

# Impedance of copper electrode in acid Cu(II) solutions containing gluconic acid

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Electrochemical impedance spectroscopy was applied to study the processes taking place on the Cu electrode in 0.01 M Cu(II) solutions containing 0.04 M gluconic acid and 0.3 M  $K_2SO_4$  (pH 3.0). The Nyquist plots obtained under open-circuit and cathodic polarization conditions present the arcs centred below the abscissa axis. The description code of the adequate equivalent circuit is  $R_{\Omega}(C_{dl}[R_1W_1][R_2W_2])$  (here, elements in series are written in angle brackets and parallel elements are given in parentheses). The settled exchange current densities obtained for the two-step charge transfer process ( $i_{01} = 4.8 \mu A cm^{-2}$  and  $i_{02} = 440 \mu A cm^{-2}$ ) are in good agreement with the quantities obtained earlier from voltammetric data.

The double-layer admittance was found to increase with the cathodic overvoltage approaching the values that are typical of additive-free Cu(II) solutions. Desorption of gluconate is supposed to occur at potentials adjacent to the plateau of the limiting current.

**Key words:** copper, gluconic acid, impedance, equivalent circuit

## INTRODUCTION

Gluconic acid,  $HO-CH_2-(CH-OH)_4-COOH$ , falls into the category of substances that can be industrially applied without bringing harm to the environment. Much information concerning this ecological substance may be obtained from Sawyer's review [1]. Due to the presence of OH-groups which release protons in alkaline media, gluconic acid is an effective ligand capable of forming complex compounds with most metals, copper included [1–4]. Therefore, a high complexation degree of Cu(II) is typical of alkaline media in which polynuclear complexes can be also formed [5–7]. However, the stability constants given in the literature [1–7] are rather *exiguous* and somewhat different, because they depend on the ionic strength of solutions and the nature of the supporting electrolyte.

In the case of acid media, gluconic acid may be symbolized as LH to show that only one hydrogen atom can split out from the carboxylic group, yielding the gluconate anion  $L^-$ . This particle is classified as an active form of the ligand that forms complexes with  $Cu^{2+}$  ions. Mononuclear complexes are weaker and the composition of acidic solutions becomes simpler [8, 9].

Among other applications, gluconate complexes found their use in different plating baths. Copper [10], as well as Cu–Sn alloys [11, 12] can be deposited from plating baths containing gluconates. Various practicalities are concerned in most of these works, whereas less attention is given to studies of the mechanism and kinetics of cathodic processes. According to [5], reversible polarograms were recorded in Cu(II) gluconate solutions. In contrast, the cathodic process on a solid copper electrode proceeds irreversibly via a consecutive transfer of two electrons. Voltammetric investigations have shown [9] that the limiting step  $Cu^{2+} + e \rightarrow Cu^+$  is characterized by relatively low ( $1-20 \mu A cm^{-2}$ ) exchange current densities which depend on the ligand concentration and pH.

More information could be obtained from the impedance data that carry information on the kinetics of faradaic processes as well as on characteristics of a double electric layer. As for gluconate systems, such investigations are scarce. A great variety of Nyquist plots (relationships between real and imaginary components of impedance) is demonstrated in Ref. [13] that deals with the deposition of tin from neutral gluconate baths, but no quantitative analysis is presented.

Impedance characteristics of the copper electrode, obtained for acid (pH 3) Cu(II) solutions containing gluconic

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acid are analyzed in the present paper. The kinetic parameters determined on the basis of a proper equivalent circuit are compared with similar data obtained from voltammetric measurements [9].

## EXPERIMENTAL

Solutions were prepared using thrice-distilled water,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Mallinckrodt, USA, chlorides less than 0.005%), sodium gluconate (Sigma-Aldrich, 99% pure), and 0.3 M  $\text{K}_2\text{SO}_4$  (high purity, Reakhim Russia) as a supporting electrolyte. Argon stream had been passed through solutions for 0.5 h before measurements. The argon atmosphere was kept also under solutions throughout the experiments.

