J Appl Electrochem (2011) 41:713–719
DOI 10.1007/s10800-011-0285-0

ORIGINAL PAPER

Impedance studies of copper electro-reduction on a disc-shaped ultramicroelectrode in industrial electrolytes

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Received: 27 January 2011 / Accepted: 7 March 2011 / Published online: 22 March 2011

Abstract The electrodeposition of copper from industrial sulphate electrolytes has been studied using electrochemical impedance spectroscopy on the gold disc ultramicroelectrode. The influence of dc potential E_{dc}, temperature, cupric ions and animal glue concentration on electrochemical impedances has been investigated. The mechanism of the copper electro-reduction process in industrial electrolytes has been proposed and experimental impedance data have been analyzed by proper equivalent circuits. According to our knowledge the faradaic and non-faradaic impedance parameters of the process on ultramicroelectrode's have been estimated for the first time in complex matrix copper industrial electrolytes. The role of animal glue in copper industrial electrolytes has been discussed in the present paper.

Keywords Industrial electro-refining · Animal glue · Impedance · Ultramicroelectrodes

1 Introduction

Since electrolysis is widely applied in copper refineries and the electronic industry, there has been a large number of publications concerning the mechanism and kinetics studies of copper electro-reduction. However, a detailed mechanism of the process has not been established. One of the methods to analyze the elementary steps of metal electrodeposition [1] is Electrochemical Impedance Spectroscopy [2]. By combining EIS technique with ultramicroelectrodes a promising and broadly applicable tool has been created to investigate the mechanisms and kinetics of electrode reactions [3]. The term "ultramicroeletrode" describes an electrode the size of which is decreased to micrometer scale [4–6] and thus the critical dimension of the UME is smaller than the diffusion layer.

Copper electrodeposition in an acidic bath has been investigated in the current study using the EIS method. In our previous studies, a mechanism of copper electrocrystallization was studied using chronoamperometry and cyclic voltammetry on the ultramicroelectrodes in concentrated industrial and laboratory prepared electrolytes [7–14]. One of the key parameters of the industrial copper electrorefining process has been the concentration of the active animal glue in the electrolyte. In the past we used the EIS method in industrial electrolytes for analytical purposes as an indirect method of active animal glue detection [7, 14].

It should be added that in general there are not many experimental electrochemical studies concerning either concentrated or complex matrix industrial electrolytes. These studies are important because the relationships governing thermodynamic and electrochemical properties of the concentrated electrolytes are in general non-linear and the kinetic effects are not additive in many cases. Consequently, extrapolation of the electrochemical behaviour of the concentrated electrolytes from the results obtained in diluted electrolytes is very difficult. Therefore, we believe that despite the experimental difficulties, the measurements in industrial electrolytes can be a source of very important information concerning both the fundamental research and the industrial process which is quite often carried out

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largely in accordance with empirically established rules and conditions.

There have been a large number of published ac impedance studies concerning copper electrodeposition [1, 15–23], but the majority of these papers concern electrolytes prepared in a laboratory and often copper ion concentrations were relatively low. The mechanisms of copper ion reduction proposed in the literature have been different depending on the experimental parameters and especially the electrolyte composition. There were several processes discussed in the published papers: electron transfers, adsorptions of reactants, products and intermediates as well as mass transport from the solution and surface diffusion. Also likely pathways for copper electrodeposition in presence and in absence of Cl^- as additive agent are proposed [16–19]. These interactions influence the kinetics of copper electrodeposition and in fact complex composition of industrial electrolytes obviously makes the interpretation of all processes more difficult. The knowledge concerning relatively diluted simulated electrolytes might not be sufficient for the investigation of real concentrated tank house solution. These electrodeposition steps (ion transport, adsorption, nucleation, crystal growth and charge transfers) might be sensitive to electrolyte composition especially in the case of the presence of inhibiting molecules, e.g. animal glue. It is known that animal glue is a hydrolysis product of animal tissue collagen and its average molar mass is in the range of 10,000–250,000 g mol^{-1}. Neither collagen protein interactions in water are established completely nor the interactions between adsorbed glue molecules and copper surface. Animal glue is hydrolyzed by acid and is incorporated into copper deposit during electro reduction. It is assumed that positively charged proteins are attracted by negatively charged cathode and there is a change in viscosity of double layer [24]. Smoothing action of animal glue consists in its adsorption on copper nucleus. Animal glue layer inhibits too extensive growth of copper crystals and it is used in concentration range of 1–10 ppm [25]. The chemical and physical properties of animal glues used in the electrorefining process and their water solutions/suspensions are given in paper [24]. Additionally the effects of temperature, thiourea, Cl^- and Cu^{2+} ions on animal glue degradation are presented in the same paper. The recommended procedures of preparing glue solution involve glue soaking at room temperature followed by heating to about 50 °C.

