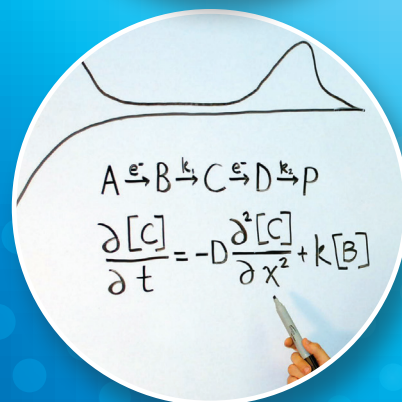
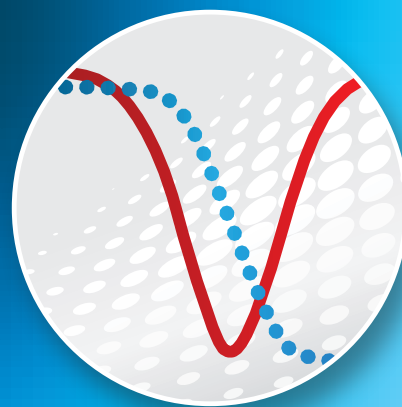


Introduction to Experimental Electrochemistry

Teacher 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	$8.314\,46 \text{ J mol}^{-1} \text{ K}^{-1}$
ϵ_0	Permittivity of free space	$8.854\,19 \times 10^{-12} \text{ F m}^{-1} \text{ or } \text{C}^2 \text{ N}^{-1} \text{ m}^{-2}$

*Introduction to
Experimental Electrochemistry*

Teacher's Guide

***Introduction to
Experimental Electrochemistry***

Teacher's Guide

***Cynthia A. Schroll
Stephen M. Cohen***

***Gamry Instruments, Inc.
Warminster, Pennsylvania***



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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, 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.

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

Faraday's Law

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 .

$$\begin{aligned} 1 F &= 96\,485\text{ C} \\ &= 96\,485\text{ A}\cdot\text{s} \end{aligned}$$

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 cm^2 ,

D is the analyte's diffusion coefficient, in cm^2/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.

► Materials Available from Gamry Instruments

Below is a table of all materials Gamry Instruments supplies in a complete electrochemistry course kit to perform all eleven experiments for ten pairs of students.

Part number	Description	Quantity
820-00005	Sample of mild steel	30
930-00015	Ag AgCl reference electrode	1
932-00003	Platinum working electrode	1
932-00009	Platinum microelectrode	1
935-00065	Micro stirring bar	1
935-00120	Carbon screen-printed electrode	36
935-00122	Platinum screen-printed electrode	60
972-00065	Cuvette cap	1
987-00099	DigiElch student edition	1
988-00049	Student edition book	20
988-00050	Teacher edition book	1
990-00193	Dr. Bob's Cell kit	1
990-00195	Polishing kit	1
990-00196	EuroCell kit	1
990-00419	AC Dummy Cell	1
990-00420	Screen-printed electrode cell stand for 4 mm banana plugs	1
990-00421	Screen-printed electrode adapter for 4 mm cable	1

► Non-Gamry Materials Required

Below is a table of all materials Gamry Instruments does not supply but are required to perform all eleven experiments for ten pairs of students. All chemicals should be 95+% pure.

Material	Quantity
1000 ppm std aqueous Cu with 2% w/w HNO ₃	100 mL
1000 ppm std aqueous Pb with 2% w/w HNO ₃	100 mL
3-methylthiophene (monomer)	2 mL / 2 g
acetaminophen (paracetamol) elixir	8 fl. oz. or 250 mL
acetaminophen (paracetamol) tablet	1 bottle of 50 tablets
acetaminophen (paracetamol)	7 g
acetonitrile	275 mL
citric acid	20 g
dialysis membrane	1 package
disposable cuvette, 4.5 mL capacity	1
ferrocene	1 g
glucose	5 g
glucose oxidase, from <i>Aspergillus niger</i> , Type II, ≥15 000 units/g solid (no added oxygen)	10 000 units
perchloric acid	5 mL
potassium chloride	44 g
potassium ferricyanide	1 g
pyrocatechol	1 g
sodium phosphate dibasic heptahydrate	5 g
sodium phosphate monobasic monohydrate	8 g
sodium sulfate	3 g
sulfuric acid	140 mL
tetrabutylammonium hexafluorophosphate	10 g
tetrabutylammonium tetrafluoroborate	4 g
PTFE tubing (L × O.D. × I.D.) 10 ft × 1/16 in. × 0.023 in.*	1 package

* This is the tubing that fits into the cap of the SPE cuvette cell. You also must supply your own fittings to connect this tubing to your in-house nitrogen-system outlet.

