
EIS characterization of laprol 2402C adsorption on copper, tin and bronze electrodes

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Adsorption of laprol 2402C (a copolymer of ethene and propene oxides) on copper, tin and bronze was investigated in 0.6 M H₂SO₄ solutions by means of impedance spectroscopy. Analysis of selected equivalent circuits revealed a weak and kinetically controlled adsorption similar for both copper and bronze electrodes. On the contrary, a strong and fast adsorption of inhibitive nature was found to occur in the case of tin electrode. An increase in the impedance from tin to bronze correlates with the corrosion resistance of respective coatings.

Key words: laprol 2402C, adsorption, copper, tin, bronze, impedance

INTRODUCTION

Plating baths used for electrodeposition of copper and its alloys usually contain various additives favourable for producing coatings of high quality. For instance, properly selected ligands make it possible to bring closer the equilibrium potentials of the metals to be codeposited. Optimal conditions for alloy deposition can be also realized by adding certain surface-active substances (SAS) that exert a selective influence on partial processes. Some SAS of organic nature, such as polymers involving -CH₂-CH₂-O- chains, are in common use for bronze plating. Poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), laprol (the copolymer of ethene and propene oxides), sintanols OS-20 and DS-10, moisteners OP-7 and OP-10 fall into this category of SAS. Though the processes involving such substances have been investigated rather extensively [1–13], the adsorption phenomena have not been sufficiently explored so far.

PEG was found to act as an inhibitor at low (up to 0.15 V) cathodic polarizations [7], especially in the presence of Cl⁻ ions. According to [8], two adsorption states are possible on copper electrode. Comparatively thick (*ca.* 1 nm) layers involving copper chloride and PEG give rise to the inhibition effects, whereas only thin adsorption layers were found to be present at higher cathodic polarizations. The influence of PEG on Cu(II) reduction has been generalized by Stoychev in review articles [9, 10].

The inhibition effects mentioned above are also known for tin and its alloys [6, 11–13]. A deep minimum on voltammograms has been observed in a

certain region of potentials with a significant decrease in double layer capacitance [13]. The special attendant effect is the rise of current oscillations in the region of the negative slope of voltammograms [6, 14, 15].

Recently, the laprol 2402 C has found its use as an effective SAS for producing bright Cu–Sn coatings [16]. Since its adsorption has not been studied in more detail, there is a good reason to fill some gaps in this problem. Electrochemical impedance spectroscopy (EIS) as one of the most informative methods was preferred for this purpose.

EXPERIMENTAL

The solutions under investigation contained 0.6 M H₂SO₄ (analytical grade) and different amounts of laprol 2402 C with an average molecular mass of *ca.* 3200. They were deaerated by the argon stream over 0.5 h. Thrice-distilled water was used for the preparation of solutions.

A Pt wire with 0.3 cm² surface area was used as a substrate for preparation of working electrodes. It was coated at 10 mA cm⁻² by a 5–7 μm thick copper layer in a solution containing (g dm⁻³): CuSO₄·5 H₂O – 125, H₂SO₄ (*d* = 1.84 g cm⁻³) – 50. A similar procedure was used to obtain tin coatings in acid Sn(II) sulphate solution of the following composition (g dm⁻³): SnSO₄ – 50, H₂SO₄ – 160, laprol 2402C – 1. Bronze (89% of Cu and 11% of Sn) coatings were deposited in a solution containing (g dm⁻³): CuSO₄·5 H₂O – 30, SnSO₄ – 50, H₂SO₄ – 140, Na₂SO₄ – 40, the brightener Br-1 – 6, laprol 2402C – 1. A saturated Ag|AgCl, KCl electrode

served as a reference electrode. To protect the solutions under investigation from traces of Cl^- ions, a special Cl^- -free electrolytic key was used. Electrode potentials were converted to the standard hydrogen scale. All the experiments were carried out at 20°C .

Impedance measurements were carried out within the frequency (f) range from 10^{-1} to 5×10^4 Hz using a Zahner Elektrik (Germany) IM6 Impedance Spectrum Analyzer. Each experiment was repeated 3–4 times. A reproducibility of impedance accounted for 5% at $f > 1$ Hz. Computer programs elaborated by Boukamp [17] were used to analyze the impedance spectra.

