

Cu(II) electroreduction kinetics in acidic sulphate solutions containing tetraethyleneglycol and small amounts of chlorides

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Voltammetry and electrochemical impedance spectroscopy were used to investigate the effect of tetraethyleneglycol (TEG) on Cu(II) reduction kinetics in the presence of micromolar amounts of chloride ions. TEG was found to be the shortest molecule among polyethyleneglycols that are capable to show the inhibitive adsorption on copper substrate in the presence of halides. An analysis of normalized Tafel plots has showed that TEG suppresses mainly transfer of the first electron to Cu²⁺ ion. The possible structure of adsorption layer is proposed, in which chloride ions act as the particles bonding the copper surface with pseudo-crowns involving Cu⁺ and TEG.

Key words: copper, reduction, tetraethyleneglycol, chloride, adsorption

INTRODUCTION

Polyethers in combination with some sulphur-containing organic substances are widely employed in modern plating industry to obtain bright copper coatings of high quality. Different polyethyleneglycols (PEG) should be mentioned among such surface-active substances (SAS) first of all. A more comprehensive information on their electrochemical behaviour and adsorption properties may be found in [1–3]. Though some contradictory data concerning PEG surface activity on copper substrates have been reported in the earlier publications, now it is possible to conclude that PEG surface activity is rather low when Cu(II) solutions are carefully protected from traces of chlorides. The effect of PEG on Cu(II) reduction kinetics is also weak in this case [4–10].

Investigations involving PEG of different molecular mass have shown that the halide-enhanced inhibitive adsorption depends not only on PEG concentration [1] but also on the length of hydrocarbon chain [11]. Moreover, no significant surface activity was detected in the solutions containing too short polyether molecules. Specifically, no significant inhibition was observed in Cu(II) solutions involving mono-, di- or three-ethyleneglycols even in the presence of halides [12]. It was established that only tetraethyleneglycol (TEG) $\text{HO(CH}_2\text{)}_4\text{OH}$ or other derivatives with a higher molecular mass can give rise to inhibition of Cu(II) reduction.

Chlorides are known as the necessary components that improve the anodic process in copper plating baths. Alternatively, these ions, as well as other halides, are able to influence adsorption properties of the SAS used in copper plating, and therefore their effect should be controlled. Since the data concerning bromide-enhanced TEG adsorption have been mainly presented in [12], we consider that the data obtained for chloride-containing solutions are worth of being reported in more detail. At the same time, a presumptive structure of the adsorption layer is discussed in the article.

EXPERIMENTAL

Solutions under investigation contained 0.01 M CuSO₄ (Mallinckrodt, USA), 0.6 M H₂SO₄ (high purity) as a supporting electrolyte, 30 μM of potassium halides (high purity) and different amounts of tetraethyleneglycol. The latter substance was used as received. Thrice-distilled water was used for the preparation of solutions. A pure argon stream was passed through solutions for 0.5 h before measurements.

The conventional rotating disc electrode (RDE) technique was used in voltammetric measurements. To prepare working electrodes, a 1 cm² platinum disc was coated at 10 mA cm⁻² with a 5–7 μm thick copper layer in the solution containing (g dm⁻³): CuSO₄ · 5 H₂O – 200, H₂SO₄ – 50. The working electrode was rinsed with water, immediately immersed into a solution under investigation and kept

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in it for a controlled time τ . A similar procedure was applied to prepare electrodes for impedance measurements. A platinum wire with 0.36 cm^2 surface area, fused into a glass holder, was used as a substrate in this case. Electrochemical cells also contained a copper anode and an Ag|AgCl|KCl(sat) reference electrode. In the case of impedance measurements, an additional electrode (platinum cylinder) was embedded for perturbation by alternating current. Electrode potentials were converted to the standard hydrogen scale. All experiments were performed at 20°C .

Voltammetric characteristics were recorded under forced convection conditions at a potential sweep rate $\nu = 5 \text{ mV s}^{-1}$ using a PI-50-1 potentiostat (Russia). It should be mentioned that a small background current was observed in Cu(II)-free solutions. It varied approximately linearly with the electrode potential E and accounted for $\sim 3\text{--}4\%$ of i_d at $E = -0.4 \text{ V}$. This current was eliminated from the experimental data obtained for respective Cu(II) containing solutions.

Impedance spectra were obtained within a frequency f range from 0.1 to 40 000 Hz 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 for analyzing the impedance data.

