

Electrochemical Impedance Spectroscopy

▶ Goals

- To learn the effect of placing capacitors and resistors in series and parallel
- To model electrochemical impedance spectroscopy data

▶ Experimental Apparatus

- Gamry Instruments Interface 1000T potentiostat
- Gamry Instruments Framework™ software package installed on a host computer
- Gamry Instruments AC Dummy Cell (Gamry part number 990-00419)
- Two 2.7 V, 3 F capacitors
- 20 Ω , ¼ W (or higher power-rating) resistor
- 100 Ω , ¼ W (or higher power-rating) resistor

▶ Background

Electrochemical impedance spectroscopy (EIS) is a popular method for studying an electrochemical interface. EIS is a “two-part” technique, that is:

- First, the electrical response of the electrochemical interface is recorded when a small alternating current (AC) potential is applied, and
- Second, the data are fitted to a theoretical electronic circuit that is designed to be “equivalent” to the actual system.

In the first part (applying AC to the sample), the system is immersed in electrolyte, and an AC potential is applied, with the AC frequency carefully stepped from a high frequency (1 MHz or more) down to a low frequency (~1 Hz or less), usually in a logarithmic sequence. While perfect resistors respond without delay or loss in amplitude to AC input, all real electrical components (including surfaces undergoing corrosion) respond to such AC with a loss in amplitude, and a slight delay in time (phase-shift). How the electrochemical system responds to the AC input reveals much about the internal physical and chemical structure of the system. Therefore we cannot use the ideal Ohm’s Law equation to describe our electrochemical surface,

$$R = \frac{E}{I}$$

where R is the resistance of the system, E is the potential applied to the system, and I is the current applied to the system. Instead, we must consider the actual phase-shifted response of the system to the applied potential.

Now we can describe the AC excitation potential applied to the system as a sine wave:

$$E = E_0 \sin(\omega t)$$

where

E is the applied potential as before,

E_0 is the AC amplitude,

t is time,

and ω is radial frequency (and $\omega = 2\pi f$).

The electrochemical system's response (Figure 10.1), then, is

$$I = I_0 \sin(\omega t + \phi)$$

where the phase-shift away from the applied AC is ϕ . The amplitude of the excitation signal is kept small so that the cell's response is pseudo-linear. In a pseudo-linear system the cell's frequency response is the same frequency as the excitation signal.

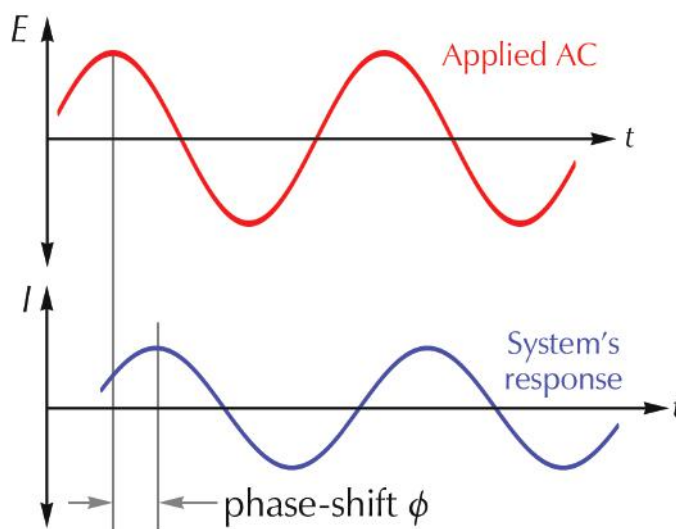


Figure 10.1. An applied AC potential (upper graph); a system's response is shifted in phase and amplitude (lower graph).

We cannot use the term “resistance” to describe the electrochemical system’s ability to resist current flow because we are not operating under the conditions of an ideal resistor. Instead we must introduce the term **impedance** with symbol Z , analogous to an electrical inductor or coil of wire. The impedance can be described using complex numbers as:

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

where j is imaginary. Note that this expression has a real component ($\cos \phi$) and an imaginary component ($j \sin \phi$). If we plot the real part on the x -axis, and the imaginary part on the y -axis, we create a **Nyquist plot** (Figure 10.2).

