Experimental Electrochemistry:

an Introduction for Educators

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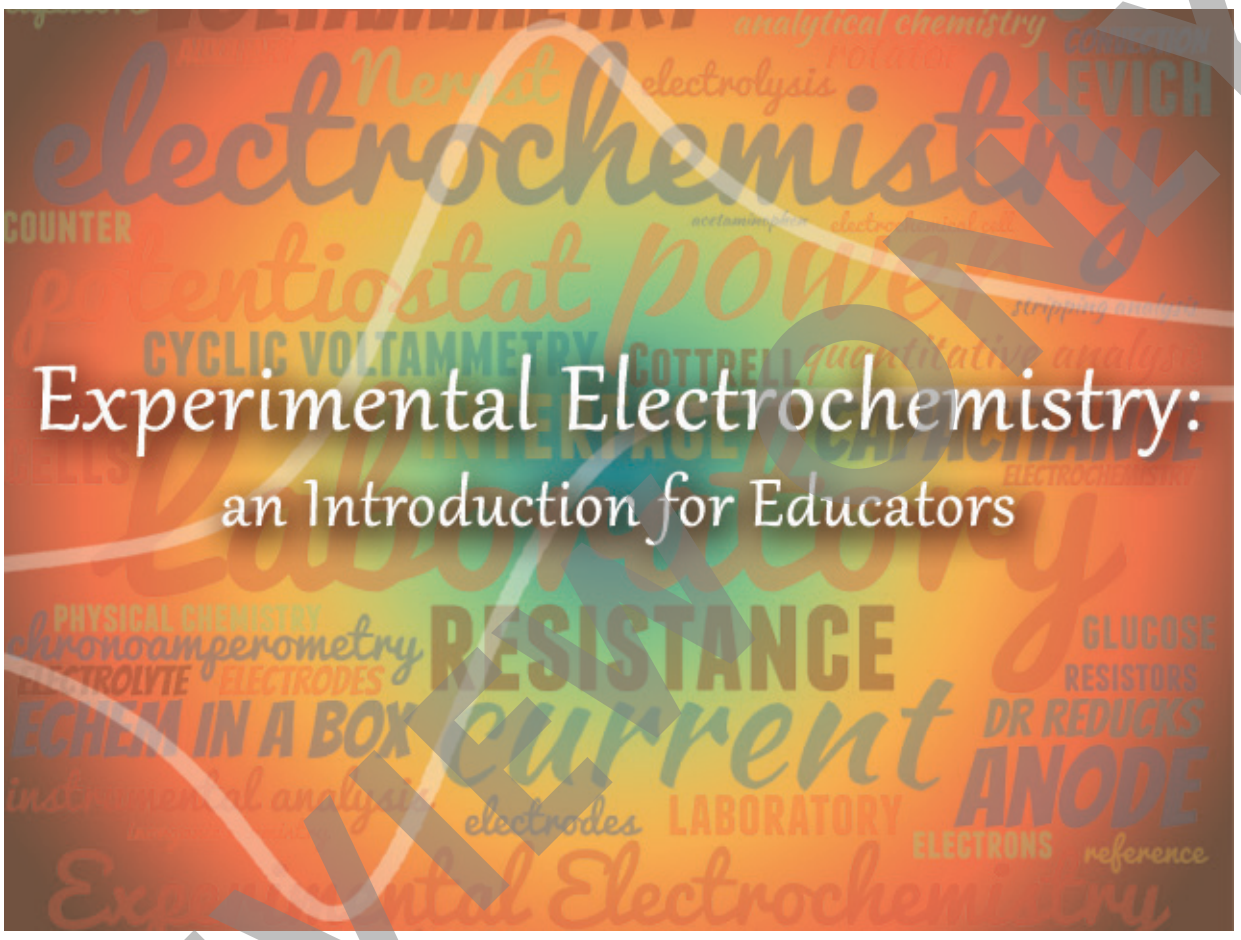
Experimental Electrochemistry: an Introduction for Educators



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Frequently Used Equations

Free Energy Relationship to Cell Potential	$\Delta G^\circ = -nFE^0_{cell}$
Diffusion Layer Thickness Estimate	$l = \sqrt{2Dt}$
Nernst Equation	$E = E^0 - \frac{RT}{nF} ln\left(\frac{a_O}{a_R}\right)$
	$E = E^0 - \frac{RT}{nF} ln\left(\frac{C^*_O}{C^*_R}\right)$
	$E = \frac{0.0592}{n} log\ Q\ at\ 25℃$
Ohm's Law	$V = iR$
Capacitor Behavior	$C = \frac{q}{E}$
Faradaic Current Relationship to Electrolysis Rate	$Q = it = \frac{m}{Z} = \frac{mnF}{M}$
Cottrell Equation	$i(t) = nFAC\left(\frac{D}{\pi t}\right)^{1/2}$
Randles-Ševćik Equation	$i_p = 0.4463\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D_O^{1/2} C_O^* v^{1/2}$
	$i_p = (2.687 \times 10^5) n^{3/2} v^{1/2} D^{1/2} AC\ at\ 25℃$
Levich Equation	$i_L = (0.620) nFAD^{2/3} \omega^{1/2} v^{-1/6} C$

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Common Units with Cross-Reference

Symbol	Meaning	Common Units	Section
A	area	cm^2	3.5
a	activity coefficient	none	6.4.2
β	operational amplifier gain	none	6.1.1
C	(a) capacitance	F	3.5
	(b) concentration	mol/cm^3	3.3
D	diffusion coefficient	cm^2/s	5
d	distance between parallel plate capacitors	m	3.5
E	(a) emf of a reaction	V	3.3
	(b) amplitude of an AC voltage	V	6.1.1
	(c) potential of an electrode vs. reference	V	6.4.2
E^0	standard potential	V	3.3
e^-	electron	none	3.2
ε_r	relative static permittivity	$F \cdot m^{-1}$	3.5
ε_0	electric constant	$F \cdot m^{-1}$	3.5
F	Faraday's constant	C	3.3
G	Gibbs free energy	$kJ,\ kJ/mol$	3.4
$G°$	standard Gibbs free energy	$kJ,\ kJ/mol$	3.4
i	current	A	3.5
$\bar{\mu}$	electrochemical potential	J/mol	3.3
n	stoichiometric number of electrons in a redox event	none	3.3
Φ	electric potential	V	3.3
Q	reaction quotient	depends on order	3.4
q	charge	C	3.5
R	(a) resistance	Ω	3.5
	(b) ideal gas constant	$J \cdot mol^{-1} \cdot K^{-1}$	3.4
R_s	solution resistance	Ω	4.4.1
T	absolute temperature	K	3.4
t	time	s	
v	scan rate	V/s	
v	kinematic viscosity	m^2/s	5.2.4
ω	angular rotation rate	rad/s	5.2.4

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2. Introduction

2.1 Focus

Experimental Electrochemistry: an Introduction for Educators is designed to assist educators who, having little to no prior electrochemical experience, are assigned to teach an undergraduate chemistry course that may include electrochemistry (e.g., analytical chemistry/quantitative analysis, inorganic chemistry, instrumental analysis, physical chemistry, etc.). The guide will detail significant theory and experimental aspects of electrochemistry. It should be noted, however, that this guide is not a substitute for a text book; it is recommended that the instructor use a standard text book and supplement it with this guide where applicable. An appendix of text books and other resources can be found at the end of the guide (see: Appendix A: References, Journals, and Texts).

Pine Research has also developed a video supplement for the *Experimental Electrochemistry: an Introduction for Educators*. The videos reflect the knowledge of trained electroanalytical chemists but are condensed into segments that are easy to understand. They are based upon the content of the educational guide herein; the educational guide extends beyond the videos' limited time/space. We encourage you to first view our short video series at your own leisure and then read this educational guide.

2.2 Background

To say that most college-aged students have a mobile electronic device on their person at all times is a plausible generalization; the electronic device may be a mobile phone, tablet, e-reader, music player, personal computer, etc. These energy (battery) dependent systems have intercalated into nearly every aspect of life and have caused an increased dependence on energy. The additional consumption of energy is standard in many areas of life, including transportation, entertainment, communication, and more. This guide is not the appropriate place to discuss energy policy, but rather to point out that our physical world is energy hungry. A great deal of successful research over the last 30 + years in the broad area of electrochemistry has focused on this energy hunger. Technological innovations in electrochemistry have made significant changes to the energy horizon: higher efficiency batteries, efficient fuel cells which convert chemical fuels into electrical energy, and solar based technologies such as dye-sensitized solar cells and photoelectrochemical systems to split water to source electrical current.

Modern electrochemistry is a powerful tool that is utilized for a large number of applications in addition to the energy regime: small microelectrodes probe biochemical events on the cellular level, rotating disk electrodes monitor industrial corrosion processes, and electrochemical methods with amazingly low detection limits are used to monitor lead levels in the bloodstream. Additional applications in water purification, and chlorine and hydroxide refinement by the chlor-alkali process, are also seen. Moreover, electrodes coated with special polymers are finding use as glucose detectors for diabetics and even the synthesis of metallic nanoparticles is based on electrochemical principles. The common thread across these innovations is electrochemistry and electrochemical methods.

