Digital simulation of electrochemical diffusion for the case of concentration dependent diffusion coefficient

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The problem of concentration dependent diffusion coefficient for the case of electrochemical diffusion is solved using the method of digital simulation. The procedure and results are demonstrated on the example of diffusion of Al(III) ions in the melt NaCl—KCl deposited on aluminium electrode.

Цифровым симулированием решается проблема концентрационно зависимого коэффициента диффузии при электрохимической диффузии. Ход и результаты решения показаны для случая диффузии ионов Al(III) в расплаве NaCl—KCl, которые выделяются на алюминиевом катоде.

In studying the kinetics of electrode reaction, our aim is to elucidate the relation between the rate of reaction and the experimental variables and so deduce the reaction mechanism. If we postulate a particular reaction mechanism then the kinetics of reaction can be calculated by solving a set of equations describing single reaction steps. If the theoretical and observed relations between experimental variables (potential, concentration, current, *etc.*) agree in limits of error we may accept the proposed mechanism.

However, at the study of kinetics of electrode processes it often happens that analytical relationships between current, potential, time, and kinetics parameters cannot be derived. If we wish to deal with real systems, in which the electrochemical reactions and transport of species can be described by more complicated schemes which are not analytically soluble, one of the ways how to overcome the mathematical obstacles is the digital simulation of electrochemical processes by means of a computer. For the case of constant diffusion coefficient this topic is treated in a comprehensive review [1]. In this paper we shall deal with concentration dependent diffusion coefficient for the case of metal deposition on a planar electrode formed by the same metal.

The equation for one-dimensional diffusion when the diffusion coefficient D is a function of concentration c is

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial x}\left(D\,\frac{\partial c}{\partial x}\right) \qquad (1)$$

If the rate of cathodic electrochemical reaction is determined only by a linear diffusion then for the case of chronopotentiometry when the current flowing through the system is constant it holds in the vicinity of electrode

$$j=-nFD_0\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_{x=0} \tag{2}$$

where n is the charge number of the electrode reaction, F is the Faraday constant, and D_0 is the diffusion coefficient in the vicinity of electrode. The boundary conditions are chosen so that at time $t=0$ the concentration of electroactive species equals c^0 for all x. In the infinity distance from electrode the concentration c^0 remains constant also during electrolysis.

The basis of the conceptual model for digital simulation is discretization of space and time. Let us divide the electrolyte into the volume elements ΔV the thickness of which is Δx (Fig. 1). The average distance of the I-th volume element from the electrode surface is

$$x=(I-0.5)\Delta x \tag{3}$$

and the average concentration in the I-th volume element is c_I. (I is an integer.) It should be noted that the term 0.5 is especially important for proper treatment of the boundary conditions at $I=1$ [1].

The rate of diffusion is given by empirical Fick's first law

$$J=-D\frac{\partial c}{\partial x} \tag{4}$$

The change in amount of substance in the I-th volume element is given by the difference between the fluxes of substance entering and exiting the element. For the case of concentration dependent diffusion coefficient the transport across an element boundary can be described using average diffusion coefficient between the two adjacent volume elements. The change in concentration occurring during time interval Δt in the I-th volume element ($I\geqslant 2$) can be expressed in the difference form as

$$c_I^+-c_I=\frac{\Delta t}{2(\Delta x)^2}\left[(D_{I+1}+D_I)(c_{I+1}-c_I)-(D_I+D_{I-1})(c_I-c_{I-1})\right] \tag{5}$$

where c_I^+ is the concentration in the I-th element at time $t+\Delta t$. If the diffusion coefficient is constant eqn (*5*) is identical with the Schmidt relation [2].

Similarly as in the case of Schmidt method the stability of eqn (*5*) is given by condition

$$D\Delta t/(\Delta x)^2\leqslant 0.5 \tag{6}$$

The stability conditions of numerical solution of diffusion equations are discussed in detail in the monograph [3]. The time interval Δt was chosen according to eqn *(6)* for the highest value of diffusion coefficient in the studied concentration range. In our case the diffusion coefficient decreased with increasing concentration and, therefore, for estimation of Δt the limit value of diffusion coefficient at zero concentration was used.

In the first volume element at the vicinity of electrode besides transport phenomena (diffusion from the second volume element) also the electrochemical reaction takes place which is responsible for the decrease of the amount of substance in this element. It holds

$$c_1^+ - c_1 = \frac{\Delta t}{2(\Delta x)^2}(D_1 + D_2)(c_2 - c_1) - \frac{j\Delta t}{nF\Delta x} \tag{7}$$

where the first term on the right side corresponds to diffusion from the second to the first volume element and the second term corresponds to consumption of the electroactive substance in electrochemical reaction.

In the experimental study of electrode reactions at chronopotentiometric conditions we follow the dependence of potential of working electrode *vs.* time. Potential of electrode is given by the Nernst relationship

$$E = E^0 + (RT/nF)\ \ln a_{\mathrm{Ox}}/a_{\mathrm{Red}} \tag{8}$$

where a_{Ox}, a_{Red} are the activities of an oxidation-reduction couple in the vicinity of electrode. In the case of metal deposition on the electrode formed by the same metal a_{Red} approaches 1. If the activity (and therefore also concentration) of deposited metal approaches zero at the electrode vicinity, the electrode potential changes rapidly. Time at which a_{Ox} equals zero is the transition time τ. This time is important characteristic of an electrode process.

