

Electrochemical Impedance Spectroscopy (EIS)

Gamry Interface 1010E

Potentiostat/Galvanostat/ZRA

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Electrochemical impedance spectroscopy (EIS) is a powerful technique that utilizes a small amplitude, alternating current (AC) signal to study the impedance characteristics of a cell. The AC signal is scanned over a wide range of frequencies to generate an impedance spectrum for the electrochemical cell. This impedance technique differs from direct current (DC) techniques as it allows the study of capacitive, inductive, and diffusion processes taking place inside the electrochemical cell.

In this experiment we will use the Physical Electrochemistry to study the Circuit Elements, their common Equivalent Circuit Models and then extract Model Parameters from Impedance Data. We will talk about the generation of Lissajous Figure and how this figure helps us to obtain the Nyquist Plot that gives us the whole set of information regarding our electrochemical cell.

1. Theoretical Introduction

The principles of electrochemical impedance spectroscopy can be understood by understanding the basic circuit elements and the parameters that are associated with them.

1.1. AC Circuit Theory

The simplest electrical circuit is the resistor itself that obeys the Ohm's law which means that the current is always proportional to the voltage. Thus, the resistance is defined as a ratio of voltage, E and current, I .

$$R = \frac{E}{I} \quad (1)$$

When a voltage is applied to a resistor, the response of this signal is a current that depends upon the resistance of that specific resistor. This current does not have a reactive part (i.e., would be in-phase with the voltage) and the resistance would not be dependent on the frequency. However, many of the circuits used in daily life contains elements that exhibit much more complex behaviors. Thus, rather than resistance, we use a more generalized term called impedance, Z which is defined as ability of the circuit to resist the flow of electrical current. In this case, however, the impedance includes the reactive part and would also be dependent on

the frequency. Thus, impedance can be written in terms of the capacitive response with the capacitance C and frequency $\omega=2\pi f$ as [1]:

$$Z = \frac{1}{j\omega C} \quad (2)$$

Electrochemical impedance can be obtained by measuring the current through an electrochemical cell when an AC voltage is applied. Let us assume that a sinusoid voltage is applied to a system, the response of which would be a sinusoid current with same frequency but shifted in phase as shown in Figure 1.

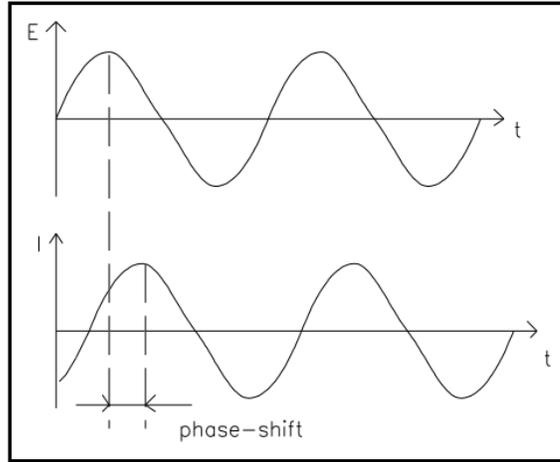


Figure 1: Sinusoidal applied voltage and current response as a function of time t .

The applied sinusoid voltage can be expressed as a function of time:

$$E_t = E_0 \sin(\omega t) \quad (3)$$

where E_t is potential at time t and E_0 is the amplitude of the signal. The response signal I_t would be shifted in-phase (ϕ) and has a different amplitude I_0 :

$$I_t = I_0 \sin(\omega t + \phi) \quad (4)$$

Thus, the expression for Ohm's law will allow us to calculate the impedance of the circuit:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (5)$$

If the applied voltage signal E_t is plotted on x-axis and the response signal I_t on y-axis, then an oval is obtained which is called as Lissajous Figure. Lissajous Figure (as shown in Figure 2) can give all the details regarding impedance measurement of the system and can be easily obtained on an oscilloscope.

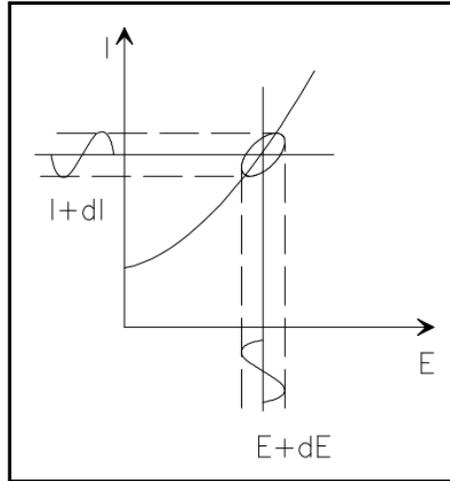


Figure 2: Lissajous Figure with E on x-axis and I on y-axis.