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

Solution Preparation

- 0.1 M KCl
Weigh out 0.74 g KCl for every 100 mL of water needed. 100 mL of solution provides 80–90 aliquots of 1 mL each.
- 2 mM potassium ferricyanide in 0.1 M KCl
Weigh out 0.74 g KCl and 0.06 g potassium ferricyanide for every 100 mL of water needed. 100 mL of solution provides 80–90 aliquots of 1 mL each.

The laboratory instructor has already purged the solutions of dissolved O₂. Purging the dissolved O₂ from these solutions prevents spurious peaks from appearing in your data.

Solution Purging

1. Purge both solutions with an inert gas (preferably N₂) for 10 min.
2. Blanket each solution with the inert gas.
3. Stopper immediately.

CAUTION:

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

► 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.

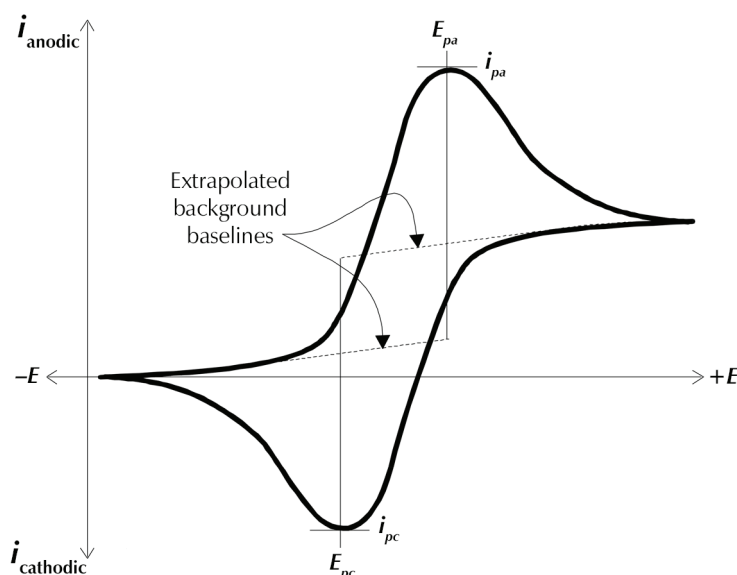


Figure 1.1. A generic CV. A CV plot reveals the reversibility of the redox couple. (Adapted from P. T. Kissinger and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, New York: Marcel Dekker, Inc., 1984, p. 88.)

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° , 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 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.

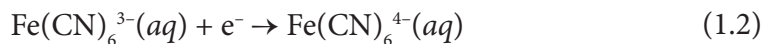
The initial direction of the first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) or negative (cathodic) direction, as determined by the characteristics of the analyte. For an oxidizable analyte, the first sweep starts in the positive direction, whereas for a reducible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

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

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 present, 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 extrapo-

$$i_p = 0.4463nFAC\sqrt{\frac{nF\nu D}{RT}} \quad (1.4)$$

lated baseline.

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

$$E^\circ = \frac{E_{\text{pa}} + E_{\text{pc}}}{2} \quad (1.5)$$

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.

In this equation,

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

ν 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^2),

R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),

T is the absolute temperature (K), and

D is the diffusion coefficient of the analyte(cm^2/s).

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

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

where the constant has units of $2.686 \times 10^5 \text{ C mol}^{-1} \text{ V}^{-1/2}$.

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.

4. 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.
5. 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

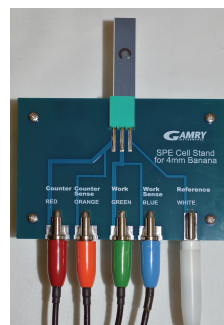
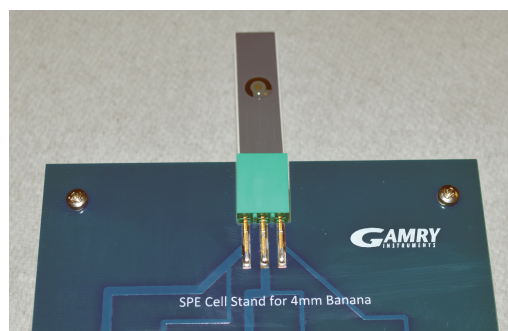


Figure 1.2. Left: Screen-printed electrode inserted into SPE cell stand. Right: Complete set-up.

