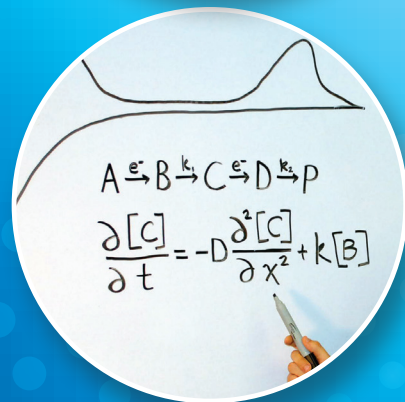
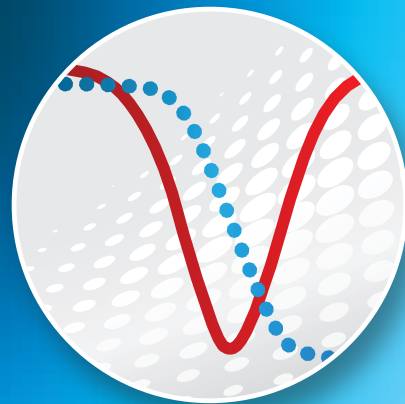


# Introduction to Experimental Electrochemistry

*Student Edition*



Cynthia A. Schroll  
Stephen M. Cohen

**GAMRY**  
INSTRUMENTS

## ► Basic equations

---

### *Nernst equation*

---

$$E = E^\circ - \left( \frac{RT}{nF} \right) \ln Q$$

$$E = \frac{0.0592}{n} \log Q \text{ at } 25^\circ\text{C}$$

### *Cottrell equation*

---

$$i(t) = nFAC \sqrt{\frac{D}{\pi t}}$$

### *Levich equation*

---

$$i_L = 0.620nFAD^{2/3} \omega^{1/2} \nu^{-1/6} C$$

### *Randles-Ševčík equation*

---

$$i_p = 0.4463nFAC \sqrt{\frac{nF\nu D}{RT}}$$

$$i_p = (2.686 \times 10^5) n^{3/2} \nu^{1/2} D^{1/2} AC \text{ at } 25^\circ\text{C}$$

## ► Physical constants

---

(2014 CODATA Recommended Values)

$c$	Speed of light in vacuum	$2.997\,92 \times 10^8 \text{ m s}^{-1}$
$e$	Elementary charge	$1.602\,18 \times 10^{-19} \text{ C}$
$F$	Faraday constant	$96\,485.3 \text{ C mol}^{-1}$
$h$	Planck constant	$6.626\,07 \times 10^{-34} \text{ J s}$
$k$	Boltzmann constant	$1.380\,65 \times 10^{-23} \text{ J K}^{-1}$
$N_A$	Avogadro constant	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$
$R$	Molar gas constant	$8.314\,46 \text{ J mol}^{-1} \text{ K}^{-1}$
$\epsilon_0$	Permittivity of free space	$8.854\,19 \times 10^{-12} \text{ F m}^{-1} \text{ or } \text{C}^2 \text{ N}^{-1} \text{ m}^{-2}$

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Stephen M. Cohen*

*Gamry Instruments, Inc.  
Warminster, Pennsylvania*



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**Gamry Instruments, Inc., 734 Louis Drive, Warminster, Pennsylvania 18974**

**[www.gamry.com](http://www.gamry.com)**

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# Foreword

*I have been so electrically occupied of late that I feel as if hungry for a little chemistry: but then the conviction crosses my mind that these things hang together under one law & that the more haste we make onwards each in his own path the sooner we shall arrive, and meet each other, at that state of knowledge of natural causes from which all varieties of effects may be understood & enjoyed.*

—Michael Faraday, 1838

Electrochemistry often gets short shrift in modern undergraduate chemistry curricula. A student sees the Nernst equation in first-year General Chemistry, and revisits it during a discussion of thermodynamics in Physical Chemistry—but there the topic rests.

Yet the modern technological world is driven by electrochemistry, in the form of compact batteries for the myriad of portable electronic devices, and—more and more—in the form of powerful electric batteries to run our cars. How to prevent or minimize corrosion of metals has been a crucial subject for engineers for centuries. Conversion and storage of electrical energy is an active research topic for energy conservation. Even biology and neuroscience is very much a subject of ionic gradients across cell membranes. In fact, one of the most common consumer medical devices—the glucose meter—is based on an electrochemical measurement. Thus every scientist and engineer must know some basics about our truly electrochemical world.

This book is an attempt to introduce the undergraduate, in one semester, to some of the present-day techniques found in modern electrochemistry and electroanalytical chemistry. We assume that the student has had one full year of General Chemistry lecture and laboratory. Organic Chemistry and Physical Chemistry are decidedly helpful, but not required. The laboratory experiments are designed to be run in the order presented in this book. All data-collection, analysis, and questions are on separate pages from the background and procedure; they may be torn out from the book and handed in with graphs and plots that the student generates. Occasionally we offer a “Bonus Question” to give the student a deeper consideration of the techniques and theory.

