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The Differentiating Polarization Curve Technique for the Tafel Parameter Estimation

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Abstract: An experimentally obtained polarization curve for the hydrogen evolution reaction on silver in a 0.5 mol dm^{−3} solution was investigated using an electrochemical curve technique named the differential polarization method (DPM). The exchange current density estimated by the Tafel extrapolation method (TEM) and the DPM were compared and assessed from points of simple and more accurate handling. It is shown that the DPM has two advantages: (1) proper reading of the Tafel slope region and (2) elimination of the undesirable physical factors such as oxide film and solution resistance.

Keywords: hydrogen evolution reaction; exchange current density; silver electrode; electrochemical measurement; irreversible reaction

1. Introduction

Special attention has been paid to the hydrogen evolution reaction (*her*) in not only academic fields but also industrial applications such as fuel cell research, battery development, and corrosion engineering. From an engineering standpoint, the major interest has been in the kinetic area, especially the rate of *her*, because mass production of hydrogen becomes a key technology to sustain the future energy society.

The kinetic *her* is usually evaluated from the exchange current density (i_0). In 1905 Tafel proposed the experimental methodology known as the Tafel extrapolation method [1]. The TEM has been widely accepted as one of the most important analytical tools for determining the i_0 . Although numerous papers and books have been published, different i_0 values have been reported [2–7]. For instance, some reports on silver electrode in the same H₂SO₄ solution environments vary from 10^{−2.7} to 10^{−4.9} mA cm^{−2}—a difference of about two orders of magnitude [4]. The i_0 for other metals also shows the same tendencies [4–7]. It is often said that some of them cannot be accurately reproduced and hence are probably unreliable [5,6]. Such inconclusiveness data may be due to individual errors and difficulties in reading the proper region when applying the TEM. In addition, it is necessary to pay more attention to the physical factors such as solution resistance and oxide film on the electrode [8–11]. Authors believe that there is a need for a more reliable technique for determining the i_0 in addition to the conventional TEM. To address this need, we have developed a technique termed the “differential polarization method (DPM)” [8]. Our previous work using the DPM reported that the i_0 for the *her* on the platinum electrode in the 0.5 mol dm^{−3} H₂SO₄ solution is limited by the amount of dissolved hydrogen. In addition, we showed that the above reaction is the same rate as the current density of the hydrogen oxidation reaction (*hor*), because the reversible reaction is the reciprocal reaction between

the *her* and the *hor* at an equilibrium state; the reaction is determined by a smaller amount of the dissolved hydrogen.

The purpose of this study is to extend the application of the DPM to an irreversible reaction from two points: (1) how to find the accurate region that satisfied the Tafel slope and (2) how to remove unnecessary physical resistances.

2. Results

2.1. Polarization Curve for Silver Electrode

An experimentally obtained polarization curve, $E_{\text{exp}}(i)$ for Ag electrode, was measured in a $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution which was continuously bubbled with H_2 gas. Typical and stationary $E_{\text{exp}} \sim \log|i|$ curves are shown in Figure 1.

Figure 1. Experimental polarization curve for Ag electrode in a moderately stirred $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution saturated with H_2 gas bubbling at about 298 K. The (A) is a starting point and (D) is a finishing point for polarization, via point (B) and (C).

First, to clean up the Ag electrode surface by H_2 bubbling, the cathodic treatment was performed from starting point (A) to point (B); this route is shown as the gray color. Around point (B), at which the vigorous hydrogen gas bubbles were observed, the polarization operation was reversed to point (C). The anodic current began to be observed around point (C). Beyond the point (C), the anodic current hardly flowed at the potential range of 0–0.4 V vs. SHE. At point (D) the polarization operation was finished. The smoothed $E_{\text{exp}}(i)$ curve between points (B) via point (C) and point (D) is also shown in Figure 1. This curve shows the red color for the anodic branch and the blue color for the cathodic branch, together with the experimental raw data of their light colors. The overlapped blue and red curves confirmed that the smoothed $E_{\text{exp}}(i)$ is representative of the experimental raw data. We can read that $E_{\text{exp}}(0) \approx -0.02 \text{ V vs. SHE}$.

2.2. Polarization Resistance Curve for Silver Electrode

The smoothed $E_{\text{exp}}(i)$ for (B)-(C)-(D) was finite-differentiated. The result for $h_{\text{exp}}(i) (= \Delta E_{\text{exp}} / \Delta i)$ was plotted in Figure 2.

The $h_{\text{exp}}(i)$ was shown as a form of $\log h - \log|i|$. For reference, an orange straight line with a gradient of $d \log h / d \log|i| = -1$ was added on the cathodic branch data. We can see that the overlaid line region exists at approximately $0.1 \text{ mA cm}^{-2} \leq |i| \leq 3 \text{ mA cm}^{-2}$. This line region is a geometric characteristic for an irreversible reaction, which will be discussed later.

Figure 2. Polarization resistance curve, $h_{\text{exp}}(i)$ obtained by differentiating the $E_{\text{exp}}(i)$ shown in Figure 1. For reference, an orange broken line with gradient of $d \log h / d \log |i| = -1$ is added. The (B), (C), and (D) correspond to that in Figure 1.