The main aim of this paper is to investigate the influence of animal glue concentration and potential E_{dc}, temperature as well as the concentration of cupric ions on the electrochemical impedances using original complex electrolytes coming from a copper tank house. To our knowledge our study is the first systematic analysis of EIS data using such electrolytes. Knowledge of these relations could bring about better understanding of the mechanism of copper deposition in a sulphate bath used in a copper refinery.

2 Experimental

The ac impedance results were recorded from 200 kHz to 0.5 Hz and the sinusoidal wave of 10 mV amplitude was applied. The frequency response analyzer (FRA) was a module of the AUTOLAB GSTST30 system (Eco Chemie), and Frequency Response Analyzer version 2.4 Software was used for data acquisition.

The measurements for different E_{dc} potentials and temperatures were carried out in a two-electrode system. A gold disc UME of 25 μm diameter was used as a working electrode. The 0.3 cm^2 copper plate was used as an auxiliary electrode. A copper sulphate solution containing 44.3 g dm^{-3} cupric ions was supplied by Nordeutsche Affinerie (currently Aurubis) Hamburg, Germany.

One of the most important factors determining the kinetics and mechanism of copper electro-reduction is a type of the copper base. In our previous studies we used different UME materials such as gold, platinum and stainless steel [11]. In the present study we selected gold UME because it is characterized by the strongest interactions with deposited copper which leads e.g. to the application of gold to the stripping analysis of copper at room temperature [26].

The measurements for different cupric ions and animal glue concentrations were carried out in a three-electrode system with a saturated calomel electrode SCE as a reference electrode, 0.3 cm^2 platinum plate as an auxiliary electrode and a gold disc UME (25 μm diameter) as a working electrode. KGHM S.A. Glogow (Poland) industrial copper sulphate solutions containing 36.4–51.9 g dm^{-3} cupric ions were used. The other components of the electrolytes were 170–200 g dm^{-3} H_2SO_4, and 0.02–0.05 g dm^{-3} Cl^-; the electrolyte contains numerous impurities (e.g. 25 g dm^{-3} Ni, 20 g dm^{-3} As, 2 g dm^{-3} Fe, 0.7 g dm^{-3} Sb, 0.6 g dm^{-3} Bi) and also 1–10 parts per million of leveling and grain-refining agents (e.g. animal glue and thiourea). When influence of temperature, animal glue and cupric ion concentrations were investigated, potentials E_{dc} −130 mV (vs. copper electrode), −60 and −50 mV (vs. SCE electrode) were applied, respectively. It is claimed that under such experimental conditions dissolution of deposited copper in gold [26] on ultramicroelectrode's surface took place enabling to keep constant electrochemical surface area of UME during EIS measurements.

In order to study the influence of animal glue on the copper electrodeposition process it was removed from the industrial electrolyte by heating the electrolyte for 4 h.

The animal glue removal procedure was presented in our previous paper [8]. When the influence of the leveling agents' concentrations were studied, fresh portions of them were added. Animal glue manufactured by Smits Vuren B.V (Netherlands) was used. The same product was used in the industrial copper electro-refining process.