All of the specialized electrochemical instrumentation mentioned herein may be purchased from Gamry Instruments, Inc. in order to set up a complete electro-

chemistry laboratory. Contact Gamry at +1-215-682-9330 (toll-free 1-877-367-4267 in the USA and Canada), fax us at +1-215-682-9331, send us an e-mail at [sales@gamry.com](mailto:sales@gamry.com), or contact your local distributor, for more information.

# Introduction

From your chemical education, you should be familiar with certain electrochemical ideas already.

These basic ideas include

- Half-reactions,
- Formal potentials,
- Reference electrodes,
- The Nernst equation,
- Free-energy calculations,
- Simple dual-electrode cells.

This laboratory manual deals with potentiostatic and galvanostatic methods. Techniques where the potential of an electrode is the controlled variable, while the current is measured are called potentiostatic methods. Galvanostatic methods reverse the situation (current is controlled, while voltage is measured).

## ► Basic Theory

### *Nernst Equation*

The **Nernst equation** describes a relationship between electrode potential and solution concentration:

$$E = E^\circ - \left(\frac{RT}{nF}\right) \ln Q$$

Here  $Q$  is the reaction quotient is the product of the activity times concentration for the products divided by the product of the activity times concentration for the reactants.

At room temperature ( $25^\circ\text{C} = 298\text{ K}$ ), using the Ideal Gas Constant and base-10 logarithms,  $RT / F = 0.0592\text{ V}$ , so the Nernst equation becomes

$$E = E^\circ - \frac{0.0592\text{ V}}{n} \log Q$$

The Nernst equation is used for predicting the concentrations of species near the electrode surface at a given applied potential. The Nernst equation is relatively accurate only when the electrochemical system responds quickly to changes in the ap-

*Walther Nernst (1864–1941), physicist, derived his relationship in 1888.*

*In most cases (when concentrations of species are not too high), you may use concentrations instead of activities.*

plied potential. Such redox systems remain in quasi-equilibrium with the electrode surface. These systems sometimes are known as “Nernstian” or reversible systems because they are in quasi-equilibrium.

The potential of the working electrode determines what kind of redox processes may occur at the electrode’s surface. Extremely negative potentials will probably reduce analytes while positive potentials are likely to oxidize them. Should oxidation or reduction happen, a current flows through the electrode, and the magnitude of this current is proportional to concentrations in the solution. Thus, the current gives the detectable signal that can be used as a calibration curve relating signal to concentration.

## ***Heterogeneous States***

Electrochemical systems must be heterogeneous. Worthwhile chemical and electrochemical reactions occur at or near the surface of the working electrode. This means that the electrode affects the volume of solution close to the electrode. In general, the electrode influences a volume of solution extending just a few micrometers away from the surface of the electrode. Concentrations of analyte in this very local diffusion layer can vary dramatically from those measured in the rest of the solution. The volume of the diffusion layer is tiny compared to the total amount of solution in the electrochemical cell. Hence any changes in concentration in the diffusion layer created by the electrode rarely influence the bulk solution.

## ***Faraday’s Law***

*Michael Faraday (1791–1867), physicist and chemist, was active in electrochemical research around 1833.*

**Faraday’s Law** states that the amount of charge in an electrochemical process is directly proportional to the underlying stoichiometry of that half-reaction. Most half-reactions involve simple transfers of one electron, therefore application of Faraday’s Law leads to the general statement that, for every mole of a species that is oxidized or reduced at an electrode, a mole of electrons (with a charge  $Q$  of 96 485 coulombs) enters or leaves the electrode.

$$m = \frac{QM}{Fz}$$

where  $m$  = mass,

$Q$  = charge,

$M$  = molar mass,

$F$  = Faraday’s constant, and

$z$  = valence number.

*This  $Q$  is not the same as the reaction quotient  $Q$ .*

$$1 F = 96\,485\text{ C} \\ = 96\,485\text{ A}\cdot\text{s}$$

For half-reactions requiring two, three, or four electrons,  $Q$ , the quantity 96 485 C/mol, is multiplied by the corresponding whole number.

Faraday's Law is integral, for it describes the connection between the observed current and concentration of the species. Generally higher concentrations give higher currents. When the electrode potential is perturbed far enough from its equilibrium value, the current is limited solely by how fast the analyte can diffuse to the surface of the electrode. For solutions that are not stirred, the analyte must diffuse passively across the diffusion layer from the bulk solution to the surface of the electrode. The diffusion rate is governed by a concentration gradient—that is, diffusion transfers material from a volume of high concentration to one of low concentration. Not only that, but the larger the difference between the two concentrations, the faster the species diffuses. (This is similar to the behavior of gases.) Therefore the current at an electrode is highest when the gradient in concentration of analyte across the diffusion layer is highest.

