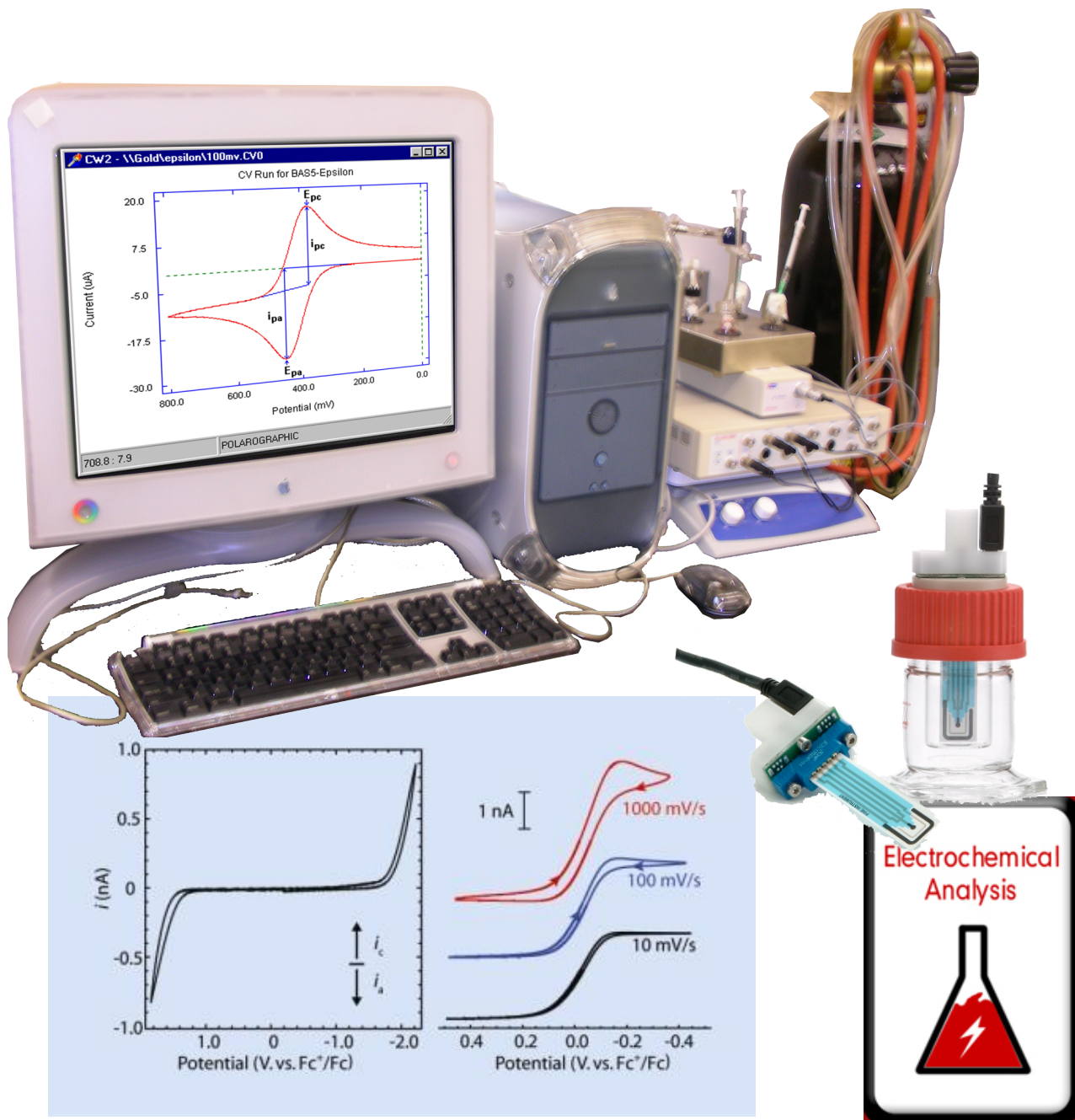# Standard Operating Procedure

eDAQ Potentionstat

Miramar College Potentiostat

-Report by Marianne Samonte, Dec 2009

I. Instrument

Description of Potentiostat and eCorder

The components of the eDAQ eCorder and PowerChrom for Electrochemistry instrument are EA 161 eDAQ Potentiostat, eCorder unit and the Pine printed screen electrode. The Potentiostat is a software-controlled three-electrode potentiostat that is hooked up to the eCorder, which records electrochemical reactions. The Pine printed screen electrode is an advanced version of the 3-electrode electrochemical cell with the 3-electrodes already printed on the screen. The 3-electrodes are the working, reference, and counter electrodes. The potential is applied between the working and reference electrodes and the current flow is measured between the working and counter electrodes. The 3-electrodes are placed in the chemical solution in a pattern electrode cell (vial) with cap. The important of the potentiostat is that it reads the potential and current flow of the chemical solution. The instrument configuration of the 3-electrode cell differs in that the 3-electrode cell has a nodule for each electrode and alligator clips that connect to the potentiostat. With the Pine printed screen electrode, the electrode is hooked up to the potentiostat with a USB cable. External gas that is used with the instrument is nitrogen gas. A nitrogen supply is placed into the electrode vial with a needle to degas the sample. Nitrogen removes oxygen that could interfere with the signal. Generally after degassing, the voltammogram signal will be cleaner and have less noise. The potentiostat varies the potential to the chemical solution and the current flow is measured. The current and voltage are then plotted by the EChem software. The component of the instrument that is responsible for sample stimulation is the Pine printed screen electrode that is hooked up to the potentiostat. The results are detected on the computer as a voltammogram, graph of current versus voltage.

