Electrochemical Impedance Spectroscopy (EIS)

Overview & Test Procedure

Introduction

Electrochemical Impedance Spectroscopy (EIS) is a laboratory technique that performs impedance characterization for electrode-electrolyte interfaces. From EIS measurements we obtain magnitude and phase parameters of the impedance with respect to frequency and can generate Bode and Nyquist Plots. These plots are useful because they provide complete and concise information on the performance of electrodes in an implantable neural probe, for example.

Because we are measuring impedance, the electrode-electrolyte interface can be modeled as an electric circuit consisting of lump elements such as resistors and capacitors. As we will investigate later, the interface impedance response is typically different to an ideal resistor-capacitor network. Other elements such as Warburg or constant-phase elements can be used to better model the interface and fit the data more accurately. For a high-level understanding, electric circuit models are commonly used in biomedical applications, such as modeling a skin electrode (figure 1), where each circuit element corresponds to the interpretation of a physical property of the system. In this text we will explore well known circuit models such as the Randles Cell, or the Gouy-Chapman-Stern model.

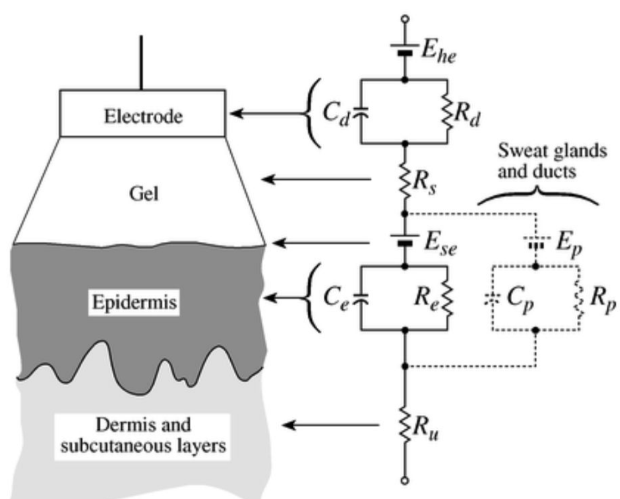

Figure 1. Skin electrode equivalent circuit. [1]

The main criticism of using electric circuit models is that they rely on intuition or interpretation of the physical phenomena at the interface. A more rigorous approach is to consider the electrode-to-electrolyte interface as a boundary value problem with the corresponding governing equations and initial/boundary conditions, as illustrated in figure 2. The Modified Poisson-Nernst-Planck (MPNP) model[1] analyzes this problem as such and characterizes the interface based on material properties, size, mobility and diffusion coefficients, among other parameters. This model is more complex and cumbersome to work with and it is beyond the scope of the research we are conducting in our lab, to date.

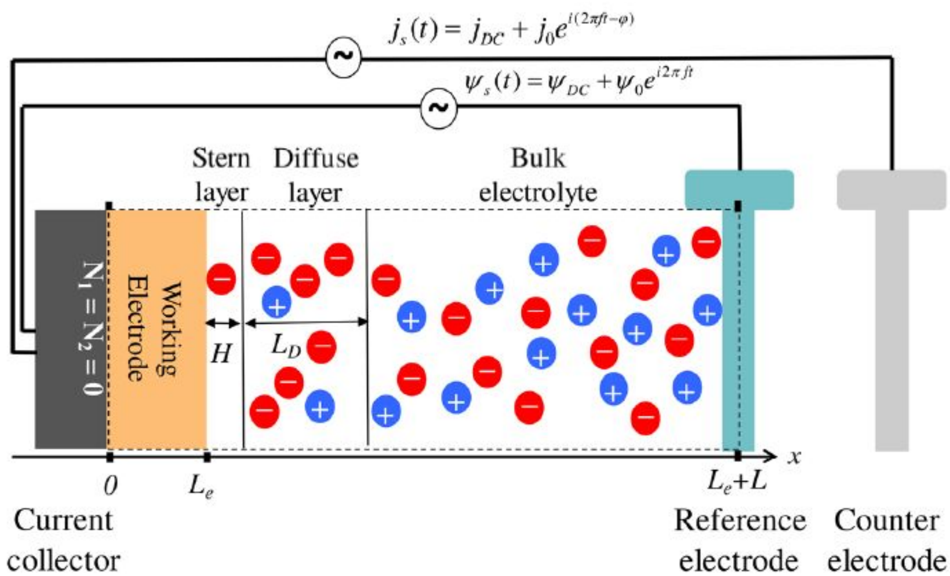

Figure 2. Electrode-to-electrolyte interface 1D Boundary Value Problem. [2]