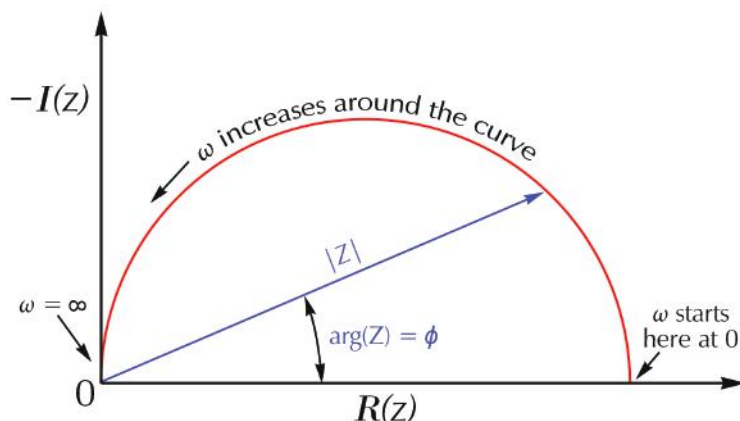


Figure 10.2. Typical Nyquist plot.

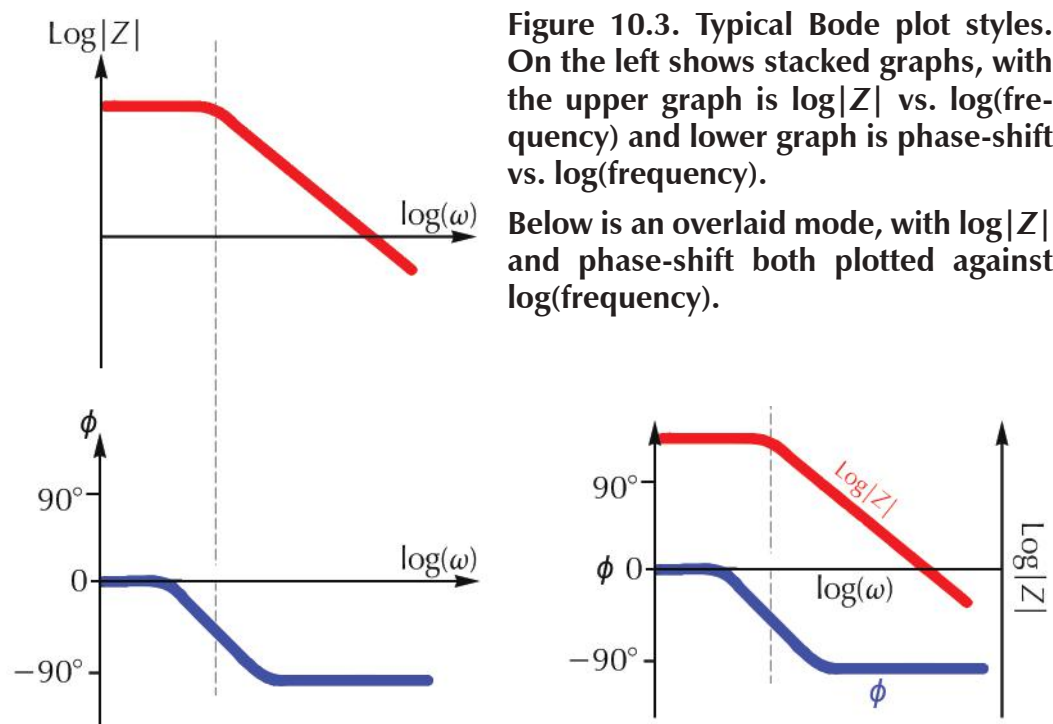
In a Nyquist plot, the absolute value of the impedance Z is the length of the vector. The angle between the vector and the x -axis is referred to as the **phase angle** ϕ (or often ω). A problem with Nyquist plots is that the frequency used for each point on the curve is not determinable. Therefore another popular plotting scheme is the **Bode** (pronounced “BOH-dee”) **plot**, which incorporates two distinct curves, usually plotted separately but sometimes overlaid (Figure 10.3 shows both styles). The x -axis is $\log(\text{frequency}, f)$. The y -axis uses the logarithm of the absolute values of the impedance ($|Z|=Z_0$) for the impedance curve, and the phase-shift (plotted on a linear scale) for the phase-shift curve.

