

APPLICATION OF DIMENSIONAL ANALYSIS AND SIMILARITY THEORY IN ELECTROCHEMISTRY: A REVIEW

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Similarity theory and dimensional analysis were shown to be suitable both in electrochemical kinetics and in electrochemical engineering. The corresponding original and literature data were reviewed. The use of dimensionless groups in electrochemical mass transfer problems was described; the similarity criteria involved were summarized. Similarity theory and dimensional analysis may be successively applied for a kinetic analysis of an electrochemical reaction described both by the equations of the slow discharge theory and by the Marcus–Hush–Chidsey formalism. The corresponding dimensionless quantities (similarity criteria) were derived and approximating interrelations between them were analyzed. The results of numerical simulation of the kinetics of a two-stage electrochemical reaction with partial transfer of intermediates between the electrode surface and the bulk solution in conditions of linear nonsteady-state diffusion of reactants are analyzed with the use of dimensional analysis and similarity theory (i.e. a theory of generalized variables). Some dimensionless complexes utilized in applied electrochemistry were reviewed. The main advantages of the application of similarity theory and dimensional analysis in pure and applied electrochemistry were generalized.

Introduction

Multistage electrochemical processes are described by mathematical expressions which commonly contain a great number of various parameters and variables. One may cite as an example the reactions of consecutive charge transfer with the participation of stable intermediates [1–4]. When analyzing the corresponding bulky equations of polarization curves one has either to use numerical simulation or to consider easier particular cases. As a consequence, the clearness of the analysis results declines and the generality of the conclusions derived fails.

Applying similarity theory as well as dimensional analysis might be an effective way to analyze behavior of complex multiple-factor systems and processes, these two theories may be named as the theory of generalized variables [5–8]. Dimensional analysis is a tool to find or check relations among physical quantities by using their dimensions. Dimensional analysis is based on the fact that a physical or physicochemical law must be independent of the units used to measure the physical variables. A straightforward practical consequence is that any meaningful equation must have the same dimensions in the left and right sides. Checking this is the basic way of performing dimensional analysis. Dimensional analysis is usually used to check the plausibility of derived equations and computations. It is also used

to form reasonable hypotheses about complex physical situations that can be tested by experiment or by more developed theories of the phenomena, and to categorize types of physical quantities and units based on their relations to or dependence on other units, or their dimensions if any.

The similarity theory (i.e. similitude concept) [9] is inseparably connected with the dimensional analysis. Similitude is a concept applicable to the testing of engineering models. A model is said to have similitude with the real application if the two share geometric similarity, kinematic similarity, dynamic similarity and (or) other types of similarity. Similitude can be used to predict the performance of a new design based on data from an existing, similar design. In this case, the model is the existing design. Another use of similitude and models is in validation of computer simulations (or numerical simulation) with the ultimate goal of eliminating the need for physical models altogether.

The basic principle of dimensional analysis was known to Isaac Newton (1686) who referred to it as the «Great Principle of Similitude». James Clerk Maxwell played a major role in establishing modern use of dimensional analysis by distinguishing mass, length, and time as fundamental units, while referring to other units as derived. The 19th-century French mathematician Joseph Fourier made important contributions based on the idea that every physical

law should be independent of the units employed to measure the physical variables. This led to the conclusion that meaningful laws must be homogeneous equations in their various units of measurement, a result which was eventually formalized in the Buckingham π theorem. This theorem describes how every physically meaningful equation involving n variables can be equivalently rewritten as an equation of $n-m$ dimensionless parameters, where m is the number of fundamental dimensions used. Furthermore, and most importantly, it provides a method for computing these dimensionless parameters from the given variables.

In dimensional analysis, a dimensionless quantity or quantity of dimension one is a quantity without an associated physical dimension. It is thus a «pure» number, and as such always has a dimension of 1. Dimensionless quantities are widely used in mathematics, physics, engineering, economics, and so on. Let us enumerate several well-known dimensionless quantities as follows: (i) Reynolds number, (ii) Fourier number, (iii) Péclet number.

Dimensionless quantities are often defined as products or ratios of quantities that are not dimensionless, but whose dimensions cancel out when their powers are multiplied.

The Buckingham π theorem [9] is a key theorem in dimensional analysis. It is a formalization of Rayleigh's method of dimensional analysis. The theorem loosely states that if we have a physically meaningful equation involving a certain number, n , of physical variables, and these variables are expressible in terms of k independent fundamental physical quantities, then the original expression is equivalent to an equation involving a set of $p=n-k$ dimensionless parameters constructed from the original variables: it is a scheme for nondimensionalization. This provides a method for computing sets of dimensionless parameters from the given variables, even if the form of the equation is still unknown. However, the choice of dimensionless parameters is not unique: Buckingham's theorem only provides a way of generating sets of dimensionless parameters, and will not choose the most "physically meaningful".

