POTENTIOSTAT SOFTWARE SETUP, SIMULATIONS, AND ANALYSES

Introduction

According to Prof. Ardo, electrochemical processes are "Those that occur when the electrochemical potential of electrons in a solid influence, or are influenced by, chemical reactions, including those involving the motion/transport of charge – carried by entities other than unsolvated electrons and holes – through phase(s), or the transfer of charge across interface(s)." Therefore, in order to perform electrochemical processes and study electrochemistry we need a tool that can assist us in driving this charge motion through phases and across interfaces. That tool is the potentiostat. Potentiostats allow one to vary the driving force for electron transfer and transport (i.e. the electrode potential) between a (working) electrode relative to the potential of a reference electrode (and not vacuum, unless you are Trassati). It then enables current to flow (recall that the direction of positive current is opposite to the direction of electron transport) by transporting electrons from one electrode to another electrode, where these electrodes can be the aforementioned working and reference electrodes (two-electrode measurement), or the working electrode and another electrode (three-electrode measurement), or neither of the working or reference electrodes and thus between two other electrodes (four-electrode measurement). At this time, we are not concerned with the number or nature of the electrodes, but we must know how to control their potential and current using a software program that is freely available online.

Purpose

The purpose of this laboratory, I mean hands-on discussion activity, is to become familiar with the software that you will use throughout the hands-on discussion sessions. A high level of proficiency in using the software will ensure that you spend most of your time performing simulations, analyzing data, setting up electrochemical experiments, taking data, and troubleshooting electrochemical issues, but not dealing with problems using the software. The software is only available for PC so between you and your $1 - 2$ "lab" partner(s) someone needs a PC laptop that can be brought to discussion section and used for the hands-on activities. Depending on how long the assignments take you to complete, you may need access to the software, and thus a PC, outside of the discussion session.

Safety

Carpel tunnel syndrome can be hazardous to your health. Also, software viruses can be hazardous to your computer and so only perform the steps outlined below to download and run the BioLogic software, EC-Lab. If you follow them exactly, you will not install a software virus.

Procedures

Part A: Installing the potentiostat software (EC-Lab by BioLogic) on PC only

(1) To download the BioLogic software (EC-Lab) follow the link: https://www.biologic.net/support-software/ec-lab-software/. Click the "Download" button on the left and then click the blue "Log in" text on the right. Locate the installation file in the folder indicated by the Prof. Ardo. Alternatively, enter a "Username or Email Address" and "Password" and click the "Log In" button, if that information was given to you. Then click the "Download now" text on the right to download the file "ec-lab-##-##-setup.exe". (If the website mistakenly navigates you away from the "Software" menu, hover your mouse over "Support" on the banner at the top and select "Support Software", and then click on "BioLogic EC-Lab® Software" and then click the "Download" button on the left).

(2) Locate your Downloads folder and double click on the installation application to perform the installation, and when prompted with choices or questions, just click "Yes" and then "Next" several times and finally "Install". Note: If you wish to use your computer and EC-Lab to communicate with a BioLogic potentiostat in the future, you will have to restart your computer to finish the installation so that the USB and Ethernet port communications work with the potentiostat. Do this by clicking "OK" at the end of installation.

Part B: Starting up EC-Lab

(1) Locate the EC-Lab program on your desktop and double click on it to open it.

(2) When prompted for a "User name:" just click the "OK" button to skip that step. (Sometimes when you run the program, a box titled "Global View" and with the side text "VSP – virtual" will appear and if so, just click the "Close" button.)

(3) In the "Devices" region at the upper left side, click on the "virtual potentiostat" icon (it's the one on the far right; hover over icons to see their names) and if it is not already there, in the "Instrument" region select "VSP" and click the "Add" button.

(4) In the "Experiment" region at the lower left under the "Parameter Settings" tab, click on the yellow key image to enter "Modify mode". *This is the number one reason why it is not possible to enter or edit data in the software, so keep that in mind for future troubleshooting.*

Part C: Loading and modifying experiments and general settings

(1) Under the "Experiment" menu bar at the top far left, choose "New" (or in the "Experiment" region at the lower left under the "Parameter Settings" tab, click the light blue PLUS sign) and if prompted to "Switch to Modify mode?" click "Yes".

