

UNIVERSITY OF SOUTH CAROLINA

ECHE 460 CHEMICAL ENGINEERING LABORATORY

Electrochemical Methods: Voltammetry

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Introduction

Electrochemical reactors can be used to concentrate, recover, or destroy soluble aqueous ions. From another viewpoint, a battery is an electrochemical reactor. An example is a redox battery, which is an attractive class of electrochemical storage devices for utility load-leveling applications. In these batteries, both the reactants and products are completely soluble in the electrolyte and are stored in tanks outside the cell. For example, the Fe^{+3} in the cyanide complex $\text{Fe}(\text{CN})_6^{-3}$ can be reduced to Fe^{+2} at the cathode and Cr^{+2} can be oxidized to Cr^{+3} at the anode. The active species are dissolved in an aqueous electrolyte and the fluids are pumped past their respective electrodes. The anode and cathode are separated by an ionic separator which prevents the active species from mixing but allows ions to flow freely thus completing the electrical circuit. Figure 0.1 below is a simple schematic of a redox battery.

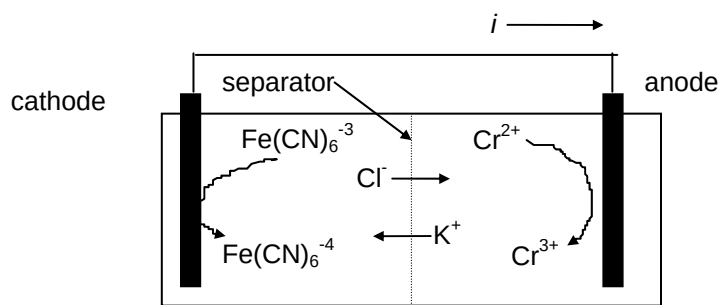


Figure 0.1: A redox battery utilizing the reduction of iron cyanide complex.

Regardless of whether we meet our future energy needs by harnessing the energy derived from nuclear fuels, fossil fuels, hydroelectric, geothermal, sunlight, wind, waves, or ocean thermal gradients, the storage of energy is an inherent requirement of modern technology. Storage systems not only conserve energy, but they also provide flexibility at lower cost by matching the production of energy with consumer's needs. The typical load demand of the utilities, for example, varies so much during the day, over the weekend, and seasonally, that the capacity of the electric power system is much larger than the average capacity used. As a result, rarely utilized equipment must be kept available. Large-scale energy storage in batteries allows energy to be produced at a constant rate to meet the average capacity. When demand for electricity is less than average the batteries are charged and when the demand exceeds the average the batteries are discharged.

Desirable attributes for batteries, like other power generation equipment, are related to cost, performance, durability, safety, and environmental considerations. Energy and power densities are examples of important performance criteria for battery applications. Energy density is equal to the voltage difference between the anode and cathode (i.e., cell voltage) divided by the mass of the battery per electron available for transfer to the external circuit. Redox batteries are sought for their favorable cost and durability, which are important attributes for load-leveling applications.

The rate of mass transfer of an electrochemically-active species to an electrode surface is critical to the proper design and operation of an electrochemical reactor. Power is the rate at which energy is delivered, and therefore the power density of the battery is greatly influenced by the kinetics of the reaction and the rate of mass transfer of the active species to the electrode surface. In order to quantify the mass transfer and properly design a battery the diffusion coefficient of the active species must be known. In addition, batteries can generate a significant amount of heat, especially at high rates of discharge, which requires diffusion coefficients to be correlated with temperature.

Of the three main divisions of analytical chemistry—spectroscopy, chromatography, and electrochemistry—the latter generally receives the least attention in an undergraduate Chemical Engineering laboratory course. In many cases, undergraduate students complete their degree without ever having a “hands-on” experience with a modern electroanalytical instrument. This experimental module is an effort to correct this situation by making it as easy as possible for the laboratory instructor to include modern electrochemistry techniques in the Unit Operations Laboratory.

Although its roots can be traced all the way back to Michael Faraday, modern electrochemistry is being applied to a number of current chemical problems. Incredibly small microelectrodes are being used to probe biochemical events on the cellular level. Industrial corrosion processes are being monitored using rotating disk electrodes. Voltammetric methods with amazingly low detection limits are being used to monitor lead levels in the bloodstream. Electrodes coated with special polymers are finding use as glucose detectors for diabetics. The use of electrochemical detection is also expanding the range of analyses that can be performed using liquid chromatography.

The purposes of these experiments are to compare and contrast three different voltammetric methods. The methods studied are *cyclic voltammetry*, *rotated disk voltammetry*, and *chronoamperometry*. Each of these different methods are used to examine the very same analyte solution to determine the diffusion coefficient of the analyte. The teaching assistant or laboratory instructor will direct each group of students as to which of these voltammetric method(s) they will be required to perform.

NOTE: Before starting the PineChem software ensure the potentiostat is turned on and the CONTROL SOURCE is in the EXTERNAL mode by pressing and holding down the button for approximately one second.

1. Cyclic Voltammetry

Objective

The goal of this experiment is to become familiar with using a modern electrochemical potentiostat, when given the concentration of ferricyanate in solution, to measure the diffusion coefficient and measure the formal solution potential. This procedure illustrates how the current observed in a cyclic voltammetry experiment depends upon experimental parameters such as sweep rate and temperature.

Experimental Apparatus

Pine Instrument Company AFCBP1 Bipotentiostat
5-neck electrode cell
Platinum disk electrode
Platinum auxiliary electrode
SCE reference electrode
Constant Temperature Refrigerated Circulating Bath
Alumina polishing solution

Reagents and Chemicals

100 ml of electrolyte (0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KCl) to a 125 ml jacketed 5-neck cell.
100 ml of 1.0 M KCL to a 125 ml jacketed 5-neck cell.
HPLC Grade water

Discussion

Cyclic voltammetry is perhaps the most often used electroanalytical technique. A cyclic voltammogram (or CV) is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. 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. The magnitude of this current is proportional to the diffusion coefficient of the analyte in solution.

The equipment required to perform cyclic voltammetry consists of a conventional potentiostat connected to three electrodes (working, reference, and counter) immersed in a test solution. The potentiostat applies and maintains the potential between the working and reference electrode while at the same time measuring the current at the working electrode. (Charge flows between the working electrode and the counter electrode.) A recording device is used to record the resulting cyclic voltammogram as a graph of current versus potential.

