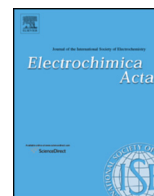




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Differentiating polarization curve technique for determining the exchange current density of hydrogen electrode reaction

Osami Seri*, Yoshiki Itoh

Muroran Institute of Technology, 27-1, Mizumoto, Muroran, Hokkaido, 050-8585, Japan

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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 *hers* in 0.005, 0.05 and 0.5 mol dm⁻³ H₂SO₄ 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 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.

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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 [1c]. 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 H₂ 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.

* Corresponding author.

E-mail address: seri@mmm.muroran-it.ac.jp (O. Seri).

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



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:

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

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]:

$$i(\eta) = i_0 \left\{ \left(1 - \frac{i}{i_{\text{Red,L}}} \right) \exp(f_a \eta) - \left(1 - \frac{i}{i_{\text{Ox}^{z+,L}}} \right) \exp(-f_c \eta) \right\} \quad (3)$$

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 $y_{\text{Ox}^{z+}}$ which are usually unknown. To circumvent these problems, the E^0 was introduced. Substitution of the following equations into Eq. (3) yields the following practical Eq. (6):

$$\left\{ \begin{array}{l} \eta = E - E_{\text{eq}} = E - E^0 + E^0 - E_{\text{eq}} = \eta^0 + (E^0 - E_{\text{eq}}) \end{array} \right. \quad (4)$$

$$\left\{ \begin{array}{l} i_0 = z F k^0 [\text{Red}]_{\text{bulk}}^\beta [\text{Ox}]_{\text{bulk}}^\alpha \end{array} \right. \quad (5)$$

$$\left\{ \begin{array}{l} E_{\text{eq}} - E^0 = \frac{RT}{zF} \ln \frac{[\text{Ox}^{z+}]_{\text{bulk}}}{[\text{Red}]_{\text{bulk}}} \end{array} \right. \quad (2')$$

Then,

$$i(\eta^0) = k^0 \left\{ \left(\frac{i_{\text{Red,L}} - i}{k_{\text{Red}}} \right) \exp(f_a \eta^0) - \left(\frac{i - i_{\text{Ox}^{z+,L}}}{k_{\text{Ox}^{z+}}} \right) \exp(-f_c \eta^0) \right\} \quad (6)$$

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

$$\frac{i_{\text{Red,L}}}{k_{\text{Red}}} \exp(f_a \eta^0) = \frac{-i_{\text{Ox}^{z+,L}}}{k_{\text{Ox}^{z+}}} \exp(-f_c \eta^0) \quad (7)$$

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:

$$\frac{A + B + C}{B i_{\text{Red,L}} + C i_{\text{Ox}^{z+,L}}} i(\eta^0) = 1 \quad (8)$$

where A , B , and C are abbreviations for $1/k^0$, $\exp(f_a \eta^0)/k_{\text{Red}}$, and $\exp(-f_c \eta^0)/k_{\text{Ox}}$, respectively. From a mathematical point of view, each of $1 (= \exp(0))$, $\exp(f_a \eta^0)$, and $\exp(-f_c \eta^0)$ are interpreted as weighted functions on respectively the k^0 , k_{Red} and k_{Ox} . Term A

shown as $1/k^0 (= \exp(0)/k^0)$ is related to the activation process. Term B and term C are related to the diffusion processes. The term $B (= \exp(f_a \eta^0)/k_{\text{Red}})$ emerges in anodic diffusion processes and will show either a large/negligible effect when the η^0 has a positive/negative value. Conversely, the term $C (= \exp(-f_c \eta^0)/k_{\text{Ox}})$ shows the opposite effect: a negligible/large value when the η^0 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 $i(\eta^0)$, 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^0). The (B) group shows slow kinetics with irreversible reaction characteristics (small value of k^0). 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^0 , is classified as follows:

$$\left\{ \begin{array}{l} \text{(A)-1 : } \frac{B+C}{B \cdot i_{\text{Red,L}} + C \cdot i_{\text{Ox}^{z+,L}}} i(\eta^0) \approx 1 \end{array} \right. \quad (9)$$

$$\left\{ \begin{array}{l} \text{(A)-2 : } \frac{B}{B \cdot i_{\text{Red,L}} + C \cdot i_{\text{Ox}^{z+,L}}} i(\eta^0) \approx 1 \end{array} \right. \quad (10)$$

$$\left\{ \begin{array}{l} \text{(A)-3 : } \frac{C}{B \cdot i_{\text{Red,L}} + C \cdot i_{\text{Ox}^{z+,L}}} i(\eta^0) \approx 1 \end{array} \right. \quad (11)$$

and the (B) group, which always includes k^0 , is classified as follows:

$$\left\{ \begin{array}{l} \text{(B)-1 : } \frac{A}{B \cdot i_{\text{Red,L}} + C \cdot i_{\text{Ox}^{z+,L}}} i(\eta^0) \approx 1 \end{array} \right. \quad (12)$$

$$\left\{ \begin{array}{l} \text{(B)-2 : } \frac{A+B}{B \cdot i_{\text{Red,L}} + C \cdot i_{\text{Ox}^{z+,L}}} i(\eta^0) \approx 1 \end{array} \right. \quad (13)$$

$$\left\{ \begin{array}{l} \text{(B)-3 : } \frac{A+C}{B \cdot i_{\text{Red,L}} + C \cdot i_{\text{Ox}^{z+,L}}} i(\eta^0) \approx 1 \end{array} \right. \quad (14)$$

In the field of electrochemistry, electrochemical kinetics are usually expressed in three functional forms: $i(\eta^0)$, $E(i)$ and $h(i)$. Each function has its own merits. For instance, the $i(\eta^0)$ 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 another function which can be obtained by differentiating the $E(i)$:

$$h(i) = \frac{dE}{di} = \frac{dE}{d(i_a + i_c)} = \frac{1}{1/h_a(i_a) + 1/h_c(i_c)} \quad (15)$$

The $h(i)$ is expressed as a parallel circuit of the anodic polarization resistance $h_a(i_a)$, and the cathodic polarization resistance $h_c(i_c)$. The $h(i)$ expression has a merit of requiring fewer experimental readings. Although $i(\eta^0)$, $E(i)$, 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.

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