The application of dimensionless quantities in quantitative analysis allows diminishing the number of variables analyzed, simplifying and clarifying the forms of relationships that reflect the content of mathematical models involved.

The similarity theory and dimensional analysis are widely used in studies on mass transfer, heat exchange, continuum mechanics, designing of different machines and aggregates, electrical engineering and so on. The basic methods of the similarity theory and dimensional analysis are described in detail in monographs and manuals [5–7].

The possibility of the usage of the similarity theory in the field of physical-chemical processes

was firstly considered in works by D'yakonov [10]. D'yakonov utilized not only common similarity criteria (such as Péclet number, Grashof number, Reynolds number etc.), which describe the processes of mass transfer, heat transfer and motion of continuum, but also suggested new specific similarity criteria relating to the chemical reactions (the criteria of chemical transformation). However, these studies have not been further developed.

Attempts to apply the methods of the similarity theory and dimensional analysis in electrochemistry have been made long ago [11–13]. However, these attempts were restricted to the processes of mass and heat transfers in electrochemical systems; they did not refer to the electrochemical kinetics proper.

It seems that just one exception in this respect was a criterion of electrochemical similarity which spread in monographs and textbooks. This criterion may be given as follows:

$$\frac{\partial E}{\partial i} \cdot \frac{\chi}{L_0}, \quad (1)$$

where χ is the electrical conductivity of the electrolyte; $\frac{\partial E}{\partial i}$ is the polarizability of the electrode;

L_0 is the crucial geometrical size of the system [14,15]. The criterion of electrochemical similarity is dimensionless; it generalizes the effects of geometrical and electrochemical parameters upon the uniformity of current distribution in an electrochemical bath. This criterion is often named as the Wagner number in the English scientific literature [16].

In connection with the above, another aspect that deserves reference is related with the fact that the development and analysis of the kinetic models of various electrochemical reactions creates in the general case a very difficult task. The difficulties are caused both by the intricate physicochemical content of mass and charge transfer through the interface «first-class conductor / second-class conductor» and by the complicated form of mathematical apparatus involved. A great number of diverse variables obscure the general view of phenomena concerned and impede the progress in ascertaining hidden intrinsic relations in systems and consolidating these relations in clear quantitative laws.

Applying the dimensional analysis and similarity theory in the analysis of electrochemical systems behavior may and should be very fruitful. This work is devoted to generalizing the literature data dealing with the topic concerned.

Dimensional analysis and similarity theory in electrochemistry for the description of mass transfer

The applications of dimensional analysis in electrochemical mass transfer problems were firstly discussed in work by Ibl [11]. Mass transfer to or

from the electrode surface plays an important role in electrolysis. At a given current density the transport processes determine the concentration at the electrode surface. The transport processes also determine the limiting current at which the concentration at the interface is zero, and which corresponds to the maximum rate with which an electrode process can be carried out under a given set of experimental conditions.

The mass transfer processes in electrolysis are: convection, diffusion and electric migration. As a first approximation the flux N_i of the i th ionic species is given by the following equation:

$$N_i = -\vec{D}_i \overrightarrow{\text{grad}C_i} - \frac{z_i F D_i C_i}{RT} \overrightarrow{\text{grad}\phi} + C_i \vec{V}, \quad (2)$$

where D_i means the diffusion coefficient of the ionic species considered; C_i its concentration; z_i its valency; \vec{V} is the velocity vector of the hydrodynamic flow and ϕ is the electric potential. F , R and T have their usual meaning.

The first, second and third term on the right hand side of equation (2) correspond to the mass transfer by diffusion, electrical migration and convection, respectively. From Eq. (2) the relation expressing the conservation of mass for the i th species can be derived:

$$\frac{dC_i}{d\tau} = -\text{div} \vec{N}_i = -D_i \text{div} \overrightarrow{\text{grad}C_i} + \frac{z_i F D_i C_i}{RT} \text{div} (C_i \overrightarrow{\text{grad}\phi}) - \vec{V} \overrightarrow{\text{grad}C_i}. \quad (3)$$

Equation (3) gives the change of concentration with time in an elementary solution volume of an incompressible liquid. Eq. (3), the Navier-Stokes relation and the continuity equation of hydrodynamic form the three fundamental differential equations of convective mass transfer. If a complete calculation of the limiting current or the concentration at the interface is to be achieved these three equations must be integrated simultaneously.