RESULTS AND DISCUSSION

In general, impedance spectra carry information on both faradaic and non-faradaic processes occurring in an electrochemical system. Ideally, the adsorption, as a quantity, may be obtained from the capacitance of double electric layer (C_{dl}). The latter element needs to be extracted from a more general, sometimes rather intricate equivalent circuit of the electrode. Direct measurements of C_{dl} are available only in special cases. Smooth liquid mercury in an indifferent supporting electrolyte containing SAS may be an example. Electric properties of such a system may be represented by ohmic resistance of the solution (R_Ω) and C_{dl} in series with the proviso that the adsorption is fast and reversible, and no faradaic process occurs. Then the dependence of the imaginary part of impedance (Z'') upon its real part (Z') (the so-called Nyquist plot) takes the form of a line parallel to the ordinate. This is not valid for rough electrodes when the dispersion of C_{dl} with frequency f arises. Then C_{dl} should be replaced by a constant phase element (CPE) with an admittance

$$Y = Y_0 (j\omega)^n, \quad (1)$$

where $j = \sqrt{-1}$ and $\omega = 2\pi f$. The parameter Y_0 represents the capacitance at $n = 1$ [17, 18].

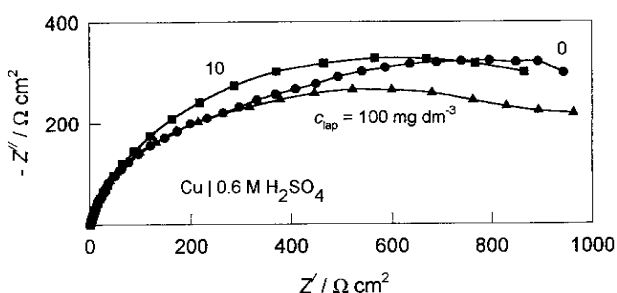
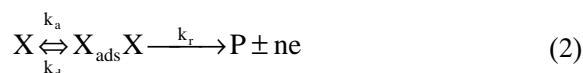


Fig. 1. Nyquist plots obtained for Cu electrode under open circuit conditions ($E = 0.21$ V). The laprol concentrations are indicated at the curves

The Nyquist plots obtained at the open circuit potential of Cu electrode (Fig. 1) take the form of arcs. It may be seen even at the first sight that an addition of laprol up to 0.1 g dm^{-3} has a little effect on the electrode impedance, this being indicative of a low surface activity of this substance.

Some equivalent circuits for a simple electrochemical process involving adsorption



have been given by Koper [19]. There k_a , k_d and k_r are rate constants of adsorption, desorption and electrochemical processes, respectively. According to [19], the equivalent circuit shown in Fig. 2 conforms this process when the adsorption is not potential-dependent. Its description code [17] may be given as $R_\Omega([R_{ct}(R_a C_a)]C_{dl})$: elements in series are given in square brackets and elements in parallel are in parentheses. The adsorption resistance (R_a) and capacitance (C_a) depend on the rate constants given in Eqn. (2).

It seems appropriate to present here the relationships corrected for a misprint found in [19]:

$$R_{ct}^{-1} = nF \frac{k_a}{k_a + k_d + k_r} \frac{\partial k_r}{\partial E} \quad (3)$$

$$R_a = \frac{k_r R_{ct}}{k_a + k_d} \quad (4)$$

$$R_{ct} C_a k_r = 1, \quad (5)$$

where Γ is an adsorption and E is an electrode potential.

Some faradaic process with the charge transfer resistance R_{ct} is supposed to occur. It can hardly be identified for the system under discussion. In general, the formation of some Cu^{2+} or Cu^+ ions may be expected under polarization conditions with the sinusoidal current. The alternative process might be corrosion, which seems to be more pronounced for a tin electrode in a strongly acid medium (see below).

