

The comparison of two electrochemical process models involving chemical steps

J. Dabulytė-Bagdonavičienė · F. Ivanauskas

Received: 19 April 2009 / Accepted: 10 July 2009 / Published online: 28 July 2009
© Springer Science+Business Media, LLC 2009

Abstract In this paper the comparison of two models of the same electrochemical process involving chemical steps has been made with the aim of accomplishing two tasks: (1) the analysis of concentration of each of components taking part in the electrochemical process, and (2) the analysis of the total metal or total ligand concentration. An assumption that the increase of the system lability makes the two systems' solutions close was tested out. The numerical investigation was proposed. The suggestions for finding the values of parameters giving the same concentrations were made by computational experiments.

Keywords Electrochemical reaction · Electrically active complex · Chemical equilibrium · Ligand

1 Introduction

Some chemical materials such as hydrogen, oxygen, leaches as well as chemical compounds like pharmaceutical, perfume are obtained by electrolysis [1–4]. The electrochemical extraction of some materials is very simple and the materials extracted

J. Dabulytė-Bagdonavičienė (✉)
Faculty of Fundamental Science, Kaunas University of Technology, Studentų 50,
51368 Kaunas, Lithuania
e-mail: jurgita.dabulyte@ktu.lt

F. Ivanauskas
Faculty of Mathematics and Informatics, Vilnius University, Naugarduko 24,
03225 Vilnius, Lithuania

F. Ivanauskas
Institute of Mathematics and Informatics, Akademijos 4, 08663 Vilnius, Lithuania
e-mail: feliksas.ivanauskas@maf.vu.lt

Fig. 1 The schematic view of the electrochemical process

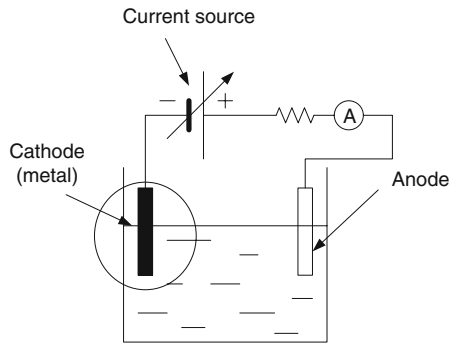
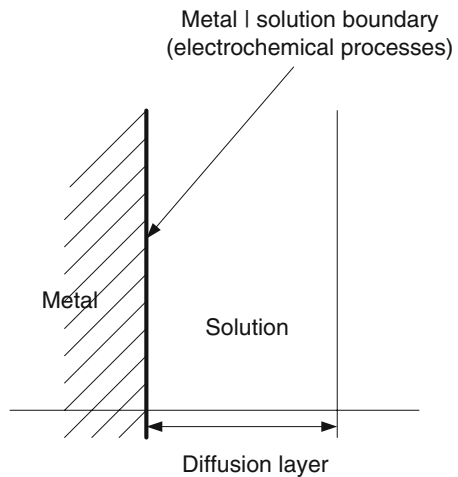


Fig. 2 The schematic view of metal|solution boundary



are very clean. Usually the electrolysis is the cheapest way of getting some materials (sodium, chlorine). The metallic, anticorrosive covering, electrochemical manufacturing of metals (cutting, boring, etching) are also evidential by electrolysis.

In the present paper we consider electrochemical processes which take place at the metal|solution boundary [5]. We compare two models of the same electrochemical process involving chemical steps with the aim of exploring two tasks: (1) investigating the concentration of each of components involved in the electrochemical process and (2) investigating the total metal or total ligand concentration and in that way finding out the concentration profile of each of components. We test out the assumption that the increase of the system lability could make the two systems' solutions close.

The simplest electrochemical process (Fig. 1) is a redox reaction



during which the reactant O, gaining n electrons, converts into product R [6]. This process takes place at the metal|solution boundary and can proceed in both direct and reverse directions (Fig. 2).

To initiate the macro-process, the electrode potential E should be shifted from its equilibrium value. In other terms, a certain overvoltage η should be applied using an external circuit involving a power source. This results in the respective concentration changes at the electrode surface (denoted further by subscript s).