Unfortunately, the number of variables occurring in convective mass transfer problems is usually large, and serious mathematical difficulties arise. A considerable simplification can be achieved by grouping the variables together in a suitable manner, so that new dimensionless variables (i.e. similarity criteria) are formed, whose number is smaller than that of the original dimensional variables [11]. It should also be mentioned that such dimensionless similarity criteria can be employed even under intricate flow conditions when the integration of the fundamental differential equations becomes too complicated and has not yet been performed.

The advantages of using dimensionless groups in electrochemical mass transfer problems were illustrated in [11] by a few examples. A first example referred to the steady state mass transfer rate in metal deposition at a flat electrode along which the solution is flowing. The following expression is valid in such a case at the limiting current:

$$j = f(D, \Delta C, \nu, V, l), \quad (4)$$

where j means the steady state mass transfer rate of metal deposition; ΔC is the difference between the metal ions concentration at the interface and in the bulk, which is the driving force for the diffusion process; ν is the kinematic viscosity; V is the flow velocity of the solution and l is the length of the electrode in the direction of the flow.

The equation (4) may be transformed into the form:

$$Nu = F(Sc, Re), \quad (5)$$

where $Nu = \frac{j l}{D \Delta C}$ is the Nusselt number; $Sc = \frac{\nu}{D}$ is the Schmidt number; and $Re = \frac{V l}{\nu}$ is the Reynolds number.

It is seen that the original six dimensional variables have been replaced by the three dimensionless variables Nu , Sc , and Re . The number of such dimensionless groups which have to be introduced in order to describe the problem completely is definitely given by the π -theorem.

A second example, which was described in [11], concerned the steady-state mean mass transfer rate in metal deposition at a plane vertical electrode in a solution which is not artificially stirred. Then a buoyancy force acts on the liquid and gives rise to an ascending hydrodynamic flow along the cathode. We will have the following equation:

$$j = f\left(D, \Delta C, \nu, g \frac{\Delta \rho}{\rho}, l\right), \quad (6)$$

where g is the gravitational acceleration; $\Delta \rho$ is the density difference between interface and bulk, ρ is the density in the bulk, and the other variables are the same as in the preceding forced convection example.

The problem can be reduced to a relationship between three dimensionless similarity criteria. Two of these, Nu and Sc , are formed in the same manner as before. The third criterion commonly used in natural convection is the Grashof number

$$Gr = \frac{g \Delta \rho l^3}{\rho \nu^2} = \frac{g \alpha \Delta C l^3}{\nu^2}. \quad \text{Furthermore, it can be shown}$$

that at high Schmidt numbers usually prevailing in

electrolysis Sc and Gr need not be considered separately. Their product, $Sc \times Gr$, may be taken as a single variable. Therefore we can write:

$$Nu = F(Sc \times Gr) = F(Ra). \quad (7)$$

The product $Sc \times Gr$ is called Rayleigh number (Ra). The data obtained by various authors were analyzed in work [11] in dimensionless form. These data were found to be in good agreement and a simple generalized correlation was obtained when dimensionless groups were used, whereas the representation of the experimental results would be incomparably more complicated if the original variables were used.

Later dimensional analysis was applied to the generation of electrostatic streaming currents accompanying the flow of a liquid [12,13,17]. The choosing of those dependent and independent variables that are of significance was discussed. These variables were then collected into non-dimensional groups and the physical significance of these groups (i.e. similarity criteria) was also derived. The data given in the papers under consideration differ somewhat in the concrete forms of similarity criteria that is not surprising in view of the aforesaid. Let us consider the results which have been stated in the most detailed paper [12].

The governing equations were taken in the following form:

$$\frac{\partial \sigma_{\pm}}{\partial \tau} = D_{\pm} \nabla^2 \sigma_{\pm} - \nabla \cdot (\lambda_{\pm} E) + \alpha C_m - \beta C_+ C_-, \quad (8)$$

where σ is the charge density; ϵ is the dielectric coefficient; E is the electric field; λ_{\pm} is the electrical conductivity; C_m is the concentration of molecular species; α is the dissociation coefficient and β is the recombination coefficient. The signs \pm are related to the cations and anions, respectively.

These two equations together with the Poisson relation:

$$\sigma = \nabla \cdot (\epsilon E) \quad (9)$$

and the summation of charge density:

$$\sigma = \sigma_+ + \sigma_-, \quad (10)$$

provide a set of equations for the case under consideration. After some their transformations which are here omitted and with due regard for boundary conditions; the authors of [12] formed five dimensionless groups as follows

$$\frac{i_s^2}{\rho U^4 \epsilon l^2}, \frac{\epsilon U}{\lambda_0 l}, \frac{D \epsilon}{\lambda_0 l^2}, \frac{D_+}{D_-},$$

$\frac{\rho U l}{\mu}$. In these complexes new designations appeared:

i_s is the streaming current; ρ is the fluid density; U is the reference fluid velocity; l is the typical length; λ_0 is the electrical conductivity for $\sigma=0$; μ is the fluid viscosity; $2D \equiv D_+ + D_-$.