The somewhat modified circuit $R_\Omega([R_2(R_3 Q_3)]Q_4)$ with CPE instead of C makes it possible to describe the experimental data with an accuracy of $\pm 3\%$. A comparison of the experimental and the simulated data is given in Fig. 3; the established parameters are listed in Table 1. The constant phase elements Q_3 and Q_4 may be interpreted as capacitive elements (n is close to 1). Besides, Q_4 may be treated as a measure of C_{dl} , which depends only weakly on both the laprol concentration and the electrode potential. Investigation of Cu(II) reduction in solutions containing laprol has shown that this SAS also has

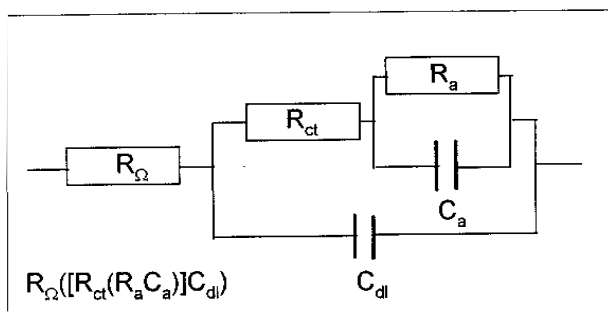


Fig. 2. Equivalent circuit [19] involving ohmic resistance of solution (R_{Ω}), charge transfer resistance (R_{ct}), adsorption resistance (R_a), adsorption capacitance (C_a) and double layer capacitance (C_{dl})

a little influence on the voltammetric characteristics up to the plateau of the limiting current

Assuming that the equivalent circuit under discussion is suitable for the Cu electrode, the rate

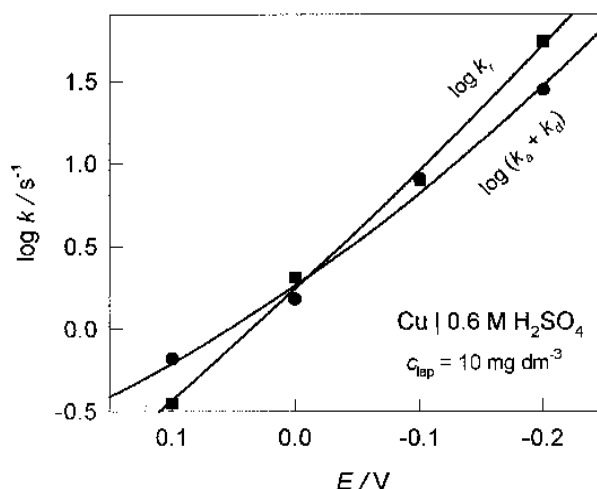


Fig. 4. Variations of rate constants indicated at the curves with Cu electrode potential in 0.6 M H_2SO_4 solutions containing 10 mg dm^{-3} of laprol

Table 1. Elements of $R_1([R_2(R_3Q_3)]Q_4)$ equivalent circuit obtained for Cu electrode in 0.6 M H_2SO_4 solutions containing 10 mg dm^{-3} of laprol

E, V	$R_1, \Omega \text{ cm}^2$	$R_2, \Omega \text{ cm}^2$	$R_3, \Omega \text{ cm}^2$	Q_3		Q_4	
				$Y_{03}, \text{ S cm}^{-2} \text{ s}^n$	n_3	$Y_{04}, \text{ S cm}^{-2} \text{ s}^n$	n_4
0.21	0.40	600	690	1.51×10^{-3}	0.62	2.68×10^{-4}	0.822
0.10	0.44	8900	4760	3.19×10^{-4}	1	1.73×10^{-4}	0.874
0.00	0.44	5800	7830	8.44×10^{-5}	1	1.58×10^{-4}	0.887
-0.10	0.44	1440	1410	8.81×10^{-5}	1	1.52×10^{-4}	0.893
-0.20	0.44	480	950	3.78×10^{-5}	1	1.47×10^{-4}	0.899

constant of electrochemical reaction (k_r) may be given by the equation:

$$k_r \approx (R_2 Y_{03})^{-1} \tag{6}$$

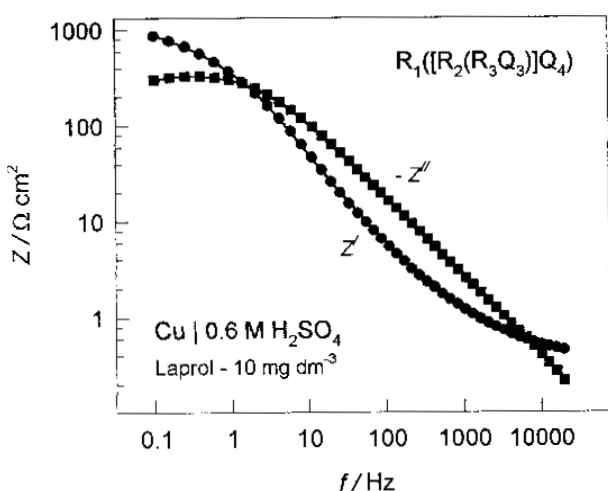


Fig. 3. Experimental (points) and simulated (lines) spectra of real (Z') and imaginary (Z'') parts of Cu electrode impedance under open circuit conditions. Values of circuit elements are given in Table 1

It follows from the formal electrode kinetics that k_r is exponentially dependent on the electrode potential at sufficiently high overvoltages. The data in Fig. 4 support this statement. Besides, the value $\alpha n = 0.42$ obtained from the slope of “ $\log k_r - E$ ” plot is quite acceptable.

Other rate constants are not available from the experimental data. It is only possible to obtain the sum $k_a + k_d$ using the relationship that follows from Eqns. (4) and (5):

$$k_a + k_d \approx (R_2 Y_{03})^{-1} \tag{7}$$

The results presented in Fig. 4 show that k_a and k_d are potential-dependent. Another equivalent circuit, namely $R_{\Omega}([R_{ct}(R_a L)]C_{dl})$, has been proposed for this case in [19]. However, an analysis shows that the latter circuit is identical to that described above. In other words, both circuits offer the same impedance spectra over an unlimited range of frequencies under specified relations between their elements. Besides, Eqn. (3) remains valid for both circuits.

When the adsorption exhibits a stronger potential dependence than does electron transfer, a nega-

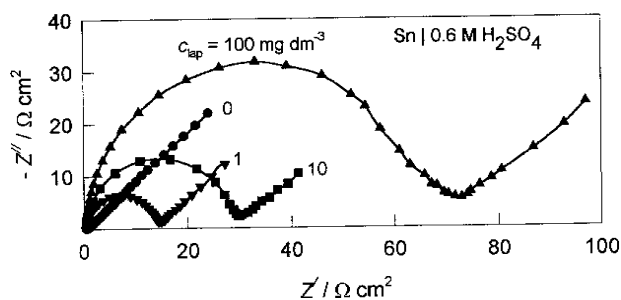


Fig. 5. Nyquist plots obtained for Sn electrode under open circuit conditions ($E = -0.26$ V). The laprol concentrations are indicated at the curves

tive R_{ct} may give rise to a negative impedance over a certain frequency range [19], but this is not pertinent to the Cu electrode.

A completely different situation occurs in the case of Sn electrode (Fig. 5). The Nyquist plot is actually the line with the slope close to 1 in the absence of laprol. Such shape is typical of diffusion-controlled processes. An addition of very small (1 mg dm^{-3}) SAS amount radically changes the shape of the plots, giving rise to well-defined semicircles. Though the impedance increases with laprol concentration, it remains more than one order of magnitude lower than that of Cu electrode.

An analysis shows that the above equivalent circuit is also acceptable for Sn electrode, with the only difference that the resistance R_3 cannot be reliably defined and may be considered as infinitely high. This gives grounds to delete R_3 from the circuit, simplifying it to $R_1([R_2Q_3]Q_4)$. This circuit makes it possible to describe the electrical properties of Sn electrode with a $\pm 2\%$ accuracy (Fig. 6).

Another peculiarity of the system lies in the fact that the nature of CPE Q_3 changes radically as well. Now, the parameter n_3 is close to 0.5 (Table 2), which is characteristic of Warburg impedance [18]. Elements R_2 and Q_4 retain their previous meaning. A very small amount of laprol gives rise to a significant (*ca.* 6-fold) decrease in double-layer capacitance (parameter Y_{04} in Table 2) with an even greater increase in charge transfer resistance (element R_2). With further addition of the SAS, Y_{04} varies weaker, whereas R_2 continues to increase to a great extent.

