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THEORY OF THE GALVANOSTATIC TRANSIENT METHOD ON POROUS ELECTRODE

Part 3. Distribution of current and potential on porous electrode

By

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Abstract

Expressions are derived theoretically for the current and potential distribution on a porous electrode whose surface consists of a flat part and pores of different sizes, as a function of time in response to application of a step function of current I . An electron-transfer process across the electric double layer at the electrode-solution interface is taken into consideration by introducing a reaction resistance of the process parallel to the double layer capacity. The resistance is taken constant in the region of overvoltage much less than RT/F .

It is pointed out that the shorter the time constant of the electron-transfer process, which is defined as a product of the double layer capacity and the reaction resistance of the process, and the lower the conductivity of the solution, the more inhomogeneous the current and potential distribution on the electrode surface becomes especially in the initial stage of polarization. Because of this inhomogeneity the overvoltage changes at a different rate with time at each position on the electrode surface, which causes the relation between $\log(I/\phi)$ and time obtained by analysing the initial stage of the overvoltage-time ($\phi-t$) curve to deviate from a linear one.

The numerical calculation was performed and the results are illustrated for the distribution along a pore axis of the overvoltage, the current passing through the cross section, and the current density which flows into the electrode. The current which flows into the electrode at the flat part of the electrode surface is given as a function of time.

Introduction

In Part 2¹⁾, the distribution of current and potential in a pore electrode was given as a function of time and position under the condition that a constant current flowed into the pore from its orifice and was used for charging up of the double layer and the electron-transfer process.

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On a porous electrode whose surface has a flat part and pores of different sizes, however, it is necessary to reconsider the current and potential distribution on the electrode surface by taking into consideration the geometrical configuration of the surface when applying the galvanostatic transient method. In the present paper, the current and potential distribution was formulated on a porous electrode whose surface consists of a flat part and pores of different sizes.

§ 1. Theory of current and potential distribution on porous electrode

1. The differential equation for current and potential in a pore

We must first define the model of the electrode surface and deduce the differential equations for the current and potential in a pore on the basis of the model.

Let us assume here that the electrode surface consists of a flat surface and N pores of different sizes each of which has a cylindrical form and its axis normal to the electrode surface. The differential equations for the current and potential in a pore have been discussed in Part 2 by regarding the pore as an one-dimensional transmission-line which has along its axis the distributed Ohmic resistance of the solution, the double layer capacity and the reaction resistance of the electron-transfer process across the electric double layer at the electrode-solution interface in the pore.

The equivalent circuit of the k -th pore is shown in Fig. 1, where z is the distance from the orifice of the pore along its axis, e is the overvoltage of the electron-transfer process at z , *i.e.*, the potential difference across the double layer at z referred to the difference at the reversible potential, i is the current passing through the cross section of the pore at z , $R_{1,k}$, $r_{1,k}$ and $C_{1,k}$ denote respectively the solution resistance, the reaction resistance of the electron-transfer process, and the differential capacity of the double layer per unit length of the pore, $r_{b,k}$ and $C_{b,k}$ denote respectively the reac-

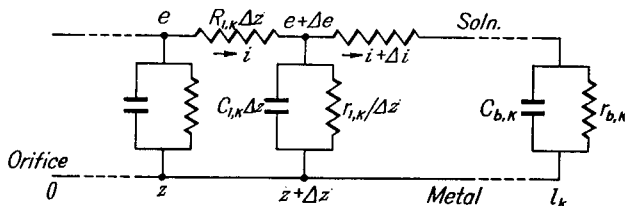


Fig. 1. An equivalent circuit of the k -th pore.

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tion resistance and the double layer capacity at the bottom of the pore and l_k is the length of the k -th pore. Both i and e should be suffixed by k in this case, but it is neglected for simplicity in what follows.

As described in part 2, the gradient of the potential at z in the pore is given by

$$\frac{\partial e}{\partial z} = -iR_{1,k}. \quad (1)$$

The gradient of the current i is given by the sum of the Faradaic and capacitive components as

$$\frac{\partial i}{\partial z} = -C_{1,k} \left(\frac{\partial e}{\partial t} + \frac{e}{\tau} \right), \quad (2)$$

assuming that the absolute value of e is much lower than RT/F , where the Faradaic current can be regarded as proportional to e with a proportionality constant $r_{1,k}$. τ , the time constant of the electron-transfer process, is given by $C_{1,k}r_{1,k}$. t is the time measured from the beginning of polarization of the electrode by a step current I . From Eqs. (1) and (2), we have a differential equation for the potential in the k -th pore as

$$\frac{\partial^2 e}{\partial z^2} = R_{1,k}C_{1,k} \left(\frac{\partial e}{\partial t} + \frac{e}{\tau} \right). \quad (3)$$

The distributions of the current and potential in the k -th pore will be discussed on the basis of Eqs. (1), (2) and (3) using the initial and the boundary conditions which depend on the geometrical configuration of the electrode surface.

2. Initial and boundary conditions of the potential and current

The initial condition of the potential is given by

$$e(z, 0) = 0, \quad (4)$$

since the potential is referred to the reversible state.

The boundary condition of the current at the bottom of the k -th pore is given by

$$i(l_k, t) = C_{b,k} \left\{ \left(\frac{\partial e}{\partial t} \right)_{z=l_k} + \frac{e(z=l_k)}{\tau} \right\}. \quad (5)$$

