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THEORY OF THE GALVANOSTATIC TRANSIENT METHOD ON POROUS ELECTRODE

Part. 1. Theory of the overvoltage-time curve and determination of the differential capacity of the electric double layer and the time constant of an electron-transfer step.

By

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Abstract

A theoretical treatment for the change of overvoltage $\varphi(t)$ with time on porous electrode in response to application of a step function of current I was developed in the region of overvoltage much less than RT/F . $\varphi(t)$ was estimated as the change of the potential difference across the impedance at the electrode-solution interface on the basis of the *Carson's* integral equation. The electrode surface was assumed to consist of a flat part and N -cylindrical-pores of different sizes. The impedance at the electrode-solution interface was considered as a parallel combination of the impedance at the flat part and those of pores. The impedance of a pore was estimated by regarding the pore as an one-dimensional transmission line which consisted of the solution resistance, double layer capacitance and reaction resistance of the electron-transfer reaction.

It was shown that the feature of the $\varphi(t)$ - t curve on porous electrode is affected not only by the time constant τ of the electron-transfer reaction which is defined by a product of the double layer capacitance and the reaction resistance of the reaction, but also by the time constants of the pores. τ_k 's ($k=1, 2, \dots, N$), each of which is defined by a product of the double layer capacitance and the solution resistance in the pore.

The relation between $\log(I/\varphi)$ and time was found to deviate from a linear one in the initial region of time earlier than the largest one of the time constants of the pores, τ_N . It was shown, however, that the differential capacity C of the double layer and τ will be determined from the linear relation between $\log(I/\varphi)$ and time in the region of time later than τ_N on the basis of the equation

$$\ln(I/\varphi) = \ln C + t/\tau,$$

when τ is larger than τ_N . This case was shown to be the one for the hydrogen electrode on evaporated films of *Platinum*, *Nickel* and *Silver* in alkaline solutions.

The above expressions for the impedance and the $\varphi(t)$ - t curve were found to have simplified forms in the initial region of time earlier than τ_1/π , where τ_1 is the smallest one of the τ_k 's. It was shown that τ and the differential capacity of the double layer at the

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flat part will be determined by the analysis of the initial region of $\varphi(t)-t$ curve where time is less than τ_1/π on the basis of the simplified expressions for the $\varphi(t)-t$ curve.

$\varphi(t)$ and $\log(I/\dot{\varphi})$ were calculated numerically as the functions of time respectively for the case of uniform pore size, and the results were shown graphically.

Introduction

The galvanostatic transient method has been used to determine the constituent elementary steps of the hydrogen evolution reaction and to elucidate the mechanism of setting up of the hydrogen overvoltage¹⁻⁴. In this method, the differential capacity C of the electric double layer at the electrode-solution interface and the time constant τ of the electron-transfer step are determined from the initial region of the overvoltage-time curve on the basis of Eq. (1)¹⁾

$$\ln(I/\dot{\varphi}) = \ln C + t/\tau, \quad (1)$$

where I , φ and $\dot{\varphi}$ denote respectively the polarizing current of a constant value, the overvoltage and its time derivative. However, it has been found that the $\log(I/\dot{\varphi})-t$ curve deviates from Eq. (1) on rough evaporated films of Platinum^{1,2)}, Nickel³⁾ and Silver⁴⁾ in dilute alkaline solutions and that the deviation tends to increase with the decrease of the solution concentration and is not observed on smooth plate electrodes.

On the other hand, it has been pointed out by several authors⁵⁻⁷⁾ that the roughness of the electrode surface affects the impedance at the electrode-solution interface and that the change of the impedance brings about the change of the feature of the potential-time curve or the frequency dependence of the capacitive component of the interfacial impedance.

Thus, the analysis of the overvoltage-time curve based on Eq. (1) is required to be reconsidered by taking into account the roughness of the electrode surface, since Eq. (1) was derived from an uniformly flat surface of the electrode. The present work is devoted to develop a theoretical treatment of the overvoltage-time curve in the galvanostatic transient method and to discuss how to determine the time constant of the electron-transfer step and the differential capacity of the double layer on the electrode with a rough surface. Several authors have discussed this problem for some special cases. The results and their applicability will be discussed in detail in the following sections.

§ 1. The overvoltage-time curve on porous electrode

1.1 The time function of potential and Carson's integral equation

When a step function of current I is applied to an impedance, the time

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function of potential across the impedance is expressed by the *Carson's* integral equation. Applying this equation to an electrode system, W. LORENZ⁸⁾ expressed the change of the electrode potential $\varphi(t)$ with time in terms of the impedance $Z(s)$ at the electrode-solution interface as

$$Z(s)/s = \int_0^{\infty} \exp(-st) \frac{\varphi(t)}{I} dt, \quad (2)$$

where $s=j\omega$, $j=\sqrt{-1}$ and $\omega/2\pi$ is the frequency of the alternating current. We will discuss the potential-time curve on the basis of Eq. (2) in what follows.

Equation (2) is rewritten by the Laplace transform L of variable s , as

$$L\{\varphi(t)\} = IZ(s)/s. \quad (3a)$$

The Laplace transform of the time derivative of potential is derived from Eq. (3a), as

$$L\{\dot{\varphi}(t)\} = IZ(s) - \varphi(0_+).$$

Putting $\varphi(0_+) = 0$ as the initial condition in this equation, we have

$$L\{\dot{\varphi}(t)\} = IZ(s). \quad (3b)$$

The potential $\varphi(t)$ is thus reduced to overvoltage.

From Eqs. (3a) and (3b), we have

$$\varphi(t) = L^{-1}\{IZ(s)/s\} \quad (4a)$$

and
$$\dot{\varphi}(t) = L^{-1}\{IZ(s)\} \quad (4b)$$

where L^{-1} denotes the inverse Laplace transform of variable s . As seen from Eqs. (4a) and (4b), the problem of mathematical formulation of $\varphi(t)$ and $\dot{\varphi}(t)$ is reduced to that of finding the expression for the impedance $Z(s)$. The impedance $Z(s)$ will be given in what follows by assuming a distribution of pores of different sizes on the electrode surface.

