

A Noble Approach to Measure The Interfacial Resistance

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A noble approach to measure the interfacial resistance is presented. This approach is appropriate particularly for the systems having very high electrolyte resistance which results in a long time constant and disables conventional electrochemical methods. This method consists of several current steps such that each step has same magnitude and duration. In this method, the ohmic contribution can be eliminated via measuring the transient potential response when a very small current step is applied repeatedly. A theoretical analysis of signal response and method of analyzing such response to obtain the interfacial resistance are presented.

1. Introduction

Determination of a interfacial polarizing resistance(R_p) constitutes a vital electrochemical experiments. Numerous methods such as linear polarization^{1~3}, AC impedance^{4,5} have been proposed to measure R_p . In the linear polarization method, for example, R_p can be determined by either potentiodynamic or galvanodynamic method where a potential(or current) ramp is applied while the resulting current(or potential) response is analyzed.

It should be noted, however, that the system should attain steady-state for precise determination of R_p . A sweep rate(linear polarization) and frequency(AC impedance) have a significant influence on the accuracy of measured R_p ^{4,6} and should be selected so that a steady-state proximity can be maintained. A system's time constant, which determines how fast the system attains steady-state, varies with the electrochemical nature of po-

larizing interface. The time effect may be obtained by representing the polarizing interface with an electrical model consisting of an appropriate combination of passive circuit elements. The simplest, but mostly commonly used, model is the simplified Randles circuit(Figure 1) consisting of the electrolyte resistance(R_e), the double-layer capacitance (C) and the polarization resistance(R_p).

The time constant of polarizing interface is a function of system's electric component. As will be shown later, it increases with C and resistances. Hence systems having high electrolyte resistance (metals in organic coating or concrete) and charge transfer resistance(passive metal, kinetically slow reactions) are subjected to problems of large time constant and the measurement of R_p via conventional steady-state method becomes ineffective. In other words, a very slow sweep rate(linear polarization) or ultra low frequency(AC impedance) is required to measure R_p of such systems. This

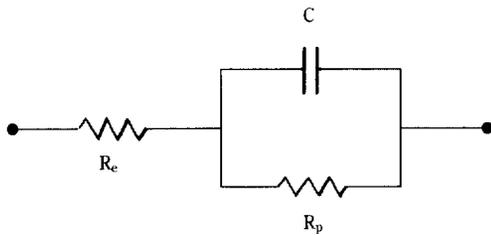


Fig. 1 Randles equivalent circuit
 R_e : Electrolyte resistance
 R_p : Polarization resistance
 C : Double layer capacitance

study presents a noble method which is suitable for such systems having large time constants.

2. Time Constant of Various Electrochemical Methods

When an Randles circuit is subjected to a potential ramp, of magnitude ΔE , it exhibits the following current response

$$I(t) = \frac{\Delta E}{R_e(R_e + R_p)} \left\{ R_e + R_p \exp\left(-t/\frac{CR_e R_p}{R_e + R_p}\right) \right\} \quad (1)$$

This response has two components of stationary

$$I_\infty = \frac{\Delta E}{R_e + R_p} \quad (2)$$

and transitory

$$I_{tr} = \frac{\Delta E R_p}{R_e(R_e + R_p)} \left\{ R_e + R_p \exp\left(-t/\frac{CR_e R_p}{R_e + R_p}\right) \right\} \quad (3)$$

The current attains steady-state when the transitory component of response disappear, i. e., $I_{tr} = 0$. Time constant (τ_E), therefore, can be written as follow from equation(3) :

$$(\tau_E) = \frac{CR_e R_p}{R_e + R_p} \quad (4)$$

For majority of metals in solution systems, the polarization resistance(R_p) is much greater than the electrolyte resistance(R_e), and equation(4) can be written as

$$\tau_E \approx CR_e \quad (5)$$

τ_E represents a time constant for potentiostatic case.