Using Euler's relationship:

$$\exp(j\phi) = \cos \phi + j\sin(\phi) \quad (6)$$

impedance can be written as a complex function:

$$Z(\omega) = Z_0 \exp(j\phi) = Z_0(\cos \phi + j\sin \phi) \quad (7)$$

The above expression is composed of real and imaginary part which we can represent as an Argand diagram, plotting the real part on x-axis while the imaginary part on y-axis. This plot for impedance is called Nyquist plot and is shown in Figure 3. Each point on Nyquist plot defines the impedance at one frequency. For a simple RC parallel circuit, one might obtain a single semi-circle. This semi-circle is the characteristic of a single time constant.

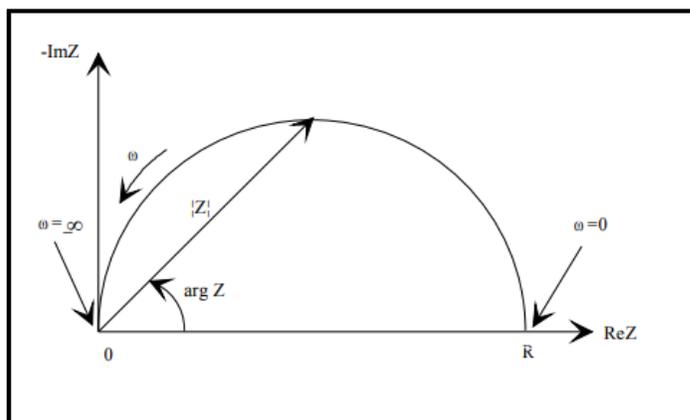


Figure 3: Nyquist Plot with impedance vector Z .

1.2. Electrical Circuit Elements and their Applications

EIS data can be analyzed by fitting it into the equivalent electrical circuit models. Most common circuit elements are resistors, capacitors and inductors and models the physical electrical systems. For example, a combination of resistors models the cell's solution resistance. In actual, very few electrochemical cells can be modeled using a single equivalent circuit element like resistor or capacitor. Usually, a combination of these elements is responsible for the accurate demonstration of the impedance. Such combinations are called serial or parallel combinations of elements [2]. The simple formulas for series and parallel combinations of resistors and capacitors can describe the impedance of the system.

EIS, in this way, is most useful to determine the resistance of the ionic solutions. The resistance of such a solution depends upon the ionic concentration, temperature, ion type and the geometry of the area in which the current is carried. Thus, resistance can be calculated using the equation:

$$R = \frac{l}{\kappa A} \quad (8)$$

where κ is called the conductivity of the solution, l is the length and A is the area of the geometry carrying the current. Using EIS, one can determine the resistance of the ionic solution directly without calculating the ionic conductivity.

Thus, using EIS one can calculate the double layer capacitance, polarization resistance, charge transfer resistance, diffusion of reactants, coating capacitance and much more.

1.3. Cyclic Voltammetry

Cyclic voltammetry (CV) is the most useful electrochemical technique in the world as it allows to study the electrochemical systems revealing not only fundamental knowledge but also application-oriented information. CV is helpful in extracting the qualitative kinetic data about a capacitive electrochemical cell such as capacitance, voltage window and cycle life.

Capacitors can operate within a range of voltage called the "voltage window". Wider this window is, efficient would be our capacitor. Voltages outside this window causes the decomposition of the electrolyte which can eventually damage the device. Electrolytes may be aqueous or non-aqueous depending upon the application and geometry of the cell. Aqueous electrolytes are easier and safer in use however non-aqueous electrolytes have wide voltage window.

Capacitors also have a cycle life. They can be charged and discharged for several times, but they eventually degrade. Super-capacitors that are operating now days have 10^5 charge/discharge cycles. The cycle life of all the rechargeable capacitors depends upon the conditions under which the cycling occurs. These conditions involve the current magnitude, voltage limits and temperature.

1.3.1. Description of Cyclic Voltammetry

In CV, current that flows across the electrochemical cell is plotted as the voltage is swept over a voltage range. The voltage is repetitively sweeps between the two limit potentials and a pair of sweeps in opposite direction is called a cycle.