The focus in the lab is not to investigate the most accurate model of the electrode-to-electrolyte interface between our neural probes and the cerebrospinal fluid, but to make sure the impedance is *low enough* and compatible with the rest of the system. In addition, design parameters of our neural probes and electrodes are mostly not modified based on EIS measurements or tweaked to evaluate the validity of the MPNP model.

A good compromise for our purposes is to use electric circuit models where each parameter represents a macroscopic physical quantity, in line with the microscopic MPNP model. Despite potential disparities between the circuit model and the EIS data, this exercise will provide us with context and intuition of the behaviour of the electrodes of our neural probes[2].

[1] More information on MPNP: *J. Phys. Chem. C* 2018, 122:1, 194–206. doi
[2] How important is the electrode impedance model? *Neto et al. (2018) Front. Neurosci. 12:715.* doi.

Electrode-Electrolyte Circuit Models[3]

Depending on the characteristics of the electrode: material, size, electrolyte-compatibility, etc. the electrode-electrolyte interface might be modeled by one type of circuit or another. A common practice for electrode characterization is to reverse engineer a circuit model that fits the data set based on observed physical phenomena.[4] This practice is described by many as an *art* rather than a meticulously scientific procedure. To help with this task, knowing the response of common circuits will provide intuition on the kind of circuit model the interface corresponds to.

Purely Capacitive Coating

Given a hypothetical electrode with an insulating coating material, the behavior appears to be purely capacitive. For a 1 cm^2 electrode with a 25 μm deep coating and relative permittivity, ε_r = 6, we can model the interface as a capacitor in series with the electrolyte resistance, assumed to be poorly conductive: $R_{electrolyte}$ = 500 **Ω** shown in fig. 3 with equivalent impedance in eq. (1).

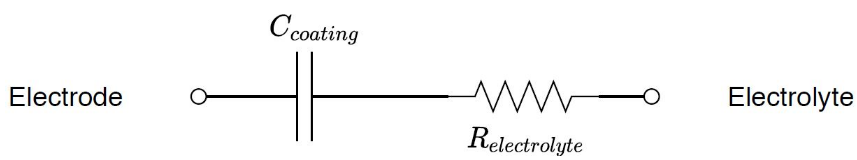

Figure 3. Circuit model of Pure Capacitive electrode

$$Z = \frac{1}{jC} + R \qquad \text{(Eq. 1)}$$

The corresponding Bode and Nyquist plots are:

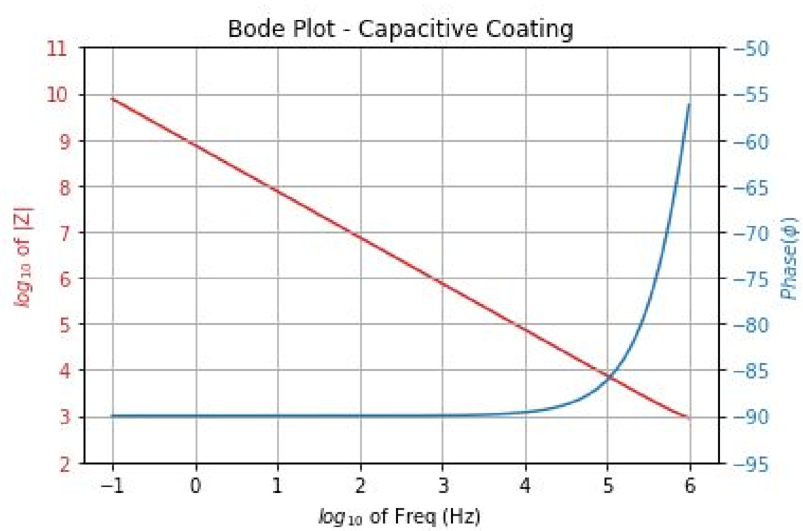

Figure 4. Magnitude and Phase Bode Plot for purely capacitive electrode

[3] Python scripts and modules Git repo.
[4] More on basics of EIS: Gamry Instruments App note & *Franks et al. (2005) IEEE Biomed. Eng. 52:7* doi.