*Technically the current at higher potentials is not related to how fast analyte diffuses to the electrode surface, but rather how the energy states overlap. Very large overpotentials will actually see a decrease in current.*

## ***Fick's First Law of Diffusion***

We need to describe diffusion of atoms, molecules, and ions, and so we add **Fick's First Law of Diffusion**:

$$J = -D \frac{\partial \phi}{\partial x}$$

*Adolf Fick (1829–1901), physiologist, derived his laws of diffusion in 1855.*

This equation describes diffusion (under steady-state conditions) in terms of flux  $J$  (amount of substance flowing through a given area during a given time), that is, diffusion occurs from high concentration to low concentration. When we combine Faraday's Law with Fick's First Law of Diffusion, we obtain a general expression for the diffusion-limited current,  $i_d$ , at a working electrode,

$$i_d = nFAD \left( \frac{dC}{dx} \right)_0$$

where

$n$  is the number of electrons involved in the half-reaction,

$F$  is Faraday's constant (96 485 C/mol)

$A$  is the electrode area in  $\text{cm}^2$ ,

$D$  is the analyte's diffusion coefficient, in  $\text{cm}^2/\text{s}$ , and

$(dC/dx)_0$  is the concentration gradient at the surface of the electrode.

This expression may be new to you. The key point of this combined expression is the direct proportion between current and concentration gradient.

# Cyclic Voltammetry

## ▶ Goals

The goals of this experiment are to:

- Learn how to set up a screen-printed electrode
- Learn how to operate the Gamry potentiostat
- Determine the redox potential of potassium ferricyanide
- Calculate the diffusion coefficient of potassium ferricyanide

## ▶ Experimental Apparatus

- Gamry Instruments Interface 1000T
- Gamry Instruments Framework™ software package installed on a host computer
- Screen-printed electrode (SPE) cell stand (Gamry part number 990-00420)
- Platinum working screen-printed electrode (Gamry part number 935-00122)

## ▶ Reagents and Chemicals

- 0.1 M potassium chloride, pre-purged to remove dissolved O<sub>2</sub>
- 2 mM potassium ferricyanide in 0.1 M potassium chloride, pre-purged to remove dissolved O<sub>2</sub>

### CAUTION:

Cyanide-containing compounds can hydrolyze to form hydrogen cyanide gas, which is highly poisonous. Never pour potassium ferricyanide down the drain!

*The laboratory instructor has already purged the solutions of dissolved O<sub>2</sub>. Purging the dissolved O<sub>2</sub> from these solutions prevents spurious peaks from appearing in your data.*

## ▶ Background

**Cyclic voltammetry** is the most commonly used electroanalytical technique for obtaining rapid quantitative data about an electrochemical reaction. The importance of cyclic voltammetry is that it provides a quick result concerning the kinetics of a heterogeneous electron-transfer, diffusion coefficients, and thermodynamic information for a process. Cyclic voltammetry also can give data on subsequent chemical reactions or adsorption processes.

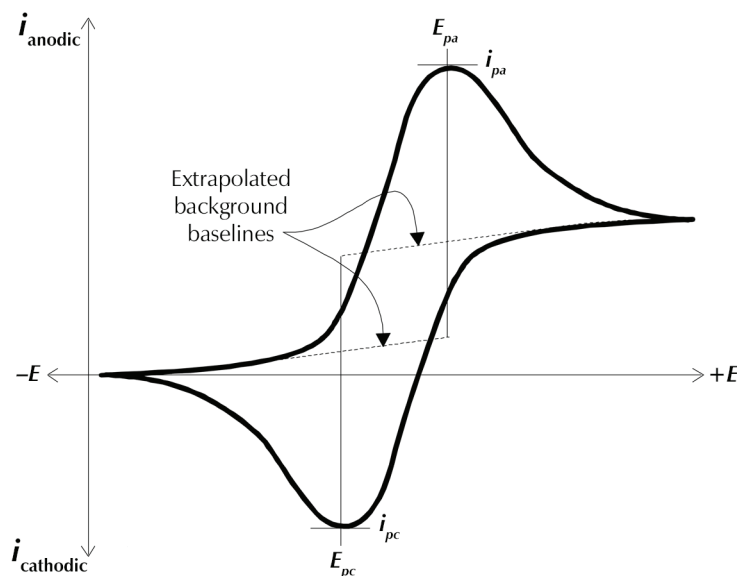
Cyclic voltammetry is usually the first experiment performed on an electroactive analyte because of its ability to provide the redox potential of that analyte. This technique also allows fast evaluation of the effect that a particular matrix may have on a redox process.

During a typical cyclic voltammetry experiment, a component of the solution is electrolyzed (oxidized or reduced) by placing the solution in contact with an electrode, and then applying a potential to that electrode that is sufficiently positive or negative with respect to a reference half-cell (e.g., calomel or Ag|AgCl). The electrode's voltage is adjusted higher or lower linearly, and finally, the voltage is returned to the original value at the same linear rate.

