

# Impedance characterization of *p*- and *n*-Cu<sub>2</sub>O layers developed in Cu(II) solutions containing ligands

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Electrochemical impedance spectroscopy (EIS) data were used for characterization of the oxide layers developed in Cu(II) solutions containing different ligands. Oxide layers of usual *p*-type conductivity are formed in the ethylenediamine solutions, whereas *n*-Cu<sub>2</sub>O prevails in the layers formed in the β-alanine system. According to the EQCM data, the oxide layers are most stable in slightly acidic ligand-free Cu(II) solutions at pH 4.1–4.9. The electrochemical properties of Cu | *p*-Cu<sub>2</sub>O electrodes can be modelled with two subcircuits in series. One of them reflects the consecutive charge transfer typical of Cu<sup>2+</sup> reduction, and another subcircuit represents the properties of the oxide layer. The impedance of Cu | *n*-Cu<sub>2</sub>O electrode can be described using more complicated equivalent circuits that contain negative resistances, negative capacitances or inductive elements.

**Key words:** cuprous oxide, ethylenediamine, β-alanine, impedance, equivalent circuit

## INTRODUCTION

Spontaneous formation of copper oxides often attends the electroreduction of Cu(II) and may affect not only the kinetics but also the mechanism of charge transfer reaction, as it takes place in the Cu(II)–glycine system [1]. It has been found that Cu(II) reduction may be described quantitatively by equations of formal electrochemical kinetics, if sufficiently thin oxide layers are formed. However, such an approach fails when surface layers are considerably thicker as, *e.g.*, in the case of a Cu | Cu(II), β-alanine system [2]. Furthermore, oxide layers developed in electrochemical systems containing ligands are interesting as such, because their properties may be essentially different from those known for monocrystals or polycrystalline compacts.

The thermodynamic stability of Cu<sub>2</sub>O in ligand-containing systems has been analysed and the respective diagrams have been constructed [3, 4]. At present, there is no doubt that the electrochemical characteristics of oxide layers strongly depend on conditions under which they are built up. It has been established [5] that oxide formation is conditioned to a great extent by the complexation degree of Cu(II): the higher the stability of Cu(II) complexes, the lower is the rate of Cu<sub>2</sub>O formation. Though the

nature of the ligand seems to be of secondary importance in this case, it acquires significance as a factor responsible for some properties of the oxides formed. Though cuprous oxide is known as a substance exhibiting *p*-type semiconductor properties, quite often electrochemically formed Cu<sub>2</sub>O layers display the so-called “anomalous” *n*-type conductivity. Both species of oxides can be also formed in the presence of ligands [5–9]. For instance, *p*- and *n*-Cu<sub>2</sub>O prevail in ethylenediamine [4, 8, 10, 11] and β-alanine [2, 5–7] systems, respectively.

The type of conductivity may be easily defined from photoelectrochemical experiments, *i.e.* from signs of photocurrent or photopotential that are opposite for *p*- and *n*-Cu<sub>2</sub>O. It was also established [12] that impedance characteristics largely depend on the type of conductivity. We did not find any proper information on this subject in the available literature. Therefore, it was of interest to perform more detailed investigations in this field, focussing on a retrieval of equivalent circuits that give the best fit to the experimental data.

## EXPERIMENTAL

A Pt wire with a surface area of 0.36 cm<sup>2</sup>, fused into a glass holder, was used as a substrate for preparation of the working electrode. It was coated at 10 mA cm<sup>-2</sup> with a 5–7 μm thick copper layer in the

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solution containing ( $\text{g dm}^{-3}$ ):  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  – 200,  $\text{H}_2\text{SO}_4$  – 50. The next procedures were performed with the solutions containing 0.01 M  $\text{CuSO}_4$  (Mallinckrodt, USA), 0.3 M  $\text{K}_2\text{SO}_4$  (high purity) as a supporting electrolyte and, in special cases, some ligands. All of them were prepared using thrice-distilled water and were deaerated with a pure argon stream passed through solutions for 0.5 h before measurements.