The boundary condition of the current at the orifice of the k -th pore is given by estimating the fractional current which flows into the k -th pore when the electrode is polarized by a constant current I . The expressions for the current which flows into the k -th pore and onto the flat part of

the electrode surface are given in what follows. The total impedance $Z(s)$ of the electrode is given by a parallel combination of the impedance $Z_f(s)$ at the flat part and the impedances $Z_k(s)$'s of the pores, where $s = j\omega$, $j = \sqrt{-1}$, and ω is the angular frequency of the alternating current. The overvoltage which can be measured on the electrode in response to application of a step current I is given by the potential difference across the impedance $Z(s)$ as described in Part 1²). Thus, the potential difference $\varphi(t)$ is imposed equally to the impedances $Z_f(s)$ and $Z_k(s)$'s. Let us denote the current which flows into the flat part as $i_f(t)$ and that into the k -th pore as $i_k(t)$. The current I is given as the sum of these fractional currents as

$$I = i_f(t) + \sum_{k=1}^N i_k(t). \quad (6)$$

Generally, the time function of the current which flows in a circuit when a voltage source $e(t)$ is applied to an impedance is given by the Duhamel's integrals. Thus, $i_f(t)$ and $i_k(t)$ are given by the Duhamel's integrals. The expressions in the Laplace transforms for $i_f(t)$ and $i_k(t)$ are given by

$$\bar{i}_f = IZ(s)/sZ_f(s), \quad (7)$$

$$\bar{i}_k = IZ(s)/sZ_k(s), \quad (8)$$

where \bar{i}_f and \bar{i}_k denote respectively the Laplace transforms for $i_f(t)$ and $i_k(t)$. Equation (8) shows the current which flows into the k -th pore from its orifice and it gives the boundary condition of the current at the orifice of the k -th pore in the Laplace transform dropping the suffix k as

$$\bar{i}(z=0) = IZ(s)/sZ_k(s) \quad (9)$$

3. The current $i(z, t)$ and potential $e(z, t)$ in a pore

The potential and current in the k -th pore will be expressed here as functions of t and z by solving Eq. (3) applying the Laplace transformation. Equation (3) is transformed under the initial condition Eq. (4) as

$$\frac{d^2 \bar{e}}{dz^2} = R_{1,k} C_{1,k} (s + \tau^{-1}) \bar{e}, \quad (10)$$

where \bar{e} denotes the Laplace transform of potential e . The general solution of Eq. (10) is given by

$$\bar{e} = A \exp \left\{ z \sqrt{R_{1,k} C_{1,k} (s + \tau^{-1})} \right\} + B \exp \left\{ -z \sqrt{R_{1,k} C_{1,k} (s + \tau^{-1})} \right\}, \quad (11)$$

where A and B are the constants determined by the boundary conditions. The Laplace transform of the current is obtained from Eq. (1) as

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$$\bar{z} = -\frac{\sqrt{R_{1,k}C_{1,k}(s+\tau^{-1})}}{R_{1,k}} \left[A \exp \left\{ z \sqrt{R_{1,k}C_{1,k}(s+\tau^{-1})} \right\} - B \exp \left\{ -z \sqrt{R_{1,k}C_{1,k}(s+\tau^{-1})} \right\} \right]. \quad (12)$$

The boundary condition (5) is transformed as

$$\bar{z}(z=l_k) = C_{b,k} \bar{e}(z=l_k)(s+\tau^{-1}). \quad (13)$$

The constants A and B can be determined from Eqs. (9), (11), (12) and (13). Introducing A and B thus determined into Eq. (11), we obtain the Laplace transform of potential;

$$\bar{e} = \frac{IR_k Z(s)}{s Z_k(s)} \times \frac{C_k \cosh \left\{ \left(1 - \frac{z}{l_k} \right) \sqrt{\tau_k(s+\tau^{-1})} \right\} + C_{b,k} \sqrt{\tau_k(s+\tau^{-1})} \sinh \left\{ \left(1 - \frac{z}{l_k} \right) \sqrt{\tau_k(s+\tau^{-1})} \right\}}{\sqrt{\tau_k(s+\tau^{-1})} \{ C_k \sinh \sqrt{\tau_k(s+\tau^{-1})} + C_{b,k} \sqrt{\tau_k(s+\tau^{-1})} \cosh \sqrt{\tau_k(s+\tau^{-1})} \}}, \quad (14)$$

where $R_k = l_k R_{1,k}$, $C_k = l_k C_{1,k}$ and τ_k is the time constant of the k -th pore defined by $\tau_k = R_k C_k$. The expressions for $Z_k(s)$ and $Z(s)$ in Eq. (14) have already been given in Part 1 as

$$Z_k(s) = \frac{Z_k^0(s) + C_{b,k} R_k / C_k}{C_{b,k}(s+\tau^{-1}) Z_k^0(s) + 1}, \quad (15)$$

and

$$Z(s)^{-1} = C_f(s+\tau^{-1}) + \sum_{k=1}^N \frac{C_{b,k}(s+\tau^{-1}) Z_k^0(s) + 1}{Z_k^0(s) + C_{b,k} R_k / C_k}, \quad (16)$$

where

$$Z_k^0(s) = \frac{R_k}{\sqrt{\tau_k(s+\tau^{-1})}} \coth \sqrt{\tau_k(s+\tau^{-1})}. \quad (17)$$

Introducing Eqs. (15), (16) and (17) into (14), we can rewrite the \bar{e} as

$$\bar{e} = \frac{I p(s)}{s(s+\tau^{-1}) \cdot q(s) \cdot F(s)}, \quad (18)$$

where

$$p(s) = C_k \cosh \left\{ \left(1 - \frac{z}{l_k} \right) \sqrt{\tau_k(s+\tau^{-1})} \right\} + C_{b,k} \sqrt{\tau_k(s+\tau^{-1})} \sinh \left\{ \left(1 - \frac{z}{l_k} \right) \sqrt{\tau_k(s+\tau^{-1})} \right\}, \quad (19)$$

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$$q(s) = C_k \cosh \sqrt{\tau_k(s + \tau^{-1})} + C_{b,k} \sqrt{\tau_k(s + \tau^{-1})} \sinh \sqrt{\tau_k(s + \tau^{-1})}, \quad (20)$$

and

$$F(s) = C_f + \sum_{k=1}^N \frac{C_k \left\{ C_{b,k} \cosh \sqrt{\tau_k(s + \tau^{-1})} + \frac{C_k \sinh \sqrt{\tau_k(s + \tau^{-1})}}{\sqrt{\tau_k(s + \tau^{-1})}} \right\}}{C_k \cosh \sqrt{\tau_k(s + \tau^{-1})} + C_{b,k} \sqrt{\tau_k(s + \tau^{-1})} \sinh \sqrt{\tau_k(s + \tau^{-1})}}. \quad (21)$$

The potential $e(z, t)$ can be obtained by performing the inverse Laplace transformation of \bar{e} given by Eq. (18). The problem of the inverse Laplace transformation of Eq. (18) is reduced to that of finding the pole points of the function $\bar{e} \cdot \exp(st)$ and the sum of the residues at these points according to Jordan's lemma and the residue theorem, since $\bar{e} \cdot \exp(st)$ is a single-valued function of s and it is readily shown $\lim_{s \rightarrow \infty} \bar{e}$ equals zero*.

