

Electrochemistry of Redox Reaction

I. On the Kinetic Equations for Rotating Disk Technique

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SYNOPSIS

An equation on the current-polarization voltage characteristics of single charge transfer redox reaction on a rotating disk electrode (RDE) was given and a curve-fitting method to determine kinetic parameters from an observed polarization curve was proposed therefrom. The method was demonstrated for $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction in acidic aqueous electrolyte on Pt-RDE and the limitation of the method was discussed. The extension of the method to multistep charge transfer reaction was also considered.

1. INTRODUCTION

Electrochemical redox reactions of soluble transition metal ions in aqueous solution have been of great interests since the practical use of redox reaction as a large-scale electrical energy storage system based on electrochemical reaction of soluble species was indicated.

Although many redox reactions were investigated and the basic concepts of electrode kinetics were summarized in several monographs and textbooks¹⁻⁹⁾, the electrochemistry of redox reaction has not been well established mainly due to the lack of the effort to fill the gap between theoretical electrochemistry and electrochemical engineering.

Overall objectives of this series of theoretical and experimental

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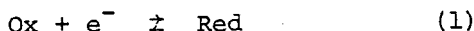
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works are to establish a unifying kinetic equation with which one can predict electrochemical characters for redox reaction from basic kinetic parameters and to understand the nature of redox electrode system. This paper is dealt with the basic kinetic equations for redox reaction on rotating disk electrode.

2. THEORETICAL BACKGROUND OF THE METHOD

2.1 Kinetics of the Charge Transfer

For a single elementary charge transfer reaction



which involves two soluble species, neglecting the double layer effect^{3, 8, 26}, the current-overvoltage characteristics may be given³⁻⁹ as

$$J = J_0 \left\{ \exp\left(\frac{\alpha F}{RT}\eta\right) - \exp\left(-\frac{(1 - \alpha)F}{RT}\eta\right) \right\} \quad (2)$$

with

$$\eta = E - E_e \quad (3)$$

where J_0 is the apparent exchange current density in $\text{A}\cdot\text{cm}^{-2}$, E_e is the equilibrium potential with respect to reference electrode in V (vs.RE), and E is the polarization voltage in V(vs.RE). Reacting species and supporting electrolyte were assumed not to be specifically adsorbed. The transfer coefficient α in eq.(2) corresponds to the anodic process and $1 - \alpha$ corresponds to the cathodic process. Then a net reduction current is negative and a net oxidation current is positive. The derivation of the equation for more general form can be found in the literatures^{3-5, 7-10}.

It should be noted that J_0 and η in eq.(2) are operative with respect to the concentration of the soluble species Ox and Red, that is, equation (2) does not hold in any cases involving rate processes except charge transfer.

Applying the Nernst equation¹¹, the equilibrium potential E_e can be represented as

$$E_e = E_0 - \frac{RT}{F} \ln \frac{C_R(0)}{C_O(0)} \quad (4)$$

where E_0 is the standard electrode potential in V (vs.RE), $C_R(0)$ and $C_O(0)$ are the concentrations of soluble species Red and Ox, respectively, at the vicinity of the electrode in $\text{moles}\cdot\text{cm}^{-3}$, not the concentrations of bulk solution because of the heterogeneous nature of the charge transfer process. Although activities rather than concentrations, in all rigor, should be written in eq.(4) and thereafter, concentrations in $\text{moles}\cdot\text{cm}^{-3}$ are used here.

According to the kinetic theory on the charge transfer process¹²⁻¹⁴,

the apparent exchange current density has a form

$$J_O = Fk^O (C_R(O))^{1-\alpha} (C_O(O))^\alpha \quad (5)$$

where k^O is the apparent standard rate constant in $\text{cm}\cdot\text{sec}^{-1}$.

Introducing eqs. (3), (4), and (5) in eq. (2), one obtains

$$J = Fk^O \left[C_R(O) \exp\left\{\frac{\alpha F}{RT}(E - E_O)\right\} - C_O(O) \exp\left\{-\frac{(1-\alpha)F}{RT}(E - E_O)\right\} \right] \quad (6)$$

In eq. (6), the k^O and E_O are independent of J , E , $C_R(O)$, and $C_O(O)$. The net current J and polarization voltage E can be controlled or determined in an experiment. The $C_R(O)$ and $C_O(O)$, however, can not be controlled experimentally, because if a finite current is passed through, the $C_R(O)$ and $C_O(O)$ should be increased or decreased.

