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Differentiating polarization curve technique for determining the exchange current density of hydrogen electrode reaction

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(Abstract)

The authors propose a new method to easily and reliably determine the exchange current density (i_0) of hydrogen evolution reaction (*her*). The validity of a novel method named the differential polarization method (DPM) was ascertained by the estimation of i_0 on platinum electrode in acid solutions. The *her*s in 0.005, 0.05 and 0.5 mol dm^{-3} H_2SO_4 solutions were visually categorized as reversible reactions. The obtained i_0 had constant values of about 0.5 mA cm^{-2}, corresponding to the appearance of a vertical line on the anodic polarization resistance curve. This DPM shows the i_0 is corresponds to the limiting diffusion current density of the hydrogen oxidation reaction. We believe that the DPM has the potential to be a beneficial and reliable method for estimating electrochemical parameters.

Keywords: Hydrogen evolution reaction; Exchange current density; Platinum electrode; Polarization resistance; Tafel relation

1. Introduction

The hydrogen electrode reaction is one of the most fundamental electrolytic reactions in the field of electrochemistry. It is a single electrode reaction between hydrogen oxidation reaction (*hor*) and hydrogen evolution reaction (*her*). The exchange current density i_0 is an important parameter in evaluating the relevant catalyst performance in industrial applications such as fuel cell research, battery development, and corrosion engineering. Numerous papers about i_0 have been published since Tafel established the experimental relation in 1905 [1]. In almost all cases, the i_0 has been estimated by the Tafel extrapolation method, $\eta = a + b \log|i|$. The linear relationship between the logarithm of the cathodic current density ($\log|i|$) and its overvoltage (η) has been established as a determinant of the i_0. However, some unresolved issues still hamper the Tafel method [2], [3]. For example, in some cases different values are observed [1]-[4]. The i_0 of gold electrode varies from $10^{-0.15}$ to $10^{-4.04}$ mA cm^{-2} [2]; a difference of more than four orders of magnitude. Similarly, another result showed that the i_0 on platinum in sulfuric acid solutions ranged from $10^{-1.0}$ to $10^{0.4}$ mA cm^{-2} [1-c]. In simple experiments, the Tafel slope of -0.03 V for the *her* in an acid solution can be determined in a high overvoltage region. This platinum electrode polarized in a cathodic potential region is fully absorbed in hydrogen bubbles and probably encounters turbulence due to vigorous H_2 evolution. On the other hand, the most preferable and reliable determination of i_0 is done in a low overvoltage region [5],[6]. Furthermore, physical factors such as solution resistance due to the hydrogen bubbles and the existence of oxide film on the electrode must be considered [7],[8]. We think that the main reasons for the variation in measured experimental values are because of the solution or oxide film or adsorption layer resistances. We believe that there is another suitable method to solve or decrease these problems concerning the hydrogen electrode reaction. Such a method should be sufficiently rigorous to accurately predict the i_0 from experimental data. Furthermore, the new method must be both theoretically sound and experimentally verifiable.

In this paper, we propose a new method, the differential polarization method (DPM), which is intended to be used as a complementary approach to the Tafel method. The application of the DPM to estimate corrosion rates has shown positive results. A few experimental results of the mass loss from aluminum alloys corroded in a mineral acid solution were in good agreement with the mass losses predicted by the DPM [9,10]. These successful experimental results lead us to believe that the DPM could be applicable to the determination of the i_0 of *her*. The purpose of this paper is twofold: firstly, to explain the methodology behind the DPM; and secondly, to demonstrate its reliability in experiments. The validity of the DPM was verified in an experiment involving the *her* of a platinum electrode in different sulfuric acid solutions.

2. Explanation of the DPM expression

2.1 Electrochemical reaction and its expression

Before discussing the DPM, it is necessary to explain the relationship between electrochemical kinetics and the DPM. A single-electrode reaction shown as

$$\mathrm{Red} \rightleftarrows \mathrm{Ox}^{z+} + ze^{-} \qquad (1)$$

is electrochemically characterized by the Nernst equation which will play a very important role in the explanation of DPM. By definition, the E_{eq} is expressed as follows:

$$E_{\mathrm{eq}} = E^{0} + \frac{R\,T}{z\,F} \ln \frac{\{\mathrm{Ox}^{z+}\}_{\mathrm{bulk}}}{\{\mathrm{Red}\}_{\mathrm{bulk}}} = E^{\emptyset} + \frac{R\,T}{z\,F} \ln \frac{[\mathrm{Ox}^{z+}]_{\mathrm{bulk}}}{[\mathrm{Red}]_{\mathrm{bulk}}} \qquad (2)$$

The electrochemical polarization phenomena at the stationary state are expressed by two main processes: activation and diffusion. When both of them occur simultaneously, the following well-known equation is obtained [11]:

$$i\,(\eta) = i_0 \left\{ \left(1 - \frac{i}{i_{\mathrm{Red,L}}}\right) \exp(f_{\mathrm{a}}\,\eta) - \left(1 - \frac{i}{i_{\mathrm{Ox}^{z+},\mathrm{L}}}\right) \exp(-f_{\mathrm{c}}\,\eta) \right\} \qquad (3)$$

When using Eq. (3), we often confront problems such as poor data collection and the tedious task of calculating the activity coefficients for y_{Red} and $y_{\mathrm{Ox}^{z+}}$ which are usually unknown. To circumvent these problems, the $E^{\emptyset}$ was introduced. Substitution of the following equations into Eq. (3) yields the following practical Eq.(6):

$$\begin{cases} \eta = E - E_{\mathrm{eq}} = E - E^{\emptyset} + E^{\emptyset} - E_{\mathrm{eq}} = \eta^{\emptyset} + (E^{\emptyset} - E_{\mathrm{eq}}) & (4) \\ i_0 = z\,F\,k^{\emptyset}\,[\mathrm{Red}]_{\mathrm{bulk}}^{\beta}\,[\mathrm{Ox}]_{\mathrm{bulk}}^{\alpha} & (5) \\ E_{\mathrm{eq}} - E^{\emptyset} = \frac{R\,T}{z\,F} \ln \frac{[\mathrm{Ox}^{z+}]_{\mathrm{bulk}}}{[\mathrm{Red}]_{\mathrm{bulk}}} & (2') \end{cases}$$

Then,

$$i\,(\eta^{\emptyset}) = k^{\emptyset} \left\{ \left(\frac{i_{\mathrm{Red,L}} - i}{k_{\mathrm{Red}}}\right) \exp\left(f_{\mathrm{a}}\,\eta^{\emptyset}\right) - \left(\frac{i - i_{\mathrm{Ox}^{z+},\mathrm{L}}}{k_{\mathrm{Ox}^{z+}}}\right) \exp(-f_{\mathrm{c}}\,\eta^{\emptyset}) \right\} \qquad (6)$$

At the equilibrium state, which is the equal state of $i\,(\eta^{\emptyset}) = 0$, we can obtain the following relation:

$$\frac{i_{\mathrm{Red,L}}}{k_{\mathrm{Red}}} \exp\left(f_{\mathrm{a}}\,\eta^{\emptyset}\right) = \frac{-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{k_{\mathrm{Ox}^{z+}}} \exp(-f_{\mathrm{c}}\,\eta^{\emptyset}) \qquad (7)$$

After arranging the above, we found that Eq.(7) arrives at the Nernst equation. For this paper it is important to remember that the $E(0)$ is identical to the E_{eq}.

For the sake of further simplification, Eq. (6) is arranged as follows:

$$\frac{A+B+C}{B\ i_{\mathrm{Red,L}}+C\ i_{\mathrm{Ox^{z+},L}}}\ i(\eta^{\emptyset})\ =1 \tag{8}$$

where *A*, *B*, and *C* are abbreviations for $1/\ k^{\emptyset}$, $\exp(\ f_{\mathrm{a}}\ \eta^{\emptyset})\ /\ k_{\mathrm{Red}}$, and $\exp(\ -f_{\mathrm{c}}\ \eta^{\emptyset})/\ k_{\mathrm{Ox}}$, respectively. From a mathematical point of view, each of $1(=\exp(0))$, $\exp(\ f_{\mathrm{a}}\ \eta^{\emptyset})$, and $\exp(\ -f_{\mathrm{c}}\ \eta^{\emptyset})$ are interpreted as weighted functions on respectively the $k^{\emptyset}$, k_{Red} and k_{Ox}. Term *A* shown as $1/\ k^{\emptyset}(=\exp(0)/k^{\emptyset})$ is related to the activation process. Term *B* and term *C* are related to the diffusion processes. The term *B* $(=\exp(\ f_{\mathrm{a}}\ \eta^{\emptyset})\ /\ k_{\mathrm{Red}})$ emerges in anodic diffusion processes and will show either a large/negligible effect when the $\eta^{\emptyset}$ has a positive/negative value. Conversely, the term *C* $(=\exp(\ -f_{\mathrm{c}}\ \eta^{\emptyset})/\ k_{\mathrm{Ox}})$ shows the opposite effect: a negligible/large value when the $\eta^{\emptyset}$ has a positive/negative value.