The potential $e(z, t)$ is finally given as

$$e(z, t) = \frac{I\tau \cdot F_k(z)}{B} - I r_0 e^{-t/\tau} - 2I \sum_{n=1}^{\infty} \frac{f_k(q_n, z)}{(q_n^2 + \tau^{-1}) \{C_f + A(q_n)\}} \exp \left\{ -(q_n^2 + \tau^{-1}) t \right\}, \quad (22)$$

where

$$F_k(z) = \frac{C_k \cosh \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\} + C_{b,k} \sqrt{\alpha_k} \sinh \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\}}{C_k \cosh \sqrt{\alpha_k} + C_{b,k} \sqrt{\alpha_k} \sinh \sqrt{\alpha_k}}, \quad (23)$$

$$B = C_f + \sum_{k=1}^N \frac{C_k (C_{b,k} \sqrt{\alpha_k} + C_k \tanh \sqrt{\alpha_k})}{\sqrt{\alpha_k} (C_k + C_{b,k} \sqrt{\alpha_k} \tanh \sqrt{\alpha_k})}, \quad (24)$$

$$f_k(q_n, z) = \frac{C_k \cos \left\{ q_n \sqrt{\tau_k} \left(1 - \frac{z}{l_k} \right) \right\} - C_{b,k} q_n \sqrt{\tau_k} \sin \left\{ q_n \sqrt{\tau_k} \left(1 - \frac{z}{l_k} \right) \right\}}{C_k \cos q_n \sqrt{\tau_k} - C_{b,k} q_n \sqrt{\tau_k} \sin q_n \sqrt{\tau_k}}, \quad (25)$$

$$A(q_n) = \sum_{k=1}^N \frac{C_k (C_k^2 + C_k C_{b,k} + C_{b,k}^2 q_n^2 \tau_k)}{(C_k \cos q_n \sqrt{\tau_k} - C_{b,k} q_n \sqrt{\tau_k} \sin q_n \sqrt{\tau_k})^2}, \quad (26)$$

the q'_n 's are the positive roots of the following equation ;

$$C_f + \sum_{k=1}^N \frac{C_k (C_{b,k} q \sqrt{\tau_k} \cos q \sqrt{\tau_k} + C_k \sin q \sqrt{\tau_k})}{q \sqrt{\tau_k} (C_k \cos q \sqrt{\tau_k} - C_{b,k} q \sqrt{\tau_k} \sin q \sqrt{\tau_k})} = 0, \quad (27)$$

* For more details of inverse Laplace transformation, see Part 1 or 2.

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r_0 is the reaction resistance of the electron-transfer process with respect to the total surface area of the electrode and α_k is defined by $\alpha_k = \tau_k / \tau$.

The expression for the current $i(z, t)$ is obtained by differentiating $e(z, t)$ with z according to Eq. (1), as

$$\frac{i(z, t)}{I} = \frac{C_k G_k(z)}{\sqrt{\alpha_k} B} + 2C_k \sum_{n=1}^{\infty} \frac{q_n \sqrt{\tau_k} g_k(q_n, z)}{\sqrt{\tau_k} (q_n^2 + \tau^{-1}) \{C_f + A(q_n)\}} \exp \left\{ -(q_n^2 + \tau^{-1}) t \right\}, \quad (28)$$

where

$$G_k(z) = \frac{C_k \sinh \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\} + C_{b,k} \sqrt{\alpha_k} \cosh \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\}}{C_k \cosh \sqrt{\alpha_k} + C_{b,k} \sqrt{\alpha_k} \sinh \sqrt{\alpha_k}}, \quad (29)$$

and

$$g_k(q_n, z) = \frac{C_k \sin \left\{ q_n \sqrt{\tau_k} \left(1 - \frac{z}{l_k} \right) \right\} + C_{b,k} q_n \sqrt{\tau_k} \cos \left\{ q_n \sqrt{\tau_k} \left(1 - \frac{z}{l_k} \right) \right\}}{C_k \cos q_n \sqrt{\tau_k} - C_{b,k} q_n \sqrt{\tau_k} \sin q_n \sqrt{\tau_k}}. \quad (30)$$

The expression for the potential can be more simplified by its initial condition. Putting $e(z, 0) = 0$, we have from Eq. (22)

$$\frac{I \tau \cdot F_k(z)}{B} - I r_0 = 2I \sum_{n=1}^{\infty} \frac{f_k(q_n, z)}{(q_n^2 + \tau^{-1}) \{C_f + A(q_n)\}}. \quad (31)$$

Introducing Eq. (31) into (22), we have the expression for the potential in more simplified form as

$$e(z, t) = I r_0 (1 - e^{-t/\tau}) + 2I \sum_{n=1}^{\infty} \frac{f_k(q_n, z)}{(q_n^2 + \tau^{-1}) \{C_f + A(q_n)\}} \left[1 - \exp \left\{ -(q_n^2 + \tau^{-1}) t \right\} \right] \quad (32)$$

From the current and potential given by Eqs. (28) and (32), we can derive the expressions for the overvoltage-time curve which has already been given in Part 1, the Ohmic potential in the pore and the current density which flows into the electrode at the position z in the pore.

