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THEORY OF THE GALVANOSTATIC TRANSIENT METHOD ON POROUS ELECTRODE

Part 2. Current and potential distribution in a pore

By

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Abstract

A mathematical treatment was given for the current and potential distribution in a pore when the electrode was polarized by a step function of current. The pore was assumed to be equivalent to an one-dimensional transmission line consisting of the solution resistance, the double layer capacitance and the reaction resistance of the electron-transfer reaction across the double layer. The expressions are given for the potential difference across the electric double layer at the electrode-solution interface inside the pore referred to that at the equilibrium potential, the current passing through the cross section of the pore, the current density which flows into the electrode and the Ohmic potential in the pore respectively as functions of time and the position in the pore. The distribution of the current and potential was found to depend greatly not only on the time constant of the pore defined by a product of the solution resistance inside the pore and the double layer capacitance of the pore wall, but also on that of the electron-transfer reaction.

It is shown that in concentrated solutions the current density distributes homogeneously throughout the whole surface inside the pore, while in dilute solutions most of the polarizing current flows into the electrode near the orifice of the pore in the early stage of time and that the current density distribution becomes more inhomogeneous with decreasing the time constant of the electron-transfer reaction. This inhomogeneity causes the deviation of the $\log (I/\dot{\varphi})$ *vs. time* curve from a linear relation in the initial stage of time.

Introduction

The distribution of current and potential in a pore in steady states has been discussed by many authors. However, there has been reported few works concerning the problem in the transient state. KSENZHEK and STENDER[1-3] discussed the potential distribution in a pore in the transient state, but they did not give explicitly the analytical solution of the potential as a function of time and the position in the pore. DE LEVIE[4] has given an

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expression for the current and potential in a pore of infinite length in the transient state for an ideal polarized state, and similar relations have been reported by BONNEMAY, BRONOËL, LEVART, PILLA, and d'ORSAY[5]. POSEY and MOROZUMI[6] have discussed the current and potential distribution in the pore of definite length in an ideal polarized state. Thus, it is needed to reconsider the distribution of the current and potential in a pore caused by applying a step function of current taking into consideration an electron-transfer reaction across the double layer to elucidate the mechanism of the electrochemical reaction by the galvanostatic transient method using a porous electrode.

The time function of the electrode potential on a porous electrode caused by a step function of a polarizing current was given in Part 1[7] by taking into consideration the random distribution of pores on the electrode surface. It was found that the electrode potential $\varphi(t)$ depends not only on the time constant of an electron-transfer step which is given by the product of the double layer capacitance and the reaction resistance of the step, but also on the time constant of each pore which is expressed as the product of the double layer capacitance and the solution resistance inside the pore.

In the present paper, the distribution of current and potential in a pore caused by applying a step function of current to the pore electrode will be theoretically expressed as a function of time on the basis of the one-dimensional transmission-line model of the equivalent circuit of the pore in which an electron-transfer reaction is taken into consideration.

§1. Theory of current and potential distribution in a pore

We assume here a pore of cylindrical form of length l and radius r. The equivalent circuit of the pore is given by an one-dimensional transmission-line model as shown in Fig. 1 by taking into consideration the solution resistance, the double layer capacitance at the electrode-solution interface
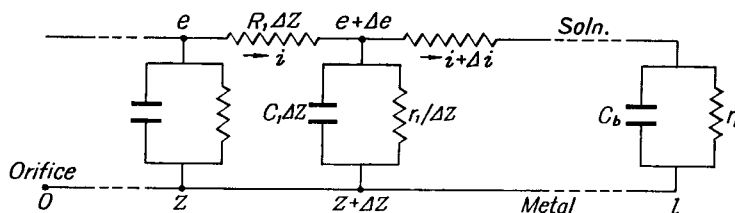

Fig. 1. An equivalent circuit of the pore

and the reaction resistance of the electron-transfer reaction across the double layer inside the pore.

In Fig. 1, z is the distance from the orifice of the pore measured along the axis of the pore, e is the overvolage of the electron-transfer step at z, i.e., the difference of the potential drop across the double layes at z between the reversible state and the working one of the electrode, i is the current strength passing through the cross section of the pore at z. R_1, r_1 and C_1 denote, respectively, the Ohmic resistance of the solution in the pore, the reaction resistance of the electron-transfer step and the differential capacitance of the double layer, each of which is referred to the unit length of the pore. r_b and C_b denote, respectively, the reaction resistance and the double layer capacitance at the bottom of the pore.