To prepare the working electrodes, Pt wire with the surface area  $0.36 \text{ cm}^2$  was coated with copper in solutions containing ( $\text{g dm}^{-3}$ ):  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} - 250, \text{H}_2\text{SO}_4 - 50$ . The thickness of smooth coatings was 5–7  $\mu\text{m}$ . The electrodes were rinsed with water, immediately immersed into the solution under investigation and kept in it for a controlled time  $\tau$ . The electrode potentials  $E$  were measured in reference to the  $\text{Ag} | \text{AgCl} | \text{KCl}(\text{sat})$  electrode and converted to the standard hydrogen scale.

Impedance measurements were carried out under potentiostatic conditions within the frequency ( $f$ ) range from 0.05 to  $5 \times 10^4$  Hz, using a Zahner Elektrik (Germany) IM6 impedance spectrum analyzer. All experiments were performed at 20 °C. Computer programs elaborated by Boukamp [14] were used for analyzing impedance spectra.

## RESULTS AND DISCUSSION

The kinetic parameters of electrochemical processes as well as characteristics of the double electric layer can be obtained from impedance data. For this purpose, an appropriate equivalent circuit (EC) of the electrode / solution interphase should be selected. It is well known that the electrochemical reduction of Cu(II) involves two consecutive charge transfer steps resulting in the formation of intermediate Cu(I) com-

pounds. Theoretical treatment of such systems under sinusoidal perturbation conditions made it possible to describe quantitatively real ( $Z'$ ) and imaginary ( $Z''$ ) components of impedance [15–18]. The further inspection [19] allowed us to compose an adequate equivalent circuit which rigorously followed from analytical relationships obtained earlier in [15, 17]. According to [19], the faradaic part of EC is represented by two parallel sub-circuits, each containing the charge transfer resistance ( $R$ ) and Warburg impedance ( $W$ ) in series. Next, the faradaic impedance is shunted with the capacitance of a double electric layer ( $C_{dl}$ ) and, finally, the ohmic resistance of the solution ( $R_{\Omega}$ ) is attached. Following Boukamp's symbolism [14], the description code of such general EC may be written as follows:  $R_{\Omega}(C_{dl}[R_1W_1][R_2W_2])$  (here, elements in series are written in angle brackets and parallel elements are given in parentheses).

It follows from the above-mentioned investigations that the Nyquist plots (interrelations between impedance components) present the arcs (quarters of a circle) centred below the  $Z'$  axis. Experimental data obtained under open-circuit conditions (Fig. 1) are essentially consistent with this statement. However, the duration of staying of the Cu electrode in the solution somewhat affect the experimental data: the impedance increases with the exposure time  $\tau$ . It should be mentioned that the full record of impedance spectra lasts about 8 minutes, but the record of its major part (at  $f > 10$  Hz) takes only some tens of seconds. In this connection, the question arises to what degree the characteristics of the object could shift in the course of the measurement. To obtain certain answers, we made use of the Kramers–Kronig (KK) transforms. The essence of this mathematical procedure is that the real part of impedance ( $Z'$ ) can be obtained from the imaginary component ( $Z''$ ) and vice versa, if the following constraints are satisfied: linearity of the system, causality, stability and finiteness [20, 21]. Using the equations

$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_0^{\infty} \frac{x Z''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx, \quad (1)$$