Time constant for galvanostatic case can also be obtained from the potential response. Potential response upon current ramp exhibits simpler behavior which can be represented as

$$E(t) = I [R_e + R_p \{1 - \exp(-t/CR_p)\}] \quad (6)$$

and the time constant can be written as

$$\tau_I = CR_p \quad (7)$$

Bearing in mind that $R_p \gg R_e$ for most of systems, a potentiodynamic method using a potential ramp has an advantage over a galvanodynamic one in that the time to attain steady-state is shorter for the former ($\tau_E \ll \tau_I$). Even for a potentiodynamic method, however, a proper scan rate should be selected to obtain reliable results.

It has been shown that an apparent R_p value between R_p and $(R_e + R_p)$ may be obtained depending on the scan rate. Generally the scan rate may be such that the scanning time to apply $\Delta E = \pm 10$ mV is larger than $5 \sim 6\tau$. Faster scan rate results in underestimated R_p close to R_e whereas slower rate gives overestimated R_p close to $(R_e + R_p)$.

A similar scan rate problem is encountered with AC impedance method where a sinusoidal perturbation is applied. The ratio $\Delta E/\Delta I$, i. e., impedance Z , is a sinusoidal function which can be decompo-

sed in a resistive term in phase with input signal and a capacitive term with a phase shift of 90° . Impedance vector describes a semicircle in a complex plot when the frequency is varied from 0 to ∞ . The parameters of this semicircle enable one to calculate R_e , R_p and C .

It has been awared that the advantage of AC impedance method is that it does not perturb the system significantly because of it's AC nature that does not produce transport phenomena. At very low frequencies, however, a significant perturbation is expected. Moreover, in systems of high interfacial resistance, frequency should be very low like 10^{-3} Hz or lower in order to obtain kinetic information. In this low frequency range, the equilibrium potential becomes unstable due to the substantial transport phenomena effect.

Mansfeld⁽⁴⁾ proposed a limit of low frequency signal where R_p can be measured without a significant contribution of transport phenomena as follow

$$f_{\max} = \frac{1}{4\pi R_e C} \left(1 - \frac{1}{R_p} \sqrt{R_p^2 - 4R_e R_p - 4R_e^2} \right) \quad (8)$$

Since the limit frequency (f_{\max}) decreases with increasing R_e and R_p , impedance can not be used for systems having high R_e and R_p .

3. Galvanostatic Transient Linear Polarization Method

Galvanostatic Transient Linear Polarization (GTLP) method is proposed for systems where the conventional methods (linear polarization and AC impedance) can not be used to measure the interfacial resistance due to high R_p and/or R_p . The GTLP method consists of several current step

such that each current step has the same magnitude and duration. The current of the n^{th} step is n times that of the first step ($I_n = nI_1$). The schematic representation is shown in Figure 2.

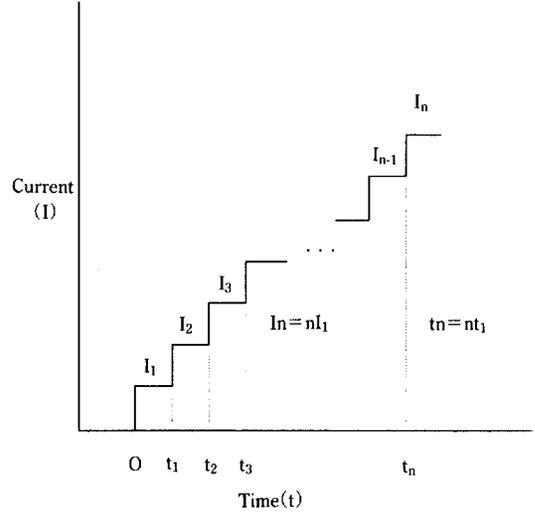


Fig. 2 The applied current signal of the GTLP method.

I_i represents the current of the i^{th} step.

The electrode potential upon external current exhibits transient behavior as equation(6). The electrode potential corresponding to the i^{th} step will be measured at time t_i such that $(t_i - t_{i-1}) < \tau_i$. As a result, the measured potential, E_i , is not a steady potential as the duration of the applied signal is smaller than the time constant τ_i . From equation(6)

$$E_i = I_i [R_p \{ 1 - \exp(-t/CR_p) \} + R_e] + E_{i-1} \exp(-t/CR_p) \quad (9)$$

where E_i and I_i are the potential and current at the i^{th} step and $E_{i-1} \exp(-t/CR_p)$ is the overvoltage present when I_i is applied.