When Eq.(8) is expressed in a coherent system of units [12,13], this equation provides specific numerical sets for its approximation. In other words, a combination of numerators of *A*, *B*, and *C* accounts for a contribution ratio for the whole $i(\eta^{\emptyset})$, because Eq.(8) is equivalent to both the physical equation and the numerical equation. Since the right-hand side of Eq.(8) is 1, a combination of the left-hand-side terms corresponds to a numerical contribution ratio.

To grasp the gist of this approximation, the expression of Eq.(8) is divided into two groups: group (A) and group (B). The (A) group shows fast kinetics with reversible reaction characteristics (large value of $k^{\emptyset}$). The (B) group shows slow kinetics with irreversible reaction characteristics (small value of $k^{\emptyset}$). The (A) and (B) groups are further classified into three equations based on possible electrochemical reactions. The (A) group, which includes k_{Red} and k_{Ox} but omits $k^{\emptyset}$, is classified as follows:

$$\begin{cases} \text{(A)-1 : } \dfrac{B+C}{B\cdot i_{\mathrm{Red,L}}+C\cdot i_{\mathrm{Ox^{z+},L}}}\, i(\eta^{\emptyset}) \approx 1 & (9) \\ \text{(A)-2 : } \dfrac{B}{B\cdot i_{\mathrm{Red,L}}+C\cdot i_{\mathrm{Ox^{z+},L}}}\, i(\eta^{\emptyset}) \approx 1 & (10) \\ \text{(A)-3 : } \dfrac{C}{B\cdot i_{\mathrm{Red,L}}+C\cdot i_{\mathrm{Ox^{z+},L}}}\, i(\eta^{\emptyset}) \approx 1 & (11) \end{cases}$$

and the (B) group, which always includes $k^{\emptyset}$, is classified as follows:

$$\begin{cases} \text{(B)-1 : } \dfrac{A}{B\cdot i_{\mathrm{Red,L}}+C\cdot i_{\mathrm{Ox^{z+},L}}}\, i(\eta^{\emptyset}) \approx 1 & (12) \\ \text{(B)-2 : } \dfrac{A+B}{B\cdot i_{\mathrm{Red,L}}+C\cdot i_{\mathrm{Ox^{z+},L}}}\, i(\eta^{\emptyset}) \approx 1 & (13) \\ \text{(B)-3 : } \dfrac{A+C}{B\cdot i_{\mathrm{Red,L}}+C\cdot i_{\mathrm{Ox^{z+},L}}}\, i(\eta^{\emptyset}) \approx 1 & (14) \end{cases}$$

In the field of electrochemistry, electrochemical kinetics are usually expressed in three functional forms: $i(\eta^{\emptyset})$, $E(i)$ and $h(i)$. Each function has its own merits. For instance, the $i(\eta^{\emptyset})$ function enables the easy superimposition of anodic and cathodic branch currents, whereas the $E(i)$ function suggests thermodynamically feasible reactions by referring to electrode potential–pH diagrams [14]. The polarization resistance $h(i)$ is an another function which can be obtained by differentiating the $E(i)$:

$$h(i) = \frac{\mathrm{d}E}{\mathrm{d}i} = \frac{\mathrm{d}E}{\mathrm{d}(i_{\mathrm{a}}+i_{\mathrm{c}})} = \frac{1}{1/h_{\mathrm{a}}(i_{\mathrm{a}})+1/h_{\mathrm{c}}(i_{\mathrm{c}})} \tag{15}$$

The $h(i)$ is expressed as a parallel circuit of the anodic polarization resistance $h_{\mathrm{a}}(i_{\mathrm{a}})$, and the cathodic polarization resistance $h_{\mathrm{c}}(i_{\mathrm{c}})$. The $h(i)$ expression has a merit of requiring fewer experimental readings. Although $i(\eta^{\emptyset})$, $E(i)$, and $h(i)$ are exhibited in different forms, they are interchangeable with each other. To understand the distinctions among them, we used some algebraic and geometrical examples. However, the explanation of the (B) group is beyond the scope of the present paper. This will be treated in detail elsewhere.

2.2. Approximations for reversible reactions: group (A) approximations

(A)-1 approximation

The (A)-1 approximation is applicable in the case of reversible reactions with diffusion phenomena in both anodic and cathodic directions. The $i(\eta^{\emptyset})$, $E(i)$ and $h(i)$ are expressed as follows:

The $i(\eta^{\emptyset})$ is expressed as:

$$\begin{cases} i(\eta^{\emptyset}) \approx \frac{B \cdot i_{\mathrm{Red,L}} + C \cdot i_{\mathrm{Ox^{z+},L}}}{B+C} \left(= i_{\mathrm{a}}(\eta^{\emptyset}) + i_{\mathrm{c}}(\eta^{\emptyset})\right) & (16) \\ i_{\mathrm{a}}(\eta^{\emptyset}) = \frac{B}{B+C}\, i_{\mathrm{Red,L}} & (17) \\ i_{\mathrm{c}}(\eta^{\emptyset}) = \frac{C}{B+C}\, i_{\mathrm{Ox^{z+},L}} & (18) \end{cases}$$

The $E(i)$ is obtained by arranging Eqs. (16)–(18):

$$\begin{cases} E(i) = E^{\emptyset} + \frac{R\,T}{z\,F} \ln \frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}}\, \frac{i - i_{\mathrm{Ox^{z+},L}}}{i_{\mathrm{Red,L}} - i} & (19) \\ E_{\mathrm{a}}(i_{\mathrm{a}}) = E^{\emptyset} + \frac{R\,T}{z\,F} \ln \frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}}\, \frac{i_{\mathrm{a}}}{i_{\mathrm{Red,L}} - i_{\mathrm{a}}} & (20) \\ E_{\mathrm{c}}(i_{\mathrm{c}}) = E^{\emptyset} + \dfrac{R\,T}{z\,F} \ln \dfrac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}}\, \dfrac{i_{\mathrm{c}} - i_{\mathrm{Ox^{z+},L}}}{-i_{\mathrm{c}}} & (21) \end{cases}$$

Close examination finds that $E(i)$ at $i_{\mathrm{Red,L}} \to 0$ and $i_{\mathrm{Ox^{z+},L}} \to 0$ completely matches both the $E_{\mathrm{a}}(i_{\mathrm{a}})$ and $E_{\mathrm{c}}(i_{\mathrm{c}})$, respectively. The following is an easy mathematical protocol to directly obtain $E_{\mathrm{a}}(i_{\mathrm{a}})$ and $E_{\mathrm{c}}(i_{\mathrm{c}})$ from $E(i)$ [7]:

$$\begin{cases} E_{\mathrm{a}}(i_{\mathrm{a}}) = [E(i)]_{\substack{i_{\mathrm{Ox^{z+},L}} \to 0 \\ i = i_{\mathrm{a}}}} & (22) \\ E_{\mathrm{c}}(i_{\mathrm{c}}) = [E(i)]_{\substack{i_{\mathrm{Red,L}} \to 0 \\ i = i_{\mathrm{c}}}} & (23) \end{cases}$$

The $h(i)$ is expressed through differentiation of the Eqs. (19)–(21):

$$\left\{\begin{aligned}
&h(i)=\frac{\mathrm{d}E}{\mathrm{d}i}=\frac{R\,T}{z\,F}\left(\frac{1}{i_{\mathrm{Red,L}}-i}+\frac{1}{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\right) && (24)\\
&h_{\mathrm{a}}(i_{\mathrm{a}})=\frac{\mathrm{d}E_{\mathrm{a}}(i_{\mathrm{a}})}{\mathrm{d}i_{\mathrm{a}}}=\frac{R\,T}{z\,F}\left(\frac{1}{i_{\mathrm{a}}}+\frac{1}{i_{\mathrm{Red,L}}-i_{\mathrm{a}}}\right) && (25)\\
&h_{\mathrm{c}}(i_{\mathrm{c}})=\frac{\mathrm{d}E_{\mathrm{c}}(i_{\mathrm{c}})}{\mathrm{d}i_{\mathrm{c}}}=\frac{R\,T}{z\,F}\left(\frac{1}{-i_{\mathrm{c}}}+\frac{1}{i_{\mathrm{c}}-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\right) && (26)
\end{aligned}\right.$$

Since *h*(*i*) is an one order differential equation, *E*(*i*) is obtained by solving the *h*(*i*) under an initial condition such as (0, *E*(0)):

$$\int_{E(0)}^{E(i)}\mathrm{d}E\;=\frac{R\,T}{z\,F}\int_{0}^{i}\left(\frac{1}{i_{\mathrm{Red,L}}-i}+\frac{1}{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\right)\mathrm{d}i \tag{27}$$

Then,

$$E(i)=E(0)+\frac{R\,T}{z\,F}\ln\frac{i_{\mathrm{Red,L}}}{-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\,\frac{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{i_{\mathrm{Red,L}}-i} \tag{28}$$

And as $E(0)=E_{\mathrm{eq}}$,

$$E(i)=E^{\varnothing}+\frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox}^{z+}}}\,\frac{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{i_{\mathrm{Red,L}}-i} \tag{29}$$

The Eq.(29) above is the same expression as Eq.(19).