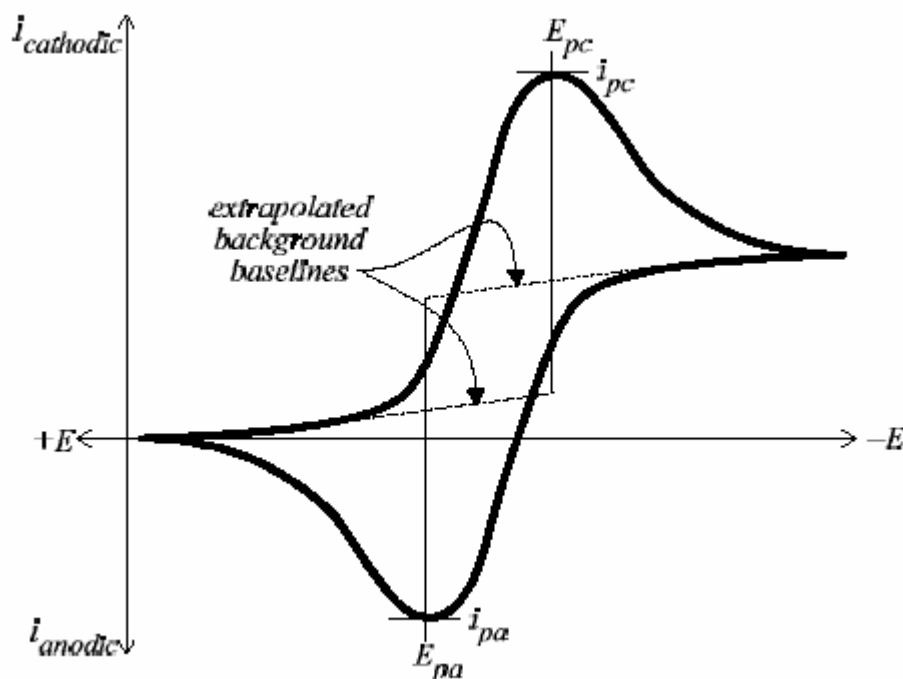


FIGURE 1.1: A Typical Cyclic Voltammogram.

Figure 1.1 depicts a generic cyclic voltammogram. The potential is graphed along the *x*-axis with more positive (or oxidizing) potentials plotted *to the left*, and more negative (or reducing) potentials *to the right*. The current is plotted on the *y*-axis of the voltammogram, with cathodic (*i.e.*, reducing) currents plotted *up* along the positive direction, and anodic (*i.e.*, oxidizing) currents plotted *down* in the negative direction. (A voltammogram is almost always plotted in this fashion by North American electrochemists, but in Europe, the axes are typically reversed.)

The peaks appearing in a voltammogram are similar to those found in a spectrum or chromatogram. Each peak corresponds to a particular electroactive analyte in the test solution, and the height of a peak is proportional to the concentration of that analyte. The peaks in a cyclic voltammogram are asymmetric, with the leading side being very steep and the trailing side falling off gradually. The peaks observed during the reverse sweep have the same general shape as those seen in the forward sweep, but they are inverted because the direction of current flow is reversed. The first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) direction or in the negative (cathodic) direction.

There is a great deal of quantitative information that can be gleaned from a good cyclic voltammogram. First, it can be a test to see if a redox couple is indeed reversible. The peak potential for the anodic sweep, E_{pa} , and the peak potential for the cathodic peak, E_{pc} , can be directly read from the voltammogram, and the difference between them, ΔE_{peak} , can be calculated. If the redox couple is reversible, then the relationship,

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

holds true, where n is the number of electrons involved in the redox couple (usually just one).

In addition, the cyclic voltammogram for a reversible redox couple has an anodic peak current, i_{pa} , that is equal to the cathodic peak current, i_{pc} , so that the relationship,

$$i_{pa} / i_{pc} = 1 \quad (1.2)$$

also holds true. It is important to note that the peak currents are not measured using the x -axis as a baseline. Rather, a background current baseline must first be extrapolated out to the peak potential (see Figure 1.1). Then, the peak current is measured (vertically) from the peak down to the extrapolated baseline.

The background current is always present, even in a test solution that contains no electroactive analyte. It is due to a *double layer* of ions in the solution immediately adjacent to the surface of the electrode. This double layer behaves like a capacitor, alternately being charged and discharged as the potential is swept back and forth. Thus, the background current is sometimes referred to as a *charging current*.

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

$$E^\circ = (E_{pa} + E_{pc}) / 2 \quad (1.3)$$

Formal potentials measured using cyclic voltammetry are usually accurate to within 50 mV of the true value. More accurate values can be obtained using other electrochemical techniques.

Quantitative information regarding analyte diffusion coefficient or concentration can be obtained from the voltammogram using the Randles-Sevcik equation (Eqn. 1.4). This equation specifies the peak current, i_p (either anodic or cathodic), in terms of the analyte concentration, C (mole/liter) or D diffusion coefficient (cm^2/sec).

$$i_p = 0.4463nFAC(nFvD/RT)^{1/2} \quad (1.4)$$

In this equation, n is the number of electrons appearing in half-reaction for the redox couple, v is the rate at which the potential is swept (V / sec), F is Faraday's constant (96485 Coulombs / mol), A is the electrode area (cm^2), R is the universal gas constant (8.314 J / mol K), and T is the absolute temperature (K). Note that if the temperature is assumed to be 25°C (298.15K), the Randles-Sevcik can be written in a more concise form,

$$i_p = (2.687 \times 10^5) n^{3/2} v^{1/2} D^{1/2} AC \quad (1.5)$$

where the constant is understood to have units (*i.e.*, $2.687 \times 10^5 \text{ mol}^{-1} \text{V}^{-1/2}$). Note that the peak current is directly proportional to the analyte concentration. Also note that if the analyte concentration is a known quantity, then cyclic voltammetry can be used to measure the analyte's diffusion coefficient. The diffusion coefficient is a measure of how fast the analyte moves through the solution as a result of random collisions with other molecules.

Procedure

All glassware used for electrochemistry should be as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. It is a good idea to use deionized, ultrafiltered (DIUF) water or “conductivity water” or “HPLC grade water” for the final rinsing of glassware and for all solution preparation.

Background Scan: A simple background cyclic voltammogram of the pure 1.0 M Potassium Chloride solution is a good way to confirm the purity of the solution, the cleanliness of the glassware, and the preparation of the polished working electrode all in a single step. Electrochemists frequently perform such a background scan before moving on to the main experiment just to make sure everything is okay. Any electroactive impurities from the solvent or dirty glassware will show up as unexplained peaks in the background scan. In addition, a fouled or improperly polished electrode surface usually causes a larger background current. Note, however, that even clean platinum electrodes will exhibit some peaks due to oxide deposition and stripping.

