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KINETIC ANALYSIS OF THE MIXED POTENTIAL, THE REACTION RESISTANCE AND THE CORROSION CURRENT

By

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Abstract

General expressions for the reaction resistance at the mixed potential, V_r, and for the concentration dependences of V_r and the corrosion current are derived and applied to the systems where the concentration polarizations are present.

The condition subjected to V_r was that (i) V_r is far from the equilibrium potentials of the respective reaction, $V_{t\cdot eq}$, $t=1,2,\cdots$, and (ii) V_r is far from some of $V_{t\cdot eq}$'s, $t=1,2,\cdots f$, and close to the rest, $t=f+1,\cdots$.

Resulting formulae were then extended to the cases of (a) a diffusion-controlled anodic (or cathodic) reaction (b) a cathodic (or anodic) reaction with concentration polarization (c) surface process-controlled anodic and cathodic reactions. Special case where the diffusing species are common for both of the anodic and cathodic reactions is also discussed.

Introduction

In the previous papar[1], the present authors developed the general expressions for the concentration dependence of the mixed potential, V_r, and the reaction resistance at V_r, and then discussed the systems where no concentration polarization is present. These general expressions cover all relations reported for limiting cases[2,3].

It is now desirable to derive the concentration dependence of the corrosion current and also to apply the above general treatment to the system where the concentration polarizations are present as will be the case in many systems. However, reported treatments on such a system seem to be rather qualitative or limited under certain conditions. STERN[3] discussed only the shape of the polarization curve. Recently, HERBLIN *et*

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al[4]. analyzed the mixed potential of the two-reaction system where one of the two reactions is under diffusion control, and showed the method for obtaining the Tafel constant of the non-diffusion controlled reaction from the behaviour of V_r. Their treatment, however, is based upon the assumption that the mixed potential is far apart from the equilibrium potentials of the respective reactions and is not applicable to other more complicated cases, *e.g.*, no allowance for neglecting the reverse rate of the respective reactions, and the presence of more than two electrode reactions.

The purpose of the present papar is to extend our previous general treatment to the system where the concentration polarizations are present. Expressions for the concentration dependence of V_r, the concentration dependence of the corrosion current, and the reaction resistance at V_r are obtained in a general manner and will be discussed for several cases which will be most probable to occur.

Fundamental

The mixed potential, V_r, will be determined in general by several electrochemical reactions of the type,

$$aA+bB+\cdots = xX+yY+\cdots+ne^- , \qquad (1)$$

some of them proceeding in the anodic direction and the others in the cathodic direction, respectively. These reactions will be symbolized in the text as

$$\sum_s m_{ts}M_s - n_t e^- = 0 , \qquad t=1, 2, \cdots , \qquad (2)$$

where m_{ts} represents the stoichiometric coefficient of the t-th reaction with respect to the species, M_s, being positive or negative in accordance with M_s being the reduced ($M_s = A, B, \cdots$) or oxidized species ($M_s = X, Y, \cdots$), respectively, and n_t designates the number of electron involved in the t-th reaction.

The net rate of the respective reactions, I_t, will be a function of the electrode potential, V, and the concentrations, C_s's,

$$I_t = f_t(V, C_1, C_2, \cdots, C_s) , \qquad t=1, 2, \cdots . \qquad (3)$$

By denoting the net rate of the t-th reaction at V_r as I_{tr}, the condition for the mixed potential is expressed as[5]

$$\sum_t I_{tr} = 0 , \qquad t=1, 2, \cdots . \qquad (4)$$

This is the most fundamental relation on which the following treatments are based.

When the concentration of any species is changed, the mixed potential will shift so that condition (4) is satisfied. Hence, the resulting change in I_{tr} is expressed from Eq. (3) as

$$dI_{tr}=\left(\frac{\partial I_{tr}}{\partial V_r}\right)_{C_s} dV_r+\sum_s\left(\frac{\partial I_{tr}}{\partial C_s}\right)_{V_r,C_{s'}} dC_s\,, \qquad t=1, 2, \cdots, \tag{5}$$

where the subscript C_s stands for the concentration of all species concerned and $C_{s'}\neq C_s$. Since the summation of dI_{tr} equals zero, we have from the above equation,

$$dV_r=-\frac{\sum_t\left[\sum_s(\partial I_{tr}/\partial \ln C_s)_{V_r,C_{s'}} d\ln C_s\right]}{\sum_t(\partial I_{tr}/\partial V_r)_{C_s}}\,. \tag{6}$$