The $i_{\mathrm{a}}(i)$ and $i_{\mathrm{c}}(i)$ as functions of i are directly obtained when $E(i)=E_{\mathrm{a}}(i_{\mathrm{a}})$ and $E(i)=E_{\mathrm{c}}(i_{\mathrm{c}})$:

$$\left\{\begin{aligned}
&i_{\mathrm{a}}(i)=\frac{i_{\mathrm{Red,L}}(i-i_{\mathrm{Ox}^{z+},\mathrm{L}})}{i_{\mathrm{Red,L}}-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\left(=i_0+\frac{i_{\mathrm{Red,L}}}{i_{\mathrm{Red,L}}-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\,i\right) && (30)\\
&i_{\mathrm{c}}(i)=\frac{-i_{\mathrm{Ox}^{z+},\mathrm{L}}(i-i_{\mathrm{Red,L}})}{i_{\mathrm{Red,L}}-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\left(=-i_0+\frac{-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{i_{\mathrm{Red,L}}-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\,i\;=i-i_{\mathrm{a}}(i)\right) && (31)
\end{aligned}\right.$$

Because $i_0=i_{\mathrm{a}}(0)$ or $i_0=-i_{\mathrm{c}}(0)$, the i_0 is expressed as:

$$i_0=\frac{i_{\mathrm{Red,L}}(-i_{\mathrm{Ox}^{z+},\mathrm{L}})}{i_{\mathrm{Red,L}}-i_{\mathrm{Ox}^{z+},\mathrm{L}}}=\frac{1}{1/i_{\mathrm{Red,L}}+1/-i_{\mathrm{Ox}^{z+},\mathrm{L}}} \tag{32}$$

Substituting Eq. (32) into the *h*(0) in Eq. (24) gives that the i_0 in diffusion process is expressed as:

$$h(0)=\frac{R\,T}{z\,F}\left(\frac{1}{i_{\mathrm{Red,L}}}+\frac{1}{-i_{\mathrm{Ox}^{z+},\mathrm{L}}}\right)=\frac{R\,T}{z\,F}\frac{1}{i_0} \tag{33}$$

The detailed condition when the (A)-1 approximation is available is expressed as:

$$\frac{B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}}}{A+B+C} \approx \frac{B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}}}{B+C} \tag{34}$$

This can be simplified to:

$$(A \approx 0) \cup (B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}} \approx 0) \tag{35}$$

The ($A \approx 0$) has the same meaning for a large value of $k^{\emptyset}$, because $A = 1/k^{\emptyset} \approx 0$ ($\ll 1$). The arrangement of ($B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}} \approx 0$) yields the Nernst equation. This is:

$$E(0) \approx E^{\emptyset} + \frac{R\,T}{z\,F} \ln \frac{[\mathrm{Ox^{z+}}]_{\mathrm{bulk}}}{[\mathrm{Red}]_{\mathrm{bulk}}} (= E_{\mathrm{eq}}) \tag{36}$$

Thus, approximation of the (A)-1 is valid where $1 \ll k^{\emptyset}$ or $E(0) \approx E_{\mathrm{eq}}$.

(A)-2 approximation

The (A)-2 approximation is applicable in the case of reversible reactions with a diffusion process occurring in an anodic direction. The same procedures described for the (A)-1 can be applied.

The $i(\eta^{\emptyset})$ expressions are:

$$\left\{\begin{array}{ll} i(\eta^{\emptyset}) \approx \dfrac{B \cdot i_{\mathrm{Red,L}} + C \cdot i_{\mathrm{Ox^{z+},L}}}{B} (= i_{\mathrm{a}}(\eta^{\emptyset}) + i_{\mathrm{c}}(\eta^{\emptyset})) & (37) \\ i_{\mathrm{a}}(\eta^{\emptyset}) = i_{\mathrm{Red,L}} & (38) \\ i_{\mathrm{c}}(\eta^{\emptyset}) = \dfrac{C}{B}\, i_{\mathrm{Ox^{z+},L}} & (39) \end{array}\right.$$

The $E(i)$ expressions are:

$$\left\{\begin{array}{ll} E(i) = E^{\emptyset} + \dfrac{R\,T}{z\,F} \ln \dfrac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}} \dfrac{-i_{\mathrm{Ox^{z+},L}}}{i_{\mathrm{Red,L}} - i} & (40) \\ E_{\mathrm{a}}(i_{\mathrm{a}}) = \ ?\ (\text{unknown}) & (41) \\ E_{\mathrm{c}}(i_{\mathrm{c}}) = E^{\emptyset} + \dfrac{R\,T}{z\,F} \ln \dfrac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}} \dfrac{-i_{\mathrm{Ox^{z+},L}}}{-i_{\mathrm{c}}} & (42) \end{array}\right.$$

A similar expression for Eq.(23) is:

$$E_{\mathrm{c}}(i_{\mathrm{c}}) = [E(i)]_{\substack{i_{\mathrm{Red,L}}\to 0 \\ i=i_{\mathrm{c}}}} \tag{43}$$

Unfortunately, the $E_{\mathrm{a}}(i_{\mathrm{a}})$ cannot be expressed.

The *h*(*i*) expressions are:

$$\left\{\begin{aligned}
&h(i) = \frac{R\,T}{z\,F}\,\frac{1}{i_{\mathrm{Red,L}}-i} && (44)\\
&h_{\mathrm{a}}(i_{\mathrm{a}}) = \frac{1}{\mathrm{d}i_{\mathrm{a}}/\mathrm{d}E_{\mathrm{a}}(i_{\mathrm{a}})}, \text{ then} && (45)\\
&\qquad\quad = \frac{1}{\mathrm{d}i_{\mathrm{Red,L}}/\mathrm{d}E_{\mathrm{a}}(i_{\mathrm{a}})} \to \frac{1}{0} \to \infty && (46)\\
&h_{\mathrm{c}}(i_{\mathrm{c}}) = \frac{\mathrm{d}E_{\mathrm{c}}(i_{\mathrm{c}})}{\mathrm{d}i_{\mathrm{c}}} = \frac{R\,T}{z\,F}\,\frac{1}{-i_{\mathrm{c}}} && (47)
\end{aligned}\right.$$

Applying the previous procedures of Eqs. (27) - (29) to the *h*(*i*), the *E*(*i*) can be solved under the initial condition of (0, *E*(0)) . This solution is:

$$\int_{E(0)}^{E(i)} \mathrm{d}E = \frac{R\,T}{z\,F}\int_0^i \frac{1}{i_{\mathrm{Red,L}}-i}\,\mathrm{d}i \tag{48}$$

Then,

$$E(i) = E(0) + \frac{R\,T}{z\,F}\ln\frac{i_{\mathrm{Red,L}}}{i_{\mathrm{Red,L}}-i} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}}\,\frac{-i_{\mathrm{Ox^{z+},L}}}{i_{\mathrm{Red,L}}-i} \tag{49}$$

The Eq.(49) above is the same expression as Eq.(40). The $i_{\mathrm{a}}(i)$ and $i_{\mathrm{c}}(i)$ expressions are:

$$\left\{\begin{aligned}
&i_{\mathrm{a}}(i) = i_{\mathrm{Red,L}} && (50)\\
&i_{\mathrm{c}}(i) = i - i_{\mathrm{a}}(i) = i - i_{\mathrm{Red,L}} && (51)
\end{aligned}\right.$$

The i_0 and $h(0)$ are:

$$i_0 = i_{\mathrm{a}}(0) = -i_{\mathrm{c}}(0) = i_{\mathrm{Red,L}} \tag{52}$$

$$h(0) = \frac{R\,T}{z\,F}\,\frac{1}{i_{\mathrm{Red,L}}} = \frac{R\,T}{z\,F}\,\frac{1}{i_0} \tag{53}$$

It is interesting to note that the i_0 and $h(0)$ in the (A)-2 correspond to the special state of $i_{\mathrm{Red,L}}/-i_{\mathrm{Ox^{z+},L}} \ll 1$ in the (A)-1approximation.