The electrical double layer is an array of charged species and oriented dipoles existing at the metal-solution interface. At a given potential the electrode-solution interface is characterized by a double-layer capacitance, C_d , typically in the range of 10 to 40 $\mu\text{F}/\text{cm}^2$. for a cyclic linear potential sweep given by

$$C_d = C / V \quad (1.6)$$

where C is the charge in Coulombs, C_d is the capacitance in Farads, and V is the potential sweep rate in Volts/second, knowing the typical range of capacitance you can calculate the maximum current required to charge the double layer capacitance. By comparing this to the experimental results, you may be able to explain any or the irregularities that were explained above

Analog Sweep Experiment Setup Panel

File Instrument Experiment

Experiment Type
Collection (sweep E1 only)

General Sweep Controls
Sweep Rate: 100 mV/s
Total Sweeps: 2
Initial Direction: ☐ UP ☒ DOWN

K1 Sweep Potentials
☐ Unique Initial: 0 mV
Limits: 0 to 900 mV
☐ Unique Final: 0 mV

K2 Potential
Hold at: 0 mV

Delay Periods
Initial: 1 sec
Final: 1 sec

Data Acquisition Period
☒ Expt Length: 18 sec
☐ Number of Points: 360
☒ Point Interval: 5 mV
Sampling Rate: 20,000 Hz
Memory Required: 28,800 kB

Electrode Sensitivities
K1 Current (max): 50 μ A
☒ K1 post-experiment range check
K2 Current (max): 100 nA
☐ K2 post-experiment range check

Post Experiment Idle Conditions
K1 Potential: 0 mV
K2 Potential: 0 mV
☒ Dummy Normal ☐ Open Connected

Other Options
☐ Perform Using Dummy Cell
☐ Use 10 V Potential Input Range
☐ Ignore Y2 Electrode

Load... Save... Default Cancel Perform

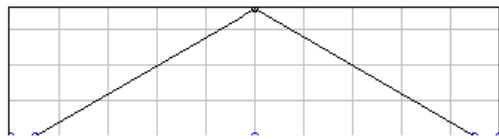


Figure 1.2 Experiment setup for background scan.

Analog Sweep Experiment Setup Panel

File Instrument Experiment

Experiment Type
Collection (sweep E1 only)

General Sweep Controls
Sweep Rate: 100 mV/s
Total Sweeps: 3
Initial Direction: ☐ UP ☒ DOWN

K1 Sweep Potentials
☒ Unique Initial: 0 mV
Limits: -500 to 1200 mV
☒ Unique Final: 0 mV

K2 Potential
Hold at: 0 mV

Delay Periods
Initial: 1 sec
Final: 1 sec

Data Acquisition Period
☒ Expt Length: 34 sec
☐ Number of Points: 680
☒ Point Interval: 5 mV
Sampling Rate: 20,000 Hz
Memory Required: 54,400 kB

Electrode Sensitivities
K1 Current (max): 5 mA
☒ K1 post-experiment range check
K2 Current (max): 100 nA
☐ K2 post-experiment range check

Post Experiment Idle Conditions
K1 Potential: 0 mV
K2 Potential: 0 mV
☒ Dummy Normal ☐ Open Connected

Other Options
☐ Perform Using Dummy Cell
☐ Use 10 V Potential Input Range
☐ Ignore Y2 Electrode

Load... Save... Default Cancel Perform

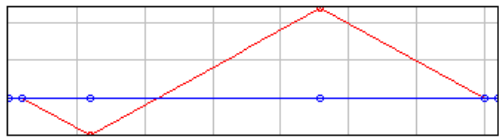


Figure 1.3 Setup for an expanded background scan.

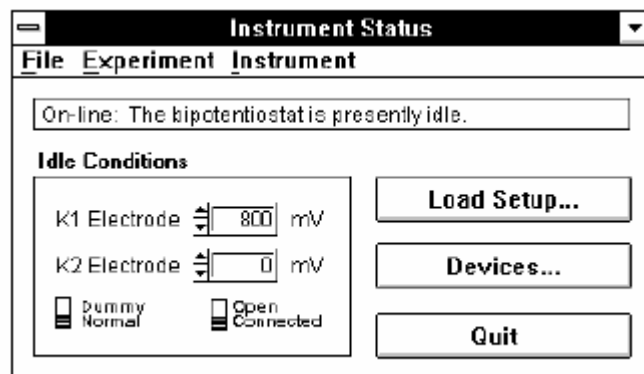


Figure 1.3. Initial Instrument Status Panel Settings

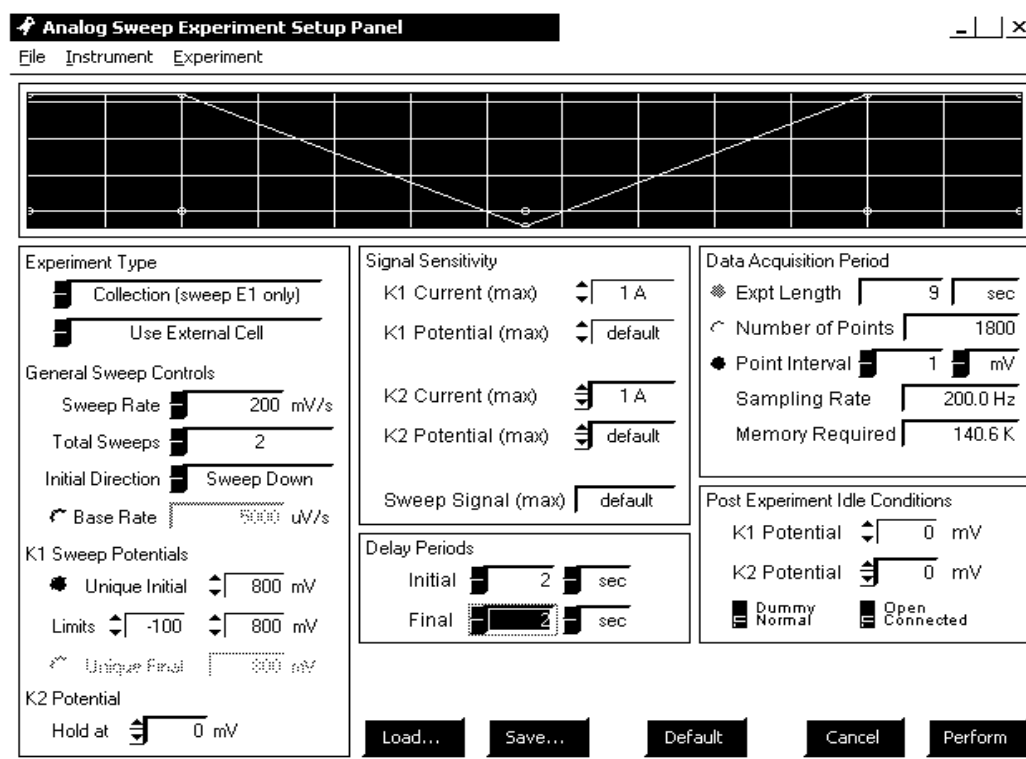


Figure 1.4. Experimental Setup for Cyclic Voltammetry

To accomplish a cyclic voltammogram perform the following steps.

