

Mechanistic Modeling of the Impedance Response of Cathodic Reduction of Hydrogen Ion in Strong Acidic Environments

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ABSTRACT

Studying the mechanism of electrochemical reactions benefits from implementation of steady state and transient techniques such as electrochemical impedance spectroscopy (EIS). To develop an understanding of experimental results and how they relate to corrosion mechanisms requires their comparison with a mechanistic model. In this study, a physico-chemical model was used to simulate both the steady state potentiodynamic sweep, and the EIS response of cathodic reduction of H^+ in an acidic environment. The modeled steady state potentiodynamic sweep, Nyquist plot and Bode plot were validated by comparison with experimental data.

INTRODUCTION

EIS is one of the techniques which is frequently used for studying electrochemical reactions on a metal surface in an aqueous environment. However, one of the main challenges in using EIS is the interpretation of results. Various interpretation methods and their associated uncertainties lead to ambiguous outcomes and often end up with a biased analysis. One of the methods frequently used is the so-called “equivalent electrical circuit” method which models the response of an electrochemical system by matching it to that of a combination of “analogous” electrical circuit components, such as resistors, inductors, capacitors, etc.^{1,2} However, it is often seen that several different equivalent electrical circuits match the impedance response of an electrochemical system and therefore, the analysis of the results using this approach can be misguided and ambiguous¹. Furthermore, it is not always easy to assign physical meaning to all the various electrical components of an equivalent circuit that seems to match the electrochemical data best.

Therefore, the main motivation of the present work is to directly model the impedance response of an electrochemical system by directly building a model involving electrochemical reactions and other associated processes such as mass transfer, chemical reactions, etc.^{3,4}

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Consequently, the simulated impedance response using this type of model can be directly used to analyze the experimental results and evaluate mechanisms of electrochemical reactions in a complex system. In this work, the transient electrochemical/physico-chemical models behind the mechanistic corrosion prediction package MULTICORP™, have been used as a base for building a new module, LABCORP-AC™, focused modeling the current response to an imposed alternating potential perturbation in an electrochemical system³. The physico-chemical, mathematical, and numerical aspects of this model are explained in detail in a previous paper⁵. The model describes the main reactions and processes in an electrochemical system such as electrochemical and chemical reactions at the steel surface, transport of species between the steel surface and the bulk solution, and formation/growth of corrosion product layers. All these mechanistic features make this particular model a suitable tool for simulating the impedance response of electrochemical reactions associated with the corrosion of mild steel.

RESULT AND DISCUSSION

Modeling Steady State Potentiodynamic Sweep

As the first step, the modeling of the steady state potentiodynamic sweep is required in order to establish whether the model can properly generate the steady state sweeps which would enable us to choose the desired DC potential at which the impedance response will be simulated. In an experiment, generating a potentiodynamic sweep initially requires waiting for the concentrations of the ions to get established near the metal surface in order to obtain a constant open circuit potential (OCP). Similarly, when the simulation is started it takes a certain amount of time to obtain a constant OCP.

Table 1 shows the simulation parameters for generating a steady state potentiodynamic sweep. The velocity in the simulation is the superficial velocity in a pipe with 0.1 m internal diameter, 0.02 m thickness, 20 μm roughness and conductivity of 60 W/m.K. The model was modified to output the open circuit potential at a specified time step (0.01 sec). Consequently, as shown in Figure 1, it only required about 0.1 sec to establish a stable OCP in the simulation.

Table 1. Simulation parameters for generating steady state potentiodynamic sweep.

Parameters	Values
pN ₂	1 bar (de-aerated environment)
Temperature	30°C
pH	4
Electrolyte	0.1 M NaCl
velocity	2.6 m/s