An impedance experiment can be run in two ways: galvanostatic or potentiostatic. In a potentiostatic EIS experiment the amplitude of the applied voltage for a sinusoidal wave is controlled, and the current response of the system from that signal is measured. In a galvanostatic EIS experiment the amplitude of the applied current for a sinusoidal wave is controlled, and the potential response of the system from that signal is measured. When you choose the appropriate technique,

The term **impedance** was invented by physicist-mathematician-electrical engineer Oliver Heaviside (1850–1925) in 1886.

The Nyquist plot was named for the electrical engineer Harry Nyquist (1889–1976).

The Bode plot was invented by the electrical engineer and inventor Hendrik Bode (1905–1982).



the general rule of thumb is to control the smaller signal and measure the larger signal, so that experimental noise is reduced. Typically that means that you choose potentiostat EIS; however in today's experiment we are using galvanostatic EIS because the current response of the systems under study are small.

The second part of EIS is the analysis of a Nyquist or Bode plot. Here the researcher starts with a hypothetical electrical-circuit model composed of networks of resistors, capacitors, and other elements. The model is used to mathematically calculate the response of this network, and that response is compared to the experimental data taken. The researcher then tries to explain the physical or chemical rationale behind each circuit element in the model equivalent circuit. Each component of the electrical circuit model must have a corresponding real element. This means that elements are not added to the model unless they can be physically explained, even if adding elements produces a model that statistically fits to the data better.

Some circuit elements are:

- **Solution resistance** (the resistance that the ions in solution offer to a current),
- **Double-layer capacitance** (the capacitance that adsorbed ions create when sitting on a conductive surface),
- **Polarization resistance** (the resistance generated by electrochemical reactions at an electrode surface), and

- **Coating capacitance** (when an insulating coating such as paint sets up a capacitance between the electrolyte solution and underlying metal).

Many other physico-chemical circuit elements exist. There are quite a few models for equivalent circuits; this text does not have sufficient space to treat them in detail. You can imagine various electrical scenarios, especially with corroding or rusting metals covered by a failing protective coating perforated with holes and pores. Hence EIS is a common technique for studying and modeling the behavior of corroding metallic surfaces, especially when covered by a layer of paint.

In today's experiment you examine two elements of a cell model in the form of capacitors and resistors. You will also evaluate and analyze a traditional **Randles cell**.

The Randles model was first described by electrochemist John Edward Brough Randles (1912–1998) in 1947.

► Procedure

1. Turn on the potentiostat.
2. Open the Gamry Framework™ software on the host computer.
3. Take capacitor measurements.
 - a. Prepare the first capacitor for testing by connecting the green (working) and blue (working sense) alligator clips to the negative lead on the capacitor. Connect the red (counter), orange (counter sense), and white (reference) alligator clips to the other lead of the capacitor.



Single capacitor attached to potentiostat.

NOTE: Be sure of the proper polarity. Improper connections can damage the capacitor.

- b. When the Framework registers that the potentiostat is connected to the host computer, charge the capacitor:

Go to **Experiment > Physical Electrochemistry > Chronopotentiometry**. Set the parameters equal to those found in Figure 10.4.

- c. Run the experiment.
- d. After the experiment ends, go to **Experiment > Electrochemical Impedance > Galvanostatic EIS**. Set the parameters



Capacitors in parallel attached to potentiostat.

Chronopotentiometry


Default Save Restore OK Cancel

Pstat ☒ IFC1000-05065

Test Identifier

Output File

Electrode Area (cm²)

Notes... 

Pre-step Current (A)

Pre-step Delay Time (s)

Step 1 Current (A)

Step 1 Time (s)

Step 2 Current (A)

Step 2 Time (s)

Sample Period (s)

Decimate ☒ On

Lower Limit V (V)

Upper Limit V (V)

Equil. Time (s)

Init. Delay ☐ Off Time(s) Stab. (mV/s)

Conditioning ☐ Off Time(s) E (V)

Sampling Mode ☐ Fast ☒ Noise Reject

Advanced Pstat Setup ☐ Off

Electrode Setup ☐ Off

Figure 10.4. Experiment set-up window for chronopotentiometry.

equal to those found in Figure 10.5.