The ultramicroelectrodes were mechanically polished with wet alumina powder before each measurement. The estimate of the equivalent circuit's parameters was made using the Levenberg–Marquardt algorithm (LMA), i.e. non-linear least squares routine [27], was implemented in MATLAB.

3 Results and discussion

In general, EIS results depend on both the faradaic and non-faradaic parameters of the studied system. Nyquist plots were obtained for different dc potentials, E_{dc} (Fig. 1) and temperatures (Fig. 2). The complex plane plots show only one semicircle: either well-defined or depressed/distorted one. The second small distorted semicircle is observed in the low frequency range when animal glue concentration increases (Fig. 3) or Cu^{2+} ion (Fig. 4) concentration decreases. There are two different aspects of this small distorted semicircle. At the lowest frequency range an inductive loop is observed, which according to the literature, is difficult to assess [17]. In Gabrielli's paper [17] it is attributed to "the adsorption–desorption of inhibiting species, e.g. anions, or to a nucleation process on the facets of the copper crystallites, which, both give rise to the relaxation of the surface area with potential." In our paper we assumed that the second distorted semicircle is related to the second step of copper deposition described by Eq. (5). Similarly, Reid [15] suggested that low frequency semicircle related to this fast reaction was surface-diffusion controlled. The concentrations of Cu^{2+} and Cu^{+} ions in the reaction layer close to the electrode are related by the equilibrium constant of disproportionation reaction [28]. Taking into account the equilibrium constant it is clear that decreasing Cu^{2+} ion concentration, the concentration of Cu^{+} ions decreases. Since the second reaction step depends on the concentration of Cu^{+} and its diffusion [15] it is more pronounced when the Cu^{2+} ion concentration decreases.

The equivalent circuit used to analyze experimental EIS data for one semicircle is shown in Fig. 5 (solid line). In this case the faradaic impedance Z is given by the Eq. (1) [29]:

$$Z(f) = R_z + \frac{1}{\frac{1}{R_{ct1}} + (2\pi fi)^{CPA} \cdot Q_1} \tag{1}$$

where R_z solution resistance, CPA constant phase angle, R_{ct1} charge transfer resistance of the process described by Eq. (4), Q_1 capacitance constant phase element (CPE) parameter, f frequency.

The equivalent circuit applied to fit experimental EIS data for two semicircles is shown in Fig. 5 (solid and dotted lines). The faradaic impedance Z is then given by the following equation:

$$Z(f) = R_z + \frac{1}{\frac{1}{R_{ct1}} + (2\pi fi)^{CPA} \cdot Q_1} + \frac{1}{\frac{1}{R_2} + 2\pi fi \cdot C_2 + \frac{1}{2\pi fi \cdot L_k}} \tag{2}$$

where Q_1 capacitance constant phase elements (CPE) parameters, R_2, L_k and C_2 resistance, inductance and capacitance, respectively, related to the new, copper phase creation on the gold UME surface.

The CPE semi-empirical parameters [30, 31] were used to describe the capacitance Q_1, which has been equal to the double layer capacitance, C_{dl} when CPA = 1. According to theory [29, 30, 32] when the distributed double layer capacitance is coupled with charge transfer resistance its value can be estimated from the following equation:

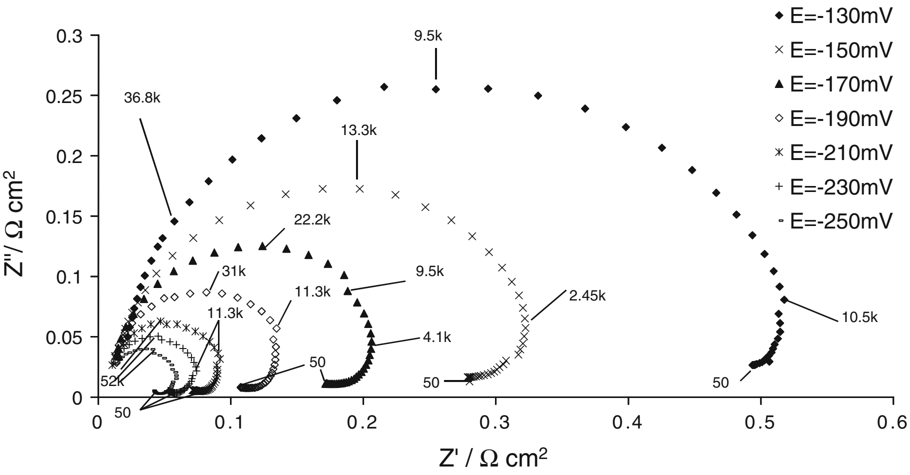

Fig. 1 Complex plane EIS plots obtained at different E_{dc} (vs. copper) in tank house electrolyte containing 44.3 g dm^{-3} Cu^{2+}, at temperature 22 °C, using a gold disc UME of diameter 25 µm. Frequencies in Hz

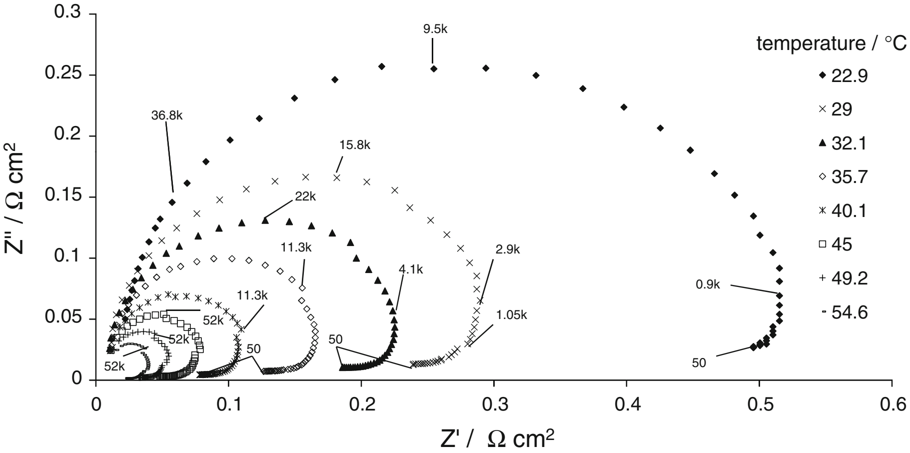

Fig. 2 Complex plane EIS plots obtained at different temperatures and $E_{dc} = -130$ mV (vs. copper) in tank house electrolyte containing 44.3 g dm^{-3} Cu^{2+}, using a gold disc UME of diameter 25 µm and frequencies in Hz

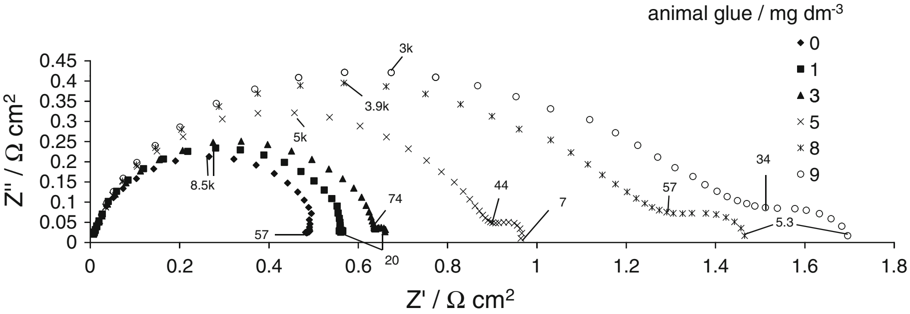

Fig. 3 Complex plane EIS plots obtained at different animal glue concentrations in tank house electrolytes containing 51.9 g dm^{-3} Cu^{2+}, at temperature 23.3 °C and $E_{dc} = -60$ mV (vs. SCE) using a gold disc UME of diameter 25 µm. Frequencies in Hz