RESULTS AND DISCUSSION

According to the literature data cited above, PEGs of the general formula $\text{H}-(\text{CH}_2-\text{CH}_2-\text{O})_m-\text{H}$ exhibit a rather weak influence on Cu(II) reduction kinetics in chloride-free solutions. Experiments carried out with short PEG molecules ($m < 6$) have shown that halides are not able to enhance the inhibitive adsorption of PEG when it contains less than 3 etheral bonds. Thus, tetraethyleneglycol (TEG) is the initial potential surface-active substance in the homologous series of PEGs. The adsorption power of TEG depends on the nature of halide that enhances its adsorption. This may be seen from EIS data shown in Fig. 1: the effect of halides increases in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$ with a respective increase in the total electrode impedance. Chlorides influence mainly the real component Z' of impedance, whereas its imaginary part Z'' remains close to that obtained for chloride-free solutions.

An increase in surface activity of TEG in the presence of chlorides is also seen from voltammetric data (Fig. 2). This effect manifests itself as a certain increase in cathodic polarization that takes place on addition of TEG and does not clearly depend on the intensity of forced convection. Therefore, a certain generalization of experimental data

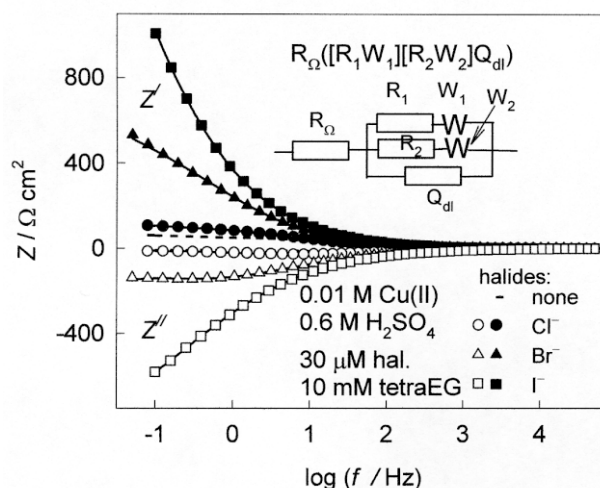


Fig. 1. Spectra of real (Z') and imaginary (Z'') components of electrode impedance obtained for solutions containing 0.01 M of Cu(II), 10 mM of tetraethyleneglycol and 30 μM of indicated halides. Experimental data (symbols) are compared with impedance spectra (lines) calculated for the given equivalent circuit

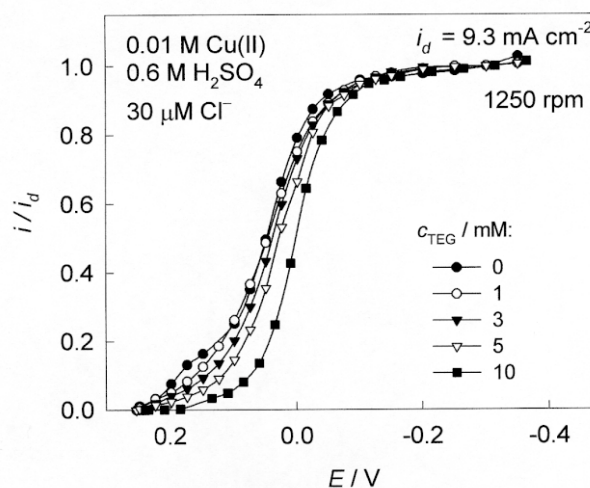


Fig. 2. Voltammograms normalized to the limiting current density, obtained at 1250 rev per min for 0.01 M Cu(II) solutions containing 30 μM of chloride and indicated amounts of tetraethyleneglycol

is possible: the voltammograms recorded at different rotating velocity of RDE but normalized with respect to the limiting current density (i_d) are positioned very closely, though they do not coincide completely. At the same time, the limiting current follows the Levich equation, which is indicative of its diffusive nature. The latter fact provides a way for an easy account of the surface concentration of Cu^{2+} ions (see below).