1.2 Impedance at the electrode-solution interface on porous electrode

When the electrode surface consists of a flat part and pores, the impedance $Z(s)$ at the electrode-solution interface is expressed by a parallel combination of the impedance of the flat part $Z_f(s)$ and those of pores $Z_k(s)$'s, *i. e.*,

$$\frac{1}{Z(s)} = \frac{1}{Z_f(s)} + \sum_{k=1}^N \frac{1}{Z_k(s)}, \quad (5)$$

where the suffix f means the flat part of the electrode surface, k means the

k -th pore and N is the number of the pores on the electrode surface.

Now, we estimate the pore impedance $Z_k(s)$ on the basis of the one-dimensional transmission-line model assuming that the pore is of cylindrical shape and has an axis normal to the electrode surface. According to this model, the potential in the pore depends only on the position along the axis of the pore and the k -th pore is expressed by the equivalent circuit in Fig. 1. Here, z is the distance from the orifice of the pore measured along the axis, e the potential difference between the solution and the electrode at z , i is the strength of the current passing through the cross section of the pore at z , $Z_{1,k}$ and $R_{1,k}$ are the impedance at the electrode-solution interface and solution resistance both per unit length respectively and $Z_{b,k}$ is the impedance at the bottom of the pore.

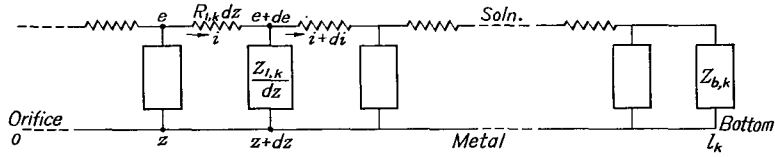


Fig. 1. The equivalent circuit of the k -th pore.

First, we express e and i at z as a function of $R_{1,k}$ and $Z_{1,k}$. As seen from Fig. 1, we have the following equation for the gradients of e and i at the point z

$$\frac{de}{dz} = -iR_{1,k} \quad (6)$$

and
$$\frac{di}{dz} = -e/Z_{1,k}. \quad (7)$$

Differentiating Eqs. (6) and (7), we obtain

$$\frac{d^2e}{dz^2} - \frac{R_{1,k}}{Z_{1,k}} e = 0. \quad (8)$$

The general solution of Eq. (8) is

$$e = A \exp(z\sqrt{R_{1,k}/Z_{1,k}}) + B \exp(-z\sqrt{R_{1,k}/Z_{1,k}}), \quad (9)$$

where A and B are the integration constants.

The current i is obtained from Eqs. (9) and (6) as

$$i = -\frac{1}{\sqrt{R_{1,k}Z_{1,k}}} \left\{ A \exp(z\sqrt{R_{1,k}/Z_{1,k}}) - B \exp(-z\sqrt{R_{1,k}/Z_{1,k}}) \right\}. \quad (10)$$

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The constants A and B are determined from the following boundary conditions at the orifice and at the bottom of the pore

$$e(z=0) = E, \quad (11)$$

and
$$e(z=l_k) = i(z=l_k)Z_{b,k}, \quad (12)$$

where l_k is the length of the k -th pore. Using the values of A and B thus determined, we have from Eq. (10) the current which flows into the k -th pore

$$i(z=0) = E \left/ \frac{R_{1,k}Z_{1,k} + Z_{b,k}\sqrt{R_{1,k}Z_{1,k}} \coth(l_k\sqrt{R_{1,k}/Z_{1,k}})}{\sqrt{R_{1,k}Z_{1,k}} \coth(l_k\sqrt{R_{1,k}/Z_{1,k}}) + Z_{b,k}} \right. . \quad (13)$$

The impedance of the k -th pore is defined as $E/i(z=0)$, and hence we have from Eq. (13)

$$Z_k(s) = \frac{R_{1,k}Z_{1,k} + Z_{b,k}Z_k^0}{Z_k^0 + Z_{b,k}}, \quad (14)$$

where
$$Z_k^0 = \sqrt{R_{1,k}Z_{1,k}} \coth(l_k\sqrt{R_{1,k}/Z_{1,k}}). \quad (15)$$

It can be seen from Eq. (14) that $Z_k(s)$ is reduced to Z_k^0 by putting the impedance $Z_{b,k}$ infinite. Z_k^0 of Eq. (15) is identical with the expression for the impedance of an infinite pore derived by DE LEVIE⁹⁾ and LEIKIS, SEBASTIANOV and KNOTZ⁶⁾.

On the other hand, the impedances $Z_{b,k}$ and $Z_{1,k}$ can be expressed by the double layer capacitance and the time constant of the electron-transfer step, as^{*)}

$$Z_{b,k}(s)^{-1} = C_{b,k}(s + \tau^{-1}), \quad (16)$$

and
$$Z_{1,k}(s)^{-1} = C_{1,k}(s + \tau^{-1}), \quad (17)$$

where $C_{b,k}$ and $C_{1,k}$ are the differential capacity of the double layer at the bottom of the pore and that per unit length of the pore, respectively.

Introducing Eqs. (16) and (17) into (14) and (15), we can express $Z_k(s)$ as

$$Z_k(s) = \frac{Z_k^0(s) + C_{b,k}R_k/C_k}{C_{b,k}(s + \tau^{-1})Z_k^0(s) + 1}, \quad (18)$$

where
$$Z_k^0(s) = \frac{R_k}{\sqrt{\tau_k(s + \tau^{-1})}} \coth \sqrt{\tau_k(s + \tau^{-1})}. \quad (19)$$

*) The time constant of the electron-transfer step changes in general depending on the overvoltage and consequently on the position inside the pore. However, our consideration will be confined to the region of overvoltage much less than RT/F . In this case, the time constant of the electron-transfer step is regarded as constant independent of the position in the pore.