The overvoltage-time curve is obtained from Eq. (32) putting $z=0$, *i.e.*,

$$e(o, t) = \varphi(t) \quad (33)$$

The difference between $e(o, t)$ and $e(z, t)$ is the Ohmic potential $e_o(z, t)$ at z in the pore, *i.e.*, the potential difference between the orifice of the pore and the position z . Thus, we have

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$$e_d(z, t) = e(o, t) - e(z, t), \quad (34)$$

which is given from Eq. (32) as

$$e_d(z, t) = 2I \sum_{n=1}^{\infty} \left\{ 1 - f_k(q_n, z) \right\} \frac{1 - \exp \{ -(q_n^2 + \tau^{-1}) t \}}{(q_n^2 + \tau^{-1}) \{ C_f + A(q_n) \}}. \quad (35)$$

The current which flows into the electrode between z and $z + \Delta z$ is given by the difference $i(z) - i(z + \Delta z)$. Thus, the current density $i^*(z, t)$ which flows into the electrode at the position z is given by

$$i^*(z, t) = \frac{1}{2\pi r_k} \lim_{\Delta z \rightarrow 0} \frac{i(z) - i(z + \Delta z)}{\Delta z} = -\frac{1}{2\pi r_k} \frac{\partial i(z, t)}{\partial z}, \quad (36)$$

where r_k is the radius of the k -th pore. Introducing Eq. (2), we can rewrite Eq. (36) as

$$i^*(z, t) = \frac{C_{1,k}}{2\pi r_k} \left(\frac{\partial e}{\partial t} + \frac{e}{\tau} \right) = C^* \left(\frac{\partial e}{\partial t} + \frac{e}{\tau} \right), \quad (37)$$

where C^* denotes the double layer capacity per unit area. Equation (37) shows that $i^*(z, t)$ is given by the sum of the capacitive and the Faradaic components. The $i^*(z, t)$ can be obtained from Eqs. (28) and (36) as

$$\frac{i^*(z, t)}{I} = \frac{C^* F_k(z)}{B} + 2C^* \sum_{n=1}^{\infty} \frac{q_n^2 \cdot f_k(q_n, z)}{(q_n^2 + \tau^{-1}) \{ C_f + A(q_n) \}} \exp \left\{ -(q_n^2 + \tau^{-1}) t \right\}. \quad (38)$$

The current $i_f(t)$ which flows into the electrode at the flat part of the electrode surface can readily be obtained as the inverse Laplace transform of Eq. (7). As shown in Part 1, the impedance at the flat part $Z_f(s)$ is given by the double layer capacity C_f at the flat part and τ as

$$Z_f(s)^{-1} = C_f(s + \tau^{-1}). \quad (39)$$

Putting Eq. (39) into (7), we have

$$\bar{i}_f = C_f \left\{ IZ(s) \cdot (s + \tau^{-1})/s \right\} = C_f \left\{ IZ(s) + \frac{1}{\tau} \frac{IZ(s)}{s} \right\}. \quad (40)$$

The inverse Laplace transforms of $IZ(s)$ and $IZ(s)/s$ give respectively $\varphi(t)$ and $\phi(t)$ as shown in Part 1. Thus, we have from Eq. (40) the expression for $i_f(t)$, as

$$i_f(t) = C_f \left\{ \phi(t) + \frac{\varphi(t)}{\tau} \right\}. \quad (41)$$

§ 2. Discussion

The currents $i(z, t)$ and $i^*(z, t)$ and the overvoltage $e(z, t)$ in the pore depend not only on the time constant of the electron-transfer process τ , but also on those of the pores τ'_k s as seen from Eqs. (28), (38) and (32). We will discuss here the influence of τ and τ'_k s on these current and overvoltage in the pore.

1. Influence of the time constants of the pores

In the case when the time constants of the pores can be regarded as practically zero, we can put $\alpha_k=0$ and $q'_k s=\infty^*$. This is the case when the conductivity of the solution is enough high, *i.e.*, in the concentrated solutions.

In this case, i , i^* and e are given by

$$\frac{i(z, t)}{I} = \frac{C_k + C_{d,k}}{C} - \frac{C_k}{C} \frac{z}{l_k}, \quad (42)$$

$$e(z, t) = I r_0 (1 - e^{-t/\tau}), \quad (43)$$

$$\frac{i^*(z, t)}{I} = C^*/C = 1/S, \quad (44)$$

$$e_d(z, t) = 0, \quad (45)$$

where S is the total surface area of the porous electrode.

It can be seen from these results that the overvoltage in a pore depends only on τ and t independently of the position in the pore, and i^* also remains constant. The electrode behaves as if it were a flat one in this case, *i.e.*, a linear relation between $\log(I/\phi)$ and time can be observed. This

* If $q\sqrt{\tau_k}$ becomes zero with decreasing τ_k , the left-hand side of Eq. (27) tends to $C_f + \sum_{k=1}^N (C_{d,k} + C_k)$ which equals the total double layer capacity C . For the validity of Eq. (27) when the τ'_k s reach zero, $q\sqrt{\tau_k}$ should not reach zero, *i.e.*, the q'_k s should be infinite in such a case. On the other hand, when τ_k becomes infinite, the q'_k s should reach zero as described below. The left-hand side of Eq. (27) can be rewritten as

$$C_f + \sum_{k=1}^N \frac{C_k \left(C_{d,k} \cos q\sqrt{\tau_k} + \frac{C_k \sin q\sqrt{\tau_k}}{q\sqrt{\tau_k}} \right)}{C_k \cos q\sqrt{\tau_k} - C_{d,k} q\sqrt{\tau_k} \sin q\sqrt{\tau_k}},$$

which tends to C_f if $q\sqrt{\tau_k}$ becomes infinite with increasing τ_k and $\sin q\sqrt{\tau_k} \neq 0$. We have $\sin q\sqrt{\tau_k} \neq 0$, *i.e.*, $q\sqrt{\tau_k} \neq n\pi$, because the left-hand side of Eq. (27) does not equal zero when $q\sqrt{\tau_k} = n\pi$. Therefore, the left-hand side of Eq. (27) does not equal zero if $q\sqrt{\tau_k}$ becomes infinite with increasing τ_k , *i.e.*, the q'_k s should tend to zero with increasing τ_k . This is the case in very dilute solutions.