In light of all of this recent activity, it is clear that modern electroanalytical techniques should be included in the undergraduate curriculum. However, despite its powerful applications, electrochemistry generally receives the less attention than other common instrumental topics, such as spectroscopy, spectrometry, separations, and microscopy, across the undergraduate chemistry curriculum. In fact, electrochemistry is typically only discussed in theory with little to no hands-on laboratory experience to validate the pedagogy. Furthermore, in many undergraduate programs, electrochemistry and electrochemical methods are completely removed from the chemistry curriculum. Students at these

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institutions are only exposed to electrochemistry through general chemistry courses when redox potentials are discussed.

The lack of emphasis placed on teaching electrochemistry in bygone days is most likely attributed to its ease of use, or lack thereof, in comparison to spectroscopic and separation techniques. The instructor, faced with a bewildering number of instrumental methods, likely chooses to emphasize the more popular spectroscopic and separations techniques over the less familiar electrochemical methods because old-fashioned polarographs and clumsy dropping mercury electrodes made cuvettes and columns look more attractive. Now, however, electrochemical instrumentation has a simple design, and several interesting experiments can be added to the instrumental analysis course with a minimum investment of time and money.

Pine Research created the *Experimental Electrochemistry: an Introduction for Educators* guide to make it as easy as possible for the analytically-minded college instructor to implement, update, and include electrochemistry into new and existing curriculum. The required equipment is quite inexpensive–an institution can now purchase a fully functional potentiostat system for less than the cost of a UV/vis spectrophotometer or a gas chromatograph. Pine Research offers everything required to start teaching modern electrochemistry in the undergraduate laboratory and has developed a durable, robust, and easy-to-implement system that is low-cost and easy to use by students.

Of course, the lab instructor needs suitable experiments for undergraduates to perform during a single lab period. *Experimental Electrochemistry: an Introduction for Educators* includes several tested electrochemical laboratory exercises, complete with notes for the instructor, which have been successfully used to teach undergraduate level experimental electrochemistry. The laboratory exercises are designed with an analytical objective in mind, such as determination of an unknown concentration or measurement of a diffusion coefficient. It is important to note, however, that there are many non-analytical uses for electrochemistry. A modern potentiostat can be used to measure the fundamental thermodynamic and/or kinetic properties of chemical systems in an inorganic or physical chemistry laboratory. The *Experimental Electrochemistry: an Introduction for Educators* is likely to be a useful resource for many chemistry courses from general chemistry to instrumental analysis.

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3. Prior Learning Concepts

Many basic electrochemical concepts—half-reactions, formal potentials, reference electrodes, the Nernst equation, free energy calculations, and simple dual electrode cells—are likely introduced during high school or introductory college-level chemistry and physics courses. As a result, most students in upper level laboratory courses are already familiar with basic electrochemical concepts (whether they realize/remember is another issue). Unfortunately, the introduction of electrochemistry in early courses can be rather dull: most students are given stoichiometric and concentration data of systems that do not pass current, but rather rest at an equilibrium potential, and are expected to predict the cell potential under these potentiometric conditions (see: Section 5 for more information about potentiometry). At best, this early emphasis on "number crunching" leaves students with a very narrow view of electrochemistry. At worst, the students emerge quite confused, worrying far too much about how to tell which electrode is the cathode or which half-reaction gets "flipped." The student rarely learns why it might be useful to perform an otherwise mundane redox reaction in that special container known as the electrochemical cell.

Fortunately, analytical chemistry and instrumental analysis provide an opportunity to re-introduce electrochemistry to the student in a more engaging and realistic manner. The point should be made (early and often) that the real power behind modern electrochemical techniques derives from a very simple idea: carrying out a redox process in an electrochemical cell forces electron transfer between reactants to occur through an external electronic circuit. Because the design and control of the external circuit belongs to the electrochemist, the electron flow may be used in whatever way is desired. For example, it can be used as a source of power, the basis for a chemical measurement, or the driving force for an electrosynthesis reaction. Rather than passively observing a redox process, the modern electrochemist takes control of the process, adjusting how fast it occurs (by regulating the current) or to what extent it occurs (by regulating the potential).

The next sections of this guide address prior learning areas that are essential to the fundamental understanding of electrochemistry and electrochemical-based experiments. Only a casual review of these topics is provided, leaving a more rigorous and robust treatment of the topics to traditional textbooks and material typically covered in early-career college courses.

3.1 Reduction-Oxidation (Redox) Reactions

The reduction-oxidation (redox) reaction is a fundamental type of chemical reaction that is very important to electrochemistry. Redox reactions are at the core of many energy-based systems such as batteries, fuel cells, and solar cells, and are also the fundamental reaction of interest in corrosion or tarnish of sterling silver (simple oxidation). Energy production, storage, and transfer within living systems are linked to redox-based cascades of reactions as well.

In redox reactions, electrons are transferred between two species. One species is reduced and, equivalently, another species is oxidized. If an atom gains an electron during the chemical reaction, its oxidation state decreases (i.e., reduces) and so the species is said to be reduced. Similarly, if an atom loses an electron during the chemical reaction, its oxidation state increases (i.e., oxidizes) and so the species is said to be oxidized.

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The cell potential at standard conditions has been correctly determined as $1.76\ V$. Real world chemistry (especially in an educational laboratory) are far from standard conditions. To determine the electrochemical potential at conditions other than standard state, it is necessary to utilize the Nernst Equation which will be discussed in the next section.

3.4 Free Energy and Thermodynamics

A brief foray into thermodynamics is appropriate to establish the relationship between cell potential and analyte concentration. Recall that Gibbs free energy, ΔG, is related to the reaction quotient, Q, by:

$$\Delta G = \Delta G^0 + RT\ ln\ Q \qquad \textbf{(3-14)}$$

where ΔG^0 is the standard Gibbs free energy, R is the universal gas constant $8.314\ J\ mol^{-1}\ K^{-1}$, and T is the temperature in $Kelvin$. As discussed earlier, Gibbs free energy is directly proportional to the cell potential E via

$$\Delta G = -nFE \qquad \textbf{(3-15)}$$

Substitution of E into Equation 3-14 builds an expression to relate cell potential change to redox molecule concentration, otherwise known as the Nernst Equation:

$$E = E^0 - \frac{RT}{nF} ln(Q) \qquad \textbf{(3-16)}$$

The Nernst equation is powerful because it predicts the analyte concentration ratio only by measuring the cell potential (as long as the standard potential of the reaction is already known). In addition, the measured or calculated cell potential indicates whether a reaction is spontaneous: when $E > 0$, the reaction is spontaneous and when $E < 0$, the reaction is non-spontaneous. The sign conventions for cell potential are opposite those for Gibbs free energy: when $\Delta G > 0$, the reaction is non-spontaneous, and when $\Delta G < 0$, the reaction is spontaneous.

Spontaneity and thermodynamics were first introduced to students in general chemistry through reaction diagrams (see: Figure 3-3). On the left side of the generic reaction diagram, a "spontaneous" reaction occurs along the reaction coordinate ($x - axis$): high energy reactants overcome the activation energy barrier to form products at a lower energy level. On the right side of the generic reaction diagram, a "non-spontaneous" reaction occurs: low energy reactants overcome the activation energy barrier and form products at a higher energy level.

The thermodynamic energy diagram can be extended to represent an electrochemical system (see: Figure 3-4). The diagram differs only with respect to terminology: electrochemical potential replaces Gibbs free energy and spontaneity is defined by E and not ΔG. In addition, electrochemists use the term overpotential rather than activation energy. The terms are essentially the same and refer to the amount of energy needed beyond the thermodynamic minimum to drive the reaction forward. A chemist might increase the temperature to overcome the activation energy barrier whereas an electrochemist would adjust the applied potential to overcome the overpotential.

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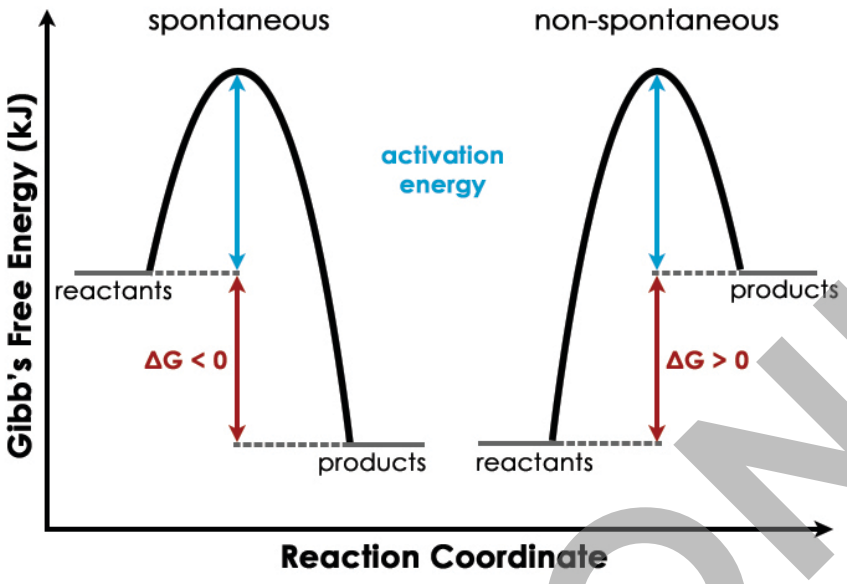