In a typical CV experiment, the electrolyte is oxidized or reduced by placing the solution in contact with the electrode. Then a potential is applied to the electrode that is kept sufficiently positive or negative with respect to the reference electrode. The electrode's voltage is swept higher or lower according to the voltage window and then the voltage is returned to the original value as shown below in Figure 4:

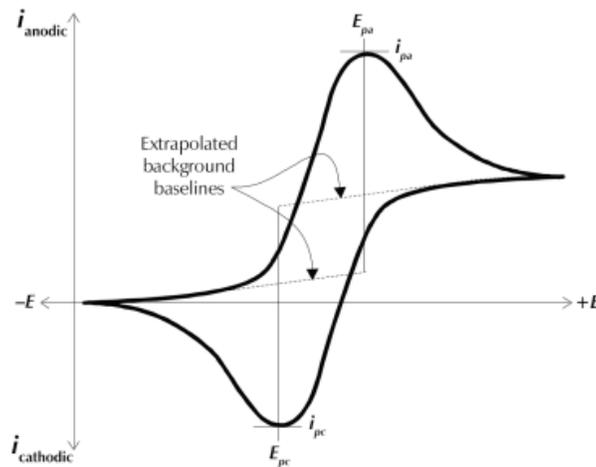


Figure 4: A typical CV voltammogram.

As the potential is swept back and forth, a current flow through the electrolyte that either oxidize or reduce the electrolyte. In other words, a species in the solution may transfer electrons to the electrode surface or may gain from the surface. Electron transfer or gain is the measurable current in the whole system that depends upon the concentration of the charges present in the electrolyte. This allows the CV to be used in an analytical determination of concentration. The result is a cyclic voltammogram with the swept potential on x-axis and current on the y-axis.

The positive potentials are plotted to the right on the voltammogram showing the oxidation process while negative potentials to the left showing reduction processes. The current that is graphed on the y-axis with cathodic currents plotted in the negative direction while anodic currents on the positive direction. The peaks in the voltammogram denotes a particular electrolytic process with the height of the peak determines the concentration of the solution. The initial direction of the first sweep in a CV experiment is thus defined whether the solution is oxidizable or reducible. Thus, for an oxidizable solution, the sweep starts in the positive direction while in negative for reducible solutions [3].

2. Experimental Apparatus

The experimental kit of Gamry Interface 1010E is available in the lab with its user-friendly software named Gamry Framework. All experiments are launched from Gamry Framework which is in actual an Explain Interpreter. Once the kit is fully assembled, the software is configured and fully calibrated and the electrochemical cells are made, one can start doing an analysis. The Gamry kit consists of the following parts:

- Gamry Interface 1010E
- Power supply with power cord
- Cell cable

The cell cable consists of a cable connector with a 25-pin female D connector at one end (that will be connected to the interface) while the other end of cell cable terminates in a number of banana plugs and pin jacks. These terminators are identified separately with a specific color as blue for working sensor, green for working electrode, white for reference electrode, red for counter electrode, orange for counter sensor and black for grounding the cell.

2.1. Potentiostat

A potentiostat is an electronic instrument that is used to control the voltage difference between a working electrode and reference electrode placed inside an electrochemical cell. This is achieved by injecting current through an auxiliary or counter electrode placed in the same cell. As a response of this injection, potentiostat measures the current flow between the working and counter electrodes.

2.2. Galvanostat

A galvanostat is an electronic instrument that is used to control the cell current in order to measure the cell voltage. Gamry's software can measure impedance spectra in either a potentiostat mode or galvanostat mode.

In potentiostat mode, a DC voltage is applied which is superimposed by an AC voltage signal. The frequency of this signal varied and a phase-sensitive AC current is measured.

In galvanostatic mode, alternatively, a DC current is applied, superimposed by an AC current to measure phase-sensitive AC voltage.

Potentiostatic mode is the most common mode of operation in EIS, but for small errors in applied DC voltage can lead to huge DC currents in low-impedance cell like for batteries, galvanostatic mode may give better results.

2.3. Zero Resistance Ammeter (ZRA)

There is also a third mode of operation, named as ZRA which force the potential difference of zero volts between two electrodes. This mode is useful in measuring the galvanic corrosions and electrochemical noise.

2.4. Standard Electrochemical Cell

A potentiostat requires a standard electrochemical cell which is composed of three electrodes, the working electrode, reference electrode and counter electrode.

2.4.1. Working Electrode

The working electrode is the specimen being tested. This is the electrode where the potential is controlled and current is measured. For many electrochemical experiments, the working electrode is an inert material such as gold, platinum or glassy carbon in which the working electrode act as a surface where the electrochemical reaction takes place.