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is the case of evaporated films of Platinum³⁾ and Nickel⁴⁾ in concentrated alkaline solutions observed by MATSUDA, NOTOYA and OHMORI.

On the other hand, if τ_k reaches practically infinite, $\alpha_k = \tau_k/\tau \gg 1$ and the q_n 's reach zero as discussed above. Therefore, we have

$$\sinh \sqrt{\alpha_k} = \cosh \sqrt{\alpha_k} = \frac{1}{2} \exp \sqrt{\alpha_k}$$

and except for the very near part to the bottom of the pore

$$\sinh \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\} = \cosh \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\} = \frac{1}{2} \exp \left\{ \sqrt{\alpha_k} \left(1 - \frac{z}{l_k} \right) \right\}.$$

In this case we have from Eqs. (22) and (31)

$$e(z, t) = I r_f (1 - e^{-t/\tau}) e^{-\sqrt{\alpha_k} \frac{z}{l_k}}, \quad (46)$$

where r_f is the reaction resistance of the electron-transfer process at the flat part of the electrode surface. This is the case in very dilute solutions. In this case i , i^* and e_d can be obtained from Eq. (46) on the basis of Eqs. (1), (36) and (34) respectively, as

$$\frac{i(z, t)}{I} = \frac{C}{C_f} (1 - e^{-t/\tau}) \frac{1}{\sqrt{\alpha_k}} e^{-\sqrt{\alpha_k} \frac{z}{l_k}}, \quad (47)$$

$$\frac{i^*(z, t)}{I} = \frac{1}{S_f} (1 - e^{-t/\tau}) e^{-\sqrt{\alpha_k} \frac{z}{l_k}}, \quad (48)$$

$$e_d(z, t) = I r_f (1 - e^{-t/\tau}) (1 - e^{-\sqrt{\alpha_k} \frac{z}{l_k}}). \quad (49)$$

where S_f is the area of the flat part.

It can be seen from these results that e , i and i^* equal practically zero except at the very near part to the orifice of the pore. The overvoltage-time curve observed in this case is obtained by putting $z=0$ in Eq. (46), as

$$\varphi(t) = I r_f (1 - e^{-t/\tau}). \quad (50)$$

Thus, the charging up of the double layer and the electron-transfer process proceed practically at the flat part of the electrode surface in very dilute solutions.

It can be seen from these results that in highly concentrated solutions the whole part of the electrode surface is polarized uniformly, while in very dilute solutions only the flat part of the electrode surface is polarized.

2. The influence of the time constant of the electron-transfer process

First, we will discuss here an ideal polarized electrode for which we can put $\tau^{-1}=0$, i. e., $\alpha_k=0$. In this case, we have from Eqs. (32) and (38) under the condition $\exp(-q_n^2 t) \rightarrow 0$

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$$\frac{\partial e(z, t)}{\partial t} = I/C = \frac{\partial e(o, t)}{\partial t} = \frac{\partial \varphi(t)}{\partial t}, \quad (51)$$

and

$$\frac{i^*(z, t)}{I} = 1/S. \quad (52)$$

These results show that in the ideal polarized state the electrode is polarized uniformly with increasing time and C can be readily obtained from $\varphi(t)-t$ curve on the basis of Eq. (51).

On the other hand, if the time constant of the electron-transfer process is so small as compared with the τ'_k s that we can put τ^{-1} and $\alpha_k (= \tau_k \tau^{-1})$ equals infinite, the same expressions for $i(z, t)$, $i^*(z, t)$ and $e(z, t)$ will be obtained as Eqs. (47), (48) and (49). In this case also only the flat part of the electrode surface is polarized.

The current $i_f(t)$ is given as the difference between the polarizing current I and the sum of the currents which flow into the pores

$$i_f(t) = I - \sum_{k=1}^N i_k t.$$

It can be seen from the above arguments that $i_f(t)$ equals I when either the solution is very dilute or τ is small enough as compared with the τ'_k s, while it equals IS_f/S in highly concentrated solutions.

3. The influence of the inhomogeneity of the current density distribution at the porous electrode on the overvoltage-time curve

In the case of an electrode of flat surface, the overvoltage-time curve can be analyzed by the following equation³⁾,

$$\ln(I/\varphi) = \ln C + t/\tau. \quad (53)$$

On the porous electrode, however, the theoretical relation between $\ln(I/\varphi)$ and time can be expressed as²⁾

$$\ln(I/\varphi) = \ln C + t/\tau - \ln \left\{ 1 + 2C \sum_{n=1}^{\infty} \frac{\exp(-q_n^2 t)}{C_f + A(q_n)} \right\}, \quad (54)$$

Equation (54) is reduced to Eq. (53) under the condition $\exp(-q_n^2 t) = 0$. We will discuss here the current and potential distribution in the pore under this condition, by which we can know the reason why the relation between $\ln(I/\varphi)$ and time deviates from a linear one in the initial stage of polarization as observed in the study of the electron-transfer process of the hydrogen electrode reaction on the evaporated films of Platinum^{3,4)}, Nickel⁵⁾ and Silver⁶⁾.