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In Eqs. (18) and (19), R_k and C_k denote respectively the solution resistance and the double layer capacitance of the k -th pore and they are given by $R_k = l_k R_{1,k}$ and $C_k = l_k C_{1,k}$. The τ_k is given by $\tau_k = R_k C_k$ which will be called the time constant of the k -th pore in what follows.

The total impedance of the electrode-solution interface is given as the parallel combination of $Z_f(s)$ and the $Z_k(s)$'s by Eq. (5). $Z_f(s)$ is expressed by the double layer capacitance C_f of the flat part and the time constant τ , as

$$Z_f(s)^{-1} = C_f(s + \tau^{-1}), \quad (20)$$

in so far as the overvoltage is much less than RT/F .

The total impedance $Z(s)$ is finally given from Eqs. (5), (18) and (20) as

$$Z(s)^{-1} = C_f(s + \tau^{-1}) + \sum_{k=1}^N \frac{C_{d,k}(s + \tau^{-1})Z_k^0(s) + 1}{Z_k^0(s) + C_{d,k}R_k/C_k}. \quad (21)$$

In the case of an ideal polarized electrode, the impedance $Z(s)$ is reduced to $Z_0(s)$ by putting $\tau^{-1} = 0$ in Eq. (21), as

$$Z_0(s)^{-1} = C_f s + \sum_{k=1}^N \frac{C_{d,k} s Z_k^0(s) + 1}{Z_k^0(s) + C_{d,k}R_k/C_k}, \quad (22)$$

$$\text{where } Z_k^0(s) = \frac{R_k}{\sqrt{\tau_k s}} \coth \sqrt{\tau_k s}. \quad (23)$$

Comparison of $Z(s)$ and $Z_0(s)$ shows that $Z(s)$ is obtained by replacing s with $s + \tau^{-1}$ in $Z_0(s)$, as

$$Z(s) = Z_0(s + \tau^{-1}). \quad (24)$$

1.3 The overvoltage-time curve on porous electrode

Applying the inverse Laplace transformation to Eq. (24), we have a general relation between the time derivatives of overvoltage in the presence and absence of the electron-transfer reaction across the electrode-solution interface on the basis of Eq. (4b)

$$\dot{\varphi}(t) = \dot{\varphi}_0(t) \cdot \exp(-t/\tau), \quad (25)$$

where $\varphi_0(t)$ and $\dot{\varphi}_0(t)$ denote respectively the overvoltage and its time derivative in the ideal polarized state. The $\dot{\varphi}(t)$ will be readily obtained from $\dot{\varphi}_0(t)$ on the basis of Eq. (25) if $\dot{\varphi}_0(t)$ is given.

When the electrode surface is geometrically flat, Eq. (25) is reduced to Eq. (1), since $\dot{\varphi}_0(t)$ is given by I/C .

The $\dot{\varphi}_0(t)$ will be given below as the inverse Laplace transform of $Z_0(s)$ on the basis of Eq. (4b).

The problem of inverse Laplace transformation of $Z_0(s)$ is reduced to

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that of finding the pole points of the function $Z_0(s) \cdot \exp(st)$ and the sum of the residues at these points according to the JORDAN'S lemma and the CAUCHY'S residue theorem since $Z_0(s)$ is a single-valued function of s and $Z_0(s) \rightarrow 0$ with the increase of s as seen from Eqs. (22) and (23).

Now, $Z_0(s)^{-1}$ can be expressed as the product of s and $F(s)$, *i. e.*,

$$Z_0(s) = \frac{1}{sF(s)}, \quad (26)$$

$$\text{where } F(s) = C_f + \sum_{k=1}^N \frac{C_k(C_{b,k} + \frac{C_k}{\sqrt{\tau_k s}} \tanh \sqrt{\tau_k s})}{C_k + C_{b,k} \sqrt{\tau_k s} \tanh \sqrt{\tau_k s}}. \quad (27)$$

The pole points of $Z_0(s) \cdot \exp(st)$ are given as the solutions of the equation $s \cdot F(s) = 0$, *i. e.* $s=0$ and the solutions of the equation $F(s)=0$,

$$C_f + \sum_{k=1}^N \frac{C_k(C_{b,k} + \frac{C_k}{\sqrt{\tau_k s}} \tanh \sqrt{\tau_k s})}{C_k + C_{b,k} \sqrt{\tau_k s} \tanh \sqrt{\tau_k s}} = 0. \quad (28)$$

On the other hand, the residues of the function $Z_0(s) \cdot \exp(st)$ are given by $F(0)^{-1}$ at $s=0$ and by $\exp(s_n t)/s_n F'(s_n)$ at the pole points given by Eq. (28), where s_n is the n -th root of Eq. (28) and $F'(s_n)$ is the derivative of $F(s)$ at $s=s_n$. Here, the s_n 's are confined to the roots on the real axis since $\phi_0(t)$ should be a real function. Thus, we have

$$\phi_0(t) = I \left\{ \frac{1}{F(0)} + \sum_{n=1}^{\infty} \frac{\exp(s_n t)}{s_n F'(s_n)} \right\}. \quad (29)$$

Next, we will estimate $s_n F'(s_n)$. For the second term in the right-hand side of Eq. (29) to be convergent, the s_n 's should be negative, and hence we can put

$$\sqrt{s_n} = j q_n, \quad q_n; \text{ positive real value.} \quad (30)$$

From Eqs. (27), (28) and (30), we have

$$s_n F'(s_n) = \frac{1}{2} \{ C_f + A(q_n) \}, \quad (31)$$

$$\text{where } A(q_n) = \sum_{k=1}^N \frac{C_k(C_k^2 + C_k C_{b,k} + C_{b,k}^2 \tau_k q_n^2)}{(C_k \cos q_n \sqrt{\tau_k} - C_{b,k} q_n \sqrt{\tau_k} \sin q_n \sqrt{\tau_k})^2}, \quad (32)$$

and the q_n 's are the positive roots of the equation

$$C_f + \sum_{k=1}^N \frac{C_k(C_{b,k} q \sqrt{\tau_k} \cos q \sqrt{\tau_k} + C_k \sin q \sqrt{\tau_k})}{q \sqrt{\tau_k} (C_k \cos q \sqrt{\tau_k} - C_{b,k} q \sqrt{\tau_k} \sin q \sqrt{\tau_k})} = 0. \quad (33)$$