Figure 3-3. Generic Reaction Diagram Expressed in terms of ΔG

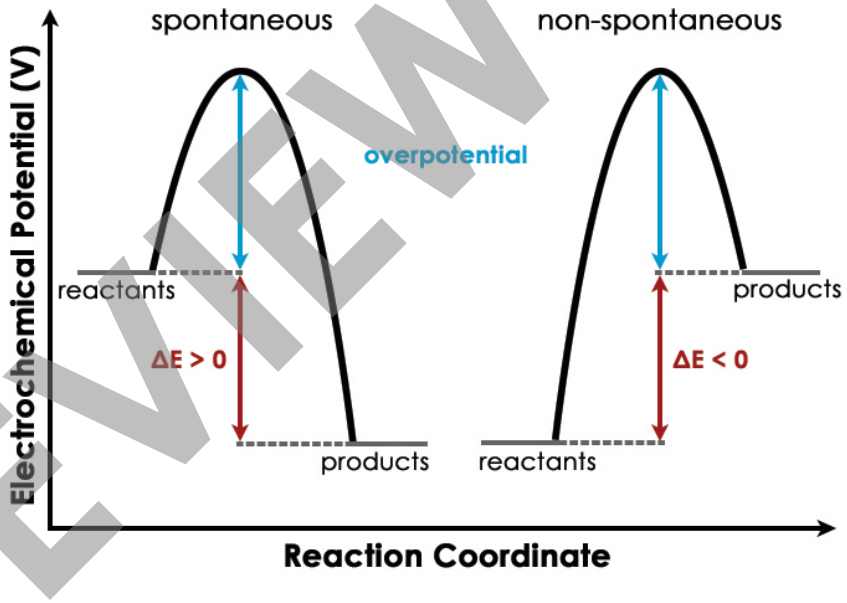

Figure 3-4. Generic Reaction Diagram Expressed in terms of E

After reviewing the similarities between ΔG and E, it is easy to describe thermodynamics from an electrochemical perspective. There are two more important ideas to remember about ΔG and E. First, recall from general chemistry that the value of ΔG only describes if the reaction is thermodynamically favorable but does not describe the kinetics of the reaction; the same is true for electrochemical potential. For example, a redox reaction may have a positive cell potential but high kinetic barriers prevent the process from occurring. Second, it is not necessary to have an electrochemical cell equipped with a salt bridge and voltmeter for an electrochemical reaction to occur. For example,

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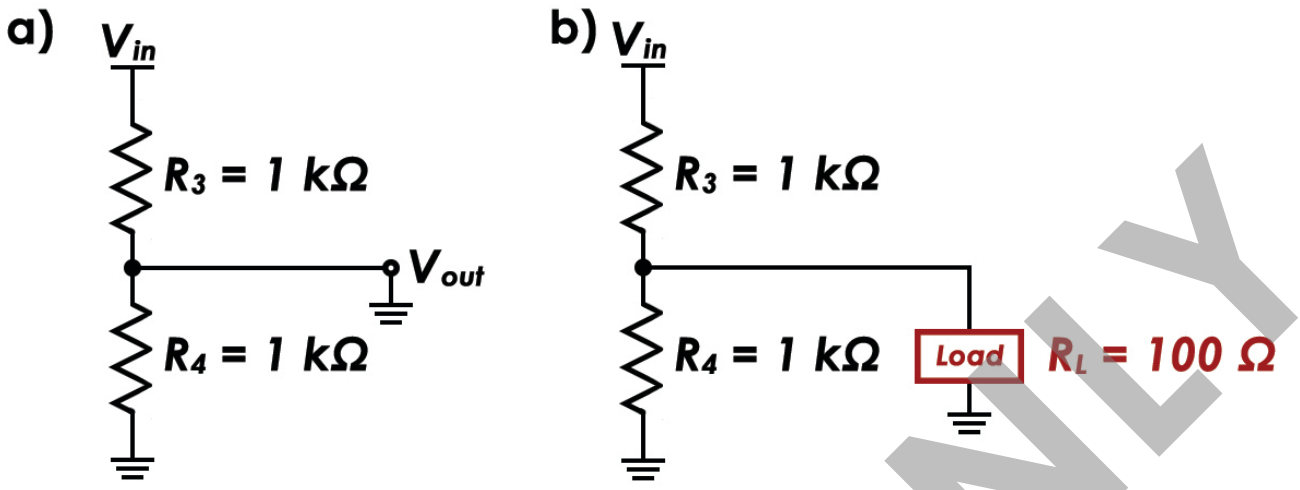

Figure 3-7. Circuit Diagrams a) a Voltage Divider and b) a Voltage Divider Attached to a Load

Physicists use the term "voltage divider" for this type of circuit (see: Figure 3-7a). The potential between the two resistors in series, V_o, for the voltage divider is determined mathematically as:

$$V_{out} = V_{in}\left(\frac{R_3}{R_3 + R_4}\right) \quad \textbf{(3-23)}$$

For the example provided, $R_3 = R_4 = 1\ k\Omega$, $R_{eq} = 2\ k\Omega$, and therefore $V_o = V_i/2$. The voltage measured between the two resistors is half the input voltage. However, when an external load requiring $5\ V$ is connected to the voltage divider circuit (with $V_i = 10\ V$), it is found that the circuit cannot power the external load. This occurs because the external load has an intrinsic impedance that affects V_o (see: Figure 3-7b). The effect of the load on V_o can be calculated: a voltage divider occurs between R_3 and $R_4//R_L$ (R_4 parallel to R_L). To compute V_{out}, the equivalent resistance (R_{eq}) for $R_4//R_L$ is found first:

$$\frac{1}{R_{eq}} = \frac{1}{R_4} + \frac{1}{R_L} = \frac{1}{1000\ \Omega} + \frac{1}{100\ \Omega} = 90.9\ \Omega \quad \textbf{(3-24)}$$

Now, the voltage divider formula can be used between R_3 and R_{eq}:

$$V_{out} = V_{in}\left(\frac{R_{eq}}{R_3 + R_{eq}}\right) = (10\ V)\frac{(90.9\ \Omega)}{1000\ \Omega + 100\ \Omega} \approx 0.083\ V \quad \textbf{(3-25)}$$

It is clear that there is not sufficient voltage at the output to operate large loads with this type of setup. However, operational amplifiers are often placed before the external load to solve this problem (see: Section 6.1.1).

For complicated circuits, which may have resistors in both series and parallel, break the circuit down into simpler parts. Typically, add parallel resistances to find a combined resistance. Then, the combines resistance is placed in series with other resistors. This can simply the daunting process of balancing circuits.

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4. Electrochemical Fundamentals

With the prior learning content reviewed (see: Section 3), it is now possible to start discussing experimental electrochemistry. The concepts in this section are not often included in the undergraduate curriculum. In many cases, they are not even covered in the graduate curriculum, save for a specific course in Electrochemistry. Thus, unless an instructor took a graduate level electrochemistry course or performed electrochemical research in graduate school, they are unlikely to intuitively understand the concepts in this section. The goal here is to provide sufficient electrochemical fundamentals to understand, teach, and answer questions about experimental electrochemistry.

4.1 Mass Transfer

Electrochemical measurements are heterogeneous in nature, meaning that liquid electrolyte solution carrying analyte must come into contact with the solid electrode (mercury electrodes, while rarely still used, are liquid but still participate in heterogeneous electron transfer). Therefore, in order for current to be sustained, mass transfer of reactive species from bulk solution to the electrode | electrolyte interface must occur. There are three such mass transfer mechanisms: migration, convection, and diffusion.

Electrochemists often strive to create a system where diffusion is the only form of mass transfer because the mathematics involved in solving for the current as a function of potential is simpler for diffusion controlled systems. Remember each mode of mass transfer in an electrochemical measurement can be variables, thus a well-designed experiment will lead to results that are easier to interpret.

NOTE:

The motion of ions (mass transfer) is experimentally observed in the form of current. Mass transfer directly affects the current results obtained in electrochemistry experiments.

4.1.1 Migration

Migration is the mode of mass transfer of a charged species moving as the result of an applied electric field. Some scientists might consider electrokinetic separations (*i.e.*, electrophoresis) to be electroanalytical methods. Most electrochemists would not make the same association, however, as efforts are often taken to intentionally eliminate migratory effects in electrochemical cells. Migration is mitigated by adding a significant amount of excess electrolyte in comparison to the analyte of interest; the excess electrolyte shields the analyte from electric charge generated by the electrode.

4.1.2 Convection

Convection is the hydrodynamic motion of molecules, based on stirring or mixing of the solution. It is common to stir solution for bulk electrolysis, where the entire bulk analyte may undergo a redox reaction at the electrode interface. Mechanical motion brings analyte to this interface. When convection is well-controlled and migration is minimized with a high electrolyte concentration, then diffusion mass transfer is well-behaved and may even be constant. As in the case of rotating disk electrochemistry, the flow of analyte past the electrode interface is well-defined and constant for a given rotation rate. While out of scope for this guide, a brief mention of hydrodynamic methods is included later (see: Section 5.2.4). In general, electrochemists eliminate the mass transfer contribution by convection by keeping solution perfectly still.