3. Discussion

3.1. Differential Form of the TEM

A single-electrode reaction shown as

is a fundamental reaction and is thermodynamically characterized by the Nernst equation. This equation will play an important role in the DPM. The E_{eq} can be expressed in two ways:

$$E_{\text{eq}} = E^0 + \frac{RT}{zF} \ln \frac{\{\text{Ox}^{z+}\}_{\text{bulk}}}{\{\text{Red}\}_{\text{bulk}}} = E^{\circ} + \frac{RT}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \quad (2)$$

In this paper, usage of the concentration rather than the activity is beneficial due to its easy accessibility to the experimental data. We also know an important kinetic relation between net current density, i and overpotential, $\eta^{\circ} (= E - E^{\circ})$ [8]:

$$i(\eta^{\circ}) = k^{\circ} \left\{ \left(\frac{i_{\text{Red,L}} - i}{k_{\text{Red}}} \right) \exp(f_a \eta^{\circ}) - \left(\frac{i - i_{\text{Ox}^{z+},L}}{k_{\text{Ox}^{z+}}} \right) \exp(-f_c \eta^{\circ}) \right\} \quad (3)$$

Arranging the above, another expression of

$$i(\eta^{\circ}) = \frac{\{\exp(f_a \eta^{\circ})/k_{\text{Red}}\} i_{\text{Red,L}} + \{\exp(-f_c \eta^{\circ})/k_{\text{Ox}^{z+}}\} i_{\text{Ox}^{z+},L}}{1/k^{\circ} + \exp(f_a \eta^{\circ})/k_{\text{Red}} + \exp(-f_c \eta^{\circ})/k_{\text{Ox}^{z+}}} = \frac{B(\eta^{\circ}) i_{\text{Red,L}} + C(\eta^{\circ}) i_{\text{Ox}^{z+},L}}{A(0) + B(\eta^{\circ}) + C(\eta^{\circ})}, \quad (4)$$

is obtained. Where, $A(0) = 1/k^{\circ} = \exp(0)/k^{\circ}$, $B(\eta^{\circ}) = \exp(f_a \eta^{\circ})/k_{\text{Red}}$ and $C(\eta^{\circ}) = \exp(-f_c \eta^{\circ})/k_{\text{Ox}^{z+}}$. From mathematical point of view, $\exp(0)(=1)$, $\exp(f_a \eta^{\circ})$ and $\exp(-f_c \eta^{\circ})$ are interpreted as weighted functions for $1/k^{\circ}$, $1/k_{\text{Red}}$, and $1/k_{\text{Ox}^{z+}}$, respectively. The term $A(0)$ related to the charge transfer process is independent of the η° . It has a constant effect of 1 on the $1/k^{\circ}$. The terms $B(\eta^{\circ})$ and $C(\eta^{\circ})$, related to the diffusion processes, have noticeable effects at $\eta^{\circ} \neq 0$. The term $B(\eta^{\circ})$ emerges in the anodic diffusion transfer process and will have an exponential influence on the $1/k_{\text{Red}}$ when the η° has a positive value. Conversely, the term $C(\eta^{\circ})$ shows the opposite effects on the $1/k_{\text{Ox}^{z+}}$ and negligible value when the η° has a positive value.

Considering the current additivity, Equation (4) can be divided into the anodic branch current density, $i_a(\eta^\circ)$ and the cathodic branch current density, $i_c(\eta^\circ)$:

$$i(\eta^\circ) = i_a(\eta^\circ) + i_c(\eta^\circ), \quad (5)$$

where, $i_a(\eta^\circ) = \frac{B(\eta^\circ)}{A(0) + B(\eta^\circ) + C(\eta^\circ)} i_{\text{Red,L}}$ and $i_c(\eta^\circ) = \frac{C(\eta^\circ)}{A(0) + B(\eta^\circ) + C(\eta^\circ)} i_{\text{Ox}^{z+},\text{L}}$.

The η° is expressed and arranged below:

$$\eta^\circ = E(i) - E^\circ = E(i) - E_{\text{eq}} + E_{\text{eq}} - E^\circ = \eta + (E_{\text{eq}} - E^\circ) \quad (6)$$

Since $\eta = 0$ is the equilibrium state, the same state using the η° expression is $\eta^\circ = E_{\text{eq}} - E^\circ$, which is equal to $\eta^\circ = \frac{R}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}}$. Therefore, the equilibrium state for Equation (5) is shown as:

$$i \left(\frac{R}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right) = i_a \left(\frac{R}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right) + i_c \left(\frac{R}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right) = 0. \quad (7)$$

Then,

$$i_a \left(\frac{R}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right) = -i_c \left(\frac{R}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right) = \frac{zF [\text{Red}]_{\text{bulk}}^{\alpha_c} [\text{Ox}^{z+}]_{\text{bulk}}^{\alpha_a}}{\frac{1}{k^\circ} + \left(\frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right)^{\alpha_a} \left\{ \frac{1}{k_{\text{Red}}} + \left(\frac{[\text{Red}]_{\text{bulk}}}{[\text{Ox}^{z+}]_{\text{bulk}}} \right) \frac{1}{k_{\text{Ox}^{z+}}} \right\}} = \frac{i_0}{1 + \left(\frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \right)^{\alpha_a} \left\{ \frac{k^\circ}{k_{\text{Red}}} + \left(\frac{[\text{Red}]_{\text{bulk}}}{[\text{Ox}^{z+}]_{\text{bulk}}} \right) \frac{k^\circ}{k_{\text{Ox}^{z+}}} \right\}} \quad (8)$$