The formation of oxide layers was performed exposing the copper electrode to a certain solution for a controlled time  $\tau$ . Two 0.01 M  $\text{Cu(II)}$  solutions with different ligands were used for this purpose. The first of them contained also 0.005 M ethylenediamine at pH 5.3 and made it possible to form  $p\text{-Cu}_2\text{O}$  on the copper surface [8]. Another  $\text{Cu(II)}$  solution, involving 0.04 M  $\beta$ -alanine at pH 6.1, was used for the formation of  $n\text{-Cu}_2\text{O}$  [6]. Then the  $\text{Cu} | \text{Cu}_2\text{O}$  electrode was rinsed with ligand-free 0.01 M  $\text{Cu(II)}$  solution and placed into the impedance measurement cell containing the latter solution.

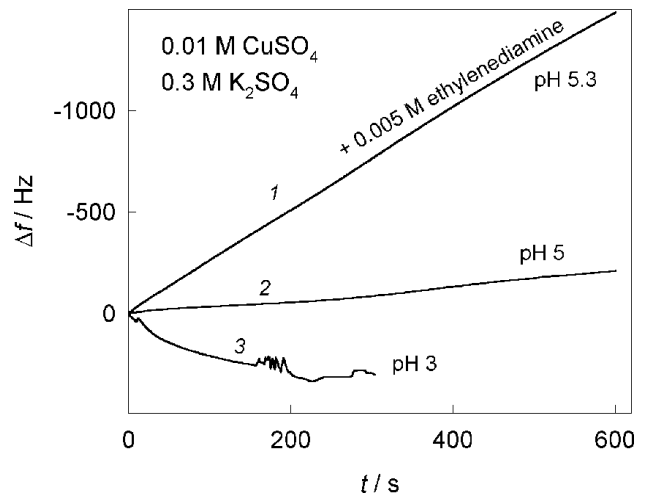
To determine the boundaries of pH at which oxide layers are most stable, special experiments using electrochemical quartz crystal microgravimetry (EQCM) were carried out. EQCM was equipped with a 6 MHz, AT-cut, plano-convex quartz crystal with a vacuum-deposited gold layer (from Intelmetrics LTD, UK). Electrodes were prepared in the same way as described above. Other details concerning this technique are given in [10].

Impedance spectra were recorded within a frequency  $f$  range from 0.1 Hz to 40 kHz using a Zahner Elektrik (Germany) IM6 impedance spectrum analyzer. Each record took about 5 min and was repeated 3–4 times. Computer programs elaborated by Boukamp [13] were used to analyze the impedance data.

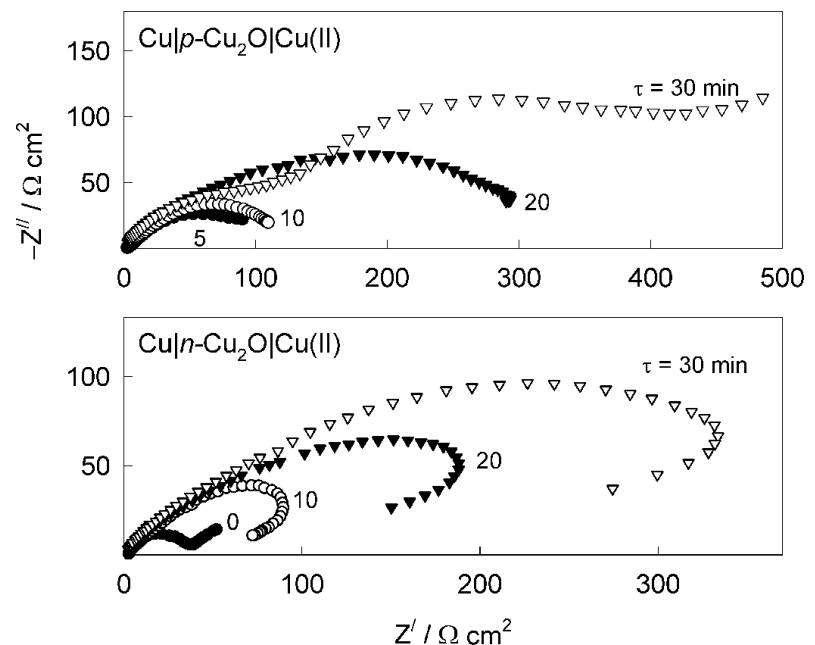
All experiments were performed at 20 °C.