- e. Run the second experiment.
- f. Repeat steps 3(a)–(e) for the second capacitor, making sure to change the **Output File** name from “Capacitor 1” to “Capacitor 2.”
- g. Connect the capacitors in parallel, making sure that both capacitors are ori-

Galvanostatic EIS

Default Save Restore OK Cancel

Pstat ☒ IFC1000-05065

Test Identifier Galvanostatic EIS

Output File GalEIS Capacitor 1.DTA

Notes... 2.7 V 3 F Capacitor #1

Initial Freq. (Hz) 20000

Final Freq. (Hz) 0.1

Points/decade 10

AC Current (A rms) 0.05

DC Current (A) 0

Area (cm²) 0.1

Conditioning ☐ Off Time(s) 15 E(V) 0

Init. Delay ☐ Off Time(s) 100 Stab. (mV/s) 0

Estimated Z (ohms) 100

Optimize for: ☐ Fast ☒ Normal ☐ Low Noise

Figure 10.5. Experiment set-up window for galvanostatic EIS.

ented in the same direction, and repeat steps 3(a)–(e), changing the **Output File** name to “Capacitors in parallel.”

NOTE: To ensure proper contact between both capacitors and the alligator clips, twist the leads of the capacitors together prior to attaching the clips.

- h. Connect the capacitors in series, making sure that both capacitors are oriented in the same direction, and repeat steps 3(a)–(e), changing the **Output File** name to “Capacitors in Series.”

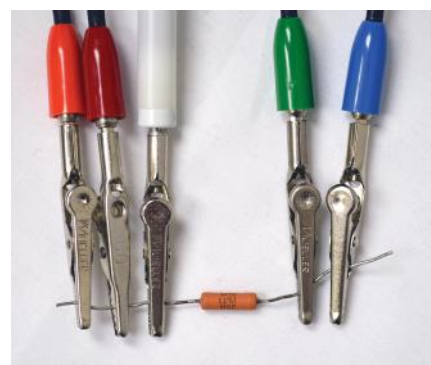
Capacitors in series attached to potentiostat.



4. Take resistor measurements.
 - a. Prepare the 20 Ω resistor for testing by connecting the green (working) and blue (working sense) alligator clips to one lead of the resistor. Connect the red (counter), orange (counter sense), and white (reference) alligator clips

to the other lead of the resistor.

- b. Resistors do not need to be charged, so chronopotentiometry is unnecessary. Go to **Experiment > Electrochemical Impedance > Galvanostatic EIS**. Set the parameters equal to those found in Figure 10.5.
 - c. Run the experiment.
 - d. Repeat steps 4(a)–(c) for the 100 Ω resistor, making sure to change the **Output File** name from “Resistor 1” to “Resistor 2.”
 - e. Connect the resistors in parallel, and repeat steps 4(a)–(c), changing the **Output File** name to “Resistors in parallel.”
 - f. Connect the resistors in series, and repeat steps 4(a)–(c), changing the **Output File** name to “Resistors in series.”
5. Measure the EIS Dummy Cell as a Randles cell.
- a. Connect the potentiostat to the **EIS Dummy Cell** side of the AC Dummy Cell as per Figure 10.6. (The AC Dummy Cell acts as a very good Randles cell.)



Single resistor attached to potentiostat.



Figure 10.6. Connections from the Universal Dummy Cell (EIS Dummy Cell side) to the potentiostat.

NOTE: Do not let the various alligator clips touch each other.

- b. The AC Dummy cell does not need to be charged, so chronopotentiometry is unnecessary. Go to **Experiment > Electrochemical Impedance > Potentiostatic EIS**. Set the parameters equal to those found in Figure 10.7.

Potentiostatic EIS

Default Save Restore OK Cancel

Pstat ☒ IFC1000-05065

Test Identifier Potentiostatic EIS

Output File PotEIS Randles Cell.DTA

Notes... AC Dummy Cell

Initial Freq. (Hz) 20000

Final Freq. (Hz) 0.1

Points/decade 10

AC Voltage (mV rms) 10

DC Voltage (V) 0 ☐ vs Eref ☒ vs Eoc

Area (cm²) 0.1

Conditioning ☐ Off Time(s) 15 E(V) 0

Init. Delay ☐ Off Time(s) 10 Stab. (mV/s) 0

Estimated Z (ohms) 100

Optimize for: ☐ Fast ☒ Normal ☐ Low Noise

Figure 10.7. Experiment set-up window for potentiostatic EIS on a Randles cell.

- c. Run the experiment.
6. After all experimental runs are complete, turn off the potentiostat. Copy or move the data that you obtained today from the folder **C:\Users\Public\Documents\My Gamry Data** to your portable storage device for later analysis.