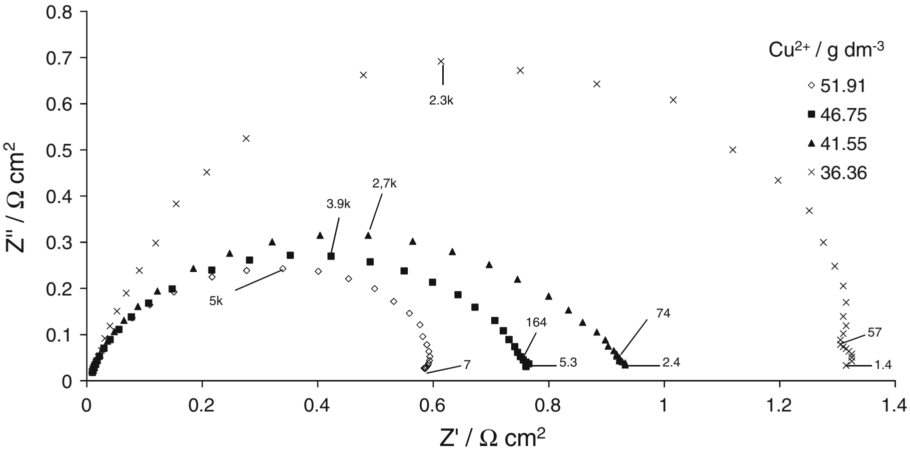

Fig. 4 Complex plane EIS plots obtained in tank house electrolytes containing different Cu^{2+} concentrations, at temperature 23.3 °C and $E_{dc} = -50$ mV (vs. SCE) using a gold disc UME of diameter 25 µm. Frequencies in Hz

$$C_{dl} = Q_1^{\frac{1}{CPA}}\left[\frac{1}{Rz}+\frac{1}{Rct}\right]^{\frac{CPA-1}{CPA}} \qquad (3)$$

Theoretically, the dimensionless constant phase angle CPA changes in the range of 0–1. The equivalent circuit represented in Fig. 5 by dotted and solid lines was proposed by Bai and Conway [2, 33] for a two-step electrode reaction involving one adsorbed species. The approximations of EIS results were made for the electrolytes containing 0–9 mg dm^{-3} of animal glue (Fig. 3). The EIS experimental data fitting the parameters are presented in Table 1. The solution resistance parameter R_z was fixed at 5×10^{-4} Ω cm^2 in all cases. For electrolytes containing 0 and 1 mg dm^{-3} of animal glue, one semicircle was observed and the average double layer capacitance, C_{dl} of 2.21×10^{-5} F cm^{-2} was estimated from the Eq. (3). This value is very close to the data [15, 34] given for concentrated laboratory-prepared copper ion electrolytes. It is interesting to note that the estimated value of the double layer capacitance in a concentrated,

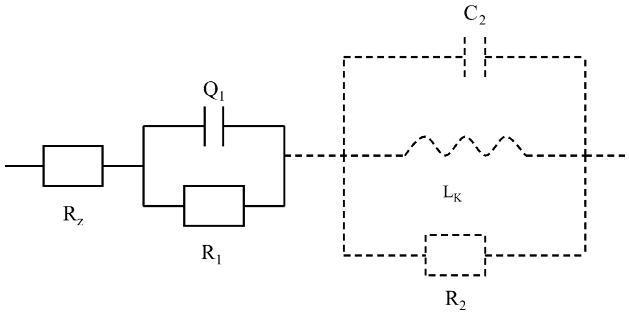

Fig. 5 Equivalent circuits used to fit experimental EIS data in the case of one semicircle at Nyquist plot (*solid line*) and in the case of two semicircles (*solid* and *dotted lines*)

complex matrix electrolyte is very similar to that of diluted electrolytes.