In digital simulation of chronopotentiometry we are looking for the point when the concentration of electroactive component at the electrode equals zero. If the concentration in the middle of the first volume element is c_1, then from the boundary condition of chronopotentiometry (eqn *(2)*) and respecting eqn *(3)* it follows

$$c_{x=0} = c_1 - \frac{j\Delta x}{2nFD_1} \tag{9}$$

Therefore the digital simulation of electrochemical diffusion is based on calculation of concentration distribution at time $(N+1)\ \Delta t$ on the basis of knowledge of this distribution at time $N\Delta t$ using eqns *(5)* and *(7)*. At the beginning the concentration of electroactive species is c^0 in the whole electrolyte. In the first time interval $(N=1)$ the transport of substance given by eqn *(5)* equals zero and the diffusion term in eqn *(7)* equals zero as well. The change in concentration in the first volume element is only due to electrochemical reaction. After each cycle we use eqn *(9)* for testing whether concentration c_0 at the electrode surface equals zero. Actually the concentration c_0 will never be zero but at some point in simulation process this concentration will become negative. Therefore the transition time is to be determined by linear interpolation of time on the basis of values c_0 at time $(NEND - 1)\ \Delta t$ and $NEND\ \Delta t$.

It should be noted that the choice of Δt and Δx must fulfil not only the condition (*6*) but also the boundary condition of chronopotentiometry (*9*). Therefore it is necessary to choose sufficiently small Δx and subsequently to calculate Δt according to relation (*6*).

The method of digital simulation is illustrated in Fig. 1 where the change of concentration *vs*. distance from the electrode is plotted. The number on each curve is the time, in seconds, elapsed since the beginning of electrolysis. The numerical data were obtained for the diffusion of Al(III) in the melt NaCl—KCl at 700°C. On the basis of 30 experiments carried out at different concentrations c^0 and current densities it was found [4] that the experimental dependence of transition time on concentration (up to 10^{-3} mol $AlCl_3$ per cm^3) and current density can be described by hyperbolic dependence of diffusion coefficient on concentration. The hyperbolic function enables to model sharp change of diffusion coefficient in the vicinity of electrode

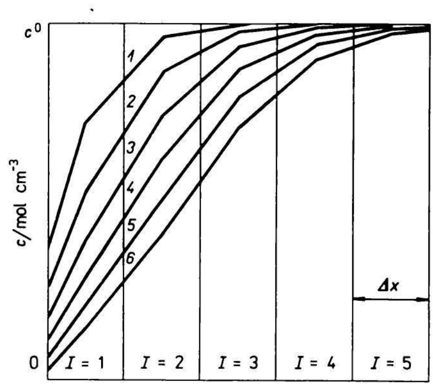

Fig. 1. Change in concentration of Al(III) ions as a function of time elapsed from the beginning of electrolysis and distance from the electrode. $c^0 = 9.392 \times 10^{-5}$ mol cm^{-3}, $j = 0.6369$ A cm^{-2}, $\Delta x = 3.742 \times 10^{-3}$ cm.
Diffusion coefficient depends on concentration according to eqn (*10*).
1. 0.05 s; *2.* 0.10 s; *3.* 0.15 s; *4.* 0.20 s; *5.* 0.25 s; *6.* 0.30 s.

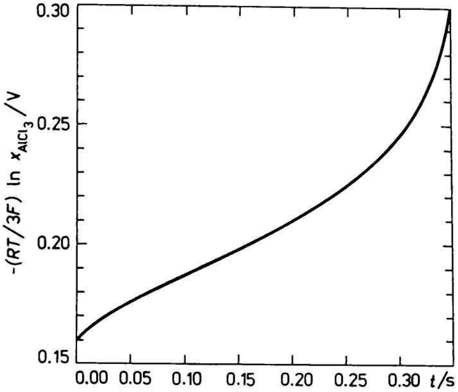

Fig. 2. Chronopotentiometric curve constructed on the basis of data obtained by digital simulation of diffusion.
The experimental conditions are the same as in Fig. 1.

$$D_I/\mathrm{cm^2\,s^{-1}} = 1/(1/7\times10^{-4} + 10^8\, c_I/\mathrm{mol\,cm^{-3}}) \qquad (10)$$

The agreement between model and experiment was tested using criterion of minimalization of the sum

$$\sum_{i=1}^{k} (\tau_{i,\mathrm{exp}} - \tau_{i,\mathrm{calc}})^2/\tau_{i,\mathrm{exp}}$$

In the example shown in Fig. 1, the experimental transition time is 0.31 s while the transition time obtained by digital simulation of chronopotentiometric diffusion is 0.35 s ($c^0 = 9.392\times10^{-5}$ mol cm^{-3}, $j = 0.6369$ A cm^{-2}).

In Fig. 2, the difference of the electrode potential and standard potential $E - E^0$ (see eqn (*8*)) *vs.* time is drawn. The experimental conditions are the same as mentioned above. The activity of Al(III) equals mole fraction of $AlCl_3$ in the electrolyte, the activity of deposited metal is assumed to be unit.

It can be concluded that in the case of concentration dependent diffusion coefficient no analytical expressions derived for constant diffusion coefficient can be correctly used, neither for determination of transition time, nor for logarithmic analysis of experimental chronopotentiometric curve. Numerical solution of diffusion equations discussed in this paper yields a universal tool for solving this problem.

References

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