Thus, the concentration dependence of V_r with respect to a species, M_s, is given in general form as[1)]

$$\boxed{\gamma_s\equiv\left(\frac{\partial V_r}{\partial \ln C_s}\right)_{C_{s'}}=\frac{-\sum_t(\partial I_{tr}/\partial \ln C_s)_{V_r,C_{s'}}}{\sum_t(\partial I_{tr}/\partial V_r)_{C_s}}}\,. \tag{7}$$

Let us consider next the polarization of the electrode with a small current, dI. In such a case, we have

$$dI=\sum_t dI_t=\sum_t\left[(\partial I_t/\partial V)_{C_s}\right]_{V=V_r} dV$$

and hence the reaction resistance, ρ, at V_r is given in general form as[1)]

$$\boxed{\rho\equiv\left[(\partial V/\partial I)_{C_s}\right]_{V=V_r}=1\Big/\sum_t\left[(\partial I_t/\partial V)_{C_s}\right]_{V=V_r}}\,. \tag{8}$$

Reciprocal of ρ is equal to the denominator of the expression for γ_s, Eq. (7).

The total current which flows in the forward direction at V_r, is equal to that in the reverse direction *i.e*,.

$$\sum_t I_{tr}^{+}=\sum_t I_{tr}^{-}\equiv I_m\,,$$

where I_{tr}^{+} or I_{tr}^{-} is a forward or backward unidirectional current of the t-th reaction at V_r and I_m will be called the corrosion current. Variation of I_m caused by the change of C_s is given as

$$dI_m = \sum_t \left[(\partial I_{tr}^+/\partial C_s)_{V_r, C_{s'}} dC_s + (\partial I_{tr}^+/\partial V_r)_{C_s} dV_r \right]$$
$$= \sum_t \left[(\partial I_{tr}^-/\partial C_s)_{V_r, C_{s'}} dC_s + (\partial I_{tr}^-/\partial V_r)_{C_s} dV_r \right].$$

Thus, the concentration dependence of I_m with respect to a species, M_s, is given by taking into account Eq. (7) as

$$\sigma_s \equiv \left(\frac{\partial I_m}{\partial \ln C_s} \right)_{C_{s'}} = \sum_t (\partial I_{tr}^+/\partial \ln C_s)_{V_r, C_{s'}} + \gamma_s \sum_t (\rho_{tr}^+)^{-1}$$
$$= \sum_t (\partial I_{tr}^-/\partial \ln C_s)_{V_r, C_{s'}} + \gamma_s \sum_t (\rho_{tr}^-)^{-1} \quad , \qquad (9)$$

where $\rho_{tr}^+ \equiv (\partial I_{tr}^+/\partial V_r)_{C_s}^{-1}$ and $\rho_{tr}^- \equiv (\partial I_{tr}^-/\partial V_r)_{C_s}^{-1}$. The expression (7) for γ_s is also derived from the above two expressions, (9), considering that $I_{tr} = I_{tr}^+ - I_{tr}^-$.

The above three fundamental expressions, (7), (8) and (9), are valid in any systems with no assumptions and save to a large extent the awkward calculations required when we attempt to obtain γ_s, σ_s and ρ directly from the rate equations by using only condition (4).

Application

In this section, we apply the general expressions of γ_s, ρ and σ_s to the systems where the concentration polarizations are present.

We first assume that one of the reactants of each reaction d(t), is of samll concentration and that one of the products of each reaction, $D(t)$, accumulates on the surface in large excess of the bulk concentration. Applying Fick's 1st law to the respective diffusion processes of the t-th reaction, we have the following relation at the steady state,

$$I_{tr} = k_{d(t)} \left[C_{d(t)} - C_{d(t)}(s) \right] = k_{D(t)} \left[C_{D(t)}(s) - C_{D(t)} \right],$$

where $k_{d(t)}$ or $k_{D(t)}$ is the constant including the factor for the difference in the stoichiometric coefficients in the chemical equation, and $C_{d(t)}(s)$ or $C_{D(t)}(s)$ is the surface concentration of d(t) or $D(t)$. From the above equations,

$$C_{d(t)}(s) = C_{d(t)}(1 - I_{tr}/I_{tL}^+)$$
$$C_{D(t)}(s) = C_{D(t)}(1 + I_{tr}/I_{tL}^-),$$

where

$$I_{tL}^+ \equiv k_{d(t)} C_{d(t)} \text{ and } I_{tL}^- \equiv k_{D(t)} C_{D(t)}.$$

When the reaction occurs in the reverse direction, d(t) accumulates on the surface and $D(t)$ is of small concentration at the surface, since I_{tr} is negative in this case.