Using the common concentration C^* in $\text{moles}\cdot\text{cm}^{-3}$, the equation (6) can also be represented as

$$J = Fk^O C^* \left[\frac{C_R(O)}{C^*} \exp\left\{\frac{\alpha F}{RT}(E - E_O)\right\} - \frac{C_O(O)}{C^*} \exp\left\{-\frac{(1-\alpha)F}{RT}(E - E_O)\right\} \right] \quad (7)$$

Putting $C^* = 1 \text{ moles}\cdot\text{cm}^{-3}$ as a standard, one can define the apparent standard exchange current density J_O^S in $\text{A}\cdot\text{cm}^{-2}$ as

$$J_O^S = Fk^O \quad (8)$$

Introducing eq. (8) in eq. (6), one has

$$J = J_O^S \left[C_R(O) \exp\left\{\frac{\alpha F}{RT}(E - E_O)\right\} - C_O(O) \exp\left\{-\frac{(1-\alpha)F}{RT}(E - E_O)\right\} \right] \quad (9)$$

Although $C_R(O)$ and $C_O(O)$ are not known, the equation (9) is one of the general expression of the charge transfer process for an elementary step involving one electron transfer. In order to apply eq. (9) to experimental results on the current-polarization voltage characteristics, one should determine the $C_O(O)$ and $C_R(O)$ with the aid of mass transfer theory.

2.2 Kinetics of the Mass Transfer on the Rotating Disk Electrode

The rotating disk electrode technique is popular among the electrochemists and electrochemical engineers, partly because the hydrodynamic conditions are analytically known, and partly because the mass flux is controllable using rather simple equipment.

Convective-diffusion problems on the rotating disk system have solved and reviewed by several authors^{16-19,21)}. According to Newman¹⁸⁻²⁰⁾, the rate of mass transfer or corresponding current density for the rotating disk under the steady laminar flow of an incompressible fluid has the form ;

$$J_O = F(C_O(O) - C_O(\infty)) \cdot \sqrt{\omega \nu} \cdot f(Sc_O) \quad (10)$$

and

$$J_R = F(C_R(\infty) - C_R(O)) \cdot \sqrt{\omega \nu} \cdot f(Sc_R) \quad (11)$$

with

$$f(\text{Sc}_i) = \frac{0.62048 \text{Sc}_i^{-2/3}}{1 + 0.2980 \text{Sc}_i^{-1/3} + 0.14514 \text{Sc}_i^{-2/3}} \quad (12)$$

for $\text{Sc}_i > 100$, and

$$f(\text{Sc}_i) = 0.88447 \exp(-1.611 \text{Sc}_i) [1 + 1.961 \text{Sc}_i^2] \quad (13)$$

for $\text{Sc}_i \ll 100$, where Sc_i is the Schmidt number of species i ($\text{Sc}_i = \nu/D_i$), ν is the kinematic viscosity in $\text{cm}^2 \cdot \text{sec}^{-1}$, ω is the angular velocity of disk electrode in $\text{radians} \cdot \text{sec}^{-1}$, $C_O(\infty)$ and $C_R(\infty)$ are the bulk concentrations of the diffusing species Ox and Red, respectively, while D_i is the diffusion coefficient of species i in $\text{cm}^2 \cdot \text{sec}^{-1}$.

Since the Schmidt number is usually on the order of 10^3 for aqueous electrolyte, i.e., $\nu = 10^{-2} \text{cm}^2 \cdot \text{sec}^{-1}$ and $D = 10^{-5} \text{cm}^2 \cdot \text{sec}^{-1}$, it is appropriate to use eq.(12) for the Schmidt number correction. For large Schmidt number, that is, the diffusion coefficient is very small and then the concentration variation occurs very close to the disk surface, the approximation of eq.(12) can be done in this case.