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$F(0)$ in Eq. (29) is given from Eq. (27) as

$$F(0) = C_f + \sum_{k=1}^N (C_{d,k} + C_k) = C, \quad (34)$$

where C is the total double layer capacity at the electrode-solution interface. Finally, we have from Eqs. (29), (30), (31) and (34) the expression for $\dot{\varphi}_0(t)$ as

$$\dot{\varphi}_0(t) = \frac{I}{C} + 2I \sum_{n=1}^{\infty} \frac{\exp(-q_n^2 t)}{C_f + A(q_n)} \quad (35)$$

Integrating Eq. (35), we have the expression for $\varphi_0(t)$ as

$$\varphi_0(t) = \frac{I}{C} t + 2I \sum_{n=1}^{\infty} \frac{1 - \exp(-q_n^2 t)}{q_n^2 \{C_f + A(q_n)\}}. \quad (36)$$

Equation (35) indicates that the second term in the right-hand side due to the presence of pores on the electrode surface disappears with the increase of time and that a linear $\varphi_0(t) - t$ curve is observed whose slope gives the total double layer capacity.

On the other hand, in the case of the electrode on which the electron-transfer occurs through the electrode-solution interface, $\dot{\varphi}(t)$ is obtained from $\dot{\varphi}_0(t)$ by Eq. (25) as

$$\dot{\varphi}(t) = I \exp(-t/\tau) \left\{ \frac{1}{C} + 2 \sum_{n=1}^{\infty} \frac{\exp(-q_n^2 t)}{C_f + A(q_n)} \right\}. \quad (37)$$

Integrating Eq. (37), we have the expression for $\varphi(t)$

$$\varphi(t) = I r_0 \{1 - \exp(-t/\tau)\} + 2I \sum_{n=1}^{\infty} \frac{1 - \exp\{-(q_n^2 + \tau^{-1})t\}}{(q_n^2 + \tau^{-1}) \{C_f + A(q_n)\}}, \quad (38)$$

where r_0 is the reaction resistance of the electron-transfer step relevant to the total surface area of the electrode and is related to the exchange current i_0 as $r_0 = RT/F i_0$.

1.4 The relation between $\log(I/\dot{\varphi})$ and time on porous electrode

From Eq. (37), we have the relation between $\log(I/\dot{\varphi})$ and time on porous electrode, as

$$\ln(I/\dot{\varphi}) = \ln C + t/\tau - \ln \left\{ 1 + 2C \sum_{n=1}^{\infty} \frac{\exp(-q_n^2 t)}{C_f + A(q_n)} \right\}. \quad (39)$$

It can be seen that Eq. (39) is reduced to Eq. (1) with the increase of time. Note that C and τ will also be determined on porous electrodes on the basis of Eq. (1).

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1.5 The case of uniform pore size

In the special case of uniform pore size, *i. e.*

$$C_k = C_p, \quad C_{b,k} = C_p, \quad R_k = R_p \quad \text{and} \quad \tau_k = \tau_p \quad (k=1, 2, \dots, N)$$

$\varphi(t)$, $\varphi_0(t)$ and $\ln(I/\bar{\varphi})$ are reduced respectively to the following equations

$$\varphi(t) = Ir_0 \left\{ 1 - \exp(-t/\tau) \right\} + 2I\tau_p \sum_{n=1}^{\infty} \frac{1 - \exp\left\{ -\left(q_n^2 + \frac{\tau_p}{\tau} \right) t/\tau_p \right\}}{\left(q_n^2 + \frac{\tau_p}{\tau} \right) \{ C_f + A(q_n) \}}, \quad (40)$$

$$\varphi_0(t) = \frac{I}{C} t + 2I\tau_p \sum_{n=1}^{\infty} \frac{1 - \exp(-q_n^2 t/\tau_p)}{q_n^2 \{ C_f + A(q_n) \}}, \quad (41)$$

and

$$\ln(I/\bar{\varphi}) = \ln C + t/\tau - \ln \left\{ 1 + 2C \sum_{n=1}^{\infty} \frac{\exp(-q_n^2 t/\tau_p)}{C_f + A(q_n)} \right\}, \quad (42)$$

where
$$A(q_n) = \frac{(N^2 C_p^2 + C_f^2 q_n^2)(C_p^2 + C_p C_b + C_b^2 q_n^2)}{N C_p (C_p^2 + C_b^2 q_n^2)}, \quad (43)$$

and the q_n 's are the positive roots of the following equation

$$\tan q = \frac{C_p(C_f + N C_b)q}{C_f C_b q^2 - N C_p^2}. \quad (44)$$

Equation (42) indicates that the second term due to the presence of pores on the electrode surface affects the $\log(I/\bar{\varphi})-t$ curve and causes a deviation from Eq. (1) to longer time when τ_p becomes larger. Thus, the deviation from Eq. (1) increases with the increases of the specific resistance of the solution, *i. e.*, with the decrease of the solution concentration.

Several authors^{7,10,11)} have derived the overvoltage-time equation on a porous electrode assuming the uniform pore size but neglecting the existence of a flat part and the bottom of the pore. It will be seen that the equations derived by these authors are obtained from Eqs. (40) and (44) by putting $C_f = C_b = 0$ and $N = 1$. POSEY and MOROZUMI¹²⁾ have given the overvoltage-time equation on an ideal polarized electrode in the presence of the external flat surface, which is obtained by putting $C_b = 0$ and $N = 1$ in Eqs. (41) and (44).

