

Journal of Electroanalytical Chemistry 379 (1994)43-37

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Effects of electromigration on polarization curves for parallel electrode reactions in the absence of supporting electrolyte

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Received 20 December 1993: in revised form 23 March 1994

Abstract

Polarization curves are analyzed for two different types of parallel clcctrochemical reactions, with no supporting electrolyte in the solution. The consideration of the problem is based on an analytic solution in parametric form of Nernst–Planck equations for electrodiffusion with boundary conditions of the Butler-Volmer type. It is found that the current–voltage curves for such systems clearly display the interaction of ionic components due to migration current exaltation phenomena.

Keywords: Polarization curves; Electromigration

1. Introduction

The first experimental observation of the important role of electromigration in parallel electrochemical processes was made by Kemula and Michalski [1], who studied the increase of the limiting current of polarographic cation reduction in the presence of parallel reduction of oxygen. This phenomenon was called "migration current exaltation" and its first quantitative description was given by Heyrovsky and Bures [2]. They studied the polarographic irreversible reduction of Na' ions from dilute NaCl solutions. First, the polarographic wave corresponding to the discharge of Na⁺ ions was recorded, then the solution was saturated with atmospheric oxygen from the air, and a new polarographic wave was recorded. The limiting current in the second case was higher than the sum of oxygen reduction current i_{O} , and the limiting current of Na' reduction i_{Na^+} in the absence of oxygen. Heyrovsky and Bures called this additional current the "exaltation current" i_{exal}:

 $i = i_{0,} + i_{Na^+} + i_{exal}$

The explanation of the migration current exaltation effect given in Refs. [3] and [4] was based on the

approximate method of calculation of migration current presented by Heyrovsky. In this method the limiting current of discharging ions was taken as the sum of diffusion and migration currents, the last being assumed to be proportional to the total current with the proportionality coefficient being equal to the transport number of discharging ions. Heyrovsky's theory gives us a qualitative description of this phenomenon.

In a series of publications [5-18] a theory of migration current effects for parallel electrode reactions was presented, based on exact analytic solutions of coupled Nernst-Planck equations for electrodiffusion for two parallel electrode reactions. In particular, in contrast to the Heyrovsky theory, it was taken into account that as a result of reduction of neutral substance (oxygen) negatively charged reduction products OH- ions) appear in the diffusion layer close to the electrode:

$$O_{2} + 2H_{2}O + 4e^{-} \rightarrow 4OH^{-}$$

It was shown that the exaltation current depends on the mobility of OH- ion u_{OH^-} but not on anion mobility u_{CI^-} :

$$i_{\text{exal}} = i_{o_2} \frac{u_{\text{Na}}}{u_{\text{OH}}}$$

For the case of two parallel reactions involving reduction of two different cations, an extended theory of correlational exaltation of migration current describing the mutual influence of ionic transport due to

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electrodiffusion process was presented in Refs. [5] and [7].

In the above-mentioned papers, only the relations between the partial limiting diffusion-migration currents were found. In the present paper we describe the behaviour of total current-voltage curves for parallel electrode processes described by Butler-Volmer reaction kinetics with account of electromigration effects. For simplicity only the case of a stationary processes at a planar electrode with a one dimensional Nernst diffusion layer is considered. This analysis can be generalized for corresponding non-stationary problems, such as parallel reactions at a growing mercury drop electrode, as considered in Ref. [9].

2. Problem formulation

Consider a reaction with reduction of cations with simultaneous reduction of neutral species in the absence of supporting electrolyte in the solution. The concentrations C, of cations (Na⁺, for instance), C_2 of anions (Cl⁻, for instance), C_3 of negatively charged products (OH-) of reduction of neutral molecules (O₂) together with the electric potential Φ in the diffusion layer can, for dilute solutions, be computed from the Nernst-Planck equations for electrodiffusion

$$D_1 \frac{\mathrm{d}C_1}{\mathrm{d}X} + z_1 C_1 \frac{FD_1}{\mathrm{RT}} \frac{\mathrm{d}\Phi}{\mathrm{d}X} = \frac{i_1}{Fz_1} \tag{1}$$