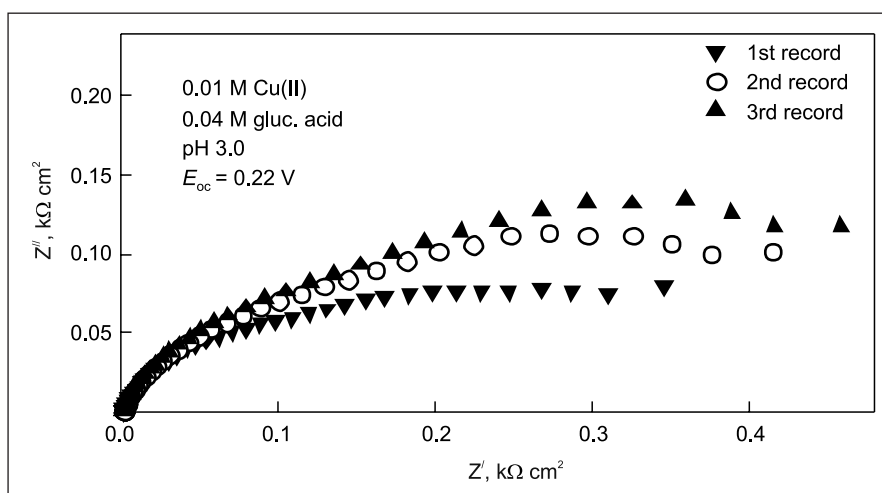


Fig. 1. Nyquist plots obtained at open-circuit potential  $E_{oc} = 0.22 \text{ V}$  for the solution of indicated composition

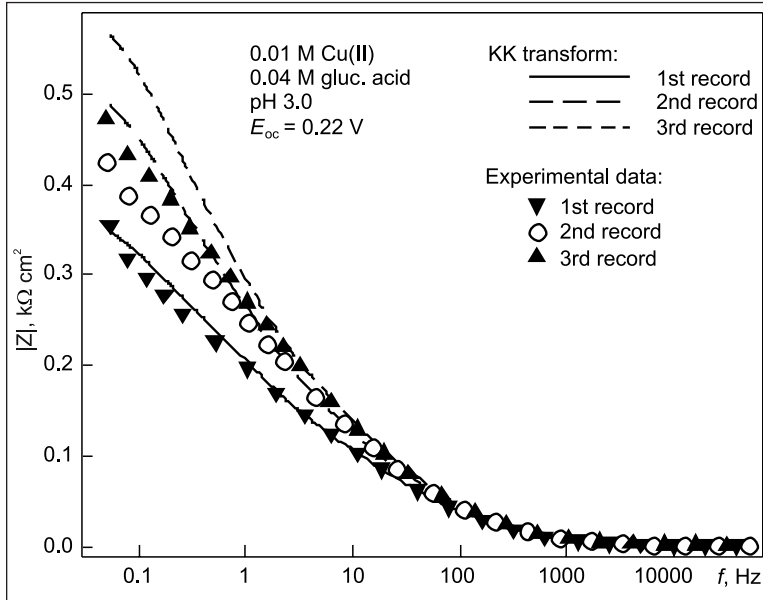


Fig. 2. Comparison of experimental impedance spectra (symbols) with those obtained by Kramers–Kronig transform (lines)

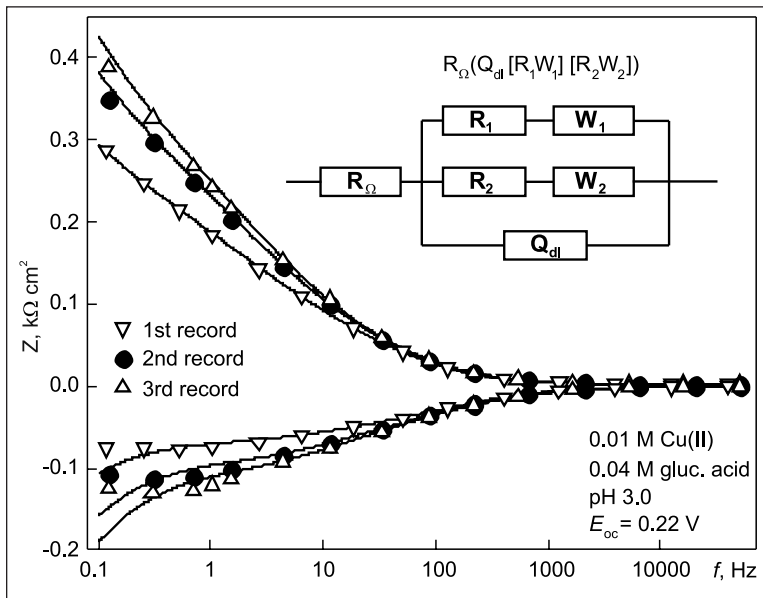


Fig. 3. Comparison of experimental impedance spectra (symbols) with those simulated for a given equivalent circuit (lines)

$$Z''(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx, \quad (2)$$

where  $\omega = 2\pi f$  and  $x$  is an auxiliary variable, the impedance modules  $|Z| = \sqrt{(Z')^2 + (Z'')^2}$  were calculated and compared with the respective experimental quantities. It can be seen from Fig. 2 that transformed and experimental data coincide quite well over the large area of frequencies applied, viz. at  $f > 3$  Hz. Hence, the results obtained in this region seem to characterize a certain steady-state state.