It was stated that these five dimensionless groups have the physical significances as follows:

– the first non-dimensional group $\left(\frac{i_s^2}{\rho U^4 \epsilon l^2} \right)$

indicates the ratio between fluid field force and fluid inertia force;

– the second non-dimensional group $\left(\frac{\epsilon U}{\lambda_0 l} \right)$

indicates the ratio between convection current and conduction current;

– the third non-dimensional group $\left(\frac{D \epsilon}{\lambda_0 l^2} \right)$

indicates the ratio between diffusion current and conduction current;

– the fourth non-dimensional group $\left(\frac{D_+}{D_-} \right)$ may

be replaced with the Knudsen number;

– the fifth non-dimensional group $\left(\frac{\rho U l}{\mu} \right)$ was

shown to be the Reynolds number.

Dimensional analysis and similarity theory in electrochemical kinetics¹

Using the dimensional analysis and similarity theory in electrochemical kinetics was for the first time thoroughly examined in a series of works [4,18–23]. Thus, it was shown in [18] that the similarity theory and dimensional analysis (i.e. the theory of generalized variables) is applicable for a kinetic analysis of a simple electrochemical reaction described by the following conventional equation of the slow discharge theory:

$$i = i_0 \left\{ \exp \left[\frac{\alpha F \eta}{RT} \right] - \exp \left[- \frac{(1-\alpha) F \eta}{RT} \right] \right\} \times \exp \left[\frac{(\alpha - z_0) F \psi_1}{RT} \right], \quad (11)$$

where i is the measured cathodic current density of

¹ It should be especially stressed that the same letter designations are sometimes applied for diverse variables in the different subsections of the present work. This is caused by the large variety of the variables which have been utilized in works by different authors. Nevertheless, the letter designations of different variables are homogeneous within each of the subsections.

a one-electron reaction $O + e^- \rightleftharpoons R$; $i_0 = Fk_s C_O^{1-\alpha} C_R^\alpha$ is the true exchange current density; $\eta = (E^0 - E) > 0$ is the cathodic polarization; α is the transfer coefficient; k_s is the heterogeneous rate constant; C_O and C_R are the concentrations of oxidized and reduced forms; z_0 is the charge of species O; and ψ_1 is the potential in the plane accommodating reacting species O and R, respectively.

The four corresponding dimensionless complexes were derived and quantitative interrelation between them is analyzed. These complexes have the form:

$$\pi_1 = \frac{i}{i_0}, \quad \pi_2 = \frac{F\eta}{RT}, \quad \pi_3 = \frac{z_0 F \psi_1}{RT}, \quad \pi_4 = \frac{F\psi_1}{RT}. \quad (12)$$

Let us elucidate the physical meaning dimensionless complexes obtained. The first complex presents the ratio of the measured current density to the true exchange current density; it characterizes a relative (i.e. dimensionless) rate of the electrode process. The second complex reflects balance between the electric work consumed in charge transfer connected with the electrode polarization ($F\eta$) and the energy of the thermal motion (RT).

Thus, the second complex $\frac{F\eta}{RT}$ is a dimensionless form of polarization which is the driving force of an electrochemical process.

The third and fourth complexes with a similar structure compare the work of the electric field consumed for the transfer of species O (the third complex) and the electron (the fourth one) to the plane where the activated complex is localized with the thermal motion. These two dimensionless similarity criteria describe the relative intensity of two effects connected with the influence of the electric double layer (EDL) upon the discharge rate [24].

The very interesting finding which was shown in [18] lies in the fact that the transfer coefficient α also is a similarity criterion. Indeed, the transfer coefficient enters the Bronsted relationship for an electrochemical process as follows:

$$\Delta G^\ddagger = \Delta G_0^\ddagger + \alpha F \eta, \quad (13)$$

where ΔG_0^\ddagger is the activation free energy at an equilibrium potential; and ΔG^\ddagger is the activation energy at a given value of polarization η .

Then the transfer coefficient is the ratio between the change in the activation energy resulted from electrode polarization and the electric work consumed for the electron transfer due to polarization:

$$\alpha = \frac{\Delta G^\ddagger - \Delta G_0^\ddagger}{F\eta}. \quad (14)$$

Taking into account the fact that every similarity criterion is a quantitative measure of balance between the intensities of two physical effects essential for the process involved, one can conclude that $\alpha \equiv \pi_5$ should be viewed as a special electrochemical similarity criterion (the fifth in the series criteria under consideration).