II. Procedure and Operation

Electrode Set-up (Procedure for Pines' Screen Printed Electrode)

**1.** Use Pines' screen printed electrode and the pattern electrode cell (vial) with cap. Fill the cell with about 10-mL of the solution to be analyzed. Sample solution is prepared in the appropriate solvent and electrolyte. Alumina may be added to remove impurities such as water especially if organic solvents are used. Connect the alligator plug terminal of the Pine's wire harness to the appropriate electrode connection to eDAQ's potentiostat wire harness. Attach the printed screen electrode to the cell cap, screw the cap to the vial and attach the wire harness to the USB plug on the cell cap. (If Pines' screen printed electrode will not be used, three electrodes in electrode chamber will be used. The green electrode is the working electrode, the red electrode is the reference electrode and the yellow electrode is the reference electrode with Teflon II (counter electrode). Place about 5-ml of sample solution to be analyzed into the electrode chamber then put all three electrodes into the chamber at the same height.) Sit the electrode chamber onto the chamber instrument.
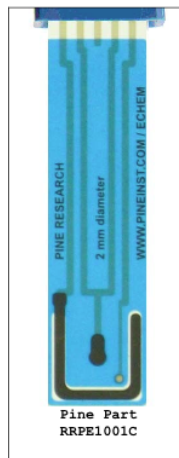
2. Degas the solution with nitrogen by placing the needle valve from the nitrogen supply to one of the holes in the cell cap. Adjust the cylinder regulator to give a pressure reading of not more than 0.5 bar. (0.1 bar ideal). Slowly open the needle valve, adjusting the flow to give a steady stream of small gas bubbles.

3. Turn on the attached Macintosh computer and log in as Chemstudent. Type the password Chemstudent

Familiarization with EChem software

1. Turn on the eDAQ potentiostat by reaching behind the e-corder 410 and turn on the rocker switch located at the bottom left. The overload light on the potentiostat should go away in a few seconds. Next, double-click the EChem icon "EChem Version 2.51" (displayed as a hand on a voltammogram) on the computer desktop on the right side bar to launch the EChem program. The screen shows an X-Y graph of potential applied to the working electrode (V, x-axis) against the current passed (μA, y-axis) by the working electrode. If the overload light on the potentiostat does not go away, it can be over-ridden by clicking on the Potentiostat under the iChannel heading.