The result obtained offers the further analysis using a slightly modified equivalent circuit  $R_{\Omega}(Q_{dl}[R_1W_1][R_2W_2])$  containing a constant phase element (CPE)  $Q_{dl}$  instead of  $C_{dl}$  (vide supra). Fitting procedures were applied to obtain the parameters of EC elements; they are summarized in Table. This circuit enabled us to describe experimental data quantitatively with a frequency error of 2–3% over the range from 0.3 Hz to 30 kHz (Fig. 3).

Firstly, it is appropriate to discuss the data obtained under open-circuit conditions. Three records of the impedance (Table) correspond to exposure times  $\tau$  equal to 5, 15 and 25 minutes, respectively. According to the definition [20, 21], the admittance ( $Y_{dl}$ ) of the CPE  $Q_{dl}$  can be expressed as follows:

$$Y_{dl} = Y_0(j\omega)^n, \quad (3)$$

where  $j = \sqrt{-1}$ . When the index  $n = 1$ , the CPE transforms into pure capacitance. However, the experimentally determined  $n$  values are lower than 1 (Table). This could mean that the CPE  $Q_{dl}$  stands for a more complex sub-circuit which renders the properties of the non-equilibrium double layer. For instance, when adsorption processes are not

Table. Parameters of the equivalent circuit  $R_{\Omega}(Q_{dl}[R_1W_1][R_2W_2])$

$$R_{\Omega} = 1.65 \pm 0.01 \Omega \text{ cm}^2$$

| $E/V$        | $\tau/\text{min}$ | $Q_{dl}$   |       | $R_1$ | $W_1$         | $R_2$ | $W_2$         | Note       |
|--------------|-------------------|------------|-------|-------|---------------|-------|---------------|------------|
|              |                   | $10^5 Y_0$ | $n$   | $R_1$ | $10^3 Y_{01}$ | $R_2$ | $10^4 Y_{02}$ |            |
| 0.221        | 5                 | 9.59       | 0.815 | 273   | 9.72          | 84.4  | 7.49          | 1st record |
|              | 15                | 7.41       | 0.833 | 343   | 6.15          | 70.2  | 6.06          | 2nd record |
|              | 25                | 6.79       | 0.839 | 375   | 4.92          | 65.7  | 5.69          | 3rd record |
| 0.05         |                   | 3.12       | 0.925 | 690   | 8.38          | 577   | 2.63          |            |
| -0.10        |                   | 4.94       | 0.920 | 330   | 19.3          | 274   | 1.12          |            |
| -0.25        |                   | 13.6       | 0.866 | ~     | ~             | 176   | 44.3          |            |
| Rel. err., % |                   | 7          | 1     | 6     | 12            | 6     | 7             |            |

Dimensions:  $[R] = \Omega \text{ cm}^2$ ,  $[Y_0] = \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$ ,  $[Y_{01}] = [Y_{02}] = \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$ .

fast enough, the aforementioned sub-circuit can acquire the following structure: ( $C_{dl}$ [RWC]) [22–24]. Unfortunately, addition of such extra elements overloads the basic EC, and its analysis becomes impossible. Nevertheless, the diminution of  $Y_0$  with  $\tau$  indicates that the adsorption intensifies and the double-layer capacitance decreases.