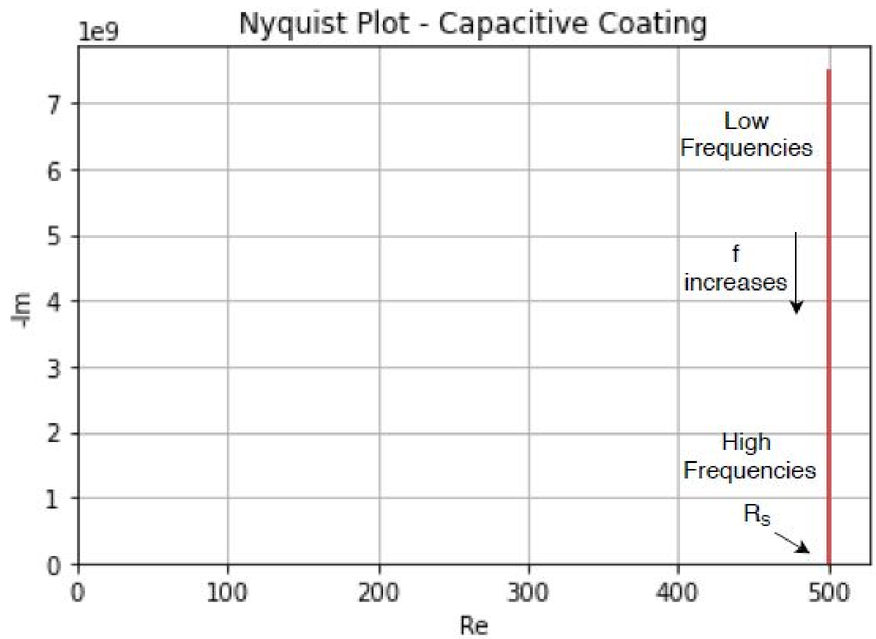

Figure 5. Nyquist Plot for purely capacitive electrode

The Bode plot was obtained from calculating the $\log_{10}$ of the magnitude of the impedance:

$$log_{10}(|Z|) \qquad \text{(Eq. 2)}$$

showed as the red curve, −, in fig. 4, and the phase, −, is simply the angle of the complex impedance:

$$\angle = tan^{-1}\left(Im/Re\right) \qquad \text{(Eq. 3)}$$

where both parameters are plotted versus the $\log_{10}$ of the frequency. For a pure capacitive electrode, we see the negative slope of the magnitude as the frequency increases and a constant phase at -90° for low frequencies that increases with higher frequencies.

The Nyquist plot is the curve of the negative imaginary component (-*Im*) vs the real component (*Re*) of the impedance. In this plot (fig. 5), we see a vertical line at the 500**Ω** (R_s) mark in the horizontal axis corresponding with many -*Im* values $(1/jC)$. Considering the equation of the impedance of this interface (eq. 1), we can reason how the Nyquist plot goes downwards at the vertical line as the frequency increases, since the imaginary component vanishes with large values of ω.

A purely capacitive electrode is often not the desired response for an electrode. However, this simplified model serves as a good introduction for circuit models and provides an illustration for the response expected from highly capacitive interfaces.

