Modelling and Parameter Identification of Electrochemical Cu-Cu Cell

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Abstract: An electrochemical cell consisting of two copper electrodes and copper sulphate solutions is modeled. The presented model takes into account both electrode interfaces and the activity of copper(II) ions. The current-potential equation is derived and a method for identifying mass-transfer parameters as well as kinetic parameters is proposed for a specific case. The created model is simulated and verified against measurements.

Keywords: electrochemical cell modelling, electrode kinetics, parameter identification

1. INTRODUCTION

An electrochemical system includes two electrodes. When analyzed, the other electrode, where the chemical reaction of interest occurs, is called the working electrode (WE) and, the other that completes the electric circuit, the auxiliary electrode (AUX). Typically, voltammetric studies discuss only the working electrode and reactions on it, without considering the auxiliary electrode and processes occurring there. This is reasonable when areas of the electrodes differ significantly and the electric conductivity of the electrolyte so good that the ohmic voltage drop can be neglected. The current density on a large electrode is small and therefore the overpotential there practically does not change. Thus the potential of a large auxiliary electrode can be assumed zero and the potential of the working electrode is approximately equal to the voltage applied over the cell. In practical cases the auxiliary electrode is an essential part of the system and its area, material and corresponding electrochemical reactions affect on the overall behaviour of the electrochemical cell. Thus a model, which considers both electrodes, is required for a detailed study of an electrochemical system.

2. BACKGROUND

The basic relation between the cell current and the voltage applied for the electrode reaction $O + ne \rightleftarrows R$, where both oxidized (O) and reduced (R) species are soluble in the solution, is given by the current-overpotential equation (Bard and Faulkner, 2001) as

$$I_e = I_{e,0} \left[\frac{c_R(0,t)}{c_R^b} e^{k\alpha_{e,a}\eta_e} - \frac{c_O(0,t)}{c_O^b} e^{-k\alpha_{e,c}\eta_e} \right], \quad (1)$$

where I_e – total cell current ($I_e = I$), A, $I_{e,0}$ – exchange current (constant), A, c_O – concentration of oxidized species, mol/m³, c_R – concentration of reduced species, mol/m³, c_O^b, c_R^b – bulk concentration of species, mol/m³, $\alpha_{e,a}$ – anodic apparent transfer coefficient, dim. less, $\alpha_{e,c}$ – cathodic apparent transfer coefficient, dim. less, η_e – surface overpotential of electrode, V, k – temperature voltage, $k=nF/RT$, V⁻¹, n – number of electrons, dim. less, F – Faraday's constant, 96485 A·s/mol, R – ideal gas constant, 8.314 J/(mol·K), T – absolute temperature, K. The subscript e denotes the electrode in question: WE or AUX.

Often the reaction in question is considered to be of first order, meaning that the reaction rate is assumed linearly proportional to the species' concentration.

ASSUMPTION A1. The reaction rate is linearly proportional to the reacting species' concentration at the reaction interface.

Surface overpotential of electrode e is defined as in (2):

$$\eta_e = \phi_e - \phi_{e,eq}, \quad (2)$$

where ϕ_e – electrode potential with external EMF applied, V, and $\phi_{e,eq}$ – electrode potential in equilibrium, V.

The electromotive force (EMF) is the algebraic sum of the electrode potentials and ohmic voltage drop in the cell

$$E = \phi_{WE} - \phi_{AUX} + IR. \quad (3)$$

ASSUMPTION A2. If the auxiliary electrode area is large enough ($A_{AUX} \gg A_{WE}$) one can assume that $\phi_{AUX} = 0$.

ASSUMPTION A3. The ohmic voltage drop in the cell is insignificant.

Following A1 concentration enters (1) linearly. From A2 and A3 follows $\phi_{WE}=E$ and that the current-overpotential equation (1) can be written in terms of EMF rather than potentials:

$$I_e = I_{e,0} \left[\frac{c_R(0,t)}{c_R^b} e^{k\alpha_{e,a}(E-E_{eq})} - \frac{c_O(0,t)}{c_O^b} e^{-k\alpha_{e,c}(E-E_{eq})} \right]. \quad (4)$$

Equation (4) underlies a numerical means for computing the current-potential curve as well as for identifying the mass-transfer parameters and kinetic parameters for the reversible, totally irreversible, and quasi-reversible electrochemical reactions as both species are soluble in the solution (Bard and Faulkner, 2001).