It is of interest to analyze the faradaic sub-circuits so as to obtain the exchange current densities  $i_{01}$  and  $i_{02}$  of the charge transfer processes  $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$  and  $\text{Cu}^+ + e \rightarrow \text{Cu}$ , respectively. The following relationships, obtained in [17, 19], may be used for this purpose:

$$i_{01} + i_{02} = \frac{RT}{F} \left( \frac{1}{R_1} + \frac{1}{R_2} \right), \quad (4)$$

$$\frac{1}{i_{01}} + \frac{1}{i_{02}} = \frac{R_1 + R_2}{\sigma_1 + \sigma_2} \frac{1}{F\sqrt{D}} \left( \frac{1}{[\text{Cu}^{2+}]} + \frac{4}{[\text{Cu}^+]} \right), \quad (5)$$

where  $\sigma_1$  and  $\sigma_2$  are coefficients of the respective Warburg impedances (see EC elements  $W_1$  and  $W_2$ ). Generally,

$$Z_w = \sigma(1-j)/\sqrt{\omega}, \quad (6)$$

then the Warburg admittance

$$Y_w \equiv (Z_w)^{-1} = Y_0 \sqrt{j\omega} = Y_0(1+j)\sqrt{2\omega}/2 \quad (7)$$

and

$$\sigma = (\sqrt{2}Y_0)^{-1}. \quad (8)$$

Hence,  $\sigma_1$  and  $\sigma_2$  can be easily obtained from  $Y_{01}$  and  $Y_{02}$  quantities given in Table. The equilibrium concentration of  $\text{Cu}^{2+}$  ions ( $[\text{Cu}^{2+}] = 2.14 \text{ mM}$ ) was obtained using well-known material balance equations and stability constants determined and listed in Ref. [9]. It follows from the analysis of standard potentials of  $\text{Cu} | \text{Cu}^{2+}$  and  $\text{Cu} | \text{Cu}^+$  electrodes that the equilibrium constant of the process  $\text{Cu} + \text{Cu}^{2+} \rightleftharpoons 2 \text{Cu}^+$  is equal to  $4.5 \times 10^{-7} \text{ M}$ ; then,  $[\text{Cu}^+] = 3.1 \times 10^{-5} \text{ M}$ . The value of the diffusion coefficient

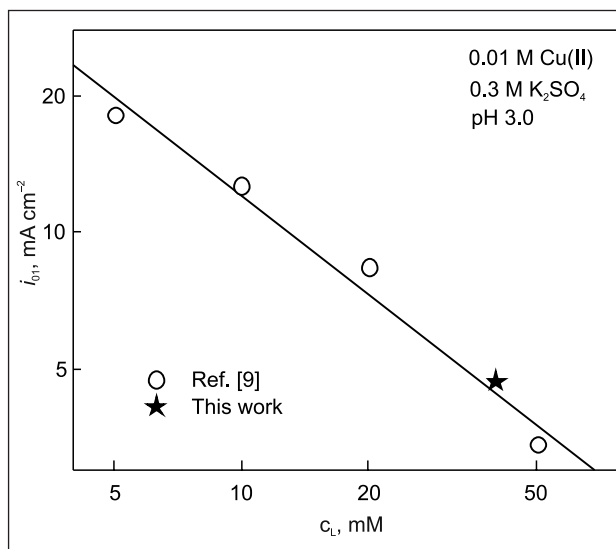


Fig. 4. Exchange current densities of the process  $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$  vs. total ligand concentration

$D = 4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  was also taken from Ref. [9]. Simulations, carried out by Eqns. (4) and (5), yield the following values of  $i_{01}$  and  $i_{02}$  (in  $\mu\text{A cm}^{-2}$ ): 4.30 and 383 (1st record), 4.69 and 424 (2nd record) 4.75 and 442 (3rd record). It can be seen primarily that  $i_{01} \ll i_{02}$ , i. e. the transfer of the first electron is the rate-determining step. Secondly, the variations in  $i_0$  are rather lower as compared with the changes in  $Y_0$  (see element  $Q_{dl}$  in Table). Thus, it could be concluded that a certain restructuring of the double layer has a rather weak effect on the exchange current densities.

The kinetic parameters of  $\text{Cu(II)}$  reduction were also determined by us from voltammetric data, using analysis of normalized Tafel plots [9]. The  $i_{01}$  values obtained by two different methods are in good agreement (Fig. 4), what does not always happen. This gives all reasons to state that  $\text{Cu}^{2+}$  aqua-complexes can be actually treated as electrically active particles.