2.4.2. Reference Electrode

The reference electrode such as silver/silver chloride (Ag/AgCl) electrode is used to measure the working electrode potential.

2.4.3. Counter Electrode

The counter electrode is the output of the Interface. The counter electrode is generally a platinum or graphite, which act as a conductor that completes the cell. The current that enters the cell from the working electrode, leaves the solution via counter electrode.

The schematic diagram of Gamry Instrument's potentiostat is shown below in Figure 5. In this schematic, $\times 1$ on an amplifier indicates that the amplifier is a unity-gain differential amplifier. The output voltage of this circuit is the difference between its two inputs.

The blocks labeled Voltage and Current $\times R_m$ are the voltage and current signals that are sent to the system A/D converters for digitization. The electrometer circuit measures the voltage difference between the reference and working electrodes. Its output has two major functions: it is the feedback signal in the potentiostat circuit, and it is the signal that is measured whenever the cell voltage is needed.

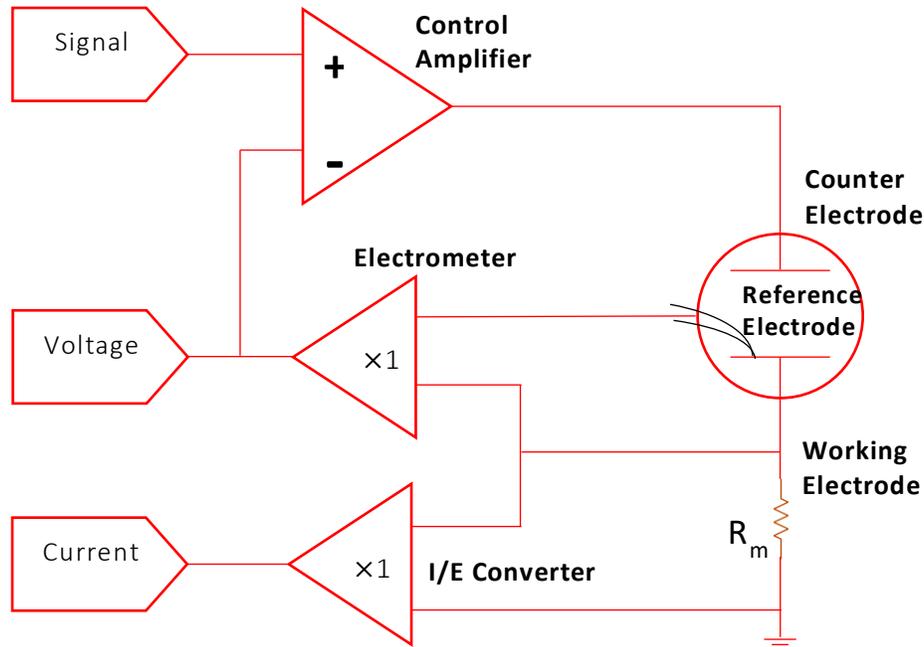


Figure 5: Schematic of Gamry Instrument's Potentiostat

The current-to-voltage (I/E) converter in the schematic measures the cell current. It forces the cell current to flow through a current-measurement resistor, R_m . The voltage drop across R_m is a measure of the cell current.

The control amplifier is a servo amplifier. It compares the measured cell voltage with the desired voltage and drives current into the cell to force the voltages to be the same.

3. Experiment I: Randles Cell

In the first experiment, we will learn how to calculate a solution resistance (R_s), double layer capacitance (C_{dl}) and a charge transfer or polarization (R_{ct}/R_P) resistance. This experiment can be simplified if a simple combination of resistor and capacitor is selected. We will perform this experiment as a dummy experiment by just making a series and parallel combination of RC circuit.

3.1. Apparatus

This experiment is designed to perform as a two-electrode system in which working and working sense terminals are attached at one end of the circuit while the counter and reference terminals are attached to the other end. A proposed circuit is shown in Figure 6.

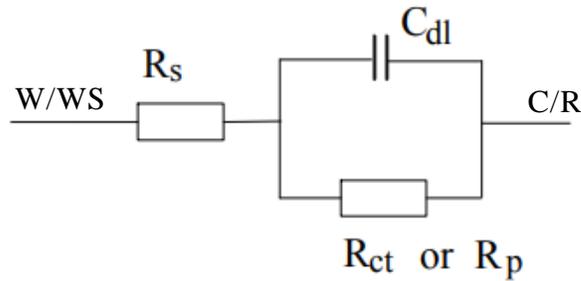


Figure 6: Proposed Randle circuit for EIS measurement with one end connected to working and working sense (W/WS) terminal and the other end to counter and reference (C/R) terminal.