Simplified Randles Cell

A more precise model of the electrode-electrolyte interface takes into account the physical phenomena at the interface. As shown in figure 2, in the interface between the electrode and the electrolyte there is a double layer of charged ions, the stern and diffuse layer. Based on parameters describing this double layer, an equivalent double layer capacitance can be obtained, C_{dl}. In addition, we consider the chemical RedOx reaction at the interface which converts the charge carrier from electrons to ions. A half-cell reaction of a metal electrode is given in (4).

$$M \rightarrow M^{+} + e^{-} \qquad \text{(Eq. 4)}$$

In the RedOx reaction, the dynamics governing the transfer of charge-carriers does not result directly in a one-to-one exchange. A lot more electrons might be present and *awaiting* for the reaction at the interface, or vice versa. The delayed exchange can be modeled as a charge-transfer resistance, R_{ct}.

Therefore, the simplified Randles Cell circuit model can be used to model the interface, where R_s is the resistance of the electrolyte.

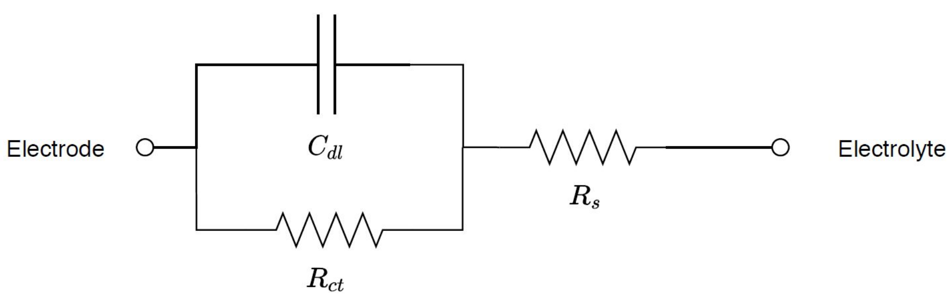

Figure 6. Simplified Randles Cell for double layer ion interface.

The equivalent impedance of this circuit is:

$$Z = \frac{R_{ct}}{1 + jC_{dl}R_{ct}} + R_s \qquad (5)$$

Considering a solution as our electrolyte with R_s = 20 **Ω**, a charge-transfer resistance, R_{ct} = 250**Ω** and a double layer capacitance, C_{dl} = 40 μF. The Bode and Nyquist plots are given in figures 7 and 8.