Secondly, we assume the following rate equations

$$\begin{aligned} I_{tr} &= I_{tr}^{+} - I_{tr}^{-} \\ &= k_t^{+} \overset{s'}{\Pi} C_{ts}^{z_{ts}^{+}} \left[C_{d(t)} (1 - I_{tr}/I_{tL}^{+}) \right]^{z_{td(t)}^{+}} \exp(\alpha_t^{+} V_r F/RT) \\ &\quad - k_t^{-} \overset{s'}{\Pi} C_{s}^{z_{ts}^{-}} \left[C_{D(t)} (1 + I_{tr}/I_{tL}^{-}) \right]^{z_{tD(t)}^{-}} \exp(-\alpha_t^{-} V_r F/RT), \end{aligned} \tag{10}$$

where s' $\neq$ d(t) or $D(t)$, k's the rate constants, z_{ts}^{+} or z_{ts}^{-} the reaction order with respect to M_s, $z_{td(t)}^{+}$ or $z_{tD(t)}^{-}$ that of d(t) or $D(t)$, and α_t^{+} or α_t^{-} the Tafel constant of the respective unidirectional rates of the t-th reaction.

When the diffusion rate is sufficiently large, I_{tr}/I_{tL}^{+} or I_{tr}/I_{tL}^{-} becomes zero and the surface concentrations equal the bulk ones. This is the case which we have treated previously[1]. On the other hand, when the concentration of, say, d(t) is so small that the diffusion step of d(t) governs the reaction rate, I_{tr} becomes I_{tL}^{+}.

Case (1); All of d(t)'s and D(t)'s are different species.

Each derivatives in Eqs. (7) and (8) will be easily obtained from rate equation (10). Thus, we obtain finally the following relations for the concentration dependences of V_r with respect to the species, M_s, d(t) and $D(t)$,

$$\gamma_s = -\left[\sum_t (I_{tr}^{+} z_{ts}^{+} - I_{tr}^{-} z_{ts}^{-})/\delta_t \right] \times \rho \tag{11}$$

$$\gamma_{d(t)} = -\left[I_{tr}^{+} z_{td(t)}^{+}/(1 - \Delta_{+t})\,\delta_t \right] \times \rho \tag{12}$$

$$\gamma_{D(t)} = \left[I_{tr}^{-} z_{tD(t)}^{-}/(1 + \Delta_{-t})\,\delta_t \right] \times \rho \tag{13}$$

$$1/\rho = (F/RT) \sum_t \left[(I_{tr}^{+}\alpha_t^{+} + I_{tr}^{-}\alpha_t^{-})/\delta_t \right] \tag{14}$$

where

$$\left.\begin{aligned} &\delta_t \equiv 1 + \delta_t^{+} + \delta_t^{-}, \qquad \delta_t^{+} \equiv \Delta_{+t}^{+} z_{td(t)}^{+}/(1 - \Delta_{+t}), \\ &\delta_t^{-} \equiv \Delta_{-t}^{-} z_{tD(t)}^{-}/(1 + \Delta_{-t}) \end{aligned}\right\} \tag{15}$$

and

$$\left.\begin{aligned} &\Delta_{+t}^{+} = I_{tr}^{+}/I_{tL}^{+}, \qquad \Delta_{+t} = I_{tr}/I_{tL}^{+}, \qquad \Delta_{-t}^{-} = I_{tr}^{-}/I_{tL}^{-}, \\ &\Delta_{-t} = I_{tr}/I_{tL}^{-}. \end{aligned}\right\}$$

The above equations, (11) to (14), are more general than those derived previously[1] since the concentration polarizations are taken into account.