## RESULTS AND DISCUSSION

The dynamics of development or destruction of oxide layers in different  $\text{Cu(II)}$  solutions may be seen from frequency variations  $\Delta f$  of the quartz crystal oscillator under open-circuit conditions (Fig. 1). Rapid changes of  $\Delta f$  are observed in  $\text{Cu(II)}$ -ethylenediamine solutions, and they are indicative of an intense formation of oxide layers. They are not stable when immersed into acidic  $\text{Cu(II)}$  solutions. A certain increase in  $\Delta f$  (consequently, the respective decrease in the electrode mass) is observed at pH 3 due to the disintegration of  $\text{Cu}_2\text{O}$ . Minimal mass



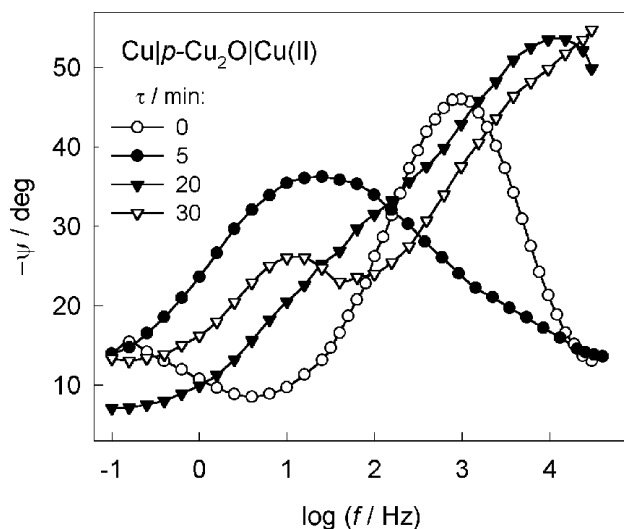
**Fig. 1.** EQCM data for freshly prepared (curve 1) and covered with  $\text{Cu}_2\text{O}$  layer (curves 2 and 3) copper electrodes exposed to the solutions of indicated composition



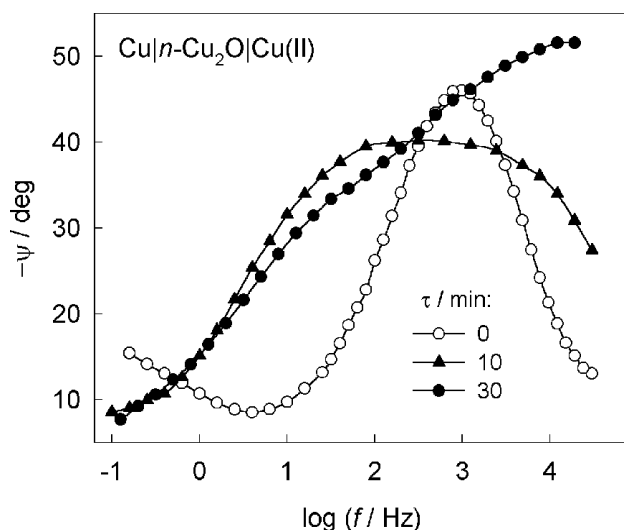
**Fig. 2.** Nyquist plots obtained for electrodes covered with  $p$ - (upper part) and  $n\text{-Cu}_2\text{O}$  (lower part). The length of exposure time is indicated at the curves

changes were found to occur in slightly acidic media, specifically, at pH 4.1–4.9. This condition was kept on obtaining the EIS data.