$$\frac{\mathrm{d}C_2}{\mathrm{d}X} - z_2 C_2 \frac{F}{RT} \frac{\mathrm{d}\Phi}{\mathrm{d}X} = 0 \tag{2}$$

$$D_3 \frac{\mathrm{d}C_3}{\mathrm{d}X} - z_3 C_3 \frac{FD_{\circ}}{\mathrm{RT}} \frac{\mathrm{d}\Phi}{\mathrm{d}X} - \frac{i_0}{Fz_3} \tag{3}$$

$$z_1 C_1 = z_2 C_2 + z_3 C_3 \tag{4}$$

Here D_1 and D_3 are the diffusion coefficients for cations (Na⁺) and anions (OH-), F the Faraday constant, R the gas constant, and T the absolute temperature i_0 and i, are the electric current densities for neutral substance (O₂) reduction and discharge of cations (Na⁺), respectively. X is the coordinate perpendicular to the electrode and z_1 , z_2 and z_3 the charge numbers for cations (Na⁺), anions (Cl⁻) and product of the second electrode reaction (OH-). It is assumed that the product of cation reduction is neutral. Below we shall consider the simple case $z_1 = z_2 = z_3 = 1$.

The boundary conditions at X = L, where L is the thickness of the Nernst diffusion layer, are

$$C_1(L) = C^0, C_2(L) = C^0; C_3(L) = 0; \Phi(L) = 0$$
 (5)

In terms of the dimensionless coordinate x = X/L,

concentrations $c_m = C_m/C^0$, (m= 1, 2, 3) and electric potential $\psi = F\Phi/RT$, Eqs. (1-4) may be written in the form

$$\frac{\mathrm{d}c_1}{\mathrm{d}x} + c_1 \frac{\mathrm{d}\psi}{\mathrm{d}x} = j_1 \tag{6}$$

$$\frac{\mathrm{d}c_2}{\mathrm{d}x} - c_2 \frac{\mathrm{d}\psi}{\mathrm{d}x} = 0 \tag{7}$$

$$\frac{\mathrm{d}c_3}{\mathrm{d}x} - c_3 \frac{\mathrm{d}\psi}{\mathrm{d}x} = -j_0 \tag{8}$$

$$c_1 = c_2 + c_3 \tag{9}$$

Here $j_1 = i_1 L / FD_1 C^0$ and $j_0 = i_0 L / FD_3 C^0$. The solution of Eqs. (6-9) is, see e.g. Refs. [5] and [6]:

$$c_1 = \frac{(j_1 - j_0)}{2} (x - 1) + 1 \tag{10}$$

$$\psi = \frac{(j_1 - j_0)}{(j_1 + j_0)} \ln \left[\frac{(j_1 - j_0)}{2} (x - 1) + 1 \right]$$
(11)

The current density at the electrode surface (x = 0) is assumed to be given by the following form of the Butler-Volmer law

$$j_{1} = j_{1}^{0} \{ c_{1}(0) \exp(-(1-\alpha) [V - \psi(0)]) - \exp(\alpha [V - \psi(0)]) \}$$
(12)

where j_1^0 is the exchange current density, *a* transfer coefficient, $c_1(0)$ the surface concentration of discharging cations, $\psi(0)$ the potential drop in the diffusion layer and $V - \psi(0)$ the reaction overvoltage.