§ 2. Discussion

2.1 The features of $\varphi_0(t)$, $\varphi(t)$ and $\log(I/\bar{\varphi})$ functions

In section 1, the expressions for $\varphi_0(t)$, $\varphi(t)$ and $\log(I/\bar{\varphi})$ functions were

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given taking into consideration the presence of pores on the electrode surface. The features of these functions will be understood better by performing the numerical calculation of them as the functions of time. The results of the numerical calculation of $\varphi_0(t)$, $\varphi(t)$ and $\log(I/\bar{\varphi})$ against t/τ_p are illustrated in Figs. 2, 3 and 4, which were calculated for the case of uniform pore size under the conditions given in Table 1.

TABLE 1. Values of some parameters employed in the numerical calculation

apparent surface area of the electrode	1 cm ²
pore radius (r)	5×10^{-3} cm
pore length (l)	10^{-2} cm
double layer capacity per unit area	20 μ F
specific resistance of solution (in 10^{-3} N-NaOH)	4.65 K Ω ·cm
time constant of the pore (τ_p)	3.72 msec

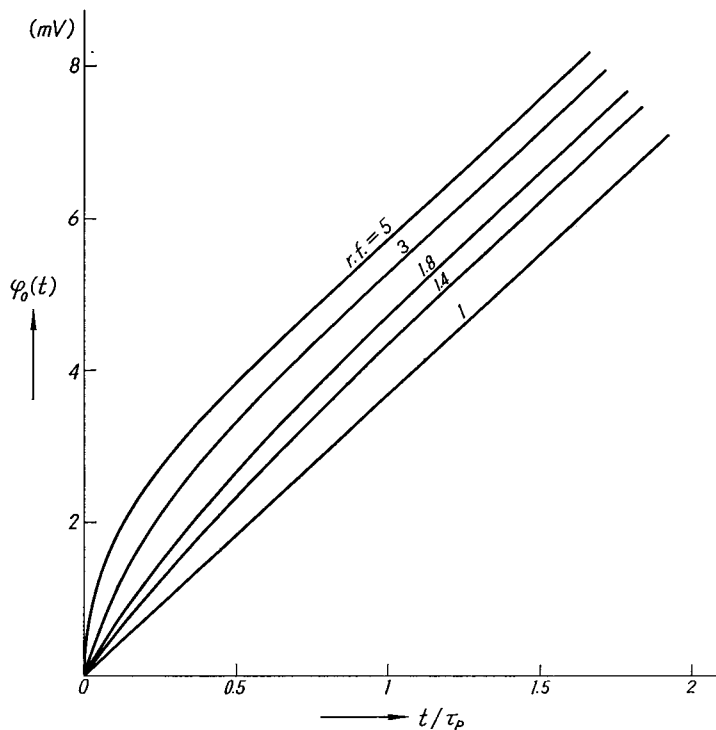


Fig. 2. Overvoltage-time curves in an ideal polarized state. The roughness factor 5 and 1.4 correspond to the number of pores $N=1.27 \times 10^4$ and $N=1.27 \times 10^3$ respectively per apparent unit surface area.

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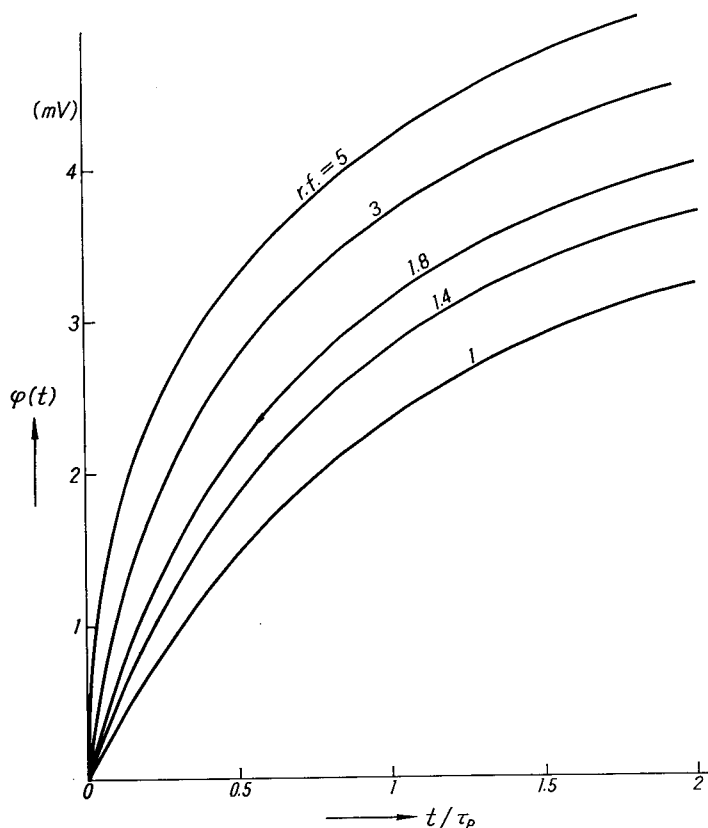


Fig. 3. Overvoltage-time curves in the case $\tau = \tau_p$.

In these calculations, true current density was kept constant (2×10^{-5} Amp/cm²) and hence the current strength increases with the increase of the roughness factor of the electrode surface. As mentioned in the foregoing section the influence of the pores on the time derivative of overvoltage decreases with the increase of time and disappears in the region of approximately $t > \tau_p$ as seen from Figs. 2 and 4.

2.2 The overvoltage-time curve in the initial time region

Now, we discuss here the initial part of the overvoltage-time curve observed on the electrode with N -pores of different size where t is shorter than τ_1/π and discuss what kind of parameters can be determined from the overvoltage-time curve in the time region $t < \tau_1/\pi$. We assume here that the order of the time constants of the pores is $\tau_1 < \tau_2 < \dots < \tau_k < \dots < \tau_N$.