1. Use the INSTRUMENT STATUS panel (Fig. 1.2) of the **PineChem** software package to place the AFCBP1 Bipotentiostat in DUMMY mode. Assemble the electrochemical cell and fill it with the potassium ferricyanide solution (or the

- supporting electrolyte alone for a background scan). Ensure the potentiostat is in the “Dummy” mode as observed on the instrument’s front panel. Mount the three electrodes in the cell. Connect the platinum working electrode to the K1 input. Connect the platinum counter electrode to the CE input. Connect the SCE reference to the REF input. Bubble nitrogen through the ferricyanide solution for about 10 minutes to displace dissolved oxygen from the solution. You may perform steps 2 through 6 while bubbling.
2. From the INSTRUMENT STATUS panel of the **PineChem** software package, adjust the IDLE CONDITIONS as shown in Figure 1.2. From the instrument’s front panel confirm that the AFCBP1 Bipotentiostat is now in NORMAL mode, and that the K1 electrode is idling near +800 millivolts. Use the Rotator as necessary to remove any gas bubbles on the electrode surface.
 3. Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 1.3. Note that these settings are for a cyclic voltammetry experiment in which the potential is swept from +800 mV down to –100 mV and back using a sweep rate of 200 mV/sec. Note also that the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.
 4. Click on the PERFORM button to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +800 mV to –100 mV. On the return sweep, an anodic wave of equal size should be apparent.
 5. After acquiring a satisfactory voltammogram, save it on the disk ensuring to denote the sweep rate and temperature.
 6. Using sweep parameters similar to those in section A above, acquire voltammograms at the following sweep rates: 225, 170, 120, 80, and 50 mV/sec and at 3 different temperatures. Be sure to save each voltammogram to a separate file. Note that the ELECTRODE SENSITIVITY (current range) should be adjusted from time to time as progressively lower sweep rates are used.

Data Analysis and Report Items

- 1 Using the cathodic peak currents measured from the series of voltammograms acquired at different sweep rates, prepare a plot of peak current versus the square root of the sweep rate. (Make sure that each of the voltammograms was acquired using the same standard solution.)
- 2 Perform a linear least squares analysis on the data to find the equation of the best straight line that fits the data.
- 3 Use the slope of the line to calculate the diffusion coefficient for the ferricyanate cation in 1.0M potassium chloride.
- 4 Using the voltammogram obtained with the slowest sweep rate, determine the formal potential, E° , for the ferricyanate/ferrocyanide redox couple. Express the result in volts versus the standard hydrogen electrode (SHE), and compare it to an accepted value from a reference textbook.
- 5 Using the diffusion coefficient obtained from the RDE experiment (if performed), calculate the concentration of the solution you are using and compare with actual solution concentration.

- 6 Explain, in terms of what happens in the diffusion layer immediately adjacent to the electrode surface, why faster sweep rates give higher peak currents.

2. Rotating Disk Voltammetry

Objective

The primary objective of this experiment is to measure the diffusion coefficient of $\text{Fe}(\text{CN})_6^{-3}$ (ferricyanate) ions in an aqueous solution of KCl as a function of temperature using a rotating-disk electrode (RDE). Secondary objectives include determining the concentration profiles for ferricyanate in the diffusion layer, the diffusion-layer thickness as a function of rotation speed, and the surface concentration of ferricyanate as a function of potential. The purpose of these secondary objectives is to gain a general understanding of some of the principles governing electrochemical reactors.

Experimental Apparatus

Pine Instrument Company AFCBP1 Bipotentiostat
5-neck electrode cell
Platinum disk electrode
Platinum auxiliary electrode
SCE reference electrode
Constant Temperature Refrigerated Circulating Bath
Cannon-Fenske Viscometer
Alumina polishing solution

Reagents and Chemicals

100 ml of electrolyte (0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KCl) to a 125 ml jacketed 5-neck cell.
100 ml of 1.0 M KCL to a 125 ml jacketed 5-neck cell.
HPLC Grade water

Discussion

Electrochemical techniques are frequently used to measure the diffusion coefficients of electrochemically active species. The key to extracting accurate diffusion information from electrochemical data is to use a system for which the mass transfer is well described. One such technique is to measure the limiting current at a rotating-disk electrode (RDE). In this experiment, the potential difference between the disk and the reference electrode is changed until the current reaches a maximum or limiting value. Figure 2.1 shows a schematic of the current (i) versus the potential difference for the reduction of $\text{Fe}(\text{CN})_6^{-3}$ to $\text{Fe}(\text{CN})_6^{-4}$ at the electrode surface.

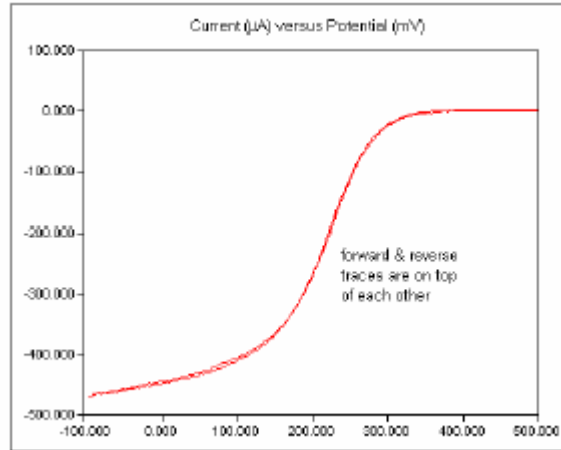


Figure 2.1: A schematic of the current versus the potential difference between the disk and the reference electrode for the reduction of Fe(CN)_6^{-3} to Fe(CN)_6^{-4} [3]. A limit in the current is reached at a large potential difference.

Increasing the potential difference will increase the rate at which Fe(CN)_6^{-3} is reduced at the electrode. The concentration of Fe(CN)_6^{-3} at the surface of the disk decreases as the potential difference increases, causing the observed current increase. The current is a direct measure of the rate of reduction of the ion. The relationship between the current i , the bulk concentration C^o , and the concentration at the surface of the electrode C_s in a well-stirred system is given by

$$i = (nFAD/\delta) (C^o - C_s) \quad (2.1)$$

where n is the number of electrons transferred per mole of the active species, F is Faraday's constant ($F = 96,485 \text{ C/mol}$), A is the area of the rotating disk, D is the diffusion coefficient of the reacting species, and δ is the diffusion-layer thickness.

Since the surface concentration cannot go below zero, there is a potential at which the concentration difference between the electrode surface and the bulk is a maximum. A maximum in the concentration difference means a maximum mass transfer rate and hence a maximum current (*i.e.*, limiting current). The advantage of using a rotating disk is that the diffusion-layer thickness can be predicted by solving the convective-diffusion equation to give the following relationship (see reference 3 for a detailed derivation).

$$\delta = \frac{1.61 D^{1/3} \nu^{1/6}}{\omega^{1/2}} \quad (2.2)$$

where ω is the rotation speed of the electrode and ν is the kinematic viscosity of the electrolyte solution. Equation 2.2 indicates that the diffusion-layer thickness decreases with increasing rotation speed which results in an increasing limiting current. Also, combining equations 2.1 and 2.2, and setting $C_s = 0$ indicates that a plot of the limiting current versus the square root of the rotation speed will result in a straight line. The slope of that line can be used to determine the diffusion coefficient of the active species once ν is known. The kinematic viscosity can be obtained from a capillary-tube kinematic viscometer.