The circuit in Figure 6 is regarded as the equivalent circuit of the simplified Randle cell. This circuit can be made easily on a breadboard through resistors and capacitors connected with each other as shown.

3.2. Procedure

1. After making the right connections to the circuit press the power button on the front panel of the Gamry Interface 1010E.
2. Open the Gamry Framework.
3. Go to Experiment >> Electrochemical Impedance >> Galvanostatic EIS.

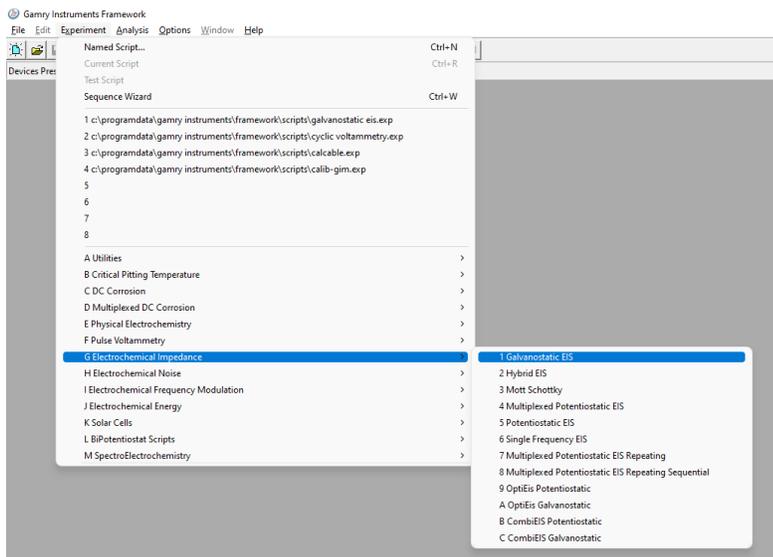


Figure 7: Procedure to open Galvanostatic EIS.

4. Another window will appear as shown in Figure 8 below. Type the name of the file in Output File option. After putting the values as shown for rest of the parameters press the OK button to start the measurement.

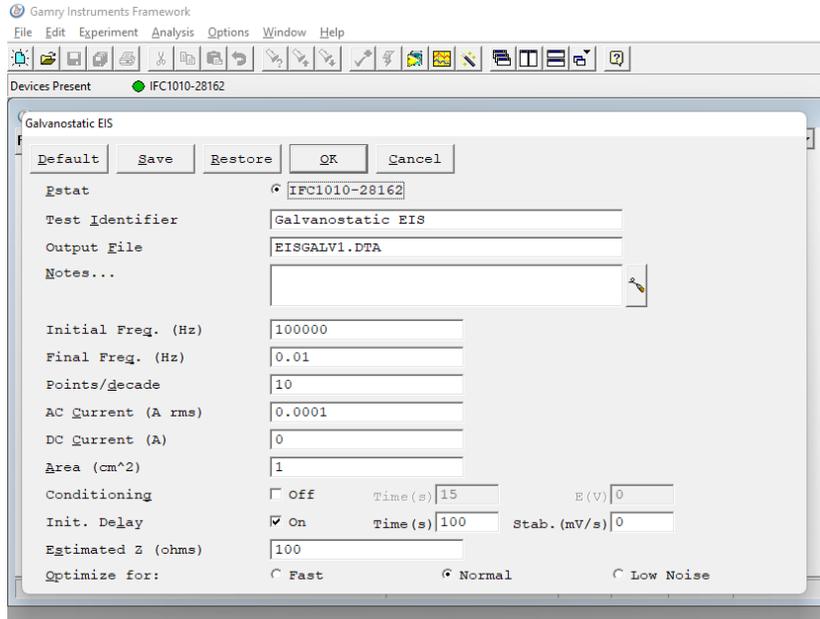


Figure 8: Galvanostatic EIS window for EIS measurement.

The software will automatically start taking the data and will save it to your desired destination as a DTA file type. This file then can be open from the Gamry Echem Analyst. The Echem Analyst shows the impedance data in the form of Nyquist plot. The data can be saved from the copy to clipboard button at the top left side.