2. Double-click on the Potentiostat button to the right of the main window to open the potentiostat dialog box. Change the radio button from Standby to dummy, which internally connects
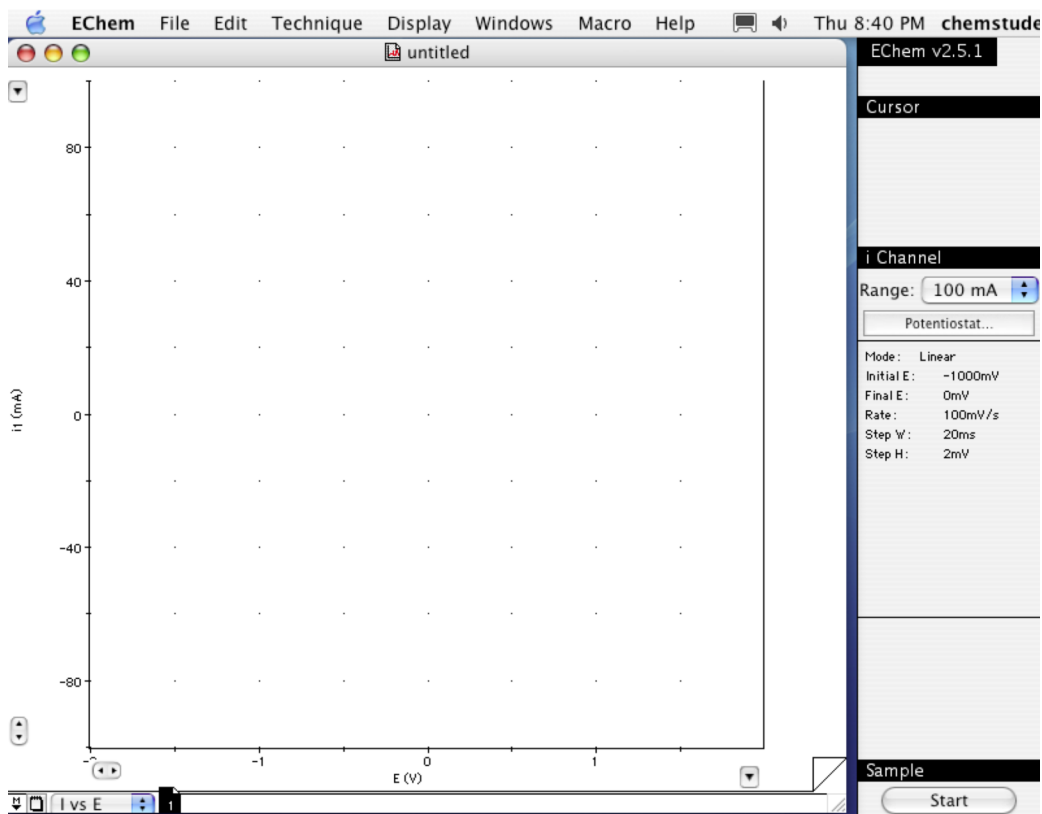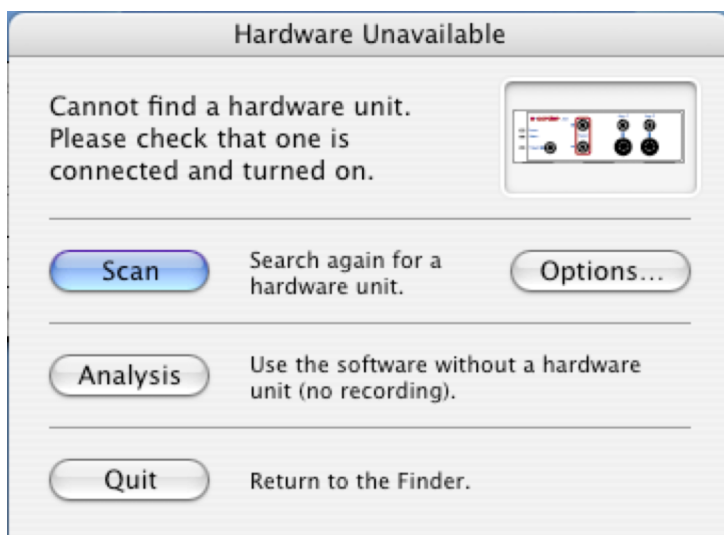
a resistor between the electrodes. Set the current range to 100 μA and alter the applied potential using either the slider control or by typing a value into the potential display. Increase the potential in 0.1 V jumps, the current trace should vary as you change the potential. The relationship should be linear as expected from Ohm's law (Voltage = I (current) * R (resistance)). Finally reset the potential to 0 V.
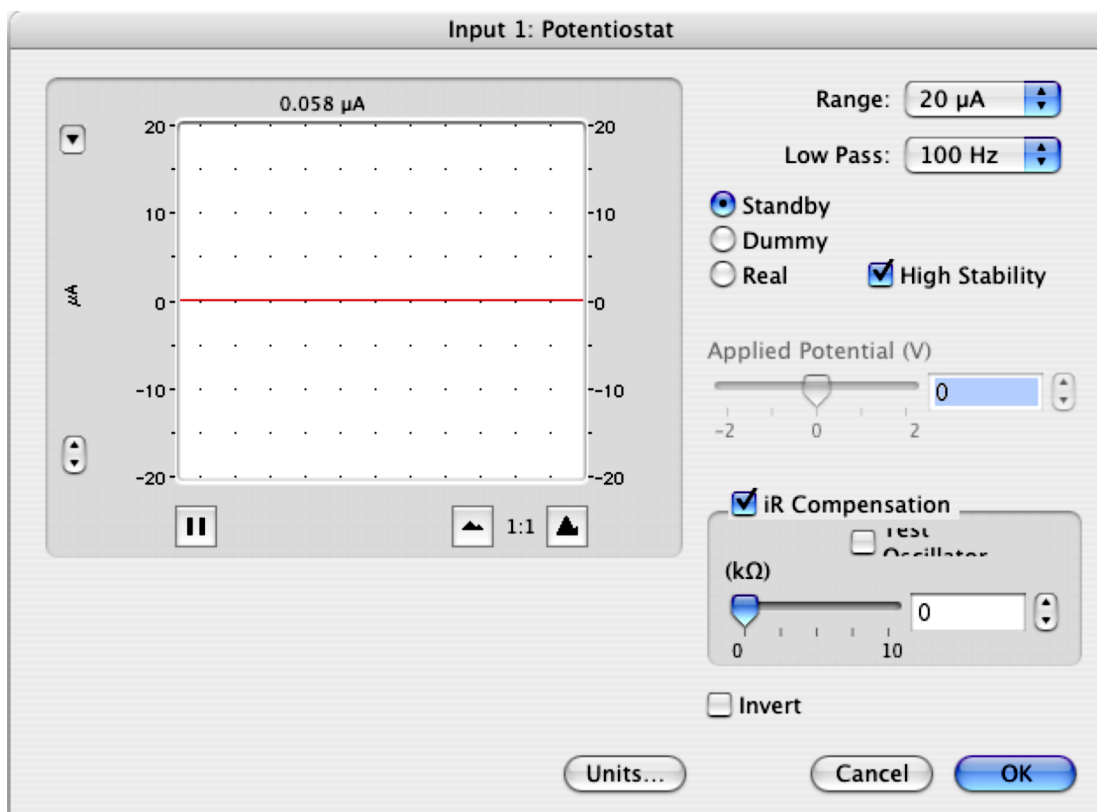
3. Change the radio button from dummy to cell. The potential will now be applied across the electrodes. Repeat the procedure in Step **2**, keeping the potentials between −0.2 V and +1.0 V. Do NOT exceed these limits. It will be necessary to change the current range (try 200 μA) to see the current responses. Notice that there is a small range of potentials over which the current is very sensitive to applied potential.

4. Reset the potential to 0 V and click OK to close the potentiostat dialog box. The potentiostat will automatically switch to standby mode.

Cyclic Voltammetry of Sample Solution

1. Double-click on the Potentiostat button again and switch the current range to 10 μA on the potentiostat dialog box. Click on OK to close the Potentiostat dialog box.

2. From the techniques menu select Cyclic Voltammetry. This opens the Staircase Cyclic Voltammetry dialog box, which is used to set the limits and ramp rate of the voltage waveform applied to the working electrode.

Staircase Cyclic Voltammetry		Range:	2 V

Ramp
Initial	0	mV
Final	0	mV
Rate	100	mV/s
Width	20	ms
Height	2	mV
Steps	1400	

Limits
| Upper | 400 | mV |
| Lower | −1000 | mV |

Speed: 10 kHz

S. Period
| 5 | ms |

Cycles
| Number of Cycles | 3 |
☑ + Initial Direction

Rest Time
| 2 | s |

View...