When the electrode becomes sufficiently negative or positive, a species in solution may gain electrons from the electrode's surface, or transfer electrons to that surface. As the potential is swept back and forth past the formal potential,  $E^\circ$ , of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. Electron-transfer is a measurable current in the electrode's circuitry. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration.

The result is a **cyclic voltammogram** (or CV), in the form of a cycle between current and potential, where potential is plotted on the  $x$ -axis, and current is plotted on the  $y$ -axis.

Figure 1.1 shows a generic cyclic voltammogram. The potential is graphed along the  $x$ -axis with more positive (or oxidizing) potentials plotted to the right, and more



**Figure 1.1.** A generic CV. A CV plot reveals the reversibility of the redox couple. (Adapted from P. T. Kissinger and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, New York: Marcel Dekker, Inc., 1984, p. 88.)

negative (or reducing) potentials to the left. The current is graphed on the  $y$ -axis of the voltammogram, with cathodic (i.e., reducing) currents plotted in the negative direction, and anodic (i.e., oxidizing) currents plotted in the positive direction.

The peaks in a voltammogram look something like those in a spectrum or chromatogram. Each peak denotes a particular electrolytic process in the analytical solution, and the height of a peak is proportional to the concentration of that analyte. The peaks in a cyclic voltammogram are asymmetrical, with the leading side steep and the trailing side showing a gradual fall-off. The peaks seen during the reverse scan have the same overall form as those in the forward sweep, but they are inverted because the current is flowing in the opposite direction.

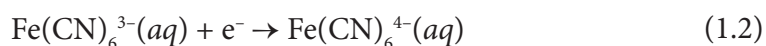
The initial direction of the first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) or negative (cathodic) direction, as determined by the characteristics of the analyte. For an oxidizable analyte, the first sweep starts in the positive direction, whereas for a reducible analyte, the first sweep begins in the negative direction.

Much quantitative information can be extracted from a high-quality cyclic voltammogram. First, the plot can serve as a test if a redox couple is actually electrochemically reversible. The peak potential for the anodic sweep,  $E_{pa}$ , and the peak potential for the cathodic peak,  $E_{pc}$ , can be read right from the voltammogram, and the difference between them,  $\Delta E_{peak}$ , can be calculated. If the redox couple is reversible, then, based on the Nernst equation,  $E = E^\circ + 2.303 (RT/nF) \log[\text{Ox}/\text{Red}]$ , the relationship between the  $\Delta E_{peak}$  and the number of electrons involved in the redox couple is

$$n \Delta E_{peak} = 59 \text{ mV} \quad (1.1)$$

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

In fact, for this particular experiment, ferricyanide ion undergoes a reversible one-electron transfer according to the following reaction:



The anodic peak current  $i_{pa}$  is equal to the cathodic peak current  $i_{pc}$ , so that the relationship,

$$\frac{i_{pc}}{i_{pa}} = 1 \quad (1.3)$$

also holds true. A ratio of the peak currents deviating from 1 is an indication of chemical or electrochemical irreversibility. If the ratio is  $<1$  but a return peak is pres-



ent, then the electrochemical reaction is said to be **pseudo-reversible**. The peak currents are not measured using the  $x$ -axis as a baseline. Rather, you must first extrapolate a background current baseline out to the peak potential (see Figure 1.1). Then, the peak current is measured vertically from the peak down to the extrapolated baseline.

The formal potential,  $E^\circ$ , for a reversible redox couple is easily found as the average of the two peak potentials:

$$E^\circ = \frac{E_{pa} + E_{pc}}{2} \quad (1.4)$$

Quantitative information about concentration of the analyte can be determined from the voltammogram via the Randles-Ševčík equation (Eqn. 1.5). This equation calculates the peak current,  $i_p$  (either anodic or cathodic), in terms of the concentration  $C$  of the analyte.

$$i_p = 0.4463nFAC\sqrt{\frac{nF\nu D}{RT}} \quad (1.5)$$

In this equation,

$n$  is the number of electrons appearing in half-reaction for the redox pair,

$\nu$  is the scan-rate for the potential sweep (V/s),

$F$  is Faraday's constant (96 485 C/mol),

$A$  is the electrode area (cm<sup>2</sup>),

$R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),

$T$  is the absolute temperature (K), and

$D$  is the diffusion coefficient of the analyte (cm<sup>2</sup>/s).

If we assume standard temperature (25°C, 298.15 K), the Randles-Ševčík equation can be written concisely as

$$i_p = 2.686 \times 10^5 n^{\frac{3}{2}} AC\sqrt{\nu}\sqrt{D} \quad (1.6)$$

where the constant has units of 2.686 × 10<sup>5</sup> C mol<sup>-1</sup> V<sup>-1/2</sup>.

The peak current is directly proportional to the concentration of the analyte. If the analyte concentration is known, then cyclic voltammetry can be used to find the analyte's diffusion coefficient. The diffusion coefficient shows how fast the analyte moves through the solution because of random collisions with other molecules.