It is often supposed that the concentration gradients arise only in some boundary layer the thickness of which δ does not depend on current density i . The latter quantity characterizes the rate of the electrochemical process according to the kinetic equation [7]:

$$i = i_0 \left\{ \frac{[\text{O}]_s}{[\text{O}]_b} \exp\left(\frac{anF}{RT}\eta\right) - \frac{[\text{R}]_s}{[\text{R}]_b} \exp\left(-\frac{(1-a)nF}{RT}\eta\right) \right\}, \quad (2)$$

where i_0 is an exchange current density; a is a cathodic charge transfer coefficient; R is universal gas constant; T is absolute temperature; F is Faraday's constant; $[\text{O}]_s$, $[\text{R}]_s$, $[\text{O}]_b$, $[\text{R}]_b$ are the reactant and product surface (subscript s) and bulk (subscript b) concentrations. The rate of the electrochemical process is controlled by the overvoltage and depends both on the surface concentrations of the reactants and the products. The latter quantities may be obtained from the regularities of diffusive mass transport that takes place in the δ , i. e. thick diffusion layer. Generally, the differential equation reflecting the second Fick's law and supplemented by relevant initial and boundary conditions should be solved. In the case of plane infinite electrode, only one space coordinate x , perpendicular to the electrode surface, may be taken into account. Then the equation under discussion takes the form:

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}, \quad (3)$$

where c is the respective (O or R) concentration, dependent on space coordinate x and time t , and D is a diffusion coefficient.

This task has been successfully solved earlier [4]. However, the similar problem becomes more complicated when the process (1) is accompanied by chemical interactions between different components of the electrochemical system [8–10]. A typical example of this case might be electrolysis of solutions containing cyanide complexes of silver. It is known (see, e.g. [11]) that Ag^+ ions form complex compounds with such ligand as cyanide anion CN^- yielding AgCN , $\text{Ag}(\text{CN})_2^-$, $\text{Ag}(\text{CN})_3^{2-}$ and $\text{Ag}(\text{CN})_4^{3-}$. All these species are in labile chemical interactions and may be formed (e.g. $\text{AgCN} + \text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$) or decomposed (e.g. $\text{Ag}(\text{CN})_3^{2-} \rightleftharpoons \text{Ag}^+ + 3 \cdot \text{CN}^-$). Such processes occur both in the bulk of solution and in diffusion layer. The species taking part in the charge transfer process similar to (1) is called an electrically active complex (EAC). Usually, the composition of EAC is not known a priori and its establishment requires special investigation.

The main goal of this task is to model the electrochemical process (1) in two different ways with a limited number of components, also to explore what parameters values makes two tasks' solutions close and to give some recommendations on faster finding these solutions.

2 Mathematical model

To describe quantitatively the mass transport, the rate of chemical interactions should be taken into account. To make the mathematics simple, we shall consider only a limited number of components emphasizing that their increase has no effect on general conclusions.

The electrochemical system containing “free” metal ions M^{n+} , ligand L and complexes ML^{n+} , ML_2^{n+} is considered [12]. For simplicity, ligand L is supposed to be uncharged. Then the main chemical transformations may be written as the following reactions:



where k are rate constants of respective direct (a positive index) and reverse (a negative index) reactions. In turn, the rates of (4) and (5) reactions may be written as:

$$w_1 = k_1 c_0 c_3, \tag{6}$$

$$w_{-1} = k_{-1} c_1, \tag{7}$$

$$w_2 = k_2 c_1 c_3, \tag{8}$$

$$w_{-2} = k_{-2} c_2, \tag{9}$$

where c_0 is the concentration of metal ions M^{n+} , c_1 and c_2 —the concentrations of complexes ML^{n+} and ML_2^{n+} , c_3 —the concentration of ligand L.

Equations reflecting the second Fick’s law and supplemented by kinetic terms should be written for all the above processes. We assume that the diffusion coefficients (D) are the same for all species.

Differential equations describing linear diffusion in the system under consideration take the following form:

$$\frac{\partial c_0}{\partial t} = D \frac{\partial^2 c_0}{\partial x^2} + w_{-1} - w_1, \tag{10}$$

$$\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} + w_{-2} - w_2 - w_{-1} + w_1, \tag{11}$$

$$\frac{\partial c_2}{\partial t} = D \frac{\partial^2 c_2}{\partial x^2} + w_2 - w_{-2}, \tag{12}$$

$$\frac{\partial c_3}{\partial t} = D \frac{\partial^2 c_3}{\partial x^2} + w_{-1} - w_1 + w_{-2} - w_2. \tag{13}$$

The rate constants k involving kinetic terms are positive if a diffusing particle is formed in a respective chemical process, and they are negative if it dissociates.