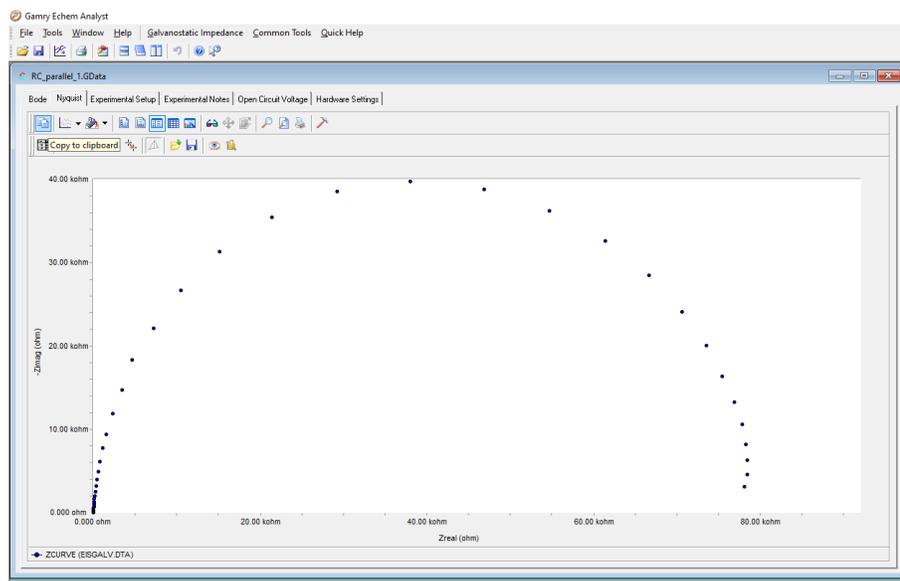


Figure 9: Nyquist plot from Echem Analyst.

The data obtained from the Echem Analyst then can be plotted on any software and can be optimized. Further information on how to use Echem Analyst can be seen from reference [4].

4. Experiment II: Cyclic Voltammetry of Ferricyanide

In this experiment Gamry Interface 1010E was used to study the cyclic voltammetry of Ferricyanide. Here, $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ couple is used as an electrochemical reversible redox system. A platinum working electrode of 2 mm diameter (CH Instruments Inc., CHI102), Ag/AgCl reference electrode (CHI111) and platinum wire counter electrode (CHI115) was used in this three-electrode system. Before starting each experiment, the working electrode under usage should be initially polished with alumina and rinsed with water.

4.1. Reagents

First a 2 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution was prepared using stoichiometric amount of $\text{K}_3\text{Fe}(\text{CN})_6$ crystals. Then, a stock solution 50 mL of 2mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 1 M KNO_3 was prepared.

4.2. Apparatus

50 mL solution of $\text{K}_3\text{Fe}(\text{CN})_6$ and KNO_3 was added to cell. The cell consists of a beaker with three electrodes named working, reference and counter electrode. The working electrode was connected to the green and blue terminals named working and working sense terminals. Reference electrode to the white and counter electrode to the red terminal.



Figure 10: Experimental apparatus and electrode setup for CV measurement.

4.3. Procedure

1. When the cell connections were made, power on the Gamry Interface 1010E and then open the Gamry Framework software.

2. Go to Experiment >> Physical Electrochemistry >> Cyclic Voltammetry.

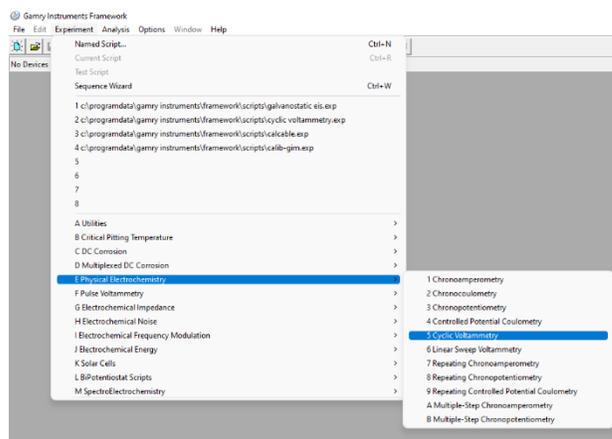


Figure 11: Procedure to open Cyclic Voltammetry.

3. Another window will appear as shown in Figure 12 below. Type the name of the file in Output File option. After putting the values as shown for rest of the parameters press the OK button to start the measurement.

