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The description of the copper deposition/dissolution process in ammonia buffer with the application of mathematical two-plate model

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ABSTRACT

The experimental $Cu^{2+}/Cu^{+}/Cu^{0}$ system in ammonia buffer (pH = 9.25) has been investigated by cyclic voltammetry method and described by the advanced two-plate model with BET adsorption equation. A change of electrode properties during electrode process is included into the applied model. The model reproduces four one-electron peaks of electronation/deelectronation process together with a characteristic loop on cathodic part of CV response and covers 0.1; 0.2, 0.5; 1; 2; 5; 10; 20; 50 mM concentrations of Cu^{2+} at scan rate range 0.05–5 V/s. The values of elementary kinetic parameters have been determined, validated and discussed. It has been proved that CV technique and two-plate model is adequate to cover complete description of the deposition process for the wide range of concentration. The parameters of applied BET adsorption model coupled with kinetic parameters of electrochemical process model have been extensively discussed.

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1. Introduction

The problem of investigating and modeling of metal deposition/dissolution process at solid electrodes was raised by Brainina [1,2], Chevalier and co-authors [3], Mouhandes [4–6] and Grygar [7,8]. Advanced mathematical models of respective metal deposition/dissolution process investigated by stripping analysis are described by Compton and co-authors [9,10].

A change of electrode properties during the electrode process is the key problem in describing deposition/dissolution process. It results in a significant change of values of kinetic parameters and forms a characteristic loop in cathodic part of current response. For this purpose we proposed two-plate model with BET adsorption isotherm. The model was verified by the use of not fully resolved experimental data: three peaks $Cu^{2+}/Cu^{+}/Cu^{0}$ system in 0.5 M HCl solution [11] as well as two peaks Cu^{2+}/Cu^{0} system in 1 M $NaClO_4$ (pH = 3) solution [12] at different scan rates. To complete the experiment/model relationship, the present paper deals with the system fully resolved into four one electron steps, namely

$Cu^{2+}/Cu^{+1}/Cu^{0}$ system in 1 M NH_4Cl/1 M NH_4OH ammonia buffer pH = 9.25. Such a system with two diffusion cathodic peaks and two anodic (adsorption and diffusion) peaks, is appropriate especially for estimation of kinetic parameters. Mechanism aspects of Cu^{2+} electroreduction process were investigated by several authors mainly in the sixties e.g. [13–17] and they were followed by a number of authors ([18–26] and literature therein).

A characteristic type of cyclic voltammetry (CV) response is often met in deposition of metals. It is the response in which the reverse cathodic current line crosses over the forward deposition line in two points and, as a result, forms a loop on its cathodic part (c.f. respective figures in [11,12,27]). The rigorous general theory coherently describing the system regarding cathodic-diffusion/anodic-adsorption peaks of different properties at solid electrode is presented in [11,12]. The model describes different scan rate experimental responses with the loop on its cathodic parts where the description of a change of electrode reaction rate constant during a scan time interval with growing coverage of electrode is included. The latter problem is connected with under- and over-potential deposition of metals. Mathematical models of deposition/dissolution systems should be useful in modeling of actual problems which occur in stripping analysis, such as data processing and prediction of current response of multicomponent deposits at solid electrodes, as well as deposition of alloys.

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In this paper it is shown that the two-plate model is suitable to describe precisely a very complicated system of four one electron peaks for both different scan rate values as well as for a wide range of metal ion concentrations. The latter parameter diversity is rarely considered. The problem of concentration of ions of deposited metal is important from both scientific and practical points of view i.e. there is a need to establish a link between high concentration deposition technologies (electroplating) and CV investigation in both experimental and theoretical aspects.

2. Numerical procedures and experimental part

The presented problems were solved with the use of *ESTYM_PDE* program by K. Kaczmarski, previously described and compared with other relevant electrochemical software [28–30]. Various examples of solving electrochemical problems by means of *ESTYM_PDE* software are described in our earlier papers [11,12,28–36]. The applied theory of electrochemical simulations is described in refs. [37–46]; simulation packages are described in papers [43–45] (*DigiSim®*) and [41,46] (*ELSIM*). The correctness of our calculations with *ESTYM_PDE* program was confirmed by the test published in [29]; we showed [29,34] that our results obtained

where electrochemical $(cm\,s^{-1})$ rate constants $^1k_1 = {}^1k_{-1}$, $^1k_2 = {}^1k_{-2}$ concern first plate reaction, $^2k_1 = {}^2k_{-1}$, $^2k_2 = {}^2k_{-2}$ concern second plate reaction (the left superscripts denote the number of plate: (1) or (2)).