Neglecting the second and third term in the denominator of eq.(12) and putting it into eqs.(10) and (11), the equations become simple

$$\text{forms ; } J_O = 0.62048 F (C_O(0) - C_O(\infty)) \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot D_O^{2/3} \quad (14)$$

$$J_R = 0.62048 F (C_R(\infty) - C_R(0)) \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot D_O^{2/3} \quad (15)$$

Equations (14) and (15) are first derived by Levich^{16,21}.

It should be recalled here in the application of eqs.(14) and (15) that the numeral coefficient varies with the Schmidt number as was indicated in eq.(12).

2.3 The Current-Polarization Voltage Characteristics for a Process with Mixed Control by Mass and Charge Transfer

Since the rate of mass transfer of the species Ox and Red is equal to the rate of the charge transfer under the steady state condition, eliminating $C_O(0)$ and $C_R(0)$ in eq.(9) by using eqs.(10) and (11), the current-polarization voltage curve can then be expressed in the form

$$J = \frac{C_R(\infty) \exp\{\frac{\alpha F}{RT}(E - E_O)\} - C_O(\infty) \exp\{-\frac{(1 - \alpha) F}{RT}(E - E_O)\}}{\frac{1}{J_S} + \frac{1}{F \sqrt{\nu \omega} f(\text{Sc}_R)} \exp\{\frac{\alpha F}{RT}(E - E_O)\} + \frac{1}{F \sqrt{\nu \omega} f(\text{Sc}_O)} \exp\{-\frac{(1 - \alpha) F}{RT}(E - E_O)\}} \quad (16)$$

where $f(\text{Sc}_R)$ and $f(\text{Sc}_O)$ are given in eq.(12). It was assumed that the current distribution on a disk is uniform below and at the limiting current, i.e., no edge effect²²). Variables in eq.(16), such as $J, E,$

$C_R(\infty)$, $C_O(\infty)$, ω and v , are measureable or controllable, therefore, one can examine the validity of the equation and possibly determine the kinetic parameters from a polarization curve if experimental conditions fit into the conditions required from eq.(16).

Prior to the experimental confirmations on eq.(16), it is appropriate to perform mathematical assessments.

At high polarization voltage, one has $|E - E_O| \gg RT/\alpha F$ (or $|E - E_O| \gg RT/(1-\alpha)F$) and then two of the exponentials in eq.(16) can be dropped, and if J_O^S is extremely large, equation (16) becomes

$$J_L = F \cdot \sqrt{v\omega} \cdot f(Sc_R) \cdot C_R(\infty) \quad (17)$$

or

$$J_L = -F \cdot \sqrt{v\omega} \cdot f(Sc_O) \cdot C_O(\infty) \quad (18)$$

where J_L is the limiting current density.

When the first term in the denominator of eq.(16) is fairly large compared with the sum of the second and third term, i.e., small value of J_O^S , equation (16) becomes

$$J = J_O^S \left[C_R(\infty) \exp\left\{\frac{\alpha F}{RT}(E - E_O)\right\} - C_O(\infty) \exp\left\{-\frac{(1-\alpha)F}{RT}(E - E_O)\right\} \right] \quad (19)$$

Equation (19) has the form of Tafel equation which was named after the work of Tafel²³.

When $J = 0$, one has the Nernst equation

$$E = E_O - \frac{RT}{F} \ln \frac{C_R(\infty)}{C_O(\infty)} \quad (20)$$

As the Nernst and Tafel equation as well as the equation for the limiting current appear in a special case, equation (16) may cover the Nernst, Tafel and limiting current region in a polarization curve. Consequently, the equation (16) may be one of the general formulas for a process with mixed control by mass and charge transfer.

Another way to assess the equation (16) is to figure out polarization curves by putting the numbers into the kinetic parameters in eq.(16).

Figure 1 shows polarization curves, calculated from eq.(16) with the given kinetic parameters, as a function of $C_R(\infty)$ at constant $C_O(\infty)$ for low standard exchange current density. The shape of polarization curves in Fig.1 is quite similar to the results obtained by Vetter²⁴ for Tl^{3+}/Tl^+ redox reaction and also if one apply the graphic method to determine apparent exchange current density as a function of $C_R(\infty)$, one would have the same conclusion reached by Gerischer²⁵ for Fe^{2+}/Fe^{3+} redox reaction. Graphic method, however, can not apply for polarization curves with no clear Tafel lines, i.e., large standard exchange current density, as was illustrated in Fig.2.

