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PROPERTIES OF POLARIZATION CURVES FOR ELECTROCHEMICAL CELLS DESCRIBED BY BUTLER–VOLMER KINETICS AND ARBITRARY VALUES OF THE TRANSFER COEFFICIENT

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Abstract — Theoretical investigation of potentiostatic electrolysis of a metallic salt in three component electrolyte solution was carried out for a cell consisting of two identical parallel electrodes. Analytical and numerical results are given for polarization curves for electrochemical cells with arbitrary values of transfer coefficient α and exchange current density. Theoretical analysis of the electrodiffusion problem, based on an exact solution of the Nernst–Planck equations with boundary conditions of Butler–Volmer type, led to a formula for the polarization curve that is similar to the Tafel equation but with an effective transfer coefficient $\alpha_{eff} = \alpha(1 - \alpha)$. It was shown that, under certain conditions, the polarization curve can have two inflection points.

Key words: electrochemical kinetics, electrodiffusion, polarization curves, transfer coefficient.

INTRODUCTION

In a recently published paper [l], a theoretical investigation of potentiostatic one-dimensional electrolysis of a metallic salt in a three-component electrolyte solution was carried out for an electrochemical cell having two identical parallel electrodes. The analysis led to an exact solution of the system of Nernst–Plank transport equations accounting ion transfer by diffusion and migration mechanisms [2-5]. The polarization curves were derived in parametric analytic form for the special case where the transfer coefficient a in the Butler–Volmer law is equal to 0.5 and for an arbitrary concentration of supporting electrolyte.

Qualitatively, the polarization curves found in [1] for $\alpha = 0.5$ were similar to those found for a wide class of different systems in which ionic diffusion and migration transport were analysed at the surface of one electrode [6-10]. In particular, polarization curves of this type were studied in recently published papers [11-16]. On the other hand, for $\alpha \neq 0.5$, one may expect effects on the current–voltage curve due to the asymmetry of the reaction. In this paper, this issue is examined in some detail for arbitrary values of the exchange current density.

1. *Problem statement*

Consider a binary electrolyte with ionic charge numbers z_1 and z_2 for cations and anions, respectively. The following reduction reaction occurs at the cathode:

$$M^{z_1 +} + z_1 e^- \rightarrow M.$$
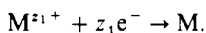
At the anode the same reaction proceeds in the opposite direction. We shall analyse the current–voltage characteristic of the cell assuming that there is no convective motion of the electrolyte in the space between electrodes, and that ionic transport takes place owing to diffusion and migration in the $\vec{e}_x$-direction, which is perpendicular to the electrodes' surfaces at $X = 0$ (cathode) and $X = L$ (anode).

Let the cathode electric potential be equal to 0 and the anode potential equal to V. We shall assume that there is no redistribution of the electric potential Φ in the diffuse double layers during current flow.

In the case of dilute electrolyte, the Nernst–Einstein relation for the diffusion and mobility coefficients can be used. The concentrations of cations and anions, C_1 and C_2, respectively, and the electric potential Φ can then be computed from the following system of equations:

$$D_1 \frac{dC_1}{dX} + z_1 C_1 \frac{FD_1}{RT} \frac{d\Phi}{dX} = -\frac{i}{Fz_1}, \quad (1)$$

$$\frac{dC_2}{dX} - z_2 C_2 \frac{F}{RT} \frac{d\Phi}{dX} = 0, \quad (2)$$

$$z_1 C_1 - z_2 C_2 = 0. \quad (3)$$

Here D_1 is the diffusion coefficient for cations, F is the Faraday constant, R is the gas constant, T is the absolute temperature, and i is the electric current density.

From the Butler–Volmer law, the electric current density can be expressed in terms of overpotentials for electrode reactions, which are $\Phi(0)$ and $V - \Phi(1)$

for the cathode and anode, respectively:

$$i = i_0 \left\{ e^{-[\alpha z_1 F\Phi(0)/RT]} - \frac{C_1(0)}{C_1^0} e^{[(1-\alpha)z_1 F\Phi(0)/RT]} \right\}. \quad (4)$$

$$i = i_0 \left\{ \frac{C_1(0)}{C_1^0} e^{[(1-\alpha)z_1 F(\Phi(L)-V)/RT]} - e^{-[\alpha z_1 F(\Phi(L)-V)/RT]} \right\}. \quad (5)$$

In these formulae, i_0 is the exchange current density, for a concentration of cations equal to C_1^0, and a is the transfer coefficient.