It is reasonable to suppose that laprol shows a strong and fast adsorption on the Sn electrode, since no other elements responsible for adsorption kinetics were detected. The inhibitive character of the adsorption follows from R_2 variations described above.

Similar effects were also detected at low cathodic polarizations, but

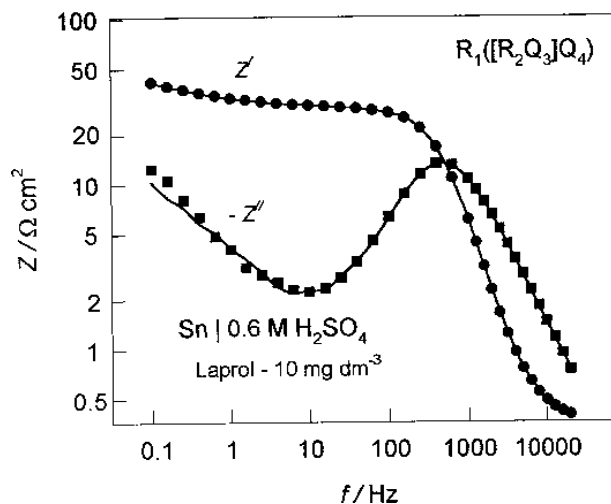


Fig. 6. Experimental (points) and simulated (lines) spectra of real (Z') and imaginary (Z'') parts of Sn electrode impedance under open circuit conditions. Values of circuit elements are given in Table 2

the influence of the electrode potential was not revealed in more detail due to the evolution of hydrogen. A preliminary investigation has shown that laprol retards the current of Sn(II) reduction within a wide region of potentials including the area of the limiting current.

Impedance characteristics of the bronze electrode do not substantially differ from those of copper. Generally, it comes as no surprise, since copper prevails in bronze coatings (see Experimental). A rather weak kinetically controlled adsorption of laprol was observed as well. Irregular variations of the impedance with the electrode potential shown in Fig. 7 are also peculiar for copper. The same equivalent circuit can be applied for both electrodes. Some distinctions may be seen from Tables 1 and 3. The main of them consists in significantly different values of R_2 . The reason for such an effect is still elusive. An analysis of the experimental data obtained with a bronze electrode offers more problems as compared with copper or tin. Finally, it may be stated that the total impedance increases from tin to bronze. This effect is consistent with the corrosion resistance of respective coatings.

Table 2. Elements of $R_1([R_2Q_3]Q_4)$ equivalent circuit obtained for Sn electrode in $0.6 \text{ M H}_2\text{SO}_4$ solutions with different concentrations of laprol (c_{lap}). Open circuit ($E = -0.26$ V) conditions

c_{lap} , mg dm^{-3}	R_1 , $\Omega \text{ cm}^2$	R_2 , $\Omega \text{ cm}^2$	Q_3		Q_4	
			Y_{03} , $\text{S cm}^{-2} \text{ s}^n$	n_3	Y_{04} , $\text{S cm}^{-2} \text{ s}^n$	n_4
0	0.45	0.24	0.037	0.49	9.76×10^{-5}	0.90
1	0.41	13.1	0.070	0.46	1.51×10^{-5}	0.98
10	0.35	27.8	0.071	0.42	1.47×10^{-5}	0.97
100	0.36	66.0	0.039	0.38	1.33×10^{-5}	0.98