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.

Cyclic Voltammetry

Default Save Restore OK Cancel

Pstat ☒ IFC1000-05065

Test Identifier Cyclic Voltammetry

Output File BLANK.DTA

Electrode Area (cm²) 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

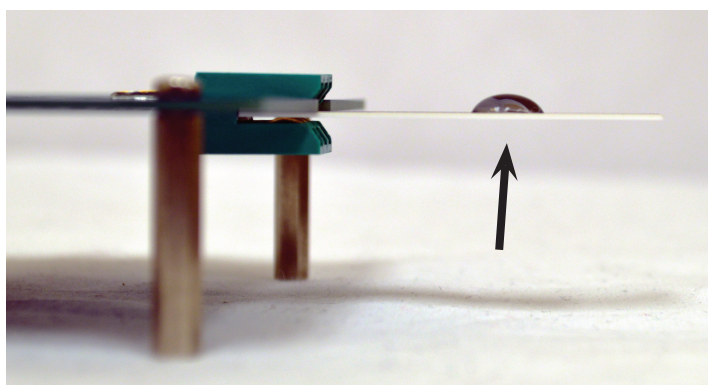
Sampling Mode ☐ Fast ☒ Noise Reject ☐ Surface

Advanced Pstat Setup ☐ Off

Electrode Setup ☐ Off

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

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



3. Set the experimental fields in the **Cyclic Voltammetry** window to those shown in Figure 1.3, with the file name as **blank**.
4. Place a drop of the blank solution, 0.1 M KCl, onto the electrodes of the SPE. (See Fig. 1.4.)
5. Click the **OK** button to run the experiment.

Perform scans using sample solution.

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

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.

- On the host computer's desktop, open Gamry Echem Analyst™ software.
- Use Echem Analyst to determine the potential of cathodic and anodic peaks and cathodic and anodic peak currents.
 - Open the CV file you want to evaluate.
 - 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.
 - Repeat for both cathodic and anodic peaks.
 - Fill in the appropriate column in the table below.
- Repeat step 2 for all the other scan rates.

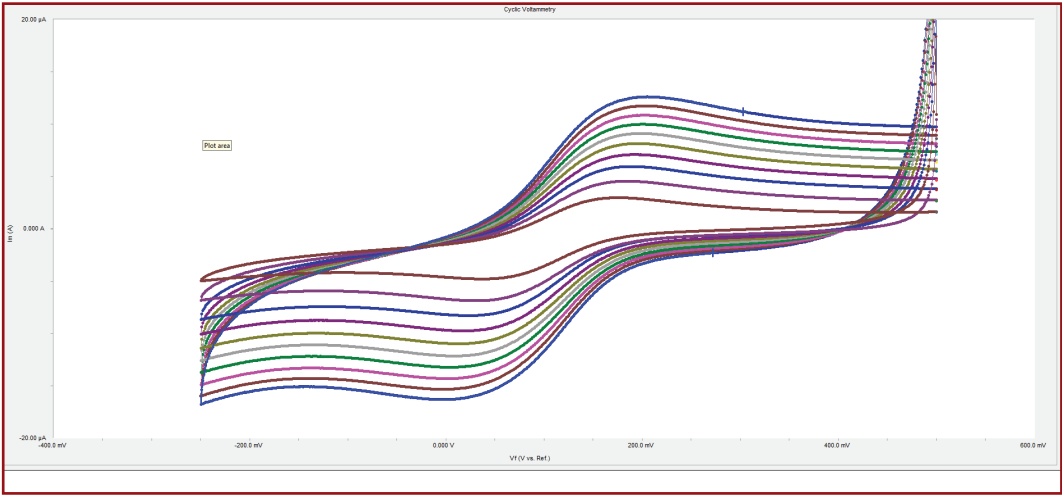
Scan Rate (mV/s)	10	20	30	40	50	60	70	80	90	100
E_{pc} (mV)	36	29	23	16	13	9	2	0	-2	-4
E_{pa} (mV)	174	184	190	190	195	198	201	203	206	205
I_{pc} (μA)	-3.679	-5.289	-6.896	-8.098	-8.591	-9.478	-9.657	-11.08	-11.09	-12.27
I_{pa} (μA)	3.190	4.135	4.783	5.636	5.964	6.447	7.717	8.426	8.610	8.723

Sample data

Print graphs.