The set of differential equations (10–13) has a characteristic feature. An addition of Eqs. (10–12) yields a simple relationship

$$\frac{\partial c_M}{\partial t} = D \frac{\partial^2 c_M}{\partial x^2} \quad (14)$$

containing no kinetic terms. Here

$$c_M = c_0 + c_1 + c_2 \quad (15)$$

is a total metal concentration. A similar expression may be obtained for total ligand [13] concentration

$$c_L = c_1 + 2 \cdot c_2 + c_3. \quad (16)$$

Linear combination of (11–13) yields

$$\frac{\partial c_L}{\partial t} = D \frac{\partial^2 c_L}{\partial x^2}. \quad (17)$$

Hence, a mass transfer of total metal is subject to the same regularities as that of M^{n+} aqua-complexes in the absence of ligand L.

The usage of simple relationships (14), (17) is very tempting, since the solution of such an equation supplemented with corresponding initial and boundary conditions has been discussed in literature in considerable detail. However, it is necessary to consider some conceptions that make it possible to formulate specific relations between various concentrations as functions of coordinate x and time t .

The components of the system are in chemical equilibrium when the rate of their formation is equal to the rate of their disintegration: $w_1 = w_{-1}$ and $w_2 = w_{-2}$ [14]. Then the following relationships can be obtained from (6–9):

$$\beta_1 = \frac{k_1}{k_{-1}} = \frac{c_1}{c_0 c_3}, \quad (18)$$

$$\beta_2 = \frac{k_1 k_2}{k_{-1} k_{-2}} = \frac{c_2}{c_0 c_3^2}. \quad (19)$$

Hence, the equilibrium state can be described in terms of cumulative stability constants β . The higher β is the more stable is the complex particle. Since β is dependent on the ratio of respective rate constants k , the same β values may be realized at different k . The latter terms determine the degree of system lability: high and low k values characterize them as labile or inert systems respectively.

Generally, the problem under discussion is given by (10–13) and further it will be named as the *problem A*. The kinetics of the charge transfer process



described by (2) modified as follows

$$i = i_0 \left\{ \frac{[\text{ML}_j^{n+}]_s}{[\text{ML}_j^{n+}]_b} \exp\left(\frac{anF}{RT}\eta\right) - \left(\frac{[\text{L}]_s}{[\text{L}]_b}\right)^j \exp\left(-\frac{(1-a)nF}{RT}\eta\right) \right\}, \quad (21)$$

where j determines the EAC composition and is equal to 0, 1 or 2. If $i_0 \rightarrow \infty$ (a reversible charge transfer), the kinetic relationship takes the form of the Nernst equation. Then voltammetric and similar characteristics become independent of the assumption on EAC composition, i.e. on the charge transfer mechanism.

It is necessary to note that labile systems are often considered as a limiting case of general *problem A*. Then the relations between concentrations at any fixed t and x may be determined on the basis of cumulative stability constants of complexes (18, 19). The last statement is used below in *problem B*. In this case the system is supposed to be in an equilibrium state with respect to purely chemical processes, but this statement is not valid for the charge transfer process the degree of reversibility of which may be different.

As has been noted above, the differential equations should be supplemented with corresponding initial and boundary conditions. If the first task is simple and clear (the system is in equilibrium state at $t = 0$), some problems are encountered during the formulation of boundary conditions. In *problem A*, the boundary condition usually reflects the first Fick's law

$$i = nFD \left. \frac{\partial c^*}{\partial x} \right|_{x=0}, \quad (22)$$

where c^* is the concentration of an electrically active particle given in (20). As can be seen from different publications [7] dealing with processes involving chemical steps, the gradients of concentrations of other particles are set to zero, except for the product of EAC transformation (ligand L) if the latter is soluble and is capable of diffusing into the bulk of solution

$$\begin{aligned} \left. \frac{\partial c_0}{\partial x} \right|_{x=0} + \left. \frac{\partial c_1}{\partial x} \right|_{x=0} + \left. \frac{\partial c_2}{\partial x} \right|_{x=0} &= \frac{i(t)}{96500D}, \\ \left. \frac{\partial c_1}{\partial x} \right|_{x=0} + 2 \left. \frac{\partial c_2}{\partial x} \right|_{x=0} + \left. \frac{\partial c_3}{\partial x} \right|_{x=0} &= 0. \end{aligned}$$