The Nyquist plots retain their shape under cathodic polarization conditions as well (Fig. 5). The three values of the

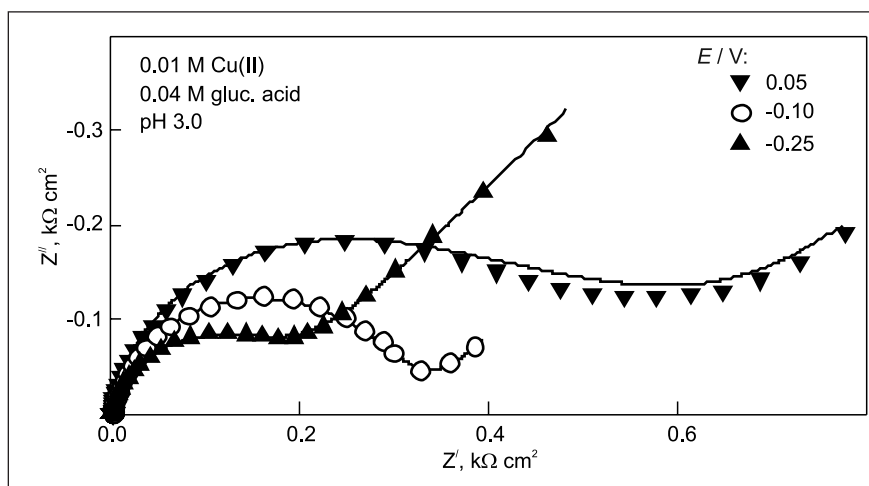


Fig. 5. Nyquist plots obtained at indicated potentials. Comparison of experimental (symbols) and simulated (lines) data

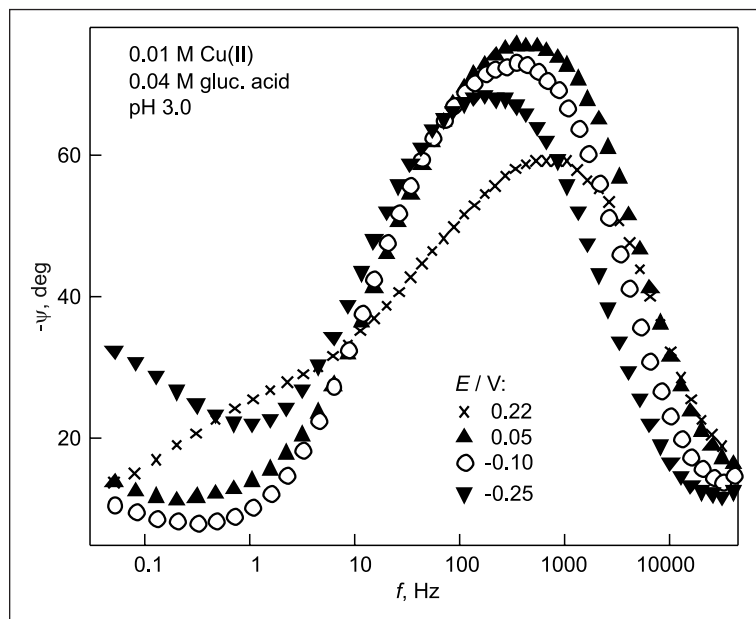


Fig. 6. Spectra of electrical phase angle obtained at indicated potentials

potentials applied (0.05, -0.10 and -0.25 V) correspond to the current densities that comprise ~10, 25 and 90% of the limiting current density. The same EC that was used above (see Fig. 3) fits experimental data quite well (Fig. 5). The lowest double-layer admittance  $Y_0$  was obtained at 0.05 V (Table). It increases with the cathodic overvoltage approaching the values that are typical of additive-free Cu(II) solutions [19, 25]. This is an indication of a significant desorption of gluconate at sufficiently negative electrode potentials. A comparison of data given in [26–29] leads to the conclusion that the zero-charge potential of Cu electrode in sulphate-containing solutions falls on 0 V. Thus, as should be expected, the main region of gluconate absorption is located at moderate (positive and negative) surface charge densities. When the negative charge becomes too high, gluconate ions are displaced from the double layer.