Taking into account that the reactions at anode and cathode have equal rates, conservation conditions for C_1 and C_2 may be written in the form

$$\int_0^L C_m \, dX = C_m^0 L, \quad m = 1, 2, \quad (6)$$

where C_m^0 are the initial (homogeneous) concentrations of species in the electrolyte.

Equations (2–6) can be written in dimensionless form in terms of the coordinate $x = X/L$, the concentrations $c_m = C_m/C_1^0$, $(m = 1, 2)$ and the electric potential $\phi = F\Phi/RT$:

$$\frac{dc_1}{dx} + z_1 c_1 \frac{d\phi}{dx} = -\frac{j}{z_1}, \quad (7)$$

$$\frac{dc_2}{dx} - z_2 c_2 \frac{d\phi}{dx} = 0, \quad (8)$$

$$z_1 c_1 - z_2 c_2 = 0. \quad (9)$$

The boundary conditions (4–5) can be written in the form

$$j = j_0 \{ c_1(0) e^{(1-\alpha)z_1\phi(0)} - e^{-\alpha z_1\phi(0)} \}, \quad (10)$$

$$j = j_0 \{ e^{-\alpha z_1(\phi(1)-v)} - c_1(1) e^{(1-\alpha)z_1(\phi(1)-v)} \} \quad (11)$$

where $j = -iL/FD_1 C_1^0$, $j_0 = i_0 L/FD_1 C_1^0$ and $v = V/RT$.

For the normalization conditions (6), one obtains the following expressions

$$\int_0^1 c_1 \, dx = 1, \quad \int_0^1 c_2 \, dx = \frac{z_1}{z_2}, \quad (12)$$

Integration of equations (7–9) after consideration of the conditions (12), gives the following expressions for the concentrations:

$$c_1(x) = 1 + \frac{jz_2}{z_1(z_1 + z_2)} (\tfrac{1}{2} - x) = \frac{c_2(x)z_1}{z_2}. \quad (13)$$

From equation 8, for example, one then finds the expression for the total potential drop in electrolyte:

$$\Delta\phi = \phi(1) - \phi(0) = \frac{1}{z_2} \ln \frac{c_2(1)}{c_2(0)} = \frac{1}{z_2} \ln \frac{j^1 + j}{j^1 - j}, \quad (14)$$

where

$$c_1(0) = 1 - \frac{j}{j^1}, \quad (15)$$

$$c_1(1) = 1 + \frac{j}{j^1}, \quad (16)$$

and

$$j^1 = \frac{2z_1(z_1 + z_2)}{z_2}. \quad (17)$$

j^1 is the dimensionless limiting diffusion–migration current in the cell, corresponding to the condition $c_1(0) = 0$.

Rewriting the boundary conditions (10–11) by using expressions (14–16) one obtains the following two relations between $\phi(0)$, v and j:

$$j = j_0 \left\{ \left(1 - \frac{j}{j^1} \right) e^{(1-\alpha)z_1\phi(0)} - e^{-\alpha z_1\phi(0)} \right\}, \quad (18)$$

and

$$j = j_0 \left\{ e^{-\alpha z_1[\phi(0)-v+(1/z_2)\ln[(j^1+j)/(j^1-j)]]} \right.$$
$$\left. - \left(1 + \frac{j}{j^1} \right) e^{(1-\alpha)z_1[\phi(0)-v+(1/z_2)\ln[(j^1+j)/(j^1-j)]]} \right\}. \quad (19)$$

Elimination of $\phi(0)$ from these expressions leads to an implicit expression for the polarization curve $j(v)$. A convenient form is obtained by solving for $e^{z_1\phi(0)}$, which gives the following result

$$E = e^{z_1\phi(0)}$$

$$= \frac{e^{\alpha z_1[v-(1/z_2)\ln(j^1+j/j^1-j)]} + 1}{1 - \frac{j}{j^1} + \left(1 + \frac{j}{j^1} \right) e^{(1-\alpha)z_1[(1/z_2)\ln[(j^1+j)/(j^1-j)]-v]}}. \quad (20)$$

Substitution into relation (18) then gives

$$j = j_0 E^{-\alpha} \left[\left(1 - \frac{j}{j^1} \right) E - 1 \right]. \quad (21)$$

Expressions (21) and (20) define j as an implicit function of v.