3. Analysis of migration current exaltation

Substitution of expressions for $c_1(0)$ and $\psi(0)$ obtained from Eqs. (10) and (11) into the Butler-Volmer law gives the current-voltage curve for cation reduction process in the presence of a parallel reaction

$$j_{1} = j_{1}^{0} \left(1 - \frac{j_{1} - j_{0}}{2} \right)^{-\frac{j_{1} - j_{0}}{j_{1} + j_{0}}} \left\{ \left(1 - \frac{j_{1} - j_{0}}{2} \right)^{\frac{2j_{1}}{j_{1} + j_{0}}} \times \exp(-(1 - \alpha)V) - \exp(\alpha V) \right\}$$
(13)

From this relation, one can in the simplest case with a = 1/2, compute V in terms of j,, which gives:

$$\mathcal{V} = -\frac{2}{j_1 + j_0} \ln\left(1 - \frac{j_1 - j_0}{2}\right) - 2 \operatorname{arcsinh}\left\{\frac{j_1}{2j_1^0} \left(1 - \frac{j_1 - j_0}{2}\right)^{-1/2}\right\}$$
(14)



Fig. 1. Current-voltage curves determined by Eq. (14) $j_1^0 = 0.001$; 1: $j_0 = 0$; 2: $j_0 = 1$; 3: $j_0 = 2$; 4: $j_0 = 3$; 5: $j_0 = 4$.

In the general case with an arbitrary value of the transfer coefficient α , it is possible to express the current-voltage curve in parametric form. Denoting $\eta = V - \psi(0)$ and substituting the expression for $c_1(0)$ into the Butler-Volmer law (Eq. (12)) gives the following relation between j_1 and η

$$j_{1} = j_{1}^{0} \frac{1 + \frac{j_{0}}{2} - \exp(\eta)}{\exp((1 - \alpha)\eta) + \frac{j_{1}^{0}}{2}}$$
(15)

This relation and the definition of η written in the form $V = \eta + \psi(0)$, where $\psi(0)$ is given in terms of j_1 by the solution (Eq. (11)), gives the current-voltage curve in parametric form (with η as a parameter).

Fig. 1 shows the function $j_1(V)$ for a fixed (small) value of j_1^0 and different values of j_0 . All curves have a wave-like shape. The limiting current density j_1^l , say, depends on j_0 as shown by the following formula

$$j_1^l = 2 + j_0 \tag{16}$$

For $j_0 = 0$, one recovers $j_1 = 2$, which, in the present scaling, is the limiting diffusion-migration current in the binary electrolyte.

As can be seen from Fig. 1, the value of the half-wave potential is a monotonically increasing function of j_0 .

The total dimensional current density in the system under consideration is

$$i_t = i_1 + i_0 = \frac{FD_1C_1^0}{L}j_1 + \frac{FD_3C_1^0}{L}j_0$$
(17)

and the limiting total current density is

$$i^{l} = 2\frac{FD_{1}C_{1}^{0}}{L} + \left(\frac{D_{1}}{D_{3}} + 1\right)i_{0}.$$
 (18)

From these results, it follows that the current-voltage curve for the cation reduction depends, as expected, on the current of the parallel reduction. The current-voltage curve for the latter reaction is, however, independent of the former reaction.

4. Analysis of correlation exaltation of migration current

Consider now the parallel reduction of two different cations X^+ and Y^+ in the absence of supporting electrolyte. For $z_1 = z_2 = z_3 = 1$, the corresponding dimensionless equations for electrodiffusion are

$$\frac{\mathrm{d}c_1}{\mathrm{d}x} + c_1 \frac{\mathrm{d}\psi}{\mathrm{d}x} = j_1 \tag{19}$$

$$\frac{\mathrm{d}c_2}{\mathrm{d}x} + c_2 \frac{\mathrm{d}\psi}{\mathrm{d}x} = j_2 \tag{20}$$

$$\frac{\mathrm{d}c_3}{\mathrm{d}x} - c_3 \frac{\mathrm{d}\psi}{\mathrm{d}x} = 0 \tag{21}$$

$$c_1 + c_2 = c_3 \tag{22}$$

Here $j_1 = i_1 L / FD_1 C_1^0$ and $j_2 = i_2 L / FD_2 C_2^0$ are dimensionless exchange current densities and $c_m = C_m / C_3^0$, (m = 1, 2, 3). At the edge of the diffusion layer (x = 1) the following boundary conditions are prescribed

$$c_1(1) = c_1^0; c_2(1) = c_2^0; c_3(1) = 1; \psi(1) = 0$$
(23)