☐ Deposition
| Pot. | −1000 | mV | ☐ Stirrer |
| Time | 60 | s | ☐ Gas |

☐ Clean Time
| Pot. | 0 | mV |
| Time | 5 | s |

Cancel

OK

In the dialog box, select the following parameters:

Initial = 0 mV   Ramp Rate = 100 mV/s

Final = 0 mV   Step Width = 20 ms

Upper Limit = 700 mV   Step Height = 2 mV

Lower Limit = -700 mV   Sampling Period = 5 ms
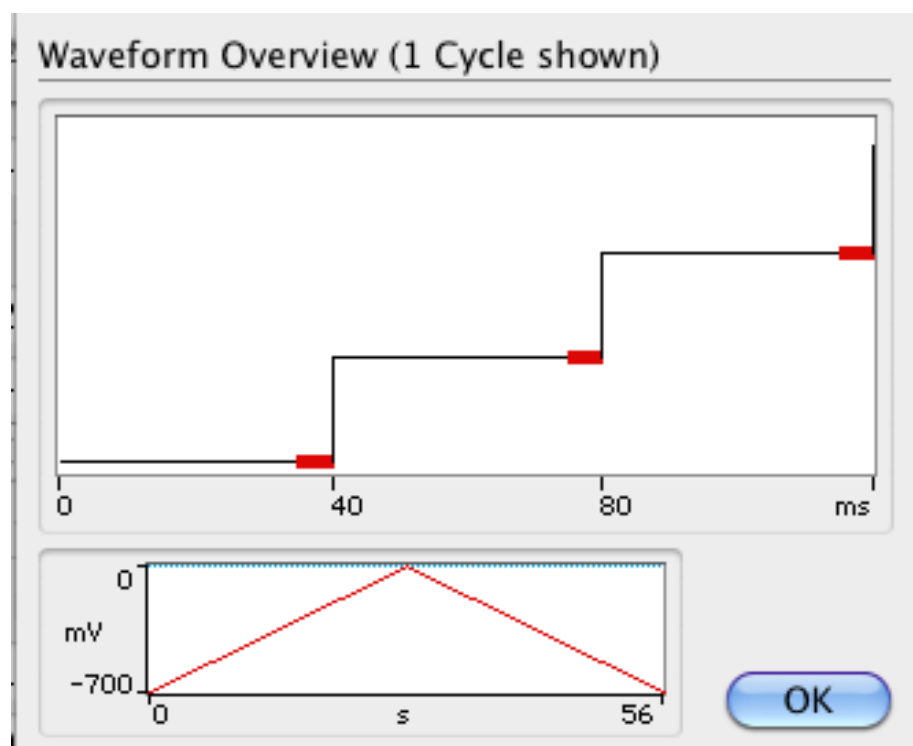
Rest Time = 5 s   Number of Cycles = 3

(These parameters are for Ferrocene Carboxylic Acid. The parameters can be changed for the particular sample that will be analyzed. Glossary for parameters is located at the end of the procedure.)

Click on View to preview the waveform defined. Waveform Overview Window figure.

Waveform Overview (1 Cycle shown)


3. Select the Notebook under the Windows menu. Write some general notes on the experiment including your name, Date, time and solution details. Close the window and save the file using a suitable filename.

4. Lift the nitrogen line out of the solution. Check that there are no bubbles trapped on the surface of the electrode. If there are, lightly tap the cell to dislodge them.

5. Click on Start to begin the potential scans. After the scans, place the nitrogen line back into the solution. The scan should look like the voltammogram below.
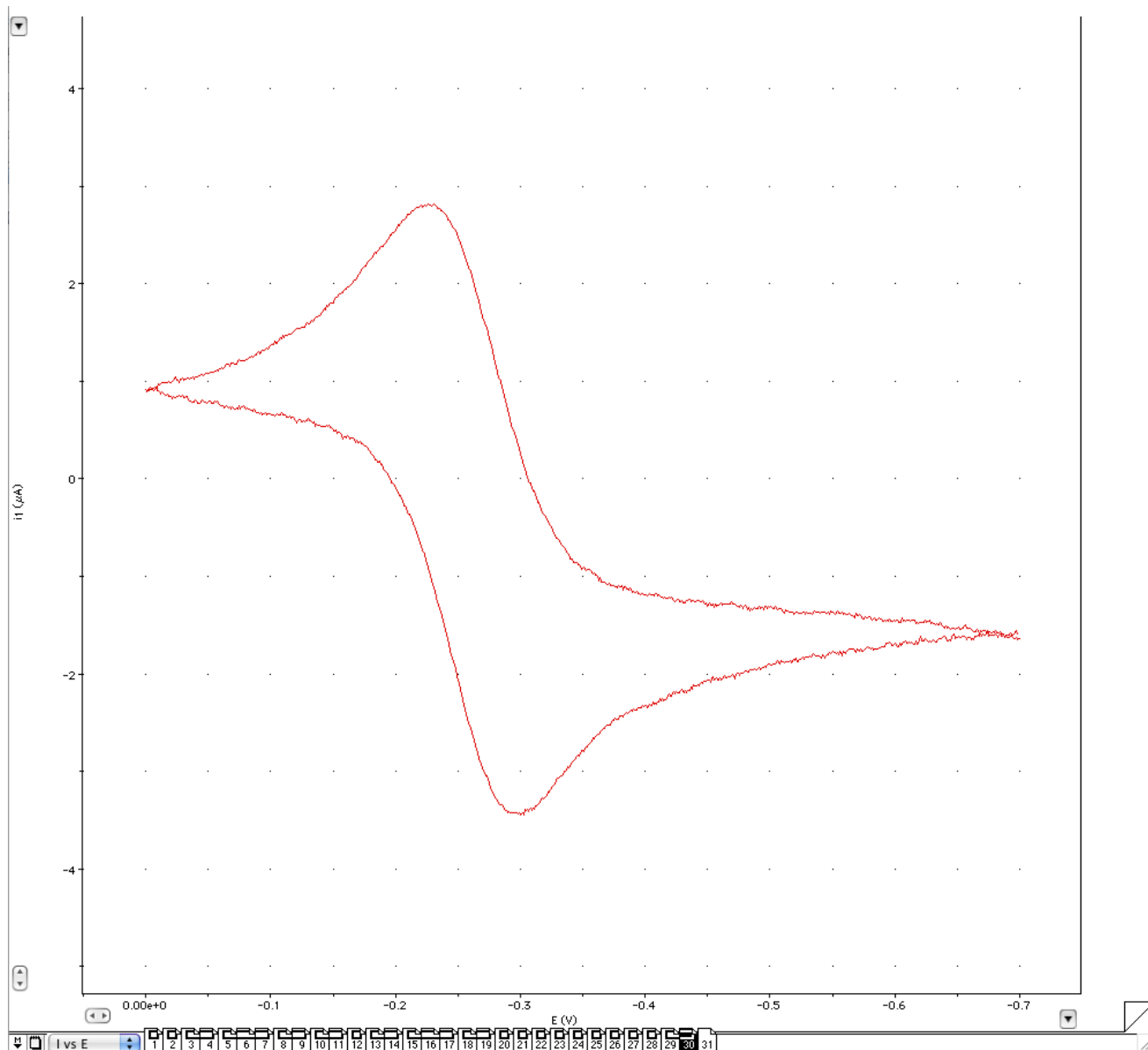
6. Adjust the current range under the potentiostat menu and apply the low pass filter if the signal is too noisy. Change the settings in the staircase Cyclic Voltammetry dialog box by adjusting the upper and lower limit so that the scan is zoomed to the oxidation reduction potential (0 to -700mV). If the current reading goes off scale, adjust the current range, and repeat the scans. If the signal has too much noise, adjust the Low Pass filter to a lower number. Adjust the other parameters after each scan to optimize