2. Analysis of some limiting cases

2.1. For small values of j and v, expansion of expression (20) gives, to the lowest order, that

$$E \approx 1 + \frac{z_1}{2} \left(v - \frac{2}{z_2} \frac{j}{j^1} \right). \quad (22)$$

Substitution of this expression into expression (21) gives the explicit linearized form of the polarization curve

$$\frac{j}{j_0} \approx \frac{z_1}{2} v - \frac{(z_1 + z_2)}{z_2} \frac{j}{j^1}. \quad (23)$$

Thus, the slope of j(v) curve at small values of v depends on the ratio between j_0 and j^1. In the case of $j_0 \ll j^1$ expression (23) may be written in the form

$$j \approx j_0 \frac{z_1}{2} v, \quad (24)$$

and in the opposite case, *ie* $j_0 \gg j^1$, as

$$j \approx j^1 \frac{z_1 z_2}{2(z_1 + z_2)} v. \tag{25}$$

2.2. Consider now the case of small values of j_0. Assuming that the values of v such that $j_0 \ll j(v) \sim j^1$ are of the order 10^0–10^1 or larger, one obtains from expression (20) the approximate relation

$$E = e^{\alpha z_1 v} \left(1 - \frac{j}{j^1} \right)^{(\alpha z_1/z_2) - 1} \left(1 + \frac{j}{j^1} \right)^{-(\alpha z_1/z_2)}. \tag{26}$$

For $E \gg 1$, one then finds from expression (21) that the polarization curve is given by the following approximate expression

$$j \approx j_0 \frac{\left(1 - \dfrac{j}{j^1} \right)^{[\alpha(1 - \alpha)z_1/z_2] + \alpha}}{\left(1 + \dfrac{j}{j^1} \right)^{\alpha(1 - \alpha)z_1/z_2}} e^{\alpha(1 - \alpha)z_1 v}. \tag{27}$$

This result shows that for values of j that are not too close to j^1, he polarization curve $j(v)$ can be represented as a Tafel-like law with the effective transfer coefficient

$$\alpha_{eff} = \alpha(1 - \alpha). \tag{28}$$

The maximum value of α_{eff} is equal to 0.25 and the dependence of $j(v)$ on α is symmetrical with respect to $\alpha = 0.25$. Again, it should be stressed that this symmetry property is valid for small j_0 values only.

2.3. For $j_0 \ll j(v) \sim j^1$ formula (27) simplifies to

$$j \approx j_0 e^{\alpha(1 - \alpha)z_1 v}. \tag{29}$$

A comparison between formulas (24) and (29) shows that in the transition region from the linear behavior of $j(v)$, which is independent of α, to the exponential one, there is an inflection point for values of α larger than 0.5. This inflection point is similar to that of the current–voltage curve for the reaction at one electrode, which is described by the Butler–Volmer law. For $j_0 \ll 1$ and $j_0 \ll j \ll j_1$ one then has

$$j = j_0 \{ e^{(1 - \alpha)z_1 v} - e^{-\alpha z_1 v} \}. \tag{30}$$

The position $v = v_c$, say, of the inflection point in this case can be readily computed and one finds that

$$v_c = \frac{2}{z_1} \ln\left(\frac{\alpha}{1 - \alpha} \right). \tag{31}$$

It turns out that this expression can also be used as an estimate of the location of one of the inflection points of the polarization curve for the cell with two electrodes. The closer α is to 1, the higher is the accuracy of equation (31).

The second inflection point of the polarization curve is found in the region of high values of v where the current limitation due to diffusion and migration becomes important.

2.4. For high values of the exchange current density, j in the left hand side of expression (21) can be neglected and the polarization curve is approxi-

mately determined by the relation

$$j \approx j^1 \left[1 - \frac{1}{E(v)} \right], \tag{32}$$

where $E(v)$ is given by expression (20). This relation is, of course, invalid when j is very close to the limiting current density.

3. The role of the supporting electrolyte in a system with three species

In the presence of a supporting electrolyte, the system of dimensionless equations for the concentrations and distributions of electroactive cations, indifferent cations, anions and the electric potentiai distribution reads as:

$$\frac{dc_1}{dx} + z_1 c_1 \frac{d\phi}{dx} = -\frac{j}{z_1}, \tag{33}$$

$$\frac{dc_2}{dx} + z_2 c_2 \frac{d\phi}{dx} = 0, \tag{34}$$

$$\frac{dc_3}{dx} - z_3 c_3 \frac{d\phi}{dx} = 0, \tag{35}$$

$$z_1 c_1 + z_2 c_2 = z_3 c_3. \tag{36}$$

In these equations, the dimensionless concentrations are defined as

$$c_i = \frac{C_i}{C_3^0} \tag{37}$$

and the electric current density is normalized according to the relation $j = -iL/FD_1 C_3^0$. It turns out to be convenient to introduce the parameter $k = C_1^0/C_3^0$. Then,