In case of metal deposition (reduced species are not soluble in the solution) (4) takes the form

$$I_e = I_{e,0}\left[a_M e^{k\alpha_{e,a}(E-E_{eq})} - \frac{c_O(0,t)}{c_O^b}e^{-k\alpha_{e,c}(E-E_{eq})}\right], \quad (5)$$

where a_M is the activity of a metal at the electrode surface (White and Lawson, 1970).

The benefit of equations (4)-(5) and, thus, the motives for the assumptions A1-A3 is that together with a linear, diffusion-controlled concentration model at the cathode surface and sweep form of the applied voltage, it leads to a linear, first order Volterra integral equation, which can be tabulated and utilized under any experimental conditions (Bard and Faulkner, 2001; Nicholson, 1965). Particularly current-potential equation for the irreversible reactions is given by (6)

$$I_e = -I_{e,0}\frac{c_O(0,t)}{c_O^b}e^{-k\alpha_{e,c}(E-E_{eq})}, \quad (6)$$

and corresponding integral equation is

$$\int_0^{bt}\frac{\chi(z)}{\sqrt{bt-z}}dz = 1-\chi(bt)e^{u-bt}, \quad (7)$$

where χ stands for dimensionless current function, bt is dimensionless voltage and u is parameter, that depends on kinetic and mass-transfer parameters and sweep rate. The properties of (7) are well documented in the literature (Bard and Faulkner, 2001; Nicholson and Shain, 1964) and enable to estimate the mass-transfer parameters and kinetic parameters of the electrochemical cell.

The method limitations also follow the assumptions A1-A3. Assumption A1 is reasonable only in dilute solutions, where the ion activity coefficient is close to unity and, thus, concentrations can be applied instead of activities. Generally, the ion activity coefficient dependence on concentration is nonlinear (Lide, 2006). Assumption A2 again is valid only when the electrode areas differ significantly. However, there are industrial systems with electrodes of essentially the same area. Assumption A3 assumes good enough conductivity of the solution (which requires a concentrated electrolyte, thus contradicting with A1) or perfect compensation of the voltage drop.

3. ELECTROCHEMICAL CU-CU CELL MODEL

When some of the assumptions A1-A3 fail, activity coefficients, overpotentials and voltage drop have to be taken into consideration in order to obtain a proper current-potential curve.

3.1 Electrode kinetics model

Consider an industrial Cu-Cu plating system which consists of two planar copper electrodes. In this system essentially the same reaction occurs on both electrodes, regardless of cell voltage polarity:

$$Cu^{2+} + 2e^- \rightleftarrows Cu. \quad (8)$$

Copper ions will be produced at the anode, while copper is deposited at the cathode. Assume A3 and start from electrode current densities

$$i_e = i_{e,0}\left[a_M e^{k\alpha_{e,a}\eta_e} - \frac{a_{e,c}(0,t)}{a_{e,c}^b}e^{-k\alpha_{e,c}\eta_e}\right], \quad (9)$$

where $i_{e,0}$ is the exchange current density A/m^2, $a_{e,c}$ and $a_{e,c}^b$ are activities of the copper(II) ions at the electrode surface and at the bulk concentration, dimensionless. The apparent transfer coefficients and exchange current densities for both electrodes are assumed equal, because material of the electrodes (copper) and the electrode reactions are essentially the same (but opposite in direction) $\alpha_{AUX,a}=\alpha_{WE,a}=\alpha_a$, $\alpha_{AUX,c}=\alpha_{WE,c}=\alpha_c$, $i_{AUX,0}=i_{WE,0}=i_0$.

Equations (9) involve electrode overpotentials, which can be calculated upon (2) when the electrode potentials and the electrode equilibrium potentials are known. The equilibrium potentials are given by the Nernst equation:

$$\phi_{e,eq} = U_e + k^{-1}\ln\frac{a_{e,c}^b}{a_M}, \quad (10)$$

where U_e refers to the reaction standard equilibrium potential equal for (8) to 0.337 V vs. standard hydrogen electrode.

The current densities are coupled by the total cell current and the electrode areas:

$$A_{AUX}i_{AUX} + A_{WE}i_{WE} = 0. \quad (11)$$

Equation (11) enables to calculate numerically the electrode overpotentials and the electrode current densities when activity of copper(II) ions is known. Furthermore, for them approximate analytical expressions can be derived for a specific case. Indeed, if it can be assumed that $A_{WE} \approx A_{AUX}$ the electrode current densities can be approximated by a single-directional model, which is valid if large cell voltage is applied.