σ_s becomes

$$\left.\begin{aligned}
\sigma_s &= \sum_t \left[I_{tr}^+ z_{ts}^+ + \left(\frac{\gamma_s F}{RT}\right) I_{tr}^+ \alpha_t^+ \right] \\
&\quad - \sum_t \frac{z_{td(t)}^+ \Delta_{+t}^+}{(1-\Delta_{+t})\delta_t} \left[I_{tr}^+ z_{ts}^+ - I_{tr}^- z_{ts}^- + \left(\frac{\gamma_s F}{RT}\right)(I_{tr}^+ \alpha_t^+ + I_{tr}^- \alpha_t^-) \right] \\
\sigma_{d(t)} &= \frac{(1+\delta_t^-) I_{tr}^+ z_{td(t)}^+}{(1-\Delta_{+t})\delta_t} \\
&\quad + \left(\frac{\gamma_{d(t)} F}{RT}\right) \sum_t \left[I_{tr}^+ \alpha_t^+ - \frac{\delta_t^+ (I_{tr}^+ \alpha_t^+ + I_{tr}^- \alpha_t^-)}{\delta_t} \right] \\
\sigma_{D(t)} &= \frac{\delta_t^+ I_{tr}^- z_{tD(t)}^-}{(1+\Delta_{-t})\delta_t} + \left(\frac{\gamma_{D(t)} F}{RT}\right) \sum_t \left[I_{tr}^+ \alpha_t^+ - \frac{\delta_t^+ (I_{tr}^+ \alpha_t^+ + I_{tr}^- \alpha_t^-)}{\delta_t} \right].
\end{aligned}\right\} \quad (16)$$

When the diffusion rates are sufficiently large, *i.e.*, when Δ's approach zero, δ_t of Eq. (15) becomes unity and hence we have the previous equations[1]:

$$\gamma_s = -\sum_t (I_{tr}^+ z_{ts}^+ - I_{tr}^- z_{ts}^-) \times \rho$$

$$\gamma_{d(t)} = -I_{tr}^+ z_{td(t)}^+ \rho, \qquad \gamma_{D(t)} = I_{tr}^- z_{tD(t)}^- \rho$$

$$1/\rho = (F/RT) \sum_t (I_{tr}^+ \alpha_t^+ + I_{tr}^- \alpha_t^-).$$

σ's of Eq. (16) becomes at Δ's$=0$, *i.e.*, at $\delta_t=1$, $\delta_t^+=\delta_t^-=0$,

$$\left.\begin{aligned}
\sigma_s &= \sum_t \left[I_{tr}^+ z_{ts}^+ + \gamma_s (F/RT) \alpha_t^+ I_{tr}^+ \right] \\
\sigma_{d(t)} &= I_{tr}^+ z_{td(t)}^+ + \gamma_{d(t)} (F/RT) \sum_t \alpha_t^+ I_{tr}^+ \text{ *)} \\
\sigma_{D(t)} &= \gamma_{D(t)} (F/RT) \sum_t \alpha_t^+ I_{tr}^+ .
\end{aligned}\right\} \quad (17)$$

Now let us consider the two-reaction system, where the mixed potential is determined by two reactions, one of which is the anodic ($t=1$) and the other is the cathodic reaction ($t=2$). In the two-reaction system, Eq. (4) gives

$$I_{1r} = -I_{2r} = I_m .$$

(i): When V_r is far apart from the equilibrium potentials of the respective reactions ($t=1, 2$),

*) The term, $\delta_t^+(1+\delta_t^-) I_{tL}^+/\delta_t$, of $\sigma_{d(t)}$ becomes $I_{tr}^+ z_{td(t)}^+$ at Δ's$=0$ from the expressions for δ_t^+, δ_t^- and δ_t of Eq. (15).