$$C_2^0/C_3^0 = z_3/z_2 - k z_1/z_2, \quad 0 < k < z_3/z_1.$$

The case of the aqueous solution of $CuSO_4$ with H_2SO_4 as a supporting electrolyte will be considered below. In this case at relatively low H_2SO_4 concentrations H_2SO_4 dissociates mainly into H^+ and HSO_4^- and, correspondingly, $z_1 = 2, z_1 = z_3 = 1$.

For the three-component system under consideration, the dimensionless version of the Butler-Volmer law for the electrode reactions, *ie* formulas (4) and (5), read

$$j = j_0 \left\{ \frac{c_1(0)}{k} e^{2(1 - \alpha)\phi(0)} - e^{-2\alpha\phi(0)} \right\}, \quad \text{at } x = 0, \tag{38}$$

$$j = j_0 \left\{ e^{-2\alpha(\phi(1) - v)} - \frac{c_1(1)}{k} e^{2(1 - \alpha)(\phi(1) - v)} \right\},$$
$$\text{at } x = 1. \tag{39}$$

The dimensionless conservation conditions, *cf.* formula (6), take the form

$$\int_0^1 c_1 \, dx = k, \tag{40}$$

$$\int_0^1 c_2 \, dx = 1 - 2k, \tag{41}$$

$$\int_0^1 c_3 \, dx = 1. \tag{42}$$

In order to compute the polarization curve, some algebraic simplifications result if the solutions of

equations *(34)* and *(35)* are written in the following form:

$$c_2 = c_2(0)e^{-[\phi(x)-\phi(0)]}, \tag{43}$$

$$c_3 = Nc_3(0)e^{[\phi(x)-\phi(0)]}, \tag{44}$$

where $c_2(0)$ and N are two constants of integration. As in Ref. [1], it is found expedient to express these constants in terms of the potential drop in solution $\Delta\phi = \phi(1) - \phi(0)$.

Combining equations *(33–36)* we have

$$\frac{dx}{d\phi} = \frac{1}{j}(3c_3 - c_2). \tag{45}$$

Substituting of this equation into normalization condition *(42)* gives the following relation between $c_2(0)$, N and $y = e^{2\Delta\phi}$:

$$\frac{Nc_2(0)^2}{2j}[3N(y-1) - \ln y] = 1. \tag{46}$$

A second relation between $c_2(0)$, N and y follows from the second conservation condition *(41)*

$$\frac{c_2(0)^2}{2j}[3N \ln y + y^{-1} - 1] = 1 - 2k. \tag{47}$$

A combination of relations *(46)* and *(47)* gives $N(y)$:

$$N = \frac{(2-k)\ln y + \sqrt{(2-k)^2 \ln^2 y + 3(y-1)(y^{-1}-1)(1-2k)}}{3(y-1)(1-2k)}. \tag{48}$$

Taking use the identity

$$\int_{\phi(1)}^{\phi(0)} \frac{dx}{d\phi}\,d\phi = 1, \tag{49}$$

and equations *(43)* and *(44)*, one can express $c_2(0)$ and j in terms of y

$$c_2(0) = \frac{2(3N - y^{-1/2})(y^{1/2} - 1)}{N[3N(y-1) - \ln y]}, \tag{50}$$

$$j = \frac{2[3N(y^{1/2}-1) + y^{-1/2} - 1]^2}{N[3N(y-1) - \ln y]}. \tag{51}$$

Combinating these expressions with the electroneutrality condition *(36)* and formulas *(43)* and *(44)* leads to the following expressions for $c_1(0)$ and $c_1(1)$ in terms of y:

$$c_1(0) = \tfrac{1}{2}(N-1)c_2(0), \tag{52}$$

$$c_1(1) = \tfrac{1}{2}(Ny^{1/2} - y^{-1/2})c_2(0). \tag{53}$$

Formulas *(48)* and *(50)–(53)* and expressions

$$j = j_0\left\{\frac{c_1(0)}{k}e^{2(1-\alpha)\phi(0)} - e^{-2\alpha\phi(0)}\right\}, \tag{54}$$

$$j = j_0\left\{e^{-2\alpha(\phi(0)+\sqrt{y}-v)} - \frac{c_1(1)}{k}e^{2(1-\alpha)(\phi(0)+\sqrt{y}-v)}\right\}, \tag{55}$$

which follow directly from expressions *(38)-(39)* and the definition of y, determine the current–voltage characteristic $j(v)$ of the cell.