The quantitative analysis of voltammetric data is based on the following statements. Cu(II) reduction in acidic sulphate solutions is known to proceed by two one-electron transfers:





Both steps are characterized by respective exchange current densities (i_{01} and i_{02}) and cathodic charge transfer coefficients (α_{c1} and α_{c2}). It is also well known that the net process is controlled by step (1) and, therefore, $i_{01} \ll i_{02}$. Then the kinetic equation takes the form:

$$i = 2i_0 \left\{ \frac{[\text{Cu}^{2+}]_s}{[\text{Cu}^{2+}]_b} \exp\left(\frac{\alpha_{c1}F}{RT}\eta\right) - \exp\left(-\frac{(2-\alpha_{c1})F}{RT}\eta\right) \right\}, \quad (3)$$

where the surface concentration $[\text{Cu}^{2+}]_s$ is dependent on the cathodic current density i (or overvoltage η). To obtain linear Tafel plots, this concentration should be moved to the left side. In the case of diffusive limiting current, the ratio of surface and bulk concentrations of Cu^{2+} ions may be expressed as

$$\frac{[\text{Cu}^{2+}]_s}{[\text{Cu}^{2+}]_b} = 1 - \frac{i}{i_d}. \quad (4)$$

Then, the next relationship is valid for sufficiently high cathodic overvoltages:

$$\log \frac{i}{1-i/i_d} = \log 2i_{01} + \frac{\alpha_{c1}F}{2.303RT}\eta_c, \quad (5)$$

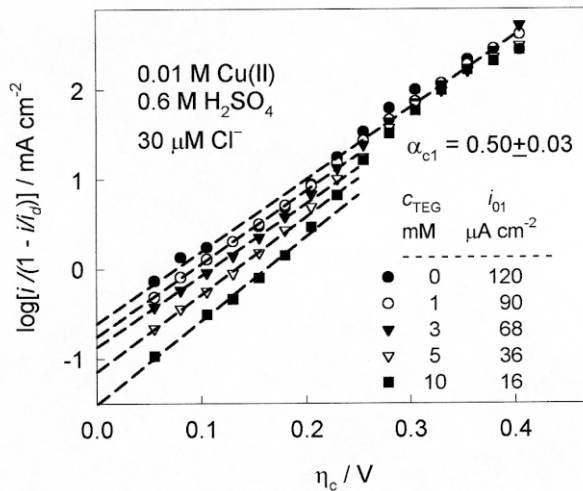


Fig. 3. Normalized Tafel plots obtained from the data in Fig. 2. The kinetic parameters were obtained from the linear regions of the plots (dashed lines)

The normalized Tafel plots constructed according to Eq. (5) are shown in Fig. 3. Transformed voltammetric data obtained for TEG-free solutions may be approximated by a line in a wide region of cathodic overvoltages (η_c). However, this region narrows when TEG is added, and then the linear part of the plots ranges up to $\eta_c \approx 0.25$ V ($E \approx 0$ V). The further increase of cathodic polarization results in a suppression of TEG action and the Tafel plots actually coincide at $\eta_c > 0.3$ V. Such a behaviour

could be conditioned by a certain destruction of the adsorption layer in which the desorption of Cl^- ions seems to play the main role.

According to [14], in the case of surface-inactive electrolytes, the zero charge potential E_{zc} varies from -0.26 to 0.15 V, depending on the method of measurement and experimental conditions. As a rule, E_{zc} established for mechanically renewed surfaces is substantially more negative [15]. Besides, in the case of sulphate solutions, it also depends on pH and becomes *ca.* 0.2 V higher when pH decreases from 6 to 1 [15]. Chlorides as well as other halides are known as surface-active anions exhibiting a specific adsorption on copper substrate and shifting E_{zc} to more negative values. This shift (ΔE_{zc}) also depends on halide concentration. A rough estimation of ΔE_{zc} caused by the specific adsorption of Cl^- and Br^- and based on the data reported in [15] yields *ca.* -0.02 and -0.07 V, respectively. The value of E_{zc} around 0 V [16–18] seems to be an acceptable quantity consistent with the conditions of the present investigation. Then, the expected value of the zero charge potential for chloride-containing solutions (*ca.* -0.02 V) corresponds to $\eta_c \approx 0.27$ V. It is exactly the overvoltage at which the onset of the desorption process occurs (see Fig. 3).

The regularities observed in bromide-containing solutions [12] are in accordance with the above propositions. Really, the desorption potential was accordingly more negative in this case ($E \approx -0.1$ V, $\eta_c \approx 0.35$ V). Besides, the established values of i_{01} were about 2.5 times lower as compared to the solutions involving chlorides. Iodides further enhance inhibition effects under open-circuit conditions, but cathodic voltammograms become more complicated [12] and their interpretation remains problematic.