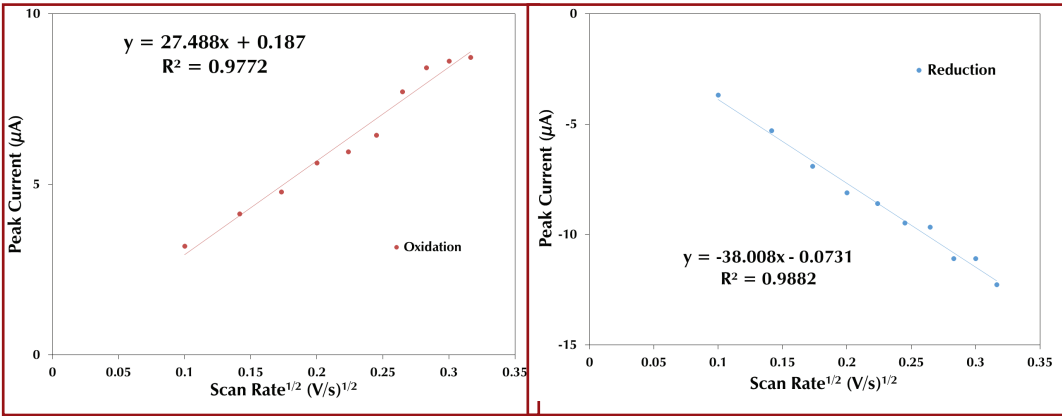
- Print a graph of the ten different scan-rates overlaid onto one plot.
 - Open the **FeCN6 1000mVs-1.DTA** file.
 - Choose **File > Overlay**.
 - Select the other graphs to be overlaid.
 - Print the complete plot.

Typical 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^{1/2}, and i_{pa} versus scan rate^{1/2}.
3. Print these two plots.

Sample data



4. Include these two plots in your laboratory report.

Calculate your results.

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

Scan Rate	10	20	30	40	50	60	70	80	90	100
(mV/s)										
ΔE_p (mV)	138	155	167	174	182	189	199	203	208	209

Sample data

$E_{1/2}$ (mV)	105	106	106	103	104	104	102	102	102	100
i_{pc}/i_{pa}	1.15	1.3	1.4	1.4	1.4	1.5	1.3	1.3	1.3	1.4

- From the plots of the i_p versus scan rate^{1/2}, determine the slope of the best-fitting line.
 - Slope of the graph i_{pc} versus scan rate^{1/2} = -38.0
 - Slope of the graph i_{pa} versus scan rate^{1/2} = 27.5
- Using the Randles-Ševčík equation and the slope from the graph of i_{pc} versus scan rate^{1/2}, calculate the diffusion coefficient for potassium ferricyanide.

Use the Randles-Ševčík equation,

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

Square both sides and rearrange to solve for D :

$$D = \frac{i_p^2 RT}{(0.4461)^2 n^3 F^3 A^2 C^2 \nu}$$

Substitute in the appropriate values with units:

$$D = \frac{(3.8 \times 10^{-5} \text{ A})^2 \cdot 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K}}{(0.4463)^2 (1)^3 (96485 \text{ C mol}^{-1})^3 (0.0314 \text{ cm}^2)^2 \left(2 \times 10^{-6} \frac{\text{mol}}{\text{cm}^3}\right)^2 (1 \text{ Vs}^{-1})}$$

$$D = 5.0 \times 10^{-6} \text{ cm}^2/\text{s}$$

► Questions

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

As the temperature increases, the diffusion coefficient would increase, because as the temperature increases the square root increases because T is in the denominator of the fraction in the square root. Also, as the temperature increases there is an increase in molecular kinetic energy and thus an increase in the diffusion rate. Answers to questions

- 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?

$$t = \frac{l^2}{2D} = \frac{0.1^2}{(2)(7.6 \times 10^{-6})} = \frac{0.01}{1.52 \times 10^{-5}} = 658 \text{ s} = 11 \text{ min}$$

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?