the signal. Note the changes of the voltammogram at different settings. Example: the lower the ramp rate is, the longer it takes to make a graph but the more accurate the graph will be. Rate is related to step height and width by Rate = Step Height * Step Width. After the scans are done, click on the Page comment button (bottom left of screen) and enter a comment for the middle scan (solution, scan rate etc.). The arrows on the horizontal and vertical axis make the graph wider or slimmer.

7. Degas the solution again with nitrogen remember that the solution should be degassed after each trial.   In the Staircase Cyclic Voltammetry dialog box, change the following parameters- • Ramp Rate to 200 mV/s, • Step Width to 10 ms • Sampling Period to 2.5 ms. Repeat Steps **4** to **6** to obtain a new set of three voltammograms.

8. Repeat Step **7**, with the following parameters-

•Ramp Rate of 500 mV/s •Step Width of 4 ms •Sampling Period of 1 ms, adjusting the current range if necessary. Next repeat Step **7** again, with the following parameters-

•Ramp Rate of 1000 mV/s •Adjust the other parameters accordingly to optimize the voltammogram.

9. Switch the current range to an optimum value and obtain scans at Ramp Rate of 10 mV/s, Step Width of 200 ms, Sampling Period of 50 ms, and Current Range to 50 μA.
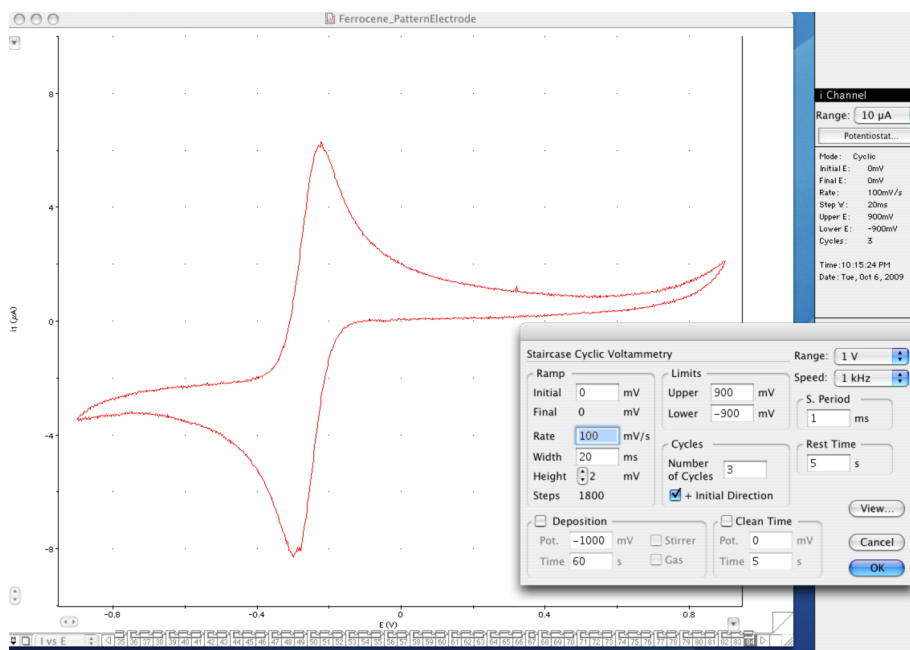
Data Analysis

1. Overlay the middle cyclic voltammogram (CV) scan of the four obtained for the sample solution at the different scan rates (ramp rates at 100, 200, 500 and 10 mv/s), by highlighting the corresponding page tabs while holding down the Command key (Apple symbol is on the key) on the keyboard. Print and label the overlain CVs. Annotate a single CV on the printout with the peak potentials (E_p Ox and E_p Red) and peak currents (ip Ox and ip Red).

2. As with many electrochemical techniques, cyclic votammograms often have sloping baselines, and the peak currents cannot be read directly. In EChem, two marker points can be used to define an estimated baseline from which the peak currents can be determined.

