Electrochemistry of Redox Reaction

II. On the Kinetic Equations for Chronopotentiometry

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SYNOPSIS

Basic kinetic equations of chronopotentiometric potential-time curves, in which the equations for reversible, quasi-reversible and irreversible electron transfer process appeared in special cases, were given and a chronopotentiometric method for determining kinetic parameters was proposed therefrom. The method was demonstrated for Fe^{3+}/Fe^{2+} redox reaction in acidic aqueous media. The limitations of the method and the double-layer charging effects on the potential-time curve were discussed. The extension of the method to more general electrode processes was also considered.

1. INTRODUCTION

There have been many excellent treatments on chronopotentiometric potential-time equations for various electrode processes[1-7]. In all of these, however, the equations have restricted applications, i.e., the equations for reversible, quasi-reversible and irreversible electron transfer process.

In the present work, we have considered a general chronopotentiometric potential-time relationship without any restricted conditions with respect to kinetics of charge transfer, in which the equations

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for reversible and irreversible electron transfer process appear in special cases. A discussion is given of the significance of the equations together with the experimental confirmation of the treatments and a chronopotentiometric technique for determining kinetic parameters on redox reaction is proposed therefrom.

2. THEORETICAL BACKGROUND OF THE METHOD

In the case of a single elementary charge transfer reaction,

$$Ox + e^- \rightleftarrows Red \qquad (1)$$
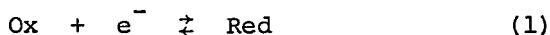
which involves two soluble species, neglecting the double layer effects, the current-polarization voltage characteristics under the galvanostatic condition may be described[8] as

$$\frac{J_C}{J_0^S} = C_R(0,t)\exp\{\frac{\alpha F}{RT}(E(t) - E_0)\} - C_O(0,t)\exp\{-\frac{(1 - \alpha)F}{RT}(E(t) - E_0)\} \qquad (2)$$

where J_C is the controlled current density in $A \cdot cm^{-2}$, J_0^S is the apparent standard exchange current density in $A \cdot cm^{-2}$, α is the transfer coefficient for oxidation process, E_0 is the standard electrode potential in V with respect to reference electrode (vs. RE) and $E(t)$ is the polarization voltage in V (vs.RE) as a function of time, while $C_R(0,t)$ and $C_O(0,t)$ are the surface concentrations of the species Red and Ox, respectively, in $moles \cdot cm^{-3}$ as a function of time.

In order to derive the chronopotentiometric potential-time equations, the surface concentration of Red and Ox must be obtained by solving Fick's equation for linear diffusion under the following initial and boundary conditions,

$$C_O(x,t) = C_O^O \quad and \quad C_R(x,t) = C_R^O, \text{ for } t = 0 \qquad (3)$$

$$C_O(x,t) = C_O^O \quad and \quad C_R(x,t) = C_R^O, \text{ at } x \to \infty \qquad (4)$$

$$J_C = -FD_O(\frac{\partial C_O(x,t)}{\partial x})_{x=0} = FD_R(\frac{\partial C_R(x,t)}{\partial x})_{x=0} \qquad (5)$$

where C_O^O and C_R^O are the bulk concentrations of Ox and Red, respectively, in $moles \cdot cm^{-3}$. It was assumed that no rate processes except diffusion participated in a mass transfer and that the conditions of semi-infinite linear diffusion were fulfilled.

Employing the Laplace transform method to the boundary value problem

and putting x = 0 in the final solution, $C_O(0,t)$ and $C_R(0,t)$ can be obtained[1]

$$C_O(0,t) = C_O^O + P_O \cdot t^{1/2} \quad (6) \qquad C_R(0,t) = C_R^O - P_R \cdot t^{1/2} \quad (7)$$

with
$$P_O = \frac{2J_C}{FD_O^{1/2}\pi^{1/2}} \quad \text{and} \quad P_R = \frac{2J_C}{FD_R^{1/2}\pi^{1/2}} \qquad (8)$$

No hypothesis on the kinetics of charge transfer was made in the derivations of $C_R(0,t)$ and $C_O(0,t)$ in eqs.(6) and (7), and consequently the equations can be combined with eq.(2) to derive a chronopotentiometric potential-time equation.

Combination of eqs.(2),(6) and (7) with the elimination of $C_R(0,t)$ and $C_O(0,t)$ yields the expression

$$\frac{J_C}{J_O^S} = (C_R^O - P_R \cdot t^{1/2}) \exp\{\frac{\alpha F}{RT}(E(t) - E_O)\}$$
$$- (C_O^O + P_O \cdot t^{1/2}) \exp\{-\frac{(1-\alpha)F}{RT}(E(t) - E_O)\} \quad (9)$$

where t is the time in seconds elapsed since the controlled current J_C was applied.