It can be calculated in the following way. Expressing $c_1(0)$ and $c_1(1)$ in terms of y one has three different expressions for current density, *ie* equation *(51)*, which describes current density j in terms of y only, equation *(54)*, which describes current density j in terms of y and $\phi(0)$, and equation *(55)*, which describes j in terms of y, $\phi(0)$ and v.

Equating the right-hand sides of expressions *(54)* and *(55)* one finds that $\phi(0)$ can easily be expressed in terms of y and v:

$$e^{2\phi(0)} = \frac{1 + e^{2\alpha(x - \sqrt{y})}}{\frac{c_1(1)}{k}e^{2(1-\alpha)(\sqrt{y}-v)} + \frac{c_1(0)}{k}}. \tag{56}$$

Substitution of this expression for $e^{2\phi(0)}$ into expression *(54)* leads to a relation between j, y and v. For each value of y, together with formula *(51)*, which determines $j(y)$, this relation permits numerical computation of v as a function of y and j. Thus this procedure gives the polarization curve $j(v)$ in parametric form for arbitrary values of the exchange current density j_0 and the transfer coefficient a.

4. Numerical simulation and discussion

Some results of numerical calculations of polarization curves are presented in Figs *1-3*. Figure *1* represents a set of curves for a binary electrolyte,
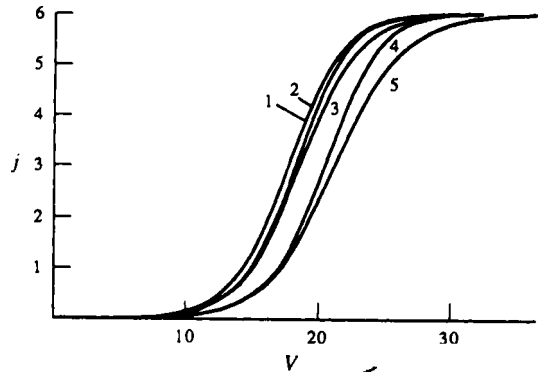

Fig. 1. Polarization curves $j(v)$ determined by equations (51), (54) and (56) corresponding to different a values. $k = 0.4$; $j_, = 6$; $j_1^0 = 0.001$; $1 - \alpha = 0.5$; $2 - \alpha = 0.4$; $3 - \alpha = 0.6$; $4 - \alpha = 0.3$; $5 - \alpha = 0.7$.
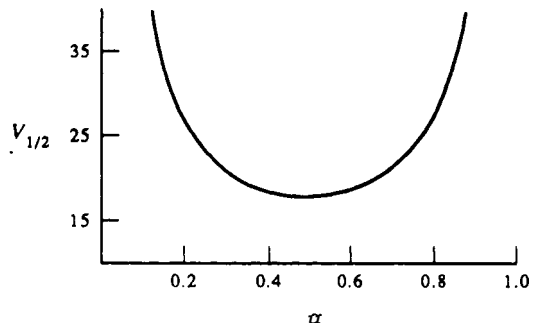

Fig. 2. Dependence of the potential $v_{1/2}$ value corresponding to current density $\mathbf{j} = j_1/2$ on the transfer coefficient α for binary solution. $j_1^0 = 0.001$; $j_, = 6$.
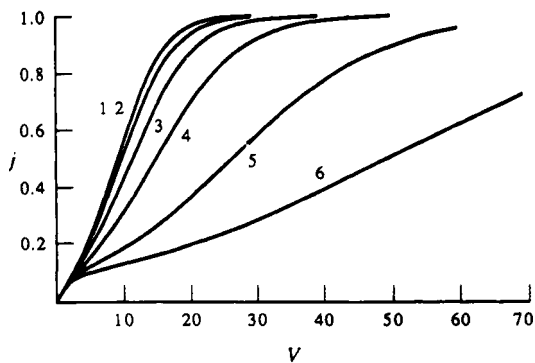
Fig. 3. Polarization curves $j(v)$ determined by equations (20) and (21) corresponding to different α values. $j_, = 1$; $j_1^0 = 0.01$; $1 - \alpha = 0.5$; $2 - \alpha = 0.6$; $3 - \alpha = 0.7$; $4 - \alpha = 0.8$; $5 - \alpha = 0.9$; $6 - \alpha = 0.95$.

calculated according to equations **(51)**, **(54)** and **(56)** and different values of a. One can see that the curves corresponding to values of α that are different from **0.5** are shifted towards higher v values with respect to the curve corresponding to a equal to **0.5**.