The differential equation of e and i with respect to t and z will be deduced on the basis of this model in what follows. It can be seen from Fig. 1 that the gradient of e at z is given by

$$\frac{\partial e}{\partial z} = -iR_1 . \tag{1}$$

The decrease of the current $-\Delta i$ between z and $z+\Delta z$ is balanced equally with the Faradaic and copacitative current which flows into the wall of the pore in this interval Δz. The capacitative part of the current is given by $C_1 \Delta z \dot{e}$ and the Faradaic one is given by $e \Delta z / r_1$, assuming that the rate of the electron-transfer step is proportional to e. This assumption is valid in the potential region much lower than RT/F. The potential in this treatment is thus limited in the region $|e| \ll RT/F$. It follows that

$$\frac{\partial i}{\partial z} = -\left(C_1 \frac{\partial e}{\partial t} + \frac{e}{r_1} \right) = -C_1 \left(\frac{\partial e}{\partial t} + \frac{e}{\tau} \right), \tag{2}$$

where τ is the time constant of the electron-transfer step and is expressed as $C_1 r_1$. e and i are given as functions of z and t by solving the differential equations (1) and (2). From Eqs. (1) and (2), we have

$$\frac{\partial^2 e}{\partial z^2} = R_1 C_1 \left(\frac{\partial e}{\partial t} + \frac{e}{\tau} \right). \tag{3}$$

The initial condition for the potential can be taken as

$$e(z, 0) = 0 , \tag{4}$$

since we start from the reversible state. The boundary conditions for the current are given as

$$i(0, t) = I , \tag{5}$$

and

$$i(l, t) = C_b \left\{ \left(\frac{\partial e}{\partial t} \right)_{z=l} + \frac{e(l, t)}{\tau} \right\},$$ (6)

where I is the polarizing current and $i(l, t)$ is the current which flows into the electrode at the bottom of the pore. Equation (3) can be solved under these conditions applying the Laplace transformation. Equation (3) is transformed as

$$\frac{d^2 \bar{e}}{dz^2} = R_1 C_1 (s + \tau^{-1}) \bar{e},$$ (7)

where $\bar{e}$ denotes the Laplace transform of e, and s is the variable. The general solution of Eq. (7) is given as

$$\bar{e} = A \exp \left\{ z \sqrt{R_1 C_1 (s + \tau^{-1})} \right\} + B \exp \left\{ -z \sqrt{R_1 C_1 (s + \tau^{-1})} \right\},$$ (8)

where A and B are the constants. Applying the Laplace transformation to Eq. (1), the Laplace transorm of the current can be expressed as

$$\bar{\imath} = -\frac{\sqrt{R_1 C_1 (s + \tau^{-1})}}{R_1} \Big[A \exp \left\{ z \sqrt{R_1 C_1 (s + \tau^{-1})} \right\}$$

$$- B \exp \left\{ -z \sqrt{R_1 C_1 (s + \tau^{-1})} \right\} \Big],$$ (9)

taking into consideration Eq. (8). The constants A and B can be determined using the boundary conditions expressed in the Laplace transforms. The boundary conditions (5) and (6) can be transformed as

$$\bar{\imath}(z = 0) = I/s,$$ (10)

$$\bar{\imath}(z = l) = C_b (s + \tau^{-1}) \bar{e}(z = l).$$ (11)

Introducing Eqs. (10) and (11) into (8) and (9), the constants A and B can be determined. Finally we have

$$\frac{\bar{\imath}}{I} = \frac{1}{s}$$

$$\times \frac{C_p \sinh \left\{ \left(1 - \frac{z}{l} \right) \sqrt{\tau_p (s + \tau^{-1})} \right\} + C_b \sqrt{\tau_p (s + \tau^{-1})} \cosh \left\{ \left(1 - \frac{z}{l} \right) \sqrt{\tau_p (s + \tau^{-1})} \right\}}{C_p \sinh \sqrt{\tau_p (s + \tau^{-1})} + C_b \sqrt{\tau_p (s + \tau^{-1})} \cosh \sqrt{\tau_p (s + \tau^{-1})}},$$

(12)

$$\bar{e} = \frac{IR_p}{s\sqrt{\tau_p(s+\tau^{-1})}}$$

$$\times \frac{C_p \cosh\left\{\left(1-\frac{z}{l}\right)\sqrt{\tau_p(s+\tau^{-1})}\right\} + C_b\sqrt{\tau_p(s+\tau^{-1})}\sinh\left\{\left(1-\frac{z}{l}\right)\sqrt{\tau_p(s+\tau^{-1})}\right\}}{C_p \sinh\sqrt{\tau_p(s+\tau^{-1})} + C_b\sqrt{\tau_p(s+\tau^{-1})}\cosh\sqrt{\tau_p(s+\tau^{-1})}},$$

$$(13)$$

where $R_p = lR_1$ and $C_p = lC_1$. τ_p is called the time constant of the pore which is defined as $\tau_p = R_p C_p$.