The condition where the (A)-2 approximation comes into effect occurs when:

$$\frac{B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}}}{A+B+C} \approx \frac{B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}}}{B} \tag{54}$$

Equation (54) can be simplified to:

$$(A\ + C \approx 0)\ \cup (B\, i_{\mathrm{Red,L}} +\ C\, i_{\mathrm{Ox^{z+},L}} \approx 0) \tag{55}$$

The expression $(B\, i_{\mathrm{Red,L}} +\ C\, i_{\mathrm{Ox^{z+},L}} \approx 0)$ is the Nernst equation. When $1/\, k^{\emptyset} \approx 0$, the detail of $(A\ + C \approx 0\ )$ is:

$$1/\, k^{\emptyset} + \exp\!\left(\, -f_{\mathrm{c}}\, \eta^{\emptyset}\, \right) /\, k_{\mathrm{Ox}} \approx \exp\!\left(\, -f_{\mathrm{c}}\, \eta^{\emptyset}\, \right) /\, k_{\mathrm{Ox}} \approx 0\ (\ll 1) \tag{56}$$

Hence, the (A)-2 approximation will be valid for the following condition:

$$\eta^{\emptyset} > \frac{-R\, T}{\beta\, z\, F} \ln k_{\mathrm{Ox}} \left(= \frac{-R\, T}{z\, F} \ln k_{\mathrm{Ox}}\right) \ \text{or}\ \ E \approx E_{\mathrm{eq}}. \tag{57}$$

(A)-3 approximation

The (A)-3 approximation is applicable in the case of reversible reactions with diffusion control phenomena occurring in a cathodic direction.

The $i(\eta^{\emptyset})$ expressions are:

$$\left\{\begin{aligned} & i(\eta^{\emptyset}) \approx \frac{B\, i_{\mathrm{Red,L}} + C\, i_{\mathrm{Ox^{z+},L}}}{C} \left(= i_{\mathrm{a}}(\eta^{\emptyset}) + i_{\mathrm{c}}(\eta^{\emptyset})\right) && (58) \\ & i_{\mathrm{a}}(\eta^{\emptyset}) = \frac{B}{C}\, i_{\mathrm{Red,L}} && (59) \\ & i_{\mathrm{c}}(\eta^{\emptyset}) = i_{\mathrm{Ox^{z+},L}} && (60) \end{aligned}\right.$$

The $E(i)$ expressions are:

$$
\begin{cases}
E(i) = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}}\,\frac{i - i_{\mathrm{Ox^{z+},L}}}{i_{\mathrm{Red,L}}} & (61) \\[2ex]
E_{\mathrm{a}}(i_{\mathrm{a}}) = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox^{z+}}}}\,\frac{i_{\mathrm{a}}}{i_{\mathrm{Red,L}}} & (62) \\[2ex]
E_{\mathrm{c}}(i_{\mathrm{c}}) = \ ?\ (\mathrm{unknown}) & (63)
\end{cases}
$$

The same procedure gives us the $E_{\mathrm{a}}(i_{\mathrm{a}})$ expression:

$$
E_{\mathrm{a}}(i_{\mathrm{a}}) = [E(i)]_{\substack{i_{\mathrm{Ox^{z+},L}} \to 0 \\ i = i_{\mathrm{a}}}} \tag{64}
$$

The $h(i)$ expressions are:

$$
\begin{cases}
h(i) = \frac{R\,T}{z\,F}\,\frac{1}{i - i_{\mathrm{Ox^{z+},L}}} & (65) \\[2ex]
h_{\mathrm{a}}(i_{\mathrm{a}}) = \frac{\mathrm{d}E(i_{\mathrm{a}})}{\mathrm{d}i_{\mathrm{a}}} = \frac{R\,T}{z\,F}\,\frac{1}{i_{\mathrm{a}}} & (66) \\[2ex]
h_{\mathrm{c}}(i_{\mathrm{c}}) = \frac{\mathrm{d}E_{\mathrm{c}}(i_{\mathrm{c}})}{\mathrm{d}i_{\mathrm{c}}} = \frac{1}{\mathrm{d}i_{\mathrm{c}}/\mathrm{d}E_{\mathrm{c}}(i_{\mathrm{c}})},\ \text{then} & \\[2ex]
\qquad = \frac{1}{\mathrm{d}i_{\mathrm{Ox^{z+},L}}/\mathrm{d}E_{\mathrm{c}}(i_{\mathrm{c}})} \to \frac{1}{0} \to \infty & (67)
\end{cases}
$$

The $i_{\mathrm{a}}(i)$, $i_{\mathrm{c}}(i)$, i_0 and $h(0)$ are:

$$
\begin{cases}
i_{\mathrm{a}}(i) = i - i_{\mathrm{c}}(i) = i - i_{\mathrm{Ox^{z+},L}} & (68) \\[2ex]
i_{\mathrm{c}}(i) = i_{\mathrm{Ox^{z+},L}} & (69)
\end{cases}
$$

$$
i_0 = i_{\mathrm{a}}(0) = -i_{\mathrm{c}}(0) = -i_{\mathrm{Ox^{z+},L}} \tag{70}
$$

$$
h(0) = \frac{R\,T}{z\,F}\,\frac{1}{-i_{\mathrm{Ox^{z+},L}}} = \frac{R\,T}{z\,F}\,\frac{1}{i_0} \tag{71}
$$

The i_0 and $h(0)$ of the (A)-3 can be interpreted as special state of $i_{\mathrm{Red,L}}/-i_{\mathrm{Ox^{z+},L}} \gg 1$ in the (A)-1. The condition where the (A)-3 comes into effect is:

$$
\eta^{\emptyset} < \frac{R\,T}{\alpha\,z\,F}\ln\ k_{\mathrm{Red}} \left(= \frac{R\,T}{z\,F}\ln\ k_{\mathrm{Red}}\right) \quad \text{or} \quad E \approx E_{\mathrm{eq}} \tag{72}
$$

Let us now construct polarization curves for visual understanding. The numerical values used as an example are z =2, $i_{\mathrm{Red,L}} = 1\ \mathrm{mA\ cm^{-2}}$ and $i_{\mathrm{Ox^{z+},L}} = -100\ \mathrm{mA\ cm^{-2}}$. The $E \sim \log|\ i\ |$ curve is shown in Fig.1(a). The $E(i)$ curve has asymptotes of $i = 1\ \mathrm{mA\ cm^{-2}} (= i_{\mathrm{Red,L}})$ and $i = -100\ \mathrm{mA\ cm^{-2}} (= i_{\mathrm{Ox^{z+},L}})$. The intersection of the branch curves for $E_{\mathrm{a}}(i_{\mathrm{a}})$ and $E_{\mathrm{c}}(i_{\mathrm{c}})$ indicates the i_0. Its value can be read to approximately $1\ \mathrm{mA\ cm^{-2}}$. The algebraic estimation using Eq. (32) is:

$$i_0 = \frac{1}{1/(1\ \mathrm{mA\ cm^{-2}}) + 1/(100\ \mathrm{mA\ cm^{-2}})} = 0.99\ \mathrm{mA\ cm^{-2}} \approx 1\ \mathrm{mA\ cm^{-2}} \tag{73}$$

It is shown that the calculated value of i_0 is almost same as the value read from the graph. In this case, a direct reading of $i_0 \approx i_{\mathrm{Red,L}} (= 1\ \mathrm{mA\ cm^{-2}})$ is acceptable due to the small ratio of $i_{\mathrm{Red,L}} / -i_{\mathrm{Ox^{z+},L}} (= 1\ \mathrm{mA\ cm^{-2}} / +100\ \mathrm{mA\ cm^{-2}} = 0.01) \ll 1$. The $\log h \sim \log|\ i\ |$ curve is shown in Fig. 1(b). The $h(i)$ curve has two vertical lines at $i_{\mathrm{a}} = i_{\mathrm{Red,L}}$ and $i_{\mathrm{c}} = i_{\mathrm{Ox^{z+},L}}$. Since the $h(i)$ curve approaches a horizontal line at a low current range of $|i| \leq 0.001\ \mathrm{mA\ cm^{-2}}$, we can accept that $h(0.001\ \mathrm{mA\ cm^{-2}}) \approx h(0\ \mathrm{mA\ cm^{-2}})$. Visual reading of the $h(0)$ is $\approx 0.013\ \mathrm{k\Omega\ cm^2}$. Therefore, the algebraic estimation of i_0 using Eq. (33) is:

$$i_0 \approx \frac{(8.31\ \mathrm{kJ\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{(2)(96.5\times10^3 \mathrm{A\ s\ mol^{-1}})} \frac{1}{0.013\ \mathrm{k\Omega\ cm^2}} = 1\ \mathrm{mA\ cm^{-2}} \tag{74}$$

The close agreement between the estimations for Eq.(73) and Eq.(74) firmly establish that the graphical reading of $h(i)$ provides an easy and simple way to obtain the i_0.

2.3 Approximation shortcuts

Even without the complicated procedures described in section 2.2, we can deduce the *E*(*i*) from the Nernst equation. Before the explanation of this shortcut, it is necessary to understand common criteria underlying all the approximations. Common algebraic criteria for A approximations are:

(I): $E_{\mathrm{eq}} = E(0)$ is satisfied in all approximations.