The derivation in reference 2 also provides the following expression for the concentration profile (within the diffusion layer) of the reacting species at the limiting current i_L :

$$C(y) = \left(\frac{C^0}{0.8934} \right) \int_0^Y \exp(-u^3) du \quad (2.3)$$

where $u^3 = y^3/3B$, $dy = du (3B)^{1/3}$, $Y = y/(3B)^{1/3}$, and $B = (D\nu^{1/2})/(0.51\omega^{3/2})$. A plot of this profile in dimensionless coordinates is shown in Figure 2.2.

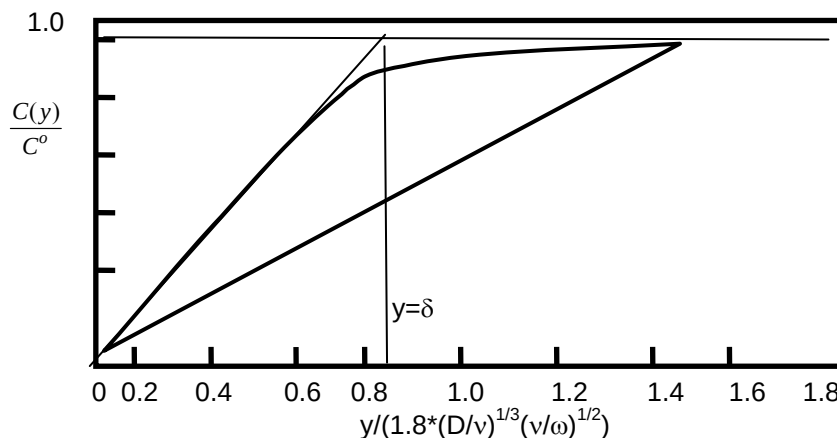


Figure 2.2: The normalized concentration profile in dimensionless coordinates near a rotating-disk electrode at the limiting current [3]. The surface of the electrode is at $y = 0$ and δ is the boundary-layer thickness.

At the limiting current the concentration is zero at the surface of the electrode ($y = 0$) and approaches the bulk value at 0.8934 dimensionless units away from the surface. The boundary-layer thickness for a RDE (*i.e.*, $y = \delta$) is the distance at which the tangent line at $y = 0$ intersects the bulk concentration (see reference 3 for details).

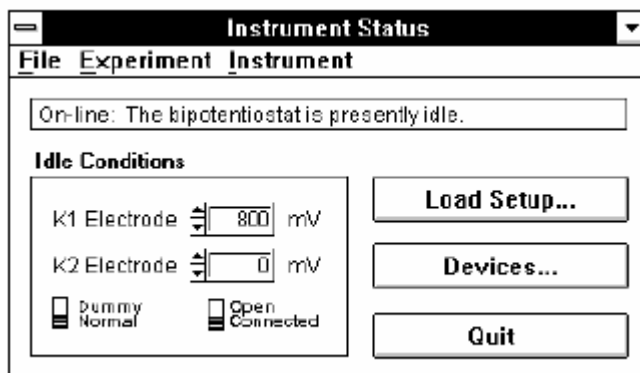


Figure 2.3. Initial Instrument Status Panel Settings

Procedure

1. Transfer approximately 100 ml of electrolyte (0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KCl) to a 125 ml jacketed cell and bring the electrolyte to the desired temperature.
2. Use the INSTRUMENT STATUS panel (Fig. 2.3) of the **PineChem** software package to place the AFCBP1 Bipotentiostat in DUMMY mode. Assemble the electrochemical cell and fill it with the potassium ferricyanide solution (or the supporting electrolyte alone for a background scan). Ensure the potentiostat is in the “Dummy” mode as observed on the instrument’s front panel. Mount the three electrodes in the cell. Connect the platinum working electrode to the K1 input. Connect the platinum counter electrode to the CE input. Connect the SCE reference to the REF input. Bubble nitrogen through the ferricyanide solution for about 10 minutes to displace dissolved oxygen from the solution. You may perform steps 2 through 6 while bubbling.
3. Turn on the electrode rotator and adjust the rotational speed of the electrode to 64 RPM. Make certain that the flow of solution in the cell is non-chaotic and that the surface of the rotating electrode remains immersed in the solution. No gas bubbles should exist on the electrode surface.
4. Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 2.4. Note that these settings are for a cyclic voltammetry experiment in which the potential is swept from +500 mV down to –100 mV and back using a sweep rate of 10 mV/sec. Note also that the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.
5. Once the experiment settings have been adjusted to match those in Figure 3.5, click on the PERFORM button to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +500 mV to –100 mV. The wave should have a sigmoidal appearance rather than the asymmetric peak shape observed during cyclic voltammetry. On the return sweep, the current signal should retrace the path followed during forward sweep. Figure 2.1 shows a typical rotated disk voltammogram for potassium ferricyanide. Note that as displayed by the software, positive potentials are plotted to the right and cathodic currents are plotted toward to the bottom of the graph.
6. After acquiring a satisfactory voltammogram, save it on the disk ensuring to note the rotational speed and temperature in the file path.
7. Plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. The voltammogram has an unusual appearance when plotted in this fashion.
8. Repeat steps 3 through 7 at rotation speeds of 144, 196, 256, 324, 400, 484, 576, 784, and 1000 rpm (why were these increments chosen?) and record the limiting current versus the rotation speed.
9. Measure the kinematic viscosity of the electrolyte using the capillary-tube kinematic viscometer.