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Under the condition $\exp(-q_n^2 t) = 0$, the time derivatives of $i(z, t)$, $i^*(z, t)$ and $e(z, t)$ are given respectively from Eqs. (28), (38) and (32), as

$$\frac{\partial i(z, t)}{\partial t} = \frac{\partial i^*(z, t)}{\partial t} = 0 \quad (55)$$

$$\frac{\partial e(z, t)}{\partial t} = \frac{I}{C} e^{-t/\tau} \quad (56)$$

It can be seen from these results that i and i^* do not depend on time and the time derivative of e does not depend on the position in the pore. From Eq. (56) we have the charging current density $i_c^*(z, t)$ of the double layer, i. e., $C^* \frac{\partial e}{\partial t}$, as

$$i_c^*(z, t) = \frac{I}{S} e^{-t/\tau}, \quad (57)$$

which is a constant independent of the position in the pore. Thus, the current density $i^*(z, t)$ and the rate of the electron-transfer process, which

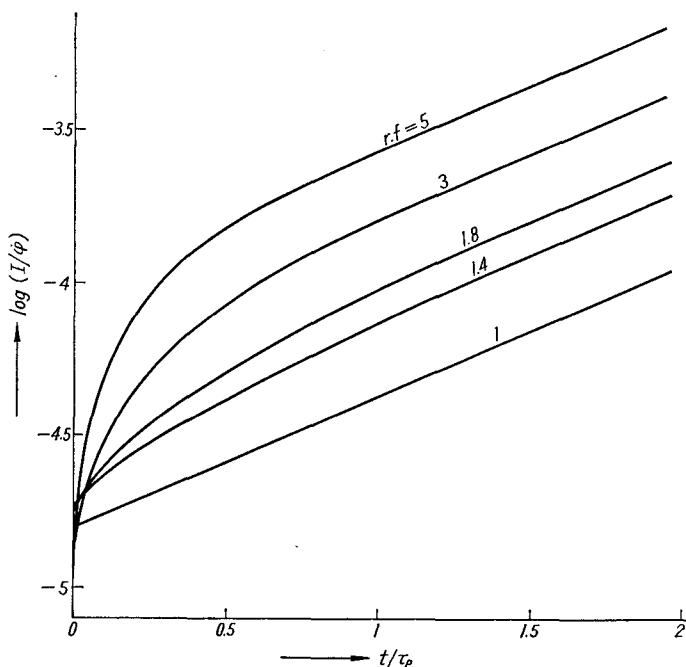


Fig. 2. The relation between $\log(I/\phi)$ and t/τ_p for the various values of the roughness factor ($r \cdot f$) of the electrode surface. $r \cdot f = 5$ and 1.4 correspond to the number of pores $N = 1.27 \times 10^4$ and $N = 1.27 \times 10^3$ respectively per apparent unit surface area.

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is given by $i^*(z, t) - i_c^*(z, t)$, vary depending on the position in the pore, while the charging current density of the double layer does not depend on z as seen from Eq. (57).

It follows from the above arguments that the relation between $\ln(I/\phi)$ and time becomes linear, *i. e.*, Eq. (54) is reduced to Eq. (53), when the charging current density of the double layer at the electrode-solution interface becomes uniform throughout the whole surface of the electrode with the increase of time. This means that the deviation from linearity in the early stage of the overvoltage-time curve is caused by the inhomogeneity of the charging current density distribution of the double layer on the electrode surface. This inhomogeneity is produced in the early stage of polarization because most of the polarizing current flows into the electrode at the flat part and near the orifice of the pores.

These characteristics of $\log(I/\phi) - t$ curves are found in Figs. 2, 3 and 4. Fig. 2 was calculated in Part 1 for the case of uniform pore size under the condition given in Table 1. Figs. 3 and 4 were obtained by the galvanostatic transient method in the study of the electron-transfer process of the hydrogen electrode on the evaporated films of Platinum³⁾ and Nickel⁵⁾ in alkaline solutions. In Part 1, the deviation from the linearity observed in the initial

stage of polarization was explained by the presence of pores on the electrode surface. According to the above arguments, however, we have now more detailed explana-

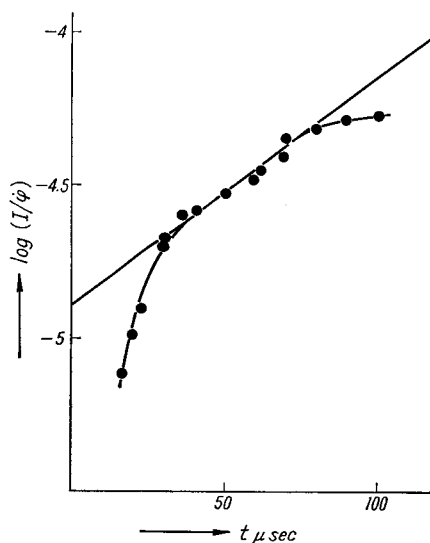


Fig. 3. The relation between $\log(I/\phi)$ and time on an evaporated film of Platinum in $\text{NaOH}_{\text{aq.}}$ solution. $\text{pH} = 13.45^{(3)}$

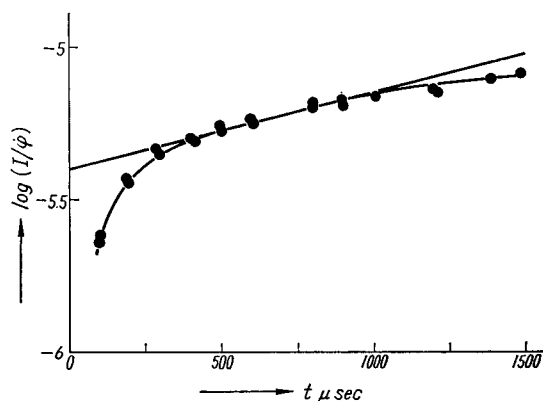


Fig. 4. The relation between $\log(I/\phi)$ and time on an evaporated film of Nickel in $\text{NaOH}_{\text{aq.}}$ solution. $\text{pH} = 11.75^{(5)}$

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tion for the deviation, *i.e.*, the inhomogeneity of the current density distribution on the electrode surface*.

4. An example of the numerical calculation of the distribution of current and potential in the pore

The results of the numerical calculation of the distributions of current and potential are given in Figs. 5-9 for the case of uniform pore size. In Table 1 the parameters used in the calculation are given.