▶ Reference

Barsoukov, E. and Macdonald, J.R., eds., *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2nd ed., Hoboken, NJ: John Wiley & Sons, 2005.

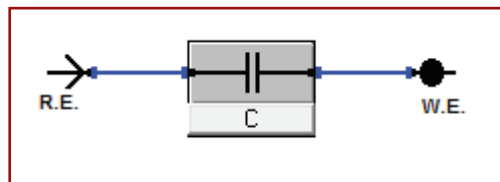
► Data Analysis

1. Open Gamry Echem Analyst™ Software.
2. Use Echem Analyst to determine the capacitance of the capacitors.
 - a. Open the **Capacitor 1** data file.
 - b. Create the appropriate electronic model circuit.

Choose **Galvanostatic Impedance > Model Editor**. In the model editor window, open the **Fuel Cell.MDL** model. Right-click on the two constant-phase elements ($\text{--}\varnothing\text{--}$) and delete them.

Then click on the capacitor icon at the top ($\text{--}||\text{--}$)—two of these are needed—and place them where the constant-phase elements were. Draw this model below, and save this file as **capacitors.MDL**. Close the model editor.

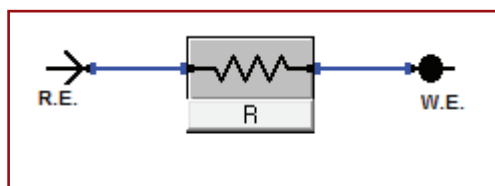
capacitors.MDL Model



Students' answers

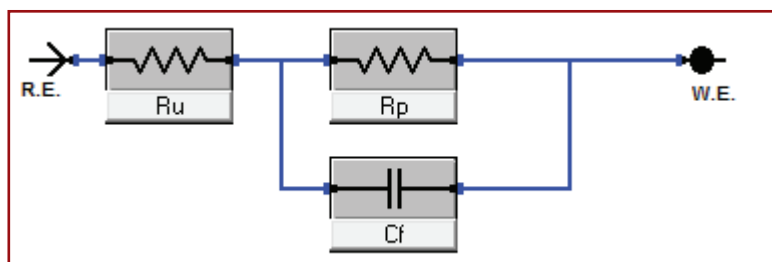
- c. In the Echem Analyst™ software, proceed to **Galvanostatic Impedance > Fit a Model (Simplex Method)**, and select the **capacitors.MDL** model you just created. A new window opens containing all of the circuit elements from the model. Click the **AutoFit** button and the model runs.
 - d. After the **Impedance Fit by the Simplex Method** window displays that the model has completed its simulation, record the total value of both capacitor values in the table in the Results section.
 - e. Open the other capacitor data files, and repeat steps 2(b)–(d) for each.
 - f. Using the known values of the capacitors from your laboratory instructor, calculate the total capacitance of the capacitors in series and parallel, also recording them in the same table.
3. Use Echem Analyst to determine the resistance of the resistors.
 - a. Open the **Resistor 1** data file. The resistor model is already created in the software. View and draw the model below by going to **Galvanostatic Impedance > Model Editor**, and opening the **R.MDL** model.

R.MDL Model



- b. In the Analyst™ software, proceed to **Galvanostatic Impedance > Fit a Model (Simplex Method)** and select the **R.MDL** model you just created. A new window opens containing the circuit element from the model. Click the **AutoFit** button and the model runs.
 - c. After the **Impedance Fit by the Simplex Method** window displays that the model has completed its simulation, record the total value of the two resistors and capacitor values within the table in the Results section.
 - d. Open the other resistor data files and repeat steps 3(b) and (c) for each.
 - e. Using the known values of the resistors from your laboratory instructor, calculate the total resistance of the resistors in series and parallel, also recording them in the same table.
4. Use Echem Analyst to determine the resistance and capacitor values of the Randles cell.
- a. Open the Randles cell data file. The resistor model is already created in the software. View and draw the model below by going to **Galvanostatic Impedance > Model Editor**. and opening **randles.MDL** model.

randles.MDL Model



- b. In the Analyst software proceed to **Galvanostatic Impedance > Fit a Model (Simplex Method)**, and select the **randles.MDL** model you just created. A

new window opens containing the circuit element from the model. Click the **AutoFit** button and the model runs.