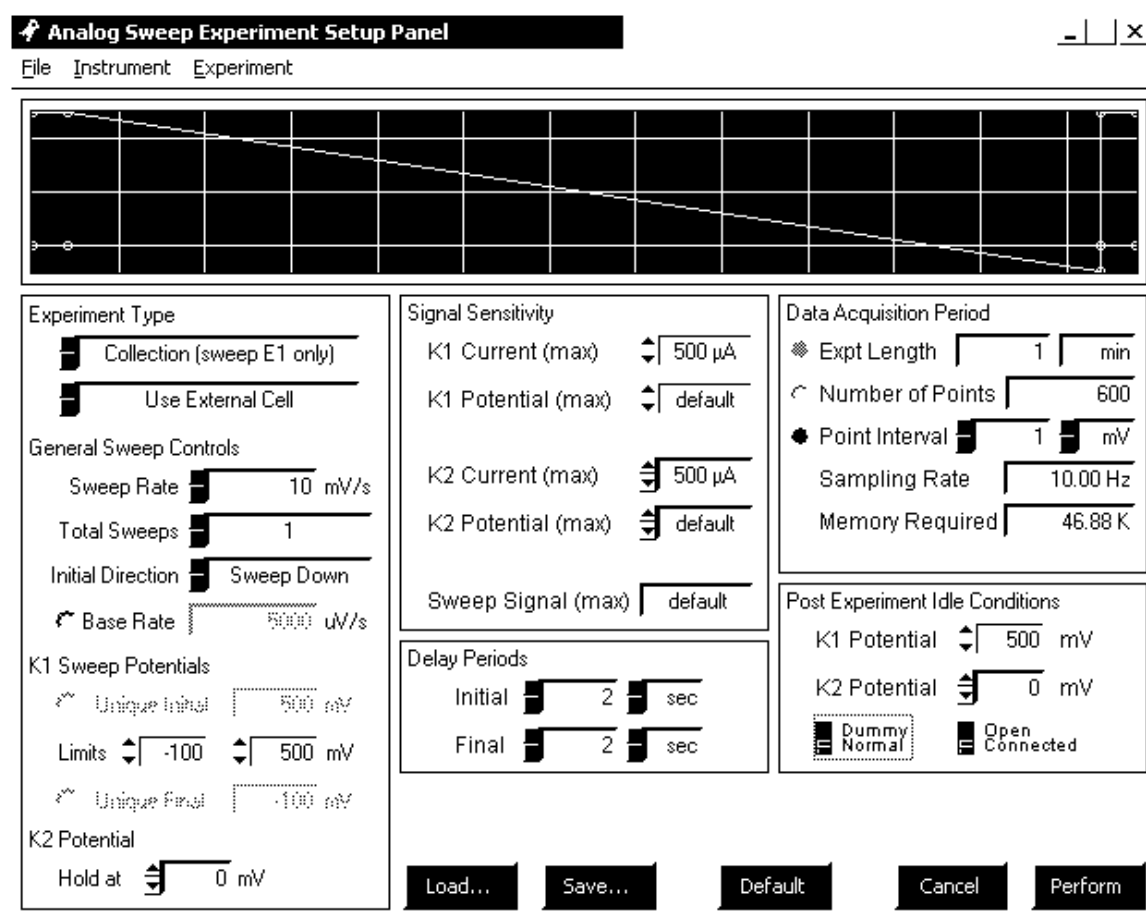


Figure 2.4. Experimental Setup for Rotated Disk Voltammetry

Data Analysis and Report Items

1. Combine equations 2.1 and 2.2 to obtain an expression for the limiting current as a function of rotation speed. Use this relationship to obtain the diffusion coefficient from the experimental data.
2. Plot the dimensional concentration profile for $\text{Fe}(\text{CN})_6^{-3}$ at the limiting current for three different rotation speeds. Indicate on the plot the diffusion-layer region at the different rotation speeds. Explain the observed trends.
3. Plot the diffusion-layer thickness as a function of rotation speed, and explain the observed trends.
4. Use the current versus potential data and equation 2.1 to plot the surface concentration as a function of potential for different rotation speeds. Explain the results.
5. The diffusion coefficient for dilute species in water is not a strong function of temperature, but there should be some dependency (see reference 4, pp. 513-516). Perform a literature

search for theories which predict the diffusion coefficient of a dilute species in water as a function of temperature. Summarize the physical significance of these theories and state whether or not they are consistent with the temperature dependency observed experimentally?

6. What terms in the material balance equation were used to obtain equation 2.2? What assumptions went into obtaining these terms? What role does KCl play in this experiment? How would the material equation have to be modified if no KCl was added (see reference 2, pp. 241-244)?

3. Chronoamperometry

Introduction

Potential Step and Pulse Methods

The simplest electroanalytical technique is called *chronoamperometry* and involves stepping the electrode potential from an initial potential to some final potential. The initial and final potentials are chosen so that they bracket the formal potential, E_o , for the analyte. At the initial potential, no significant current flows through the electrode. Once the potential is stepped to the final potential, however, the analyte begins to be consumed (via oxidation or reduction) at the electrode surface. This depletes the concentration of analyte near the electrode to such an extent that it is essentially driven to zero at the electrode surface. The sudden depletion of analyte at the electrode surface creates a very large concentration gradient, so it is not surprising that a very large current is observed immediately after the step. With time, the diffusion layer begins to extend further out into the solution, and the concentration gradient slowly relaxes. This means that the initial surge of current decays away to smaller values as time goes on. The magnitude of the current transient, $i(t)$, is proportional to the analyte concentration, C , and its decay with time is described by the Cottrell equation,

$$i(t) = n F A C (D / (\pi t))^{1/2} \quad (3.1)$$

In this equation, n is the number of electrons appearing in half-reaction for the analyte, F is Faraday's constant (96485 C / mol), A is the electrode area (cm²), and D is the analyte's diffusion coefficient (cm²/sec). The experimental data is usually plotted as $i(t)$ versus $t^{-1/2}$, yielding a straight line graph called a Cottrell plot. The slope of this line is directly proportional to concentration and may be used as the basis for an analytical determination. For solutions where the analyte concentration is already known, the slope can be used to measure the analyte's diffusion coefficient.

A variation of the simple chronoamperometry experiment that involves stepping back to the initial potential after some period of time is called *double potential step chronoamperometry (DPSCA)*. The principle strength of this experiment is its ability to probe what happens to the analyte after it is oxidized or reduced by the electrode. The oxidized or reduced forms of analytes are often unstable and may undergo various chemical reactions including decomposition. DPSCA provides a way to measure if and how fast these decomposition processes occur.

More complex potential pulse sequences may also be applied to the electrode. Techniques such as *pulse voltammetry* and *differential pulse voltammetry* involve a series of potential steps to ever increasing potentials. These techniques are able to distinguish between currents due to analyte redox processes and currents arising from background processes, and they provide both *current vs. time* and *current vs. potential* data.

Experimental Apparatus

Pine Instrument Company AFCBP1 Bipotentiostat

5-neck electrode cell

Platinum disk electrode

Platinum auxiliary electrode

SCE reference electrode

Reagents and Chemicals

100 ml of electrolyte (0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KCl) to a 125 ml jacketed 5-neck cell.

100 ml of 1.0 M KCL to a 125 ml jacketed 5-neck cell.