With a negative applied cell voltage ($\phi_{WE}<\phi_{AUX}$, WE cathode, AUX anode) the electrode current densities can be approximated by a single-directional model

$$i_{AUX} = i_0 a_M e^{k\alpha_a\eta_{AUX}}, \quad i_{WE} = -i_0\frac{a_{WE,c}(0,t)}{a_{WE,c}^b}e^{-k\alpha_c\eta_{WE}}. \quad (12)$$

By substituting (2) into (12) and then (12) into (11) we obtain

$$A_{AUX}i_0 a_M e^{k\alpha_a(\phi_{AUX}-\phi_{AUX,eq})}$$
$$-A_{WE}i_0\frac{a_{WE,c}(0,t)}{a_{WE,c}^b}e^{-k\alpha_c(\phi_{WE}-\phi_{WE,eq})} = 0. \quad (13)$$

Due to the assumption that $A_{WE} \approx A_{AUX}$, electrode areas ratio $k_A = A_{AUX}/A_{WE}$ equal to 1. The activity of a metal deposited on an electrode made of the same metal is unity and thus $a_M=1$.

Then based on the EMF definition (3) and still assuming A3 equation (13) can be solved for electrode potentials:

$$\phi_{AUX} = \frac{\alpha_a \phi_{AUX,eq} + \alpha_c \phi_{WE,eq}}{\alpha_a + \alpha_c} - \frac{\alpha_c E - k^{-1} \ln\left(a_{WE,c} / a_{WE,c}^b\right)}{\alpha_a + \alpha_c}, \quad (14)$$

$$\phi_{WE} = \frac{\alpha_a \phi_{AUX,eq} + \alpha_c \phi_{WE,eq}}{\alpha_a + \alpha_c} + \frac{\alpha_a E + k^{-1} \ln\left(a_{WE,c} / a_{WE,c}^b\right)}{\alpha_a + \alpha_c}. \quad (15)$$

Substituting equations (14) and (15) into (2), an approximation for electrode overpotentials is obtained, which is valid if large negative cell voltage is applied

$$\eta_{WE} = \frac{\alpha_a E}{\alpha_a + \alpha_c} + \frac{k^{-1} \ln\left(a_{WE,c} / a_{WE,c}^b\right)}{\alpha_a + \alpha_c}, \quad (16)$$

$$\eta_{AUX} = -\frac{\alpha_c E}{\alpha_a + \alpha_c} + \frac{k^{-1} \ln\left(a_{WE,c} / a_{WE,c}^b\right)}{\alpha_a + \alpha_c}. \quad (17)$$

An approximation of WE current density can be obtained by substituting equation (16) into (12)

$$i_{WE} = -i_0 \left(\frac{a_{WE,c}(0,t)}{a_{WE,c}^b} \right)^{\frac{\alpha_a}{\alpha_a + \alpha_c}} e^{-\frac{k \alpha_a \alpha_c}{\alpha_a + \alpha_c} E}. \quad (18)$$

By applying equation (11), knowing WE current density (18) and taking into account that $k_A = 1$ we obtain AUX current density

$$i_{AUX} = i_0 \left(\frac{a_{WE,c}(0,t)}{a_{WE,c}^b} \right)^{\frac{\alpha_a}{\alpha_a + \alpha_c}} e^{-\frac{k \alpha_a \alpha_c}{\alpha_a + \alpha_c} E}. \quad (19)$$

Using the technique presented above one can obtain an approximation of the electrode overpotentials and current densities in case of positive applied voltage. Here we present only the final expressions. The electrode overpotentials can be computed as follows

$$\eta_{WE} = \frac{\alpha_c E}{\alpha_a + \alpha_c} + \frac{k^{-1} \ln\left(a_{AUX,c} / a_{AUX,c}^b\right)}{\alpha_a + \alpha_c}, \quad (20)$$

$$\eta_{AUX} = -\frac{\alpha_a E}{\alpha_a + \alpha_c} + \frac{k^{-1} \ln\left(a_{AUX,c} / a_{AUX,c}^b\right)}{\alpha_a + \alpha_c}. \quad (21)$$