Equations (4) and (5) are derived for the equilibrium potential and are unsuitable for the description of impedance under cathodic polarization conditions. In the latter case, faradaic elements intricately depend on the partial current densities  $i_1$  and  $i_2$ , charge transfer coefficients, surface concentrations, etc. [21]. When the cathodic polarization increases, the net current density  $i = i_1 + i_2$  also increases and the surface concentration of  $\text{Cu}^{2+}$  ions ( $[\text{Cu}^{2+}]_s$ ) decreases. Variations in  $[\text{Cu}^{2+}]_s$  are more complicated and depend on the  $i_{01}/i_{02}$  ratio. All these effects are embodied in the EC parameters (Table). One of them consists in the diminution  $R_1$  and  $R_2$  until  $[\text{Cu}^{2+}]_s$  becomes sufficiently low. At -0.25 V, the impedance of  $[\text{R}_1\text{W}_1]$  increases to the extent that  $R_1$  and  $Y_{01}$  become indeterminable and this sub-circuit can be deleted from the general EC.

To sum up, it is appropriate to draw attention to the electrical phase angle  $\psi = \arctan(Z''/Z')$  that sometimes is used in diagnostic procedures. Its spectra are shown in Fig. 6. A specific maximum observed at ~1 kHz under open-circuit

conditions seems typical of most of the Cu | Cu(II) systems [19, 30, 31]. Its position shifts to lower frequencies when the cathodic polarization is increased.

## CONCLUSIONS

1. The Nyquist plots obtained for Cu electrode in 0.01 M Cu(II) and 0.04 M gluconate solutions at pH 3 present the arcs centred below the  $Z'$  axis, which are typical of two-step charge transfer reactions. They retain their shape under cathodic polarization conditions as well.

2. The equivalent circuit  $\text{R}_\Omega(\text{C}_{dl}[\text{R}_1\text{W}_1][\text{R}_2\text{W}_2])$  makes it possible to describe experimental data quantitatively with the frequency error of 2–3% over the range from 0.3 Hz to 30 kHz. It is valid under both open-circuit and cathodic polarization conditions.

3. The settled exchange current densities obtained for the two-step charge transfer process ( $i_{01} = 4.8 \mu\text{A cm}^{-2}$  and  $i_{02} = 440 \mu\text{A cm}^{-2}$ ) are in good agreement with the quantities obtained earlier from voltammetric data.

4. The double-layer admittance increases with the cathodic overvoltage approaching the values that are typical of additive-free Cu(II) solutions. Gluconate desorption is supposed to occur at potentials adjacent to the plateau of the limiting current.

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## References

1. D. T. Sawyer, *Chem. Rev.*, **64**, 633 (1964).
2. L. G. Sillen, A. E. Martell, *Stability constants of metal-ion complexes*, Special Pub. Nos. 17 and 25, L.: Chem. Soc., Vol. 1, (1964), Vol. 2 (1971).

