



Differentiating approach to the Tafel slope of hydrogen evolution reaction on nickel electrode



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ABSTRACT

A new technique was introduced to assist the Tafel extrapolation method (TEM). The hydrogen evolution reaction (*her*) on nickel electrode in H₂SO₄ solution was investigated in comparison with the TEM and proposed technique. The exchange current density (j^0) for *her* was assessed from points of simple and more accurate handling. The proposed technique has advantages: (1) proper reading of the Tafel slope region and (2) easy removing of undesirable physical factors such as oxide film and solution resistances.

1. Introduction

The *her* is one of the most fundamental reactions in the field of electrochemistry. Catalysis performance for the *her* has been evaluated by the j^0 . To assess the j^0 , the TEM has been widely used [1]. The j^0 on various metals in various environments has been extensively studied and accumulated, because mass production of hydrogen becomes a key technology to sustain future energy society. Though numerous papers have been published, some of them are poor in reliability and accuracy in numbers. We have often encountered different values [2–5]. As an example, there is reported values of $j^0 = 10^{-3.81}$ and $10^{-2.08}$ mA cm⁻² on Ni in same 0.5 mol dm⁻³ H₂SO₄ solution [2]; a difference of almost two order of magnitude. It is said that such uncertainty may be caused by difficulties in finding the proper Tafel region and ignorance of the physical resistances such as oxide film and solution resistance [6–8]. The aim of this paper is evaluation of the proposed technique from two points: (1) how to find accurate Tafel slope region and (2) how to remove the physical resistances.

2. Materials and methods [7]

2.1. Specimens

Nickel (99.99% Ni) and platinum (99.98% Pt) were used. The Ni working electrode was 15 mm length wire with 1 mm diameter. The Ni was pretreated by being immersed in H₂SO₄ solution while being ultrasonically vibrated for 300 s at an ambient temperature. The Ni was masked with insulating tape and silicone resin except for an exposure

area of 6.3 cm². The counter electrode was a coiled Pt wire with an exposure area of 5 cm². The Pt was washed with acetone and dipped into 30% HNO₃ solution at ≈ 298 K to clean up its surface and then rinsed thoroughly with deionized water.

2.2. Test solution

Chemical-grade sulfuric acid (98% H₂SO₄) was used. The test solution during the experiments was continuously bubbled with hydrogen gas (99.9999% H₂) and maintained with a moderately stirring condition. The pH and the electrical conductivity, κ of 0.5 mol dm⁻³ H₂SO₄ test solution was approximately 0.3 and > 20 S m⁻¹, respectively. The concentration of dissolved oxygen was 0.4 ppm or lower.

2.3. Measurements

An electrochemical instrument (Hokuto Denko Inc., HZ7000, Japan) was employed for the linear sweep voltammetry. The Ag/AgCl electrode in the saturated KCl solution (DKK-TOA Co., HS-305D, Japan) was used as a reference electrode. All electrode potentials experimentally measured are converted to V vs SHE. The distance between the working and reference electrode was 1 cm or less. The experimental polarization curve, $E_{\text{exp}}(j)$ was not compensated for iR drop. A slow scan rate of 0.1 mV s⁻¹ was selected for the quasi-steady state condition. Since the slow scan rate operation often produced scattering data, smoothing treatment for the $E_{\text{exp}}(j)$ was needed. They were mathematically smoothed using the commercial software Igor Pro 6.

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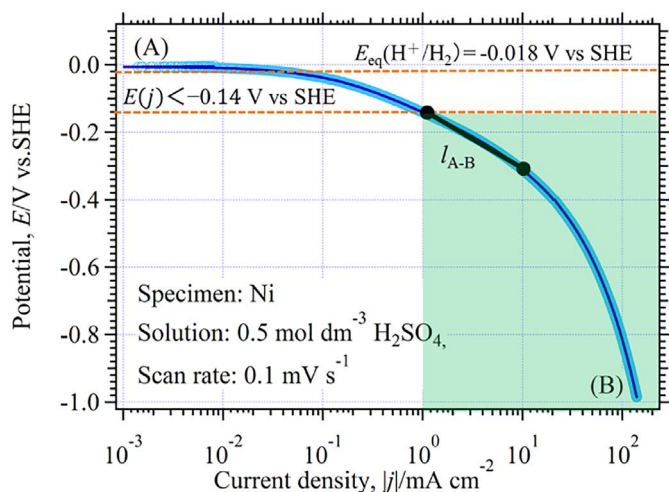