The current $i(z, t)$ and potential $e(z, t)$ can be obtained respectively as the inverse Laplace transforms of Eqs. (12) and (13). $\bar{e}$ is given as a function of $\tau_p s$, $i.e.$,

$$\bar{e} = \frac{IR_p\tau_p}{\tau_p s(\tau_p s+\alpha)}$$

$$\times \frac{C_p \cosh\left\{\left(1-\frac{z}{l}\right)\sqrt{\tau_p s+\alpha}\right\} + C_b\sqrt{\tau_p s+\alpha}\sinh\left\{\left(1-\frac{z}{l}\right)\sqrt{\tau_p s+\alpha}\right\}}{\dfrac{C_p \sinh\sqrt{\tau_p s+\alpha}}{\sqrt{\tau_p s+\alpha}} + C_b\cosh\sqrt{\tau_p s+\alpha}}, \quad (14)$$

where $\alpha = \tau_p\tau^{-1}$. Thus, we can express

$$\frac{\bar{e}(s)}{IR_p\tau_p} = F(\tau_p s),$$

where

$$F(s) = \frac{1}{s(s+\alpha)} \frac{C_p \cosh\left\{\left(1-\frac{z}{l}\right)\sqrt{s+\alpha}\right\} + C_b\sqrt{s+\alpha}\sinh\left\{\left(1-\frac{z}{l}\right)\sqrt{s+\alpha}\right\}}{\dfrac{C_p \sinh\sqrt{s+\alpha}}{\sqrt{s+\alpha}} + C_b\cosh\sqrt{s+\alpha}}.$$

$$(15)$$

We have a relation between the inverse Laplace transforms of $\bar{e}(s)$ and $F(s)$ as

$$\frac{e(z, t)}{IR_p\tau_p} = \frac{1}{\tau_p} f(t/\tau_p), \quad i.e., \quad e(z, t) = IR_p f(t/\tau_p), \quad (16)$$

where $\quad f(t) = L^{-1}\{F(s)\}.$ $\hspace{4cm}$ (17)

Thus, the problem of finding $e(z, t)$ ban be reduced to that of finding the inverse Laplace transform of $F(s)$. $F(s)$ is a single-valued function of s and it is readilly shown that $\lim_{s\to\infty} F(s) = 0$. Therefore, the problem of inverse Laplace transformation of $F(s)$ is reduced to that of finding the pole points

of function $F(s) \cdot \exp(st)$ and the sum of the residues at these points according to the JORDAN's lemma and residue theorem.

$F(s)$ is written as

$$F(s) = p(s)/s(s+\alpha)\, q(s)\,, \tag{18}$$

where
$$p(s) = C_p \cosh\left\{\left(1-\frac{z}{l}\right)\sqrt{s+\alpha}\right\} + C_b \sinh\left\{\left(1-\frac{z}{l}\right)\sqrt{s+\alpha}\right\}, \tag{19}$$

and
$$q(s) = \frac{C_p \sinh\sqrt{s+\alpha}}{\sqrt{s+\alpha}} + C_b \cosh\sqrt{s+\alpha}\ . \tag{20}$$

The pole points of the function $F(s) \cdot \exp(st)$ are given as the roots of the equation

$$s(s+\alpha) \cdot q(s) = 0\,,$$

i.e., $s = 0$, $-\alpha$ and

$$\frac{C_p \sinh\sqrt{s+\alpha}}{\sqrt{s+\alpha}} + C_b \cosh\sqrt{s+\alpha} = 0\,. \tag{21}$$

The residues at the pole points $s=0$, $-\alpha$ and those given by Eq. (21) are given respectively as

$$\frac{p(0)}{\alpha q(0)}\,, \qquad -\frac{p(-\alpha)}{\alpha q(-\alpha)}\,\exp(-\alpha t)\ \text{and}\ \frac{p(s_n)}{s_n(s_n+\alpha)\, q'(s_n)}\,\exp(s_n t)\,,$$

where s_n is the n-th root of Eq. (21) and $q'(s_n)$ is the derivative of $q(s)$ at $s = s_n$. Here, the $s_n's$ are confined to the real and negative roots, since potential e should be a real and convergent function of time. Thus, we have

$$f(t) = \frac{p(0)}{\alpha q(0)} - \frac{p(-\alpha)}{\alpha q(-\alpha)}\,\exp(-\alpha t) + \sum_{n=1}^{\infty}\frac{p(s_n)}{s_n(s_n+\alpha)\, q'(s_n)}\,\exp(s_n t)\,. \tag{22}$$

The first and the second term in $f(t)$ are given, respectively, by

$$\frac{p(0)}{\alpha q(0)} = \frac{C_p \cosh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\} + C_b\sqrt{\alpha}\,\sinh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}}{\sqrt{\alpha}\,(C_p \sinh\sqrt{\alpha} + C_b\sqrt{\alpha}\,\cosh\sqrt{\alpha}\,)}\,, \tag{23}$$

$$\frac{p(-\alpha)}{\alpha q(-\alpha)}\,\exp(-\alpha t) = \frac{C_p}{\alpha(C_p+C_b)}\,\exp(-\alpha t)\,. \tag{24}$$