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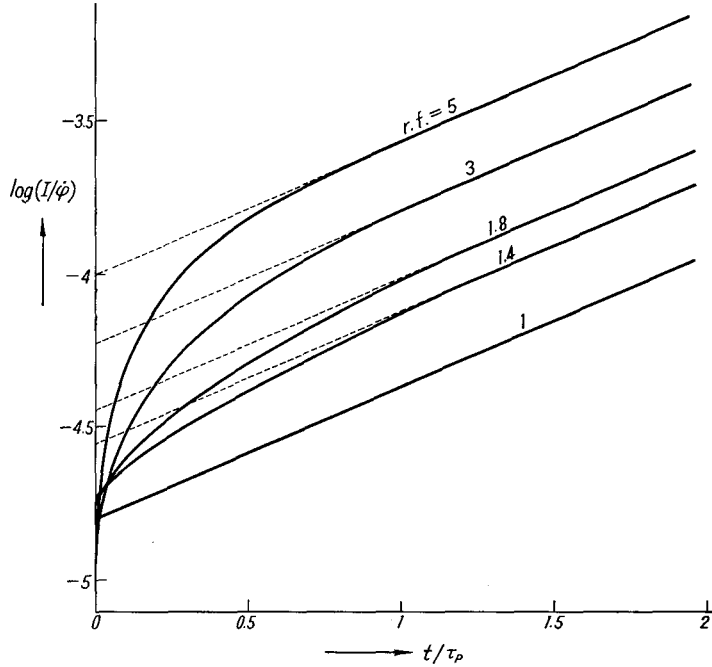


Fig. 4. The relation between $\log(I/\phi)$ and t/τ_p obtained from Fig. 3.

First, we discuss the ideal polarized electrode.

We have from Eq. (22) the expression for the impedance of the k -th pore $Z_k(s)$ in the ideal polarized state

$$Z_k(s) = \frac{Z_k^0(s) + C_{d,k}R_k/C_k}{C_{d,k}sZ_k^0(s) + 1}, \quad (45)$$

where $Z_k^0(s)$ is given by Eq. (23) as

$$Z_k^0(s) = \frac{R_k}{\sqrt{\tau_k s}} \coth \sqrt{\tau_k s}.$$

The impedance $Z_k(s)$ is reduced simply to $Z_k^0(s)$ in the time region $t < \tau_1/\pi$ as seen in what follows.

Now, we discuss $Z_k^0(s)$. Expanding $\coth \sqrt{\tau_k s}$ to a series, we have

$$\coth \sqrt{\tau_k s} = \sqrt{\tau_k s} \sum_{n=-\infty}^{\infty} \frac{1}{\tau_k s + n^2 \pi^2},$$

and hence

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$$Z_k^0(s) = \frac{1}{C_k} \sum_{n=-\infty}^{\infty} \frac{1}{s + \frac{n^2 \pi^2}{\tau_k}}.$$

Applying the inverse Laplace transformation to the expanded form of $Z_k^0(s)$, we have

$$L^{-1}\{Z_k^0(s)\} = \frac{1}{C_k} \sum_{n=-\infty}^{\infty} \exp\left(-\frac{n^2 \pi^2}{\tau_k} t\right). \quad (46)$$

In the time region $t < \tau_k/\pi$, the summation in the right-hand side of Eq. (46) can be replaced by an integral formula and calculated as

$$\sum_{n=-\infty}^{\infty} \exp\left(-\frac{n^2 \pi^2}{\tau_k} t\right) = \int_{-\infty}^{\infty} \exp\left(-\frac{n^2 \pi^2}{\tau_k} t\right) dn = \sqrt{\tau_k/\pi t}. \quad (47)$$

Thus, we have from Eqs. (46) and (47)

$$Z_k^0(s) = R_k / \sqrt{\tau_k s}. \quad (48)$$

Introducing Eq. (48) into (45), we obtain

$$Z_k(s) = R_k / \sqrt{\tau_k s} = Z_k^0(s). \quad (49)$$

It can be seen that Eq. (49) coincides with the expression given by DE LEVIE⁹ for the impedance of an infinite pore.

Introducing Eq. (49) into (22), the expression for the total impedance of a porous electrode is given by

$$Z_0(s)^{-1} = C_f s + \sum_{k=1}^N C_k \sqrt{s} / \sqrt{\tau_k}. \quad (50)$$

Applying the inverse Laplace transformation to $Z_0(s)$, we have $\dot{\varphi}_0(t)$ as

$$\dot{\varphi}_0(t) = \frac{I}{C_f} \exp(\beta^2 t) \cdot \operatorname{erfc}(\beta \sqrt{t}), \quad (51)$$

where

$$\beta = \frac{1}{C_f} \sum_{k=1}^N C_k / \sqrt{\tau_k}. \quad (52)$$

Integrating Eq. (51), we have

$$\varphi_0(t) = \frac{I}{C_f \beta^2} \left\{ \exp(\beta^2 t) \cdot \operatorname{erfc}(\beta \sqrt{t}) + 2\beta \sqrt{t/\pi} - 1 \right\}. \quad (53)$$

Differentiating Eq. (51), we obtain a relation between $\dot{\varphi}_0(t)$ and $\ddot{\varphi}_0(t)$

$$\frac{\sqrt{t} \dot{\varphi}_0(t)}{I} = \frac{1}{\beta^2} \frac{\sqrt{t} \ddot{\varphi}_0(t)}{I} + \frac{1}{\beta C_f \sqrt{\pi}}. \quad (54)$$

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This equation enables us to determine β and C_f from the very initial part of $\varphi_0(t)-t$ curve where $t < \tau_1/\pi$.

It should be noticed here that the ideal polarized state will be realized on each electrode in principle as described below. The polarizing current consists of a Faradaic and non Faradaic components and in the very initial time region much shorter than the time constant of the electron-transfer step the former is negligibly small as compared with the latter. In this region, the electrode can be regarded practically as an ideal polarized one.