These considerations on polarization curves for a process with mixed

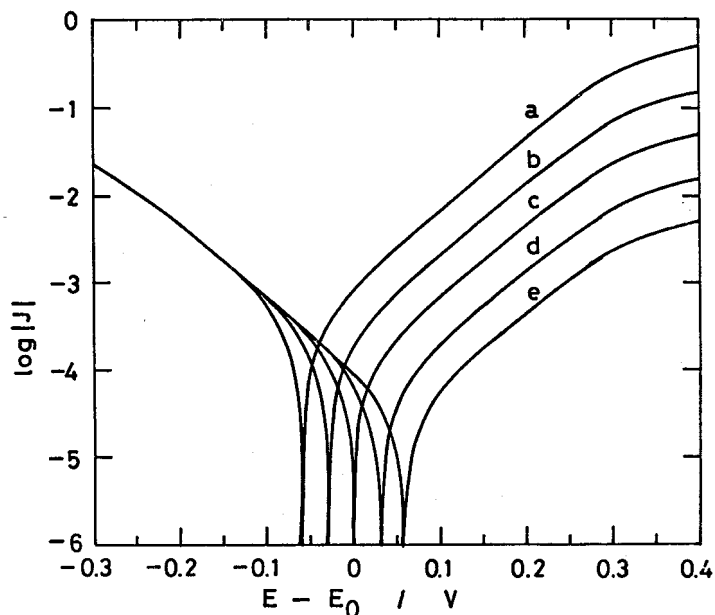


Fig.1 Theoretical polarization curves calculated from eq.(16) with the kinetic parameters : $J_O^S = 1 \text{ A}\cdot\text{cm}^{-2}$, $D_O = D_R = 1 \times 10^{-5} \text{ cm}^2\cdot\text{sec}^{-1}$, $\nu = 1 \times 10^{-2} \text{ cm}^2\cdot\text{sec}^{-1}$, $\alpha = 0.5$ and $\omega = 126 \text{ radians}\cdot\text{sec}^{-1}$ (1200rpm). $C_O(\infty)$; $1 \times 10^{-4} \text{ moles}\cdot\text{cm}^{-3}$, $C_R(\infty)$; (a) 1×10^{-3} , (b) 3×10^{-4} , (c) 1×10^{-4} , (d) 3×10^{-5} and (e) $1 \times 10^{-5} \text{ moles}\cdot\text{cm}^{-3}$

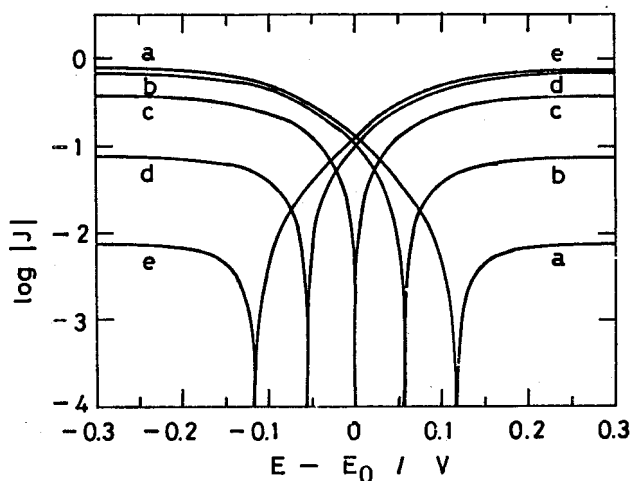


Fig.2 Theoretical polarization curves calculated from eq.(16) with the kinetic parameters : $J_O^S = 100 \text{ A}\cdot\text{cm}^{-2}$, $D_O = D_R = 1 \times 10^{-5} \text{ cm}^2\cdot\text{sec}^{-1}$, $\nu = 1 \times 10^{-2} \text{ cm}^2\cdot\text{sec}^{-1}$, $\alpha = 0.5$ and $\omega = 42 \text{ radians}\cdot\text{sec}^{-1}$ (400rpm). $C_O(\infty) + C_R(\infty) = 2 \times 10^{-3} \text{ moles}\cdot\text{cm}^{-3}$, $C_O(\infty)/C_R(\infty)$; (a) 1.98/0.02, (b) 1.80/0.20, (c) 1.00/1.00, (d) 0.20/1.80, and (e) 0.02/1.98

control by mass and charge transfer enable us to make direct method to determine kinetic parameters from an observed polarization curve.