This implies that c^* may be equated to c_M . However, the above conclusions about the values of individual gradients of concentrations do not follow back from the condition

$$i = nFD \left. \frac{\partial c_M}{\partial x} \right|_{x=0} \quad (23)$$

that can be used in *problem B*. Moreover, their predetermination is not necessary in the case of labile systems (*problem B*) because the relations between concentrations are prescribed by β values. The systems of both problems are also in equilibrium state when $x = \delta$. The equilibrium is established in such electrochemical system when

the rates of direct (cathodic) and reverse (anodic) reactions are equal. This can be expressed by the system of equations

$$\begin{aligned}\bar{c}_0 \left(1 + \beta_1 \bar{c}_3 + \beta_2 \bar{c}_3^2 \right) &= M, \\ \bar{c}_0 \left(\beta_1 \bar{c}_3 + 2\beta_2 \bar{c}_3^2 \right) + \bar{c}_3 &= L, \\ \bar{c}_1 &= \beta_1 \bar{c}_0 \bar{c}_3, \\ \bar{c}_2 &= \beta_2 \bar{c}_0 \bar{c}_3^2,\end{aligned}\tag{24}$$

where M is total metal concentration, L is total ligand concentration, \bar{X} means a concentration of X at $x = 0$.

Therefore the aim of the present investigation consists in comparing of *problems A* and *B* and their solutions. An assumption is tested that the increase of the system lability (i.e. an increase of the rate constants k) could make the solutions of the two problems close. This task is analyzed using an assumption regarding the EAC composition: EAC is the ML_2^{n+} complex prevailing in the bulk of solution ($j = 2$).

3 Results

Most science problems' mathematical models are comprised of complex equations, conditions, and loading configurations making an analytical solution impossible. In order to achieve a solution, a numerical solution technique must be employed. Therefore, we solve our mathematical models numerically. The finite—difference technique [15] and its explicit scheme are used for the discretization of *problem A* and *problem B* mathematical models. There has to be mentioned that there has to be solved the system of non-linear differential equations (10–13) in *problem A*, since in *problem B*—one linear differential equation (14) (in the case of investigation only total metal concentration). The solution of (10–13), supplemented with initial (22) and boundary (24) conditions, is the concentration of each component taking part in the electrochemical process. The total metal concentration is obtained by solving *problem B*. For the comparing of the solutions of these two tasks, the results have to be listed in the same way. So it is not enough to calculate total metal concentration, there has to be found all components concentrations. Therefore, from one point of view there has to be solved more complicated system in *problem A*, distinct *problem B*, but in the other hand the solution of *problem A* is obtained quicker. The concentration of each component is obtained after finding the total metal concentration in the *problem B*. This is attained by solving quartic equation that makes calculations more complicated. As it can be seen, the formulation of *problem A* is more complicated, but finding solution is quicker as distinct from *problem B*: the model is simpler, but the obtaining of solution is complicated. Digital simulations of the behavior of the mass transport in the electrochemical process were performed with the following values of the parameters

$$\begin{aligned}
 D &= 5 \times 10^{-6} \text{ cm}^2/\text{s}, \delta = 0.02 \text{ cm}, M = 10^{-5} \text{ mol/cm}^3, \\
 L &= 4 \times 10^{-5} \text{ mol/cm}^3, i_0 = 0.01 \text{ A/cm}^2, \\
 \beta_1 &= 10^7, \beta_2 = 10^{14}, a = 0.1, n = 1.
 \end{aligned}
 \tag{25}$$

If overvoltage changes by the following law

$$\eta = \nu t,
 \tag{26}$$

where ν is the sweep rate. The value of the sweep rate was chosen to fulfill an $F\nu/RT = 0.1$, where

$$\begin{aligned}
 F &= 96,500 \text{ C/mol}, \\
 R &= 8.31 \times 10^3 \text{ J/(kmol} \cdot \text{K)}, \\
 T &= 273.15 \text{ K}.
 \end{aligned}
 \tag{27}$$

Knowing that *problem B* uses only fixed β_1 and β_2 values, not depending on k_1 , k_{-1} , k_2 or k_{-2} , this problem is solved first.

The initial concentrations described by the system of equations (24) are

$$\begin{aligned}
 c_0(x, 0) &= 2.4751 \times 10^{-10} \text{ mol/cm}^3, \\
 c_1(x, 0) &= 4.9626 \times 10^{-8} \text{ mol/cm}^3, \\
 c_2(x, 0) &= 9.9501 \times 10^{-6} \text{ mol/cm}^3, \\
 c_3(x, 0) &= 2.0050 \times 10^{-5} \text{ mol/cm}^3.
 \end{aligned}
 \tag{28}$$