The general equation of the slow discharge theory written by using similarity criteria (12) has been derived and analyzed in [18]. The equation has the following form:

$$\pi_1 = \left\{ \exp[\pi_2 \pi_5] - \exp[\pi_2 (\pi_5 - 1)] \right\} \times \exp[-\pi_3] \exp[\pi_4 \pi_5] \quad (15)$$

Equation (15) may be simplified in some special cases. For instance, if the EDL does not influence the charge transfer kinetics (i.e. a case of the excess of supporting electrolyte, $\psi_1 = 0$), then we have $\pi_3 = \pi_4 = 0$, and the equation takes the form:

$$\pi_1 = \left\{ \exp[\pi_2 \pi_5] - \exp[\pi_2 (\pi_5 - 1)] \right\}. \quad (16)$$

Fig. 1 demonstrates the polarization curves plotted in the dimensionless complex coordinates $\ln \pi_1$ vs. $\ln \pi_2$ computed in accordance with Eq. (16). As can be seen, the section of this plot at $\pi_2 < 1$ is a straight line with a unity slope which is independent of π_5 . At $\pi_2 > 1$ this dependence is not linear, its position depends on the value of π_5 .

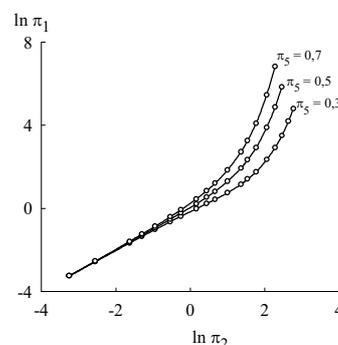


Fig. 1. Polarization dependences $\ln \pi_1$ vs. $\ln \pi_2$ at different values of π_5

Thus, when EDL has no effect on the reaction kinetics, the main concepts of the slow discharge theory may be expressed in a very simple form: the relative rate of an electrochemical reaction π_1 equals dimensionless polarization π_2 at $\pi_2 < 1$, whereas it increases proportionally to the exponent of the product of dimensionless polarization π_2 and transfer coefficient π_5 at $\pi_2 > 1$ [18].

However, the classical slow discharge theory is based on the macroscopic Butler-Volmer (BV) model, which is empirical and imperfect [25]. Thus the kinetic parameters used in this model do not

permit rational explanation of the influence of the molecular nature of the reactants, the medium and the electrode on the kinetics of the charge transfer. The Marcus theory [26] is free from these defects. The classical Marcus theory introduced a concept of the reorganization energy (λ). This value corresponds to the energy required to distort the atomic configurations of the reacting species and its solvation shells to those of the equilibrium products in the absence of electron transfer [25–27].

On the basis of Marcus theory, C. Chidsey deduced the following equations for the rate constants [25,28]:

$$k_{\text{red}}^{\text{MH}} = k_0 e^{-(1/2)\theta} \frac{I(\theta, \Lambda)}{I(0, \Lambda)}, \quad (17)$$

where $\theta = \frac{F(E-E^0)}{RT}$; E^0 is the standard potential; k_0 is

the standard rate constant (at $E=E^0$), $\Lambda = \frac{\lambda}{RT}$;

$$I(\theta, \Lambda) = \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{(\varepsilon-\theta)^2}{4\Lambda}\right]}{2 \cosh\left[\frac{\varepsilon}{2}\right]} d\varepsilon \quad \text{is an integral which}$$

cannot be determined analytically, it is evaluated numerically.

By means of the formalism developed by Chidsey three following dimensionless complexes may be derived [23]:

$$\pi_6 = \frac{F(E-E^0)}{RT} = \theta, \quad \pi_7 = \Lambda = \frac{\lambda}{RT}, \quad \pi_8 = \frac{k_{\text{red}}^{\text{MH}}}{k_0}. \quad (18)$$

Quantity π_6 reflects the ratio of the electric work consumed in the electron transfer to the energy of thermal motion. Thus, complex π_6 is a dimensionless form of polarization. The value of π_7 compares the reorganization energy with the energy of thermal motion; this criterion is a dimensionless normalized form of the reorganization energy. Complex π_8 gives the ratio of the rate constant to the standard potential of the electrochemical reaction; it characterizes a relative (dimensionless) rate of the electrochemical reaction.

Within the scope of similarity theory and dimensional analysis, the physicochemical process of electron transfer obeying the formalism under consideration should be described by the following expression [23]:

$$\pi_8 = f(\pi_6, \pi_7). \quad (19)$$

Fig. 2 presents the calculated dependence (19); some its features were discussed in detail in work [23].