To set the two marker points, switch to the view of current and applied potential against time view by selecting IE v t in the Display pop-up menu.
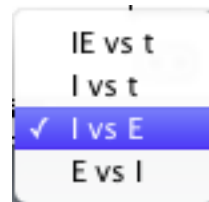

The CVs should now look similar to the graph below.:
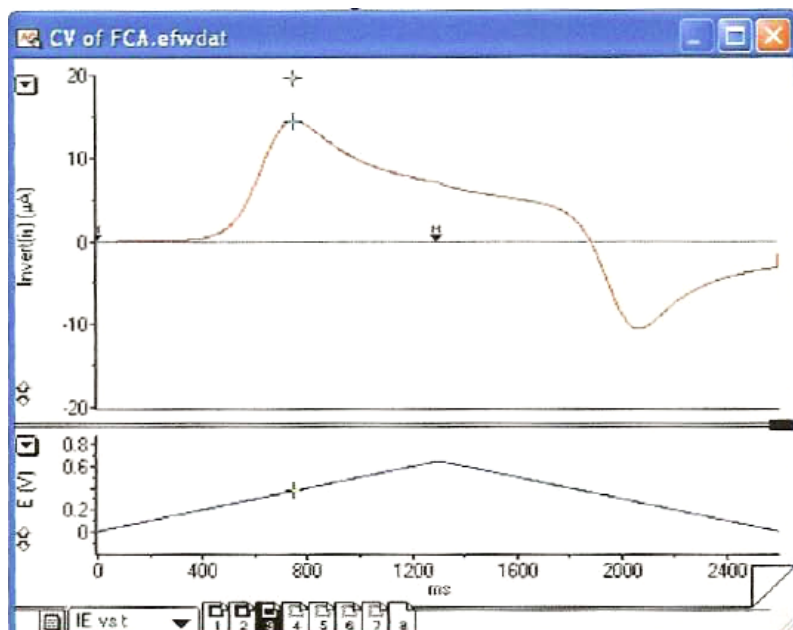
3. To measure the peak oxidation current (ip Ox), drag the marker, M, onto current (I) channel to t=0. Press Control and Command keys simultaneously, click the marker that was put at t=0 and drag a second marker with the mouse onto the CV that is independent of the waveform. Adjust the second marker so the tie line forms a tangent with the initial current slope during the oxidizing sweep. See IE Vs. t graph above for an example. Use the cursor to measure the peak current relative to the baseline. The baseline correction is also shown on the screen. Repeat measurements for each CV.