3. EXPERIMENTAL CONFIRMATION OF THE METHOD

In order to confirm the previous treatments to derive the equation (16), the polarization measurements on Pt-RDE for Fe^{3+} reduction in 2 N HCl solution were carried out. Polarization curves were measured potentiostatically and galvanostatically point-by-point for a controlled rotation speed. The diameter of platinum disk was 1.13 cm. The rotation speed was varied from 400 to 2500 rpm. The kinematic viscosities were measured by means of the Ostwald's viscometer. The Reynolds number ($\text{Re} = r^2 \omega / \nu$) for the system was calculated to be on the order of 10^3 , indicated that the flow in the boundary layer on a platinum disk was laminar.

The $1/J_L$ vs. $1/\sqrt{\omega}$ plots were shown in Fig.3 as a function of Fe^{3+} concentration. The plots gave a straight line for a given Fe^{3+} concentration and each straight line converged to zero in $1/J_L$ axis when $1/\sqrt{\omega} \rightarrow 0$ as was expected from eq.(10). This indicates that there

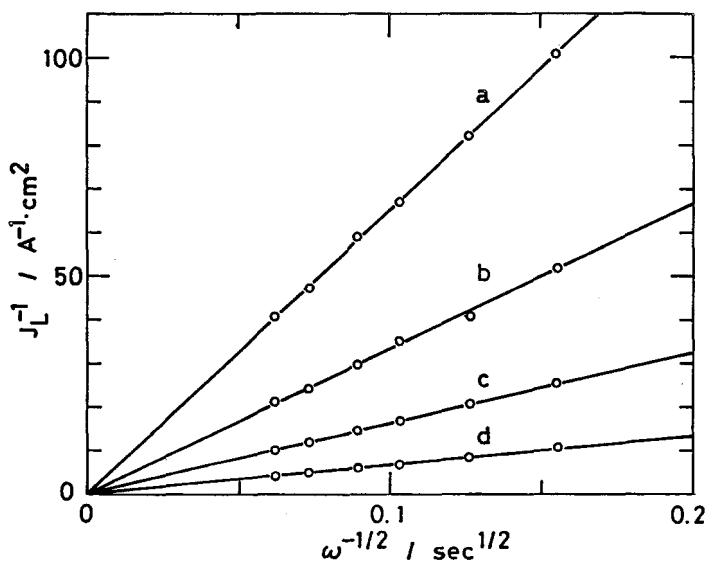


Fig.3 The $1/J_L$ vs. $1/\sqrt{\omega}$ plots for the electrochemical reduction of Fe^{3+} on Pt-RDE in 2N HCl at room temperature.

Fe^{3+} ; (a) 4.5×10^{-5} , (b) 9.0×10^{-5} , (c) 1.8×10^{-4} , and (d) 4.5×10^{-4} moles $\cdot \text{cm}^{-3}$

is no rate process except mass and charge transfer¹⁶⁾. From the slope of a straight line in Fig.3, one can determine diffusion coefficient when the kinematic viscosity is known¹⁸⁾.