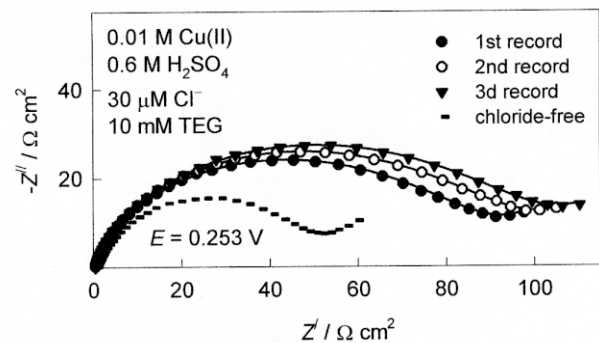


Fig. 4. Nyquist plots obtained for the solutions of indicated composition at different exposure times (τ): 10 min (the first record), 15 min (the second record) and 20 min (the third record). Experimental data (symbols) are compared with spectra (full lines) simulated for $R_{\Omega}([R_1W_1][R_2W_2]Q_{dl})$ equivalent circuit (see Table 1)

Some additional information on kinetic and double-layer parameters may be obtained from impedance measurements. The Nyquist plots (relations bet-

Table. Parameters of equivalent circuit $R_{\Omega}(Q_{dl} [R_1 W_1] [R_2 W_2])$ obtained for 0.01 M Cu(II) solutions containing 10 mM of TEG and indicated amounts of chloride. Electrodes were exposed to the solutions for time τ before measurements.

$R_{\Omega} = 0.44 \pm 0.02 \Omega \text{ cm}^2$. Dimensions: $[Y_0] = \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$, $[Y_{0w}] = \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$.

[Cl ⁻], μM	τ , min	Q_{dl} $10^6 Y_0$ n		R_1 , Ωcm^2	W_1 $10^2 Y_{0w}$	R_2 , Ωcm^2	W_2 $10^4 Y_{0w}$	i_{01} , $\mu\text{A cm}^{-2}$	i_{02} , mA cm^{-2}
0	20	178.0	0.839	51.6	9.55	6.54	7.233	89.4	4.22
30	10	97.36	0.873	94.2	11.61	30.01	8.808	34.7	1.06
30	15	98.50	0.870	102	10.89	31.32	8.622	33.1	1.01
30	20	99.78	0.867	108	10.21	30.61	8.447	32.4	1.02

ween real and imaginary components of the impedance) gain a shape of arcs centred below the abscissa axis (Fig. 4), which is typical of consecutive charge transfer. Experimental data can be described quantitatively using the equivalent circuit whose description code is $R_{\Omega}(Q_{dl} [R_1 W_1] [R_2 W_2])$ (see Fig. 1). It contains two parallel Faradaic subcircuits, each involving the charge transfer resistance R and Warburg impedance W in series. This set of elements is shunted with double-layer impedance, and finally an ohmic resistance of the solution R_{Ω} is added.

The established values of the electric analogues are listed in Table. The impedance spectra of this equivalent circuit coincides with experimental data with a frequency error less than 2%. It is necessary to note that the impedance data vary to a certain extent with exposure time (Fig. 4) and the main changes (an increase in the total impedance) occur over 10–15 min. An analysis shows (see Table) that the respective variations of charge transfer resistance R_1 are mainly responsible for this effect. We made an attempt to determine the exchange current densities using a relationships derived in [19]:

$$i_{01} + i_{02} = \frac{RT}{F} \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \quad (6)$$

$$\frac{1}{i_{01}} + \frac{1}{i_{02}} = \frac{R_1 + R_2}{W_1 + W_2} \frac{1}{F\sqrt{D}} \left(\frac{1}{[\text{Cu}^{2+}]} + \frac{4}{[\text{Cu}^+]} \right), \quad (7)$$

where the Warburg coefficients W_1 and W_2 are determined by the relationship:

$$Z_w = \frac{W(1-j)}{\sqrt{\omega}} \quad (8)$$

with $\omega = 2\pi f$, $j = \sqrt{-1}$ and $(Z_w)^{-1} = Y_{0w} \sqrt{j\omega}$.

The above equations are valid for ideally smooth electrodes under equilibrium conditions. In this connection, some comments on the possible errors should be given. Firstly, we used the equilibrium value of bulk concentration intermediate Cu^+ ions equal to 77 μM . However, no direct control for this quantity was available for us. Secondly, the

double layer impedance in the presence of surface-active substances is more complex than the constant phase element Q_{dl} and needs a respective specification. This is possible in the case of simpler systems, such as $\text{Sn} | \text{Sn(II)}$ [10], but not when the equivalent circuit contains too much elements. Therefore, the kinetic parameters given in Table should be treated as approximate quantities. Nevertheless, it might be stated that the main changes of the impedance originate from respective variations of the exchange current density i_{01} , whereas the rate of the second transfer (i_{02}) remains actually on the same level. It also follows from the impedance data that Q_{dl} considerably falls when Cl^- ions are added, this being indicative of an intensification of TEG adsorption.