Differentiating Equation (4), the following polarization conductance, $g(\eta^\circ)$, will be obtained:

$$g(\eta^\circ) = \frac{di}{d\eta^\circ} = \frac{\{f_a B(\eta^\circ) i_{\text{Red,L}} - f_c C(\eta^\circ) i_{\text{Ox}^{z+},\text{L}}\} \{A(0) + B(\eta^\circ) + C(\eta^\circ)\} - \{B(\eta^\circ) i_{\text{Red,L}} + C(\eta^\circ) i_{\text{Ox}^{z+},\text{L}}\} \{f_a B(\eta^\circ) - f_c C(\eta^\circ)\}}{\{A(0) + B(\eta^\circ) + C(\eta^\circ)\}^2} = \frac{f_a i_a - f_c i_c - i (f_a i_a / i_{\text{Red,L}} + f_c i_c / -i_{\text{Ox}^{z+},\text{L}})}{\{A(0) + B(\eta^\circ) + C(\eta^\circ)\}^2} \quad (9)$$

when being far-cathodically polarized ($0 \gg \eta^\circ$), the $i(\eta^\circ)$ will closely approximate to the cathodic branch current density, $i_c(\eta^\circ)$:

$$i(\eta^\circ) = i_a(\eta^\circ) + i_c(\eta^\circ) \approx i_c(\eta^\circ). \quad (10)$$

Then, Equation (9) is simplified to:

$$g(\eta^\circ) = -f_c i - i (f_c i / -i_{\text{Ox}^{z+},\text{L}}) = -f_c i (1 + i / -i_{\text{Ox}^{z+},\text{L}}) \quad (11)$$

Considering the mathematical relation between $g(\eta^\circ)$ and the polarization resistance, $h(i) (= dE/di)$, the following relations hold true.

$$\frac{di}{d\eta^\circ} \frac{d\eta^\circ}{di} = g(\eta^\circ) \frac{d(E - E^\circ)}{di} = g(\eta^\circ) \frac{dE}{di} = g(\eta^\circ) h(i) = 1 \quad (12)$$

Using the above relation, Equation (11) can be arranged to:

$$h(i) = \frac{1}{g(\eta^\circ)} = \frac{1}{f_c} \left(\frac{1}{1 + i / -i_{\text{Ox}^{z+},\text{L}}} \right) \left(\frac{1}{-i} \right) = \frac{RT}{\alpha_c z F} \left(\frac{1}{1 + i / -i_{\text{Ox}^{z+},\text{L}}} \right) \left(\frac{1}{-i} \right) \quad (13)$$

when $i / -i_{\text{Ox}^{z+},\text{L}} \approx 0$, the above is simplified to:

$$h(i) = \frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right). \quad (14)$$

Taking logarithms of the above is:

$$\log h(i) = \log \frac{RT}{\alpha_c z F} - \log(-i). \quad (15)$$

The gradient of the above is:

$$\frac{d \log h(i)}{d \log(-i)} = -1 \quad (16)$$

It is important to know that the relation of Equation (16) is valid for the Tafel equation. The reason is the following: the Tafel equation in the condition of Equation (10) is expressed as:

$$\eta = a + b \log|i| = a + b \log(-i) = a + \frac{b}{2.3} \ln(-i), \quad (i < 0) \quad (17)$$

Differentiating the above, the $h(i)$ expression for the Tafel equation is:

$$h(i) = \frac{-b}{2.3} \left(\frac{1}{-i} \right). \quad (18)$$

Taking the logarithms and the gradient of the above, the same relation of Equation (16) will be obtained. It is important to note that the $E(i)$ region that satisfies the Tafel equation (Equation (17)) always satisfies the gradient relation (Equation (16)); the reverse is also true. This is an extremely useful tool when finding the proper Tafel slope region in experimental data. Additionally, Equation (16) is always valid without the need for a knowledge of reaction types such as reversible, irreversible, or quasi-reversible reaction. Visual differences among the reaction types will come to the much understanding. First of all, in order to grasp the graphical characteristics of the reaction types, the $i(\eta^\circ)$ and $h(i)$ curves using the feasible data listed in Table 1 are drawn.

Table 1. Example data for drawings for graphical explanation of the $i(\eta^\circ)$ and $h(i)$. The symbols used here are explained in the last.