In the case where an electron-transfer occurs through the electrode-solution interface, we have an expression of $\dot{\varphi}(t)$ in the time region $t < \tau_1/\pi$ from Eqs. (25) and (51)

$$\dot{\varphi}(t) = \frac{I}{C_f} \exp\{(\beta^2 - \tau^{-1})t\} \cdot \operatorname{erfc}(\beta\sqrt{t}). \quad (55)$$

Integrating Eq. (55), we have

$$\varphi(t) = \frac{I}{C_f(\beta^2 - \tau^{-1})} \left[\exp\{(\beta^2 - \tau^{-1})t\} \cdot \operatorname{erfc}(\beta\sqrt{t}) + \beta\sqrt{\tau} \operatorname{erf}\sqrt{t/\tau} - 1 \right]. \quad (56)$$

From Eq. (55), we have

$$\ln(I/\dot{\varphi}) + \beta^2 t + \ln\{\operatorname{erfc}(\beta\sqrt{t})\} = \ln C_f + t/\tau. \quad (57)$$

This equation enables us to determine τ and C_f from the initial part of the $\varphi(t)-t$ curve if β is available, *e.g.* on the basis of Eq. (54).

The applicability of Eqs. (54) and (57) will be discussed in detail in the following section.

In the case of uniform pore size, Eq. (56) becomes equivalent to that which was derived by KSENZHEK¹³.

2.3 The determination of the double layer capacity and the time constant of the electron-transfer step by the analysis of overvoltage-time curves

As seen from Eq. (38), the time function of overvoltage is strongly affected by the time constants of the pores τ_k 's and of the electron-transfer step τ .

Here, a criterion of the analysis of the overvoltage-time curve will be discussed in two cases when τ is smaller or larger than τ_N . As seen from Fig. 4, in the case of uniform pore size Eq. (39) is practically reduced to Eq. (1) in the time region $t > \tau_p$ and we have the linear relation between $\log(I/\dot{\varphi})$ and time. This means that Eq. (39) is practically reduced to Eq.

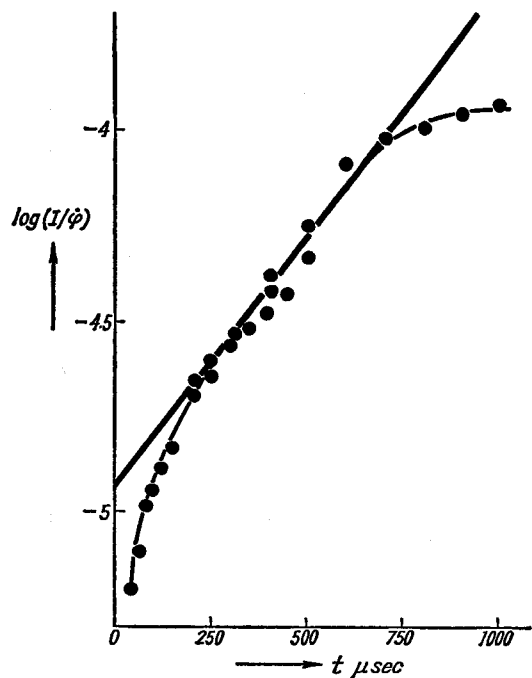


Fig. 5. The relation between $\log(I/\phi)$ and time on an evaporated film of Platinum in NaOH aq. solution. $\text{pH}=11.9^{1,2}$

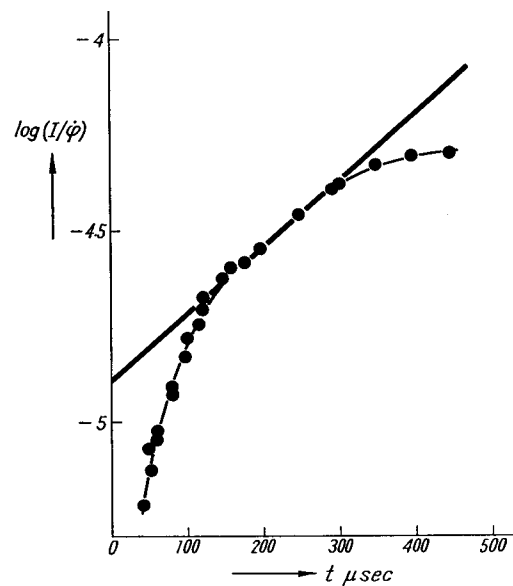


Fig. 6. The relation between $\log(I/\phi)$ and time on an evaporated film of Platinum in NaOH aq. solution. $\text{pH}=12.3^{1,2}$

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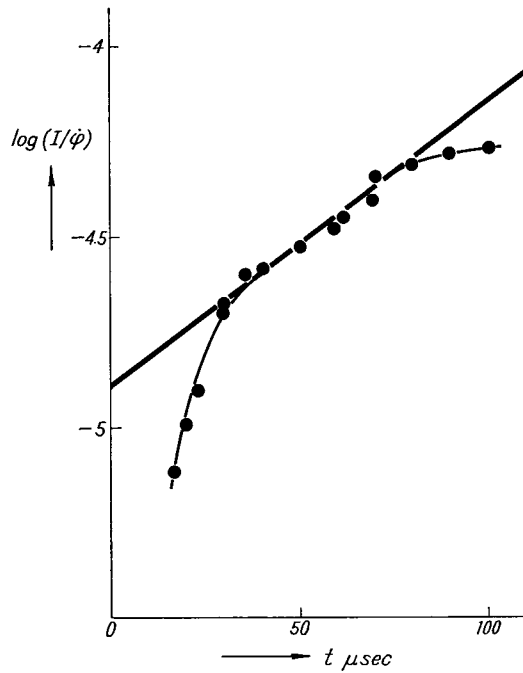


Fig. 7. The relation between $\log(I/\phi)$ and time on an evaporated film of Platinum in NaOH aq. solution. $\text{pH}=13.45^{1,2}$