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5. Experimental Electrochemical Techniques

In an electrochemical experiment, current and potential cannot be controlled simultaneously so the electrochemist must choose which of these experimental variables to control. Broad categories of electrochemical methods are as follows:

- Potentiometry – potential measured as a function of concentration and $i = 0$
- Controlled Potential Methods – current measured as a function of applied potential, which may be fixed or applied across a controlled ramp or waveform
- Controlled Current Methods – potential measured as a function of applied current, which may be fixed or applied across a controlled ramp or waveform

Methods where current is observed as a function of the controlled electrode potential are called *potentiostatic methods*. Methods where the potential is measured as a function of controlled current at the working electrode are called *galvanostatic methods*.

5.1 Potentiometry

In the familiar (and rather boring) context of potentiometry, the electrochemist assumes a passive role. The solution concentrations are determined by initial concentrations and reaction kinetics; the electrochemist only measures the working electrode potential, which, in theory, is the same as that predicted by the Nernst equation. In the more exciting context of voltammetry, the electrochemist assumes an active role by controlling the electrode potential and influencing the solution concentrations in the vicinity of the working electrode. Of course, the Nernst equation is still useful for predicting the concentrations of species near the electrode surface at a given applied potential. However, it provides an accurate picture only in cases where the redox system rapidly responds to changes in the applied potential. These kinetically facile redox systems remain in quasi-equilibrium with the electrode surface and are often called "Nernstian" or reversible systems. Therefore, readers are encouraged to review supplementary texts (see: Appendix A: References, Journals, and Texts) for more information on potentiometry as the remaining focus of this guide will be on methods more commonly used, which are also the methods implemented in the laboratory exercises provided later (see: Appendix D: Electrochemical Laboratory Exercises).

5.2 Controlled Potential Methods

The dozen or so popular controlled potential methods are often categorized as step, sweep, pulse, and hydrodynamic methods. Most of the methods within a given category are quite similar but have been named for their subtle differences by electrochemists. In all cases, the applied potential is a variable such that the analyte is oxidized or reduced at the electrode surface, a predictable concentration gradient forms, and a predictable current response arises.

In controlled potential methods, the potential of the working electrode determines what, if any, redox processes occur at the electrode surface. Extremely positive potentials are likely to oxidize species at the electrode|electrolyte interface while negative potentials are likely to reduce them. In either case, the current flux at the electrode surface is typically proportional to solution concentration; higher concentrations typically result in larger current. Thus, current provides an analytical signal that can be used to create a calibration curve relating signal to concentration. Students may have already assumed the link between current and analyte concentration after they learned Faraday's Law (see: Section 3.3).

For most potentiostatic methods there are equivalent galvanostatic methods. The laboratory exercises included in the guide focus on the more common potentiostatic methods. Several different methods

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are employed across the laboratory exercises, so a brief description of those most commonly used may prove helpful to understand the mode of perturbation and the meaning of the resulting response.

5.2.1 Potential Step Methods

In general, a potential step method involves moving the potential from some point (often at equilibrium, when $i = 0$) to a different potential. This move, or step, can be a single step or it can be multiple steps according to a specific program. The software interface is used to define a program, which sends command to the potentiostat to apply the potential step program with high temporal resolution. In general, step techniques generally give better quantitative information as compared to other controlled potential methods.

Chronoamperometry

The simplest electroanalytical technique is called chronoamperometry (CA) and involves stepping the electrode potential from an initial potential to a final potential, then holding at this stepped potential for a specific period of time. The initial and final potential are chosen so that they bracket the formal potential, E°, of the analyte (see: Figure 5-1a).

By convention, electrochemists add an induction period to CA experiments. During this induction period, a pre-selected potential is held constant for a specific amount of time. The potential during the induction period is selected such that no reaction occurs and $i = 0$. AfterMath does not record data during this induction period (see: Figure 5-1b, induction period from -1 to $0\,s$ at $0.0\,V$). Once the potential is (nearly) instantaneously stepped to the final potential (the potentiostat typically sets the potential step to occur at $t = 0\,s$), the analyte within the diffusional limit of the electrode surface begins to be undergo charge transfer (via oxidation or reduction) at the electrode surface (see: Figure 5-1b). The concentration of analyte near the electrode depletes rapidly (dependent, of course, on electron transfer kinetics) to such an extent that concentration near the electrode surface goes to zero in time. The sudden depletion of analyte at the electrode surface creates a large concentration gradient, thus, significant current is observed immediately after the step. With time, the diffusion layer grows further into solution away from the electrode, and the concentration gradient slowly relaxes, causing the initial spike in current to decay (see: Figure 5-1b).

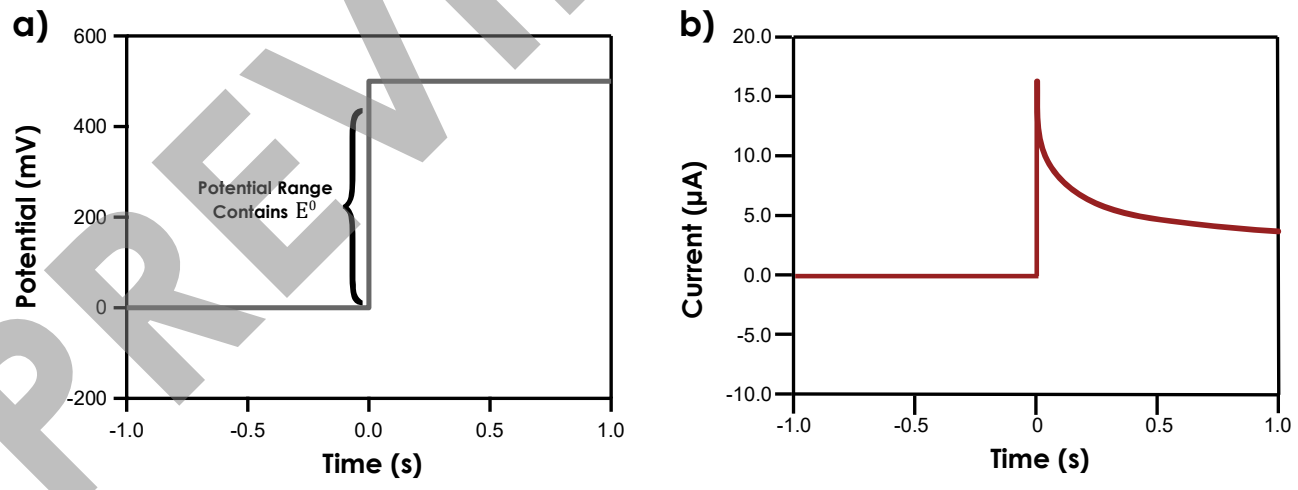

Figure 5-1. Chronoamperometry a) Potential Step Program and b) Chronoamperogram Response

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The magnitude of the current transient, $i(t)$, in a chronoamperogram is proportional to the analyte concentration, C, and is described by the Cottrell equation (see: Equation 5-1),

$$i(t) = nFAC\left(\frac{D}{\pi t}\right)^{1/2} \quad \textbf{(5-1)}$$

where variables are as previously defined. The experimental data are often plotted as $i(t)$ versus $t^{-1/2}$, which theoretically yields a straight line. Such a plot is called a Cottrell plot. The slope of this line is directly proportional to concentration and may be used for its analytical determination. For solutions where the analyte concentration is already known, the slope can be used to measure the diffusion coefficient of the analyte.

LABORATORY EXERCISE:

Chronoamperometry is the electrochemical method used for analytical determination in the Laboratory Exercise *Electrochemical Based Enzymatic Determination of Glucose in Beverages*.

There are several types of chronoamperometry, based on the number of steps. Double potential step chronoamperometry (DPSCA) provides a variation to the simple CA experiment by stepping back to the initial potential after an elapsed period of time. The principle strength of DPSCA is its ability to probe the analyte after oxidation or reduction by the electrode; oxidized and reduced analytes are often unstable and may undergo various chemical reactions including decomposition. DPSCA provides a way to measure if and how fast decomposition processes occur. Another step based experiment is Cyclic Step Chronoamperometry (CSCA). The potential step is often a combination of discreet steps, where the stepped potential is held for a specified length of time. These discreet steps can be cycled, or repeated n times. During each potential step, triggers can be applied in software, which if the trigger condition is met, the potentiostat will terminate the existing step and move on to the next. CSCA may be used for charging and discharging a battery.

5.2.2 Potential Sweep Methods

Consider expanding the basic potential step experiment like CA by performing many steps, spaced closely together in potential (*i.e.*, $1\,mV$) and for short lengths of time. The result would be a series of CA experiments in three dimensions: current (i), time (t), and potential (E).

NOTE:

Such experiments are typically called voltammetry experiments as they combine potential (in Volts), current (in Amps), and time = voltammetry.