Putting $C_R^O = P_R t^{1/2}$ at time τ_O in eq.(9), one may define the transition time τ_O, where $E(t) \to +\infty$, for an oxidation process

$$\tau_O^{1/2} = \frac{FD_R^{1/2}\pi^{1/2}C_R^O}{2J_C} \qquad (10)$$

and also define the transition time τ_R, where $E(t) \to -\infty$, for a reduction process

$$\tau_R^{1/2} = -\frac{FD_O^{1/2}\pi^{1/2}C_O^O}{2J_C} \qquad (11)$$

Equations (10) and (11), first derived by Sand[9], indicate that one can determine D_O and/or D_R from the transition time measurements.

3. ANALYTICAL RESULTS

In order to assess the previous treatments, the following special cases were considered.

When $J_C/J_O^S \simeq 0$, equation (9) reduces to the simple form

$$E(t) = E_O + \frac{RT}{F} \ln(\frac{C_O^O + P_O \cdot t^{1/2}}{C_R^O - P_R \cdot t^{1/2}}) \qquad (12)$$

which is the same formula on chronopotentiometric potential-time

equation for a reversible electron transfer process[1].

Assuming $c_O^O = 0$ (or $c_R^O = 0$) and rearrangement of eq.(12) with application of eqs.(8) and (10) (or eq.(11)) gives

$$E(t) = E_O + \frac{RT}{F} \ln(\frac{D_R}{D_O})^{1/2} + \frac{RT}{F} \ln(\frac{t^{1/2}}{\tau_O^{1/2} - t^{1/2}}) \qquad (13)$$

or

$$E(t) = E_O + \frac{RT}{F} \ln(\frac{D_R}{D_O})^{1/2} + \frac{RT}{F} \ln(\frac{\tau_R^{1/2} - t^{1/2}}{t^{1/2}})$$

By putting $t^{1/2}/(\tau_O^{1/2} - t^{1/2}) = 1$ or $(\tau_R^{1/2} - t^{1/2})/t^{1/2} = 1$ in eq.(13), one can define the quarter-wave potential[1,2] $E_{1/4}$.

$$E_{1/4} = E_O + \frac{RT}{F} \ln(\frac{D_R}{D_O})^{1/2} \qquad (14)$$

It should be noted here that the condition of $c_R^O = 0$ (or $c_O^O = 0$), at which the quarter-wave potential has the specific meaning as was expressed in eq.(14), does not hold in all rigor for any experiment because of the nature of exponential or logarithmic function in eqs.(9) or (12), respectively.

For an another special case, when the first term (or the second term) in eq.(9) is extremely larger than the second term (or the first term),i.e.,

$$E(t) \gg E_O - \frac{RT}{F} \ln(\frac{c_R^O - P_R \cdot t^{1/2}}{c_O^O + P_O \cdot t^{1/2}}) \qquad (15)$$

for an oxidation process ($J_C > 0$), or

$$E(t) \ll E_O - \frac{RT}{F} \ln (\frac{c_R^O - P_R \cdot t^{1/2}}{c_O^O + P_O \cdot t^{1/2}}) \qquad (16)$$

for a reduction process ($J_C < 0$), equation (9) becomes the following expressions

$$E(t) = E_O + \frac{RT}{\alpha F} \ln(\frac{J_C}{J_O^S \cdot c_R^O}) - \frac{RT}{\alpha F} \ln\left[1 - (\frac{t}{\tau_O})^{1/2}\right] \qquad (17)$$

for an oxidation process ($J_C > 0$), and

$$E(t) = E_O - \frac{RT}{(1 - \alpha)F} \ln(- \frac{J_C}{J_O^S \cdot c_O^O}) + \frac{RT}{(1 - \alpha)F} \ln\left[1 - (\frac{t}{\tau_R})^{1/2}\right] \qquad (18)$$

for a reduction process ($J_C < 0$), where τ_O and τ_R are the transition times for oxidation and reduction process, respectively, as were defined in eqs.(10) and (11). Equations (17) and (18) indicate that polarization voltage versus the decimal logarithm of the quantity { $1 - (t/\tau_O)^{1/2}$} or { $1 - (t/\tau_R)^{1/2}$} yields a straight line whose slope is $2.303RT/\alpha F$ for an oxidation process and $2.303RT/(1-\alpha)F$ for

a reduction process.

The equations (17) and (18) have the same formulas derived by Delahay and Berzins[2] for totally irreversible charge transfer process but the second terms in the equations and the conditions given in eqs.(15) and (16) are different. Equations (15) and (16) are more specific conditions to derive eqs.(17) and (18) because the right hand sides of the equations are the corresponding potential-time equations for a reversible charge transfer process.

Since the potential-time equations for reversible or irreversible charge transfer processes appear in a special case, equation (9) may be one of the general expressions for the chronopotentiometric potential-time characteristics.

In order to illustrate a chronopotentiometric potential-time curve and then to make visual inspection on the equation more specifically, numerical analysis was carried out. Although numerical analysis on eq.(9) was possible with the given J_C, J_O^S, α, c_O^O, c_R^O, D_O, and D_R, it is convenient to consider the following special case.