TABLE 1.

apparent surface area of the electrode	1 cm ²
pore radius (<i>r</i>)	5 × 10 ⁻³ cm
pore length (<i>l</i>)	10 ⁻² cm
number of pores (<i>N</i>)	6.4 × 10 ³
double layer capacity per unit area	20 μF
specific resistance of solution (in 10 ⁻³ N-NaOH)	4.65 KΩ cm
time constant of the pore (τ_p)	3.72 m sec

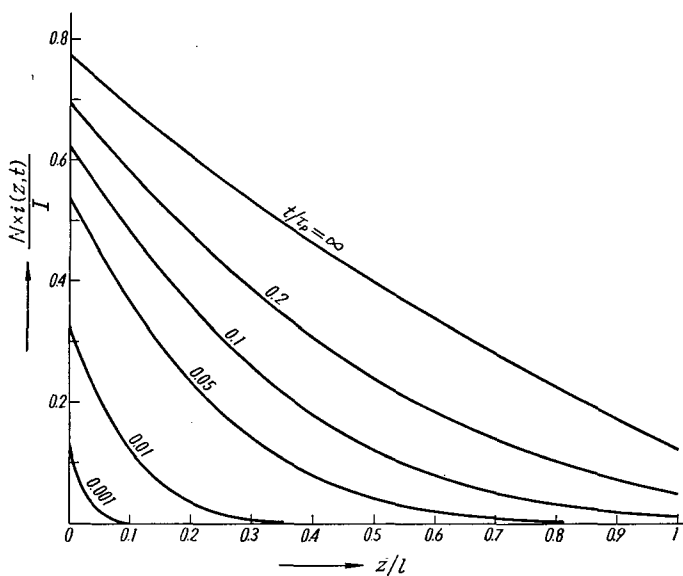


Fig. 5. Distribution of the current passing through the cross section in the pore at various values of t/τ_p . $\tau = \tau_p$

* See references 3, 4 and 5 for the reason why the relation deviates from a linear one also in the later region of time. It is caused not by the presence of pores but by the accumulation of the reaction intermediates on the electrode surface.

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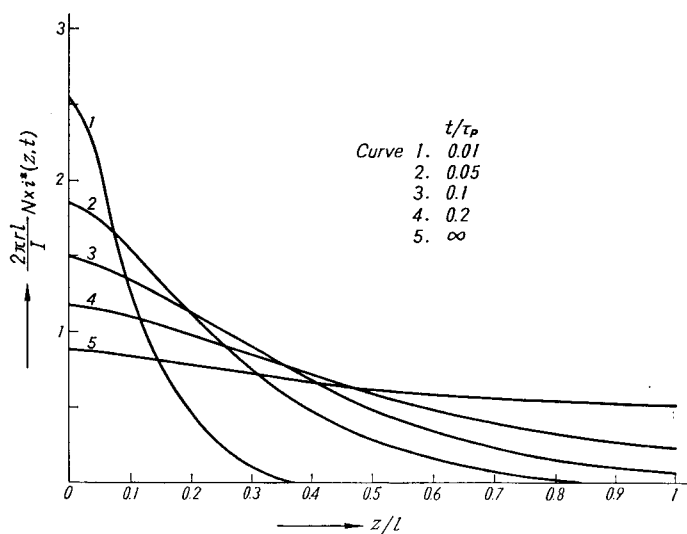


Fig. 6. Distribution of the current density flowing into the electrode in the pore at various values of t/τ_p . $\tau = \tau_p$

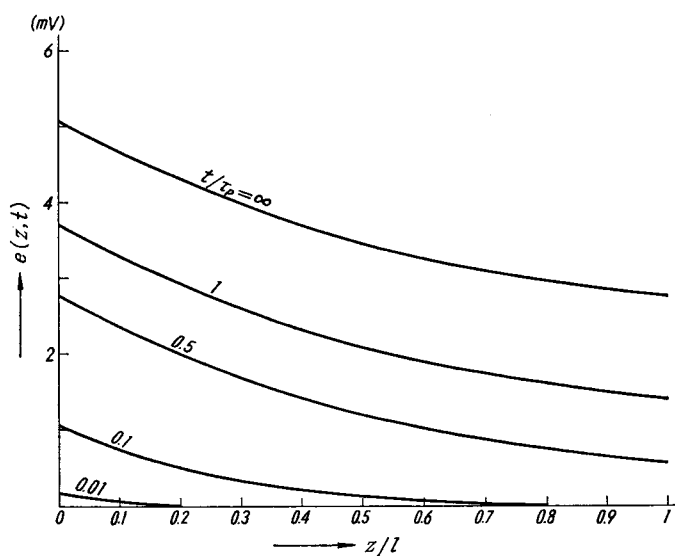


Fig. 7. Distribution of the potential in the pore at various values of t/τ_p . $\tau = \tau_p$, $I = 6 \times 10^{-5}$ Amp

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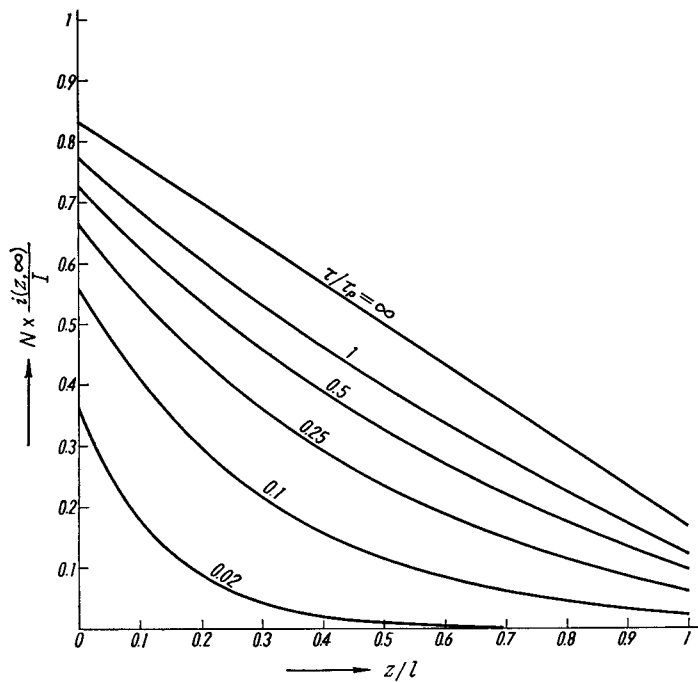


Fig. 8. Distribution of the current in steady states at various values of τ/τ_p .