In such an experiment, the potential is stepped increasingly along a ramp, linearly in time. Thus, it is as if the applied potential is swept from an initial to final value. The slope of the ramp is called sweep rate (also called scan rate). Typical sweep rates vary from $10\,mV/s$ to $1000\,V/s$. Sweep rates are a user-defined variable for sweep methods and in some cases may be very slow, such as with corrosion based

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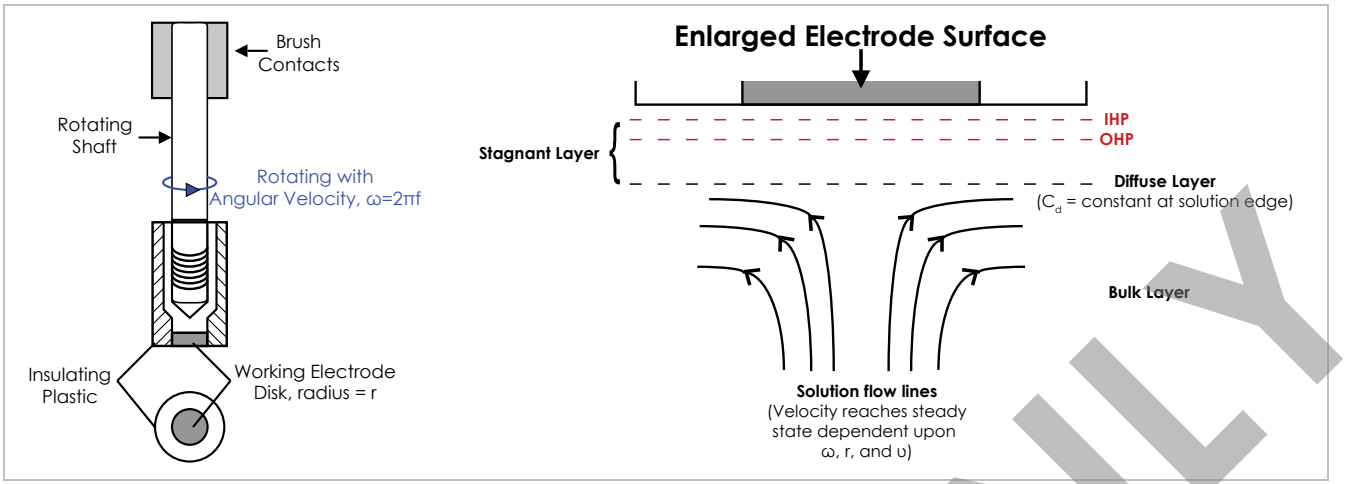

Figure 5-5. Rotating Disk Electrode Components (left) and Electrode Surface (right)

The resulting voltammogram has a sigmoidal shaped wave centered about the formal potential (see: 5-5). The limiting current, i_L, measured from the foot of the wave to its plateau, is given by:

$$i_L = (0.620)nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C \qquad \textbf{(5-5)}$$

where $\omega = 2\pi f$, f is the rotation rate $(revolutions/s)$, ν is the kinematic viscosity of the solution, and the other variables have their usual meanings. The limiting current is directly proportional to concentration and can be used for analytical determination of variables.

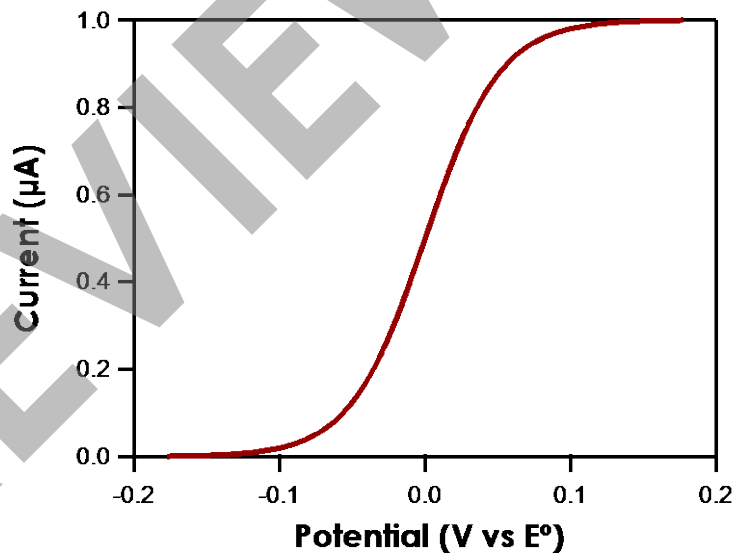

Figure 5-6. Sigmoidal Rotating Disk Electrode Voltammogram

A variation of RDE is the rotating ring-disk electrode (RRDE). The RRDE has a disk electrode with a second ring electrode concentric with the disk. When it is rotated, analyte is brought to the surface of the disk electrode and subsequently swept past the ring electrode by laminar flow. Thus, the analyte encounters

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6. Electrochemical Instruments and Tools

In most analytical chemistry techniques, a chemical system is studied through controlled perturbation and system response measurements. For example, in UV-Vis spectroscopy, a monochromator and light source are used to perturb a solution with ultraviolet and visible light. The intensity of light that passes through the solution is measured at each wavelength. The analytical signal, photons, form a response spectrum that reveals information about the electronic excited states of the molecules in solution.

Electrochemistry also uses controlled perturbations to study chemical systems. A perturbation (current or voltage) applied to the cell can elicit molecular redox events. The redox events are fully characterized by measuring the analytical response (current, charge, or voltage) as a function of the applied current or voltage perturbation. Therefore, electrochemists require instrumentation that is capable of applying a potential or current perturbation. The perturbation could be one quantity (step), a quantity that changes over time (sweep), or a quantity that discreetly changes at some repeated pattern. The same instrumentation must measure the response signal. Electrochemists use a potentiostat to accomplish this type of perturbation application/signal collection.

The fundamental instrumentation requirements for electroanalytical chemistry include a potentiostat, data acquisition system, and an electrochemical cell. The components that make up the electrochemical cell vary from experiment to experiment, most often including electrode, gas sparging tubes, stoppers, etc.

Students or researchers who are new to electrochemistry should take time to become familiar with the specialty instrumentation used in electrochemical experiments. Fortunately, setup of a potentiostat and cell is fairly straightforward and does not require a significant amount of prior knowledge. Routine electrochemical experiments are fairly easy to conduct. In some cases, it is like any other modern instrument: prepare sample, load sample, start software, adjust software settings, click a start button, and wait for the experiment to be complete. Interpretation of the data is typically the most complicated aspect of electrochemistry—at least for real world systems.

For the purpose of teaching electrochemistry, Pine Research has also developed products to lower the activation barrier of entry into a new technique. Pine Research developed Compact Voltammetry Cell (CVC) that features a simple design to significantly reduce electrochemical experiment setup time. The CVC is based around screen-printed electrodes (SPE). Just like your favorite t-shirt, these SPEs are printed in the same manner, using conductive inks, onto a substrate. The exposed electrodes on the substrate are immersed into solution, connected to the potentiostat, and disposed after use. Use of SPEs eliminates the dependency on tribal knowledge that electrochemists have about how to prepare electrodes, how to polish them, how to modify their surfaces, etc. The CVC with SPEs finds use in all of the Laboratory Exercises provided by Pine Research. Traditional electrodes could be used in the place of SPEs, however, students will gain the same insight into electrochemistry using a disposable or low-cost SPE as with traditional electrodes, which can cost 750% more than SPEs. Typically, instructors appreciate the latter and can relax during lab—knowing their students are not potentially mishandling a $1,000 electrode.

The rest of this section further details the equipment used to perform electroanalytical experiments. It also introduces the fundamental concepts of the specific instrumentation.

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6.3 The Electrochemical Cell

An electrochemical cell is a vessel that contains electrolyte solution (with analyte) and electrodes that are configured to perform an electrochemical experiment. Electroanalytical chemists often require specialized electrochemical cells for their specific research needs (*e.g.*, cells that are air-tight, UV light transparent, or composed of a specific material). However, when teaching experimental electrochemistry, most of these complicated cell designs are not needed.

Whether the electrochemical experiment is used for research or education purposes, electrochemical experiments require a greater level of care than the average titrimetric, gravimetric, or spectroscopic assay. For example, the glassware must be very clean, solvents have to be pure, students need to accurately measure smaller concentrations, and the electrode must be properly polished. Nevertheless, there is no reason why undergraduate students cannot successfully use a variety of electrochemical techniques in their laboratory work. Fortunately, to minimize this overhead, Pine Research has developed the teaching laboratories around the Compact Voltammetry Cell, which reduces (and in some cases eliminates) the traditional preparation steps and precautions that have plagued the successful outcome of electrochemical experiments.

A detailed description of the traditional components of an electrochemical cell is provided below. The Compact Voltammetry Cell kit will be described as well.

6.3.1 Glassware

In its simplest form, the electrochemical cell is a single piece of glassware capable of holding an appropriate volume of test solution. The electrochemical contains electrode ports so that the electrodes can be immersed in the test solution. Often, there are three electrodes immersed in solution: the working, reference, and counter/auxiliary. The electrodes are electrically connected to a potentiostat via the cell cable. When choosing glassware for an instructional laboratory, it is important to consider the test solution volume, ease of cell assembly, and, in the event of an accident, cost to replace the cell.

The three-neck round-bottom flask is a readily available and inexpensive piece of glassware that can be used as an electrochemical cell. These flasks can hold a considerable solution volume, and their neck opening diameters are large enough to fit most electrodes.