The ratio will be close to 1, but should be just below 1. This indicates a reversible reaction, because all of the species that were reduced are being oxidized in the back reaction. The ratio should be just below 1 because some of the reduced species will have diffused away from the face of the electrode and thus were not electrolyzed.

Common Problems

- Instrument banana plugs connected to the incorrect jacks on the SPE board. This is a fatal error, resulting in data that will not be appropriate for analysis.
- Incorrect potentials input into the software for the scan. The usability of these data for analysis will depend upon the potentials that were entered and the shape of the voltammogram. If the peaks for both the forward and reverse scans are clearly visible in the potential window used, then the data are sufficient for analysis. If the peaks are not present, then the solution will have to be rerun.

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.

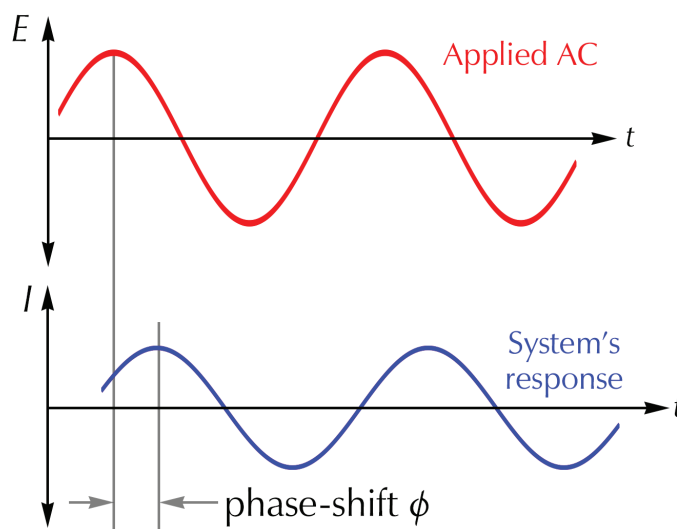


Figure 10.1. An applied AC potential (upper graph); a system's response is shifted in phase and amplitude (lower graph).

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).

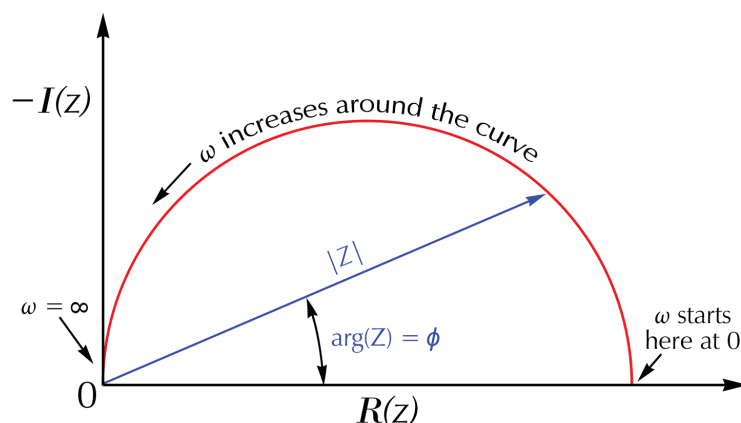


Figure 10.2. Typical Nyquist plot.

