

**Note on Selecting DC Potentials for EIS Measurements:
an Example of Determining the Diffusion Coefficient of Hydrogen Ion in Aqueous Solutions**

Negar Moradighadi, Bruce Brown and Srdjan Nesic

Institute for Corrosion and Multiphase Technology
Department of Chemical & Biomolecular Engineering, Ohio University
Athens, OH 45701

ABSTRACT

Electrochemical impedance spectroscopy (EIS) is a powerful technique that can detect and provide information about different phenomena that occur on the corroding surface using alternating current signals. Several electrochemical reactions and associated phenomena, such as mass transfer and chemical reactions happening at and near the metal surface, occur simultaneously. Therefore, the EIS data conducted at a specific DC potential often contain mixed information about several of those reactions, while at other potentials the EIS data are dominated by a single electrochemical reaction. To be able to focus on a single electrochemical reaction and its associated phenomena, it is important to identify the DC potential at which the EIS data provide the most relevant information about this reaction, otherwise, the analysis of the impedance data becomes very difficult. This work aims to show an example of how to select the DC potential range at which the hydrogen evolution reaction is dominant. Following this step, the EIS data can be used to determine the diffusion coefficient of hydrogen ion in a strong acid aqueous solution.

INTRODUCTION

EIS is a powerful tool, yet a challenging technique for studying of a corrosion electrochemical system. It can provide a broad range of information by decoupling the phenomena that occur at or near the metal surface¹⁻⁵. In the study of corrosion of mild steel in a strong acid solution, the main electrochemical reactions are anodic dissolution of iron and the cathodic reduction of hydrogen ions and water (at lower potentials). In EIS studies of these electrochemical reactions, choosing the appropriate DC potential is of great importance. For example, to study the hydrogen reduction reaction, which is often controlled by the mass transfer of hydrogen ions, a DC

potential must be chosen at which the EIS response provides mostly information about the hydrogen reduction reaction and the influence of other reactions on measured impedance is minimized. It is well known that at potentials below the open circuit potential (OCP), the measured current is dominated by hydrogen ion reduction. We are compelled to conclude that the impedance at these same potentials below the OCP is also dominated by the hydrogen reduction reaction? But, is this always the case?

In this work, a DC potential range in which the impedance associated with the hydrogen evolution reaction is dominant will be determined by building a model to determine the resistance of the key electrochemical reactions involved in the corrosion process: iron oxidation, hydrogen reduction and water reduction. Next, the EIS data, obtained at the determined DC potential, will be analyzed using a method explained in the literatures^{1,6} to determine the diffusion coefficient of the hydrogen ion in a strong acid solution.

Theory Behind Calculation of Diffusion Coefficients

For an electrochemical reaction that depends both on potential and metal surface concentration of electroactive species, the faradic impedance is related to it is a faradic resistance in series with a diffusion impedance as shown in Figure 1¹.

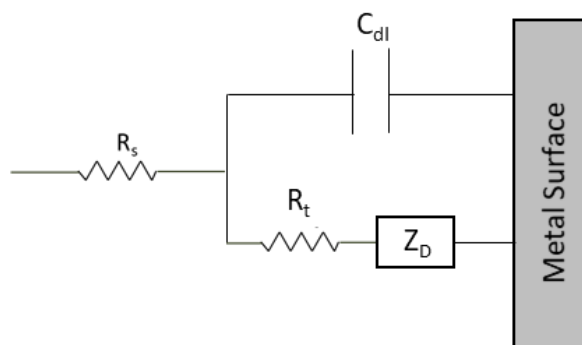


Figure 1. The schematic of the Randles circuit representing the surface phenomena and faradic reactions depending on potential and concentration of species at the metal surface.

As shown in Figure 1, the faradic impedance (Z_F) is a summation of faradic resistance (R_t) and diffusion impedance (Z_D) as shown in Equation (1) where Z_D is defined in Equation (2)¹.

$$Z_F = R_t + Z_D \quad (1)$$

$$Z_D = R_D \left(-\frac{1}{\theta_i(0)} \right) \quad (2)$$

In Equation (2), R_D is a diffusion resistance, $\theta_i(0)$ is defined as a dimensionless concentration (Equations (3)) and $\theta'_i(0)$ is its first derivative with respect to distance from the surface (Equations (4))¹.

$$\theta_i(0) = \frac{\tilde{c}_i(y)}{\tilde{c}_i(0)} \quad (3)$$

$$\theta'_i(0) = \frac{d(\frac{\tilde{c}_i}{\tilde{c}_i(0)})}{d(\frac{y}{\delta})} \quad (4)$$

To analyze the derivative of concentration with respect to time and position, a convective-diffusion equation will be used as shown in Equation (5). Moreover, any complex value such as concentration can be defined by Equation (6) having a steady state and transient part. By substituting the first derivative of Equation (6) with respect to time and distance into Equation (5), and also considering the axial velocity profile near the surface of a rotating disk electrode (Equation (7)), the dimensionless form of the convective-diffusion equation can be obtained as shown in Equation (8). The dimensionless parameters in Equation (8) are defined in Equations (9)-(11)^{1,6}.