The observed phenomena enable us to conclude that the adsorption layers are developed owing to the specific interactions between TEG, halides and copper ions. According to [20], the PEG chain is capable to wrap around a copper ion and to create six coordination bonds. In this way the so-called pseudo-crown complexes may be formed. Though the stability of such structures in water media has been questioned [1, 21], the existence of adsorbed pseudo-crowns seems to be quite probable due to the dehydration effects.

Some experimental facts give grounds to suppose that Cu^+ ions are preferable for such interactions. Firstly, an excess of TEG with respect to Cu^+ (but not to Cu^{2+}) ions was always maintained in the solutions under discussion. Secondly, a rather sluggish saturation of the surface layer with cuprous ions ($\text{Cu} + \text{Cu}^{2+} \rightarrow 2 \text{Cu}^+$) is attributable to the main factors responsible for a slow formation of the adsorption layer (see Fig. 4 and comments on it). Thirdly, a certain diminution of the open-circuit potential E_{oc} with the intensity of forced convection (rotation velocity of the electrode) was observed in the presence of TEG and halides [12]. Considering that $i_{02} \gg i_{01}$ and that the step (2) determines mainly the E_{oc} value (in accordance with the appropriate modification of Nernst equation), the observed effect might be counted in favour of the interaction between TEG and Cu^+ at the electrode surface.

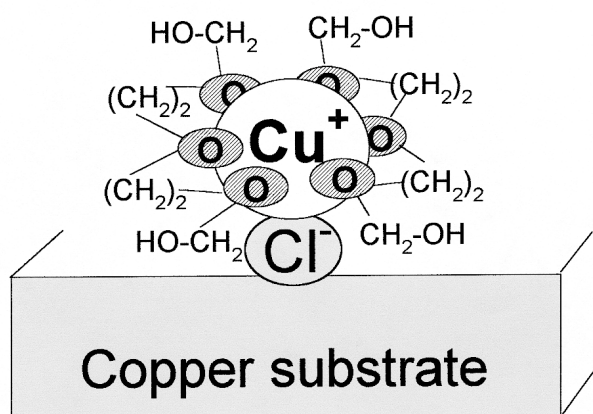


Fig. 5. Image of the structure of the adsorption layer

So, cuprous ions are able to impart positive charges to PEG, forming a pseudo-crown complex when the number of ethereal bonds is large enough. Then halide ions can act as the particles bridging pseudo-crowns with copper surface (Fig. 5). Cu^+ -O bonds can be destroyed at the certain cathodic polarizations with a release of Cu^+ and TEG and their following return to the bulk of solution.

CONCLUSIONS

1. Voltammetric and impedance investigations of Cu(II) reduction kinetics show that TEG is the shortest molecule among polyethyleneglycols capable to display the inhibitive adsorption on a copper substrate in the presence of halides.

2. It follows from the analysis of normalized Tafel plots that co-adsorption of TEG and Cl^- ions retards the transfer of the first electron to Cu^{2+} ion.

3. A possible structure of adsorption layer is proposed, in which chloride ions act as the particles bonding the copper surface with pseudo-crowns involving Cu^+ and TEG.

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Cu(II) ELEKTROREDUKCIJOS KINETIKA RŪGĖIUOSE SULFATŲ TIRPALUOSE SU TETRAETILENGLIKOLIŲ IR NEDIDELIAIS CHLORIDŲ KIEKIAIS

Santrauka

Voltamperometrijos ir elektrocheminio impedanso spektroskopijos metodais ištirta tetraetilenglikolio (TEG) ėaka Cu(II) redukcijos kinetikai, esant mikromoliniams chlorido jonŲ kiekiams. Nustatyta, kad TEG yra trumpiausia molekulė tarp polietilenglikoliŲ, kuri pasiŲymi inhibicine adsorbicija ant vario padėklo, esant halogenidŲ. SunormintŲ Tafelio priklausomybiŲ analizė rodo, kad TEG daugiausia slopina pirmojo elektrono perneðimà ė Cu^{2+} jonà. PasiŲlyta galima struktūra adsorbicinio sluoksnio, kuriame chlorido jonai veikia kaip dalelės, riðanėios vario pavirðiŲ su pseudokraunais, sudarytais ė Cu^+ ir TEG.