Applying a curve fitting method to determine kinetic parameters from an observed polarization curve, that is, calculating current density J at a given polarization voltage E with varying kinetic parameters in eq.(16) systematically again and again until the best fitting curve was obtained, the kinetic parameters were obtained while the kinematic viscosities were determined by means of the Ostwald's viscometer and summarized in Table 1. Although ferrous ion was not added initially, the finite values of Fe^{2+} , one thousandth of ferric ion, was calculated from eq.(16) due to the contamination of Fe^{2+} during the experiment and/or due to the nature of exponential function in eq.(16). Kinetic parameters, $D_{\text{Fe}^{3+}}$, $D_{\text{Fe}^{2+}}$, α , J_O^S , and E_O , separately obtained from four polarization curves gave consistent values. This means that the equation (16) works very well in this system. In order to illustrate this more specifically, the experimental and theoretical polarization curves calculated from eq.(16) with the determined kinetic parameters in Table 1 were shown in Fig.4. Although there is a small deviation at low current density region probably due to contamination of Fe^{2+} during the experiment, fairly good agreement between theoretical and experimental polarization curve was obtained.

From the analytical and experimental results, we concluded that the

Table 1 The kinetic parameters obtained from a polarization curve in Fig.4 using the equation (16)
 $\omega = 125.6 \text{ radians sec}^{-1} (1200 \text{ rpm})$, $T = 290.5 \pm 0.5^\circ \text{K}$.

Curves in Fig. 4	$C_{\text{Fe}^{3+}}^{*1}$	$C_{\text{Fe}^{2+}}$	$D_{\text{Fe}^{3+}}^{*2}, D_{\text{Fe}^{2+}}$	ν^{*3}	α	J_O^S	E_O
	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-6}$	$\times 10^{-2}$			
	moles. cm^{-3}	moles. cm^{-3}	$\text{cm}^2.\text{sec}^{-1}$	$\text{cm}^2.\text{sec}^{-1}$	--	$\text{A}.\text{cm}^{-2}$	V vs. Ag/AgCl
(a)	4.5	4.5	4.4	1.14	0.60	80	0.425
(b)	9.0	9.0	4.3	1.15	0.60	70	0.420
(c)	18	18	4.4	1.17	0.55	80	0.435
(d)	45	45	4.4	1.30	0.55	80	0.430

*1 experimental values

*2 $D_{\text{Fe}^{3+}} \approx D_{\text{Fe}^{2+}}$ was assumed

*3 from viscosity measurements

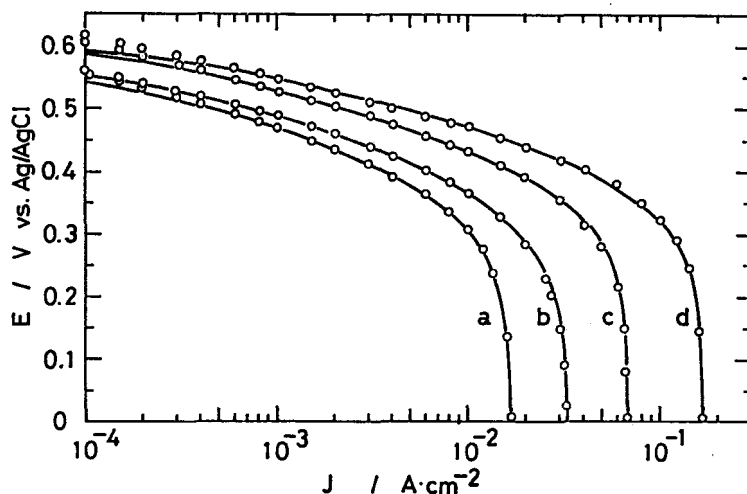


Fig.4 Comparison between the polarization curves for Fe^{3+} reduction on Pt-RDE at a rotation speed 1200 rpm in 2 N HCl solution (open circles) and the theoretical polarization curves calculated from eq.(16) with the kinetic parameters listed in Table 1.

$C_{\text{Fe}^{3+}}$; (a) 4.5×10^{-5} , (b) 9.0×10^{-5} ,
(c) 1.8×10^{-4} and (d) 4.5×10^{-4} moles·cm $^{-3}$

equation (16) was one of the general formulas on RDE for a process with mixed control by mass and charge transfer.

4. DISCUSSION

4.1 Double Layer and Edge Effect

Although the understanding on the double layer structure of non-polarizable electrode is one of the final goals of this series of investigations, no double layer effect was assumed in the present study. It is appropriate, however, to discuss briefly on the double layer effect on the electrode kinetics, which was first pointed out by Frumkin²⁶⁾ in an interpretation on hydrogen overvoltage.