Fig. 1. Experimental polarization curve (light blue circles) and its smoothed curve (dark blue dots) for the Ni electrode in 0.5 mol dm⁻³ H₂SO₄ solution bubbled with H₂ gas. The light blue area ($E(j) \leq -0.14$ V vs SHE) ($1 \text{ mA cm}^{-2} \leq |j|$) may be valid for the TEM estimation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results

3.1. Polarization curve for nickel electrode

A typical $E_{\text{exp}} \sim \log |j|$ curve is shown in Fig. 1. After holding at open circuit potential for 1 ks, the cathodic operation was performed from the start point (A) to the finish point (B). The data are plotted as light blue circles. The vigorous hydrogen gas bubbles were observed around the (B). The smoothed $E_{\text{exp}}(j)$ was also plotted in Fig. 1 as dark blue dots. The overlap of the smoothed curve on the circles confirmed that the smoothed $E_{\text{exp}}(j)$ can be representative of the experimental data.

3.2. Polarization resistance plots of nickel electrode

The smoothed $E_{\text{exp}}(j)$ was finite-differentiated. The experimental polarization resistance, $h_{\text{exp}}(j) (= \Delta E_{\text{exp}}/\Delta j)$, which was changed into a $\log h_{\text{exp}} - \log |j|$ expression, are shown in Fig. 2. We can see there are two horizontal lines of $h_{\text{exp}}(j \lesssim 3 \times 10^{-2} \text{ mA cm}^{-2}) \approx 0.35 \text{ k}\Omega \text{ cm}^2$ and $h_{\text{exp}}(j \gtrsim 10^2 \text{ mA cm}^{-2}) \approx 4 \times 10^{-3} \text{ k}\Omega \text{ cm}^2$.

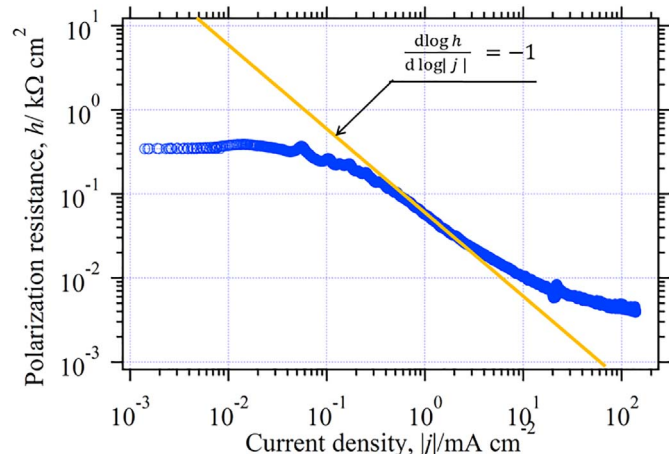


Fig. 2. Polarization resistance plots obtained by differentiating the smoothed $E_{\text{exp}}(j)$ curve shown in Fig. 1. An orange straight line with a gradient of $d \log h / d \log |j| = -1$ was added for explanation of the newly-proposed technique.

4. Discussion

4.1. Differential form of Tafel equation

The electrochemical kinetics at stationary state is expressed by two main processes: charge transfer process and diffusion transfer process:

$$j(\eta) = j^0 \left\{ \frac{[\text{Red}]_{\text{el}}}{[\text{Red}]_{\text{bulk}}} \exp(f_a \eta) - \frac{[\text{Ox}^{z+}]_{\text{el}}}{[\text{Ox}^{z+}]_{\text{bulk}}} \exp(-f_c \eta) \right\} \quad (1)$$

and

$$\begin{cases} [\text{Red}]_{\text{el}} = \left(1 - \frac{j}{j_{\text{Red},L}}\right) [\text{Red}]_{\text{bulk}}, \\ [\text{Ox}^{z+}]_{\text{el}} = \left(1 - \frac{j}{j_{\text{Ox}^{z+},L}}\right) [\text{Ox}^{z+}]_{\text{bulk}} \end{cases} \quad (2)-(3)$$