## ► Procedure

**NOTE:** Ensure that all glassware is as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. We recommend that you use deionized, ultrafiltered (DIUF) water, “conductivity water,” or “HPLC-grade water” for the final rinsing of glassware and to prepare all solutions.

### *Prepare the cell.*

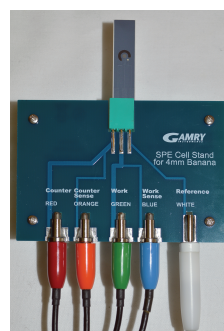
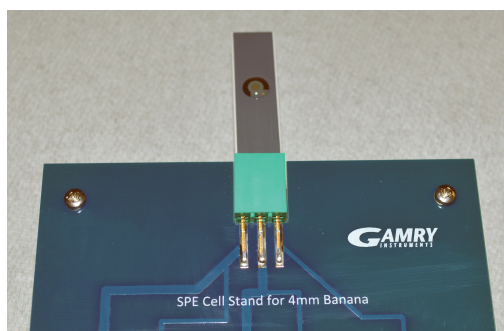
1. Connect the banana pins for the green (working), blue (working sense), white (reference), red (counter), and orange (counter sense) to the banana jacks indicated on the SPE cell stand. Leave the black (ground) pin unconnected.

2. Insert the screen-printed electrode horizontally into the connector on the SPE cell stand.

The apparatus should be set up like that shown in Figure 1.2.



Screen-printed electrode



**Figure 1.2.** Left: Screen-printed electrode inserted into SPE cell stand. Right: Complete set-up.

**NOTE:** When you add a drop of reagent, you only need enough to completely cover all three electrodes on the face of the screen-printed electrode. More reagent is unnecessary.

### *Perform a background scan.*

1. Turn on the potentiostat, and, on the host computer's Windows® desktop, open the Gamry Framework™ software.
2. When the host computer detects the potentiostat, choose **Experiment > Physical Electrochemistry > Cyclic Voltammetry**. The **Cyclic Voltammetry** window opens.

- Set the experimental fields in the **Cyclic Voltammetry** window to those shown in Figure 1.3, with the file name as **blank**.

The screenshot shows the 'Cyclic Voltammetry' dialog box with the following settings:

- Buttons:** Default, Save, Restore, OK, Cancel
- Pstat:**  IFC1000-05065
- Test Identifier:** Cyclic Voltammetry
- Output File:** BLANK.DTA
- Electrode Area (cm<sup>2</sup>):** 0.0314
- Notes...:** SPE WE-Pt, CE-C, RE-Ag/AgCl  
0.1 M KCl
- Initial E (V):** 0.5  vs Eref  vs Eoc
- Scan Limit 1 (V):** -0.25  vs Eref  vs Eoc
- Scan Limit 2 (V):** 0.5  vs Eref  vs Eoc
- Final E (V):** 0.5  vs Eref  vs Eoc
- Scan Rate (mV/s):** 100
- Step Size (mV):** 1
- Cycles (#):** 1
- I/E Range Mode:**  Auto  Fixed
- Max Current (mA):** 1.E-005
- IRComp:**  None  PF  CI
- PF Corr. (ohm):** 50
- Equil. Time (s):** 0
- Init. Delay:**  Off Time (s) 5 Stab. (mV/s) 1
- Conditioning:**  Off Time (s) 15 E (V) 0
- Sampling Mode:**  Fast  Noise Reject  Surface
- Advanced Pstat Setup:**  Off
- Electrode Setup:**  Off

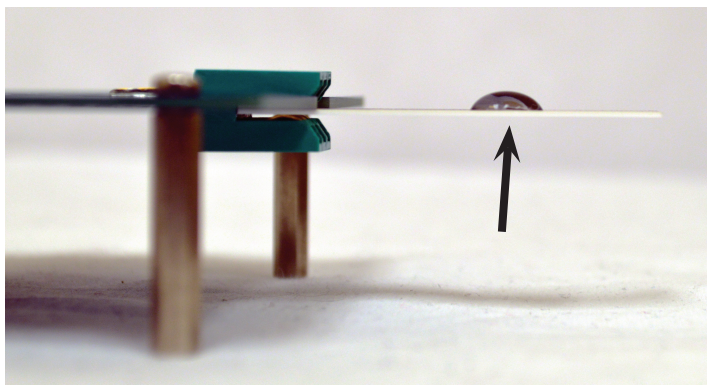
Figure 1.3. Cyclic Voltammetry window, with fields set to run a blank.

- Place a drop of the blank solution, 0.1 M KCl, onto the electrodes of the SPE. (See Fig. 1.4.)
- Click the **OK** button to run the experiment.

### ***Perform scans using sample solution.***

- Rinse the SPE with de-ionized water into a waste container. Then dab the SPE with a laboratory wiper to remove the rinsing solution.