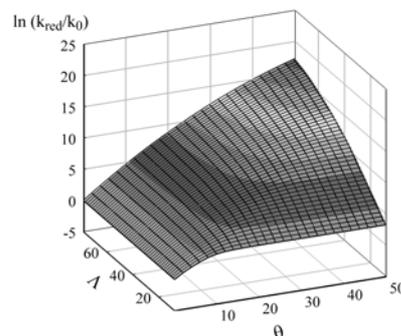


Fig. 2. Plot in coordinates $\pi_8=f(\pi_6, \pi_7)$

With reference to the issue under discussion, one should note that applying the mathematical formalism of similarity theory and dimensional analysis to the electrochemical kinetics offers some important advantages. Firstly, the number of variables decreases which is a matter of no small importance when analyzing involved multiple-factor system. Secondly, the effect of different factors is reflected in the dimensionless quantities (i.e. similarity criteria) in their interactions, revealing internal connections in the system and making quantitative pattern of phenomena more lucid. Therefore, the methods of similarity theory and dimensional analysis allow not only decreasing the number of parameters to be analyzed, but systematize them rationally. It is clear from the above discussion that the effect of reorganization energy and the energy of thermal motion on the normalized rate constant might not be analyzed separately and independently but only in aggregate, which is quantitatively expressed by the similarity criterion π_6 . The examination of the dependence shown in Fig. 2 reveals a very important fact: any point in this dependence corresponds to an infinite number of combinations of the values of overpotential, reorganization energy, temperature and rate constant, rather than to a single their combination. For example, a fixed value of dimensionless complex π_6 presents an infinite number of various sets of reorganization energy and temperature. Therefore, an investigation within the similarity theory and dimensional analysis acquires a generalized nature because it considers not isolated special cases of the combination of the parameters and conditions of a given process but an infinite number of these. Thus, the methods of the similarity theory and dimensional analysis open the way to a theoretically substantiated and optimized approach to planning electrochemical experiments and then describing and interpreting the obtained data.

However, as was observed in work [18] the application of dimensional analysis and similarity

theory for interpreting the basic equations of the slow discharge theory offers no substantial advantages over the «usual» equations of electrochemical kinetics. The benefits of the approach proposed could be fully realized only when one analyzes the behavior of electrochemical systems with complicated physico-chemical content. Such cases were considered in [4,19,21,22].

We will discuss a successive electrochemical reaction of the type:



where A, P, and B refer to the initial reactant, the intermediate, and the target product, respectively.

The following equations of non-steady-state linear diffusion describe the mass transfer of species A and P from the surface to the bulk electrolyte:

$$\frac{\partial C_A}{\partial \tau} = D_A \frac{\partial^2 C_A}{\partial x^2}, \quad \frac{\partial C_P}{\partial \tau} = D_P \frac{\partial^2 C_P}{\partial x^2}. \quad (21)$$

The initial and boundary conditions may be written by the expressions:

$$\begin{aligned} C_{A,\tau=0} &= C_{A0}, \quad C_{P,\tau=0} = C_{P0}, \\ D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=0} &= \frac{i_1}{F}, \quad D_P \left(\frac{\partial C_P}{\partial x} \right)_{x=0} = \frac{i_2}{F} - \frac{i_1}{F}, \\ C_{A,x \rightarrow \infty} &= C_{A0}, \quad C_{P,x \rightarrow \infty} = C_{P0}. \end{aligned} \quad (22)$$

Here i_1 and i_2 are the current densities in the first and second steps in the reactions chain (20).

Solutions for the set of differential equations (21) with the above initial and boundary conditions were found by means of numerical computer-aided integration [4]. Analysis of the behavior of the electrochemical system under consideration is complicated by the fact that the 14 values and parameters enter into the corresponding equations. Applying the methods of similarity theory and dimensionless analysis enables us to reduce the number of parameters involved down to 8, these dimensionless complexes values being written as follows:

$$\begin{aligned} X_1 &= \frac{\tau(k_1^0)^2}{D_A}, \quad P_1 = \frac{D_P}{D_A}, \quad P_2 = \frac{k_2^0}{k_1^0}, \quad P_3 = \frac{C_{P0}}{C_{A0}}, \\ \pi_9 &= \frac{\alpha_1 F(E_1^0 - E)}{RT}, \quad \pi_{10} = \frac{\alpha_2 F(E_2^0 - E)}{RT}, \\ Y_1 &= \frac{i_1}{F k_1^0 C_{A0}}, \quad Y_2 = \frac{i_2}{i_1}. \end{aligned} \quad (23)$$