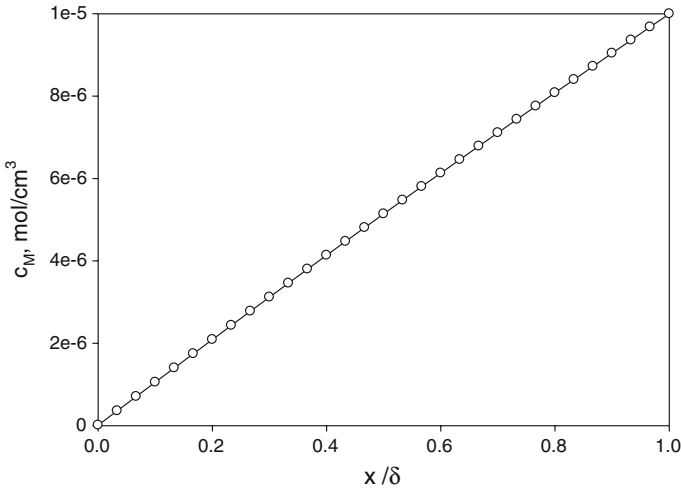


Fig. 3 The concentration c_M dependence on the x/δ , in the case of problem B. As it can be seen the dependence is linear

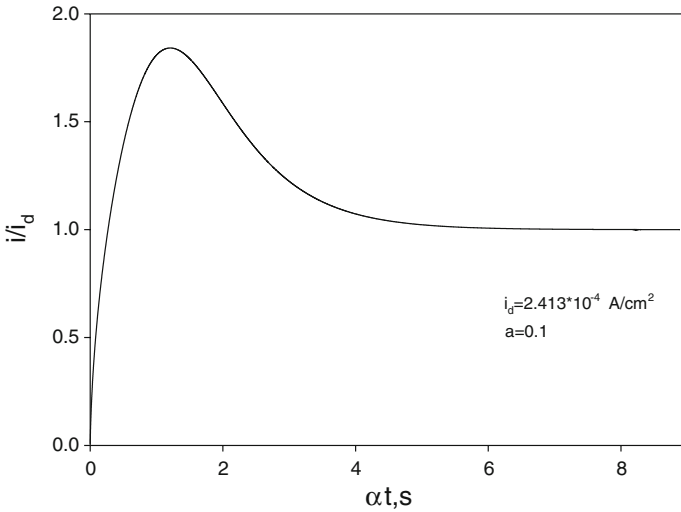


Fig. 4 The current density dependence on $\alpha = anFv/RT$. i_d is the current density in the stationary process

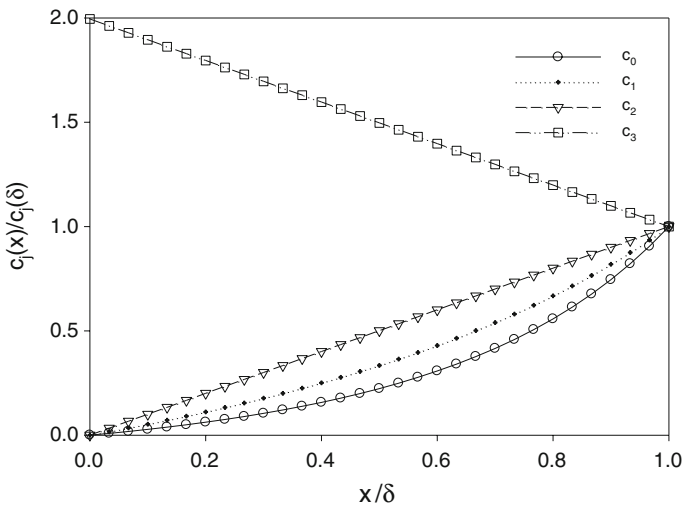


Fig. 5 All concentrations c_0 , c_1 , c_2 and c_3 profiles obtained at 8.8 s of problem B

The solution of the *problem B* is the concentration c_M (see Fig. 3). The value of c_M on the boundary $x = 0$ with fixed time t is calculated from the quartic equation obtained from (14), (23) and (24) system. The calculated current density is depicted in Fig. 4.

The total metal concentration c_M is the solution of *problem B*. There have to be obtained the concentrations of each component for comparing the concentrations with *problem A* solutions. The obtained profiles of concentrations c_0 , c_1 , c_2 and c_3 at the time of 8.8 s (stationary process) are shown in Fig. 5.