When all of them simultaneously occur, the simultaneous equations of Eq. (1)–Eq. (3) are valid:

$$j(\eta) = j^0 \left\{ \left(1 - \frac{j}{j_{\text{Red},L}}\right) \exp(f_a \eta) - \left(1 - \frac{j}{j_{\text{Ox}^{z+},L}}\right) \exp(-f_c \eta) \right\} \quad (4)$$

Arranging the above, another expression of

$$j(\eta) = \frac{\exp(f_a \eta) - \exp(-f_c \eta)}{1/j^0 + \exp(f_a \eta)/j_{\text{Red},L} + \exp(-f_c \eta)/-j_{\text{Ox}^{z+},L}} = j_a(\eta) + j_c(\eta) \quad (5)$$

is obtained. Differentiating Eq. (5), the following polarization conductance, $g(\eta)$ is obtained:

$$\begin{aligned} g(\eta) &= \frac{dj(\eta)}{d\eta} = \frac{f_a \exp(f_a \eta) + f_c \exp(-f_c \eta)}{1/j^0 + \exp(f_a \eta)/j_{\text{Red},L} + \exp(-f_c \eta)/-j_{\text{Ox}^{z+},L}} \\ &\quad - \frac{\{\exp(f_a \eta) - \exp(-f_c \eta)\} \{f_a \exp(f_a \eta)/j_{\text{Red},L} - f_c \exp(-f_c \eta)/-j_{\text{Ox}^{z+},L}\}}{\{1/j^0 + \exp(f_a \eta)/j_{\text{Red},L} + \exp(-f_c \eta)/-j_{\text{Ox}^{z+},L}\}^2} \\ &= f_a j_a(\eta) - f_c j_c(\eta) - j(\eta) \left(f_a \frac{j_a(\eta)}{j_{\text{Red},L}} + \frac{f_c j_c(\eta)}{-j_{\text{Ox}^{z+},L}} \right). \end{aligned} \quad (6)$$

When being cathodically polarizes ($\eta \ll 0$), the $j(\eta)$ will approximate closely to the cathodic branch current, $j_c(\eta)$:

$$j(\eta) = j_a(\eta) + j_c(\eta) \approx j_c(\eta). \quad (7)$$

Then, Eq. (6) is simplified to:

$$g(\eta) = -f_c j_c(\eta) - j(\eta) \frac{f_c j_c(\eta)}{-j_{\text{Ox}^{z+},L}} = -f_c j(\eta) \left(1 + \frac{j(\eta)}{-j_{\text{Ox}^{z+},L}} \right). \quad (8)$$

Considering the mathematical relation of $\frac{dj}{d\eta} = g(\eta) = g(\eta) \frac{d(E - E_{\text{eq}})}{dj} = g(\eta) \frac{dE}{dj} = g(\eta) h(j) = 1$, Eq. (8) can be changed to the polarization resistance, $h(j)$:

$$h(j) = \frac{1}{g(\eta)} = \frac{1}{f_c} \left(\frac{1}{1 + j/-j_{\text{Ox}^{z+},L}} \right) \left(\frac{1}{-j} \right) = \frac{RT}{\alpha_c n F} \left(\frac{1}{1 + j/-j_{\text{Ox}^{z+},L}} \right) \left(\frac{1}{-j} \right). \quad (9)$$

When $j/-j_{\text{Ox}^{z+},L} \approx 0$, the above is simplified to:

$$h(j) = \frac{RT}{\alpha_c n F} \left(\frac{1}{-j} \right). \quad (10)$$

The definition of α_c [9,10] is shown and arranged as:

$$\alpha_c \equiv \frac{-RT}{F} \frac{d \ln |j_c|}{dE} = \frac{-RT}{F} \frac{d \ln |j|}{dj} \frac{dj}{dE} = \frac{-RT}{F} \left(\frac{1}{j} \right) \frac{1}{h(j)}, \quad (11)$$

Substituting Eq. (11) into Eq. (10), the result of $n = 1$ is obtained. It becomes clear that the α_c can be determined without the need for a knowledge of the n . Consequently, Eq. (10) is

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