Putting $c_R^O = c_O^O = C$ and $\tau_R = \tau_O = \tau$ (i.e., $D_R = D_O$), one obtains

$$\frac{J_C}{J_O^S \cdot C} = \left[1 - (\frac{t}{\tau})^{1/2}\right]\exp\{\frac{\alpha F}{RT}(E(t) - E_O)\} - \left[1 + (\frac{t}{\tau})^{1/2}\right]\exp\{-\frac{(1-\alpha)F}{RT}(E(t) - E_O)\}$$

$$(19)$$

where $J_C/J_O^S C$ is the symbolizing kinetic factor to express " activity " of electrode system and t/τ is the symbolizing time factor. Equation (19) indicates that the shape of chronopotentiometric potential-time curve is simply determined by $J_C/J_O^S \cdot C$ and τ .

Figure 1 shows the results of numerical analysis on eq.(19) with varying $J_C/J_O^S \cdot C$ at $\alpha = 0.5$. Curve (j) in Fig.1 shows the Nernstian potential-time curve, i.e., $J_C/J_O^S \cdot C = 0$. Since the upper limit of J_O^S was calculated to be ca. 10^9 A·cm^{-2} according to the absolute rate theory[10], the curve approach to the ideal Nernstian potential-time curve as close as they can, but they can not be superimposed onto the ideal Nernstian curve.

For large value of $J_C/J_O^S \cdot C$, that is, small values of J_O^S and C with large J_C, the curve shifts systematically apart from the ideal Nernstian curve with 2.303RT/αF or 2.303RT/(1-α)F dependence on $\log|J_C|/J_O^S \cdot C$, which is corresponding to the Tafel slope. As can be seen in Fig.1, the value of $J_C/J_O^S \cdot C$ straightly affected on polarization voltage in chronopotentiometric potential-time curves for both oxidation and reduction processes.

For small value of $J_C/J_O^S \cdot C$, ca.below 10^{-1}, α does not affect so much
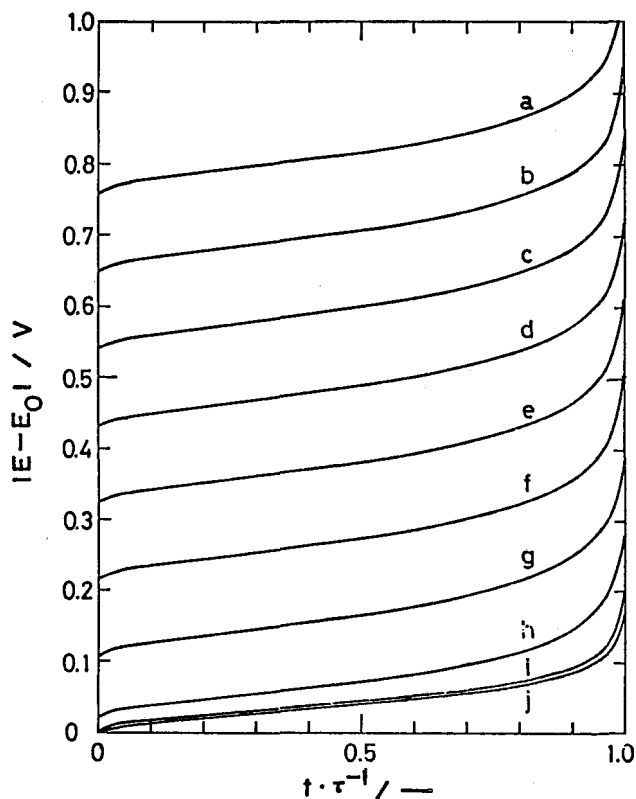
Fig.1 Theoretical chronopotentiometric potential-time curves
calculated from eq.(19) with α = 0.5 and T = 273 $^{\circ}$K as
a function of $J_C/J_O^S \cdot C$.

$J_C/J_O^S \cdot C$; (a) 10^7, (b) 10^6, (c) 10^5, (d) 10^4, (e) 10^3,
(f) 10^2, (g) 10^1, (h) 10^0, (i) 10^{-1} and
(j) 0 (Nernstian)

on the shape of chronopotentiometric potential-time curve as can be
seen in Fig.1.   The effect of α on the shape, however, is remarkable
for large value of $J_C/J_O^S \cdot C$ as shown in Fig.2.   Figure 2 indicates
that the transfer coefficient α can be determined together with J_O^S in
Fig.1 if one has specific chronopotentiometric potential-time curves
for oxidation and/or reduction process in a solution with equimolar
of Ox and Red.