**Figure 1.4. Single drop of fluid on the SPE's electrodes.**



**NOTE:** Do not get water on the SPE board.

2. Place a drop of the 2 mM potassium ferricyanide in 0.1 M potassium chloride solution onto the screen-printed electrode (Fig. 1.4).
3. In the experimental window, change the file name to **FeCN6 10mVs-1.dta**.
4. Run the experiment.
5. Redo steps 1 through 4, changing the scan rate to 20 mV/s and the file name to **FeCN6 20mVs-1.dta**.
6. Redo steps 1 through 4, this time changing the scan rate to 30 mV/s, then 40, 50, 60, 70, 80, 90, and 100 mV/s, simultaneously adjusting the file name appropriately.
7. Remove the screen-printed electrode from the connector, and discard it in the waste can.
8. Discard the analyte solution into the appropriate waste container (NEVER DOWN THE DRAIN!).


## ▶ Reference

J.J. van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston, and P.T. Kissinger, *J. Chem. Ed.*, 1983, **60**(9), 772.



## ► Data Analysis

### ***Determine cathodic and anodic peak currents and voltages.***

1. On the host computer's desktop, open Gamry Echem Analyst™ software.
2. Use Echem Analyst to determine the potential of cathodic and anodic peaks and cathodic and anodic peak currents.
  - a. Open the CV file you want to evaluate.
  - b. Using the mouse icon , select the region for the peak, and choose **Cyclic Voltammetry > Peak Find**, then choose **Cyclic Voltammetry > Automatic Baseline**. The **@ Vf (V vs. Ref)** is the potential, and the **Height (A)** is the peak current.
  - c. Repeat for both cathodic and anodic peaks.
  - d. Fill in the appropriate column in the table below.
3. Repeat step 2 for all the other scan rates.

Scan Rate (mV/s)	10	20	30	40	50	60	70	80	90	100
$E_{pc}$ (mV)										
$E_{pa}$ (mV)										
$I_{pc}$ ( $\mu$ A)										
$I_{pa}$ ( $\mu$ A)										

### ***Print graphs.***

1. Print a graph of the ten different scan-rates overlaid onto one plot.
  - a. Open the **FeCN6 1000mVs-1.DTA** file.
  - b. Choose **File > Overlay**.
  - c. Select the other graphs to be overlaid.
  - d. Print the complete plot.
  - e. Include this plot in your laboratory report.
2. Using software designated by your laboratory instructor, create plots of  $i_{pc}$  versus scan rate<sup>1/2</sup>, and  $i_{pa}$  versus scan rate<sup>1/2</sup>.
3. Print these two plots.
4. Include these two plots in your laboratory report.

### Calculate your results.

1. From your scan-rate data, calculate  $\Delta E_p$ ,  $E_{1/2}$ , and  $i_{pc}/i_{pa}$ , then fill in the table below with your results.

Scan Rate (mV/s)	10	20	30	40	50	60	70	80	90	100
$\Delta E_p$ (mV)										
$E_{1/2}$ (mV)										
$i_{pc}/i_{pa}$										

2. From the plots of the  $i_p$  versus scan rate<sup>1/2</sup>, determine the slope of the best-fitting line.
- Slope of the graph  $i_{pc}$  versus scan rate<sup>1/2</sup> = \_\_\_\_\_
  - Slope of the graph  $i_{pa}$  versus scan rate<sup>1/2</sup> = \_\_\_\_\_
3. Using the Randles-Ševčík equation and the slope from the graph of  $i_{pc}$  versus scan rate<sup>1/2</sup>, calculate the diffusion coefficient for potassium ferricyanide.

## ► Questions

1. Based on the Randles-Ševčík equation, would you expect the peak current to increase or decrease as the temperature increases? Why?

2. The average distance that molecules move in solution is expressed by the formula

$$l = \sqrt{2Dt}$$

where

$l$  is distance (cm),

$D$  is diffusion coefficient ( $\text{S}\cdot\text{m}^2/\text{s}$ ), and

$t$  is time (s).

Using your calculated diffusion coefficient, how long would it take for the analyte to diffuse 1 mm?

3. (*Bonus question*) Calculate the ratio of slopes  $i_{pc}$  and  $i_{pa}$ . Based on this number, is the reaction of ferricyanide reversible, pseudo-reversible, or non-reversible? Why?



# 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,

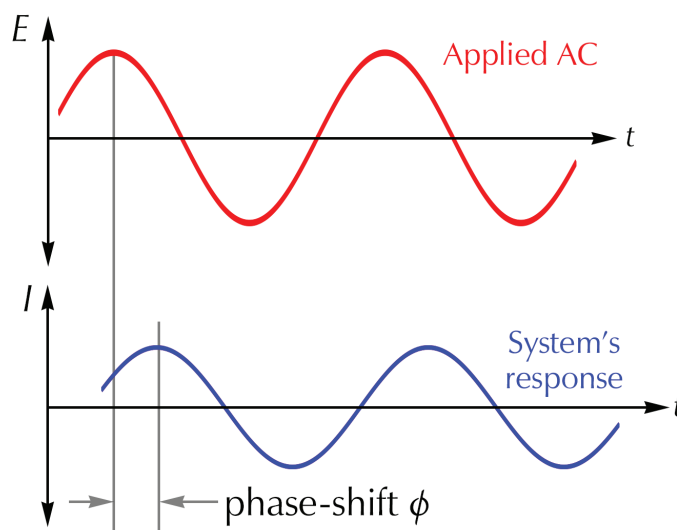
$t$  is time,

and  $\omega$  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  $\phi$ . 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.