Cathodic deposition of copper consists of two consecutive charge transfer steps [18, 20, 21]:

$$Cu^{2+} + e^{-} \leftrightarrow Cu^{+} \qquad (4)$$

$$Cu^{+} + e^{-} \leftrightarrow Cu^{o} \qquad (5)$$

where reaction Eq. (4) is a rate-determining step while the second process Eq. (5) is considered to be the fast one. The presence in the electrolyte of organic and inorganic additives increases the complexity of the copper deposition system. For example, it has been claimed that the kinetics of reactions (4) and (5) have been influenced by chloride ions due to the complex formation and adsorption of copper chloride on copper surfaces [16, 17]. Furthermore, it has been stated that animal glue has acted as an inhibitor, and due to its adsorption the electrode surface was modified [24, 35].

The first semicircle that we observed at Nyquist plots and registered in our studies could be attributed to one electron charge transfer step presented in Eq. (4). The more negative dc potential (E_{dc}) has been applied, the smaller radius of the first semi-circle was observed (Fig. 1). The relationship between charge transfer resistance (R_{ct1}) and the standard heterogeneous rate constant k_s, as a function of the applied dc potential E_{dc}, is generally described by the following equation [29]:

$$R_{ct} = \left(RT/n^2F^2k_s\right)\mathrm{V}(E_{dc}) \qquad (6)$$

where i_o exchange current densities, R gas constant, T temperature, F Faraday constant, $\mathrm{V}(E_{dc})$ a function of the applied potential E_{dc}, and charge transfer kinetic parameters [29], $n = 1$ number of electrons.

Using the above equation the value of $k_s = 6.3 \times 10^{-4}$ cm s^{-1} was calculated for data presented in Table 1 for 0 mg of added animal glue. This value is very close to the value of $k_s = 8.8 \times 10^{-4}$ cm s^{-1} [36] in diluted Cu(II) and laboratory prepared electrolytes. Lower values were presented in papers [15, 28].

Increasing the temperature to 55 °C considerably accelerated the copper electro-reduction kinetics (Fig. 2). Furthermore, when the electrolyte was boiled for 4 h, active animal glue concentration was decreased and R_{ct} decreased. This fact confirms the necessity of regular additions and on-line control of a fresh quantity of animal glue during the industrial electrorefining [7, 14]. Acid hydrolyzed animal glue and for the hydrolysis products of molar mass below approximately 10000 g × mol^{-1}, animal glue was not able to act as leveling agent and did not ensure a smooth copper deposit [24].

From our study it can be concluded that in fact animal glue acted as an inhibitor of copper electrodeposition. The increase in the glue concentration increases the charge transfer resistance R_{ct1}. The EIS results presented here show that there is a threshold of animal glue concentration of 3 mg dm^{-3} above which the mechanism of the process changes mostly due to the influence of the adsorbed animal glue on the copper nucleation process. In the first place, the small semicircle was registered when animal glue concentration was higher than 3 mg dm^{-3}. The appearance of the second, distorted semicircle might be explained by the processes of one-electron reduction Eq. (5) as well as surface diffusion of the Cu^{o} ad-atoms to copper crystals during the nucleation process:

$$Cu_{ad-atom} \rightarrow Cu_{nucleus} \qquad (7)$$

Additionally, the lowest values of CPA presented in Table 1 are registered for the animal glue concentration of 3 mg dm^{-3}. The low value of semi-empirical CPA suggests

Table 1 Parameters used for fitting the EIS data presented in Fig. 3

C_{glue} /mg dm^{-3}	R_{ct1} /Ω cm^2	Q_1 /10^{-4} F cm^{-2} s$^{\mathrm{CPA}-1}$	L_k /10^3H	R_2 /Ω cm^2	C_2 /F cm^{-2}	CPA
0	0.52	1.63	–	–	–	0.88
1	0.56	1.63	–	–	–	0.90
3	0.64	3.46	0.59	0.025	0.14	0.82
5	0.91	8.38	0.30	0.059	0.22	0.77
8	1.28	1.04	2.14	0.20	0.17	0.74
9	1.47	1.68	3.00	0.24	0.20	0.70

Solution resistance, R_z was a fixed parameter (5×10^{-4}/Ω cm^2)

strong adsorption of animal glue. Further evidence for such a threshold of animal glue concentration was found in our previous paper [8]. When glue concentration was higher than 3 mg dm^{-3} at 50–60 °C the chronoamperometric rate AN_∞ was higher than in the case of absence of leveling agent. Consequently, when glue concentration is higher than 3 mg dm^{-3} in the industrial electrolyte, animal glue can have catalytic effect rather than inhibiting on the copper electrocrystallization process. Finally, the results of our previous chronoamperometric studies suggested that the presence of leveling agent cannot change the nucleation mechanism but it influences the nucleation rate.