HPLC Grade water

Procedure

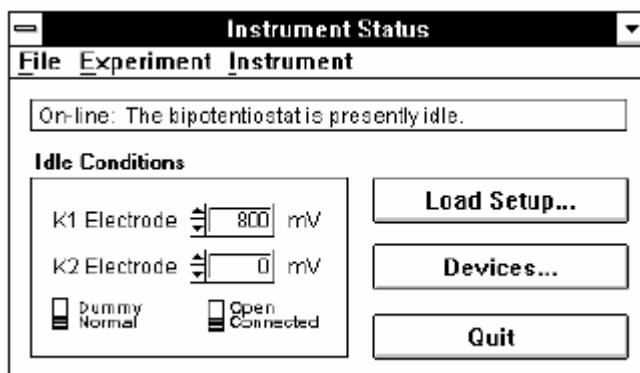


Figure 3.1. Instrument Status Panel

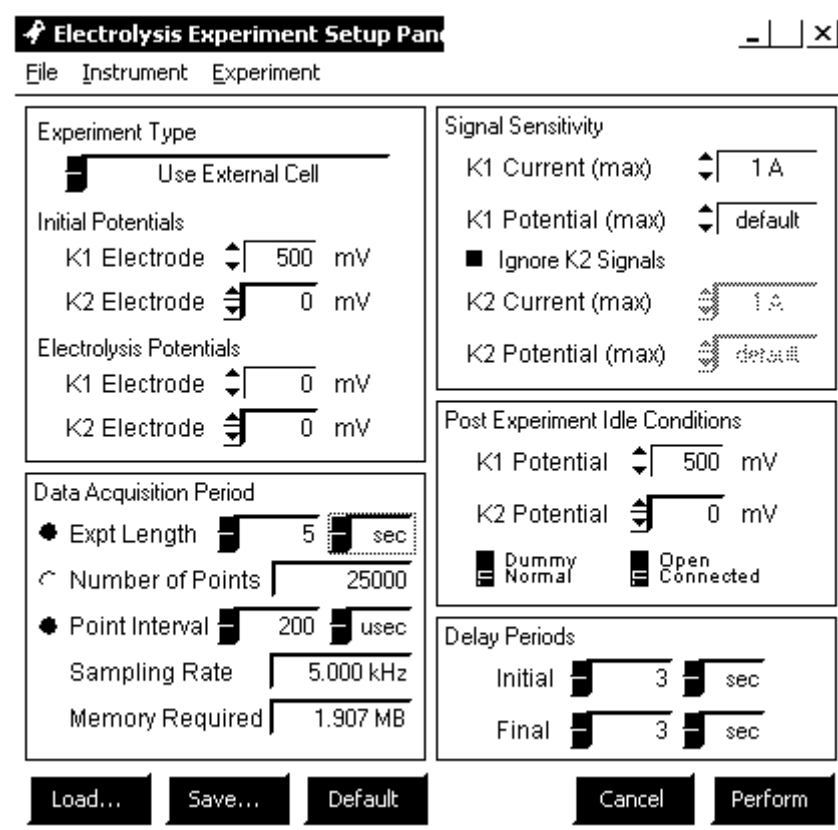


Figure 3.2. Experimental Setup for Chronoamperometry

This experiment will be performed on a static fluid.

1. Use the INSTRUMENT STATUS panel (Fig. 3.1) of the **PineChem** software package to place the AFCBP1 Bipotentiostat in DUMMY mode. Assemble the electrochemical cell and fill it with the potassium ferricyanide solution (or the supporting electrolyte alone for a background scan). Ensure the potentiostat is in the “Dummy” mode as observed on the instrument’s front panel. Mount the three electrodes in the cell. Connect the platinum working electrode to the K1 input. Connect the platinum counter electrode to the CE input. Connect the SCE reference to the REF input. Bubble nitrogen through the ferricyanide solution for about 10 minutes to displace dissolved oxygen from the solution. You may perform steps 2 through 6 while bubbling.
2. From the INSTRUMENT STATUS panel of the **PineChem** software package, adjust the IDLE CONDITIONS as shown in Figure 3.1. From the instrument’s front panel confirm that the AFCBP1 Bipotentiostat is now in NORMAL mode, and that the K1 electrode is idling near +800 millivolts. Use the Rotator as necessary to remove any gas bubbles on the electrode surface.
3. Select the ELECTROLYSIS option from the EXPERIMENT menu and adjust the experiment settings so that they match Figure 3.2. These settings are for a chronoamperometry experiment where the working electrode potential is stepped from +500 mV to zero mV. Note that the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

- Once the experiment settings have been adjusted to match those in Figure 3.2, click on the PERFORM button to initiate the experiment. A current transient that decays away rather rapidly should be observed. Figure 3.2 shows a chronoamperometry result for a solution of potassium ferricyanide. Note that as displayed by the PineChem software, cathodic currents are plotted in the downward direction.

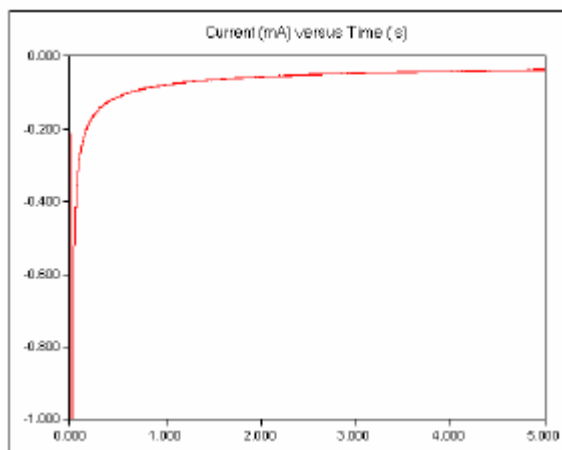


Figure 3.2. Typical Chronoamperometry Response.

After acquiring a satisfactory chronoamperometry result, save it to the disk.

Data Analysis

- Using ten data points extracted from your chronoamperometry result, prepare a plot of the current versus the reciprocal of the square root of time (*current vs. $1/\text{time}$*). Such a plot is called a Cottrell plot.
- Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.
- Use the slope of the line together with the Cottrell equation to estimate the diffusion coefficient for the ferricyanide anion. Pay close attention to proper units and report your answer in cm^2/sec .

Overall Questions

- List the three diffusion coefficient results that you obtained and compute the average result. Which of the three techniques do you believe yielded the most reliable result?
- For all three techniques, the method by which the analyte arrives at the electrode surface is diffusion. The distance that a molecule diffuses in a given amount of time is always related to the square root of the time.
- Show how this dependence on the square root of time manifests itself in each of the three voltammetric techniques studied. (*Hint: examine the units on each of the variables appearing in the Randles-Sevcik, Levich, and Cottrell equations.*)

4.0 Analyzing the Results

After each run, open the analysis panel.