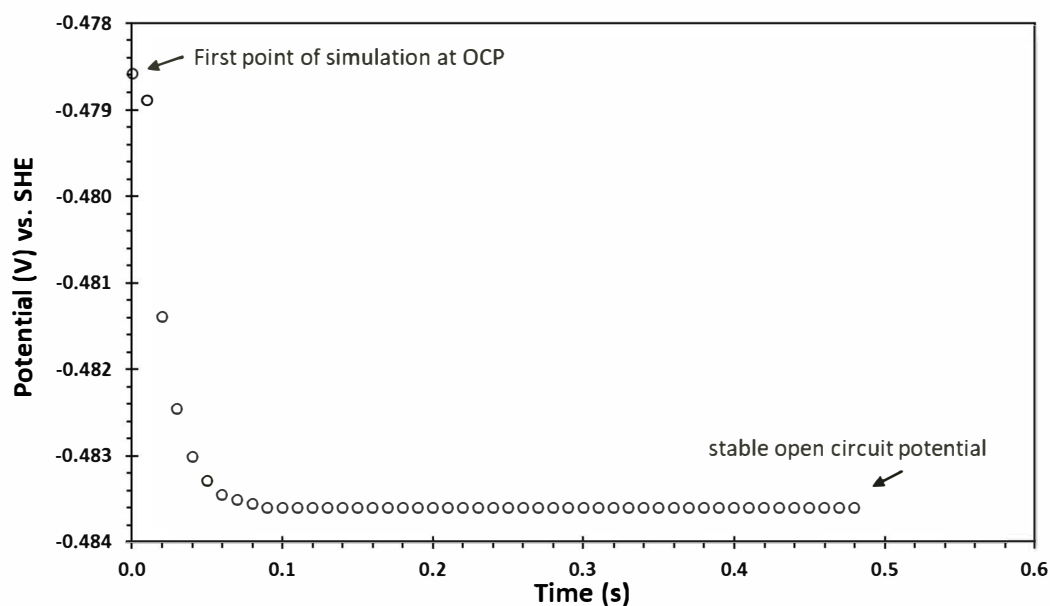


Figure 1: Calculated open circuit potential using 0.01 s time step. Simulation parameters: p_{N_2} = 1 bar, pH 4, $T=30^{\circ}\text{C}$, velocity=2.6 m/s, 0.1 M NaCl.

After obtaining a stable OCP, the potential in the simulation was changed in the cathodic direction from OCP using a -1 mV/s sweep rate (Figure 2a) and the corresponding current density was calculated, as shown in Figure 2b. It is important to note that the chosen sweep rate was small enough to obtain a steady state current density at each potential step before changing the potential. Figure 3 shows the current density response to the first potential perturbation from the OCP ($E = -1\text{ mV}$ vs. OCP). The result shows that the current density reached steady state in less than 1 s. Therefore, this analysis confirms that the potential sweep rate of -1 mV/s was acceptable for generating the steady state potentiodynamic sweep.

Both the cathodic sweep (H^+ evolution) and the anodic sweep (dissolution of iron) were generated. By summation of the anodic current density and cathodic current density, the steady state potentiodynamic sweep was obtained as shown in Figure 4.