Electroreduction of  $\text{Cu(II)}$  is known to proceed by two consecutive one-electron transfers involving formation of stable intermediate  $\text{Cu}^+$  ions. The adequate equivalent circuit that has been analysed in [14] involves two parallel subcircuits. Each of them is formed of the charge transfer resistance  $R$  and Warburg impedance  $W$  in series. The so constructed Faradaic impedance is shunted with the constant phase element (CPE) of the double electric layer  $Q_{dl}$  and then the ohmic resistance of the solution  $R_{\Omega}$  is



**Fig. 3.** Phase shift spectra obtained for Cu | *p*-Cu<sub>2</sub>O electrodes at indicated exposure times



**Fig. 4.** Phase shift spectra obtained for Cu | *n*-Cu<sub>2</sub>O electrodes at indicated exposure times

added. According to [13], the description code of the ultimate circuit may be written as  $R_{\Omega}([R_1W_1][R_2W_2]Q_{dl})$  with serial elements in square brackets and parallel elements in parentheses. Such circuit has been successfully used for modelling Cu<sup>2+</sup> reduction in acidic sulphate solutions [14].

Development of *p*- or *n*-Cu<sub>2</sub>O on the electrode surface results in growth of the total impedance (Fig. 2) and at the same time gives rise to qualitative changes in the impedance characteristics. The different character of the impedance obtained in the presence of *p*- and *n*-Cu<sub>2</sub>O may be seen for Nyquist plots (Fig. 2) that relate the real  $Z'$  and imaginary  $Z''$  components of the electrode impedance at various frequencies of the alternating current. Arcs with centres below the abscissa axis are typical of *p*-Cu<sub>2</sub>O (upper part of Fig. 2) with the peculiarity that two arcs can be separated at sufficiently long exposure

times (see curve for  $\tau = 30$  min). In the case of *n*-Cu<sub>2</sub>O, arc-shaped curves may be observed only at sufficiently high  $f$  (left parts of Nyquist plots), whereas the loops indicative of an inductive character of the impedance are inherent for lower frequencies. Similar plots have been also obtained in some investigations [15–17] dealing with formation of different surface films.

Respective differences are also embodied in other impedance characteristics, such as spectra of phase shift  $\Psi$  (Figs 3 and 4). In the case of freshly prepared copper electrodes, the  $\Psi$  values pass two extremes: the minimum at *ca.* 10 Hz and the maximum at *ca.* 3 kHz (see the data obtained for  $\tau = 0$  in Figs 3 and 4). Gradual oxidation of the electrode surface causes specific irregular changes in  $\Psi$  spectra, when *p*-Cu<sub>2</sub>O is formed (Fig. 3). Somewhat similar phenomena are also observed in the case of *n*-Cu<sub>2</sub>O (Fig. 4).

We made an attempt to interpret the experimental impedance data invoking suitable equivalent circuits. In the cases when circuit elements acquire a certain physical sense, a valuable information concerning the mechanism of electrochemical processes and other characteristics of the system under investigation can be obtained. Such analysis is somewhat simpler in the case of *p*-Cu<sub>2</sub>O. The fact that two arcs can be separated at sufficiently long exposure times gives grounds to propose the equivalent circuit  $R_{\Omega}(R_{ox}Q_{ox})([R_1W_1][R_2W_2]Q_{dl})$  shown in Fig. 5. Two subcircuits are in series with ohmic resistance of the solution  $R_{\Omega}$ . One of them,  $([R_1W_1][R_2W_2]Q_{dl})$ , represents the Cu(II) reduction proceeding by two one-electron steps and contains respective charge transfer resistances ( $R_1$  and  $R_2$ ) and Warburg impedances ( $W_1$  and  $W_2$ ), as discussed above. The subcircuit  $(R_{ox}Q_{ox})$  seems to be attributable to the oxide layer. Similar subcircuits have been involved in modelling various adsorption-related objects [18–23].