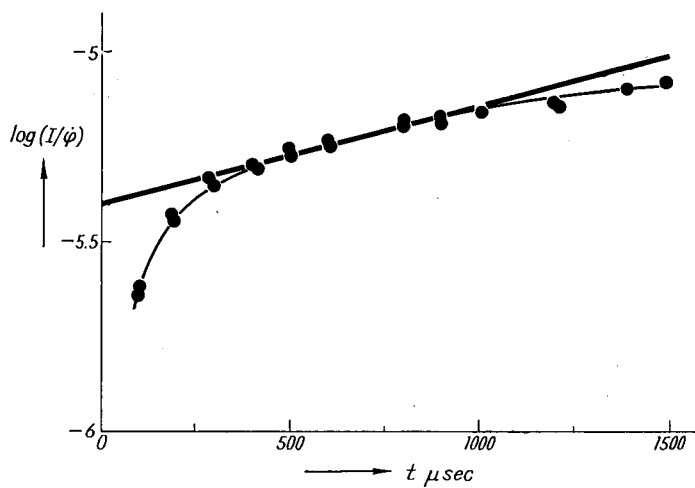


Fig. 8. The relation between $\log(I/\phi)$ and time on an evaporated film of Nickel in NaOH aq. solution. $\text{pH}=11.75^{1,2}$

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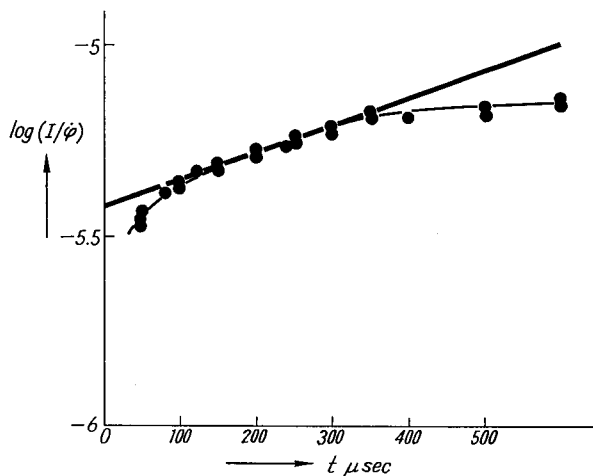


Fig. 9. The relation between $\log(I/\phi)$ and time on an evaporated film of Nickel in NaOH aq. solution. pH=12.3³⁾

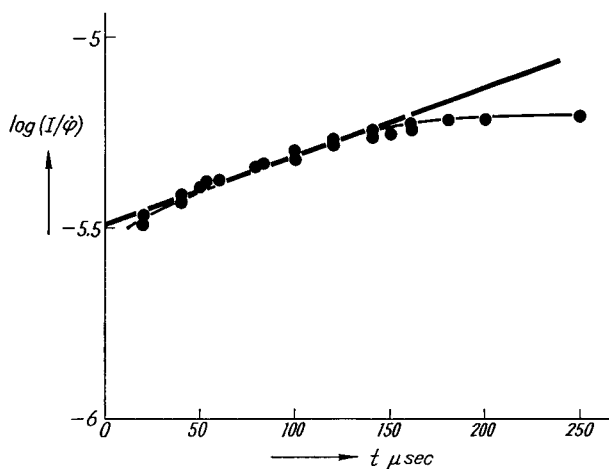


Fig. 10. The relation between $\log(I/\phi)$ and time on an evaporated film of Nickel in NaOH aq. solution. pH=12.95³⁾

(1) in the time region $t > \tau_N$ when N -pores of different sizes are distributed on the electrode surface.

If τ is larger than τ_N , in the time region between τ_N and τ Eq. (39) will be practically reduced to Eq. (1). Thus, C and τ will be determined on the basis of Eq. (1). This is the case for the hydrogen electrode on evaporated films of *Platinum*^{1,2)}, *Nickel*³⁾ and *Silver*³⁾ in alkaline solutions. Examples of the relations between $\log(I/\phi)$ and time on evaporated films

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of *Platinum* and *Nickel* observed by MATSUDA, NOTOYA^{1,2)} and OHMORI³⁾ are illustrated in Figs. 5–10. As seen from Figs. 5–10, the relation between $\log(I/\dot{\phi})$ and time deviates from a linear one in the initial time region and the deviation tends to increase with decreasing solution concentration. We can determine τ_N as the time when the relation begins to deviate from a linear one and τ and C by the analysis of the linear portion on the basis of Eq. (1) as has been done by these authors. The τ_N and τ thus determined are summarized in Table 2.

TABLE 2. The time constant of the electron-transfer step of the hydrogen electrode reaction and that of the pore on the evaporated films of Platinum and Nickel in sodium hydroxide solutions

	Pt			Ni		
pH	11.9	12.3	13.45	11.75	12.3	13.0
τ_N (μ sec)	300	150	40	450	150	50
τ (μ sec)	326	235	72.5	1770	589	226

It can be seen from these results that τ is always larger than τ_N on both electrodes and in each solution.

On the other hand, in the time region $t < \tau_1/\pi$ the electrode will be considered practically ideal polarized in this case as discussed above. Thus, Eq. (54) is applicable for the determination of C_f and β .

If τ is smaller than τ_N , it will not be possible to determine τ and C on the basis of Eq. (1), because Eq. (39) is not reduced to Eq. (1) in the time region earlier than τ_N and the electrode will be practically in the steady state in the time region later than τ_N . However, in the time region earlier than τ_1/π , Eq. (54) or (57) is applicable according as the ideal polarized state is realized or not. Thus, C_f , β and τ will be determined.

KSENZHEK^{10,13)} has discussed also how to determine the kinetic parameters on porous electrodes. However, his equations for the determination of the kinetic parameters on porous electrodes can not be applicable to the electrode system in which the pseudocapacitance plays a role in the setting up of the overvoltage, because he used the overvoltage at the steady state assuming that the change of overvoltage was caused by charging up of the double layer throughout the course of the building up of overvoltage.

Equations (39), (54) and (57) are applicable to the electrode system in which both the double layer capacitance and the pseudocapacitance play

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a role for the setting up of the overvoltage, in so far as we observe the initial change of overvoltage caused by charging up of the double layer.

The applicability of these equations are not confined to the electrode with pores of circular cylinder, but they are applicable also to the electrode with pores each of which has an axis normal to the electrode surface and an cross sectional area which remains constant independently of the position in the pore.

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