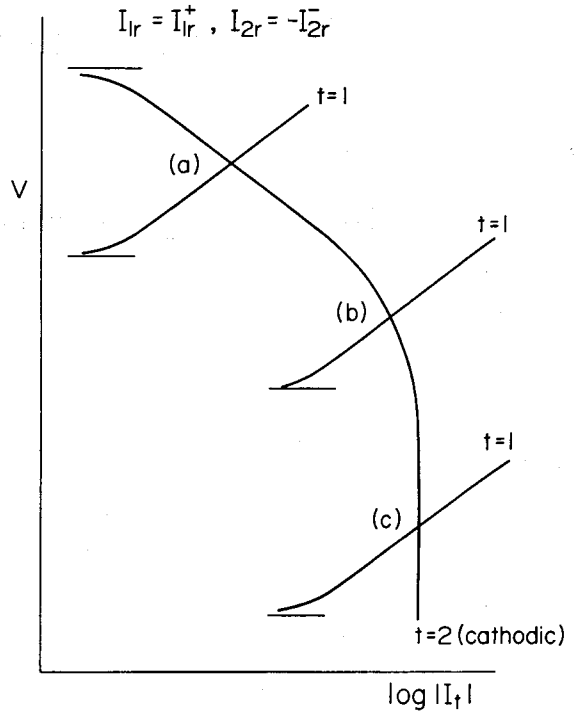

Fig. 1. Open circuit systems treated in the text as an example under the condition of $|V_r - V_{t\cdot eq}| \gg RT/\alpha_t^- F$, $RT/\alpha_t^+ F$, $t=1$ (anodic), 2 (cathodic).
(a) no concentration polarizations, (b) concentration polarization for $t=2$, and (c) diffusion control for $t=2$.

$$|V_r - V_{t\cdot eq}| \gg RT/\alpha_t^+ F, \qquad RT/\alpha_t^- F, \tag{18}$$

the unidirectional rates, I_{1r}^- ane I_{2r}^+, of the anodic and cathodic reactions are neglected and we have $I_{1r} = I_{1r}^+$ and $I_{2r} = -I_{2r}^-$. This is the case called "the mixed control" (Fig. 1). Now, Δ_{+1} and Δ_{-2} of Eq. (15) equal Δ_{+1}^+ and $-\Delta_{-2}^-$, respectively. Thus, Eqs. (11) to (15) become

$$\left.\begin{aligned} \gamma_s &= -\frac{RT}{F}\cdot\frac{z_{1s}^+/\delta_1 - z_{2s}^-/\delta_2}{\alpha_1^+/\delta_1 + \alpha_2^-/\delta_2} \\ \gamma_{d(1)} &= -\frac{RT}{F}\cdot\frac{z_{1d(1)}^+/(1-\Delta_{+1}^+)\,\delta_1}{\alpha_1^+/\delta_1 + \alpha_2^-/\delta_2}\,, \\ \gamma_{D(2)} &= \frac{RT}{F}\cdot\frac{z_{2D(2)}^-/(1-\Delta_{-2}^-)\,\delta_2}{\alpha_1^+/\delta_1 + \alpha_2^-/\delta_2} \end{aligned}\right\} \tag{19}$$

$$1/\rho = (F/RT)\, I_m(\alpha_1^+/\delta_1 + \alpha_2^-/\delta_2) \tag{20}$$

$$\delta_1 = 1 + \frac{\Delta^+_{+1} z^+_{1d(1)}}{1-\Delta^+_{+1}}, \qquad \delta_2 = 1 + \frac{\Delta^-_{-2} z^-_{2D(2)}}{1-\Delta^-_{-2}}. \tag{21}$$

From Eq. (16), σ's become

$$\left.\begin{aligned} \sigma_s &= I_m\left[z^+_{1s} + (F/RT)\,\gamma_s \alpha^+_1\right]/\delta_1 \\ \sigma_{d(1)} &= I_m\left[z^+_{1d(1)}/(1-\Delta^+_{+1}) + (F/RT)\,\gamma_{d(1)}\alpha^+_1\right]/\delta_1 \\ \sigma_{D(2)} &= I_m (F/RT)\,\gamma_{D(2)}\alpha^+_1/\delta_1, \end{aligned}\right\} \tag{22}$$