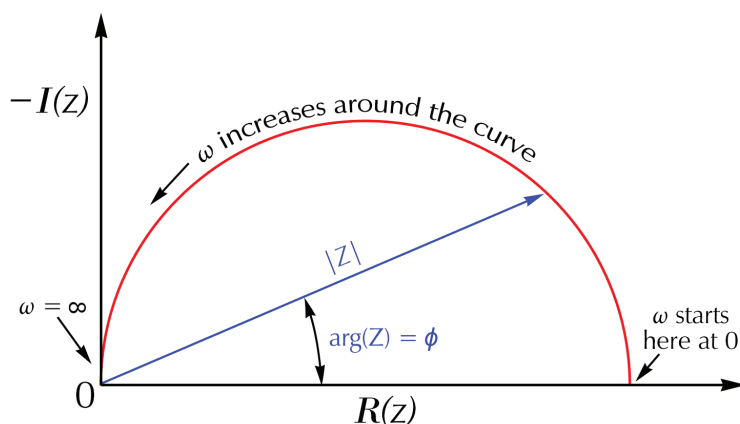


**Figure 10.1.** An applied AC potential (upper graph); a system's response is shifted in phase and amplitude (lower graph).

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.**

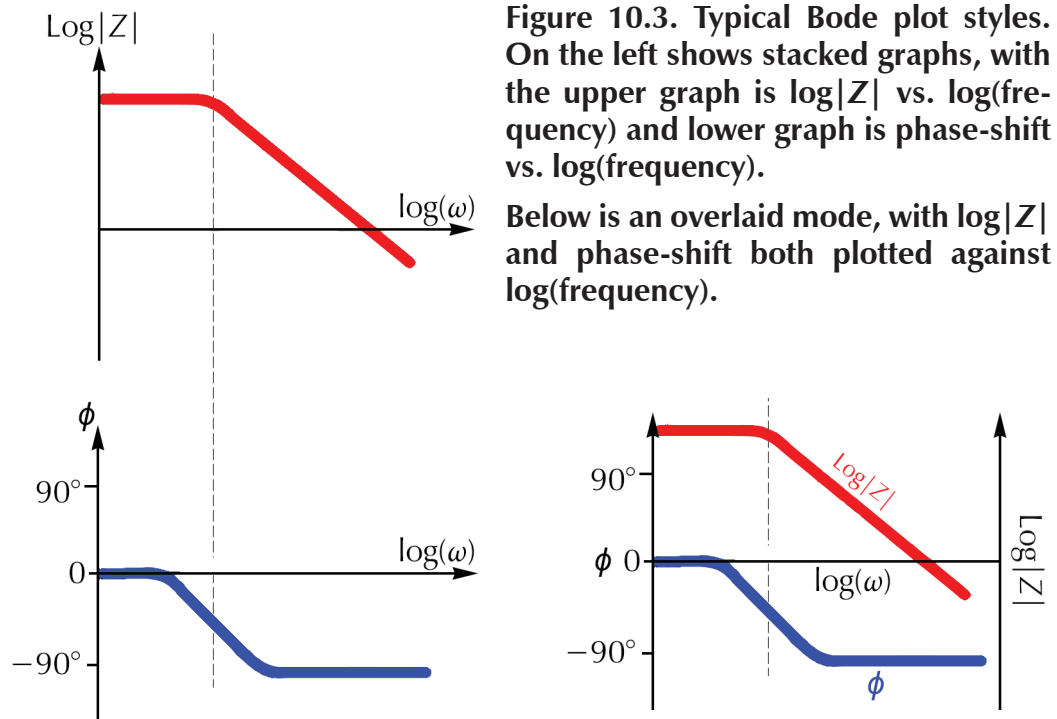
In a Nyquist plot, the absolute value of the impedance  $Z$  is the length of the vector. The angle between the vector and the  $x$ -axis is referred to as the **phase angle**  $\phi$  (or often  $\omega$ ). A problem with Nyquist plots is that the frequency used for each point on the curve is not determinable. 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.**

The screenshot shows the 'Chronopotentiometry' setup window with the following parameters:

- Pstat:** IFC1000-05065
- Test Identifier:** Chronopotentiometry Scan
- Output File:** Charging Capacitor.DTA
- Electrode Area (cm<sup>2</sup>):** 1
- Notes...:** Charging Cap 2.7 V, 3 F
- Pre-step Current (A):** 0
- Pre-step Delay Time (s):** 0
- Step 1 Current (A):** 0.1
- Step 1 Time (s):** 600
- Step 2 Current (A):** 0
- Step 2 Time (s):** 0
- Sample Period (s):** 0.01
- Decimate:**  On
- Lower Limit V (V):** 0
- Upper Limit V (V):** 2.7
- Equil. Time (s):** 5
- Init. Delay:**  Off, Time (s): 300, Stab. (mV/s): 0.1
- Conditioning:**  Off, Time (s): 5, E (V): 0
- 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-

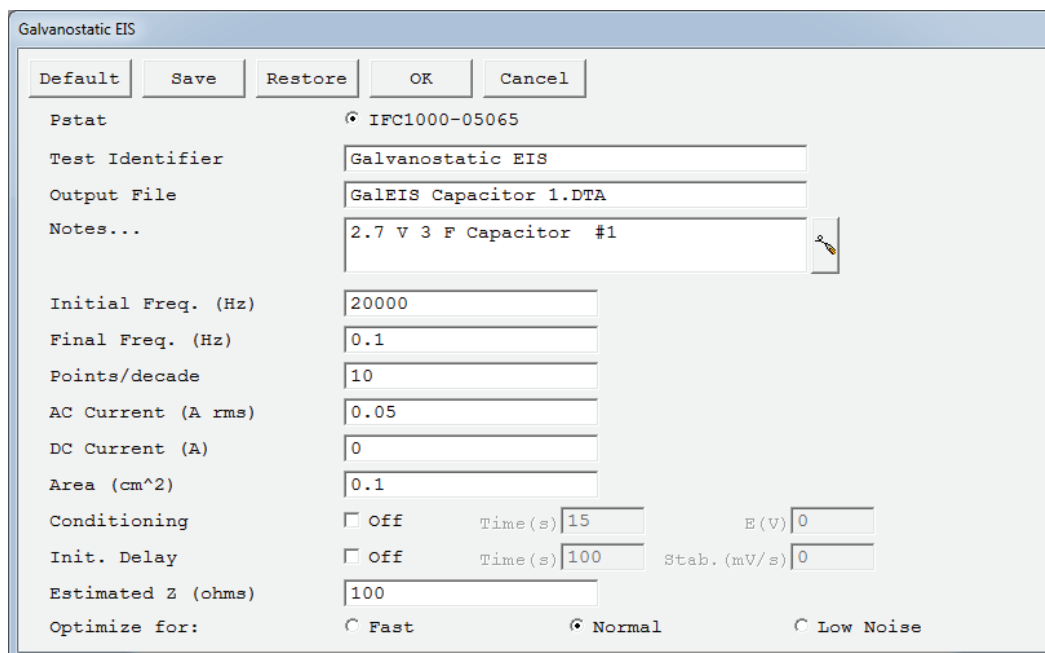


Figure 10.5. Experiment set-up window for galvanostatic EIS.

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.**

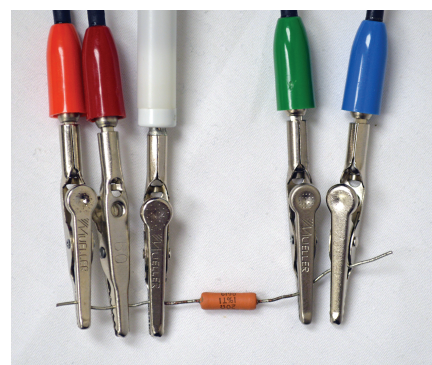


4. Take resistor measurements.
  - a. Prepare the  $20\ \Omega$  resistor for testing by connecting the green (working) and blue (working sense) alligator clips to one lead of the resistor. Connect the red (counter), orange (counter sense), and white (reference) alligator clips



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  $\Omega$  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 (cm<sup>2</sup>) 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*, 2<sup>nd</sup> ed., Hoboken, NJ: John Wiley & Sons, 2005.




## ▶ Data Analysis

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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 () and delete them.

Then click on the capacitor icon at the top ()—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

- 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  $0 \Omega$ , 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.

$-Z_{imag}$ : \_\_\_\_\_  $\Omega$

Frequency: \_\_\_\_\_ Hz

Using this frequency, calculate the radial frequency.

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

Radial frequency: \_\_\_\_\_ 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.)

## ▶ Results

### *Capacitors:*

	Model Total Capacitance (F)	Calculated Total Capacitance (F)
Capacitor 1		
Capacitor 2		
Capacitors in parallel		
Capacitors in series		

### *Resistors:*

	Model Total Resistance ( $\Omega$ )	Calculated Total Resistance ( $\Omega$ )
Resistor 1		
Resistor 2		
Resistors in parallel		
Resistors in series		

### *Randles Cell:*

Circuit Element	Model Values	Calculated Values
Resistance $R_u$		
Resistance $R_p$		
Capacitance $C_f$		

## ▶ Questions

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