Items	$i(\eta^\circ) = \frac{B(\eta^\circ) i_{\text{Red,L}} + C(\eta^\circ) i_{\text{Ox}^{z+},\text{L}}}{A(0) + B(\eta^\circ) + C(\eta^\circ)}$			Remarks
	Reversible	Quasi-Reversible	Irreversible	
	$(k^\circ \gg k_d)$	$(k^\circ \approx k_d)$	$(k^\circ \ll k_d)$	
$k^\circ / \text{cm s}^{-1}$	10	10^{-3}	10^{-6}	Charge transfer rate constant
$k_{\text{Red}} / \text{cm s}^{-1}$	$10^{-2.7}$	$10^{-2.7}$	$10^{-2.7}$	Diffusion transfer rate constant for reductant
$k_{\text{Ox}^{z+}} / \text{cm s}^{-1}$	$10^{-2.7}$	$10^{-2.7}$	$10^{-2.7}$	Diffusion transfer rate constant for oxidant
$[\text{Red}]_{\text{bulk}} / \text{mol dm}^{-3}$	10^{-3}	10^{-3}	10^{-3}	Bulk concentration of reductant
$[\text{Ox}^{z+}]_{\text{bulk}} / \text{mol dm}^{-3}$	1	1	1	Bulk concentration of oxidant
$\alpha_a (-)$	0.3	0.3	0.3	Transfer coefficient for anodic reaction
$\alpha_c (-)$	0.7	0.7	0.7	Transfer coefficient for cathodic reaction
$z (-)$	1	1	1	
$i_{\text{Red,L}} / \text{mA cm}^{-2}$	$10^{-0.71}$	$10^{-0.71}$	$10^{-0.71}$	$i_{\text{Red,L}} = zF k_{\text{Red}} [\text{Red}]_{\text{bulk}}$
$i_{\text{Ox}^{z+},\text{L}} / \text{mA cm}^{-2}$	$-10^{2.3}$	$-10^{2.9}$	$-10^{2.9}$	$i_{\text{Ox}^{z+},\text{L}} = -zF k_{\text{Ox}^{z+}} [\text{Ox}^{z+}]_{\text{bulk}}$
$i_d / \text{mA cm}^{-2}$	$10^{-0.71}$	$10^{-0.71}$	$10^{-0.71}$	$i_d = \frac{1}{1/i_{\text{Red,L}} + 1/(-i_{\text{Ox}^{z+},\text{L}})}$
$i_0 / \text{mA cm}^{-2}$	$10^{3.9}$	$10^{0.11}$	$10^{-3.1}$	$i_0 = zF k^\circ [\text{Red}]_{\text{bulk}}^{\alpha_c} [\text{Ox}^{z+}]_{\text{bulk}}^{\alpha_a}$
$i_a(0.18 \text{ V}) / \text{mA cm}^{-2}$	$10^{-0.71}$	$10^{-0.81}$	$10^{-3.1}$	$[i_a(\eta^\circ)]_{\eta^\circ = \frac{RT}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}}} = \frac{1}{1/i_0 + 1/i_d}$
$h(0) / \text{k}\Omega \text{ cm}^2$	0.13	0.17	34	$h(0) = \frac{RT}{nF} \frac{1}{i_a(0.18 \text{ V})}$

The $i(-1.0 \text{ V} \leq \eta^\circ \leq 1.0 \text{ V})$ curves are shown in Figure 3.

Figure 3. The $i - \eta^\circ$ curves for the reversible, irreversible, and quasi-reversible reaction are shown. The numerical values used for the drawings are listed in Table 1.

We can readily distinguish the $i(\eta^\circ)$ of the irreversible reaction from others, but hardly between the reversible and quasi-reversible reaction curves. Another expression ($\log h \sim \log |i|$) of their curves, which is drawn using the same data listed in Table 1, is shown in Figure 4.

Figure 4. The $\log h \sim \log |i|$ expressions for three types of reaction (reversible, irreversible, and quasi-reversible reaction) are shown for graphical explanation; (a) overviewed and (b) detailed at $|i| \approx 10 \text{ mA cm}^{-2}$. The data used for the drawings are listed in Table 1. The orange broken line in Figure 4a is the line with $d \log h / d \log |i| = -1$, which is absolutely equivalent to the Tafel slope.

Figure 4a shows that the Tafel equation ($\eta = a + b \log(-i)$) is widely satisfied in the irreversible reaction. Figure 4b shows that the Tafel slope (the b term) is always valid for all types of reactions, because we can find the geometric evidence of the parallel curve with $d \log h / d \log |i| = -1$ in all reactions when making a close observation at $|i| \approx 10 \text{ mA cm}^{-2}$.

Comparing the Figure 3 or Figure 4a, the $\log h \sim \log |i|$ expression exhibits more clear characteristics than the usual expressions such as $i(\eta^\circ)$ and the $E(i)$ expression. Making further careful observations of Figure 4a,b leads to some geometric commons, which are summarized as follows:

(I): All of the curves show a constant horizontal line at $i \approx 0$ and have the Tafel slope when $i/i_{\text{Ox}^{z+},L} \approx 0$. Namely, it is acceptable that $h(0) \approx h(i \lesssim 10^{-4})$ and $\alpha_c z = \frac{RT}{F} \left[\left(\frac{1}{h(i)(-i)} \right) \left(\frac{1}{1+i/i_{\text{Ox}^{z+},L}} \right) \right] i/i_{\text{Ox}^{z+},L} \approx 0 = \frac{0.026}{h(i)} \left(\frac{1}{-i} \right)$.

(II): The reversible reaction (red curve) has a longer horizontal line with smaller $h(0)$.

(III): The irreversible reaction (blue curve) has a shorter horizontal line with larger $h(0)$.

(IV): Especially, there are straight lines with $d \log h / d \log |i| = -1$ in the irreversible reaction.

(V): The curve for the reversible reaction has asymptotes with vertical lines corresponding to the exact $i_{\text{Red},L}$ and $i_{\text{Ox}^{z+},L}$ ($i_{\text{pa}} = i_{\text{Red},L}$ and $i_{\text{pc}} = i_{\text{Ox}^{z+},L}$).

(VI): The quasi-reversible reaction (green curve) shows almost the same shape as the reversible reaction, except for the crossing points with near $i_{\text{Red},L}$ and $i_{\text{Ox}^{z+},L}$ ($i_{\text{pa}} < i_{\text{Red},L}$ and $|i_{\text{pc}}| > |i_{\text{Ox}^{z+},L}|$).