The current densities at the electrode surface (x = 0) are assumed to be given by the following Butler-Volmer laws:

$$j_{1} = j_{1}^{0} \left\{ \frac{c_{1}(0)}{c_{1}^{0}} \exp(-(1 - \alpha_{1}) [V - \psi(0)]) - \exp(\alpha_{1} [V - \psi(0)]) \right\}$$
(24)
$$j_{2} = j_{2}^{0} \left\{ \frac{c_{2}(0)}{c_{1}^{0}} \exp(-(1 - \alpha_{2}) [V - \Delta - \psi(0)]) \right\}$$

$$= f_{2}^{0} \left\{ \frac{1}{c_{2}^{0}} \exp(-(1-\alpha_{2})[V - \Delta - \psi(0)]) - \exp(\alpha_{2}[V - \Delta - \psi(0)]) \right\}$$
(25)

In these expressions, j_1^0 and j_2^0 are the dimensionless exchange current densities for the two reactions, α_1 and α_2 are the corresponding transfer coefficients and $\Delta = \psi_2^e - \psi_1^e$ is the difference of equilibrium potentials between the two reactions. In what follows, the simplest case with α_1 and α_2 are equal to 1/2 is considered.

Eqs. (19-22) can be easily integrated [6]. One finds the following expressions for the surface concentrations of cations $c_1(0)$, $c_2(0)$ and the electric potential drop in the diffusion layer $\psi(0) - \psi(1)$:

$$\frac{c_m(0)}{c_m^0} = \frac{(j/2 - 1)j_m c_m^0 + 1}{1 - j}, \quad (m = 1, 2)$$
(26)

$$\psi(0) = \ln(1-j)$$
(27)

where

$$j = \left(j_1 c_1^0 + j_2 c_2^0\right) / 2 \tag{28}$$

From formula (26) one finds the relation between the partial limiting current J_1^l and the current j_2 , which corresponds to the condition $c_1(0) = 0$ [3,4]:

$$j_2 = \frac{4}{c_2^0} \left[1 - \frac{j_1' c_1^0}{4} - \frac{1}{j_1' c_1^0} \right]$$
(29)

Analogously, the condition $c_2(0) = 0$ leads to the relation between the partial limiting current j_2^l and the current j_1 :

$$j_1 = \frac{4}{c_1^0} \left[1 - \frac{j_2' c_2^0}{4} - \frac{1}{j_2' c_2^0} \right]$$
(30)

In terms of $y = \exp[-V/2]$ the Butler-Volmer laws (24, 25) may be written as follows

$$j_1 = j_1^0 \left[\frac{c_1(0)}{c_1^0} y - \frac{1}{y} \right]$$
(31)

$$j_2 = j_2^0 \left[\frac{c_2(0)}{c_2^0} yt - \frac{1}{yt} \right]$$
(32)

where $t = \exp[-\Delta/2]$. From expression (31), one can solve for y whereby one obtains that

$$y = \frac{1}{2} \left(\frac{c_1^0 j_1}{c_1(0) j_1^0} \right) + \sqrt{\frac{1}{4} \left(\frac{c_1^0 j_1}{c_1(0) j_1^0} \right)^2 + \frac{c_1^0}{c_1(0)}}$$
(33)

A similar expression for y can be computed from expression (32). Thus, expressions (32) and (33), after substitution of $c_1(0)$ and $c_2(0)$, expressed in terms of j, j_1 and j_2 from solutions (26) and (28), give a relation between j_1 and j_2 , that does not, remarkably enough, depend on V and $\psi(0)$. By a simple numerical method, one can compute the "trajectories" $j_1(j_2)$ in the j_1 , j_2 plane, which depend on the values of parameters j_1^0 , j_2^0 , c_1^0 , c_2^0 and t.