Electrode current densities at WE and AUX in case of positive applied voltage are given by

$$i_{WE} = i_0 \left(\frac{a_{AUX,c}(0,t)}{a_{AUX,c}^b} \right)^{\frac{\alpha_a}{\alpha_a + \alpha_c}} e^{k \frac{\alpha_a \alpha_c}{\alpha_a + \alpha_c} E}, \quad (22)$$

$$i_{AUX} = -i_0 \left(\frac{a_{AUX,c}(0,t)}{a_{AUX,c}^b} \right)^{\frac{\alpha_a}{\alpha_a + \alpha_c}} e^{k \frac{\alpha_a \alpha_c}{\alpha_a + \alpha_c} E}. \quad (23)$$

Equations (16)-(19) and (20)-(23) compose an electrode kinetics model for a Cu-Cu system in the case of the identical electrode areas correspondingly for the negative or positive cell voltage, provided that the activity of the Cu(II) ions is known. To obtain these activities we specify a mass-transfer model for the system.

3.2 1D Mass-transfer model

The bulk solution is presumed unstirred. At the cathode, surface concentration of ions is diffusion-controlled along the x-axis (normal to cathode surface) as

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D(c) \frac{\partial c(x,t)}{\partial x} \right), \quad (24)$$

where $D(c)$ is the concentration-dependent diffusivity coefficient, m²/s, and $c(x,t)$, mol/m³ is the concentration of Cu^{2+} ions, at time t and at distance x from the electrode surface. The diffusivity coefficient of copper ions was calculated as $D(c)=(-0.6\ln(c)+8.27)\cdot 10^{-10}$ (Noulty and Leist, 1987).

The initial concentration distribution of species is assumed to be uniform in the stagnation layer and equal to the bulk solution concentration

$$c(x,0) = c_b. \quad (25)$$

The condition on the cathode is given by the 1st Fick's law and states that the molar flux of Cu(II) ions is proportional to the cathode current density

$$D(c) \frac{\partial c(x,t)}{\partial x}\Big|_{x=0} = \frac{i_{WE}(t)}{2F}. \quad (26)$$

The same condition applies on the anode, though now WE current density is replaced by AUX current density

$$D(c) \frac{\partial c(x,t)}{\partial x}\Big|_{x=d} = \frac{i_{AUX}(t)}{2F}, \quad (27)$$

where d – distance between the electrodes, m.

Solving the mass-transfer equation (24) with appropriate boundary conditions (25)-(27) yields a concentration curve and successively, the Cu(II) ion activity on the copper electrode can be calculated as follows (Pohjoranta and Tenno, 2007):

$$a_{Cu} = \frac{c}{c_0} \left(\frac{c+3.5}{c_0 + 3.5} \right)^{-0.5554}, \quad (28)$$

where c_0 is standard concentration, 1000 mol/m³ and 3.5 mol/m³ is a limit concentration below which all solutions are considered dilute.

The electrode kinetics equations (16)–(19), (20)-(23) together with mass-transfer equations (24)-(28) form a model of the Cu-Cu electrolysis system in the case of the identical electrode areas.

4. PARAMETER IDENTIFICATION

If it can be assumed that diffusivity of copper(II) ions D_{Cu} is constant, then using the model developed in Section 3 a simple method for identifying mass-transfer parameters as well as kinetic parameters can be is proposed. Indeed, a common kinetic model used in voltammetry for totally irreversible reactions (6) is similar to the equation (18), only here activity is used instead of the usual concentration. It conveys the suggestion that similar identification methods and input signals can be applied for the both models. Particularly we will use the sweep-form voltage as it is used for the model (6) to obtain (7).

Though the approximation of the relationship between concentration and activity (28), that matches the estimate with concentration at infinite dilution, is known, it is strongly nonlinear and doesn't give possibility to develop analytical methods suitable for analysis and identification of the overall system. To overcome this difficulty we will use another approximation given by the following expression

$$a_{WE,c} = \left(\frac{c_{WE}(0,t)}{c_b} \right)^{\gamma}, \tag{29}$$

where $\gamma = 0.4446$ for copper(II) ions.

Substituting (29) into (18) one can write the equation for cell current I as (30)

$$\frac{I}{nFA_{WE}} = -\frac{I_0}{nFA_{WE}} \left(\frac{c_{WE}(0,t)}{c_b} \right)^{\alpha_1} e^{-k\alpha_2 E}, \tag{30}$$

where $\alpha_1 = \gamma \alpha_a / (\alpha_a + \alpha_c)$, $\alpha_2 = \alpha_a \alpha_c / (\alpha_a + \alpha_c)$.