(II): The $E(i)$, $E_{\mathrm{a}}(i_{\mathrm{a}})$, $E_{\mathrm{c}}(i_{\mathrm{c}})$ and i_0 expressions include none of α and β (or $\alpha = 1$ and $\beta = 1$).

(III): The $h(i)$, $h_{\mathrm{a}}(i_{\mathrm{a}})$ and $h_{\mathrm{c}}(i_{\mathrm{c}})$ expressions also include none of α and β (or $\alpha = 1$ and $\beta = 1$).

The common geometric criteria are:

(IV): The $\log h \sim \log|\, i\,|$ curves show a constant horizontal line at $i \approx 0$.

The common (I) provides us with some ideas: (a) there may be a simple procedure to obtain *E*(*i*); (b) *E*(*i*) also satisfies the relation of $E(0) = E_{\mathrm{eq}}$, which is probably a starting formula; and (c) *E*(*i*) must have a mathematical formula with a logarithm function. Taking these common criteria into consideration, *E*(*i*) should be expressed as:

$$E(i) = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{\mathrm{z}+}]}{[\mathrm{Red}]} \tag{75}$$

The $[\mathrm{Ox}^{\mathrm{z}+}]$ and [Red] are functions of *i*, and their variable domains are limited to:

$$\begin{cases} [\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{el}} \leq [\mathrm{Ox}^{\mathrm{z}+}] \leq [\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{bulk}} & (76) \\ [\mathrm{Red}]_{\mathrm{el}} \leq [\mathrm{Red}] \leq [\mathrm{Red}]_{\mathrm{bulk}} & (77) \end{cases}$$

Equation (75) changes to the Nernst equation when $[\mathrm{Ox}^{\mathrm{z}+}] = [\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{bulk}}$ and $[\mathrm{Red}] =$

$[\mathrm{Red}]_{\mathrm{bulk}}$:

$$[E(i)]_{\substack{[\mathrm{Red}]=[\mathrm{Red}]_{\mathrm{bulk}}\\ [\mathrm{Ox}^{\mathrm{z}+}]=[\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{bulk}}}} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{bulk}}}{[\mathrm{Red}]_{\mathrm{bulk}}} = E_{\mathrm{eq}} \qquad (78)$$

(A)-1 approximation

The diffusion phenomena play important roles in the (A) approximations. The $[\mathrm{Ox}^{\mathrm{z}+}]$ and $[\mathrm{Red}]$ should be expressed as $[\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{el}}$ and $[\mathrm{Red}]_{\mathrm{el}}$, because the (A) approximation is under the control of the diffusion phenomena. They are obtained by arranging Eq.(s4) and Eq.(s5) shown in the list of symbols. This shortcut is obtained by solving the following simultaneous equations:

$$\begin{cases} E(i) = E^{\emptyset} + \dfrac{R\,T}{z\,F}\ln\dfrac{[\mathrm{Ox}^{\mathrm{z}+}]}{[\mathrm{Red}]} & (75) \\[2ex] [\mathrm{Red}] = [\mathrm{Red}]_{\mathrm{el}} = \dfrac{i_{\mathrm{Red,L}}-i}{z\,Fk_{\mathrm{Red}}} & (79) \\[2ex] [\mathrm{Ox}^{\mathrm{z}+}] = [\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{el}} = \dfrac{i-i_{\mathrm{Ox}^{\mathrm{z}+},\mathrm{L}}}{z\,Fk_{\mathrm{Ox}^{\mathrm{z}+}}} & (80) \end{cases}$$

The same Eq. (19) can be obtained through the following procedure:

$$\begin{aligned} E(i) &= E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{\mathrm{z}+}]}{[\mathrm{Red}]} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{el}}}{[\mathrm{Red}]_{\mathrm{el}}} \\ &= E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{i-i_{\mathrm{Ox}^{\mathrm{z}+},\mathrm{L}}}{z\,Fk_{\mathrm{Ox}^{\mathrm{z}+}}}\,\frac{z\,Fk_{\mathrm{Red}}}{i_{\mathrm{Red,L}}-i} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox}^{\mathrm{z}+}}}\,\frac{i-i_{\mathrm{Ox}^{\mathrm{z}+},\mathrm{L}}}{i_{\mathrm{Red,L}}-i} \qquad (81) \end{aligned}$$

(A)-2 Approximation

The (A)-2 approximation results in a diffusion phenomenon occurring in an anodic direction. A similar procedure to that described in (A)-1 leads us to the same expression as Eq. (40).

$$\begin{cases} E(i) = E^{\emptyset} + \dfrac{R\,T}{z\,F}\ln\dfrac{[\mathrm{Ox}^{\mathrm{z}+}]}{[\mathrm{Red}]} & (75) \\[2ex] [\mathrm{Red}] = [\mathrm{Red}]_{\mathrm{el}} = \dfrac{i_{\mathrm{Red,L}}-i}{z\,Fk_{\mathrm{Red}}} & (79) \\[2ex] [\mathrm{Ox}^{\mathrm{z}+}] = [\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{el}} = [\mathrm{Ox}^{\mathrm{z}+}]_{\mathrm{bulk}} = \dfrac{-i_{\mathrm{Ox}^{\mathrm{z}+},\mathrm{L}}}{z\,Fk_{\mathrm{Ox}^{\mathrm{z}+}}} & (82) \end{cases}$$

Then,

$$E(i) = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{z+}]}{[\mathrm{Red}]} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{z+}]_{\mathrm{bulk}}}{[\mathrm{Red}]_{\mathrm{el}}}$$

$$= E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{z\,Fk_{\mathrm{Ox}^{z+}}}\frac{z\,Fk_{\mathrm{Red}}}{i_{\mathrm{Red,L}}-i} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox}^{z+}}}\frac{-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{i_{\mathrm{Red,L}}-i} \tag{83}$$

(A)-3 Approximation

Using the same procedure, we can easily obtain;

$$\left\{\begin{array}{ll} E(i) = E^{\emptyset} + \dfrac{R\,T}{z\,F}\ln\dfrac{[\mathrm{Ox}^{z+}]}{[\mathrm{Red}]} & (75) \\[2ex] [\mathrm{Red}] = [\mathrm{Red}]_{\mathrm{el}} = [\mathrm{Red}]_{\mathrm{bulk}} = \dfrac{i_{\mathrm{Red,L}}}{z\,Fk_{\mathrm{Red}}} & (84) \\[2ex] [\mathrm{Ox}^{z+}] = [\mathrm{Ox}^{z+}]_{\mathrm{el}} = \dfrac{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{z\,Fk_{\mathrm{Ox}^{z+}}} & (80) \end{array}\right.$$

Then,

$$E(i) = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{z+}]}{[\mathrm{Red}]} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{[\mathrm{Ox}^{z+}]_{\mathrm{el}}}{[\mathrm{Red}]_{\mathrm{bulk}}}$$

$$= E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{z\,Fk_{\mathrm{Ox}^{z+}}}\frac{z\,Fk_{\mathrm{Red}}}{i_{\mathrm{Red,L}}} = E^{\emptyset} + \frac{R\,T}{z\,F}\ln\frac{k_{\mathrm{Red}}}{k_{\mathrm{Ox}^{z+}}}\frac{i-i_{\mathrm{Ox}^{z+},\mathrm{L}}}{i_{\mathrm{Red,L}}} \tag{85}$$

We do wish to emphasize that these shortcuts offer an alternative way to express all of the $E(i)$ in the Nernst equation. Detailed procedures of how to apply these shortcuts to actual experiments will be presented in section 5.1.

Here, we discuss the relationship between the DPM approximation and the Tafel relation. Differentiating the Tafel relation expressed as $\eta = a + b\,\log|i|$, the following equation is obtained:

$$\frac{\mathrm{d}\eta}{\mathrm{d}i} = \frac{\mathrm{d}(E-E_{\mathrm{eq}})}{\mathrm{d}i} = \frac{\mathrm{d}E}{\mathrm{d}i} = h(i) = b\,\frac{\mathrm{d}\log|i|}{\mathrm{d}i} \tag{86}$$

When $i < 0$, then $|i| = -i$. The above equation is further arranged as:

$$\frac{\mathrm{d}\eta}{\mathrm{d}i} = h(i) = b\,\frac{\mathrm{d}\log|i|}{\mathrm{d}i} = \frac{b}{2.3}\frac{\mathrm{d}\ln(-i)}{\mathrm{d}i} = \frac{b}{2.3}\frac{1}{i} \tag{87}$$

The differential expression of the Tafel relation belongs to one of the $h(i)$ expressions. Since value of $\beta = 1$ in the case of reversible reaction, the above is rearranged and simplified to:

$$h(i)\ i = \frac{b}{2.3} = \frac{RT}{\beta zF} = \frac{RT}{zF}(\text{constant value}) \tag{88}$$

Comparing Eq.(88) and Eq.(53), the following inverse relation between $h(i)$ and i is obtained:

$$h(i)i = h(0)\ i_0 = \frac{RT}{zF}\ (\text{constant value}) \tag{89}$$

Although the value of i_0 cannot be directly obtained from experiments, we can calculate it using the graphical reading of the $h(0)$.