Table 1 The values of the rate of chemical conversion

Case	Case 1	Case 2	Case 3	Case 4	Case 5
<i>Parameter</i>					
$k_1, \text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	1	10^3	10^4	10^5	10^7
k_{-1}, s^{-1}	10^{-7}	10^{-4}	10^{-3}	10^{-2}	1
$k_2, \text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	1	10^3	10^4	10^5	10^7
k_{-2}, s^{-1}	10^{-7}	10^{-4}	10^{-3}	10^{-2}	1

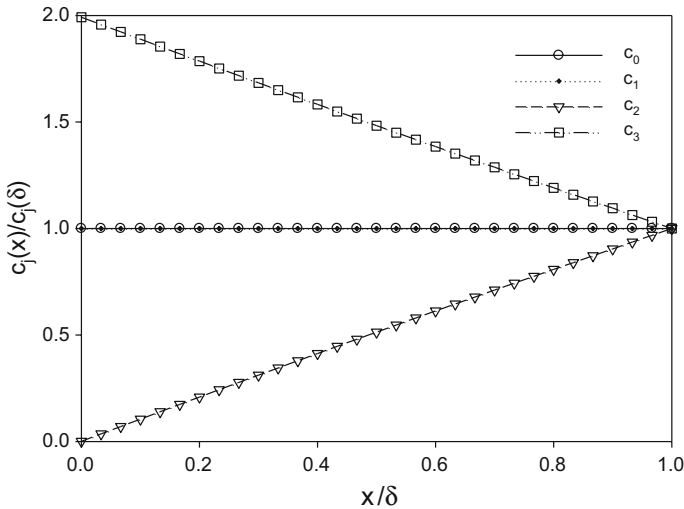


Fig. 6 The concentrations obtained by solving problem A, case 1

The solution of *problem A* differs with different rates of reactions: k_1, k_{-1}, k_2 and k_{-2} . Assume five cases of different k values (Table 1).

Figures 6 and 7 show how concentrations of *problem A* with different values of k converge to the solution of *problem B*.

As it is seen from the above figures, the *problem A* and *problem B* are close in the last case (Case 5). The main recommendation for getting both problems' solutions close is to increase the rates of direct and reverse reactions. The relative error in % of obtained current density of *problems A* and *B* is less than 0.5%, which means that the solutions are similar in that case.

Some remarks on the influence of current density i on $\alpha \cdot t$ (to be more precise, on overvoltage) can be formulated. The maximum values i_p of i , and the time t_p or $(\alpha \cdot t)_p$ of the occurrence of i_p were found. The dependences $(\alpha \cdot t)_p$ on $\ln(\alpha)$, t_p on α and i_p on $\ln(\alpha)$ are shown in Figs. 8, 9 and 10 for both problems.

One can see that the maximum value of the i increases if the value of $\ln(\alpha)$ increases and this growth is exponential. The time of the occurrence of i_p decreases with the increase of α . The $(\alpha \cdot t)_p$ of the occurrence of i_p depends on $\ln(\alpha)$ exponentially.

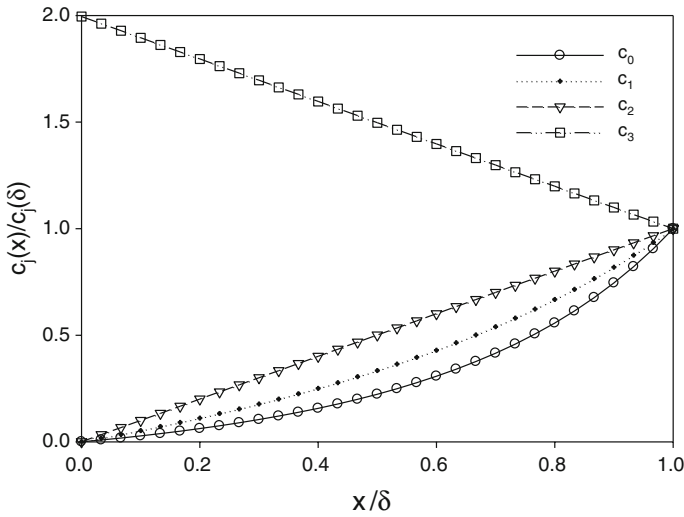


Fig. 7 The concentrations obtained by solving problem A, case 5

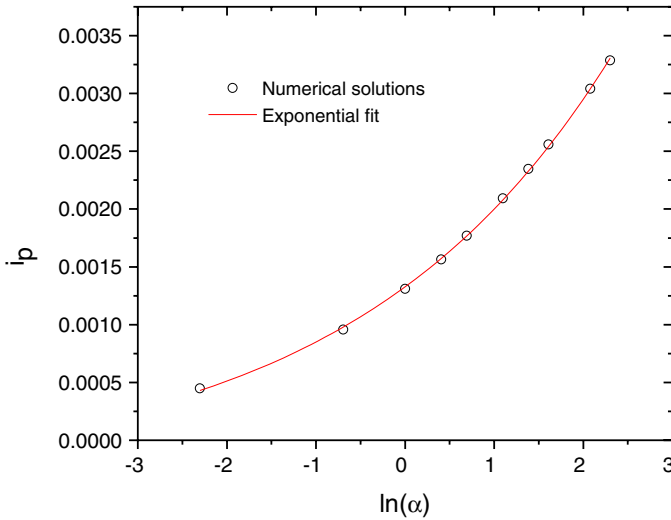


Fig. 8 The maximum current density i_p , A/cm² dependence on $\ln(\alpha)$. The white circles show the calculated value of i_p . The solid curve is an exponential function fitted to these values