The cell voltage is given by (31)

$$E(t) = E_i - \nu t, \tag{31}$$

where E_i – initial potential, where no reaction occurs, V, and ν – sweep rate, V/s.

Based on (31) equation (30) takes the form

$$\frac{I}{nFA_{WE}} = -\frac{I_0 e^{-k\alpha_2 E_i}}{nFA_{WE} c_b^{\alpha_1}} c_{WE}^{\alpha_1}(0,t) e^{k\alpha_2 \nu t}. \tag{32}$$

The left-hand side in (32) equals the flux of copper(II) ions per unit area $f(t)$

$$f(t) = I_{fi} c_{WE}^{\alpha_1}(0,t) e^{bt}, \tag{33}$$

where

$$I_{fi} = -\frac{I_0 e^{-k\alpha_2 E_i}}{nFA_{WE} c_b^{\alpha_1}}, \; b = k\alpha_2 \nu. \tag{34}$$

Due to assuming constant D_{Cu}, c_{WE} can be found by solving the semi-infinite diffusion equation and given by

$$c_{WE}(0,t) = c_b - \frac{1}{\sqrt{\pi D}} \int_0^t \frac{f(\tau)}{\sqrt{t-\tau}} d\tau. \tag{35}$$

Substituting (35) into (33), raising both sides to the power of $1/\alpha_1$ and by rearrangement, one obtains (36)

$$\int_0^t \frac{f(\tau)}{\sqrt{t-\tau}} d\tau = \sqrt{\pi D} \left(c_b - f^{\frac{1}{\alpha_1}}(t) e^{\frac{\ln(I_{fi})-bt}{\alpha_1}} \right). \tag{36}$$

Equation (36) is a nonlinear second order Volterra integral equation that enables finding the current (and corresponding mass flux) at a given sweep voltage. Note that the structure of (36) would match that of the integral equation for the totally irreversible reactions (7), provided that $\alpha_1=1$. In this case the nonlinear equation (36) becomes linear.

It is reasonable now to put the equation in a dimensionless form so that numerically obtained results will be useful under any experimental conditions. This can be done by the change of variables

$$f(\tau) = \sqrt{\pi D b} c_b \chi(b\tau).$$

Then the desired equation in terms of dimensionless variables $\chi(z), u, bt$ takes the form

$$\int_0^{bt} \frac{\chi(z)}{\sqrt{bt-z}} dz = 1 - \chi^{\frac{1}{\alpha_1}}(bt) e^{\frac{u-bt}{\alpha_1}}, \tag{37}$$

where $u = \ln\left(\sqrt{\pi D b} c_b^{1-\alpha_1} / I_{fi} \right)$.

Equation (37) can be solved numerically using the technique developed by Nicholson and Shain (1964). Then the current flowing through electrochemical cell can be obtained as (38):

$$I(t) = nFA_{WE} c_b (\pi D b)^{1/2} \chi(bt). \tag{38}$$

The solution function $\chi(bt)$ does not depend on parameter u provided that u greater than 7. However, unlike in the totally irreversible reactions case, $\chi(bt)$ depends on α_1 as shown on Fig. 1, where it plotted versus dimensionless voltage

$$E_d = \ln\left(\sqrt{\pi D b} c_b^{1-\alpha_1} / I_{fi} \right) - bt.$$
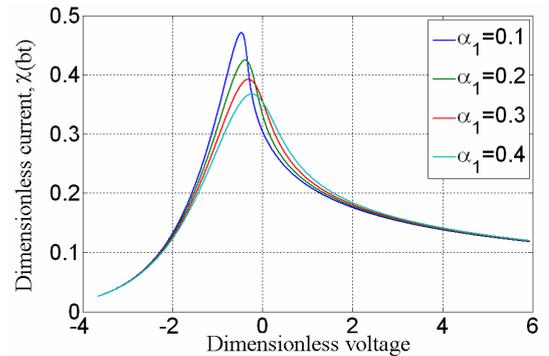