2.4 Consideration of the effect of oxide film on electrodes

In the experiments it is very important to account for the physical resistance that mainly occurs from solution resistance, oxide film, and adsorption layer resistance. These can hinder the accurate calculation of the Tafel extrapolation estimate. Hence, it is crucial that the physical resistances are calculated in a more accurate and reliable manner when reading experimental data. The DPM shows us an easy and simple way to eliminate unnecessary physical resistances. However, some caution and careful attention are needed. Since physical resistance is independent of the electrochemical phenomena, we treat the physical resistance terms as a series circuit connection to the electrochemical resistances. In experimental conditions the following expression is beneficial in the case of reversible reaction.

$$h(i) = \frac{R\,T}{z\,F}\left(\frac{1}{i_{\mathrm{Red,L}} - i} + \frac{1}{i - i_{\mathrm{Ox^{z+},L}}}\right) + \frac{l}{\kappa} \tag{90}$$

The $h(i)$ is the summation of the following three terms: $\frac{R\,T}{z\,F}\frac{1}{i_{\mathrm{Red,L}}-i}$, $\frac{R\,T}{z\,F}\frac{1}{i-i_{\mathrm{Ox^{z+},L}}}$ and $\frac{l}{\kappa}$. The contribution of each term, especially the l/κ term to the $h(i)$ shape will play a very important role to accurately and reliably estimate. The contribution becomes clear when each term is visually expressed. The $\log h(i) \sim \log|i|$ graphs plotted with a reference value of $l/\kappa = 0\ \mathrm{k\Omega\ cm^2}$ and four examples of $l/\kappa = 0.001, 0.01, 0.1$ and $1\ \mathrm{k\Omega\ cm^2}$ are shown in Fig.2. To be concrete, their numerical expressions are as follows:

$$\begin{cases} h(i) = 0.013\left(\frac{1}{1-i} + \frac{1}{i+100}\right) & (91) \\ h_1(i) = 0.013\left(\frac{1}{1-i} + \frac{1}{i+100}\right) + 0.001 & (92) \\ h_2(i) = 0.013\left(\frac{1}{1-i} + \frac{1}{i+100}\right) + 0.01 & (93) \\ h_3(i) = 0.013\left(\frac{1}{1-i} + \frac{1}{i+100}\right) + 0.1 & (94) \\ h_4(i) = 0.013\left(\frac{1}{1-i} + \frac{1}{i+100}\right) + 1 & (95) \end{cases}$$

The pink fine line of $\mathrm{d}\eta/\mathrm{d}i = h(i) = 0.013/(-i)$, on which the Tafel relation is satisfied, is also added to Fig.2 as a reference. There are some points between $h(i)$ and the Tafel relation line, but a poor line region along the line of the Tafel relation. It is extremely difficult to find the Tafel region in the case of $i_{\mathrm{Ox^{z+}},\mathrm{L}} = -100\ \mathrm{mA\ cm^{-2}}$. To make matters worse, the physical resistances make the situation more difficult: the larger value of l/κ, the more pronounced is the change in the shape of $h(i)$. It will be shown in 5.2 how to actually remove the l/κ from the $h(i)$.

3. Experimental method

3.1 Specimens

We used platinum (99.98% Pt, NILACO Ltd., Japan) working electrode wire with a diameter of 1 mm and a length of 80 mm (exposure area 2.5 $\mathrm{cm^2}$). The platinum counter electrode was a long wire with a diameter of 1mm and a length of 480mm (exposure area 15 $\mathrm{cm^2}$). The counter and working electrodes were washed with acetone and dipped into a nitric acid solution at ≈298 K (room temperature) for 300 seconds to clean their surfaces. They were subsequently rinsed thoroughly with deionized water. All electrodes were thoroughly rinsed with deionized water before the experiments.

3.2 Test solution

Chemical-grade sulfuric acid (98% H_2SO_4, Wako Pure Chemical Industries Ltd., Japan) was used. Deionized water was used to prepare the solutions. During the experiments the solutions were maintained under stagnant conditions and at an ambient temperature. The solutions were saturated with bubbling hydrogen gas (99.9999 % H_2) during the tests. In the hydrogen experiments, the electrolyte was continuously bubbled with H_2 to maintain a saturated condition under a H_2 pressure of 1 atm. The pH, dissolved oxygen (DO), and the electrical conductivity (κ) of the H_2SO_4 solution were measured. The results are listed in Table1.

3.3 Measurements

In order to have the completely same environments and the independence of the experimental operations, we used a stagnant solution and automatic voltammetry technique. An electrochemical measurement system (Hokuto Denko Inc., HZ7000, Japan) was used for the cyclic voltammetry method. As a reference electrode, an Ag/AgCl electrode (DKK-TOA Co., HS-305D, Japan) in a saturated potassium chloride solution was used. In this paper, the electrode potential related to the Ag/AgCl reference electrode (V vs. SSE) is simplified as V unless otherwise noted. The distance between the working and reference electrodes was 1 cm or less. The polarization curves were not corrected for *iR* drop. For the polarization sequence, the specimen was first kept at an open-circuit potential for 600 seconds and then cyclically polarized. A scan rate of 0.1 mV s^{-1} was selected. This rate is sufficiently slow to enable quasi-steady state conditions. Since the resulting data had a scattering tendency due to the slow scan rate operation in the stagnant solution, a smoothing treatment for the polarization curves was needed. The experimental polarization curves were mathematically smoothed using the commercial software Igor Pro 6.

4. Results

4.1 Polarization curves for platinum in H_2SO_4 solutions

The $E \sim \log|i|$ curves for the bright platinum in stagnant solutions of 0.005, 0.05 and 0.5 mol dm^{-3} H_2SO_4 were measured. A typical result from a 0.005 mol dm^{-3} H_2SO_4 solution is shown in Fig.3(a). The cyclic polarization began at the starting point (A) at approximately −0.32 V. When bubbling gas was observed on the surface at < about −0.7 V, the polarization was reversed. At point (C), the *i* changed from a negative to a positive value. Far beyond point (C), the anodic current reached a saturation value of (D). The second route for the points (E)-(F)-(G)-(H)-(I) showed almost the same route as that of the first route. The cyclic $E \sim \log|i|$ curves for 0.05 and 0.5 mol dm^{-3} H_2SO_4 solutions were measured and are shown in figures 3(b) and 3(c), respectively. Their polarization curves also showed a similar tendency to that of Fig.3; there is an anodic current saturation region observed on the anodic branch curve. We would emphasize that a noticeable current vibration was only observed on the anodic branch curve and not on the cathodic branch curve even in the same solution. Comparing the three curves, the anodic current vibration is most clearly seen in the stronger acid solution in Fig.3(c).

4.2 Polarization resistance curve

The regions of (B)-(C)-(D) in figures 3(a), 3(b), and 3(c) were differentiated by i. Their $h(i)$ curves were changed into a form of $\log h \sim \log |i|$ and shown in Fig.4(a), Fig.4(b) and Fig.4(c), respectively. Each of the $h(i)$ curves maintained an anodic vertical line. The relationship between the anodic vertical line current and the pH value are plotted in Fig.5. The anodic current values for 0.005 and 0.5 mol dm^{-3} H_2SO_4 solutions were around 0.5 mA cm^{-2}. The value for the 0.05 mol dm^{-3} H_2SO_4 solution is 0.3~0.4 mA cm^{-2}. To approximate, the anodic vertical line is independent of the solution pH

5. Discussion

5.1 Determination of i_0 by the DPM

We already know that the *her* of bright platinum in an acidic solution falls into the category of a reversible reaction [1]-[4]. This reaction is expressed as follows:

$$2H^+ + 2e^- \rightleftarrows H_2 \uparrow \qquad (96)$$

The limited solubility of H_2 gas in aqueous solutions suggests that the *her* is probably controlled by the diffusion of the H_2 gas. The DPM tells us that all of the experimental results shown in Fig.3(a)~Fig.3(c) and Fig.4(a)~Fig.4(c) indicated geometrical common characteristics of the reversible reaction. In addition, all of the results belong to the (A) approximation, particularly the

(A)-2 approximation due to the existence of a single anodic vertical line. The (A)-2 approximation tells us that the vertical line appearing on the anodic branch curve exactly corresponds to the $\mathrm{H_2}$ limiting diffusion phenomena. Therefore, the notation of z, Ox^{z+}, and Red corresponds to the actual indication of 2, H^{+}, and $\mathrm{H_2}$, respectively. Figure 5 shows that the anodic vertical currents in the H_2SO_4 solutions are around $0.5\ \mathrm{mA\ cm^{-2}}$. Hence, the actual relation of Eq. (52) is:

$$i_0 = i_{\mathrm{Red,L}} = i_{\mathrm{H_2,L}} = 0.5\ \mathrm{mA\ cm^{-2}} \tag{97}$$

The value of i_0=0.5 $\mathrm{mA\ cm^{-2}}$ in the stagnant environment corresponds to the results obtained in previously published experimental studies [1].