(a) Δ's$=0$; When both of the mass transfer steps are sufficiently fast so that Δ's of Eq. (15) equal practically zero (Fig. 1, (a)), δ's of Eq. (21) become unity. Equations (19) and (20), will then be

$$\left.\begin{aligned} \gamma_s &= -(RT/F)(z^+_{1s} - z^-_{2s})/(\alpha^+_1 + \alpha^-_2) \\ \gamma_{d(1)} &= -(RT/F)\, z^+_{1d(1)}/(\alpha^+_1 + \alpha^-_2), \\ \gamma_{D(2)} &= (RT/F)\, z^-_{2D(2)}/(\alpha^+_1 + \alpha^-_2) \\ 1/\rho &= (F/RT)\, I_m(\alpha^+_1 + \alpha^-_2), \end{aligned}\right\} \tag{23}$$

which we have already derived[1]. σ's of Eq. (22) become

$$\left.\begin{aligned} \sigma_s &= I_m(z^+_{1s}\alpha^-_2 + z^-_{2s}\alpha^+_1)/(\alpha^+_1 + \alpha^-_2) \\ \sigma_{d(1)} &= I_m z^+_{1d(1)}\alpha^-_2/(\alpha^+_1 + \alpha^-_2) \\ \sigma_{D(2)} &= I_m z^-_{2D(2)}\alpha^+_1/(\alpha^+_1 + \alpha^-_2). \end{aligned}\right\} \tag{24}$$

The above expression of σ_s has been reported by DONAHUE [6].

(b) $\Delta^+_{+1}=0$; When only the anodic reaction is controlled by the surface process (Fig. 1 (b)), Eqs. (19) to (22) become

$$\left.\begin{aligned} \gamma_s &= -(RT/F)(z^+_{1s} - z^-_{2s}/\delta_2)/(\alpha^+_1 + \alpha^-_2/\delta_2) \\ \gamma_{d(1)} &= -\frac{RT}{F}\cdot\frac{z^+_{1d(1)}}{\alpha^+_1 + \alpha^-_2/\delta_2}, \qquad \gamma_{D(2)} = \frac{RT}{F}\cdot\frac{z^-_{2D(2)}/(1-\Delta^-_{-2})\,\delta_2}{\alpha^+_1 + \alpha^-_2/\delta_2} \\ 1/\rho &= (F/RT)\, I_m(\alpha^+_1 + \alpha^-_2/\delta_2) \\ \delta_2 &= 1 + \Delta^-_{-2} z^-_{2D(2)}/(1-\Delta^-_{-2}) \\ \sigma_s &= I_m\left[z^+_{1s} - \alpha^+_1(z^+_{1s} - z^-_{2s}/\delta_2)/(\alpha^+_1 + \alpha^-_2/\delta_2)\right] \\ \sigma_{d(1)} &= I_m z^+_{1d(1)}(\alpha^-_2/\delta_2)/(\alpha^+_1 + \alpha^-_2/\delta_2) \\ \sigma_{D(2)} &= I_m z^-_{2D(2)}\alpha^+_1/(1-\Delta^-_{-2})\,\delta_2(\alpha^+_1 + \alpha^-_2/\delta_2). \end{aligned}\right\} \tag{25}$$

(c) $\Delta^+_{+1}=0$, $\Delta^-_{-2}=1$; When the rate of the anodic reaction is controlled by the surface process and that of the cathodic reaction is controlled by

which have been derived previously[1].

(b) $\Delta^{+}_{+1}=0$; When only the anodic reaction is governed by the surface process (Fig. 2, (b)), *i.e.*, $\Delta^{+}_{+1}=0$, Eqs. (29) to (31), become

$$\left.\begin{aligned} \gamma_s &= -\left[I^{+}_{1r} z^{+}_{1s} + (I^{+}_{2r} z^{+}_{2s} - I^{-}_{2r} z^{-}_{2s})/\delta_2\right] \times \rho \\ \gamma_{d(1)} &= -I^{+}_{1r} z^{+}_{1d(1)} \rho \\ 1/\rho &= (F/RT)\left[I^{+}_{1r}\alpha^{+}_{1} + (I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2})/\delta_2\right]. \end{aligned}\right\} \quad (34)$$

Equations for $\gamma_{d(2)}$, $\gamma_{D(2)}$ and δ_2 are the same as those of Eqs. (30) and (31).

(c) $\Delta^{+}_{+1}=1$; When the anodic reaction rate is governed by the diffusion step of d(1) (Fig. 2, (c)), *i.e.*, $\Delta^{+}_{+1}=1$, δ_1 becomes infinite. Hence,

$$\left.\begin{aligned} \gamma_s &= -(RT/F)(I^{+}_{2r} z^{+}_{2s} - I^{-}_{2r} z^{-}_{2s})/(I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2}) \\ \gamma_{d(1)} &= -(RT/F)\, I^{+}_{1r}\delta_2/(I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2}) \\ 1/\rho &= (F/RT)(I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2})/\delta_2 . \end{aligned}\right\} \quad (35)$$

Equations for $\gamma_{d(2)}$, $\gamma_{D(2)}$ and δ_2 are given in Eqs. (30) and (31).