Fig. 1. Dimensionless current function

It is clearly observable that the bigger α_1 is, the lower is the dimensionless current peak, and the higher is the peak potential. These features are also observable from Fig. 2-3 where the dimensionless peak current and dimensionless peak voltage are illustrated as functions of α_1.
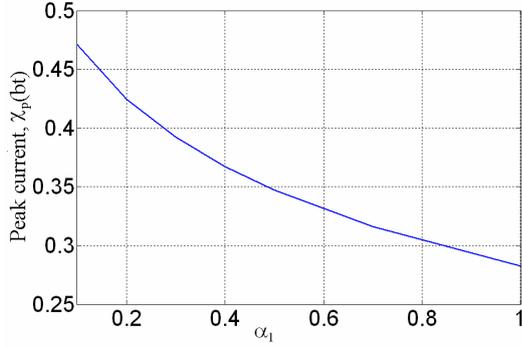

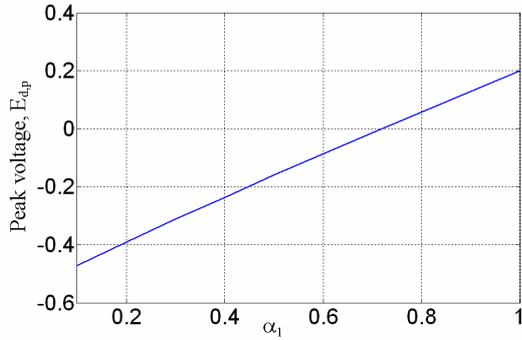Fig. 2. Dimensionless peak current as function of α_1

Fig. 3. Dimensionless peak voltage as function of α_1

According to definition of b (34), the dimensionless voltage is related to cell voltage as

$$E_d = \ln\left(\sqrt{\pi D b}\, c_b^{1-\alpha_1}/I_{fi}\right) - \frac{\alpha_2 nF}{RT}\left(E_i - E\right).$$

The E_p corresponding to peak current $\chi_p(bt)$ is a function of α_1 (see Fig. 3) and related to the dimensionless peak voltage $E_{d,p}$ as

$$E_{d,p} = \ln\left(\sqrt{\pi D b}\, c_b^{1-\alpha_1}/I_{fi}\right) - \frac{\alpha_2 nF}{RT}\left(E_i - E_p\right).$$

Solving for E_p and substituting b we obtain (39)

$$E_p = \frac{RT}{\alpha_2 nF}\left(E_{d,p}(\alpha_1) - \ln\frac{\sqrt{\pi D k \alpha_2 \nu}\, c_b nF A_{WE}}{I_0}\right). \quad (39)$$

According to (39) the peak voltage depends on the exchange current, apparent transfer coefficients and the diffusion coefficient. Considering the peak voltage at two different sweep rates and taking their difference yields (40)

$$E_{p,\nu_1} - E_{p,\nu_2} = \frac{RT}{\alpha_2 nF}\ln\sqrt{\frac{\nu_2}{\nu_1}}. \quad (40)$$

An estimate for α_2 can be created based on (40).

Still 3 parameters have to be identified (D, α_2 and I_0) but there are only two equations to utilize (χ_p and E_p), one more equation is required. The voltage at half-peak of current can be considered, as is often done in cyclic voltammetry study. The expression for the half-peak voltage can be obtained similarly as for the peak voltage. The plot of the half-peak voltage versus α_1 is depicted in Figure 4.
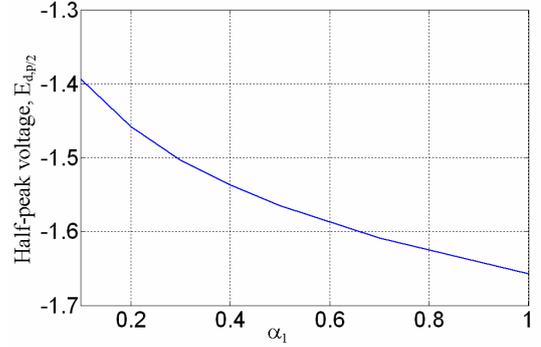

Fig. 4. Dimensionless half-peak voltage as function of α_1

Setting the expressions for peak current, peak voltage and half-peak voltage to their measured values produces a nonlinear system of 3 equations in 3 variables, and by solving the system one can estimate mass-transfer parameters and kinetic parameters of the system.

5. RESULTS AND DISCUSSION

The simulation model was built under the COMSOL Multiphysics 3.3 software package and voltammetry experiments were performed to verify the modelling results. Values of bulk Cu^{2+} ion concentration, magnitude E_M and sweep rate of the input voltage, area of the WE and areas ratio utilized in the experiment are listed in Table 1. The model parameters were optimized to minimize the mean square error between measured and predicted current densities on the WE electrode. Conventional voltammograms are depicted in Figure 5. The kinetic parameters of the model identified by direct search method are listed in Table 2.