When arriving at a decision of the reaction type, the (IV) will be helpful to judge whether $E_{\text{exp}}(i)$ belongs to the irreversible reaction or not. To roughly determine the reaction type, let us consider the graphical relationship between the charge transfer rate constant, k° , and the diffusion transfer rate constant, k_d ($=1/k_{\text{Red}} + 1/k_{\text{Ox}^{z+}}$). Since almost all D_{Red} and $D_{\text{Ox}^{z+}}$ are the order of $\approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in an aqueous solution and practical δ_{Red} and $\delta_{\text{Ox}^{z+}}$ are $\approx 0.01 \text{ cm}$ for a stirred solution and $\approx 0.05 \text{ cm}$ for the stagnant condition, respectively; then, the k_d is roughly estimated as:

$$k_d = \frac{1}{=1/k_{\text{Red}}+1/k_{\text{Ox}^{z+}}} = \frac{1}{\delta_{\text{Red}}/D_{\text{Red}}+\delta_{\text{Ox}^{z+}}/D_{\text{Ox}^{z+}}} = \frac{D}{\delta} \approx \frac{10^{-5} \text{ cm}^2 \text{ s}^{-1}}{0.01 \sim 0.05 \text{ cm}} = 10^{-3.7} \sim 10^{-3.0} \text{ cm s}^{-1} \quad (19)$$

It may be accepted that the k_d will become less changeable and is regarded as the order of $\approx 10^{-3} \text{ cm s}^{-1}$. The total rate constant, k , for the whole reaction is introduced [10] and expressed as:

$$k = \frac{1}{1/k^\circ + 1/k_{\text{Red}} + 1/k_{\text{Ox}^{z+}}} = \frac{1}{1/k^\circ + 1/k_d} \quad (20)$$

The relation between k and k° when $k_d = 10^{-3} \text{ cm s}^{-1}$ is graphically shown in Figure 5.

Figure 5. Graphical relation between the total rate constant, k , and the charge transfer rate constant, k° , when the diffusion rate is a constant of $k_d = 10^{-3} \text{ cm s}^{-1}$.

Figure 5 tells us that the k is depend on the k° : a linear relation ($k = k^\circ$) is valid for $k^\circ \lesssim 10^{-4} \text{ cm s}^{-1}$ (the irreversible reaction) and a constant relation ($k = k_d$) is valid for $k^\circ \gtrsim 2 \times 10^{-2} \text{ cm s}^{-1}$ (the reversible reaction). Roughly speaking, it may be possible to say that the $E_{\text{exp}}(i)$ having $k \lesssim 10^{-4} \text{ cm s}^{-1}$ is classified to the irreversible reaction and that having $k \gtrsim 2 \times 10^{-2} \text{ cm s}^{-1}$ is the reversible reaction.

3.2. Physical Factors Influenced on the $h(i)$ Curve

At the stage of practical treatments of the experimental $E_{\text{exp}}(i)$, it is necessary to consider the physical factors such as solution, oxide film, and adsorption gas layer resistances [11]. Considering the oxide film polarization resistance of the cathodic site (l_c/κ_c), the Equation (14) is renewed as:

$$h(i) = \frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right) + l_c/\kappa_c. \quad (21)$$

The $h_{\text{exp}}(i)$ always contains the solution polarization resistance (l_s/κ_s):

$$h_{\text{exp}}(i) = h(i) + l_s/\kappa_s. \quad (22)$$

This l_s/κ_s usually includes, to a greater or lesser degree, the adsorption gas layer resistance under cathodic polarization operation. Arranging the Equation (22),

$$h_{\text{exp}}(i) = \frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right) + l_c/\kappa_c + l_s/\kappa_s = \frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right) + l/\kappa \quad (23)$$

is obtained; where, $l/\kappa = l_c/\kappa_c + l_s/\kappa_s$. The $h_{\text{exp}}(i)$ is a summation of the two terms: $\frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right)$ and l/κ . The first term of $\frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right)$ has information about $\alpha_c z$ and the second term of l/κ is on the physical resistances. Because the l/κ is independent of the i , it will be graphically emerged as the horizontal line when the $|i|$ becomes large. We can estimate it using the following operation [8]:

$$\lim_{|i| \rightarrow \text{large}} h_{\text{exp}}(i) = \lim_{|i| \rightarrow \text{large}} \frac{RT}{\alpha_c z F} \left(\frac{1}{-i} \right) + l/\kappa \gtrsim l/\kappa \quad (24)$$

In order to visualize the influence of the l/κ on the $h(i)$, the $\log h \sim \log |i|$ curves are drawn when $l/\kappa = 0.003, 0.03, 0.3 \text{ k}\Omega \text{ cm}^2$. The results are shown in Figure 6.

Figure 6. Influence of l/κ on the shape of the $h_{\text{exp}}(i)$ curve. There are four example curves drawn using the same data in Table 1: $h_1(i) = h^*(i) + 0 \text{ k}\Omega \text{ cm}^2$ (as a blank test), $h_2(i) = h^*(i) + 0.003 \text{ k}\Omega \text{ cm}^2$, $h_3(i) = h^*(i) + 0.03 \text{ k}\Omega \text{ cm}^2$, $h_4(i) = h^*(i) + 0.3 \text{ k}\Omega \text{ cm}^2$, where $h^*(i) = 0.087 \left(\frac{1}{1+i/200} \right) \left(\frac{1}{-i} \right)$. An orange broken line of $h(i) = 0.087/(-i)$, on which the Tafel relation is completely satisfied, is added as a reference.

The orange broken line of $h(i) = 0.087/(-i)$, on which the Tafel relation is completely satisfied, is added as a reference. We can see that the $h_1(i)$ has a wide Tafel slope region but the $h_4(i)$ has a very narrow region. Namely, we can hardly catch the Tafel slope region when the $h(i)$ has the larger l/κ . Furthermore, we can hardly catch the accurate region when the $|i_{\text{Ox}^{z+},\text{L}}|$ decreases. In other words, in order to obtain the more accurate Tafel slope region it is necessary to employ a large $[i_{\text{Ox}^{z+},\text{L}}]_{\text{bulk}}$ solution and small l/κ environments which can widen the Tafel region.