4. To measure the peak reduction current (ip Red) drag an initial marker onto the current channel at the time where the reduction scan starts. Press Control and Command keys simultaneously, click the marker that was put at t=0 and drag a second marker onto the CV that is independent of the waveform. Adjust the second marker so the tie line forms a tangent with the initial current slope during the oxidizing sweep. See figure for an example. Use the cursor to measure the peak current relative to the baseline. Repeat measurements for each CV.
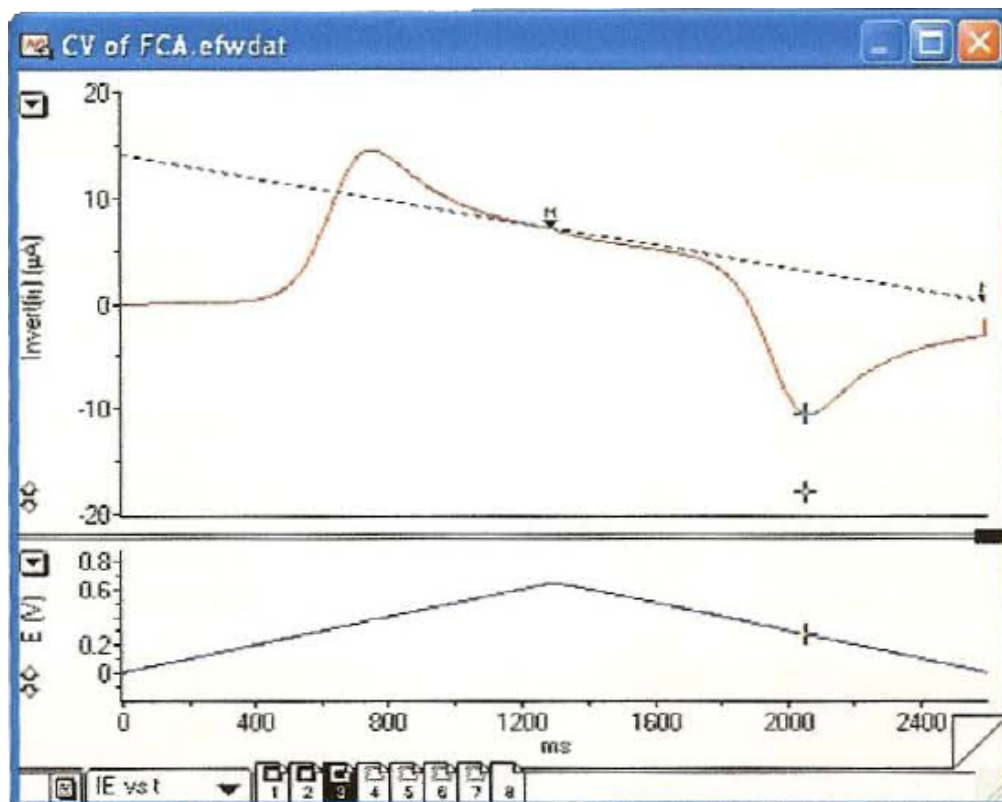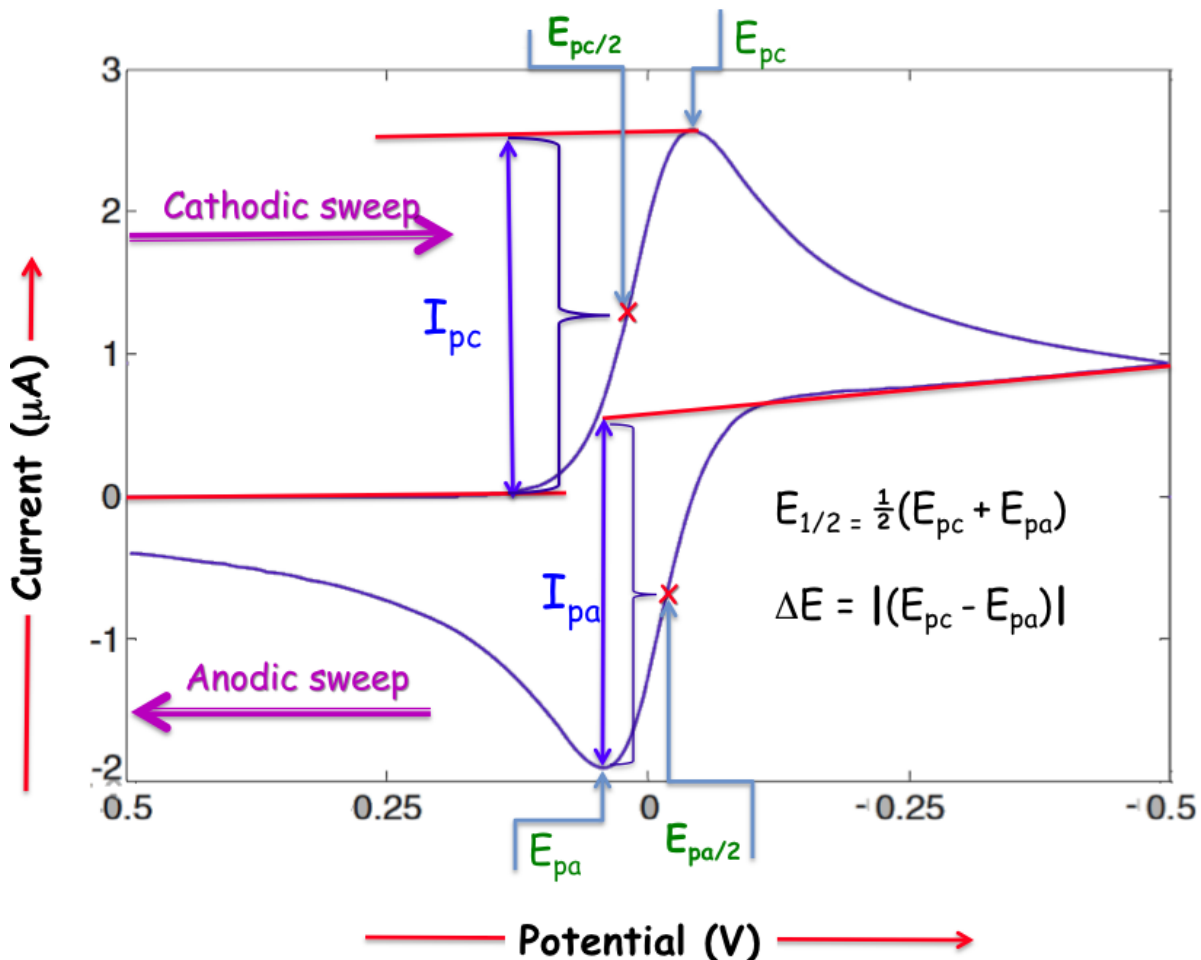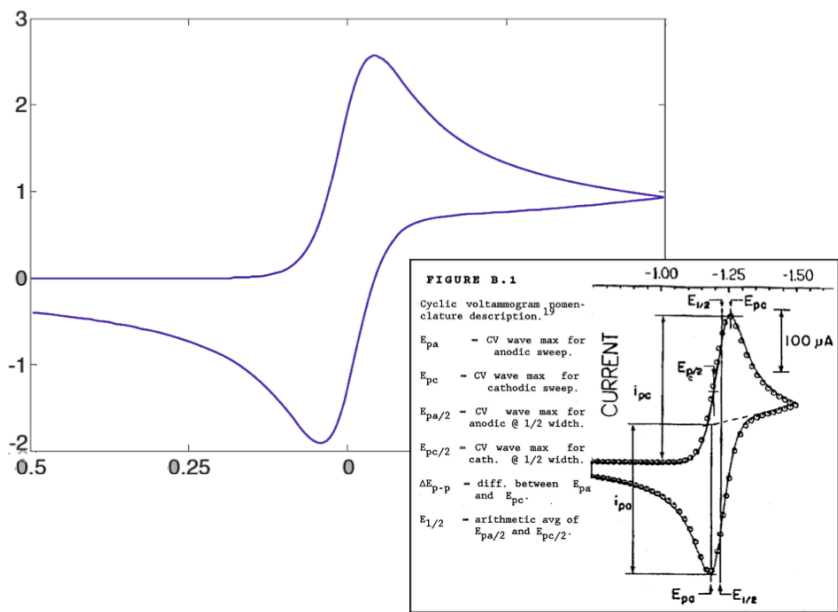

The type of data that is acquired from the instrument is a voltammogram, the curve of current (i), measured in μA, versus potential (E), measured in voltage, for half reaction

potentials. For a cyclic voltammogram, both the oxidized and reduced forms of the reaction are shown. The data is analyzed by obtaining the peak currents and peak potentials for the reduction and oxidation half-reactions. The redox reaction is diagnosed as reversible with the following criteria: if $\Delta E_p = E_p^{Red} - E_p^{Ox} = 59mV/n$ where n is number of electrons, $i_p^{Ox}/i_p^{Red} = 1$, i_p^{Ox} and $i_p^{Red} \alpha V^{1/2}$, or E_p^{Ox} and E_p^{Red} independent of V. An important equation used for analysis is the applied potential, E, and the concentration of the two redox forms in accordance with the Nernst equation: $E = E_0 + (RT/nF) \ln [Oxidized \ species]/[Reduced \ species]$.