The curves (Figs. 8, 9 and 10) through the calculated values are:

$$i_p(k) = -3.11 \times 10^{-4} + 0.00164e^{k/2.9056}, \text{ solid line in Fig. 8,} \tag{29}$$

$$t_p(k) = 0.2 + 17.94e^{-k/0.17} + 2.02e^{-k/1.49}, \text{ solid line in Fig. 9,} \tag{30}$$

$$(\alpha t)_p(k) = 1.095 + 0.23e^{k/2.42}, \text{ solid line in Fig. 10,} \tag{31}$$

where k is the $\ln(\alpha)$ or α , respectively.

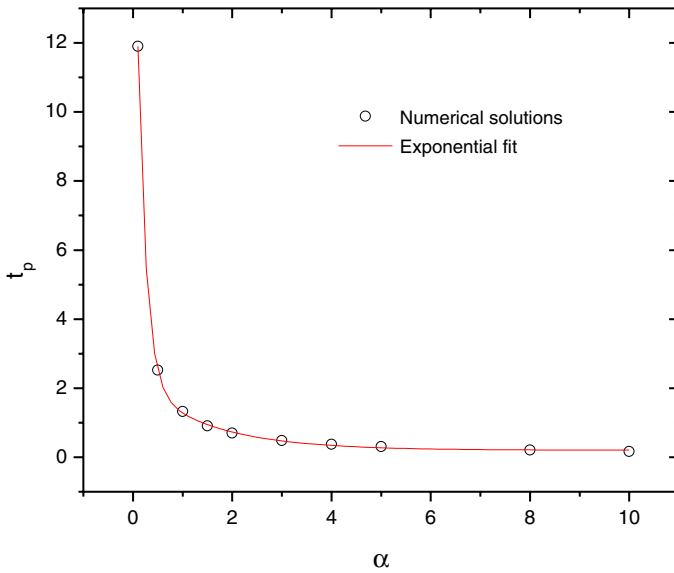


Fig. 9 The time of the occurrence of i_p dependence on α . The white circles show the calculated value of t_p, s . The solid curve is an exponential function fitted to these values

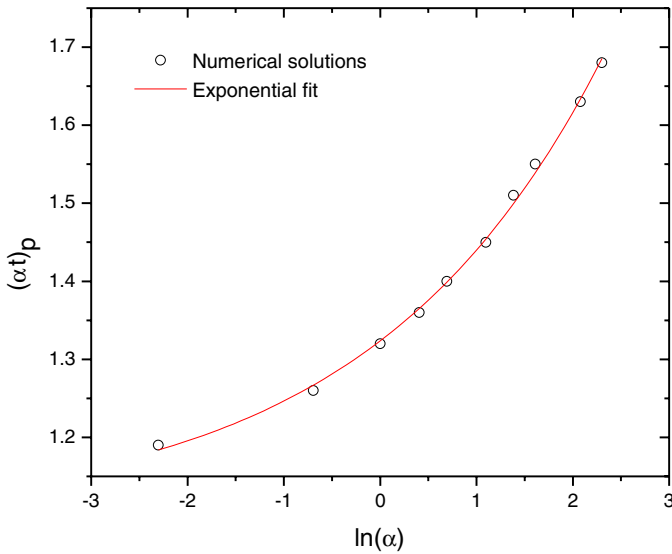


Fig. 10 The $(\alpha \cdot t)_p, s$ of the occurrence of i_p dependence on $\ln(\alpha)$. The white circles show the calculated value of $(\alpha \cdot t)_p$. The solid curve is an exponential function fitted to these values

According to these remarks the time of obtaining stationary process for the comparison of two differently described models of electrochemical process can be established.