The extremum property of the value $\alpha = 0.5$ can **be** illustrated by the dependence of the value of the potential $v_{1/2}$, which corresponds to the current density equal to one half of the limiting current density, on the values of parameter α. This relation is shown in Fig. **2.** The curve $v_{1/2}(\alpha)$ is practically symmetrical with respect to $\alpha = 0.5$ in good agreement with theoretical analysis. It should be stressed that such symmetry appears only for small values of exchange current densities.

Figure **3** shows a set of polarization curves with the exchange current density equal to **0.1** and different values of transfer coefficient α. For $\alpha = 0.5$ the polarization curve has only one inflection point corresponding to the transition into the current region, where the diffusion limitation of electrode reaction becomes important. When the transfer coeficient a increases, a second inflection point appears on the polarization curves at relatively small current densities. This inflection point is related to the transition from region of linear "ohmic-like" behaviour of polarization curves at small reaction overvoltages, which is independent of α, to the exponential "Tafel-like" region of the curve, which depends strongly on α. The inflection point of this type exists on the polarization curve only for relatively small exchange current densities j_0. At very small values of this parameter the position of this inflection point of the current–voltage curve corresponds to very low current density values.

For a binary electrolyte it should be noted that in some special cases such as a = 2/3, a = 1/3 as well as in the case of a = 1/2, which was considered in [1], the polarization curve can be found from expressions **(18)–(19)** in analytic form. Equation **(18)** can be solved easily with respect to j:

$$j = \frac{e^{(1-\alpha)z_1\phi(0)} - e^{-\alpha z_1\phi(0)}}{\dfrac{1}{j_0} + \dfrac{1}{j^1} e^{(1-\alpha)z_1\phi(0)}}. \tag{57}$$

Introducing notations

$$S = \exp\left[z_1\!\left(\phi(0) + \frac{1}{z_2}\ln\frac{j^1 + j}{j^1 - j}\right)\right], \tag{58}$$

$$p = -\frac{j}{j_0}\,S^\alpha, \quad q = -\left(1 + \frac{j}{j^1}\right)S, \tag{59}$$

one finds after some algebra, that relation (19) for $\alpha = 2/3$, can be reduced to the form

$$t^3 + pt + q = 0, \tag{60}$$

where $t = e^{(z_1 v/3)} > 0.$ The solution of equation **(60)** is (see **eg** [17]):

$$t_1 = \sqrt[3]{-\frac{q}{2} + \sqrt{\left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3}}$$

$$+ \sqrt[3]{-\frac{q}{2} - \sqrt{\left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3}}. \tag{61}$$

Taking $\phi(0)$ to be an independent parameter one can find the parametric analytic representation of the function $j(v)$ from formulas **(57)** and **(61)**, the relation $v = (3/z_1)\ln t_1$ and the definitions of S, p and q.

In a similar way the parametric form of current–voltage curve $j(v)$ can be found for case of $\alpha = 1/3$. Some examples of analytical treatment of electrode reaction kinetics for fractional values of a are considered in [18].

CONCLUSION

An exact solution of the system of Nernst–Planck equations for a one-dimensional electrodiffusion problem, with boundary conditions of Butler-Volmer type, shows that the polarization curves for a cell having two identical electrodes have some interesting general properties. At small values of the exchange current density and current densities that are not close to the limiting current density j^1, the polarization curve is of a form that is similar to the Tafel equation. One obtains that,

$$j \approx j_0 \exp(\alpha_{\text{eff}} z_1 v),$$

with the effective transfer coefficient α_{eff} related to the physical transfer coefficient a by the formula

$$\alpha_{\text{eff}} = \alpha(1 - \alpha).$$

Another general property of the polarization curves for the system under consideration is that, under certain conditions, two inflection points may appear. One of these is similar to that of the current-voltage curve for the reaction at one electrode, which is described by a Butler–Volmer law for the case of small exchange current density j_0 and current densities j, such that $j_0 \ll j < j^1$. The second inflection point can be observed on the $j(v)$ curve in the region of relatively high values of v, where the current has values of the order of the limiting current density.

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