Oxygen interferes with some electrochemical measurements because it is redox active and easily reduced. For example, if a researcher is trying to quantify cathodic current of an analyte, a minute amount of oxygen could skew the cathodic current measurement. In addition, reduced oxygen has the ability to participate in radical reactions and halt catalysis in certain systems. Therefore, airtight cells with one or two gas inlets and an outlet are often used to study analytes that are reduced at moderate to negative potentials. The gas inlets bubble an inert gas, such as nitrogen, through the solution to expel any dissolved oxygen. Over the course of the experiment, a steady stream of inert gas blankets the solution headspace under positive pressure. The steady stream of inert gas is low enough as to not disturb the solution or cause any ripples.

A four-neck cell can be configured for oxygen removal. Three cell necks are used to mount each of three electrodes in an airtight manner (simply sealing the openings with parafilm may be sufficient). The fourth opening is then sealed using a rubber septum. A small syringe needle is inserted through the septum near the outer edge of the septum. Then, a much longer needle, capable of being pushed through the septum and down into the test solution, is inserted through the center of the septum. Nitrogen gas is passed into the cell through the long needle. The small needle serves as the outlet. At first, the long needle is placed into solution, and nitrogen gas is allowed to bubble through the solution.

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When it is time to perform an experiment, the long needle is pulled out of the solution (but not all the way out of the cell), allowing a blanket of nitrogen gas to cover the solution.

A cell is available from Pine Research that is well-suited for use in common electrochemical experiments. The cell has five, $14/20$ ground glass joint openings has an upper volume limit of $125\,mL$. The five openings are designed to mount the working, reference, and counter electrodes and other gas purging and vent accessories.

6.3.2 Compact Voltammetry Cell Kit

The Compact Voltammetry Cell (CVC) Kit is the ideal electrochemical cell to introduce experimental electrochemistry to students. The CVC Kit consists of a cell cap, cell grip, $20\,mL$ scintillation vials (the cell), screen-printed electrode sample kit, and cell cable (see: Figure 6-8).

Figure 6-8. Compact Voltammetry Cell Kit

The following description of the CVC refers to the components shown below (see: Figure 6-9).

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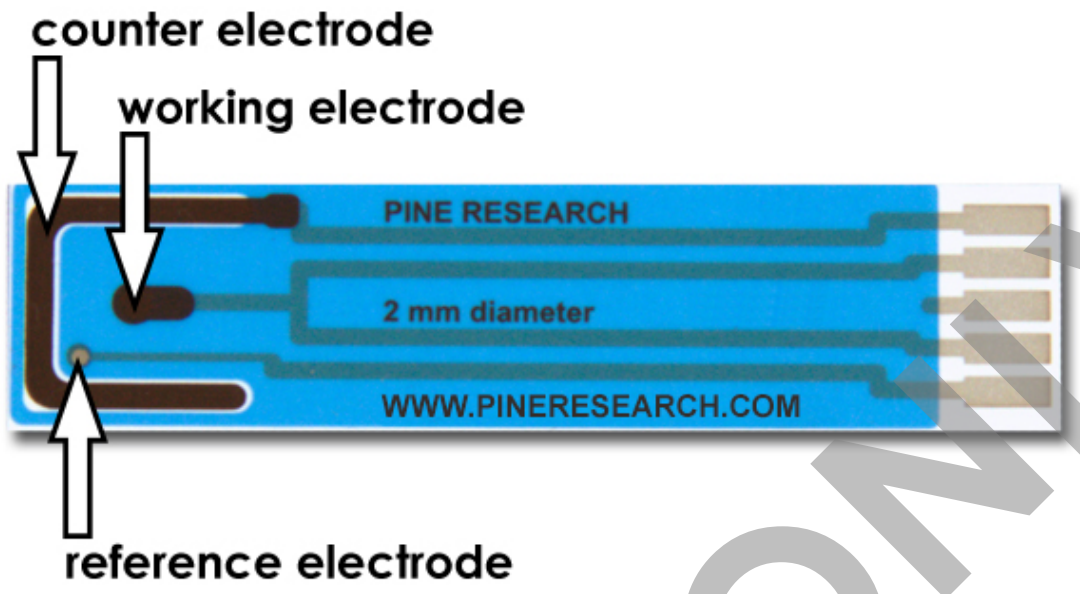

Figure 6-11. Carbon SPE with Working, Counter, and Reference Electrodes

While SPCEs are very advantageous for simple experiments, they do have their drawbacks. Unlike traditional working electrodes, it is difficult to properly clean an SPCE because SPCEs cannot be polished without risk of damage. Since the electrode is not properly polished, the surface of the screen-printed electrode is more heterogeneous than a traditional electrode. In addition, the SPCE material is not pure, but rather it contains a binding agent necessary for printing to occur. In experiments where the purity of the electrode material is critical, a screen-printed electrode cannot be applied. Finally, SPCEs are only approved for aqueous work due to a reaction between the binding agents and organic solvents.

For non-aqueous work, Pine Research manufactures ceramic screen-printed electrodes (SPEs) that are slightly thicker than SPCEs ($15 \times 61 \times 0.67\ mm$). Ceramic SPEs are more expensive than SPCEs because the working electrode material is composed of platinum or gold; there are, however, techniques to clean their surfaces so that they can be reused. Like SPCEs, ceramic SPEs have heterogeneous surfaces in comparison to traditional electrodes because they cannot be polished. Teaching laboratories should utilize SPCEs whenever possible and only use ceramic SPEs for non-aqueous or high temperature work.

INFO:

More information about screen-printed electrodes can be found on our knowledgebase:

https://www.pineresearch.com/shop/knowledgebase/

Search "Document Index" and find related article DRP10036.

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Appendix A: References, Journals, and Texts

As mentioned in the beginning of this guide, this guide is not a substitute for a text book and we encourage the user to also use a text book in developing the curriculum for the class. The following are suggested reading, some of which may serve as an advanced textbook.1–4 Additionally, references are provided in each of the laboratory exercises.

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(2) Skoog, D. A.; Leary, J. J. *Principles of Instrumental Analysis*; 4th ed.; Saunders College Publishing: Philadelphia, 1992.

(3) Kissinger, P.; Heineman, W. R. *Laboratory Techniques in Electroanalytical Chemistry*; 2nd ed.; Marcel Dekker, Inc: New York, 1996.

(4) Wang, J. *Analytical Electrochemistry*; Wiley-VCH, 2006.

(5) American Chemical Society; Committee on Chemical Safety. *Safety in Academic Chemistry Laboratories*; 7th ed.; American Chemical Society: State College, PA, 2003; Vol. 2.

(6) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L.; Sawyer, D. T. *Electrochemistry for Chemists*; Wiley, 1995.

(7) Bagotskiĭ, V. S. *Fundamentals of Electrochemistry*; Wiley-Interscience, 2006.

(8) Gileadi, E. *Physical Electrochemistry: Fundamentals, Techniques and Applications*; Wiley-VCH, 2011.

(9) Oldham, K. B.; Myland, J. C.; Bond, A. M. *Electrochemical Science and Technology: Fundamentals and Applications*; John Wiley & Sons, 2011.

(10) Zoski, C. G. *Handbook of Electrochemistry*; Elsevier, 2007.

(11) Langhus, D. L. *Fundamentals of Electroanalytical Chemistry*; 2002; Vol. 79.

(12) Holze, R. Understanding Voltammetry: Simulation of Electrode Processes. *J. Solid State Electrochem.* **2016**, *20*, 305–306.

(13) Kissinger, P. T.; Heineman, W. R. Cyclic Voltammetry. *J. Chem. Educ.* **1983**, *60*, 9242–9245.

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Appendix B: Laboratory Exercises Instrumentation and Equipment List

Pine Research has developed a unique product that combines all instrumentation, laboratory exercises, and resources in one kit. This kit is called *EChem in a Box*. *EChem in a Box* includes the instrumentation required for each laboratory exercise provided in this guide. If you have not yet purchased *EChem in a Box*, the following list represents all instrumentation and equipment needed to perform all laboratory exercises included in this guide.

Required Components

	Required Components (included in EChem in a Box)	
Pine Research Part #	**Description**	**Quantity**
AFTP1	WaveNow Potentiostat	1
—RRPA5V21	—Power Adapter, 5 V	
—EWCP6USB	—USB Cable	
—AB01DUM1-LF	—WaveNow Dummy Cell	
—EWM18B7	—Power Cord (US)	
—AKCABLE5	—WaveNow Cell Cable	
—ASTPA01	AfterMath Software (WaveNow)	
RRTPE04	WaveNow to Mini-USB Cell Cable for CVC Kit	1
RRTPE05	WaveNow to Mini-USB Cell cable with Reference Breakout	1
AKSPEKIT	Compact Voltammetry Cell Kit	1
—RRPG020	—20 mL glass vial	
—ACSPEPE	—Screen-Printed Electrode Sample Pack	
—AKSPEGRP1	—Grip Mount	
—AC01SPECAP2	—Glass Vial Cell Cap	
—RRPECBL2	—Mini-USB to Banana Post Cell Cable	
—KAA2117	—Cell Cap O-ring for Large Cell	
AKSPEJAR	Compact Voltammetry Large Volume Cell	1
RRPEAGCL	LowProfile Ag/AgCl Reference Electrode	1
AKPURGE1	Purge Kit for 1/4" Hose Barb	1
AKPURGE2	Purge Kit Conversion from 1/4" to 1/16" Tubing	1
RRSTIRBAR	Magnetic Micro Stir Bar	1
RRPE1001C-50	Screen-Printed Electrodes, Carbon, 2 mm OD, 50-pack	1
RRPE1002C-50	Screen-Printed Electrodes, Carbon, 5 × 4 mm, 50-pack	1
DRU10099	Experimental Electrochemistry: An Introduction for Educators (Book)	1
RCUSB512MB-PR	*EChem in a Box* Flash Drive with digital content (Word® Documents, videos, etc.)	1

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Electrochemical-Enzymatic Determination of Glucose in Beverages

A laboratory for quantitative determination by selective electrochemistry

This laboratory seeks to quantitatively determine glucose concentration in common beverages. The method employed is enzyme catalyzed oxidation of glucose, quantified by chronoamperometry. With an inexpensive patterned electrode and low cost glucose oxidase enzyme, an electrochemical sensor is constructed to selectively measure glucose in complicated beverages which can present as analytically challenging matrices. This lab briefly discusses conceptual information about sugars used to sweeten common beverages, enzyme-substrate interactions, glucose mutarotation, enzyme kinetics, and electroanalysis.