Equation (21) has no root in the region $s+\alpha \geqq 0$, and hence $s_n+\alpha$ should be negative. Thus, we can put

$$\sqrt{s_n+\alpha} = jq_n\,, \qquad q_n;\ \text{positive real value}. \tag{25}$$

Introduction of Eq. (25) into (21) gives

$$\tan q = -\frac{C_b}{C_p}\, q\,.\tag{26}$$

Thus, $f(t)$ is obtained finally as

$$f(t) = \frac{C_p \cosh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\} + C_b\sqrt{\alpha}\,\sinh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}}{\sqrt{\alpha}\,(C_p \sinh\sqrt{\alpha} + C_b\sqrt{\alpha}\,\cosh\sqrt{\alpha}\,)} - \frac{C_p \exp(-\alpha t)}{\alpha(C_p+C_b)}$$

$$-2\sum_{n=1}^{\infty} \frac{(C_p^2 + C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)}{(q_n^2+\alpha)(C_p^2 + C_p C_b + C_b^2 q_n^2)}\, \exp\left\{-(q_n^2+\alpha)\,t\right\}.\tag{27}$$

From Eqs. (16) and (27), we have the expression for potential $e(z,t)$ as

$$e(z,t) = \frac{IR_p\left[C_p\cosh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\} + C_b\sqrt{\alpha}\,\sinh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}\right]}{\sqrt{\alpha}\,(C_p \sinh\sqrt{\alpha} + C_b\sqrt{\alpha}\,\cosh\sqrt{\alpha}\,)} - Ir_0 \exp(-t/\tau)$$

$$-2IR_p\sum_{n=1}^{\infty} \frac{(C_p^2 + C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)}{(q_n^2+\alpha)(C_p^2 + C_p C_b + C_b^2 q_n^2)}\, \exp\left\{-(q_n^2+\alpha)\,t/\tau_p\right\}.\tag{28}$$

where $r_0(=\tau/C)$ is the reaction resistance of the electron-transfer step in the pore as a whole. The expression for the current $i(z,t)$ which passes through the cross section at z is obtained by differentiating Eq. (28) with z on the basis of Eq. (1)

$$\frac{i(z,t)}{I} = \frac{C_p \sinh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\} + C_b\sqrt{\alpha}\,\cosh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}}{C_p \sinh\sqrt{\alpha} + C_b\sqrt{\alpha}\,\cosh\sqrt{\alpha}}$$

$$-2\sum_{n=1}^{\infty} \frac{q_n(C_p^2 + C_b^2 q_n^2)\sin\left(q_n\frac{z}{l}\right)}{(q_n^2+\alpha)(C_p^2 + C_p C_b + C_b^2 q_n^2)}\, \exp\left\{-(q_n^2+\alpha)\,t/\tau_p\right\}.\tag{29}$$

On the other hand, the density of the current $i^*(z,t)$ which flows into the electrode at the point z and time t can be deduced as follows. The current whice flows into the electrode between z and $z+\Delta z$ equals $i(z)-i(z+\Delta z)$ as seen from Fig. 1. The area of the pore wall in this interval is $2\pi r\Delta z$. Thus, the current density $i^*(z,t)$ is given by

$$i^*(z,t) = \frac{1}{2\pi r}\lim_{\Delta z\to 0}\frac{i(z)-i(z+\Delta z)}{\Delta z} = -\frac{1}{2\pi r}\frac{di(z,t)}{dz}\,.\tag{30}$$

Differentiating Eq. (29), we have

$$i^*(z, t) = \frac{1}{2\pi r}\left[\frac{C_p\sqrt{\alpha}\,\cosh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}+C_b\alpha\,\sinh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}}{C_p\sinh\sqrt{\alpha}+C_b\sqrt{\alpha}\,\cosh\sqrt{\alpha}}\right.$$

$$\left. +2\sum_{n=1}^{\infty}\frac{q_n^2(C_p^2+C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)}{(q_n^2+\alpha)(C_p^2+C_p C_b+C_b^2 q_n^2)}\,\exp\left\{-(q_n^2+\alpha)\,t/\tau_p\right\}\right]. \quad (31)$$

Equation (28) can be more simplified using the initial condition of $e(z, 0)=0$. We have from Eq. (28) at $t=0$,

$$\frac{R_p\left[C_p\cosh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right\}+C_b\sqrt{\alpha}\,\sinh\left\{\sqrt{\alpha}\left(1-\frac{z}{l}\right)\right\}\right]}{\sqrt{\alpha}\,(C_p\sinh\sqrt{\alpha}+C_b\sqrt{\alpha}\cosh\sqrt{\alpha})}-r_0$$

$$=2R_p\sum_{n=1}^{\infty}\frac{(C_p^2+C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)}{(q_n^2+\alpha)(C_p^2+C_p C_b+C_b^2 q_n^2)}. \quad (32)$$