From the above considerations, we may be able to conclude that
equation (9) is one of the general formulas on the chronopotentiometric
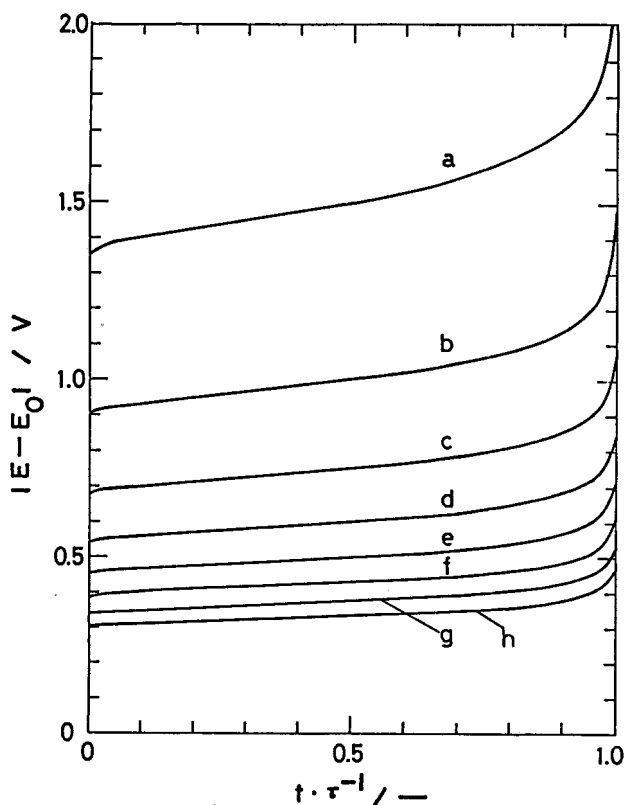potential-time curves.

Fig.2 Theoretical chronopotentiometric potential-time curves calculated from eq.(19) with $J_C/J_O^S \cdot C = 10^5$ and $T = 273$ $°K$ as a function of α.

α, $1-\alpha$; (a) 0.2, 0.8, (b) 0.3, 0.7, (c) 0.4, 0.6, (d) 0.5, 0.5, (e) 0.6, 0.4, (f) 0.7, 0.3, (g) 0.8, 0.2, and (h) 0.9, 0.1

4. EXPERIMENTAL CONFIRMATIONS ON THE TREATMENTS

In order to confirm the previous treatments, chronopotentiometry for Fe^{3+} reduction on Pt-disk (1.0 cm^2) in 2 N HCl solution was carried out. Rather highly concentrated one by one mixture of Fe^{3+} and Fe^{2+} (1.80 x 10^{-4} moles·cm^{-3}) was used in the present study to give large value of $J_O^S \cdot C$ in eq.(19). The controlled current J_C was varied from 0.2 to 11.0 mA·cm^{-2}, which gave longer transition times than 7 sec, to reduce a double layer charging effect[1,11,12] on a potential-time curve. All experiments were carried out at room temperature (12.0 ± 0.5 $°C$) to avoid a possible vibration due to an

electric fan.   In order to measure the transition time τ_R properly,
Pt-disk in polyvinyl chrolide-tubing was placed horizontally[9,13] to
avoid a semi-spherical diffusion on an edge, to minimize a natural
convection, and to maintain a linear downward diffusion, which enable
us to measure the long transition times upto 6 hours.   A Teflon
hydrophobic agent was used to avoid a possible leakage between Pt-disk
and tubing wall.   Reference electrode used here was platinum wire
in the same solution, which was calibrated to be 0.457 $\pm$ 0.002 V vs.
AgCl/Ag at room temperature (12.0 $\pm$ 0.5 ^{O}C).

The $|J_C| \cdot \tau_R^{1/2}$ vs. $|J_C|$ plots were shown in Fig.3.   The products
$|J_C| \cdot \tau_R^{1/2}$ were independent of the controlled current J_C.   This means
that the additional rate processes except diffusion was not involved
in this system.   Applying eq.(11), the diffusion coefficient $D_{Fe}3+$
was calculated to be (3.8 $\pm$ 0.1) x 10^{-6} $cm^2 \cdot sec^{-1}$ at 12.0 $\pm$ 0.5 ^{O}C.

Applying the curve-fitting method on an observed potential-time
curve, that is, calculating the $E(t/\tau_R)$ from eqs.(8),(9),and (11)
with varying J_O^S and α systematically again and again until the best
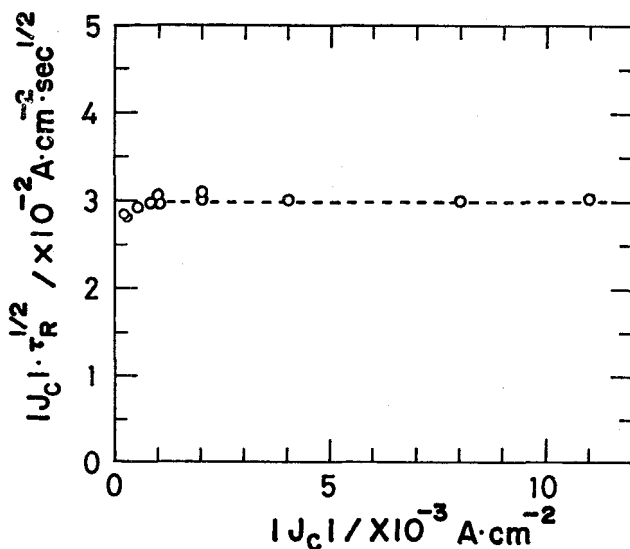