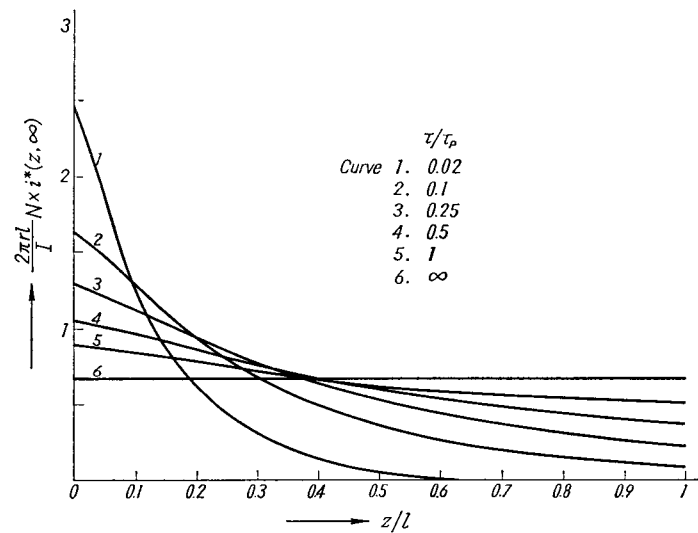


Fig. 9. Distribution of the current density in steady states at various values of τ/τ_p .

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Figs. 5 and 6 show that in the early stage of time the greater part of the current flows into the electrode at the flat part and near the orifice and with increasing time the current penetrates into the pore more deeply. Fig. 7 shows that the potential penetrates into the pore more deeply with increasing time as in the case of current. The current and potential at the steady state are strongly affected by the parameter $\alpha (= \tau_p/\tau)$. Figs. 8 and 9 show the dependence of the current distribution on the parameter α^{-1} . We see that the current flows into the electrode mainly at the flat part and near the orifice when τ/τ_p is small, while the current is uniformly distributed throughout the electrode surface when it is large as seen from the case of an ideal polarized electrode. Figs. 10 shows the change of potential with time at various positions in the pore, *i.e.*, the orifice, middle and bottom of the pore. The measured potential $\varphi(z)$ is given by the curve at $z/l=0$. Fig. 11 shows the change of the current with time which flows into the electrode at the flat part of the electrode surface for various values

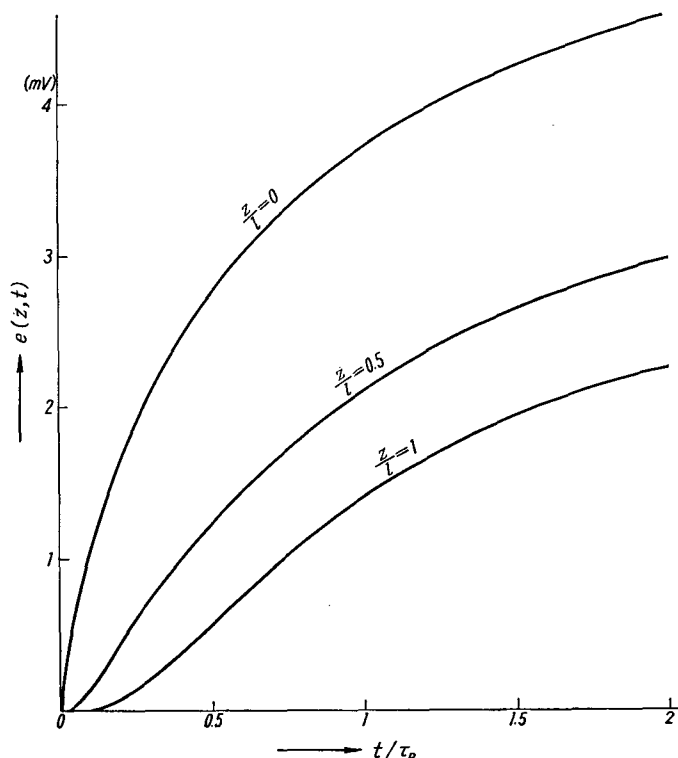


Fig. 10. Change of potential with time at the various positions in the pore when $\tau = \tau_p$. $I = 6 \times 10^{-5}$ Amp

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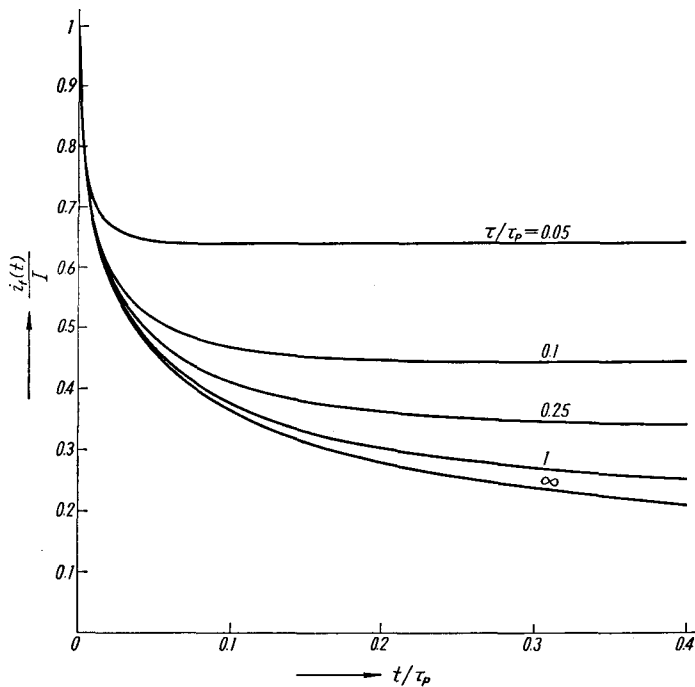


Fig. 11. Change of the current flowing into the flat part with time at various values of τ/τ_p .

of τ/τ_p . We see from Fig. 12 that in the early stage of time most part of the polarizing current flows into the electrode at the flat part and its steady value increases with decreasing τ/τ_p .

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