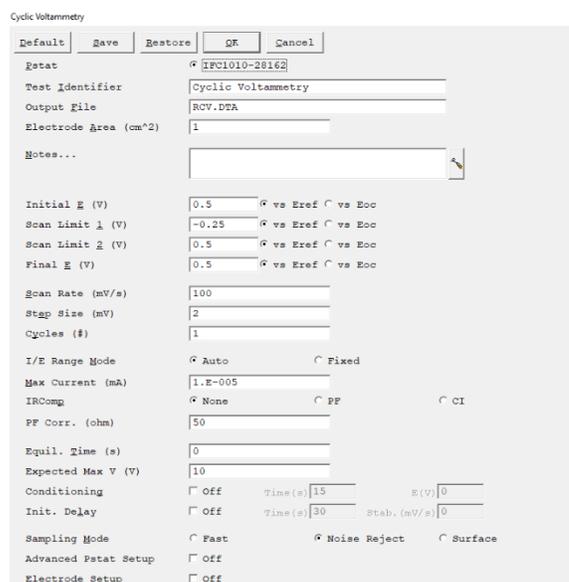


Figure 12: Cyclic Voltammetry window.

5. Results and Discussion I

Figure 13 shows the Nyquist plot obtained for simplified Randles cell. The Nyquist plot for Randles cell is always a semi-circle and it includes quantitative information regarding the solution resistance, double layer capacitance and charge transfer resistance. Double layer capacitance is the capacitance of a double layer that exists on an interface between the electrode and electrolyte. The main cause for the formation of double layer are the ions that stuck on the electrode surface. In actual, the charged electrode surface is separated by the order of angstroms from

the charged ions. This double layer capacitance is in parallel with the charge transfer resistance as can be seen from the equivalent circuit model from Figure 6.

The solution resistance can be found by noting the real axis value at the highest frequency i.e., near the origin of the plot. In our case the solution resistance is very low that is 3.5 Ω . The other real axis intercept shows the sum of the values of the solution resistance and the charge transfer resistance. Thus, the diameter of the semi-circle would be equal to the charge transfer resistance which is 78150 Ω .

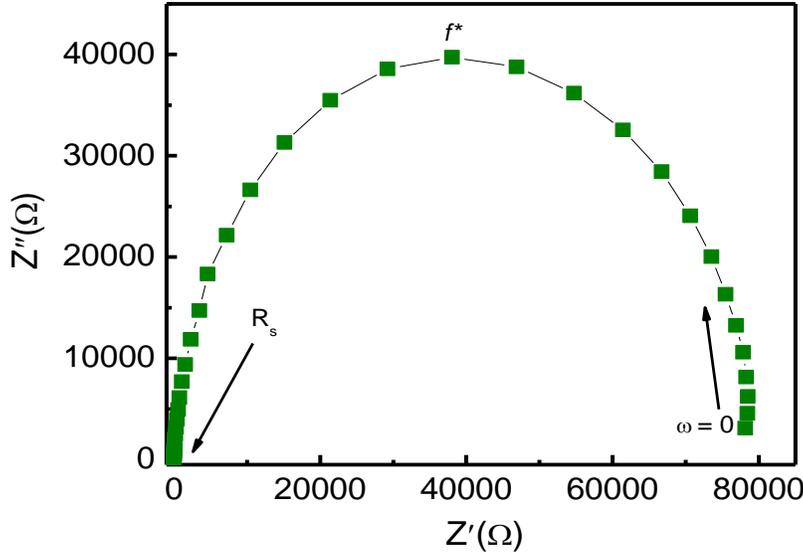


Figure 13: Nyquist Plot for Randles cell.

For the determination of capacitance, we take assistance from the relaxation frequency (f^*) which is related to RC time constant. RC time constant is directly related to the relaxation frequency as the peak of semi-circle occurs at $\omega RC = 1$. Thus, we can write:

$$\tau = \frac{1}{\omega} = \frac{1}{2\pi f} = RC \quad (9)$$

To calculate the capacitance, we must know the relaxation frequency. This is where the Bode plot comes into play. Bode plot is the graph between real/imaginary impedance and frequency. Corresponding to the highest impedance value we can point out the value of relaxation frequency and thus, calculate the capacitance from the following equation:

$$C = \frac{1}{2\pi fR} \quad (10)$$

For our Randles cell, the value of double layer capacitance was 10 μF .