3.3. Estimation by Traditional TEM

The cathodic region of (B)-(C) in Figure 1 is shown again in Figure 7 for the traditional TEM estimation.

Figure 7. The extract $E_{\text{exp}}(i)$ from Figure 1 is shown. The tacit Tafel extrapolation method (TEM) may be applied in the green area ($E(i) \lesssim -0.14$ V vs. SHE) $\cap$ $(0.4 \text{ mA cm}^{-2} \leq |i|)$. The (B) and (C) correspond to that in Figure 1.

There are not strict rules but tacit agreements when applying the TEM: (1) the linearity of $\eta = a + b \log|i|$ should exhibit at least one decade of $|i|$; and (2) the extrapolation should start at $|\eta| \gtrsim 0.12$ V [9]). The line, l , in Figure 7, is a result of fitting trials. The current range employed for the estimation and the result are shown as:

$$0.4 \text{ mA cm}^{-2} \leq |i| \leq 4 \text{ mA cm}^{-2} : \eta = -0.21 - 0.095 \log|i|. \quad (25)$$

The i_0 calculated using the Tafel coefficient relation is shown as:

$$i_0 = 10^{-a/b} = 10^{0.21/-0.095} = 10^{-2.2} \text{ mA cm}^{-2} \quad (26)$$

The result of $10^{-2.2} \text{ mA cm}^{-2}$ showed a larger value from the research results ($10^{-2.7} \sim 10^{-3.4} \text{ mA cm}^{-2}$) [4].

3.4. Estimation by DPM

For more accurate estimation, the physical resistances should be compensated. Since Figure 2 shows no vertical line of $i_{\text{Ox}^{z+},\text{L}} (= i_{\text{H}^+,\text{L}})$, its rough value was calculated using the experimental value

of pH = 0.3 shown in 4.2 and $D_{H^+} \approx 7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in a book [12]; $\delta \approx 0.01 \sim 0.03 \text{ cm}$ (moderately stirring condition), and $z = 1$ (see later Equation (31)).

$$\begin{aligned} i_{H^+,L} &= -zF k_{H^+} [H^+]_{\text{bulk}} = -zF \frac{D_{H^+}}{\delta} [H^+]_{\text{bulk}} \\ &\approx -(1) \left(96.5 \times 10^3 \text{ A s mol}^{-1} \right) \left(\frac{7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}{0.01 \sim 0.03 \text{ cm}} \right) \left(10^{-0.3} \text{ mol dm}^{-3} \right) \\ &= -113 \sim -339 \text{ mA cm}^{-2} \end{aligned} \quad (27)$$

The above large value may be a reason why Figure 2 has no vertical line of $i_{H^+,L}$. The l/κ is graphically estimated using the relation of Equation (24):

$$\lim_{|i| \approx 100 \text{ mA cm}^{-2}} h_{\text{exp}}(i) \approx 0.002 \text{ k}\Omega \text{ cm}^2 \gtrsim l/\kappa \quad (28)$$

The $l/\kappa = 0.001 \text{ k}\Omega \text{ cm}^2$ is selected due to: (1) almost saturated value and (2) making a guess by manual calculation of $h(i)$ at $|i| \approx 100 \text{ mA cm}^{-2}$. Then, Equation (23) is specifically expressed as:

$$h_{\text{exp}}(i) = \frac{R T}{\alpha_c z F} \left(\frac{1}{-i} \right) + l/\kappa \approx \frac{0.026}{\alpha_c z} \left(\frac{1}{-i} \right) + 0.001 \quad (29)$$

The revised green circles of $\log\{h_{\text{exp}}(i) - 0.001\}$ against $|i|$, together with the not-revised $h_{\text{exp}}(i)$ (blue dots) in the cathodic branch, are shown in Figure 8.

Figure 8. The revised expression of $\{h_{\text{exp}}(i) - 0.001\}$ with green circles and the not-revised $h_{\text{exp}}(i)$ with blue dots are shown. The vertical lines i_1 and i_2 are drawn for a more accurate estimation. The (B), (C) and (D) correspond to that in Figure 1.

The arrival of green circle plots having a straight line confirms that the physical resistance is practically eliminated due to the disappearance of the horizontal line (l/κ) at $|i| \approx 100 \text{ mA cm}^{-2}$. In addition, the linear relation of $\text{dlog}\{h_{\text{exp}}(i) - 0.001\} / \text{dlog}|i| = -1$ is virtually held in the green plot region. The current data for i_1 and i_2 , which fully satisfies the Tafel slope, were used for the accurate estimation. The value of -0.5 mA cm^{-2} and -3 mA cm^{-2} were employed as the i_1 and i_2 , respectively. We can estimate the $\alpha_c z$ using the following equation.

$$\alpha_c z = \frac{0.026}{\{h_{\text{exp}}(i) - 0.001\} (-i)} \quad (30)$$

The relationship between the calculated $\alpha_c z$ and the employed $|i|$ is plotted in Figure 9.

Figure 9. The relation between $\alpha_c z$ and $|i|$ is plotted using Equation (30). The value of $\alpha_c z$ was ≈ 0.7 by the least-squares approximation method.