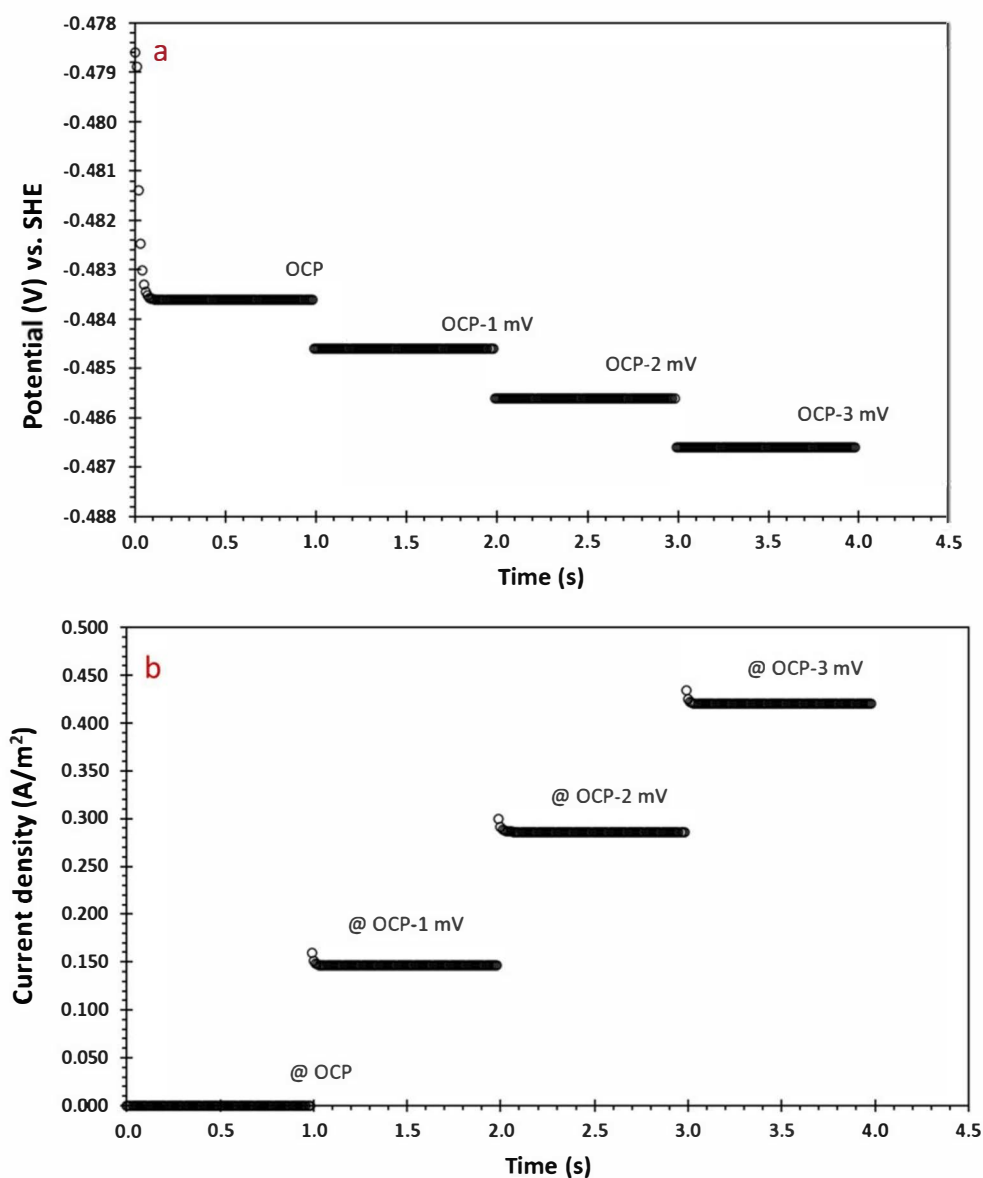


Figure 2: (a) Response when changing the potential from OCP using -1 mV/s sweep rate. (b) Current density response to each potential step. Simulation parameters: pN₂= 1 bar, pH 4, T=30°C, velocity=2.6 m/s, 0.1 M NaCl

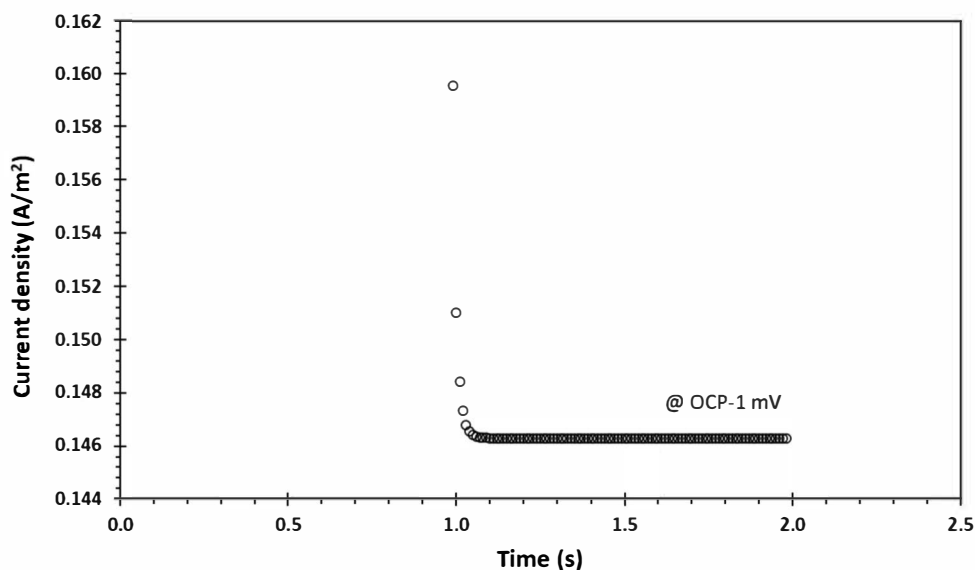


Figure 3: Calculated current density at first potential step from OCP. Simulation parameters: p_{N_2} = 1 bar, pH 4, $T=30^\circ\text{C}$, velocity=2.6 m/s, 0.1 M NaCl.