Introducing Eq. (32) into (28), we have

$$e(z, t) = Ir_0\left\{1-\exp\left(-t/\tau\right)\right\}$$

$$+2IR_p\sum_{n=1}^{\infty}\frac{(C_p^2+C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)\left[1-\exp\left\{-(q_n^2+\alpha)\,t/\tau_p\right\}\right]}{(q_n^2+\alpha)(C_p^2+C_p C_b+C_b^2 q_n^2)}. \quad (33)$$

In the ideal polarized state, the expressions for current and potential can be simplified respectively by putting $\tau^{-1}=o$, *i.e.*, $\alpha=0$, as

$$e(z, t) = \frac{I}{C}t+2IR_p\sum_{n=1}^{\infty}\frac{(C_p^2+C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)}{q_n^2(C_p^2+C_p C_b+C_b^2 q_n^2)}\left\{1-\exp\left(-q_n^2 t/\tau_p\right)\right\}, \quad (34)$$

$$\frac{i(z, t)}{I} = 1-\frac{C_p}{C}\frac{z}{l}-2\sum_{n=1}^{\infty}\frac{(C_p^2+C_b^2 q_n^2)\sin\left(q_n\frac{z}{l}\right)}{q_n(C_p^2+C_p C_b+C_b^2 q_n^2)}\exp\left(-q_n^2 t/\tau_p\right), \quad (35)$$

and

$$\frac{i^*(z, t)}{I} = \frac{1}{S}+\frac{1}{\pi rl}\sum_{n=1}^{\infty}\frac{(C_p^2+C_b^2 q_n^2)\cos\left(q_n\frac{z}{l}\right)}{C_p^2+C_p C_b+C_b^2 q_n^2}\exp\left(-q_n^2 t/\tau_p\right), \quad (36)$$

where C is the total double layer capacity of the pore which equals C_p+C_b and S is the total surface area of the pore which is given by $\pi r^2+2\pi rl$.

In the special case where the bottom of the pore is neglected, the potential $e(z, t)$ has been deduced by POSEY and MOROZUMI[6] which coincides with Eq. (34) in which C_b is put zero.

§ 2.   Discussion

We will discuss here the distribution of current density and potential inside the pore on the basis of Eqs. (31) and (33) or (34) and (36).

The potential at $z=0$, $e(0, t)$, which can be measured as the change of the electrode potential when a polarizing current is given to the electrode, is distributed in the pore between the Omhic drop $e_\Omega(z, t)$ in the solution and the potential difference across the electric double layer $e(z, t)$, i.e.,

$$e_\Omega(z, t) = e(0, t) - e(z, t).\tag{37}$$

We can express $e_\Omega(z, t)$ from Eq. (33) as

$$e_\Omega(z, t) = 2IR_p \sum_{n=1}^{\infty} \frac{(C_p^2 + C_b^2 q_n^2)\left\{1 - \cos\left(q_n \frac{z}{l}\right)\right\}}{(q_n^2 + \alpha)(C_p^2 + C_p C_b + C_b^2 q_n^2)} \left[1 - \exp\left\{-(q_n^2 + \alpha) t/\tau_p\right\}\right].\tag{38}$$

It can be seen from Eqs. (31) and (33) that $i^*(z, t)$ and $e(z, t)$ are greatly influenced by the parameter α when the pore size is fixed to a definite value. We will discuss the influence of parameter α on $i^*(z, t)$ and $e(z, t)$.

Let us consider the case when the solution is so concentrated that the Ohmic resistance of the solution practically equals zero. We can put τ_p, $\alpha = 0$ and reduce Eqs. (31) a ɪ ɾ (33) to

$$i^*(z, t) = \frac{IC^*}{2\pi rlC} = \frac{I}{S},\tag{39}$$

and

$$e(z, t) = Ir_0\left\{1 - \exp\left(-t/\tau\right)\right\}.\tag{40}$$

It can be seen from Eqs. (39) and (40) that the potential depends only on the kinetic parameter of an electron-transfer step and time independently of the position in the pore and that the current density remains constant independently of the position in the pore, i.e., the electrode can be regarded as if it were geometrically flat.