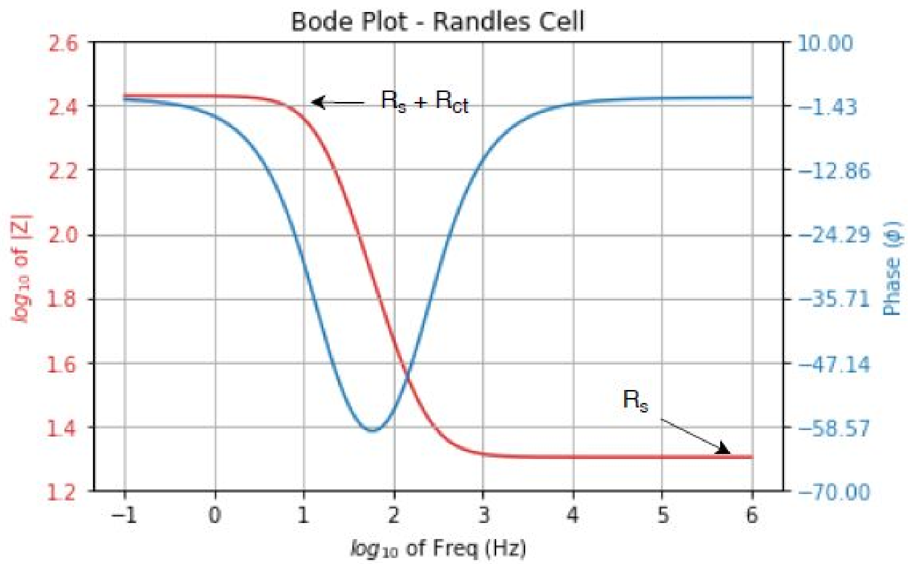

Figure 7. Magnitude and Phase Bode Plot of simplified Randles Cell

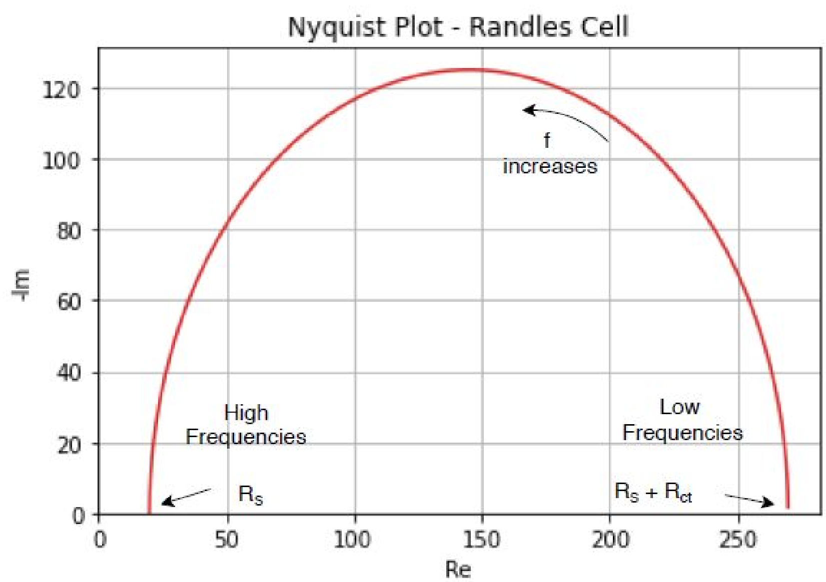

Figure 8. Nyquist Plot of simplified Randles Cell.

With a similar analysis as in the previous section, we can observe that at high frequencies the dominant parameter is the electrolyte resistance, R_s (right side of the bode plot and left side of the nyquist plot) and that at low frequencies the dominant parameters are R_s and R_{ct} (left side and right side of Bode and Nyquist plot respectively). The capacitance parameter influences the behaviour in the mid-frequency range. As it turns out, this response is seen in EIS experiments except for the phase response. As mentioned earlier, to adjust the model, we use a constant phase element, Z_{CPE}, which is similar to a capacitor but with a constant phase response.

Modified Randles Cell - Pt black electrodes (900 μm^2)

A more precise model of the electrode-electrolyte interface takes into account the physical phenomena at the interface. As shown in figure 2, in the interface between the electrode and the electrolyte there is a double layer of charged ions, the stern and diffuse layer. Based on parameters describing this double layer, an equivalent double layer capacitance can be obtained, C_{dl}. In addition, we consider the chemical RedOx reaction at the interface which converts the charge carrier from electrons to ions. A half-cell reaction of a metal electrode is given in (4).

$$M \rightarrow M^{+} + e^{-} \quad \text{(Eq. 4)}$$

In the RedOx reaction, the dynamics governing the transfer of charge-carriers does not result directly in a one-to-one exchange. A lot more electrons might be present and *awaiting* for the reaction at the interface, or vice versa. The delayed exchange can be modeled as a charge-transfer resistance, R_{ct}.

Therefore, the simplified Randles Cell circuit model can be used to model the interface, where R_s is the resistance of the electrolyte. A modified version of this Randles Cell is often used to model electrode performance.

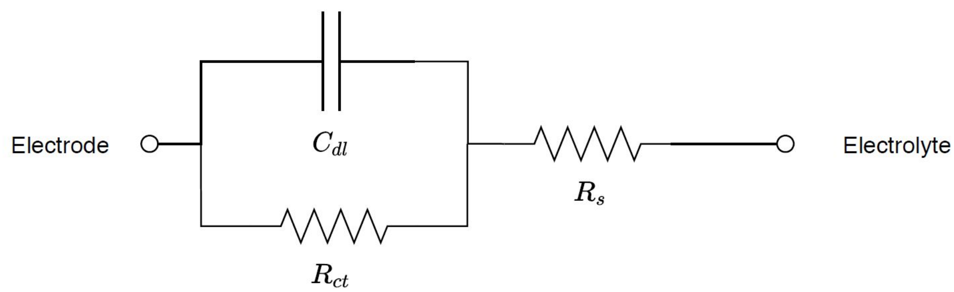

Figure 6. Simplified Randles Cell for double layer ion interface.