Other equations derived from the DPM can offer further supporting evidence. Equation (53) in the A-(2) provides a simple means for determining the i_0. Applying the Eq.(53) to an experimental data of $h(0) = 0.03\ \mathrm{k\Omega\ cm^2}$ in a 0.5 mol dm^{-3} H_2SO_4 solution which is less hindered by solution resistance:

$$i_0 = \frac{R\,T}{z\,F}\frac{1}{h(0)} = \frac{0.026\ \mathrm{V}}{(2)(0.03\ \mathrm{k\Omega\ cm^2})} = 0.43\ \mathrm{mA\ cm^{-2}} \tag{98}$$

An estimation of the physical resistance allows us to determine a more reliable and accurate value of the i_0. The l/κ value, which shows the distinctive horizontal line in Fig.4(c), is obtained using the following equation:

$$l/\kappa \lesssim \lim_{i\to -20\sim -100\ \mathrm{mA\ cm^{-2}}} h(i) \approx 0.003\sim 0.004\ \mathrm{k\Omega\ cm^2} \tag{99}$$

The modified Eq.(98) leads to a more correct value:

$$i_0 = \frac{R\,T}{z\,F}\frac{1}{h(0)-l/\kappa} = \frac{0.026\ \mathrm{V}}{(2)(0.03\ \mathrm{k\Omega\ cm^2} - 0.003\sim 0.004\ \mathrm{k\Omega\ cm^2})} = 0.48\sim 0.5\ \mathrm{mA\ cm^{-2}} \tag{100}$$

We see that the revised value agrees more closely with the value of $i_{\mathrm{H_2,L}} \approx 0.5\ \mathrm{mA\ cm^{-2}}$. When the large influence of l/κ on the $h(0)$ is observed in Fig.4(a) and Fig.4(b), which was already discussed in Fig.2, further revisions are not necessary. For instance, the i_0 in Fig.4(a) is calculated using $l/\kappa \approx 0.4\ \mathrm{k\Omega\ cm^2}$:

$$i_0 = \frac{R\,T}{z\,F}\,\frac{1}{h(0)-l/\kappa} = \frac{0.026\ \mathrm{V}}{(2)(0.3\ \mathrm{k\Omega\ cm^2} - 0.4\ \mathrm{k\Omega\ cm^2})} = -0.13\ \mathrm{mA\ cm^{-2}} \tag{101}$$

An answer of $i_0 < 0\ \mathrm{mA\ cm^{-2}}$ is utterly inconceivable. The i_0 in Fig.4(b) is similarly calculated:

$$i_0 = \frac{0.026\ \mathrm{V}}{(2)(0.08\ \mathrm{k\Omega\ cm^2} - 0.02\ \mathrm{k\Omega\ cm^2})} \approx 0.22\ \mathrm{mA\ cm^{-2}} \tag{102}$$

The value of $i_0 = 0.22\ \mathrm{mA\ cm^{-2}}$ is almost half the value of the $i_{\mathrm{H_2,L}}$. These misleading results are due to the unintended effects of the physical resistance such as the solution resistance or the oxide film. These effects are usually not compensated for in normal measurements.

The shortcut discussed in 2.3 gives us another specific way to determine the i_0. We can do this by simultaneously solving the following equations:

$$\left\{\begin{aligned} &E(i) = E^{\emptyset} + \frac{R\,T}{2\,F}\ln\frac{[\mathrm{H^+}]^2}{[\mathrm{H_2}]} && (103)\\ &[\mathrm{H_2}] = [\mathrm{H_2}]_{\mathrm{el}} = \frac{i_{\mathrm{H_2,L}} - i}{2Fk_{\mathrm{H_2}}} && (104)\\ &[\mathrm{H^+}] = [\mathrm{H^+}]_{\mathrm{bulk}} = \frac{-i_{\mathrm{H^+,L}}}{Fk_{\mathrm{H^+}}} && (105)\end{aligned}\right.$$

Then,

$$E(i) = E^{\emptyset} + \frac{R\,T}{2\,F}\ln\left(\frac{-\,i_{\mathrm{H^+,L}}}{Fk_{\mathrm{H^+}}}\right)^2\left(\frac{2Fk_{\mathrm{H_2}}}{i_{\mathrm{H_2,L}} - i}\right) = E^{\emptyset} + \frac{R\,T}{2\,F}\ln\frac{2k_{\mathrm{H_2}}}{F}\left(\frac{-i_{\mathrm{H^+,L}}}{k_{\mathrm{H^+}}}\right)^2\frac{1}{i_{\mathrm{H_2,L}} - i} \tag{106}$$

To directly determine $E_c(i_c)$ from $E(i)$, we can use Eq. (43):

$$E_{\mathrm{c}}(i_{\mathrm{c}}) = [E(i)]_{\substack{i_{\mathrm{H_2,L}} \to 0\\ i = i_{\mathrm{c}}}} \tag{107}$$

Then,

$$E_{\mathrm{c}}(i_{\mathrm{c}}) = E^{\emptyset} + \frac{R\,T}{2\,F}\ln\frac{2k_{\mathrm{H_2}}}{F}\left(\frac{-i_{\mathrm{H^+,L}}}{k_{\mathrm{H^+}}}\right)^2\frac{1}{-i_{\mathrm{c}}} = E^{\emptyset} + \frac{R\,T}{2\,F}\ln\left(2Fk_{\mathrm{H_2}}[\mathrm{H^+}]^2_{\mathrm{bulk}}\frac{1}{-i_{\mathrm{c}}}\right) \tag{108}$$

At $E_{\mathrm{eq}},\ E(0) = E_{\mathrm{c}}(-i_0)$:

$$E^{\emptyset} + \frac{R\,T}{2\,F}\ln\frac{2k_{\mathrm{H_2}}}{F}\left(\frac{-i_{\mathrm{H^+,L}}}{k_{\mathrm{H^+}}}\right)^2\frac{1}{i_{\mathrm{H_2,L}}} = E^{\emptyset} + \frac{R\,T}{2\,F}\ln\left(2Fk_{\mathrm{H_2}}[\mathrm{H^+}]^2_{\mathrm{bulk}}\frac{1}{i_0}\right) \tag{109}$$

Then,

$$i_0 = i_{\mathrm{H_2,L}} \tag{110}$$

The completely same equation as Eq.(97) was obtained using the above shortcut. Hence, this is a very advantageous and very easy technique for directly obtaining the i_0 from the Nernst equation.

5.2 The relationship between the Tafel extrapolation method and the DPM

The Tafel extrapolation method is widely used for determining the i_0 for *her*. When the η is plotted against the logarithm for i, the Tafel relation is obtained. Plotting $\log|i|$ against η will give *b* from the slope and *a* where they intersect. Under ideal conditions, the Tafel method is a powerful tool for determining electrochemical parameters, but there are many practical requirements that must be understood before this method can be used successfully. First of all, it is essential that we know the region exactly satisfied the Tafel linear relation when accurately applying the Tafel extrapolation method. In order to obtain more accurate data, the Tafel region must extend over a current range of at least one order of magnitude. In an hydrogen electrode reaction system, this cannot always be achieved because of interference from diffusion phenomena and the effects of various physical properties. As previously mentioned, the Tafel extrapolation method is often inapplicable for the determination of i_0 in a reversible *her*. However, the DPM offers a possible way to determine the i_0 value from a reading of the *h*(0). Furthermore, agreement between the experimental $E(i)$ and theoretical $E(i)$ which is obtained from the differential equation of Eq.(44) confirms the validity of this method. The theoretical $E(i)$ curve by solving the differential equation at the initial condition was (0, -0.22 V) is obtained as follows :

$$\int_{-0.22\ \mathrm{V}}^{E(i)} \mathrm{d}E \ = \int_0^i \left(\frac{0.026}{2}\frac{1}{i_{\mathrm{H_2,L}}-i} + l/\kappa\right)\mathrm{d}i = 0.013\int_0^i \frac{1}{0.5-i}\mathrm{d}i + \int_0^i 0.004\ \mathrm{d}i \tag{112}$$

Then,

$$E(i) = -0.22 + \ 0.013\ln\frac{0.5}{0.5-i} + 0.004\ i \tag{113}$$

The dark red colored $E(i)$ curve calculated from the above equation is drawn on the experimental curve region of (B)-(C)-(D) in Fi.g.3(c). The result is shown in Fig.6. This added confirmation that the theoretical $E(i)$ curve almost clearly overlaps at $i \approx 0\ \mathrm{mA\ cm^{-2}}$ with the experimental $E(i)$ curve is valid evidence of the usefulness of the DPM.