The shielded disk working electrode results in linear symmetry to the system. Therefore, it is justified to consider the problem in one dimension x representing the coordinate axis which is perpendicular to the electrode surface with $x = 0$ being the electrode surface.

Mass balance for all species in the solution consists of the following set of differential equations written for planar electrode:

$$\frac{\partial c_{Cu^{2+}}}{\partial t} = D_{Cu^{2+}}\frac{\partial^2 c_{Cu^{2+}}}{\partial x^2}$$

$$\frac{\partial c_{Cu^+}}{\partial t} = D_{Cu^+}\frac{\partial^2 c_{Cu^+}}{\partial x^2} \qquad (3)$$

$$\frac{\partial c_{Cu}}{\partial t} = D_{Cu}\frac{\partial^2 c_{Cu}}{\partial x^2}$$

with the following conditions:

1). Initial conditions: for $t = 0$ and $x > 0$: $c_{Cu^{2+}} = c^0_{Cu^{2+}}$, $c_{Cu^+} = 0$, $c_{Cu} = 0$; for $t = 0$ and $x = 0$: $\Gamma_{Cu} = 0$.

2). Boundary conditions: a). for $t > 0$ and $x = 0$ (on electrode surface):

$$D_{Cu^{2+}}\frac{\partial c_{Cu^{2+}}}{\partial x} = \begin{cases} \left(1 - \Gamma_{Cu}/\Gamma_{Cu,s1}\right) \times \left[c_{Cu^{2+}}{}^1k_1\exp\left({}^1a_1\right) - c_{Cu^+}{}^1k_{-1}\exp\left({}^1b_1\right)\right] + \left(\Gamma_{Cu}/\Gamma_{Cu,s1}\right) \times \left[c_{Cu^{2+}}{}^2k_1\exp\left({}^2a_1\right) - c_{Cu^+}{}^2k_{-1}\exp\left({}^2b_1\right)\right] & \text{for } \Gamma_{Cu} < \Gamma_{Cu,s1} \\ c_{Cu^{2+}}{}^2k_1\exp\left({}^2a_1\right) - c_{Cu^+}{}^2k_{-1}\exp\left({}^2b_1\right) & \text{for } \Gamma_{Cu} > \Gamma_{Cu,s1} \end{cases} \qquad (4)$$

$$D_{Cu^+}\frac{\partial c_{Cu^+}}{\partial x} = \begin{cases} \left(1 - \Gamma_{Cu}/\Gamma_{Cu,s1}\right) \times \begin{bmatrix} -c_{Cu^{2+}}{}^1k_1\exp\left({}^1a_1\right) + c_{Cu^+}{}^1k_{-1}\exp\left({}^1b_1\right) + \\ +c_{Cu^+}{}^1k_2\exp\left({}^1a_2\right) - c_{Cu}{}^1k_{-2}\exp\left({}^1b_2\right) \end{bmatrix} + \left(\Gamma_{Cu}/\Gamma_{Cu,s1}\right) \times \begin{bmatrix} -c_{Cu^{2+}}{}^2k_1\exp\left({}^2a_1\right) + c_{Cu^+}{}^2k_{-1}\exp\left({}^2b_1\right) + \\ +c_{Cu^+}{}^2k_2\exp\left({}^2a_2\right) - c_{Cu}{}^2k_{-2}\exp\left({}^2b_2\right) \end{bmatrix} & \text{for } \Gamma_{Cu} < \Gamma_{Cu,s1} \\ \left[-c_{Cu^{2+}}{}^2k_1\exp\left({}^2a_1\right) + c_{Cu^+}{}^2k_{-1}\exp\left({}^2b_1\right) + c_{Cu^+}{}^2k_2\exp\left({}^2a_2\right) - c_{Cu}{}^2k_{-2}\exp\left({}^2b_2\right)\right] & \text{for } \Gamma_{Cu} > \Gamma_{Cu,s1} \end{cases} \qquad (5)$$