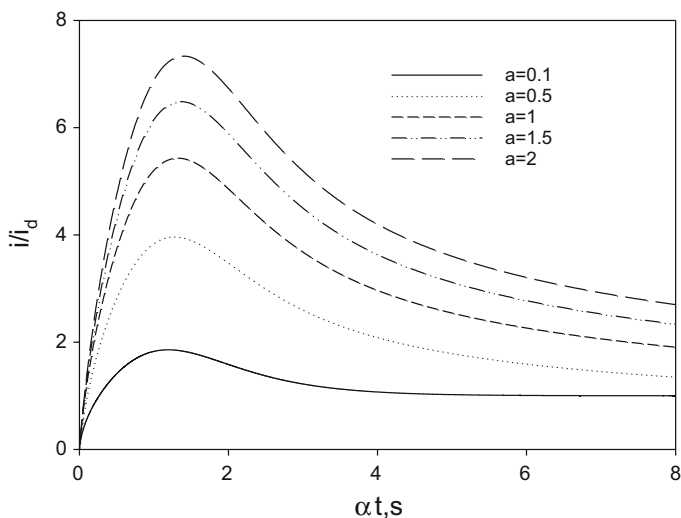


Fig. 11 The current density dependence on $\alpha = anFv/RT$ with different values of a . i_d is the current density in the stationary process

From Fig. 11 it can be seen that the change of the parameter a gives different current density, but the obtained rates of chemical conversion for one a when *problem A* and *problem B* concentrations are equal turn out to be the same.

4 Conclusions

Two mathematical models of the electrochemical process which find out the concentration profiles were given. The comparison of these models when the total metal or the concentration of each of the components is taken into account was made with different values of the parameters. The increase of the rates of the reactions (i.e. an increase of the system lability) approaches these two differently described models of the same electrochemical process. The change of the parameter a gives different current density, but the obtained rate constants of chemical conversion for single a when *problem A* and *problem B* concentrations are equal turn out to be the same. The recommendations of achieving stationary process (specifically of finding time period of achieving steady-state concentrations) were proposed.

Acknowledgments The authors express sincere thanks to Professor Arvydas Survila for his contribution into the theory of electrochemical process which takes place at the metal|solution boundary and also his continuous and helpful attention to this research. We also like to thank Professor Rolandas Vitalius Idzelis for his unremitting attention to this paper.

References

1. J. Bockris, B.E. Conway, et al., *Modern Aspects of Electrochemistry*, vol. 29 (Plenum Press, New York, 1996), 490 pp
2. Ch.M.A. Brett, A.M. Brett, *Electrochemistry: Principles, Methods and Applications* (Oxford University Press, Oxford, 1993)

3. P. Delahay, *New Instrumental Methods in Electrochemistry: Theory, Instrumentation and Applications to Analytical and Physical Chemistry* (Interscience, New York, 1954)
4. S. Kumar, V. Kumar, M.L. Sharma et al., Electrochemical synthesis of metallic micro-rose having petals in nanometer dimensions. *Superlattices Microstruct.* **4**, 324–329 (2008)
5. I. Šimkienė, Elektrocheminiai procesai optoelektroninių prietaisų technologijoje. *Lith. J. Phys.* **3**, 231 (2002)
6. P.H. Rieger, *Electrochemistry, 2nd edn.* (Chapman & Hall, New York, 1994)
7. D.D. MacDonald, *Transient Techniques in Electrochemistry* (Plenum Press, New York, 1977)
8. A. Survila, S. Kanapeckaitė, A. Survilienė, Cathodic processes in ligand-deficient Cu|Cu(II),-ethylene-diamine system. *J. Electroanal. Chem.* **501**, 151 (2001)
9. A. Survila, Z. Mockus, S. Kanapeckaitė, Kinetics of Sn and Co codeposition in citrate solutions. *Electrochim. Acta.* **46**, 571 (2000)
10. A. Survila, Z. Mockus, S. Kanapeckaitė, Effect of halides on adsorption properties of polyether laprol 2402 C on copper and tin electrodes. *J. Electroanal. Chem.* **552**, 97–103 (2003)
11. A. Survila, *Electrode Processes in Systems of Labile Complexes of Metals (in Russian)* (Mokslas, Vilnius, 1989)
12. A. Survila, P. Kalinauskas, I. Valsiūnas, Effect of ligands on formation of photosensitive oxide layers on copper electrode. *Russ. J. Electrochem.* **10**, 1068–1073 (2002)
13. S.D. Xun, J.D. Zhang, X.Z. Li et al., Synthesis and near-infrared luminescent properties of some ruthenium complexes. *Synth. Met.* **12**, 484–488 (2008)
14. J. Koryta, J. Dvorak, L. Kavan, *Principles of Electrochemistry, 2nd edn.* (Wiley, London, 1993)
15. A.A. Samarskii, *The Theory of Difference Schemes* (Nauka, Moscow, 1989, (in Russian))