When polarization is started from the equilibrium potential, E_{eq} ,

$$E_{i-1} = E_{eq} = 0 \tag{10}$$

At steady-state ($t = \infty$)

$$E_{i(t=\infty)} = I_i (R_p + R_e) \tag{11}$$

The overpotential corresponding to I_n is written from equation(9)

$$E_n = I_n \left[\frac{R_p \{ 1 - \exp(-t/CR_p) \} + R_e}{\exp(-t/CR_p)} \right] + E_{n-1} \tag{12}$$

similarly

$$E_{n-1} = I_{n-1} \left[\frac{R_p \{ 1 - \exp(-t/CR_p) \} + R_e}{\exp(-t/CR_p)} \right] + E_{n-2} \tag{13}$$

$$E_{n-2} = I_{n-2} \left[\frac{R_p \{ 1 - \exp(-t/CR_p) \} + R_e}{\exp(-t/CR_p)} \right] + E_{n-3} \tag{14}$$

$$E_2 = I_2 \left[\frac{R_p \{ 1 - \exp(-t/CR_p) \} + R_e}{\exp(-t/CR_p)} \right] + E_1 \tag{15}$$

and

$$E_1 = I_1 \left[\frac{R_p \{ 1 - \exp(-t/CR_p) \} + R_e}{\exp(-t/CR_p)} \right] \tag{16}$$

Combining equations(12)to(16),

$$\begin{aligned} E_n &= I_n R_p \left(1 - e^{-2t/\tau} + \frac{I_{n-1}}{I_n} e^{-t/\tau} - \frac{I_{n-1}}{I_n} e^{-t/\tau} \right. \\ &\quad \left. + \frac{I_{n-2}}{I_n} e^{-2t/\tau} - \dots \right) + I_n R_e \left(1 + \frac{I_{n-1}}{I_n} e^{-t/\tau} \right. \\ &\quad \left. + \frac{I_{n-2}}{I_n} e^{-2t/\tau} - \dots \right) \\ &= I_n R_p \left(1 - \frac{1}{n} e^{-t/\tau} - \frac{1}{n} e^{-2t/\tau} - \dots - \frac{1}{n} e^{-nt/\tau} \right) \\ &\quad + I_n R_e \left\{ 1 + \frac{n-1}{n} e^{-t/\tau} + \frac{n-2}{n} e^{-2t/\tau} \right. \\ &\quad \left. + \dots + \frac{1}{n} e^{-(n-1)t/\tau} \right\} \tag{17} \end{aligned}$$

Note that in deriving equation(17), the following relationship is used

$$\frac{I_{n-1}}{I_n} = \frac{(n-1)I_1}{nI_1} = \frac{n-1}{n} \tag{18}$$

The deviation of the transient overpotential from the steady-state overpotential, $\Delta\eta$, can be obtained from equations(11)and (17)

$$\begin{aligned} \Delta\eta &= E_{n(t=\infty)} - E_n \\ &= I_n (R_p + R_e) - E_n \\ &= I_1 R_p \left(e^{-t/\tau} + e^{-2t/\tau} + \dots + e^{-nt/\tau} \right) + \\ &\quad - I_1 R_e \left\{ (n-1)e^{-t/\tau} + (n-2)e^{-2t/\tau} + \dots + \right. \\ &\quad \left. e^{-(n-1)t/\tau} \right\} \tag{19} \end{aligned}$$

In case when $e^{-t/\tau} < 1$, since $t > \tau$, equation (19) converges to a maximum value, Δ_{max} , written as

$$\Delta_{max} = I_1 e^{-t/\tau} \left\{ \frac{R_p - nR_e}{1 - e^{-t/\tau}} + \frac{R_e}{(1 - e^{-t/\tau})^2} \right\} \tag{20}$$