The complex X_1 includes the value of the current time τ , and is, for the system under study, a dimensionless function of time. The value Y_1 is a dimensionless form of the current density of the first step in the successive electrochemical reaction (20). The value Y_2 is a dimensionless variable characterized the ratio between the current densities of the second and first steps in the reaction (20), respectively. According to Buckingham's π theorem, a kinetic analysis of consecutive electrochemical process (20) reduces to the investigation on the following two criterion dependences:

$$Y_1 = f_1(X_1; P_1, P_2, P_3; \pi_9; \pi_{10}), \quad (24)$$

$$Y_2 = f_2(X_1; P_1, P_2, P_3; \pi_9; \pi_{10}). \quad (25)$$

These dependences (Fig. 3, 4) were computed and analyzed in study [4]. As can be seen, all other conditions being equal, diminishing the dimensionless polarization π_9 in the first step of reaction (20) results in a decrease in Y_1 . The value of the dimensionless polarization π_{10} in the second step of electrochemical transformation affects the value of Y_1 only at negative values of π_9 (see Fig. 3). A quasi-steady-state diffusion is possible solely in the case of the simultaneous fulfillment of two conditions: $\pi_9 \leq 0$ and $\pi_{10} > 0$ [4]. The dependences $Y_2 = f_2(X_1)$ are well described by straight lines in the logarithmic coordinates (see Fig. 4). Their ascending character points to the convergence of values i_1 and i_2 with time. The position and the slope of the $\ln Y_2$ vs. $\ln X_1$ lines largely depend on the magnitude of π_{10} and are practically independent of π_9 . Thus, the inspection of criterion dependences allowed establishing the effect of different parameters on the behavior of the electrochemical system under study and ascertaining the combinations of kinetic parameters at which the reaction will proceed in a quasi-steady-state regime.

It should be observed that a kinetic analysis of the reaction under study can, in principle, be performed by considering the effect of the various initial values (E_1^0 , E_2^0 , k_1^0 , k_2^0 , etc.) on the currents i_1 and i_2 . However, then the results of the analysis could not be presented in such a laconic and illuminating form as that with the application of dimensionless variables and parameters.

In study [22], the similarity theory and dimensional analysis were applied in order to derive a universal system of dimensionless quantities (i.e. similarity criteria) which allows describing the kinetics of the metal electrodeposition reaction with the participation of stable intermediates on a rotating disc electrode. It was shown that this set of criterion includes, among others, a modified Reynolds number, a modified Stanton diffusion criterion [29], and a dimensionless variable which is the merit of nonlinearity of a given electrode reaction considered as an element of electrical circuit. The proposed

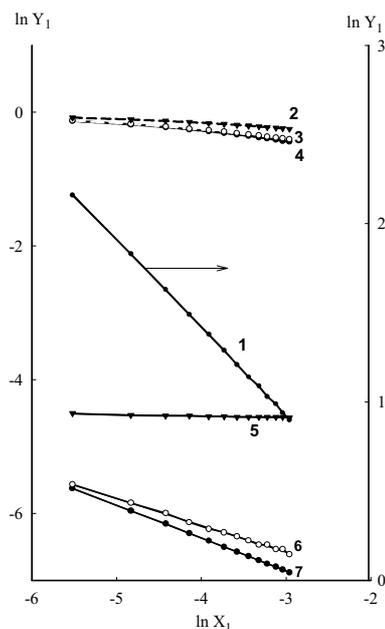


Fig. 3. Dependences of Y_1 on the value of X_1 : $P_1=1, P_2=1, P_3=0$; (1) $\pi_9=3.89, \pi_{10}=-3.89; 0; 3.89$; (2) $\pi_9=0, \pi_{10}=3.89$; (3) $\pi_9=0, \pi_{10}=0$; (4) $\pi_9=0, \pi_{10}=-3.89$; (5) $\pi_9=-3.89, \pi_{10}=3.89$; (6) $\pi_9=-3.89, \pi_{10}=0$; (7) $\pi_9=-3.89, \pi_{10}=-3.89$

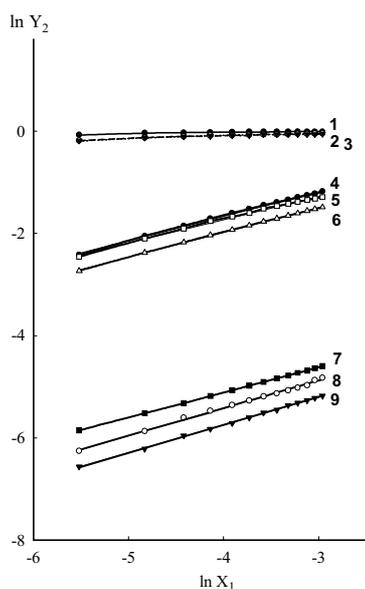


Fig. 4. Dependences of Y_2 on the value of X_1 : $P_1=1, P_2=1, P_3=0$; (1) $\pi_9=3.89, \pi_{10}=3.89$; (2) $\pi_9=-3.89, \pi_{10}=3.89$; (3) $\pi_9=0, \pi_{10}=3.89$; (4) $\pi_9=3.89, \pi_{10}=0$; (5) $\pi_9=-3.89, \pi_{10}=0$; (6) $\pi_9=0, \pi_{10}=0$; (7) $\pi_9=-3.89, \pi_{10}=-3.89$; (8) $\pi_9=3.89, \pi_{10}=-3.89$; (9) $\pi_9=0, \pi_{10}=-3.89$