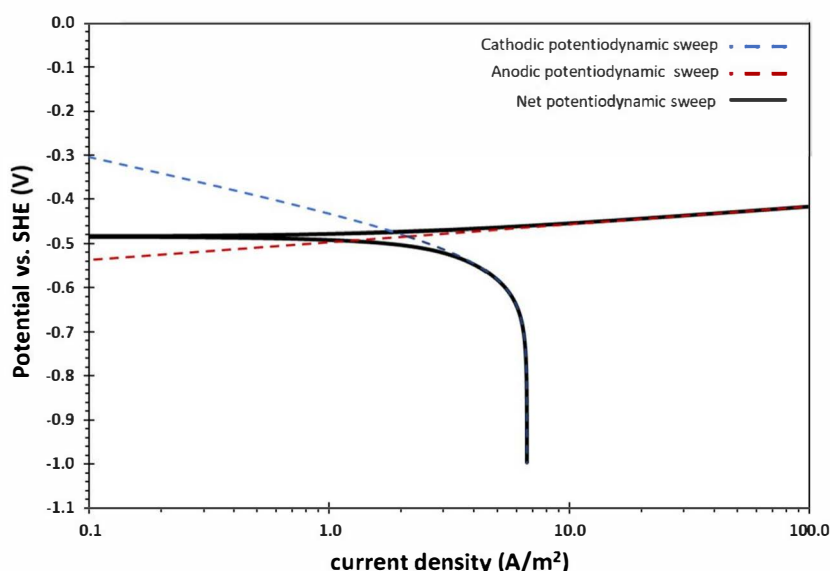


Figure 4: Calculated steady state potentiodynamic sweep. The black line represents the net current density. Simulation parameters: p_{N_2} = 1 bar, pH 4, $T=30^\circ\text{C}$, velocity=2.6 m/s, 0.1 M NaCl, sweep rate =1 mV/s.

Alternative Current (AC) Response to the Imposed Alternating Potential

In the previous section, it was described how the potential was changed linearly using a specific sweep rate, and the corresponding steady state current densities were calculated. The same approach was implemented to perturb the potential in the sinusoidal form at 10 Hz frequency (f)

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at 95 mV below the OCP where the impedance response is mainly related to the cathodic reaction, using Equation(1)¹.The imposed alternating potential is shown in Figure 5.

$$E = \bar{E}_{DC} + |\Delta E|\cos(\omega t) \quad (1)$$

$$i_T = \bar{i}_F + \Delta i_F \cos(\omega t) - C_{dl}|\Delta E|\omega \sin(\omega t) \quad (2)$$

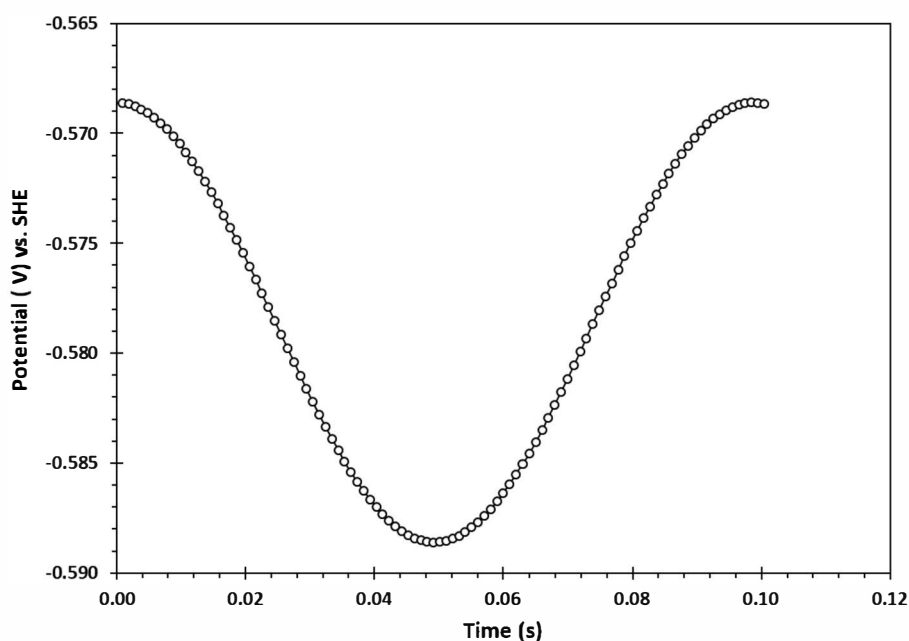


Figure 5. Imposed alternating potential using Equation (1). Simulation parameters: $\bar{E}_{DC}$ = OCP-95 mV, $|\Delta E|=\pm 10$ mV, $f=10$ Hz, $pN_2= 1$ bar = 0, pH 4, $T=30$ °C, velocity=2.6 m/s, 0.1 M NaCl.

When there is a sinusoidal perturbation in potential, the responding current density originates from the electrochemical reactions (Faradaic current) as well as the double layer (charging current) at the metal surface. The current originating from the double layer is generally modeled using capacitive charge and discharge time constants. As an example, the double layer capacitance was chosen as $50 \mu\text{F}/\text{cm}^2$ based on values reported in literature¹. As the potential was varied (Figure 5), the Faradic current density and double layer charging current density were calculated and summed according to Equation (2)¹ to obtain the total current density response as shown in Figure 6.

Once the current response to the alternating potential was obtained, the impedance was calculated using the maximum current density and the maximum perturbed potential from Equation (3)¹ and the Lissajous plot was produced, which is shown in Figure 7.