6. Conclusion

We measured the polarization curves of bright platinum in three stagnant solutions of 0.005, 0.05 and 0.5 mol dm^{-3} H_2SO_4. We developed a new method which is named the differential polarization method (DPM), and through which we obtained characteristics of the polarization resistance curve by differentiating the experimental polarization curve. The DPM showed that the exchange current density of hydrogen evolution reaction in an acid solution is equivalent to the anodic limiting current density. This can be visually ascertained by reading from a graph of an anodic vertical line on the polarization resistance curve. The DPM also shows that the hydrogen evolution reaction in the H_2SO_4 solutions was a reversible reaction and its i_0 was approximately 0.5 mA cm^{-2}, which is the limiting diffusion current density of hydrogen gas. We believe that the DPM has the potential to become a useful analytical tool in the determination of electrochemical parameters.

(List of symbols used)

E_{eq} is the equilibrium electrode potential (V vs. SHE).

E^{0} is the standard electrode potential (V vs. SHE).

$E^{\emptyset}$ is the formal electrode potential (V vs. SHE).

$$E^{\emptyset} = E^{0} + \frac{R\,T}{z\,F} \ln \frac{y_{\mathrm{Ox}^{z+}}}{y_{\mathrm{Red}}} \tag{s1}$$

$\{\mathrm{Red}\}_{\mathrm{bulk}}$ is the activity of the reductant in a bulk solution (-).

$$\{\mathrm{Red}\}_{\mathrm{bulk}} = y_{\mathrm{Red}}\,[\mathrm{Red}]_{\mathrm{bulk}} \tag{s2}$$

$\{\mathrm{Ox}^{z+}\}_{\mathrm{bulk}}$ is the activity of the oxidant in a bulk solution (-).

$$\{\mathrm{Ox}^{z+}\}_{\mathrm{bulk}} = y_{\mathrm{Ox}^{z+}}\,[\mathrm{Ox}^{z+}]_{\mathrm{bulk}} \tag{s3}$$

y_{Red} is the activity coefficient of the Red (-).

$y_{\mathrm{Ox}^{z+}}$ is the activity coefficient of the Ox^{z+}(-).

$[\mathrm{Red}]_{\mathrm{bulk}}$ is the concentration of the Red in the bulk solution (mol dm^{-3}).

$[\mathrm{Ox}^{z+}]_{\mathrm{bulk}}$ is the concentration of the Ox^{z+} in the bulk solution (mol dm^{-3}).

$[\mathrm{Red}]_{\mathrm{el}}$ is the concentration of the Red near the electrode surface (mol dm^{-3}).

$$[\mathrm{Red}]_{\mathrm{el}} = \left(1 - \frac{i}{i_{\mathrm{Red,L}}}\right)[\mathrm{Red}]_{\mathrm{bulk}} \tag{s4}$$

$[\mathrm{Ox}^{z+}]_{\mathrm{el}}$ is the concentration of the Ox^{z+} near the electrode surface (mol dm^{-3}).

$$[\mathrm{Ox}^{z+}]_{\mathrm{el}} = \left(1 - \frac{i}{i_{\mathrm{Ox}^{z+},\mathrm{L}}}\right)[\mathrm{Ox}^{z+}]_{\mathrm{bulk}} \tag{s5}$$

z is the number of electrons transferred (-).

F is the Faraday's constant ($F = 96.5 \times 10^{3}$ A s mol^{-1}).

R is the gas constant ($R = 8.31$ J mol^{-1} K^{-1}).

T is the absolute temperature (K).

$i(\eta)$ is the net current density as a function of the overvoltage (mA cm^{-2}).

η is the overvoltage between an applied potential E, and the E_{eq} $(\eta = E - E_{\mathrm{eq}})$ (V).

$\eta^{\emptyset}$ is the overvoltage according to the standard $E^{\emptyset}$ $\left(\eta^{\emptyset} = E - E^{\emptyset}\right)$ (V).

i_0 is the exchange current density (mA cm^{-2}).

f_a is α z F/RT (V^{-1}).

f_c is β z F/RT (V^{-1}).

$i_{\mathrm{Red,L}}$ is the limiting diffusion current density of the Red, (mA cm^{-2}).

$i_{\mathrm{Ox^{z+},L}}$ is the limiting diffusion current density of the $\mathrm{Ox^{z+}}$, (mA cm^{-2}).

The relations and details are shown as follows:

$$\begin{cases} i_{\mathrm{Red,L}} = zF\,\dfrac{D_{\mathrm{Red}}}{\delta_{\mathrm{Red}}}[\mathrm{Red}]_{\mathrm{bulk}} = zF\,k_{\mathrm{Red}}[\mathrm{Red}]_{\mathrm{bulk}} & \text{(s6)} \\ i_{\mathrm{Ox^{z+},L}} = -zF\,\dfrac{D_{\mathrm{Ox^{z+}}}}{\delta_{\mathrm{Ox^{z+}}}}[\mathrm{Ox^{z+}}]_{\mathrm{bulk}} = -zF\,k_{\mathrm{Ox^{z+}}}[\mathrm{Ox^{z+}}]_{\mathrm{bulk}} & \text{(s7)} \end{cases}$$

D_{Red} is a diffusion coefficient of the Red (cm^2 s^{-1}).

$D_{\mathrm{Ox^{z+}}}$ is a diffusion coefficient of the $\mathrm{Ox^{z+}}$ (cm^2 s^{-1}).

δ_{Red} is the Nernst diffusion layer thickness for the Red (cm).

$\delta_{\mathrm{Ox^{z+}}}$ is the Nernst diffusion layer thickness for the $\mathrm{Ox^{z+}}$(cm).

k_{Red} is the rate constant of the Red (cm s^{-1}).

$k_{\mathrm{Ox^{z+}}}$ is the rate constant of the $\mathrm{Ox^{z+}}$ (cm s^{-1})

i_a is the anodic branch current density (mA cm^{-2}).

i_c is the cathodic branch current density $(\mathrm{mA\ cm^{-2}})$.

i is the net current density $(i = i_\mathrm{a} + i_\mathrm{c})$ $(\mathrm{mA\ cm^{-2}})$.

$h_\mathrm{a}(i_\mathrm{a})$ is the anodic branch polarization resistance (kΩ cm^2).

$h_\mathrm{c}(i_\mathrm{c})$ is the cathodic branch polarization resistance (kΩ cm^2).

l/κ is the polarization resistance for the physical resistances containing the solution resistance and oxide film (kΩ cm^2).

l is the thickness of the physical resistances containing the solution resistance and oxide film (cm).

κ is the conductivity of the physical resistances containing the solution resistance and oxide film ((kΩ cm)$^{-1}$).

It is necessary to confirm that the units used in this paper belong to a coherent system of units. A physical quantity is expressed as the product of a numerical number and a unit of dimension. For an example, the i_0 is the product of (i_0) and $\langle \mathrm{mA\ cm^{-2}} \rangle$. Here, the character shown as (i_0) in parenthesis is numerical number. For instance, equation (5) is verified as follows:

Physical expression:

$$\frac{i_0}{z\,F\,k^{\emptyset}\,[\mathrm{Red}]_\mathrm{bulk}^{\beta}\,[\mathrm{Ox}^{z+}]_\mathrm{bulk}^{\alpha}} =$$

$$\frac{(i_0)\,\langle \mathrm{mA\ cm^{-2}} \rangle}{(z)\langle - \rangle\,(\mathrm{F})\langle \mathrm{A\ s\ mol^{-1}} \rangle\,(k^{\emptyset})\langle \mathrm{cm\ s^{-1}} \rangle\,\{([\mathrm{Red}]_\mathrm{bulk})\,\langle \mathrm{mol\ dm^{-3}} \rangle\,\}^{\beta}\,\{([\mathrm{Ox}^{z+}]_\mathrm{bulk})\,\langle \mathrm{mol\ dm^{-3}} \rangle\,\}^{\alpha}} = 1 \qquad \text{(s8)}$$

The physical expression is divided into the numerical expression and dimension expression. They are:

Numerical expression:

$$\frac{(i_0)}{(z)\ (\mathrm{F})\ (k^{\emptyset})\ ([\mathrm{Red}]_{\mathrm{bulk}}\ )^{\beta}\ ([\mathrm{Ox}^{z+}]_{\mathrm{bulk}}\ )^{\alpha}} = 1 \tag{s9}$$

Dimension expression:

$$\frac{\langle \mathrm{mA\ cm^{-2}} \rangle}{\langle - \rangle\ \langle \mathrm{A\ s\ mol^{-1}} \rangle \langle \mathrm{cm\ s^{-1}} \rangle\ \langle \mathrm{mol\ dm^{-3}} \rangle^{\beta} \langle \mathrm{mol\ dm^{-3}} \rangle^{\alpha}} = 1 \tag{s10}$$

Equation (s10) shows that the units used in this paper satisfy the requirements of a coherent system.

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