Fig.3 The $|J_{C2}| \cdot \tau_R^{1/2}$ vs. $|J_C|$ plots for Fe^{3+} reduction on Pt-disk
      (1.0 cm^2) with polyvinyl chrolide guard in 2 N HCl solution
      at 12 $\pm$ 0.5 ^{O}C.
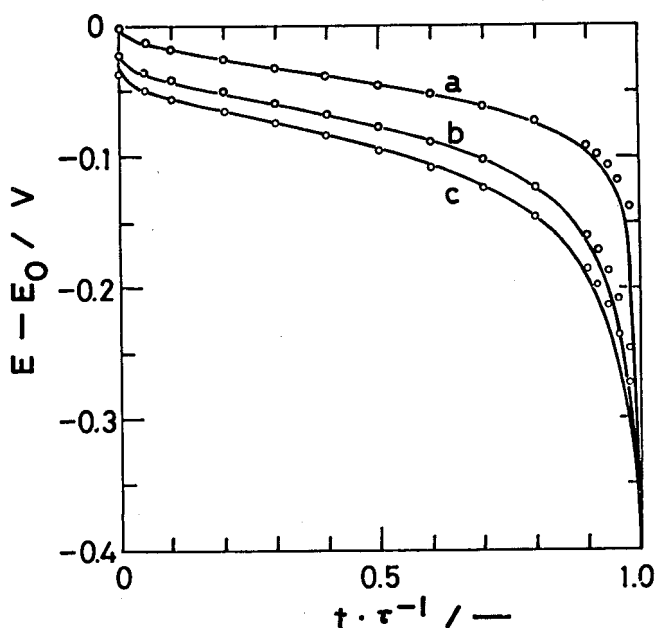 $c_{Fe}^O 2+ = c_{Fe}^O 3+ = 1.80$ x 10^{-4} moles$\cdot cm^{-3}$

Fig.4 Comparison between experimental (solid lines) and theoretical
(open circles) chronopotentiometric potential-time curves for
Fe^{3+} reduction on Pt-disk (1.0 cm^2) with polyvinyl chrolide
guard in 2 N HCl solution at 12 $\pm$ 0.5 ^{O}C.
$C_{Fe}^O{}3+ = C_{Fe}^O{}2+ = 1.80 \times 10^{-4}$ moles·cm^{-3}
(a) $J_C = -2.0 \times 10^{-4}$ A·cm^{-2}, $\tau_R = 19930$ sec, $J_O^S = 30$ A·cm^{-2},
    and $\alpha = 0.55$.
(b) $J_C = -4.0 \times 10^{-3}$ A·cm^{-2}, $\tau_R = 56.2$ sec, $J_O^S = 25$ A·cm^{-2},
    and $\alpha = 0.55$.
(c) $J_C = -8.0 \times 10^{-3}$ A·cm^{-2}, $\tau_R = 14.0$ sec, $J_O^S = 30$ A·cm^{-2}
    and $\alpha = 0.55$.

fitting curve was obtained, J_O^S and α were determined.

Figure 4 shows the comparison between observed potential-time curves
(solid lines)and the theoretical curves (open circles) calculated from
eq.(9) with the determined J_O^S and α from a curve-fitting method.
Kinetic parameters J_O^S and α separately obtained from three potential-
time curves gave consistent values and fairly good agreement between
theoretical and experimental potential-time curves was obtained.

From the analytical and experimental results, we concluded that the
equation (9) was one of the general expressions on chronopotentiometric
potential-time curves.

5. DISCUSSION

5.1 Criteria on Reversible and Irreversible Chronopotentiometric
    Potential-Time Curve

On the basis of the previous treatments, we may discuss specific
criteria on chronopotentiometric potential-time curves for reversible
and irreversible processes.

According to eq.(12), equilibrium electrode potential at any
moment during electrolysis at constant current may be given as

$$E_e(t) = E_0 + \frac{RT}{F} \ln \left(\frac{C_O^0 + P_O \cdot t^{1/2}}{C_R^0 - P_R \cdot t^{1/2}} \right) \qquad (20)$$

where $E_e(t)$ is the equilibrium electrode potential at time t.
Although a finite current is passed through, equation (20) indicates
equilibrium potential change of an electrode system.   The same
situation can be found in potentiometric titrations with constant rate
of titration.

One may be able to define concentration overvoltage η_C as

$$\eta_c(t) = E_e(t) - E_e(0) \qquad (21)$$

Although the term " concentration overvoltage" has somewhat difficulty
to use here, we obeyed the difinition reported so far[14].