The experimental impedance spectra obtained for *p*-Cu<sub>2</sub>O developed in 30 min can be fitted to the above circuit with a rather high accuracy (Fig. 6). The fitting procedure yields:  $R_{\Omega} = 0.26 \Omega \text{ cm}^2$ ,  $R_{ox} = 122 \Omega \text{ cm}^2$ ,  $Y_{ox} = 5.3 \times 10^{-5} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.628}$ ,  $R_1 = 307 \Omega \text{ cm}^2$ ,  $Y_{W1} = 8.34 \times 10^{-3} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$ ,  $R_2 = 10 \Omega \text{ cm}^2$ ,  $Y_{W2} = 1.42 \times 10^{-4} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$ ,  $Y_{dl} = 2.25 \times 10^{-4} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.776}$ . As follows from the impedance theory [24], an admittance of CPE is defined as  $Y(i\omega)^n$ , where  $\omega = 2\pi f$  and  $i = \sqrt{-1}$ . At  $n = -1, 0, 0.5$  and  $1$ , this element transforms into inductance, resistance, Warburg impedance and capacitance, respectively. It may be seen from the dimensions of  $Y$  obtained that none CPE can be rigorously classified as pure capacitance or Warburg impedance. Nevertheless, it could be reasoned that the nature of  $Q_{ox}$  is more diffusive ( $n_{ox} = 0.628$ ) than that of  $Q_{dl}$  with  $n_{dl} = 0.776$ . However, it is not possible to impart a

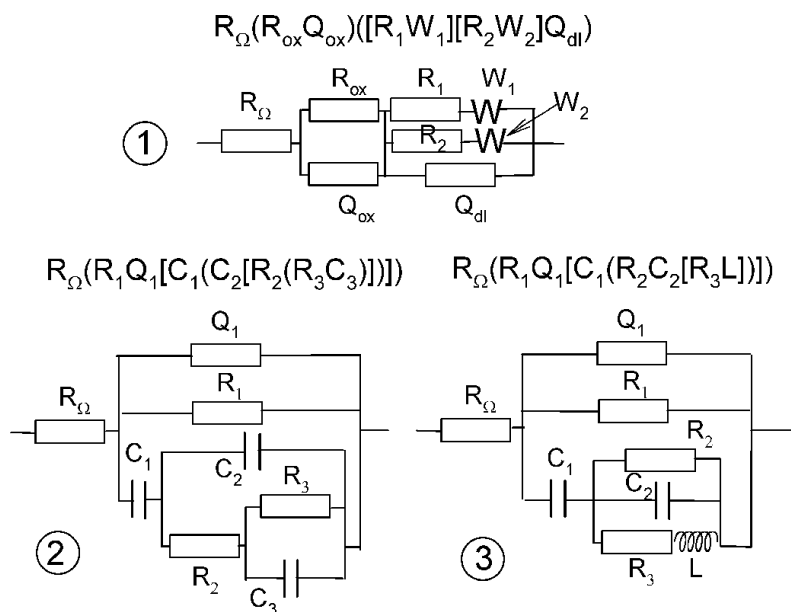


Fig. 5. Different equivalent circuits used in the present investigation

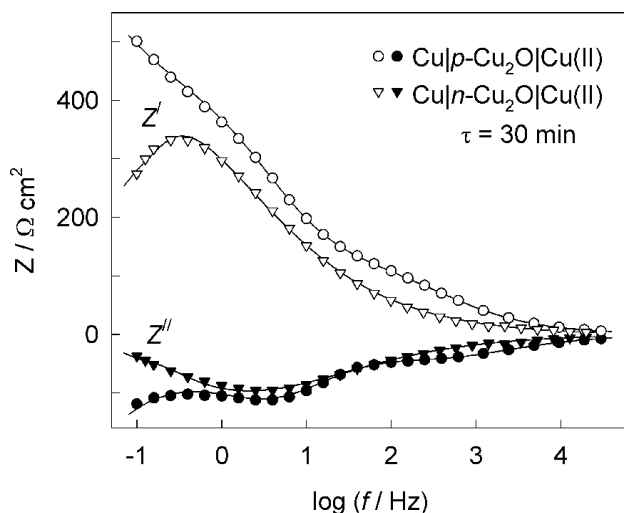


Fig. 6. Comparison of experimental (symbols) and simulated (lines) impedance spectra. Parameters of used equivalent circuits are given in the text

more precise physical sense to  $Q_{ox}$  or  $Q_{dl}$  due to the deviations of established  $n$  magnitudes from the characteristic quantities equal to 0.5 or 1.