Table 1. The values of parameters used in voltammetry experiment

Parameter	Unit	Value
c_b	mol/m^3	786
ν	V/s	0.1
E_M	V	0.47
A_{WE}	m^2	$3.5 \cdot 10^{-6}$
k_A	-	10

Table 2. The kinetics parameters used in simulation

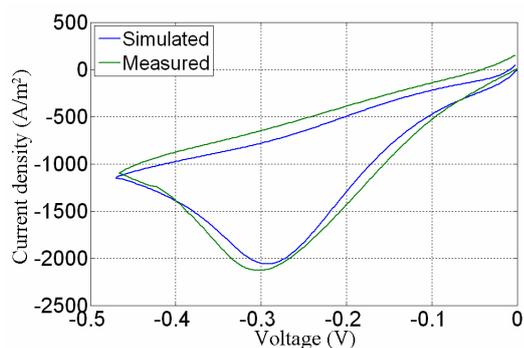| Parameter	Unit	Value
i_0	A/m^2	150
α_a	-	0.84
α_c	-	0.16

Fig. 5. Current-density – potential curve

Figure 5 shows that the model is in good agreement with experimental data. This allows us to reconstruct physical quantities which are not directly available or cannot be measured, such as the concentration of copper ions on the electrode surfaces (Fig. 6), the electrode overpotentials (Fig. 7) and the stagnation layer thickness (Fig. 8).
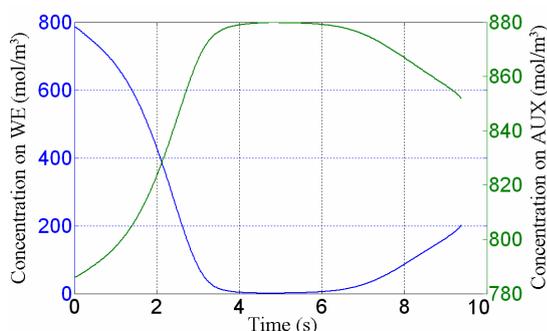

Fig. 6. Cu^{2+} ion concentration on the electrode surfaces

Figure 6 shows that the more negative is the applied cell voltage, the lower is the Cu(II) concentration on the WE and, correspondingly, the higher is the Cu(II) concentration on the AUX. However, the WE concentration changes within a wider range than that on AUX. This indicates a difference in the areas of the electrodes, namely that the area of AUX is bigger than that of WE.
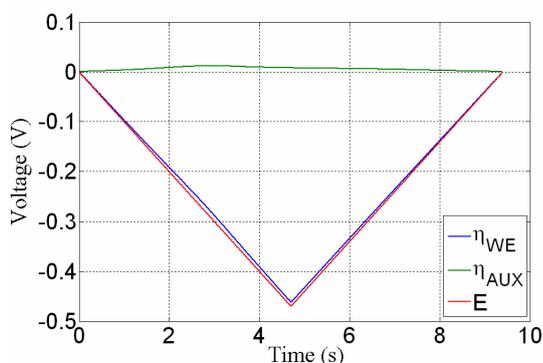

Fig. 7. Overpotentials and input voltage

Figure 8 demonstrates the growth of the stagnation layer thickness during the sweep experiment. The thickness was calculated as the distance from the electrode where the Cu^{2+}

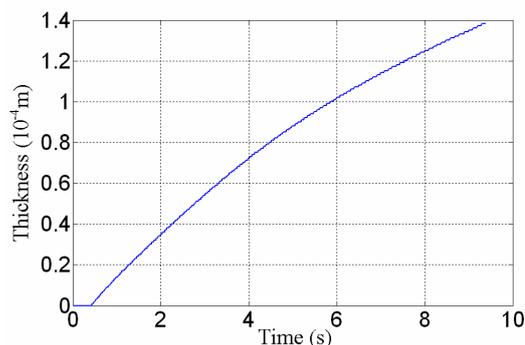ion concentration is above 95% of the bulk solution concentration.

Fig. 8. Stagnation layer thickness

6. CONCLUSIONS

A Cu-Cu electrolysis cell was modeled and method for identifying mass-transfer and kinetic parameters was proposed for a specific case. The model enables monitoring the studied system applied in industrial applications, such as copper deposition baths.

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