5. Numerical simulation and discussion

The resulting current-voltage curves for two parallel processes can be found through use of the following algorithm: for given values of parameters and some values of j_1 , the corresponding value of j_2 can, as pointed out at the end of previous section, be determined. From expressions (27) and (33) one then finds the corresponding values of $\psi(0)$ and V. In this way, one obtains curves $j_1(V)$ and $j_2(V)$ and the total dimensionless current density j_t

$$j_1 = \frac{(i_1 + i_2)L}{FD_1C_3^0} = c_1^0 j_1 + \frac{D_2}{D_1} c_2^0 j_2$$
(34)

Some numerical results are presented in Figs. 2-4.

Fig. 2 shows the effective j_1-j_2 trajectories for different values of the shift Δ between the equilibrium



Fig. 2. Functions $j_1(j_2)$ determined by Eqs. (31) and (32). $c_1^0 = 0.7$; $c_2^0 = 0.3$; 1: t = 1; 2: t = 2; 3: t = 20; 4: t = 200; 5: function $j_1^l = j_1^l(j_2)$ determined by Eq. (29); 6: function $j_2^l = j_2^l(j_1)$ determined by Eq. (30).



Fig. 3. Current-voltage curves for correlational exaltation of migration currents. 1: curve $j_1(V)$; 2: curve $j_2(V)$; $c_1^0 = 0.3$; $c_2^0 = 0.7$; $j_1^0 = j_2^0 = 0.0001$; $D_1 = D_2$; t = 200. I' and 2': curves $j_1(V)$ and $j_2(V)$ in the absence of exaltation of migration current. 3: total current density j(V).



Fig. 4. Current-voltage curves for correlational exaltation of migration currents. 1: curve $j_1(V)$; 2: curve $j_2(V)$; $c_1^0 = 0.7$; $c_2^0 = 0.3$; $j_1^0 = j_2^0 = 0.0001$; $D_1 = D_2$; t = 200. 1' and 2': curves $j_1(V)$ and $j_2(V)$ in the absence of exaltation of migration currents. 3: total current density j(V).

potentials of the reactions. All curves are located inside the region limited by coordinate axes and curves $j_1^l = j_1^l(j_2)$ and $j_2^l = j_2^l(j_1)$ that are given by expressions (29) and (30). For values of t of the order of unity, i.e. for $\psi_1^c \sim \psi_2^c$, these curves are found in the central part of this region. When $t \gg 1$, the first reaction approaches its limiting current while the current of the second reaction is still small. For high potentials, both reactions approach their limiting currents which are $j_1^l = j_2^l = 2$. In this case, it is interesting to note that two parallel processes become quasi-independent in the sense that their partial limiting currents become equal to the limiting currents for two independent reactions of cation reduction in two binary electrolytes.

Figs. 3 and 4 show the current-voltage curves for the two parallel cation reduction processes. The dashed lines correspond to the current-voltage curves for two separate processes of cation reduction with the same concentrations of cations. One notices that, due to electrodiffusional conjugation of two processes, the limiting currents of both reactions increase. This fact reflects the mutual influence of the two processes. Due to this correlational exaltation of migration currents, the total limiting current, which is always equal to the sum of both partial limiting currents, can thus exceed substantially the sum of the limiting currents of two independent processes proceeding in solutions with an excess of supporting electrolyte.

6. Conclusion

Current-voltage curves for two types of kinetically independent parallel electrode reactions have been computed. The results are based on exact solutions of the Nernst-Planck equations for electrodiffusion with boundary conditions given by Butler-Volmer laws. The one dimensional case of the Nernst diffusion layer model was used, which made it possible to find the solutions in closed analytical form. Computed polarization curves show a clearly pronounced dependence of currents of parallel reactions as a result of mutual dependence of transport processes. This dependence is caused by conjugation of electromigration processes in the absence of supporting electrolyte.

Acknowledgments

Financial support from the Royal Swedish Academy of Sciences for the participation of Yu.I.K. and A.V.S. in the present work is gratefully acknowledged. One of the authors (Yu.I.K.) would like to acknowledge the Department of Hydromechanics of the Royal Institute of Technology, Stockholm, where this work was done, for financial support and hospitality as well as partial support from the Fund of Fundamental Researches of the Russian Academy of Sciences.

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