1. Introduction

Bioanalytical chemistry, a sub-discipline of analytical chemistry, uses quantitative and qualitative methods of analysis to evaluate biological based chemical species. These biological species are commonly found in complicated matrices such as blood and may include proteins, drug metabolites, and sugars.

In a complicated matrix such as blood, it is difficult to quantitatively determine the presence and concentration of target analytes. Therefore, the matrix is often simplified by chemical separations (e.g. HPLC, GC, electrophoresis), prior to quantitative determination.

Another manner to quantify an analyte among several interferents is by increasing selectivity. Many enzymes and substrates function as a lock and key gateway. The enzyme catalyzes a reaction only when a very specific substrate binds to its active site.

Figure 1-1. Example of U.S. Nutrition facts on Edible Consumer Goods

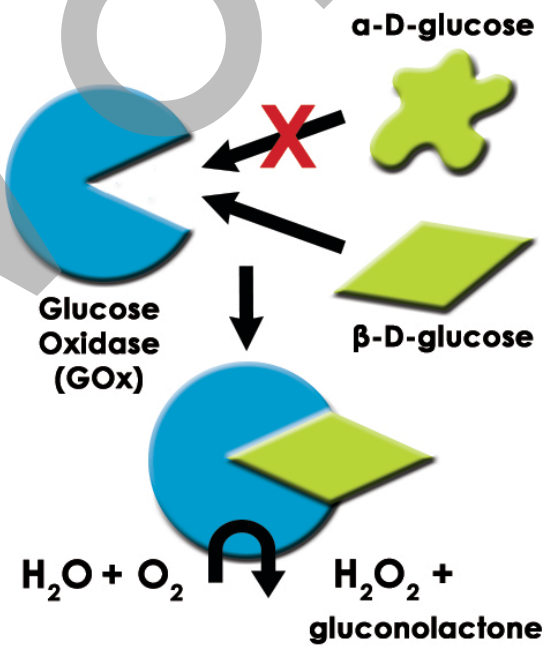

Figure 1-2. Diagram of Glucose Oxidase Enzyme with Substrate β-D-glucose and Product H_2O_2

Such is the case for glucose oxidase and its substrate, β-D-glucose. Therefore despite a complicated matrix of chemical species, an assay based on glucose oxidase will only have an analytical signal from β-D-glucose (see: Figure 1-2).

Electrochemical methods are highly sensitive. Use of electrochemistry with enzymes as described above adds selectivity. Therefore, in complicated matrices (such as common soft drinks, which could contain caffeine, sugars, preservatives, water, colorings, acids, and other chemicals), electrochemical determination

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Electrochemical-Enzymatic Determination of Glucose in Beverages Laboratory Exercise additional pages intentionally left blank.

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Electrochemical Analysis of Acetaminophen in Pain Relief Medication

An inexpensive experiment using disposable screen-printed carbon electrodes.

This experiment demonstrates the use of modern electroanalytical chemistry to determine the active ingredient in a popular children's pain relief medication. Designed for use in an instructional laboratory setting, this procedure describes the use of cyclic voltammetry to verify the concentration of acetaminophen (4-acetamidophenol) indicated on the suspension label. Advantages of the approach used here include the use of inexpensive and disposable screen-printed carbon electrodes and the use of an inexpensive consumer-grade supporting electrolyte solution that is widely available on the mass market. The only reagent grade chemical required for this procedure is a small amount of pure 4-acetamidophenol.

1. Introduction

Acetaminophen is an active ingredient in several over-the-counter pain relief medications, including the well-known brand, Tylenol®. Acetaminophen has largely replaced aspirin (acetylsalicylic acid) as the medication of choice for children and infants because aspirin has, in some cases, been linked to the development of Reye's Syndrome.

For easier delivery to young children, acetaminophen is often formulated as an oral suspension, which is a viscous aqueous suspension containing various colorings and flavorings (see: Figure 1). A typical sample of the suspension has an acetaminophen concentration in the range from 30 to 100 g/L. In this lab experiment, an electrochemical method known as cyclic voltammetry (CV) is used to determine the acetaminophen concentration in a sample of the medication, and the result is compared with the stated value provided by the manufacturer on the medication package.

2. Background

Acetaminophen, with a formal chemical name of 4-acetamidophenol, is an electroactive molecule which can be oxidized. Acetaminophen ***(A)*** can be oxidized to the quinone form ***(B)***, called N-acetyl-4-quinoneimine (abbreviated as NAPQI) in a two-electron, two-proton electron transfer process where, in the presence of an acid catalyst, NAPQI ***(B)*** is rapidly converted to a hydrate ***(C)*** called N-acetyl-4-quinoneimine hydrate (see: Figure 2). The two-electron oxidation of acetaminophen ***(A)*** is observed as an anodic (oxidizing) current when the electrode potential is swept in the positive direction.

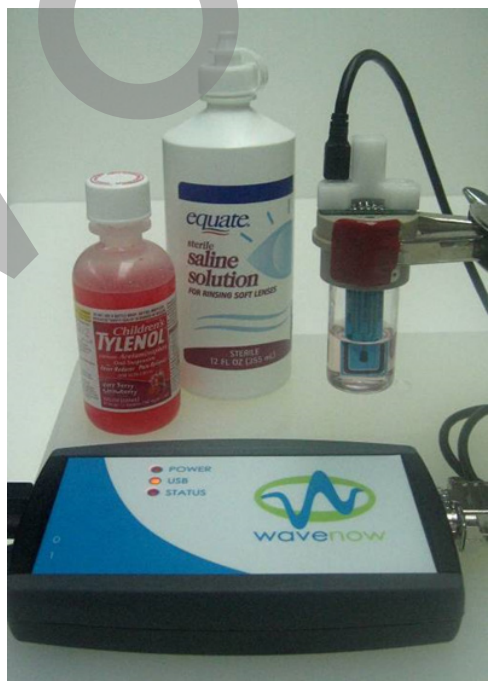

Figure 1. Experimental Apparatus and Chemicals

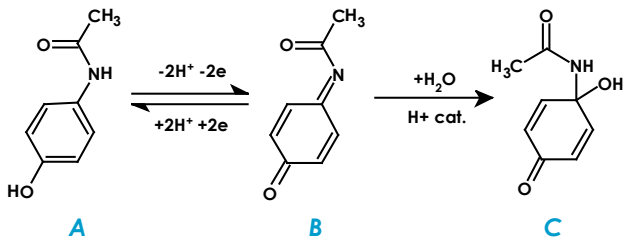

Figure 2. Electrochemical Reaction of Acetaminophen

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Highly Sensitive Electrochemical Determination of Lead in Tap Water

Anodic Stripping Voltammetry with Disposable Screen Printed Carbon Electrodes

This experiment demonstrates the use of anodic stripping voltammetry to determine lead (Pb) in tap water. Inexpensive and disposable screen-printed carbon electrodes are first coated with mercury micro-droplets (microns in diameter) by reduction of mercury acetate (Hg^{2+}) at a constant electrode potential. Then, lead ions (Pb^{2+}) in a sample are reduced and collected into the mercury droplets. This pre-concentration step allows determination of very low concentrations (ppb) of lead when anodic differential pulse voltammetry (DPV) is used as the method of detection and standard addition as the method of calibration.

1. Introduction

According to the United States Environmental Protection Agency (EPA), lead, a common element associated with many health concerns, is a significant pollutant in the environment.[1] Trace levels (ppm) of lead can have serious health effects in many animals and in humans; therefore, a highly sensitive detection method is important for environmental monitoring and clinical testing. In this lab, lead in public drinking water drinking will be determined using an electrochemical technique called anodic stripping voltammetry (ASV).

ASV is well suited for determining trace lead in liquids. The advantages of ASV include sensitivity (ppb), speed (tens of minutes), and low cost of measurement equipment, i.e., the potentiostat. In addition, the portability of some potentiostats makes it possible to do field work in remote places where access to standard AC power is prohibited.