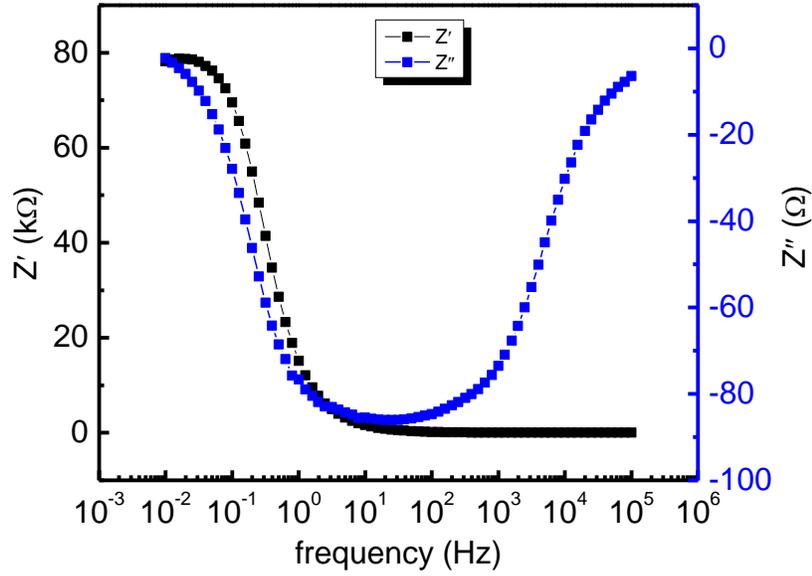


Figure 14: Bode plot for Randles cell.

6. Results and Discussion II

Figure 15 shows the cyclic voltammogram for a mixture of 2mM solution of $K_3Fe(CN)_6$ and 1 M solution of KnO_3 . The potential is drawn at the x-axis on the more positive side of the voltammogram thus, giving oxidizing potentials. While the current is plotted against the y-axis with cathodic currents on the negative side and anodic currents on the on the positive side. The peak height determining the highest current value depends upon the concentration of solution.

The quantitative information that can be obtained are the peak potential for the anodic peak E_{pa} , and the peak potential for the cathodic peak E_{pc} . The difference between them can be calculated as ΔE_{peak} , which can tell whether the redox couple we used is reversible. From the Nernst equation:

$$n\Delta E_{peak} = 59 mV \quad (11)$$

where n is the number of electrons taking part in the redox reaction.

The ferricyanide ions undergo single electron transfer as shown in the following equation:



Since the cathodic and anodic peak currents are equal so the relation $i_{pc}/i_{pa}=1$, holds which means that the reaction is reversible. If this ratio deviates from 1, this means that the reaction is irreversible.

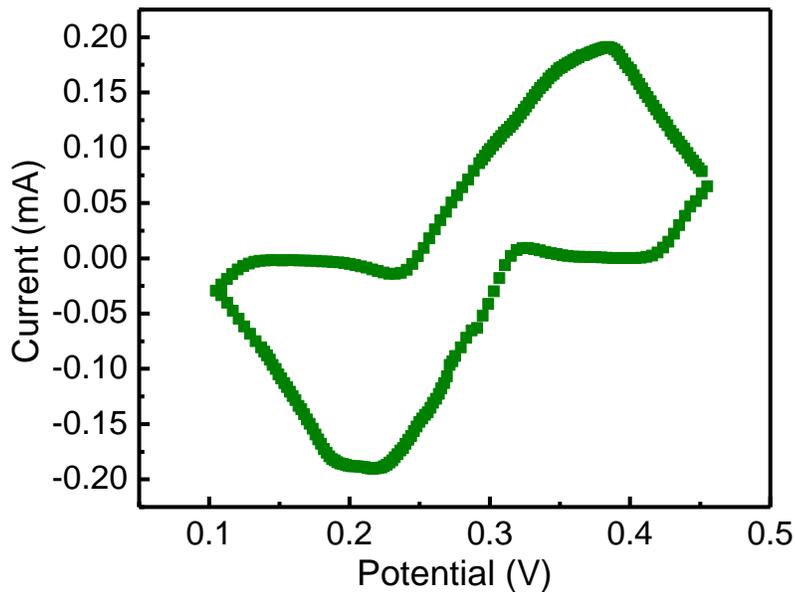


Figure 15: Cyclic Voltammogram for ferricyanide.

References

- [1] M.E. Orazem and Bernard Tribollet, "Electrochemical Impedance Spectroscopy", M.E. Orazem and Bernard Tribollet, John Wiley & Sons, 2008.
- [2] F. Mansfeld, "Electrochemical Impedance Spectroscopy (EIS) as a new tool for investigation methods of corrosion protection", *Electrochimica Acta*, 35 (1990) 1533.
- [3] J.J. van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston, and P.T. Kissinger, *Cyclic Voltammetry Experiment*, *J. Chem. Ed.*, 1983, 60(9), 772.
- [4] [Gamry Echem Analyst Software Manual](#).