For a simple case, one of the double layer effects may be represented as

$$C_i(p) = C_i(\infty) \exp\left(-\frac{z_i F}{RT} \phi_p\right) \quad (21)$$

where $C_i(p)$ is the concentration of the species i to be reacted at a pre-electrode layer, $C_i(\infty)$ is the concentration of the species i in a bulk of the solution, z_i is the valency of the reactant, and ϕ_p is the potential in a pre-electrode layer with respect to that in a bulk of the solution. Equation (21) indicates that the concentration at

a pre-electrode layer is different from that in a bulk of the solution even at the equilibrium potential unless the equilibrium potential at the point of zero charge. According to eq.(21), $C_i(p)$ should differ remarkably from $C_i(\infty)$ when the potential is apart from that at point of zero charge. If such an effect is involved in our case, the current-polarization voltage curves may be distorted from the ideal shape based on eq.(16) due to the potential change of ϕ_p with polarization voltage E . Experimental results as shown in Fig.4, however, did not show any specific deviation from the ideal shape based on eq.(16). Then, the double layer effect is negligible in the present case, possibly the effect may involve in J_0^S as was pointed out by Delahay³⁾ and Parsons⁸⁾.

Although the primary current distribution on a disk is adherently non-uniform¹⁹⁾ and the edge effect²²⁾ is not avoidable, the effect is concluded to be also negligible even at the current below limiting current owing to the beneficial effect of polarization (secondary current distribution) from the fact as shown in Fig.4.

4.2 Significance of the Curve-Fitting Method for Kinetic Study

The proposed method, a curve-fitting method based on eq.(16), can give the standard exchange current density J_0^S as a common activity scale instead of ambiguous term " activity " as was demonstrated in Figs.1 and 2.

The standard exchange current density J_0^S was defined by eq.(8), which was based on 1 mole cm^{-3} as a standard concentration to avoid the numeral coefficient in basic equations. One can also define the exchange current density i_0^S based on 1 mole l^{-1} as a standard concentration¹⁵⁾. The relationship between J_0^S and i_0^S is

$$J_0^S = 1000 \times i_0^S \quad (22)$$

Thus, the J_0^S and i_0^S are interchangeable.

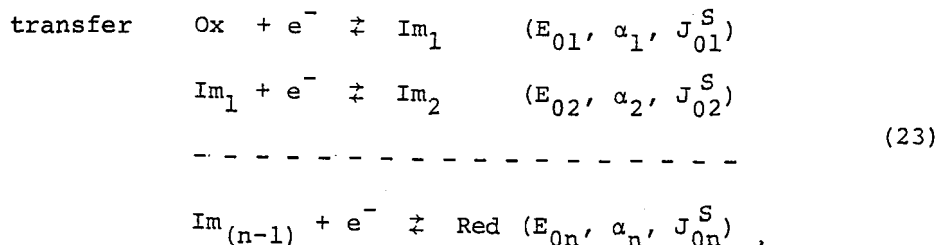
Since the kinetic parameters can be determined from a polarization curve on the rotating disk electrode using the proposed method if the electrode material can be machined to make a disk, a rapid determination of kinetic parameters can be done even for a fast electrode reaction. The proposed method will prove valuable in the study of electrode kinetics for redox reaction.

4.3 Extension to Multistep Charge Transfer Reaction

In the previous treatments to derive eq.(16), one electron transfer

was only considered. In order to apply the method for more general cases, it is necessary to extend a basic kinetic equation to multistep charge transfer reaction.

For a hypothetical n -step reaction with consecutive n electron



writing down the kinetic equations of charge transfer for each elementary step and eliminating the concentrations of the intermediates under the steady state condition, i.e., $J_1 = J_2 = \dots = J_n$, one has

$$J = \frac{C_R(0) \exp\left\{\sum_{i=1}^n \alpha_i G_i + \sum_{i=2}^n (1 - \alpha_i) G_i\right\} - C_O(0) \exp\{-(1 - \alpha_1) G_1\}}{\frac{1}{n} \left[\frac{1}{J_{01}^S} + \sum_{k=2}^n \frac{1}{J_{0k}^S} \exp\left\{\sum_{i=1}^{k-1} \alpha_i G_i + \sum_{i=2}^k (1 - \alpha_i) G_i\right\} \right]} \quad (24)$$

$$\text{with} \quad G_i = \frac{F(E - E_{0i})}{RT}$$

where J is the net current, E is the polarization voltage, while α_i , E_{0i} , and J_{0i}^S 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 are diffusing species and the intermediates do not diffused away from an electrode surface.