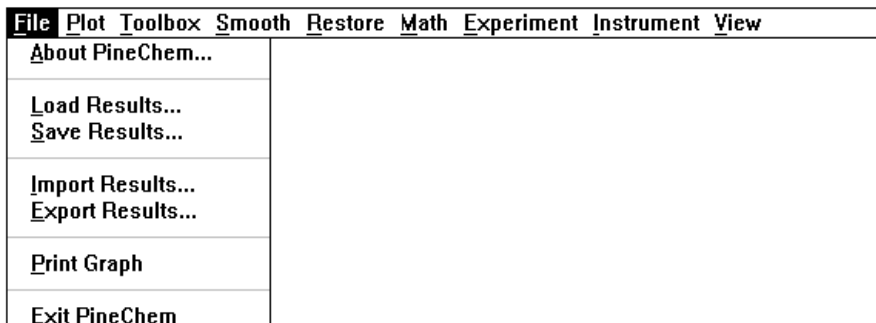


Figure 4.1. The File Menu from the Analysis Panel

All commands related to data storage, transfer, and printing is in the **File** menu. You may store and retrieve files created by this software package using commands found in this menu. You can also export data to other applications or print out a graph of the data.

Export Results...

This command allows you to store data from your experiment in an ASCII format which is readable by most other software packages, including spreadsheet and word processing applications. You may choose which signals are sent to the export file using a dialog box (see Figure 4.2). A group of check boxes lets you to select only the data that you actually need in the export file. SIGNALS should only include the ORIGINAL E1 and I1, and the SEQUENCE includes time and point numbers. The OPTIONS section on the right of Figure 4.2 is correct.

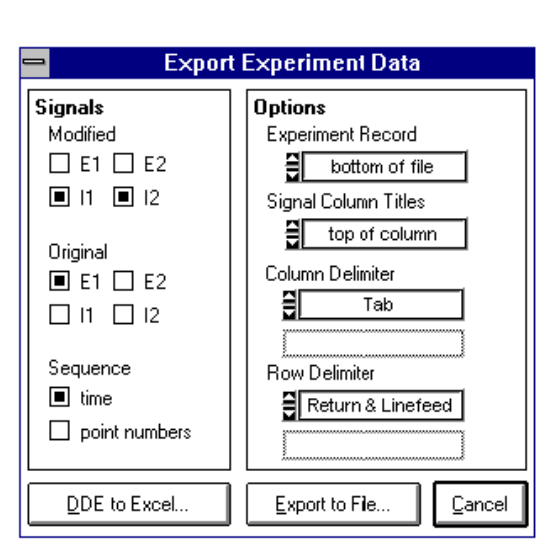


Figure 4.2. Exporting Experimental Data

The general format of the exported file is a series of lines (or rows) that are terminated with a “carriage return & linefeed” or some other “row delimiter” of your choosing. Every data point taken during the experiment occupies a single line in the export file. The information on each line is separated into different fields (or columns) using a “tab” character or some other “column delimiter” of your choosing. There can be quite a number of fields associated with each data point. Typically, these fields include the time at which the data point was acquired, and the currents and potentials at each working electrode at that point in time. You can include the ORIGINAL and/or MODIFIED data in the export file. Other information can also be included in the export file. If you intend to load the exported file into a spreadsheet or graphing program, it is a good idea to activate the SIGNAL COLUMN TITLES option. This includes a line in the export file which lets you know which data is in which column. This line can be placed at the top or bottom of the data or it can be omitted entirely. You may also choose to include an EXPERIMENT RECORD in the export file to describe, in detail, the parameters used to set up the experiment. This record can be included at the top or at the bottom of the export file. Each line in this record represents an individual experimental parameter. There are typically three pieces of information per line: the parameter title, its value, and its units. These three items are separated using the column delimiter (*i.e.*, a “tab” character).

Standard scientific notation is used to format the numeric data in the exported file. Time is specified in seconds, potentials are specified in volts, and currents are specified in amperes. The signal units for I1 ORIGINAL is always amperes.

References

1. Diffusion: Mass Transfer in Fluid Systems, E. L. Cussler, Cambridge University Press, New York, NY (1984).
2. Electrochemical Systems, 2nd Edition, J. S. Newman, Prentice Hall, Englewood Cliffs, NJ (1991).
3. Electrochemical Methods: Fundamentals and Applications, A. J. Bard and L. R. Faulkner, John Wiley and Sons, New York, NY (1980).
4. Transport Phenomena, R. B. Bird, W. E. Stewart, and E. N. Lightfoot, John Wiley and Sons, New York, NY (1960).
5. Electrochemistry at Solid Electrodes, R. N. Adams, Marcel Dekker, New York (1960).
6. Educator’s Reference Guide for Electrochemistry (Manual LMPROF1), Pine Instrument Company, Grove City, Pennsylvania (2000).

Solution Preparation

The two solutions required for this experiment should be prepared by the student or teaching assistant. The *Electrolyte Solution* is 1.0 M potassium chloride (KCL) in water. This solution provides an electrically conductive solvent suitable for use with voltammetry. The *Analyte Solution* is an 6.4 mM solution of potassium ferricyanide made using the *Electrolyte Solution* as the solvent. The *Analyte Solutions* can be of other values, but should be in the range of 10 mM.

Electrolyte Solution (250 mL)

Prepare a very clean 250 mL volumetric flask being sure that the last rinsing of this flask is done with ultra pure water. Transfer about 18.64 grams of potassium chloride (KCL) to the flask. Fill the flask with about 200 mL of ultra pure water and allow the potassium nitrate to dissolve. Once dissolution is complete, fill the flask “to the line” using ultra pure water and mix well. The resulting solution is about 1.0M KCL.

Analyte Solution (250 mL)

Prepare a very clean 250 mL volumetric flask being sure that the last rinsing of this flask is done with ultra pure water. Using a sensitive microbalance, transfer exactly 526.7 milligrams of potassium ferricyanide, $K_3Fe(CN)_6$, into the flask. Fill the flask with about 200 mL of *Electrolyte Solution* and allow the $K_3Fe(CN)_6$ to dissolve. Once dissolution is complete, fill the flask “to the line” using *Electrolyte Solution* and mix well. The resulting solution should have an analyte concentration of 6.4 mM, but the student should compute a more accurate concentration based on the actual mass of $K_3Fe(CN)_6$ that was used to prepare the solution. 100 ml of this solution will be used for experimentation and the rest for viscosity measurements.

Example:

The Randles-Sevcik equation is given below:

$$i_p = 0.4463 n F A C (n F v D / R T)^{1/2}$$

Given: $n = 1$

$$F = 96485 \text{ Coulomb/mol}$$

$$A = \pi r^2 = 0.19635 \text{ cm}^2$$

$$C = 4.5 \text{ mM} = 4.5 \times 10^{-6} \text{ mol/cm}^3$$

$$v = 200 \text{ mV/s} = 0.200 \text{ V/s}$$

$$D = 7.56 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$R = 8.314 \text{ J / mol K} = 8.314 \text{ C V / mol K}$$

$$T = 25.0^\circ\text{C} = 273.15 \text{ K}$$

Result: $i_p = 923.0 \text{ mA}$