On the other hand, the charge transfer overvoltage η_t[14] at any
moment may be given as

$$J_C = J_0(t) \left[\exp\{ \frac{\alpha F}{RT} \eta_t(t) \} - \exp\{ -\frac{(1-\alpha)F}{RT} \eta_t(t) \} \right] \qquad (22)$$

with

$$\eta_t(t) = E(t) - E_e(t) \qquad (23)$$

and

$$J_0(t) = F \cdot k^0 (C_R(0,t))^{1-\alpha} \cdot (C_O(0,t))^{\alpha} \qquad (24)$$

where $J_0(t)$ is the apparent exchange current density in A·cm^{-2} at time
t, $E(t)$ is the polarization voltage in V (vs.RE), while $C_R(0,t)$ and
$C_O(0,t)$ are the concentrations of Red and Ox, respectively, on an
electrode surface at time t.   Consequently, another expression on
chronopotentiometric potential-time curve, instead of eq.(9), may be
given by

$$E(t) = E_e(0) + \eta_t(t) + \eta_c(t) \qquad (25)$$

where $E_e(0)$ is the equilibrium potential at time t = 0, $\eta_t(t)$ is the

charge-transfer overvoltage at time t defined by eq.(23) and η_c(t) is
the concentration overvoltage at time t defined by eq.(21).

When $|\eta_t(t)| \ll RT/\alpha F$, $RT/(1-\alpha)F$ in eq.(22), η_t(t) can be dropped
in eq.(25) and then eq.(12) is a good approximation for describing the
potential-time curves, that is, if the potential difference between
an observed curve and an ideal curve calculated from eq.(12) is within
a few millivolts during electrolysis, one may call "reversible process".

When $|\eta_t(t)| \gg RT/\alpha F$, $RT/(1-\alpha)F$, one of the exponential terms in
eq.(22) can be dropped. In such a case, equations (17) or (18) are
a good approximation, that is, if the potential defference between an
observed curve and an ideal curve calculated from eq.(12) is more than
120 millivolts for $\alpha = 0.5$ and $T = 298\ ^{\circ}K$ at any moment during electro-
lysis, one may call " irreversible process ".

It should be recalled here that the shape of potential-time curve
is mainly controlled by the product $J_c/J_0^S \cdot C$ as was stated before,
therefore, the distinction between reversible and irreversible process
is highly artificial, and then it is not necessary to define which is
reversible or irreversible process.

5.2 Effect of Double-Layer Capacity on Chronopotentiometric Potential-
     Time Curve

Although the influence of double-layer charging on chronopotentio-
metric potential-time curve was not considered in the present study,
it is appropriate to discuss briefly on the double-layer charging
effects on the potential-time curves, which are frequently large
throughout the experiment.

The controlled current density J_c may be written as the algebraic
sum of faradaic current density coupled with a mass transfer and
double-layer charging current density

$$J_c = J_f(t) + J_{dl}(t) \qquad\qquad (26)$$

where t is the time elapsed since the controlled current J_c was applied.

The double-layer charging current density J_{dl}(t) in eq.(26) is given
by

$$J_{dl}(t) = C(E) \cdot \frac{dE}{dt} \qquad\qquad (27)$$

where C(E) is the differential capacity in Farads$\cdot$cm^{-2} as a function
of electrode potential.

If one assumes that no adsorption occures at the electrode surface,

charging of electrical double layer is the same as that on ideally
polarized electrode, and the differential capacity is independent of
electrode potential, one can estimate the effect of double-layer
charging on the curves[11-13]. Since the current J_{dl} is calculated
to be on the order of 10^{-5} A·cm^{-2} when $C \simeq 10^{-5}$ Farads·cm^{-2} and
$dE/dt \simeq 1$ V·sec^{-1}, such a charging effect was negligible in the present
case.

Another type of double-layer charging current is due to an adsorbed
species, especially reacting species. Reactant such as Ox and Red
should transfer from the solution of bulk to an electrode surface as
close to the place at which electron(s) transfer takes place.
Although exact location where a reactant accepts or releases electron(s)
is not known, a reactant should exisits within a double layer for non-
polarizing electrode.

When the species Ox and Red exist within double layer on an electrode
and then mass transport of species Ox and Red from the solution of
bulk does not need to proceed an electrochemical reaction

$$Ox + ne^- \rightleftarrows Red ,$$

the electrode potential may be also represented as

with
$$E = E_O - \frac{RT}{nF} \ln \frac{C_R(0,t)}{C_O(0,t)} \qquad (28)$$

$$C_O(0,t) + C_R(0,t) = C^* \qquad (29)$$

where C^* is the total concentration of Ox and Red in moles·cm^{-2} while
$C_O(0,t)$ and $C_R(0,t)$ are the surface concentrations of Ox and Red,
respectively, in moles·cm^{-2}.