(d) $\Delta^{+}_{+1}=1$, Δ_2's $=0$; In addition, let the diffusion rates of d(2) and $D(2)$ be sufficiently large, *i.e.*, Δ_{+2} and $\Delta_{-2}=0$ (Fig. 2, (d)). In this case, δ_1 is infinite and δ_2 equals unity. Hence,

$$\left.\begin{aligned} \gamma_s &= -(RT/F)(I^{+}_{2r} z^{+}_{2s} - I^{-}_{2r} z^{-}_{2s})/(I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2}) \\ \gamma_{d(1)} &= -(RT/F)\, I^{+}_{1r}/(I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2}) \\ \gamma_{d(2)} &= -I^{+}_{2r} z^{+}_{2d(2)} \rho , \qquad \gamma_{D)2)} = I^{-}_{2r} z^{-}_{2D(2)} \rho \\ 1/\rho &= (F/RT)(I^{+}_{2r}\alpha^{+}_{2} + I^{-}_{2r}\alpha^{-}_{2}) \end{aligned}\right\} \quad (36)$$

σ's for (a)~(d) will be calculated from Eq. (32) by using respective values of Δ's.

Case (2) ; One of d(t)'s and D(t)'s is common among more than one reactions

This will be the case for the system of *e.g.*, H_2O_2 which is common for the anodic and cathodic reactions, *i.e.*, $d(1)=D(2)\equiv d$. For the sake of simplicity, we treat here only the two-reaction system. Let $t=1$ and 2 be the anodic and the cathodic reactions as we did, each satisfying the condition (18). The respective rate equations are

$$\left.\begin{aligned} I_{1r} &= I^{+}_{1r} = k^{+}_{1} \overset{s'}{\Pi} C_s^{z^{+}_{1s}} \left[C_d(1 - I^{+}_{1r}/I_L)\right]^{z^{+}_{1d}} \exp(\alpha^{+}_{1} V_r F/RT) \\ I_{2r} &= -I^{-}_{2r} = -k^{-}_{2} \overset{s'}{\Pi} C_s^{z^{-}_{2s}} \left[C_d(1 - I^{-}_{2r}/I_L)\right]^{z^{-}_{2d}} \exp(-\alpha^{-}_{2} V_r F/RT), \end{aligned}\right\} \quad (37)$$

where I_L is the limiting current which is common for the reactions, $t=1$ and 2. I_L is different from the diffusion limiting current of d, since the diffused d is consumed by both reactions.

The concentration dependences of V_r and I_m are given from the expressions of (7) to (9) and Eq. (37) as

$$\left.\begin{aligned}
&\gamma_s = -\frac{RT}{F}\cdot\frac{(z_{1s}^+/\delta_1 - z_{2s}^-/\delta_2)}{(\alpha_1^+/\delta_1+\alpha_2^-/\delta_2)}\\
&\gamma_d = -\frac{RT}{F(1-\Delta)}\cdot\frac{(z_{1d}^+/\delta_1 - z_{2d}^-/\delta_2)}{(\alpha_1^+/\delta_1+\alpha_2^-/\delta_2)}\\
&1/\rho = (F/RT)\, I_m(1-\Delta)(\alpha_1^+/\delta_1+\alpha_2^-/\delta_2)\\
&\sigma_s = \left[I_m(1-\Delta)/\delta_1\right]\left[z_{1s}^+ + (F/RT)\,\gamma_s\alpha_1^+\right]\\
&\quad = \left[I_m(1-\Delta)/\delta_2\right]\left[z_{2s}^- - (F/RT)\,\gamma_s\alpha_2^-\right]\\
&\sigma_d = \left[I_m/\delta_1\right]\left[z_{1d}^+ + (F/RT)(1-\Delta)\,\gamma_d\alpha_1^+\right]\\
&\quad = \left[I_m/\delta_2\right]\left[z_{2d}^- - (F/RT)(1-\Delta)\,\gamma_d\alpha_2^-\right]\\
&\delta_1 = 1-(1-z_{1d}^+)\,\Delta\,, \qquad \delta_2 = 1-(1-z_{2d}^-)\,\Delta\\
&\Delta = I_m/I_L\,, \qquad I_m = I_{1r}^+ = I_{2r}^-\,.
\end{aligned}\right\} \quad (38)$$