- c. After the **Impedance Fit by the Simplex Method** window displays that the model has completed its simulation, record the total value of both capacitor values within the table in the Results section of the lab.
- d. Calculate resistance R_u and resistance R_p of the Randles cell. From the Nyquist plot the R_u is the associated shift in the time constant from 0Ω , while the R_p is the diameter of the semicircle created by the RC time constant.
- e. Calculate capacitance C_f . To calculate the capacitance from the **Bode** tab, change the y_2 -axis from Z_{phz} to $-Z_{imag}$. This graphs the imaginary impedance versus the frequency. Record the frequency at which the maximum negative imaginary impedance occurs.

$-Z_{imag}$: ____1776____ Ω

Frequency: ____49.87____ Hz

Using this frequency, calculate the radial frequency.

[Remember that $\omega(\max) = 2\pi f$]

$$\omega(\max) = 2\pi f$$

$$\omega(\max) = 2\pi(49.87 \text{ Hz})$$

$$\omega(\max) = 313.3 \text{ Hz}$$

Radial frequency: ____313.3____ Hz

The capacitance can now be calculated from the radial frequency, given that $\tau = RC = 1/\omega(\max)$. Record the calculated value in the Randles cell table in the Results section. (The R value is the one that you calculated from the semicircle created by the RC time constant.)

$$RC = \frac{1}{\omega(\max)}$$

$$C = \frac{1}{R\omega(\max)}$$

$$C = \frac{1}{(3000 \Omega)(313.3 \text{ Hz})}$$

$$C = 1.065 \mu\text{F}$$

► Results

Capacitors:

	Model Total Capacitance (F)	Calculated Total Capacitance (F)
Capacitor 1	1.606	
Capacitor 2	3.046	
Capacitors in parallel	4.705	6.000
Capacitors in series	0.889	0.666

Resistors:

	Model Total Resistance (Ω)	Calculated Total Resistance (Ω)
Resistor 1	20.03	
Resistor 2	100.04	
Resistors in parallel	16.02	16.66
Resistors in series	120.08	120

Randles Cell:

Circuit Element	Model Values	Calculated Values
Resistance R_u	200.1 Ω	200.0 Ω
Resistance R_p	3013 Ω	3013 Ω
Capacitance C_f	1.006 μF	1.065 μF

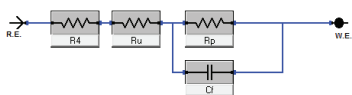
► Questions

1. Why is the amplitude of the excitation signal kept as small as possible in EIS?

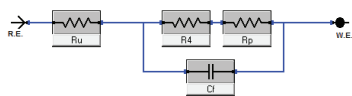
Analysis of a linear system is much simpler than a non-linear system. If the excitation signal is kept small, then the system is under a pseudo-linear response. If we measure outside of this pseudo-linear area, then the system's response will contain harmonics of the excitation signal.

2. How would the Nyquist and Bode plots change for the Randles cell measurement if a third resistor is added in series with the other circuit elements? Draw the circuit model with the extra resistor added.

Students should draw one of the following two possibilities:



If the resistor is added outside of the RC loop, then it would appear to the cell as additional solution resistance, and the semi-circle of the Nyquist plot would shift to higher resistances, but the radius would remain unchanged. In the Bode plot, the phase-angle data would decrease and shift to lower-frequency values, while the Zmod values at high frequencies would increase.



If the resistor is added inside of the RC loop, then it would appear to the cell as additional polarization resistance, and the radius of the semi-circle would increase. In the Bode plot, the phase-angle data would increase and shift slightly to lower-frequency values, while the Zmod values at lower frequencies would increase.

3. All elements of the model must have a physical representation for the model to be valid, e.g., electrolyte solution, coating, porosity, working electrode face. What do the circuit elements of the Randles cell represent?

Ru: Solution resistance.

Rp: Polarization resistance of the electrode caused by the potential at the surface not being equal to the open-circuit potential.

Cf: Double-layer capacitance at the surface of the electrode.

4. (Bonus Question) What would the Nyquist plot look like if a second RC loop (a capacitor-resistor pair in parallel) were added in series to the Randles Cell?

A second semicircle would appear on the plot, if its RC time constant is different from the original, otherwise it would convolute with the original time constant and may be hard to distinguish.

► Common Problems

- Not charging the capacitors prior to EIS measurements.
- Not having a good connection between the capacitors or resistors when twisting them into series and parallel configurations. This will be evident from noise in the data. Secure the connections and rerun the experimental setup.