When the solution is enough diluted and the solution resistance is so high that the time constant of the pore practically equals infinite, we have $\alpha = \tau_p/\tau \gg 1$.   The increase of α is also caused by the decrease of the time constant of the electron-transfer step.   We have from Eq. (33) by neglecting q_n^2 as compared with α

$$e(z, t) = I\left\{1 - \exp\left(-t/\tau\right)\right\} \left\{r_0 + 2R_p \sum_{n=1}^{\infty} \frac{(C_p^2 + C_b^2 q_n^2)\cos\left(q_n \frac{z}{l}\right)}{\alpha(C_p^2 + C_p C_b + C_b q_n^2)}\right\}. \quad (41)$$

We have also from the condition $\alpha \gg 1$, $\exp\left(\sqrt{\alpha}\right) \gg \exp\left(-\sqrt{\alpha}\right)$ and $\exp\left\{\sqrt{\alpha}\left(1 - \frac{z}{l}\right)\right\} \gg \exp\left\{\sqrt{\alpha}\left(1 - \frac{z}{l}\right)\right\}$ except for the very near position of the bottom, and hence we can put $\cosh\sqrt{\alpha} = \sinh\sqrt{\alpha} = \frac{1}{2}\exp\left(\sqrt{\alpha}\right)$ and $\cosh\left\{\sqrt{\alpha}\left(1 - \frac{z}{l}\right)\right\} = \sinh\left\{\sqrt{\alpha}\left(1 - \frac{z}{l}\right)\right\} = \frac{1}{2}\exp\left\{\sqrt{\alpha}\left(1 - \frac{z}{l}\right)\right\}$ Thus, the initial condition of potential given by Eq. (32) can be simplified as

$$\frac{R_p}{\sqrt{\alpha}}\exp\left(-\sqrt{\alpha}\frac{z}{l}\right) - r_0 = 2R_p \sum_{n=1}^{\infty} \frac{(C_p^2 + C_b^2 q_n^2)\cos\left(q_n \frac{z}{l}\right)}{\alpha(C_p^2 + C_p C_b + C_b^2 q_n^2)}. \quad (42)$$

Introducing Eq. (42) into Eq. (41), we have the expression for potential under the condition $\alpha \gg 1$ as

$$e(z, t) = \frac{IR_p}{\sqrt{\alpha}}\exp\left(-\sqrt{\alpha}\frac{z}{l}\right)\cdot\left\{1 - \exp\left(-t/\tau\right)\right\}. \quad (43)$$

From Eq. (43), we have the expressions for the current and Ohmic potential under the same condition as

$$i(z, t) = I\exp\left(-\sqrt{\alpha}\frac{z}{l}\right)\cdot\left\{1 - \exp\left(-t/\tau\right)\right\}, \quad (44)$$

$$i^*(z, t) = \frac{I}{2\pi r l}\sqrt{\alpha}\exp\left(-\sqrt{\alpha}\frac{z}{l}\right)\cdot\left\{1 - \exp\left(-t/\tau\right)\right\}, \quad (45)$$

$$e_\Omega(z, t) = \frac{IR_p}{\sqrt{\alpha}}\left\{1 - \exp\left(-\sqrt{\alpha}\frac{z}{l}\right)\right\}\left\{1 - \exp\left(-t/\tau\right)\right\}. \quad (46)$$

It can be seen from Eqs. (43), (44), (45) and (46) that the potential and current equals practically zero except for the very near part of the orifice of the pore and that the Ohmic potential in the pore practically equals $e(0, t)$. It is thus concluded that only the very near part of the orifice of the pore is polarized under the condition $\alpha \gg 1$.

In an ideal polarized state, α can be taken zero independently of the value of τ_p. The time derivative of potential at the position z becomes constant in the time region $t > \tau_p$ as seen by differentiating Eq. (34) with time, *i.e.*,

$$\dot{e}(z, t) = I/C. \quad (47)$$

It follows from Eqs. (37) and (47)

$$\dot{e}_{\Omega}(z, t) = 0 . \tag{48}$$

Thus, the distribution of the Ohmic potential drop in the pore does not depend on time. In this case di/dz equals constant as seen from Eq. (35)

$$\frac{di(z, t)}{dz} = -\frac{C_p}{lC} , \tag{49}$$

i. e., the current i passing through the cross section of the pore at z decreases linearly with the position in the pore and the current density at z which is used for the charging up of the double laper becomes constant as given by

$$i^*(z, t) = I/S . \tag{50}$$

Now, we will discuss the influence of the current density disitribution on the overvoltage-time curve observed in the galvanostatic transient study on the pore electrode. When the electrode surface is geometrically flat, the overvoltage-time curve can be analysed on the basis of the following equation[8], i. e.,

$$\ln (I/\dot{\varphi}) = \ln C + t/\tau , \tag{51}$$

where φ is the overvoltage, $\dot{\varphi}$ is its time derivative and C is the total double layer capacity. On the pore electrode, the overvoltage φ is given as $e(0, t)$ from Eq. (33) and the relation $\log(I/\dot{\varphi})$ and time is expressed as

$$\ln (I/\dot{\varphi}) = \ln C + t/\tau - \ln \left\{ 1 + 2C \sum_{n=1}^{\infty} \frac{C_p^2 + C_b^2 q_n^2}{C_p(C_p^2 + C_p C_b + C_b^2 q_n^2)} \exp (-q_n^2 t/\tau_p) \right\} . \tag{52}$$