When the net current $J = 0$, the equation becomes

$$E = E_O - \frac{RT}{nF} \ln \frac{C_R(0)}{C_O(0)} \quad (25)$$

with $E_O = \frac{1}{n} \sum_{i=1}^n E_{0i}$

which is the same formula of Nernst equation for $\text{Ox} + ne^- \rightleftharpoons \text{Red}$.

For an another extreme case, when $J_{0i}^S, i \neq m \gg J_{0m}^S$ which is corresponding to the consecutive electrochemical reaction with single rate determining step, the Tafel slope may be given

$$2.303RT/(n - m + \alpha_m)F$$

for anodic process, and

$$2.303RT/(m - \alpha_m)F$$

for cathodic process. Consequently, the equation (24) represents both the Nernst and Tafel region.

Corresponding current density of mass transfer represents as

$$J_O = nF(C_O(0) - C_O(\infty)) \cdot \sqrt{v\omega} \cdot f(Sc_O) \quad (26)$$

and

$$J_R = nF(C_R(\infty) - C_R(0)) \cdot \sqrt{v\omega} \cdot f(Sc_R) \quad (27)$$

Eliminating $C_R(0)$ and $C_O(0)$ from eq.(24) by using eqs.(26) and (27), one obtains more general formula instead of eq.(16) on the current-polarization voltage characteristics for a multistep charge transfer reaction on the rotating disk electrode. If one has specific polarization curves which may involve n electron transfer with or without Tafel lines, one may be able to determine the kinetic and thermodynamic parameters, α_i , J_{Oi}^S , and E_{Oi} of each elementary step.

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LIST OF SYMBOLS

J	Net current density ($A \cdot cm^{-2}$)
J_O	Apparent exchange current density ($A \cdot cm^{-2}$)
J_O^S	Apparent standard exchange current density based on $1 \text{ mole} \cdot cm^{-3}$ as a standard ($A \cdot cm^{-2}$)
J_{Oi}^S	Apparent standard exchange current density for i th step electrode reaction ($A \cdot cm^{-2}$)
i_O^S	Apparent standard exchange current density based on $1 \text{ mole } l^{-1}$ as a standard ($A \cdot cm^{-2}$)
J_L	Limiting current density ($A \cdot cm^{-2}$)
E	Electrode potential or polarization voltage with respect to reference electrode (V)
E_e	Equilibrium potential with respect to reference electrode (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)
$\eta (E - E_e)$	Overvoltage (V)
ϕ_p	Potential in a pre-electrode layer with respect to that in bulk solution (V)
α	Transfer coefficient (-)
α_i	Transfer coefficient for i th step electrode reaction (-)

$C_R(x), C_O(x)$	Concentration of species Ox and Red at location x (moles·cm ⁻³)
C^*	Common concentration (moles·cm ⁻³ or moles·l ⁻¹)
$C_i(p)$	Concentration of species i at a pre-electrode layer (moles·cm ⁻³)
k_0	Apparent standard rate constant for charge transfer reaction (cm·sec ⁻¹)
ν	Kinematic viscosity (cm ² ·sec ⁻¹)
ω	Rotation speed of disk electrode (radians·sec ⁻¹)
D_i	Diffusion coefficient of species i (cm ² ·sec ⁻¹)
z_i	Valency of reactant i (-)
$Sc_i (= \nu/D_i)$	Schmidt number of species i (-)
$Re^{1/2} (= r^2 \omega / \nu)$	Reynolds number (-)
F	Faraday's constant (coul·equiv ⁻¹)
R	Gas constant (joule·mole ⁻¹ ·deg ⁻¹)
T	Temperature (°K)
$G_i (= F(E - E_{O_i})/RT)$	(-)
r	Radius of disk (cm)

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