(a) $\Delta=0$; When the diffusion rate of d is sufficiently large, Δ becomes zero. Hence, the both reaction rates are controlled by the surface process. This case has been already treated and the above equations reproduce Eq. (23). σ_s is the same as that of Eq. (23) and σ_d is given as the sum of $\sigma_{d(1)}$ and $\sigma_{D(2)}$ by putting $d(1)=D(2)=d$.

(b) $\Delta=1$; On the contrary, if the diffusion rate of d is small and the both reactions are controlled by the diffusion, values of γ_s and σ_s become zero because of $z_{1s}^+=z_{2s}^-=0$ and $\Delta=1$, whereas γ_d becomes indefinite. The reaction resistance is infinite as expected from the independence of the limiting diffusion rate on the electrode potential. σ_d, *i.e.*, the change of I_m with C_d, becomes

$$\sigma_d = I_m \text{ or } \partial \ln I_m/\partial \ln C_d = 1\,.$$

Discussion

In the foregoing sections, we first developed three fundamental expressions, (7) to (9), for the concentration dependence of V_r, the concentration dependence of I_m, and the reaction resistance at V_r. These expressions

are unconditionally valid in any systems. If the rate equations of each reaction are available, one can estimate the behaviour of the mixed potential from these expressions. On the other hand, it may happen that some of the kinetic parameters are hardly determined by experiments. In such a case, the observed behaviours of the mixed potential and of I_m, *i.e.*, γ_1, γ_2, $\cdots$, σ_1, σ_2, $\cdots$, and the reaction resistance, may be used to determine these unknown parameters.

In the present analysis, we assumed the rate equation of the type given by Eq. (10). Equation (10) includes the concentration polarization of only one reactant and one product. This might be the most probable case and be taken general enough, for an introduction of other concentration polarization factors will not cause to any essential difficulty in the analysis except for the increase of terms in the expressions of γ_s and ρ.

We have treated above typical cases which may have practical importance. Some of them will be exemplified below.

i) No concentration polarization

H_2O_2–Hg system; The present authors[7] studied the kinetics of the anodic and cathodic reactions on Hg in acidic and alkaline H_2O_2 solutions and concluded that the mixed potential is determined by the anodic reaction, $2Hg + SO_4^{2-} \rightarrow Hg_2SO_4 + 2e^-$ (acidic) or $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (alkaline) and the cathodic reaction, $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (acidic) or $H_2O_2 + 2e^- \rightarrow 2OH^-$ (alkaline). This was the case of the two-reaction system, each reaction satisfying the condition (18). Calculated concentration dependences of V_r from equation (23), $\gamma_{H_2O_2}$, γ_{H^+}, $\gamma_{SO_4^{2-}}$, are in excellent agreement with the observed ones[1].

H_2O_2–Pt system; OSTROVIDOVA *et al.*[8] studied the anodic and cathodic reactions on Pt in alkaline H_2O_2 solution. This is another example of the two-reaction system which satisfies the condition (18). They calculated the value of $\gamma_{H_2O_2}$ and γ_{H^+} directly from their rate equations and showed good agreement with the observed ones.

It will be emphasized that, in principle, the behaviour of V_r must be analyzed by the rate equations obtained around the mixed potential. In the above two examples, however, the concentration dependences were calculated by using the kinetic parameters, determined experimentally in the potential range far from the mixed potential. The excellent agreement between the calculated and observed ones indicates that the rate equations observed at high anodic and cathodic polarizations are maintained around the mixed potential.

ii) Concentration polarization

Very few work have been reported on the system where the concentration polarization is present. HERBELIN *et al*[4]. analyzed the mixed potential of the two-reaction system where one of the reactions is diffusion controlled. They derived first the equation of the mixed potential and then deduced that to γ by differentiation. Such a procedure is not applicable to the cases where the formula of V_r is not given by an explicit function of the observed kinetic parameters.

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