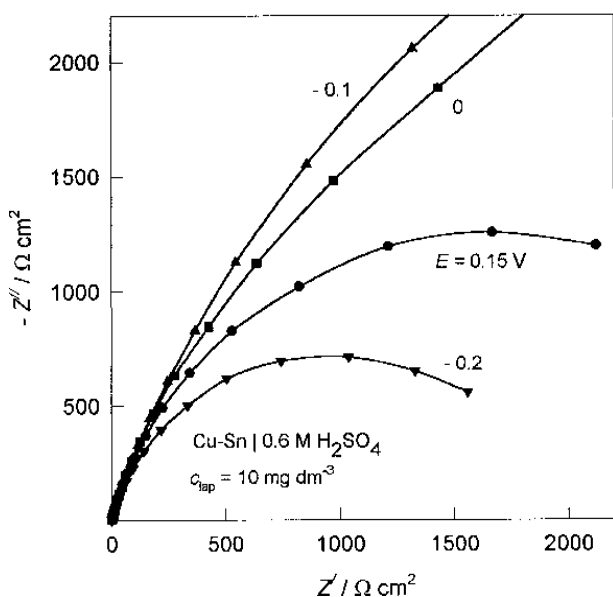


Fig. 7. Nyquist plots obtained for Cu–Sn electrode at different potentials indicated at the curves

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Table 3. Elements of $R_1([R_2(R_3Q_3)]Q_4)$ equivalent circuit obtained for Cu–Sn electrode in 0.6 M H_2SO_4 solutions containing 10 mg dm^{-3} of laprol

E, V	R_1 , $\Omega\text{ cm}^2$	R_2 , $\Omega\text{ cm}^2$	R_3 , $\Omega\text{ cm}^2$	Q_3		Q_4	
				Y_{03} , $S\text{ cm}^{-2}\text{ s}^n$	n_3	Y_{04} , $S\text{ cm}^{-2}\text{ s}^n$	n_4
0.15	0.44	10.9	3200	2.53×10^{-5}	0.97	2.65×10^{-4}	0.823
0.00	0.44	12.1	5810	1.55×10^{-5}	1	3.09×10^{-4}	0.824
-0.10	0.44	13.3	7810	1.12×10^{-5}	1	3.44×10^{-4}	0.824
-0.20	0.44	14.5	1870	1.68×10^{-5}	1	3.19×10^{-4}	0.832

CONCLUSIONS

1. An analysis of properly selected equivalent circuits shows that laprol 2402C exhibits a weak and kinetically controlled adsorption on both copper and bronze electrodes.

2. A significant decrease in double-layer capacitance caused by addition of laprol and the absence of the circuit elements responsible for the adsorption kinetics indicate a strong and fast adsorption of this substance on Sn electrode.

3. An increase in the impedance from tin to bronze correlates with the corrosion resistance of respective coatings.

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LAPROLO 2402C ADSORBCIJOS ANT VARIO, ALAVO IR BRONZOS ELEKTRODŲ CHARAKTERISTIKA, NUSTATYTA EIS METODU

S a n t r a u k a

Ištirta laprolo 2402C (eteno ir propeno oksidų kopolimero) adsorbicija ant vario, alavo ir bronzos elektrodų 0,6 M H_2SO_4 tirpaluose, taikant elektrocheminio impedanso spektroskopijos (EIS) metodą. Parinktų ekvivalentinių grandinių analizė parodo, kad silpna, kinetiškai kontroliuojama adsorbicija yra būdinga ir vario, ir bronzos elektrodams. Priešingai, stipri ir greita adsorbicija, turinti inhibicinį pobūdį, vyksta alavo elektrodo atveju. Impedanso didėjimas sekoje alavas–varies–bronzos koreliuojasi su šių dangų koroziniu atsparumu.

Received February 2001
Accepted 22 February 2001

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**ХАРАКТЕРИСТИКА АДСОРБЦИИ ЛАПРОЛА
2402С НА МЕДНОМ, ОЛОВЯНОМ И
БРОНЗОВОМ ЭЛЕКТРОДАХ, УСТАНОВЛЕННАЯ
МЕТОДОМ ЭИС**

Р е з ю м е

С помощью метода электрохимической импедансной спектроскопии (ЭИС) исследована адсорбция лапрола

2402С (кополимера оксидов этена и пропена) на медном, оловяном и бронзовом электродах в 0,6 М растворах H_2SO_4 . Анализ подобранных эквивалентных цепей показывает, что как для медного, так и для бронзового электродов типична слабая, кинетически контролируемая адсорбция. Наоборот, сильная и быстрая адсорбция ингибиционного характера имеет место в случае оловяного электрода. Увеличение импеданса в ряду олово–медь–бронза согласуется с коррозионной стойкостью этих покрытий.