The equivalent impedance of this circuit is:

$$Z = \frac{R_{ct}}{1 + jC_{dl}R_{ct}} + R_s \quad (5)$$

Considering a solution as our electrolyte with R_s = 20 **Ω**, a charge-transfer resistance, R_{ct} = 250**Ω** and a double layer capacitance, C_{dl} = 40 μF. The Bode and Nyquist plots are given in figures 7 and 8.

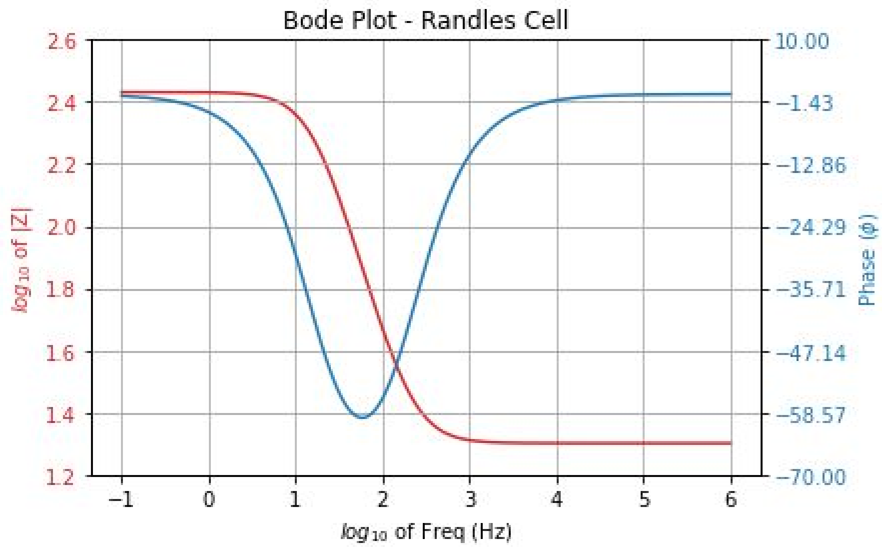

Figure 7. Magnitude and Phase Bode Plot of simplified Randles Cell

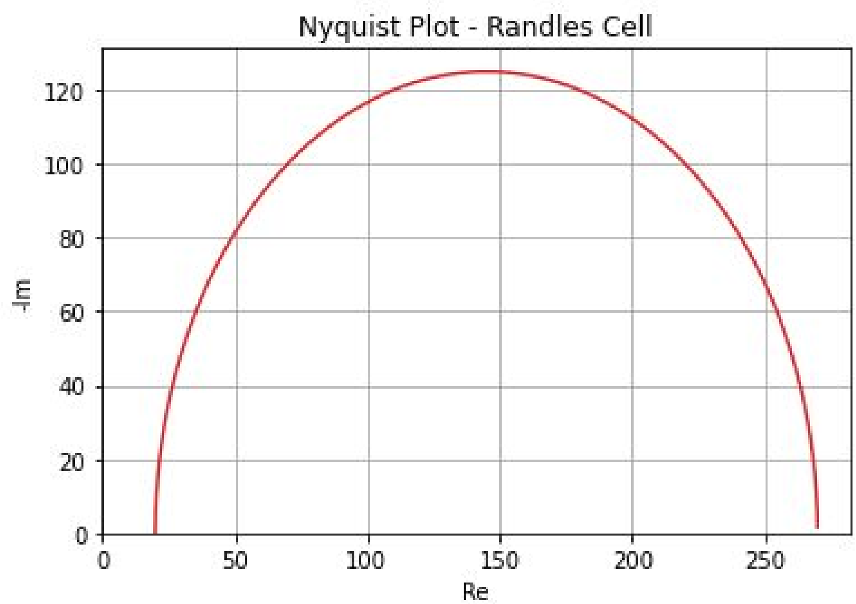

Figure 8. Nyquist Plot of simplified Randles Cell.

Experimental Set-Up

EIS measurements can be performed using a two- or three-electrode setup procedure. In our lab, we use a three electrode setup.

Three electrode Set-Up