Nomenclature and Notation

CV has been claimed to be the most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement, has resulted in its extensive use in almost every field of chemistry. CV spectroscopy can provide information about reaction kinetics and electron transfer mechanisms, this technique is used mostly to measure ground state redox potentials. The general setup for cyclic voltammogram measurements uses a three compartment cell consisting with a platinum disk working electrode, a platinum wire auxiliary electrode and a general purpose AgCl reference electrode. Room temperature measurements are obtained in a degassed (dry dinitrogen) electrolyte solution consisting of a saturated solution of tetraethylammonium hexafluorophosphate (TEAH) and alumina in 50 ml solvent (solvents used were described for each complex). Low temperature measurements (-77°C) will required a dry-ice acetone bath to house the electrode and CV cell. The first step is to scan background voltammograms for each analyte by running CV's of the electrolyte solution, after which approximately 2 mg of the complex is added to the working cell chamber and the CV recorded. In some instances, current sensitivity and switching potentials are varied to elucidate wave patterns in the voltammograms.

After measuring the voltammograms for each complex, voltammograms are measured for ferrocene (5.0mg). Since the half-wave potential $E_{1/2}$ for $Fc^{+/0}$ is insensitive to solvent and temperature, this redox potential is ideal as an internal reference. All CV's were monitored at scan rates of 1.0 V/s. The nomenclature for the CV results are illustrated and described in the figure below.

FIGURE B.1

Cyclic voltammogram nomenclature description.[19]

E_{pa} — CV wave max for anodic sweep.

E_{pc} — CV wave max for cathodic sweep.

$E_{pa/2}$ — CV wave max for anodic @ 1/2 width.

$E_{pc/2}$ — CV wave max for cath. @ 1/2 width.

ΔE_{p-p} — diff. between E_{pa} and E_{pc}.

$E_{1/2}$ — arithmetic avg of $E_{pa/2}$ and $E_{pc/2}$.

$E_{1/2} = \tfrac{1}{2}(E_{pc} + E_{pa})$

$\Delta E = |(E_{pc} - E_{pa})|$

Cathodic sweep

Anodic sweep

Current (μA)

Potential (V)

Cyclic Voltammogram Example

http://www.basinc.com/mans/EC_epsilon/Techniques/CycVolt/cv.html

This example shows a cyclic voltammogram with E_{pc}, i_{pc}, i_{pa}, and E_{pa} shown. E_{pc} (potential at cathodic peak) is about 380.0 mV and i_{pc} (current at cathodic peak) is about -23 μA. Cathodic peak is the reduction (gain electron) reaction and anodic peak is the oxidation (lose electron) reaction. E_{pa} (potential at anodic peak is about 450.0 mV and i_{pc} (current at anodic peak) is about 28 μA.

2) Cyclic voltammograms of trans-$[Rh(H_2O)_4Cl_2]^+$ at different scan rates. (http://www.chemistrymag.org/cji/2005/071005pe.htm

This example shows several cyclic voltammograms of rhodium (35 ug/mL) different scan rates overlaid over each other, as was performed in the protocol. A couple of the scan rates are 120 mV/s and 40 mV/s. The reaction is not reversible because $\Delta E_p = E_p^{Red} - E_p^{Ox} = -0.2V - (-0.16V) = -0.04V$, which does not equal 59mV or a factor of it.

3) Two scans of 5 mm Ferrocyanide in 0.1 M KNO_3.

http://www.cypresshome.com/Software/Acquire101.html

This example shows a reversible reaction because $E_p = E_p^{Red} - E_p^{Ox}$ = 180mV – 300mV = 120mV which is about 120mV/2 = 59mV. This means that 2 electrons are transferred in solution.
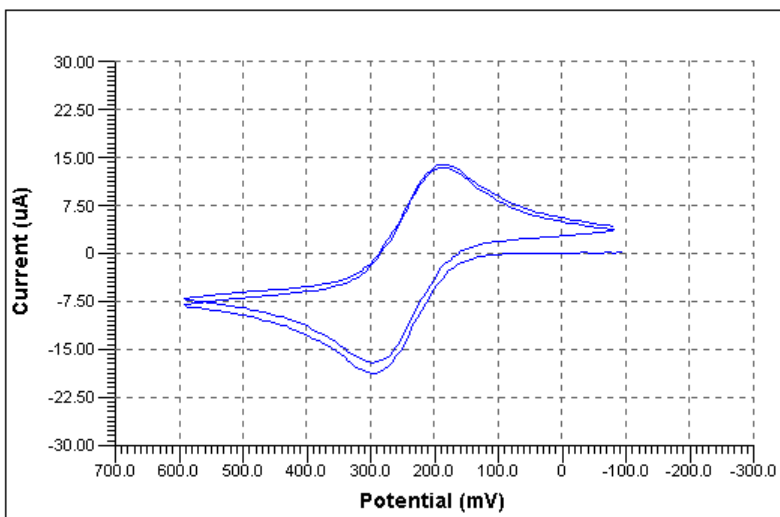
• Glossary Terms

• Initial: where the electric potential will start, measured in mV.

• Final: where the electric potential will end, measured in mV.

• Upper Limit: how much (mV) of a sweep the potentiostat is going to scan out to the sweeping potential.

• Lower Limit: how much (mV) of a sweep the potentiostat is going in opposite direction.

• Rest Time: the time (seconds) before the instrument starts so that it can stabilize itself.

• Ramp Rate: how long (mV/s) the scan will take. Ramp Rate = Step Width * Step Height

• Step Width: makes up the staircase ramp (ms).

• Step Height: makes up the staircase ramp (mV).

• Sampling Period: restricted to the final ¼ of the step width so that the capacitive current has time to decay when the potential is decayed, helps with noise, amount of time (ms) it looks at each signal at that particular point of each step.

• Number of Cycles: number of times the scan performs its sweeps.

• Range: how high or low the current is going to be.

• Speed: how fast it will take to scan each half-potential reaction.

• View: located on the bottom left corner of the menu, used to switch to the view of I vs E and IE v t.

• IE v T: view of current and applied potential against time, used to measure the peak oxidation and reduction currents because the cyclic voltammograms have sloping baselines.

• I vs E: regular view, current against applied potential of the working electrode.