$$\frac{\partial c_i}{\partial t} + v_y \frac{\partial c_i}{\partial y} - D_i \frac{\partial^2 c_i}{\partial y^2} = 0 \quad (5)$$

$$c_i(y) = \bar{c}_i(y) + Re\{\tilde{c}_i e^{j\omega t}\} \quad (6)$$

$$v_y = -\sqrt{\nu\Omega} \left(\frac{-a\Omega}{\nu} y^2 + \frac{1}{3} \left(\frac{\Omega}{\nu} \right)^{3/2} y^3 + \frac{b}{6} \left(\frac{\Omega}{\nu} \right)^2 y^4 + \dots \right) \quad (7)$$

$$\frac{d^2 \theta_i}{d\xi^2} + \left(3\xi^2 - \left(\frac{3}{a^4} \right)^{1/3} \frac{\xi^3}{Sc_i^{1/3}} - \frac{b}{6} \left(\frac{3}{a} \right)^{5/3} \frac{\xi^4}{Sc_i^{2/3}} \right) \frac{\partial \theta_i}{\partial \xi} - jK_i \theta_i = 0 \quad (8)$$

$$\xi = \frac{y}{\delta_i} \quad (9)$$

$$K = 3.2576 p Sc^{1/3} \quad (10)$$

$$p = \frac{\omega}{\Omega} \quad (11)$$

Considering the boundary conditions shown below, Equation (8) can be solved by Newman, *et al.*⁷ method. Therefore the second term in the diffusion impedance (Z_D) was determined as shown in Equation (12)^{1,6}.

$$\theta_i \rightarrow 0 \text{ as } \xi \rightarrow \infty$$

$$\theta_i \rightarrow 1 \text{ at } \xi = 0$$

$$-\frac{1}{\theta_i(0)} = \Gamma\left(\frac{4}{3}\right) [1 + 0.298Sc^{-1/3} + 0.145Sc^{-2/3} + (pSc^{1/3})^2 \alpha + j(pSc^{1/3})\beta] \quad (12)$$

According to Tribollet *et al.*, the slope of the plot shown in Figure 2 is a function of the Schmidt number as shown in Equations (13) and (14). Once the Schmidt number is obtained the diffusion coefficient can be calculated using Equation (15)^{1,6}.

$$\lim_{p \rightarrow 0} \left(\frac{dRe \left\{ -\frac{1}{\theta_i(0)} \right\}}{dpIm \left\{ -\frac{1}{\theta_i(0)} \right\}} \right) = \lambda Sc^{1/3} \quad (13)$$

$$\lambda = 1.2261 + 0.84Sc^{-1/3} + 0.63Sc^{-2/3} \quad (14)$$

$$Sc = \frac{\nu}{D} \quad (15)$$

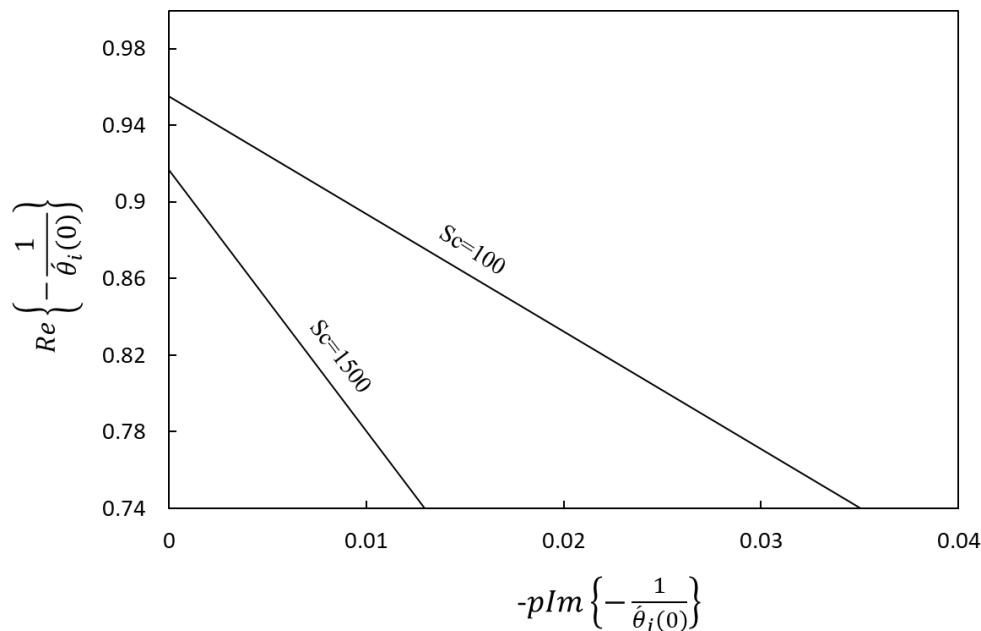


Figure 2. Determining the Schmidt number from the complex value of $\left(-\frac{1}{\theta_i(0)}\right)^6$.

METHODOLOGY

The first part of the experimental method is related to determining the DC potential at which the impedance is dominated by the hydrogen reduction reaction. The test conditions are shown in Table 1. A 3-electrode glass cell system with a rotating disk electrode is used for electrochemical experiments. The reference electrode is saturated KCl, Ag/AgCl. The counter and working electrodes are graphite and API 5L X65 mild steel respectively. Initially, the test solution is sparged with 1 bar N₂ for one hour to remove the oxygen content. The pH of the solution is adjusted using a dilute HCl solution. The metal sample is polished up to 1200 grit silicon carbide paper. Following polishing, the sample was mirror finished using a 0.25 diamond suspension liquid to avoid the generation of bubbles on the metal surface during the experiment. The sample was cleaned in an isopropanol liquid using ultrasonic for 2-3 minutes and then dried using N₂ stream.