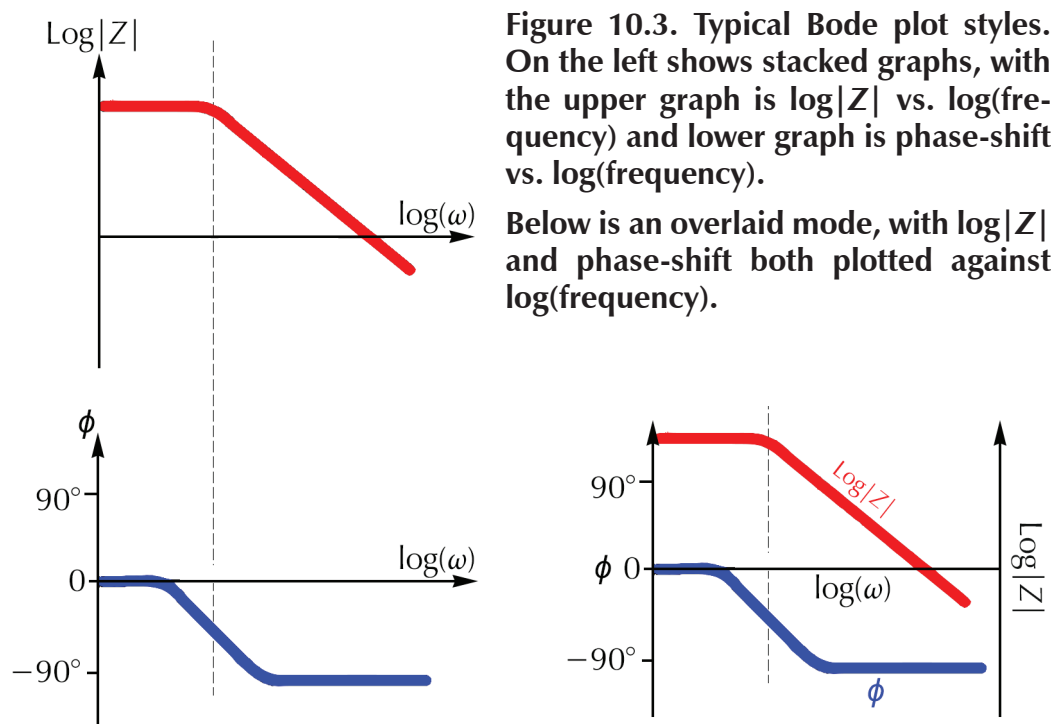
In a Nyquist plot, the absolute value of the impedance Z is the length of the vector. The angle between the vector and the x -axis is referred to as the **phase angle** ϕ (or often ω). A problem with Nyquist plots is that the frequency used for each point on the curve is not determinable. Therefore another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

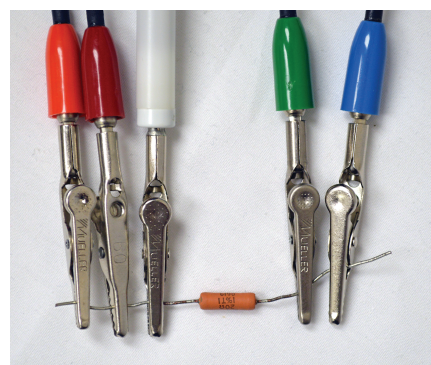
Capacitors in series attached to potentiostat.



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.

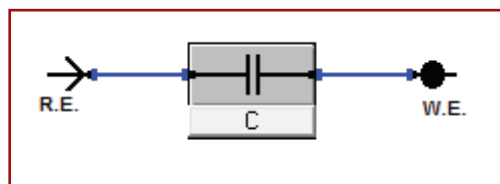
► Data Analysis

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.

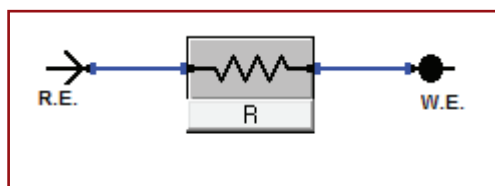
capacitors.MDL Model



Students' answers

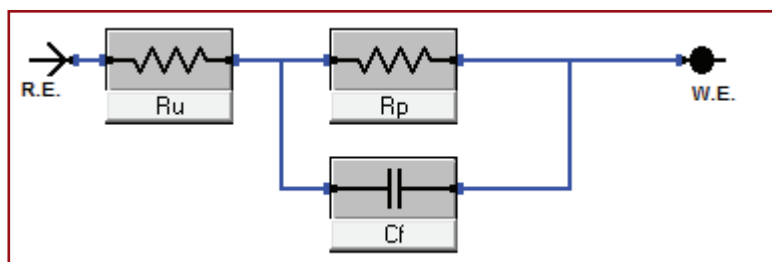
- c. In the Echem Analyst™ software, proceed to **Galvanostatic Impedance > Fit a Model (Simplex Method)**, and select the **capacitors.MDL** model you just created. A new window opens containing all of the circuit elements from the model. Click the **AutoFit** button and the model runs.
 - d. After 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

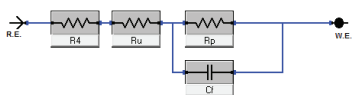
► Questions

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

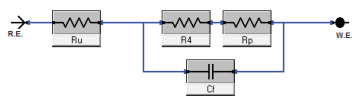
Analysis of a linear system is much simpler than a non-linear system. If the excitation signal is kept small, then the system is under a pseudo-linear response. If we measure outside of this pseudo-linear area, then the system's response will contain harmonics of the excitation signal.

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.