By solving the equations[15-17] under the given conditions, one may
have the differential capacity in Farads·cm^{-2} as a function of electrode
potential

$$C(E) = nFC^* \frac{(\frac{nF}{RT}) \exp\left[-\frac{nF}{RT}(E - E_O)\right]}{\left[1 + \exp\{-\frac{nF}{RT}(E - E_O)\}\right]^2} \qquad (30)$$

Combination of eqs.(27) and (30) yields the charging current density
and the constant charging current density gives the chronopotentiometric
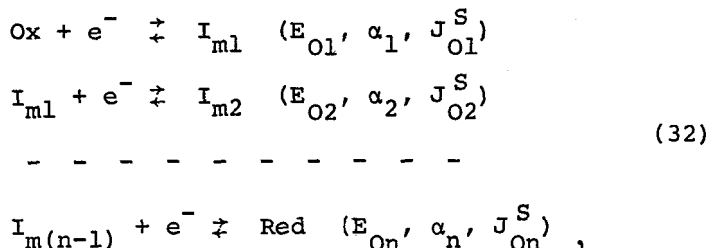potential-time curves with the transition time

$$\tau_O = \tau_R = \frac{nFC^*}{J_C} \qquad (31)$$

if the species Ox or Red only exists on an electrode surface before
electrolysis.

Although there has been an ingenious technique, first developed by Gerischer and Krause[18, 19], to remove a double-layer elect on electrode kinetics, the conpensation of such a charging current seems to be difficult because the charging current is due to the faradic current without mass transfer of reacting species, which should have essentially the same kinetics.   More specific and rigorous theoretical treatments will appear in a separate paper together with cell and electronic system design.

5.3 Extension to Multistep Charge Transfer Reaction

For a hypothetical n-step reaction with consecutive n electrons transfer[8]

$$Ox + e^- \; \overset{\rightarrow}{\leftarrow} \; I_{m1} \quad (E_{O1}, \; \alpha_1, \; J^S_{O1})$$

$$I_{m1} + e^- \; \overset{\rightarrow}{\leftarrow} \; I_{m2} \quad (E_{O2}, \; \alpha_2, \; J^S_{O2}) \tag{32}$$

$$- - - - - - - - - -$$

$$I_{m(n-1)} + e^- \; \overset{\rightarrow}{\leftarrow} \; Red \quad (E_{On}, \; \alpha_n, \; J^S_{On}) \; ,$$

the chronopotentiometric potential-time characteristics may be represented as

$$J_C = \frac{C_R(0,t)\exp\{\sum_{i=1}^{n}\alpha_i \cdot G_i + \sum_{i=2}^{n}(1-\alpha_i)G_i\} - C_O(0,t)\exp\{-(1-\alpha_1)G_1\}}{\frac{1}{n}\left[\frac{1}{J^S_{O1}} + \sum_{k=2}^{n}\frac{1}{J^S_{Ok}}\exp\{\sum_{i=1}^{k-1}\alpha_i \cdot G_i + \sum_{i=2}^{k}(1-\alpha_i)G_i\}\right]} \tag{33}$$

with

$$G_i = \frac{F}{RT}(E(t) - E_{Oi}) \; , \tag{34}$$

$$C_R(0,t) = C_R^O - \frac{2J_C}{nFD_R^{1/2}\pi^{1/2}} \cdot t^{1/2} \tag{35}$$

and

$$C_O(0,t) = C_O^O + \frac{2J_C}{nFD_O^{1/2}\pi^{1/2}} \cdot t^{1/2} \tag{36}$$

where J_C is the controlled current density, $E(t)$ is the electrode potential as a function of time while α_i, E_{Oi} and J^S_{Oi} are the transfer coefficient, the standard electrode potential and the standard exchange current density, respectively, for the elementary step i.
It was assumed that Ox and Red were diffusing species and the intermediates did not diffuse away from an electrode surface.

α When $J_{O1}^S,----, J_{O(n-1)}^S$, and J_{On}^S are extremely large, equation (33) becomes

$$E(t) = E_O - \frac{RT}{nF} \ln\frac{C_R(0,t)}{C_O(0,t)} \tag{37}$$

with

$$E_O = \frac{1}{n} \sum_{i=1}^{n} E_{Oi}$$

where $C_R(0,t)$ and $C_O(0,t)$ were given by eqs.(35) and (36), respectively. Equation (37) is the same formula of the Nernstian potential-time curves at constant current for $Ox + ne^- \rightleftarrows Red$.

For an another extreme case, when $J_{Oi,i\neq m}^S \gg J_{Om}^S$ which is corresponding to the consecutive electrochemical reaction with single rate-determining step, the potential-time curve may be given by

$$E(t) = \frac{\sum_{i=m+1}^{n} E_{Oi} + \alpha_m E_{Om}}{n - m + \alpha_m} + \frac{RT}{(n - m + \alpha_m)F} \ln(\frac{J_C}{n \cdot J_{Om}^S \cdot C_R^O})$$

$$- \frac{RT}{(n - m + \alpha_m)F} \cdot \ln\left[1 - (\frac{t}{\tau_O})^{1/2}\right] \tag{38}$$

for oxidation process ($J_C > 0$),i.e.,

$$E(t) \gg E_O - \frac{RT}{nF} \ln\frac{C_R(0,t)}{C_O(0,t)} ,$$

and

$$E(t) = \frac{\sum_{i=1}^{m} E_{Oi} - \alpha_m E_{Om}}{m - \alpha_m} - \frac{RT}{(m - \alpha_m)F} \ln\left[\frac{-J_C}{n \cdot J_{Om}^S \cdot C_O^O}\right]$$

$$+ \frac{RT}{(m - \alpha_m)F} \cdot \ln\left[1 - (\frac{t}{\tau_R})^{1/2}\right] \tag{39}$$

for reduction process ($J_C < 0$),i.e.,

$$E(t) \ll E_O - \frac{RT}{nF} \ln\frac{C_R(0,t)}{C_O(0,t)}$$

where $C_R(0,t)$ and $C_O(0,t)$ were given by eqs.(35) and (36), respectively.