Thus, the relation between $\log(I/\dot{\varphi})$ and time on the pore electrode is reduced to Eq. (51) under the condition $\exp(-q_n^2 t/\tau_p) = 0$. It was soown in part 1[7] that this condition is practically satisfisfied in the region $t > \tau_p$. It can be seen from Eq. (31) that the condition $\exp(-q_n^2 t/\tau_p) = 0$ is the one under which the current density distribution in the pore is in the steady state. Under this condition, we have from Eq. (33)

$$\frac{\partial e(z, t)}{\partial t} = \frac{I}{C} \exp (-t/\tau) \tag{53}$$

i. e., the time derivative of potential does not depend on the position in the pore. From Eq. (53), we have the charging current density of the double layer $i_c^*(z, t)$, i. e., $C^* \dfrac{\partial e(z, t)}{\partial t}$, as a constant value independent of the position in the pore

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$$i_c^*(z, t) = \frac{I}{S} \exp\left(-t/\tau\right) \tag{54}$$

where C^* is the double layer capacity per unit area.

It follows from the above arguments that the overvoltage-time curve on the pore electrode can be analysed on the basis of Eq. (51) in the region of time where the current density distribution is in the steady state and the charging current density of the double layer distributes homogenoeously in the pore. In other words, the inhomogeneity of the charging current density distribution of the double layer in the initial time region causes the high current density near the orifice of the pore and then rapid increase of overvoltage. In consequence, the relation between $\log\left(I/\dot{\varphi}\right)$ and time deviates from a linear one.