The data were scattered but their dispersion was limited. The value of $\alpha_c z$ was estimated to ≈ 0.7 using the least-squares approximation method. The $\alpha_c z$ must satisfy two restrictions: (1) the z must be a positive integer and (2) the z must be $z < 2$ because the electron number should be up to 2 of the whole reaction ($2\text{H}^+ + 2\text{e} = \text{H}_2$). Considering them, the most suitable combination is:

$$\begin{cases} z = 1, \\ \alpha_c = 0.7. \end{cases}$$

The results mean that the reaction is the irreversible and therefore the whole reaction has the rate-determining step (*rds*). Since this *rds* reaction was partially revealed to be $\text{Ox}^{z+} = \text{H}^+$, the possible *rds* reaction may be expressed as the well-known reaction in parentheses, if $\text{Red} = \text{H}_{\text{ad}}$.

Solving Equation (29) as the first order differential equation under the initial condition of $(-i_0, E_{\text{eq}} = -0.018 \text{ V vs. SHE})$, we can know the i_0 .

$$\int_{E_{\text{exp}}(i)}^{-0.018} dE_{\text{exp}} = \int_i^{-i_0} \left\{ \frac{0.026}{0.7} \left(\frac{1}{-i} \right) + 0.001 \right\} di = -0.037 \ln \left(\frac{i_0}{-i} \right) - 0.001(i + i_0). \quad (35)$$

Then,

$$E_{\text{exp}}(i) = -0.018 + 0.038 \ln \frac{i_0}{-i} + 0.001(i_0 + i) \quad (36)$$

It will be allowable that $i_0 + i \approx i$, because the i_0 in reversible reaction is usually very small. Then, the $E_{\text{exp}}(i)$ is simplified and then the relation between the i_0 and the experimental i is plotted in Figure 10.

$$E_{\text{exp}}(i) \approx -0.018 + 0.038 \ln \frac{i_0}{-i} + 0.001i \quad (37)$$

Figure 10. Relation between the i_0 calculated using Equation (37) and the values of $0.5 \text{ mA cm}^{-2} \leq |i| \leq 3 \text{ mA cm}^{-2}$. We can see that the i_0 shows approximate value of $1.4 \times 10^{-2} \text{ mA cm}^{-2}$ ($\approx 10^{-1.8} \text{ mA cm}^{-2}$).

The i_0 was $\approx 10^{-1.8} \text{ mA cm}^{-2}$, which is larger than the results of the papers ($10^{-2.7} \sim 10^{-3.4} \text{ mA cm}^{-2}$) [4]. We think the difference between them probably had its roots in the finding of the proper Tafel slope region and whether the physical resistances are compensated or not.

The $k^\varnothing$ can be estimated by the experimental reading of $\eta^\varnothing (= E_{\text{eq}} - E^\varnothing = E(0) - E^\varnothing \approx -0.02 \text{ V})$ and the experimental pH=0.3 using the i_0 equation [7,9]. Their simultaneous relations are shown as:

$$\left\{ \begin{array}{l} k^\varnothing = \frac{i_0}{zF[\text{H}_{\text{ad}}]_{\text{bulk}}^{\alpha_c} [\text{H}^+]_{\text{bulk}}^{\alpha_a}} = \frac{10^{-1.8} \text{ mA cm}^{-2}}{(1)(96.5 \times 10^3 \text{ A s mol}^{-1}) [\text{H}_{\text{ad}}]_{\text{bulk}}^{0.7} (10^{-0.3})^{(1-0.7)}} \end{array} \right. \quad (38)$$

$$\left\{ \begin{array}{l} \eta^\varnothing = -0.02 \text{ V} = \frac{0.026}{1} \ln \frac{[\text{H}^+]_{\text{bulk}}}{[\text{H}_{\text{ad}}]_{\text{bulk}}} = 0.026 \ln \frac{10^{-0.3}}{[\text{H}_{\text{ad}}]_{\text{bulk}}} \end{array} \right. \quad (39)$$

Solving the above, we can obtain that $k^\varnothing \approx 10^{-6.7} \text{ cm s}^{-1}$. Applying this $k^\varnothing$ value to the curve relation shown in Figure 5, we can reconfirm that the *her* on Ag electrode in the $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution belongs to the irreversible reaction.

4. Experimental Method

4.1. Specimens

Silver (99.99% Ag, NILACO Ltd., Tokyo, Japan), as a working electrode, and the platinum (99.98% Pt, NILACO Ltd., Tokyo, Japan), as a counter electrode, were used. The Ag electrode was 30 mm length wire with a 1 mm diameter. The Ag electrode was pretreated by being immersed in a H_2SO_4 solution while being ultrasonically vibrated for 300 s at an ambient temperature. The counter electrode was a coiled Pt wire with an exposure area of 5 cm^2 . The Pt electrode was washed with warm acetone and dipped in a HNO_3 solution at $\approx 298 \text{ K}$ to clean its surface. It was then rinsed thoroughly with deionized water. The surface of the working electrode was masked with insulating tape and silicone resin, except for an exposure area of 0.95 cm^2 .

4.2. Test Solution

Chemical grade sulfuric acid (98% H₂SO₄, Wako Pure Chemical Industries Ltd., Tokyo, Japan) was used. Deionized water was used to prepare the test solutions. During the experiments, the solution was continuously bubbled with 99.9999% H₂ and maintained with mild stirring to hold a uniform solution environment through the experiments. The pH of the 0.5 mol dm⁻³ H₂SO₄ solution was approximately 0.3. The concentration of dissolved oxygen was 0.4 ppm or lower. The electrical conductivity, κ , of the solution was ≥ 20 S m⁻¹.