mathematical model can be flexibly adapted to describing the kinetics of practically any complicated electrochemical system in which a step-wise metal electrodeposition process occurs. The derived dimensionless variables were used in interpreting the results of the study on the chromium electrodepo-

sition from oxalate and formate trivalent chromium baths on the rotating disc electrode [22].

Dimensional analysis and similarity theory in applied electrochemistry

The utility of dimensional analysis and similarity theory in electrochemical engineering was stressed in work by Kreysa [30]. It was shown that a set of electrochemical similarity criteria (Kreysa named them as «performance criteria» or «figures of merit») allow a comparable characterization of different electrochemical cells and reactions with respect both to technical and economic points of view. A set of electrochemical similarity criteria was proposed in the work abovementioned. Several criteria proposed are presented as follows¹

1) Current efficiency. The current efficiency (CE) is a «yield of charge»; it may be given as:

$$CE = \frac{Q_i}{Q_\Sigma}, \tag{26}$$

where Q_i and Q_Σ are the stoichiometric charge consumption of the product and the consumed amount of charge, respectively.

2) Fractional conversion. If reactant A undergoes an electrochemical reaction:



the fractional conversion is defined as:

$$X_A = 1 - \frac{n_A}{n_A^0}, \tag{28}$$

where n_A^0 is the starting molar amount of substrate; n_A is the final amount of substrate; ν_i is the corresponding stoichiometric coefficients.

3) Energy yield which is determined by the expression:

$$\gamma_G = \frac{U_0 \phi^e}{U_c}, \tag{29}$$

where U_c is the cell voltage; U_0 is the reversible cell voltage; ϕ^e is the current efficiency.

4) Effectiveness factor. This value is given as:

$$\gamma = \frac{i_{\text{obs}}}{i_{\text{dif}}}. \tag{30}$$

where i_{obs} and i_{dif} are the observed current density and the current density under diffusion limited conditions, respectively.

These and similar dimensionless criteria are

¹ We consider here only the most important and typical criteria. For the full list of the criteria, the reader is referred to the original paper [30].

widely used in electrochemical engineering [30].

Conclusions

As shown above, the methods of similarity theory and dimensional analysis are successfully utilized in pure and applied electrochemistry. For instance, such well known and widespread values as current efficiency and transfer coefficient proved to be typical dimensionless similarity criteria. The application of the mathematical formalism of similarity theory and dimensional analysis to electrochemistry offers a whole number of important advantages:

1) reduction in the number of variables and parameters analyzed which can sufficiently simplify a problem;

2) reflecting the effect of different factors in their interactions which allows revealing internal connections in the system under study and making quantitative relationships clear and instructive;

3) the possibility of flexible adaptation to describing various complex electrochemical systems;

4) the theory of similarity can be utilized to predict the performance of a new design based on data from an existing, similar design. Another use of similarity theory is in validation of computer simulations with the ultimate aim to eliminate the need for physical models.

5) a generalized nature of analysis since the similarity theory and dimensional analysis consider not isolated special cases of the combination of the parameters of a given process but an infinite number of those.

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APPLICATION OF DIMENSIONAL ANALYSIS AND SIMILARITY THEORY IN ELECTROCHEMISTRY: A REVIEW

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Similarity theory and dimensional analysis were shown to be suitable both in electrochemical kinetics and in electrochemical engineering. The corresponding original and literature data were reviewed. The use of dimensionless groups in electrochemical mass transfer problems was described; the similarity criteria involved were summarized. Similarity theory and dimensional analysis may be successively applied for a kinetic analysis of an electrochemical reaction described both by the equations of the slow discharge theory and by the Marcus–Hush–Chidsey formalism. The corresponding dimensionless quantities (similarity criteria) were derived and approximating interrelations between them were analyzed. The results of numerical simulation of the kinetics of a two-stage electrochemical reaction with partial transfer of intermediates between the electrode surface and the bulk solution in conditions of linear nonsteady-state diffusion of reactants are analyzed with the use of dimensional analysis and similarity theory (i.e. a theory of generalized variables). Some dimensionless complexes utilized in applied electrochemistry were reviewed. The main advantages of the application of similarity theory and dimensional analysis in pure and applied electrochemistry were generalized.

Keywords: similarity theory; dimensional analysis; similarity criterion; electrochemical system.

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