$$D_{Cu}\frac{\partial c_{Cu}}{\partial x} = \begin{cases} \frac{\partial \Gamma_{Cu}}{\partial t} - \left(1 - \Gamma_{Cu}/\Gamma_{Cu,s1}\right) \times \left[c_{Cu^+}{}^1k_2\exp\left({}^1a_2\right) - c_{Cu}{}^1k_{-2}\exp\left({}^1b_2\right)\right] + \\ -\left(\Gamma_{Cu}/\Gamma_{Cu,s1}\right) \times \left[c_{Cu^+}{}^2k_2\exp\left({}^2a_2\right) - c_{Cu}{}^2k_{-2}\exp\left({}^2b_2\right)\right] & \text{for } \Gamma_{Cu} < \Gamma_{Cu,s1} \\ \frac{\partial \Gamma_{Cu}}{\partial t} - \left[c_{Cu^+}{}^2k_2\exp\left({}^2a_2\right) - c_{Cu}{}^2k_{-2}\exp\left({}^2b_2\right)\right] & \text{for } \Gamma_{Cu} > \Gamma_{Cu,s1} \end{cases} \qquad (6)$$

for representative example of calculations are exactly the same as the ones obtained with the use of other software, e.g. *DigiSim®*. The significant aspects of mathematical modeling of electrode processes are summarized in [47].

The applied numerical method of the solution of partial differential equations (PDE) is based on orthogonal collocation method which is widely discussed in the book by Villadsen and Michelsen [48]. We have used orthogonal collocation on finite element method in the form exactly the same as depicted in papers [49–52]. The errors for determined kinetic parameters were expressed by a

standard deviation: $\mathrm{SD} = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$, where x_i–value of

parameter and $\bar{x}$ –mean value of parameters, n–number of parameters.

In the applied model, the two-electron electrode reduction runs in consecutive-parallel way on two plates i.e. on two different but mutually dependent parts of electrode surface. The same electrode reaction runs with different rate constant on the two plates:

$$Cu^{2+} + e \underset{{}^1k_{-1}}{\overset{{}^1k_1}{\rightleftarrows}} Cu^+ + e \underset{{}^1k_{-2}}{\overset{{}^1k_2}{\rightleftarrows}} Cu \qquad (1)$$

$$Cu^{2+} + e \underset{{}^2k_{-1}}{\overset{{}^2k_1}{\rightleftarrows}} Cu^+ + e \underset{{}^2k_{-2}}{\overset{{}^2k_2}{\rightleftarrows}} Cu \qquad (2)$$

$$^ja_i = -\frac{^j\alpha_i RT\left(E - {}^jE_{0,i}\right)}{F}; {}^jb_i = \frac{^j\beta_i RT\left(E - {}^jE_{0,i}\right)}{F}, i = 1, 2; j = 1, 2 \qquad (7)$$

where $c_{Cu}{}^{2+}$ and $c_{Cu}{}^+$–actual concentration of species Cu^{2+} and Cu^+ in solution, c_{Cu}–actual concentration of species Cu within double layer limit, Γ_{Cu}–actual surface concentration of Cu in mol/cm², $\Gamma_{Cu,s1}$–the value of surface concentration at which total passing of reduction on second plate takes place, α and β–cathodic and anodic transfer coefficient, E_0–equilibrium potential of redox couple. Difference E–$^jE_{0,i}$ denotes to value of overpotential on respective plate. b). For $t > 0$ and $x \rightarrow \infty$ (in bulk solution):

$$c_{Cu^{2+}} = c^0_{Cu^{2+}}, c_{Cu^+} = 0, c_{Cu} = 0 \qquad (8)$$

This condition corresponds to concentrations of species (substrate and products) in the bulk of solution. The position of this point from electrode surface depends on diffusion coefficient and experiment time and is considered to be diffusion layer thickness $(\delta = 6\sqrt{D \cdot t})$.

In the model, diffusion of species Cu^{2+}, Cu^+, Cu (Cu appears in double layer limit only) is considered (set of Eq. (3)). For species Cu, a metal of a very low solubility value, $D = 10^{-20}$ cm²s⁻¹ was assumed. The close to zero value is justified by its physical sense i.e. with the fact that Cu does not move in solution and undergoes a very strong adsorption.