It should be noted, in the above equations, that $t = \sum_i t_i$ and equation(20) holds when the total elapse time, t , is greater than system's time constant, τ . Equation(20) shows that there is a maximum in the difference between the transient and steady-state overpotentials. Therefore, after Δ_{max} is attained, the resulting non-steady-state overpotential vs. applied current will become linear and yield the same slope as for the steady-state relationship. In other words, a non-steady-state potential behavior which comprises a transient portion, can be considered as a steady-state one since the difference between the two is maintained at a constant value of Δ_{max} after a certain time of $t > \tau$. Potential response measured right after t_i , the application of a current step, can thereby utilized without wai-

ting until steady potential response appears after τ . This method accelerates the collection of data as overpotentials are measured in transient region ($t_i - t_{i,1} \ll \tau$).

4. Application of GTLP Method

Figure 3 schematically presents the approach to determine the interfacial resistance from GTLP method. The potential response curve (Figure 3-(b)) to an applied current step (Figure 3-(a)) is composed of three parts. An initial instantaneous potential rise due to the electrolyte resistance, R_e , is followed by an exponentially increasing transient part due to the capacitive nature of system. Finally, a steady state maximum appears.

Putting $t=0$ and $t=\infty$ in equation(6)

$$E_0 = IR_e \quad (21)$$

$$E_\infty = E_{\max} = I(R_e + R_p) \quad (22)$$

$\Delta E = E_{\max} - E_t$, where E_t is the transient potential.

$$\begin{aligned} \Delta E &= IR_e + IR_p - I\{R_p(1 - e^{-t/\tau}) + R_e\} \\ &= IR_p e^{-t/\tau} \end{aligned} \quad (23)$$

Taking log on both sides and rearranging

$$\log(\Delta E) = \log(IR_p) - t/\tau$$

which is a straight line in a plot of $\log(\Delta E)$ vs. time (Figure 3-(c)), with an intercept of $\log(IR_p)$ and a slope of $(-1/CR_p)$. The polarization resistance, therefore, can be obtained through determining either the intercept or the slope. It should be noted that the transient potential, measured at time t_i , is valid only when it is measured after the total elapse time, t , is sufficiently greater than time

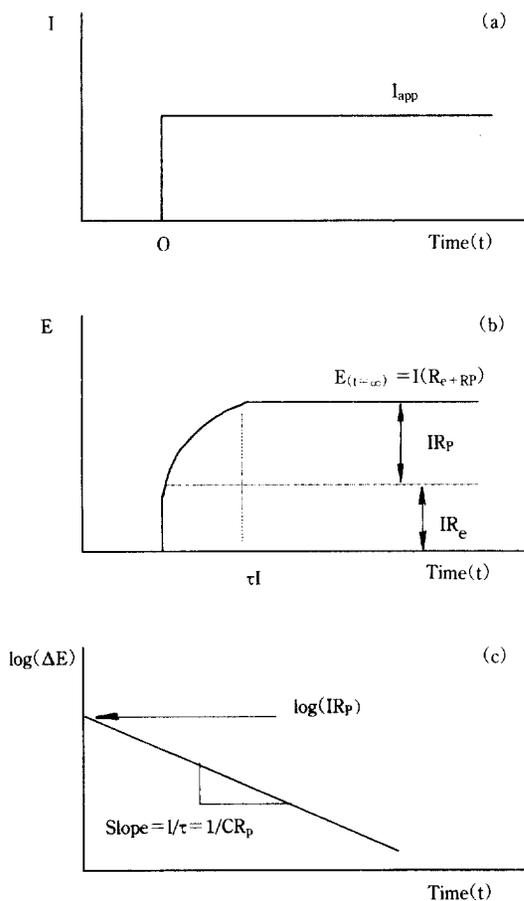


Fig. 3 Schematic representation of galvanostatic charging curve analysis.

- (a) Applied current signal
- (b) Potential response with time
- (c) Plot of $\log(\Delta E)$ vs. time

constant, τ , in order that equation (20) be satisfied. Experimental validation of GTLP method will be shown in the following works.

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