Examples of the distribution of current density $i^*(z, t)$ and potential $e(z, t)$ at definite values of time are shown respectively in Figs. 2 and 3 in the special case where the time constant of the electron-transfer step equals that of the pore. As seen from Fig. 2, in the early stage of time the large part of the current flows into the electrode near the orifice, and with the increase of time the current penetrates into the pore more deeply. As seen from Fig. 3, the potential penetrates into the pore more deeply with the
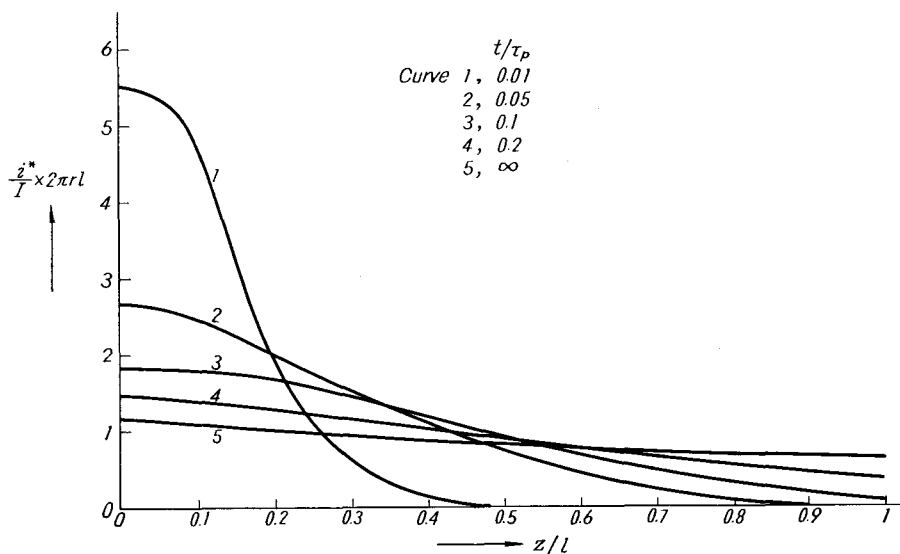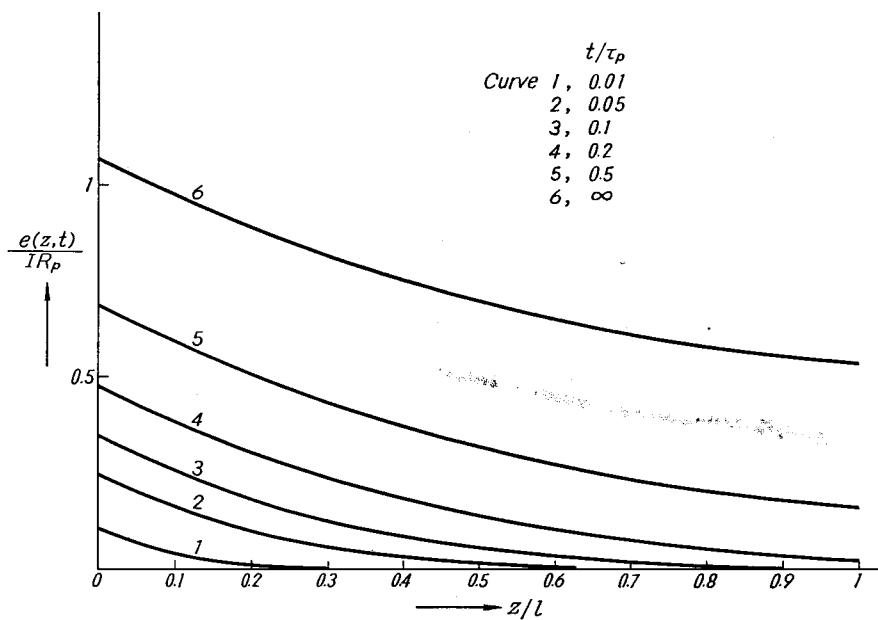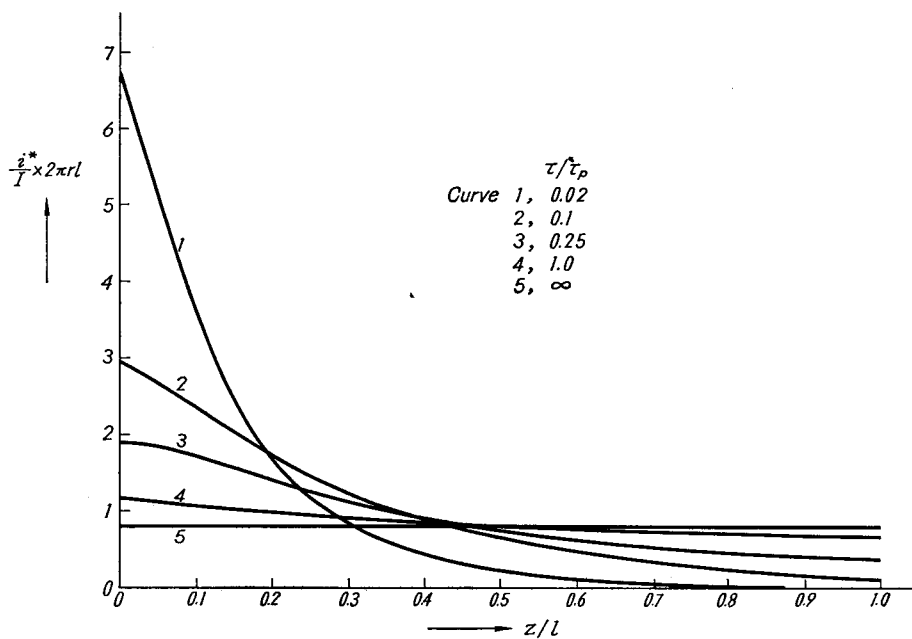

Fig. 2. Distribution of current density at the steady state.

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Fig. 3.   Distribution of potential in a pore. $\tau = \tau_p$

Fig. 4.   Distribution of current density in a pore. $\tau = \tau_p$

increase of time as in the case of the current density. It should be noted here that the measured potential is expressed by the value on the coordinate axis in Fig. 3 as a function of time. Fig. 4 shows the distribution of the current density i^* multiplied by the area of the pore wall $2\pi rl$ in the steady state at the various values of α^{-1} *i. e.*, τ/τ_p, from 0.02 to infinity. It can be seen from Fig. 4 that at small values of α^{-1}, the current flows into the electrode at the position near the orifice, while with the increase of α^{-1} the current density i^* near the bottom of the pore increases and finally at $\alpha = 0$, *i. e.*, on an ideal polarized electrode, the cureent is uniformly distributed throughout the whole surface inside the pore.

Acknowledgment

References

1) O. S. KSENZHEK, Zh. Fiz. Khim, **37**, 2007 (1963).

2) O. S. KSENZHEK, *ibid.*, **38**, 1846 (1964).

3) O. S. KSENZHEK and V. V. STENDER, Dokl. Akad. Nauk SSSR, **106**, 487 (1956).

4) R. De LEVIE, Electrochim. Acta, **8**, 751 (1963).

5) M. BONNEMAY, G. BRONOËL, E. LEVART, A. A. PILLA and E. P. d'A. d'ORSAY, Compt. rend, **258**, 4256, 6139 (1964).

6) F. A. POSEY and T. MOROZUMI, J. Electrochem. Soc., **113**, 176 (1966).

7) K. KUNIMATSU, This Journal, **20**, 1 (1972).

8) A. MATSUDA and R. NOTOYA, *ibid.*, **14**, 165 (1966).