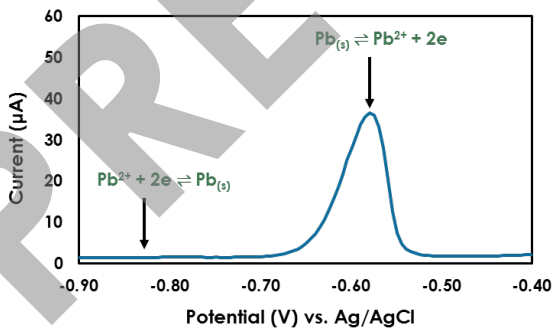

Figure 1-1. Anodic Stripping Voltammogram (ASV) of lead

2. Background

Several operational steps are involved in typical ASV analysis (see: Figure 1). These steps include pretreatment, preconcentration, and oxidative stripping. Use of small and easy to operate instrumentation is well suited to the teaching lab, however this type of analysis could be performed directly in the environment.

First, a water sample is pre-treated to convert any solid lead into its ionic form (Pb^{2+}). Chelating ligands, such as acetate, are often added to facilitate extraction, dissolution, and stabilization of lead. Other salts may also be added as ions of supporting electrolyte, or as buffer components for pH control.

Second, Pb^{2+} is converted to Pb and deposited at a mercury (Hg) electrode under a reduction potential as shown in Equation 1.

$$Pb^{2+} + 2e \rightleftharpoons Pb_{(s)} \quad \textbf{(1)}$$

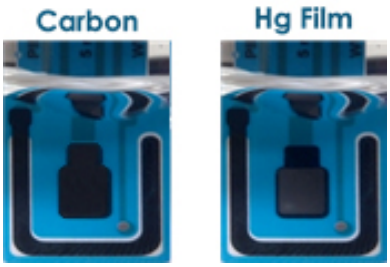

Figure 2-1. Bare Carbon Screen Printed Electrode and Mercury Plated Screen Printed Electrode

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Highly Sensitive Electrochemical Determination of Lead in Tap Water Laboratory Exercise additional pages intentionally left blank.

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Exploring Faraday's Law Using Inexpensive Screen-Printed Electrodes

A simple electroplating experiment for the general chemistry laboratory

This note describes an experimental procedure for the general chemistry laboratory student that conveniently illustrates the electroplating process. Students plate a thin film of nickel on to a screen-printed carbon electrode. The plating process is accurately controlled using a traditional three-electrode electrochemical cell arrangement. Each screen-printed electrode pattern includes all three required electrodes (working, reference, and counter). Nickel is plated on to the working electrode from a conventional Watts nickel plating solution. The light weight electrode pattern is weighed before and after deposition of the metal. By weighing the patterned electrode before and after deposition, the student obtains the mass of nickel actually deposited on to the working electrode. This mass result used with Faraday's Law allows the student to compute the efficiency of the electrodeposition process.

1. Introduction

Electroplating is an important branch of electrochemistry with many applications in modern technology. For example, the automobile industry relies upon nickel and chromium electroplating to protect steel from corrosion. Noble metal electroplating of the coinage metals (see: Figure 1) is used for decorative purposes such as fabricating jewelry. Electroplating is also an essential tool for manufacturing state-of-the-art electronic devices. Electrodeposited copper metal interconnects within integrated circuits play an important role in the devices used to build the information superhighway. In this lab experiment, basic principles of electroplating are explored by plating thin films of nickel on to screen-printed carbon electrodes.

This laboratory experiment makes use of inexpensive screen-printed electrodes (SPE) as a convenient (and disposable) alternative to larger-sized bulk metal electrodes. Each electrode consists of a carbon working electrode (WE), a carbon counter electrode (CE), and a silver/silver chloride reference electrode (REF). The student voltammetry cell (see: Figure 2) is ideal for vertically mounting the SPE, thereby making observation of the plating process easy to visualize.

For accurate control of the electrode potential used for electroplating, it is recommended that the working, counter, and reference electrodes be connected to a modern three-electrode potentiostat (such as the WaveNow from Pine Research Instrumentation). Such potentiostats are capable of applying and maintaining a constant potential between the working and reference electrodes while at the same time accurately measuring the flow of charge (current) through the working electrode.

2. Background

As the potential of working electrode moves toward more negative values, electrons at the working electrode surface become more readily available to reduce ions in the solution. Nickel(II) cations in solution are reduced to nickel metal.

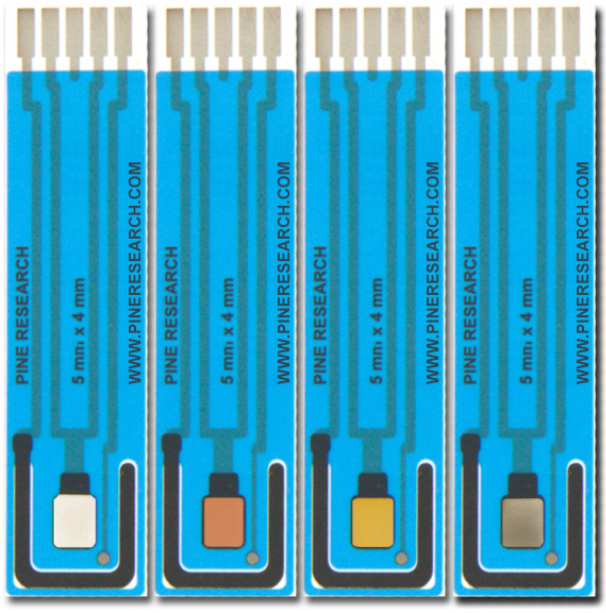

Figure 2-1. Screen-Printed Carbon Electrodes with Nickel, Copper, Gold, and Silver (left to right)

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Appendix E: Instructor's Resources for Laboratory Exercises

Pine Research has developed a unique product, which combines all instrumentation, laboratory exercises, and resources in one kit. This kit is called "Echem in a Box." The instructor's resources contain additional information, written for the instructor, to ensure a laboratory success.

STOP:

To ensure these laboratory exercises remain as free as possible from becoming "internet answer keys," please do not distribute the Instructor's Resources content in any manner.

For each of the laboratory exercises included in this guide, we have prepared what we hope is a thoughtful guide for the instructor. The general flow of these guides are to point out useful information to the course instructor. As we developed the laboratory exercises, we were mindful of aspects of the laboratory exercise that may be more difficult for the student. We also wanted to let the instructor know about a few important things such as chemical purity requirements, ways to expand the exercise, how to perform the data analysis, and ultimately, suggested answers to questions.

Each of the labs were developed from the literature, namely the *Journal of Chemical Education*. Perhaps you and your eager research students have a great idea for a laboratory exercise that should be included in this guide. We hope so! We encourage you to publish in a journal such as *J. Chem. Ed.* and alert us to its publication. We always enjoy reading ways our products have been used, and we are happy to bring attention to your publication by releasing a laboratory exercise based on it.

We are also open to feedback at Pine Research. If, in the course of teaching any of the laboratory exercises in this guide, you find additional time/cost/energy saving measures, please do not hesitate to contact us so we can add your feedback into future revisions of the instructor's resources.

TIP:

Have a tip for us? We love feedback. Please contact us at any time at pinewire@pineresearch.com.

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Electrochemical-Enzymatic Determination of Glucose in Beverages

Instructor's Resources

1. Discussion

This experiment is a good introduction to chronoamperometry as it easily relates increasing β-D-glucose concentration (and therefore increasing hydrogen peroxide concentration) to an increase in current. The enzyme-glucose reaction is time sensitive and requires that the students perform the current measurement by chronoamperometry precisely 5 $minutes$ after enzyme addition.

The major challenge of this experiment is to allot enough time for students. They need time to prepare at least four stock solutions, five calibration standards, and any beverages they wish to analyze. They will need time to rinse the electrode and change solutions. In addition, each enzyme-glucose reaction needs to sit for 5 $minutes$ before the current measurement can be performed. The instructor can prepare some stock solutions before class if desired.

INFO:

Do not let students premix the reactions as the experiment is time-sensitive.

The instructor must prepare the 100 mM Glucose Stock Solution 12 $hours$ prior to the start of the experiment. Doing so allows mutarotation of the α- and β- optical isomers of glucose to reach equilibrium. To make calculations easier for students, it may be desirable to take into account that at equilibrium in water, D-(+)-glucose will be 64% β-D-glucose and 36% α-D-glucose. Since α-D-glucose does not react with the glucose-oxidase enzyme, use enough D-(+)-glucose to make 100 mM **β-D-Glucose** stock solution (*i.e.*, for a 1 L sample, weigh 28.15 g (0.15625 mol) D-(+)-glucose to make a solution that is 156.25 mM D-(+)-glucose. Mutarotation will cause 64% of this solution to be β-D-glucose at equilibrium, and so final β-D-glucose concentration equals 156.25 $mM \times 0.64 = 100\ mM$).

TIP:

Prepare 100 mM β-D-Glucose Stock Solution 12 $hours$ in advance to allow the $\alpha -$ and β- optical isomers of glucose to reach equilibrium and to simplify calculations.

The experimental data used to prepare the figures for this document have been analyzed for your reference. All of this data was obtained using a platinum screen-printed electrode (diameter 2.0 mm, area 0.1257 cm^2) to study β-D-glucose solutions of varying concentration (0, 5, 10, 15, 20, 40, and 50 mM), constant initial glucose oxidase concentration (15 $U/\mu L$), and constant acetate buffer concentration of approximately 100 mM. Note that these substrate and enzyme concentrations and some of the time points used to obtain current from the chronoamperograms may differ from that which was called for in the Laboratory Exercise.

PREVIEW ONLY

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