Similar results may be also obtained in the case of  $n$ - $Cu_2O$  using more complicated equivalent circuits 2 or 3 shown in Fig. 5. It is necessary to note that both circuits yield fully identical impedance spectra in any range of frequencies when their elements are properly related. This property of equivalent circuits is known in the impedance theory [24]. Thus, the fitting of the 2nd circuit yields:  $R_{\Omega} = 0.2 \Omega \text{ cm}^2$ ,  $R_1 = 255 \Omega \text{ cm}^2$ ,  $Y_{Q_1} = 6.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.456}$ ,  $C_1 = 8.91 \times 10^{-4} \text{ F cm}^{-2}$ ,  $C_2 = 4.08 \times 10^{-7} \text{ F cm}^{-2}$ ,  $R_2 = -500 \Omega \text{ cm}^2$ ,  $R_3 = -4167 \Omega \text{ cm}^2$ ,  $C_3 = -8.68 \times 10^{-4} \text{ F cm}^{-2}$ . In the case of the 3rd equivalent circuit, the subcircuit  $[R_2(R_3C_3)]$  should be replaced by  $(R_2$

$[R_3L])$  with  $R_2 = -500 \Omega \text{ cm}^2$ ,  $R_3 = 560 \Omega \text{ cm}^2$ ,  $L = 217 \text{ H cm}^2$ . Though the simulated and experimental data coincide quite well (Fig. 6), the physical sense of some elements, such as inductance  $L$  or negative resistances and capacitances, is not yet clear and needs further analysis. It seems likely that a finer structure resides in some of the electric analogues.

It is well known that oxide layers developed on copper surface exhibit some peculiarities. Certain deviations from stoichiometry and inhomogeneities in the structure are among them [12]. Due to these features, the  $Cu | Cu_2O$  electrodes should be assigned to the electrochemical objects with spatially distributed electric parameters. The impedance theory of such objects is rather complicated and invites its further development.

## CONCLUSIONS

1. Oxide layers with different conductivity can be developed on the copper electrode surface in  $Cu(II)$  solutions containing different ligands. Usual  $p$ -type conductivity is acquired in ethylenediamine solutions, whereas  $n$ - $Cu_2O$  prevails in the layers formed in the  $\beta$ -alanine system.

2. Oxide layers can grow or be destroyed in ligand-free  $Cu(II)$  solutions depending on their acidity. According to the EQCM data, the layers are most stable in slightly acidic media (pH 4.1–4.9).

3. Electrochemical properties of  $Cu$  electrodes covered with  $p$ - $Cu_2O$  can be modelled with two subcircuits in series. One of them reflects the consecutive charge transfer typical of  $Cu^{2+}$  reduction, and another subcircuit represents the properties of the oxide layer.

4. The impedance of  $Cu | n$ - $Cu_2O$  electrode can be described using more complicated equivalent circuits that contain negative resistances, negative capacitances or inductive elements, the physical sense of which is not yet clear.

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***p*- IR *n*-Cu<sub>2</sub>O SLUOKSNIŲ, SUSIDARANĖIŲ CU(II) IR LIGANDŲ TIRPALUOSE, IMPEDANSO CHARAKTERISTIKOS**

**Santrauka**

Oksidų sluoksnių, susidaranėių Cu(II) tirpaluose su įvairiais ligandais, charakteristikai yra taikomas elektrocheminio impedanso spektroskopijos (EIS) metodas. Etilendiamino tirpaluose susidaro aprasto *p* tipo laidumo oksidai, tuo tarpu β-alanino sistemoje susiformavusiame sluoksnyje vyrauja *n*-Cu<sub>2</sub>O. Iš kvarco kristalo mikrogravimetrijos duomenų seka, kad oksidų sluoksniai yra stabiliausi silpnai rūgščiuose (pH 4,1–4,9) Cu(II) tirpaluose be ligando. Cu | *p*-Cu<sub>2</sub>O elektrodų elektrochemines savybes galima modeliuoti dviem nuosekliai sujungtomis subgrandinėmis. Viena iš jų atspindi nuoseklų krūvio pernešimą, tipiką Cu<sup>2+</sup> redukcijai, kita – oksidinio sluoksnio savybes. Cu | *n*-Cu<sub>2</sub>O elektrodo impedansui aprašyti reikia sudėtingesnių ekvivalentinių schemų su neigiamomis varžomis, neigiamomis talpomis ar induktyviais elementais.