4.3. Measurements

An electrochemical instrument (Hokuto Denko Inc., HZ5000, Tokyo, Japan) was employed for the voltammetry measurement. The Ag/AgCl electrode (DKK-TOA Co., HS-305D, Tokyo, Japan) in saturated potassium chloride solution was used as a reference electrode. In this paper, all electrode potentials were converted to V vs. SHE. The distance between the working and reference electrodes was 1 cm or less. The polarization curves were not corrected for the iR drop. The specimen was first maintained for 600 s at an open-circuit potential and then polarized to the anodic direction via cathodic polarization. A scan rate of 0.1 mV s⁻¹ was selected. This scan rate is sufficiently slow to hold a quasi-steady state condition. Since the resulting data often had a scattering tendency due to the slow scan operation, a smoothing treatment for the polarization curves was necessary. The experimental polarization curves were mathematically smoothed and then differentiated using the commercial software Igor Pro 6.

5. Conclusions

Verifying the DPM, the h_{er} on the silver electrode in a sulfuric acid solution was employed. The polarization resistance curves obtained by differentiating the experimental polarization data showed that the i_0 and $\alpha_c z$ can be estimated using the straight line with a gradient of $d \log h / d \log |i| = -1$ and the horizontal line emerged in a cathodically-polarized resistance curve. It was shown that the h_{er} on the silver electrode in the 0.5 mol dm⁻³ H₂SO₄ solution belongs to the irreversible reaction and its approximated i_0 is 10^{-1.8} mA cm⁻².

(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° is the formal electrode potential (V vs. SHE).

$$E^\circ = E^0 + \frac{R}{zF} \ln \frac{y_{Ox^{z+}}}{y_{Red}}$$

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

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

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

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

$[Red]_{bulk}$ is the concentration of the reductant in the bulk solution (mol dm⁻³).

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

$[Red]_{el}$ is the concentration of the reductant near the electrode surface (mol dm⁻³). It is shown as:

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

$[Ox^{z+}]_{el}$ is the concentration of the oxidant near the electrode surface (mol dm^{-3}). It is shown as:

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

z is the number of electrons transferred (-).

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

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

T is absolute temperature (K).

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

η° is the overvoltage between an applied potential $E(i)$, and the E° ($\eta^\circ = E(i) - E^\circ$) (V).

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

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

i is the net current density ($i = i_a + i_c$) (mA cm^{-2}).

i_{pa} is the least anodic current when being sufficiently far-polarized ($0 \ll i = i_a + i_c \approx i_a$) (mA cm^{-2}).

i_{pc} is the largest cathodic current when being sufficiently far-polarized ($i = i_a + i_c \approx i_c \ll 0$) (mA cm^{-2}).

$[i_a(\eta^\circ)]_{\eta^\circ = \frac{RT}{zF} \ln \frac{[Ox^{z+}]_{bulk}}{[Red]_{bulk}}}$ is the total exchange current density (mA cm^{-2}).

i_0 is the exchange current density for the charge transfer process (mA cm^{-2}). It is shown as:

$$i_0 = zFk^\circ [Red]_{bulk}^{\alpha_c} [Ox^{z+}]_{bulk}^{\alpha_a}$$

i_d is the total limiting diffusion current density for the reductant and oxidant (mA cm^{-2}). It is shown as:

$$i_d = \frac{1}{1/i_{Red,L} + 1/-i_{Ox^{z+},L}}$$

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

$i_{Ox^{z+},L}$ is the limiting diffusion current density of the oxidant, (mA cm^{-2}). They are shown as:

$$i_{Red,L} = zF \frac{D_{Red}}{\delta_{Red}} [Red]_{bulk} = zF k_{Red} [Red]_{bulk}$$

$$i_{Ox^{z+},L} = -zF \frac{D_{Ox^{z+}}}{\delta_{Ox^{z+}}} [Ox^{z+}]_{bulk} = -zF k_{Ox^{z+}} [Ox^{z+}]_{bulk}$$

D_{Red} is a diffusion coefficient of reductant ($\text{cm}^2 \text{ s}^{-1}$).

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

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

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

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

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

f_a is $\alpha_a zF/RT$ (V^{-1}).

f_c is $\alpha_c zF/RT$ (V^{-1}).

α_a and α_c are the transfer coefficients (in this paper, $\alpha_a + \alpha_c = 1$).

k° is the standard heterogeneous rate constant (cm s^{-1}).

k is the total rate constant (cm s^{-1}).

$h_a(i_a)$ is the anodic branch polarization resistance ($\text{k}\Omega \text{ cm}^2$).

$h_c(i_c)$ is the cathodic branch polarization resistance ($\text{k}\Omega \text{ cm}^2$).

l_a/κ_a is the polarization resistance for oxide film ($\text{k}\Omega \text{ cm}^2$).

l_a is the thickness of the oxide film (cm).

κ_a is the conductivity of the oxide film ($(\text{k}\Omega \text{ cm})^{-1}$).

l_c/κ_c is the polarization resistance for oxide film ($\text{k}\Omega \text{ cm}^2$).

l_c is the thickness of the oxide film (cm).

κ_c is the conductivity of the oxide film ($(\text{k}\Omega \text{ cm})^{-1}$).

l_s/κ_s is the polarization resistance for solution, produced by a current flow ($\text{k}\Omega \text{ cm}^2$).

l_s is the distance between anodic and cathodic region (cm).

κ_s is the solution conductivity ($(\text{k}\Omega \text{ cm})^{-1}$).

The units used in this paper satisfy the requirements of a coherent system [13,14].

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