Since the potential-time equations for reversible and irreversible processes for multistep electrode reaction with consecutive n electrons

transfer appeared in special cases, equation (33) may be more general expression than eq.(9) on chronopotentiometric potential-time curves.

5.4 Significance of the Chronopotentiometric Technique for Kinetic Study

   The proposed method, a curve-fitting method based on eq.(9), can give the standard exchange current density J_0^S if one has specific chronopotentiometric potential-time curve for planar electrode mater-al.   Although minor corrections on the solutions of boundary-value probelms[20] due to the difference of diffusion mode would be necessary, the proposed method, more specifically, the basic concepts of the treatments would be applicable to kinetic studies on non-planar electrode materials wuch as semi-spherical or cylindrical rods and/or whiskers.   The method will prove valuable in teh study of electrode kinetics for redox reaction.

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APPENDIX : Derivation of eq.(30)

Combination of eqs.(28) and (29) gives

$$C_R(E) = \frac{C^* \exp\left[-\frac{nF}{RT}(E - E_O)\right]}{1 + \exp\left[-\frac{nF}{RT}(E - E_O)\right]} \tag{40}$$

where E is operative with respect to time t.

The faradaic current J may be obtained by

$$J = - nF\left(\frac{dC_R(E)}{dt}\right)$$

$$= - nF\left(\frac{dC_R(E)}{dE}\right) \cdot \left(\frac{dE}{dt}\right) \tag{41}$$

On the other hand, the differential capacity C(E) may be defined as

$$C(E) = \frac{J}{\left(\frac{dE}{dt}\right)} \tag{42}$$

Comparison between eqs.(41) and (42) gives

$$C(E) = - nF\left(\frac{dC_R(E)}{dE}\right) \tag{43}$$

Differentiating eq.(40) with respect to E and then putting it into
eq.(43), one may obtain eq. (30).

It should be noted here that the current J only appears when the
electrode potential is changing, that is, the electrode system behaves
like pure capacitor as a function of electrode potential although the
current itself is a faradaic current in this special case.

LIST OF SYMBOLS

J_c Controlled current density ($A \cdot cm^{-2}$)

$J_f(t)$ Faradaic current density coupled with mass transfer as a function of time ($A \cdot cm^{-2}$)

$J_{dl}(t)$ Double-layer charging current density as a function of time ($A \cdot cm^{-2}$)

$J_o(t)$ Apparent exchange current density as a function of time ($A \cdot cm^{-2}$)

J_o^S Apparent standard exchange current density based on 1 mole $\cdot cm^{-3}$ as a standard ($A \cdot cm^{-2}$)

J_{Oi}^S Apparent exchange current density for i th step charge transfer reaction ($A \cdot cm^{-2}$)

k^O Apparent standard rate constant for charge transfer reaction ($cm \cdot sec^{-1}$)

$E(t)$ Electrode potential with respect to reference electrode as a function of time (V)

$E_e(t)$ Equilibrium electrode potential as a function of time (V)

E_O Standard electrode potential with respect to reference electrode in equation for electrode reaction (V)

E_{Oi} Standard electrode potential with respect to reference electrode for i th step electrode reaction (V)

$\eta_t(t)$ Charge-transfer overvoltage as a function of time (V)

$\eta_c(t)$ Concentration overvoltage as a function of time (V)

α Transfer coefficient (-)

α_i Transfer coefficient for i th step charge transfer reaction (-)

$C_i(x,t)$ Concentrations of species i at location x as a function of time (moles $\cdot cm^{-3}$ or moles $\cdot cm^{-2}$)

C_i^O Concentration of species i in solution of bulk (moles $\cdot cm^{-3}$)

C^* Total surface concentration of Ox and Red (moles $\cdot cm^{-2}$)

D_i Diffusion coefficient of diffusing species i ($cm^2 \cdot sec^{-1}$)

$C(E)$ differential capacity as a function of electrode potential (Farads $\cdot cm^{-2}$)

t Time elapsed since controlled current was applied (sec)

τ_O Transition time for oxidation process (sec)

τ_R Transition time for reduction process (sec)

x Distance from electrode surface (cm)

T Temperature ($^O K$)

F Faraday's constant (coul $\cdot equiv^{-1}$)

R Gas constant (joule $\cdot mole^{-1} \cdot deg^{-1}$)