3. A. E. Martell, R. M. Smith, *Critical Stability Constants*, Vol. 4, N. Y., Plenum Press (1976).
4. Yu. E. Alekseev, A. D. Garnovskii, Yu. A. Zhdanov, *Russ. Chem. Rev.*, **67**, 649 (1998).
5. R. L. Pecsoc, R. S. Juvet Jr., *J. Amer. Chem. Soc.*, **77**, 202 (1955).
6. K. Blomqvist, E. R. Still, *Anal. Chem.*, **57**, 749 (1985).
7. R. J. Motekaitis, A. E. Martell, *Inorg. Chem.*, **23**, 18 (1984).
8. M. Vicedomini, *J. Coord. Chem.*, **12**, 307 (1983).
9. A. Survila, Z. Mockus, S. Kanapeckaitė, J. Pileckienė, G. Stal-nionis, *Russ. J. Electrochem.*, **47**, 129 (2011).
10. S. S. Abd El Rehim, S. M. Sayyah, M. M. El Deeb, *Appl. Surf. Sci.*, **165**, 249 (2000).
11. S. S. Abd El Rehim, S. M. Sayyah, M. M. El Deeb, *Trans. IMF*, **76**, 74 (2000).
12. B. Subramanian, S. Mohan, Sobha Jayakrishnan, *Surf. Coat. Technol.*, **201**, 1145 (2006).
13. T. Sonoda, H. Nawafune, S. Mizumoto, *Plat. Surf. Finish*, **79**, 78 (1992).
14. B. B. Boukamp, *Equivalent Circuit (EQUIVCRT.PAS), User's Manual*, University of Twente (1989).
15. A. R. Despić, D. R. Jovanović, S. P. Bingulak, *Electrochim. Acta*, **15**, 459 (1970).
16. R. A. Slivka, D. I. Aleksandrova, B. M. Grafov, D. I. Leikis, *Elektrokhimiya*, **13**, 888 (1977).
17. A. A. Survila, A. A. Katkus, *Sov. Electrochem.*, **16**, 1483 (1980).
18. A. I. Maslij, B. Y. Pirogov, A. Ž. Medvedev, *Elektrokhimiya*, **22**, 164 (1986).
19. A. Survila, V. Baliukienė, *Chemija*, **12**, 195 (2001).
20. J. R. Macdonald, *Impedance Spectroscopy*, Wiley, New York (1987).
21. A. Lasia, *Electrochemical impedance spectroscopy and its applications*, in: B. E. Conway, J. Bocris, R. E. White (eds.), *Modern Aspects of Electrochemistry*, Vol. **32**, Kluwer Academic / Plenum Publishers, New York (1999).
22. A. Frumkin, V. I. Melik-Gaikazian, *Proc. AS USSR*, **77**, 855 (1951).
23. V. I. Melik-Gaikazian, *Zh. fiz. khim.*, **26**, 560 (1952).
24. M. Sluyters-Rehbach, J. Sluyters, *Sin-wave methods in the study of electrode processes*, in: A. Bard (ed.), *Electroanal. Chem.*, Vol. **4**, M. Dekker, New York, 75 (1970).
25. A. Survila, Z. Mockus, S. Kanapeckaitė, M. Samulevičienė, *Trans. IMF*, **84**, 94 (2006).
26. L. Y. Yegorov, I. M. Novoselskii, *Elektrokhimiya*, **6**, 869 (1970).
27. R. O. Loutfy, *Electrochim. Acta*, **18**, 227 (1973).
28. T. Agladze, A. Podobaev, *Electrochim. Acta*, **36**, 859 (1991).
29. M. Turovska, Y. Bachinski, Ya. Sokolovski, *Elektrokhimiya*, **33**, 1301 (1997).
30. A. Survila, Z. Mockus, S. Kanapeckaitė, M. Samulevičienė, *Polish J. Chem.*, **76**, 983 (2002).
31. J. Uljanionok, A. Survila, *Chemija*, **19**, 20 (2008).

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## VARIO ELEKTRODO IMPEDANSAS CU(II) IR GLIUKONO RŪGŠTIES TIRPALUOSE

### Santrauka

Elektrocheminės impedanso spektroskopijos metodu ištirti procesai, vykstantys ant vario elektrodo 0,01 M Cu(II), 0,04 M gliukono rūgšties ir 0,3 M K<sub>2</sub>SO<sub>4</sub> tirpaluose, kurių pH yra 3,0. Naikvisto grafikai, gauti atviros grandinės sąlygomis, turi lankų, kurių centrai yra žemiau abscisės, formą. Adekvačios ekvivalentinės grandinės kodas yra toks: R<sub>Ω</sub>(C<sub>dl</sub>[R<sub>1</sub>W<sub>1</sub>][R<sub>2</sub>W<sub>2</sub>]) (čia nuosekliai sujungti elementai yra patalpinti laužtiniuose skliaustuose, o sujungti lygia-grečiai – paprastuose). Dviejų krūvio pernašos stadijų nusistovėję mainų srovės tankiai (*i*<sub>01</sub> = 4,8 μA cm<sup>-2</sup> ir *i*<sub>02</sub> = 440 μA cm<sup>-2</sup>) gerai derinasi su dydžiais, gautais anksčiau iš voltamperometrinių duomenų.

Didėjant katodinei poliarizacijai, dvigubojo sluoksnio admitansas auga, pasiekdamas vertes, kurios yra būdingos Cu(II) tirpalams be priedų. Manoma, kad gliukonatas desorbuojasi, kai potencialas priartėja prie ribinės srovės srities.