Consequently, the parameter R_2 could not be unequivocally interpreted as charge transfer resistance R_{ct2} of the second reduction step Eq. (5) (see Table 1, Fig. 3). The main reason was that it was not possible to separate the two simultaneous processes: one electron electro-reduction of Cu^+ to Cu^o and adsorption and crystallization of copper atoms. The addition of animal glue inhibited the rate of the first charge transfer step reaction Eq. (4) due to the adsorption of animal glue on the electrode surface. The second step represented by Eq. (5) was influenced by the presence of animal glue mostly in the process of the new copper-phase growth and formation on the gold UME base. The surface animal-glue concentration Γ_{glue} is in general a function of animal glue concentration in bulk solution C_{glue}:

$$\Gamma_{glue} = \gamma_{glue} \cdot f(C_{glue}) \tag{8}$$

where $\mathit{\Gamma}_{glue}$ is a coefficient of surface animal-glue concentration.

Function f(C_{glue}) depends on the animal-glue adsorption isotherm that is valid for the given experimental conditions. Adsorbed animal glue (quantified by Γ_{glue}) has the ability to block the surface at the sites where copper electro-reduction takes place. This might be the reason why the higher charge transfer resistance R_{ct1} was observed for the higher animal-glue concentration. The values of the adsorption parameters R_2 and L_k increased when the concentration of animal glue increased. The model discussed here was also confirmed by the systematic decrease of the calculated CPA values (Table 1) with the addition of animal glue. In accordance with theory [29, 31, 32], the decrease of the CPA's values (see Table 1) indicates increasing physical inhomogeneity of the electrode surface due to the increased concentration, Γ_{glue} of the adsorbed animal glue.

The influence of the Cu^{2+} ion concentration on the kinetic parameters conforms well to the general theory of charge transfer. The higher the Cu^{2+} ion concentration, the faster was the first electro-reduction step (Eq. 4) and charge transfer resistance R_{ct1} is lower (see Fig. 4).

4 Conclusions

The ac impedance method on the ultramicroeletrodes is a very effective method to study the kinetics and mechanism of the copper electro-reduction process in industrial electrolytes. The experimental EIS kinetic parameters of copper electrodeposition in a complex matrix industrial refinery electrolytes are the function of temperature, copper ion and animal glue concentrations. As far as we know the current study is the first attempt to carry out a systematic EIS investigation of faradaic and non-faradaic parameters of copper reduction in industrial refinery electrolytes on UME. The experimental relationships between charge transfer resistance and temperature, and between copper concentration and dc potential are in good qualitative agreement with the theory. It is interesting to note that both the double layer capacitance, $C_{dl} = 2.21 \times 10^{-5}$ F cm^{-2} and the standard heterogeneous rate constant, $k_s = 6.3 \times 10^{-4}$ cm s^{-1} of the first step of cupric ion reduction are very similar to the published data obtained in diluted copper electrolytes. The EIS results presented here show that there is a threshold of animal glue concentration of 3 mg dm^{-3} above which the mechanism of the process changes mostly due to the influence of the adsorbed animal glue on copper nucleation process. Consequently, our results confirm the empirically established limit of 1–2 mg dm^{-3} of active animal glue used in the copper electrorefining industry.

Acknowledgments We are grateful to Dr M. Masalski for software development and to KGHM S.A. and Nordeutsche Affinerie (currentlyAurubis) for supporting in the past this work.

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