(2) Under "Electrochemical Techniques", double click "Voltamperometric Techniques", and then choose each of the following in the order listed below, each followed by clicking the

"OK" button and then repeating Step 1, so that you insert a technique a total of three times. (If the program asks you to "Reset safety limits?", click "No". If it asks you to "Set safety limits? Do no start on E overload", click "Yes".):

    a. "Chronopotentiometry – CP"
    b. "Chronoamperometry / Chronocoulometry – CA"
    c. "Cyclic Voltammetry – CV"

(3) Read the PowerPoint file, slides 1 – 12 (through and including Section 3 – Sub D – Parameter Settings), that was included with this activity to get acquainted with the general features and the settings.

(4) In summary, generally for all experiments you will want to be sure that the following boxes are checked and/or settings selected under "Experiment" region at the lower left:

    a. "Safety/Adv. Settings" tab
        i. In the "Safety Limits" region at the top, check the "Do not start on E overload" checkbox
        ii. In the "Record" region at the middle, check the "Ece/V" checkbox
        iii. In the "Electrode Connection" region at the bottom, set the drop-down box to "standard" mode, meaning that the channel is considered grounded, and not floating
    b. "Cell Characteristics" tab
        i. In the "Reference Electrode" region at the bottom, set the drop-down box to your reference electrode

(5) Read the PowerPoint file, slides 13 – 18 (through and including all Section 3 – Sub E' – Techniques), that was included with this activity to get acquainted with the features and the settings of the techniques; unfortunately, you cannot run any of these now because a connection to the potentiostat is required for that.

Part D: Simulating data – Cyclic Voltammetry

(1) Go to the "Analysis" menu bar at the top and choose "General Electrochemistry", "CV Sim…".

(2) Set the "Mechanism" drop-down box to "E", if it is not already set to "E". *If at any step in this process you receive an error message, do your best to interpret it and likely you will end up just clicking "OK" or "Yes", followed by changing a parameter.*

(3) Make other changes on each tab ("E" and "Setup") per the two screenshots below, making sure to enter the "scan rate" as "100" "mV/sec" and not "0.1" "V/s"; for some reason, at times this seems to matter.
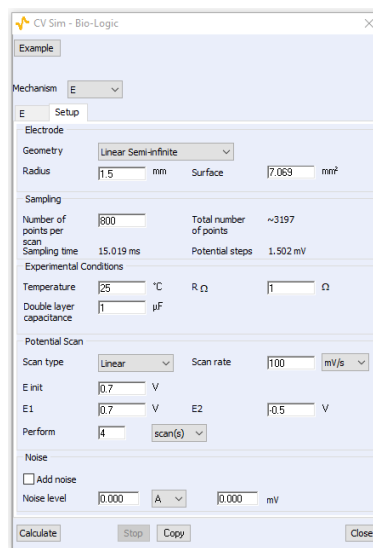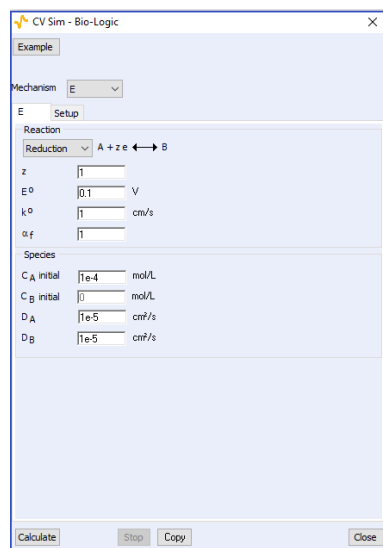
(4) At the bottom, click the "Calculate" button and then click the "Close" button. You should see a CV plot in the graph area (If you do not see a plot, then close the EC-Lab program and restart the program, but do not perform Part C of this procedure. Directly start with Part D). Right click on the plot and choose "Save Data File As…" and enter a meaningful filename for the dataset, making sure the file type is "EC-Lab text files (*.MPT)", and then click the "Save" button.

(5) Now, because the software is a bit buggy and/or I am a bit novice at using it, you must click on the "Selector" button located in the toolbar at the top middle (logo of a white piece of paper with I and E on it and check marks) (which is also "Alt+S"), and select the dataset from your most recent (only) simulation by clicking on it, then clicking the "Remove" button, then clicking the "Add" button and adding the same file back by clicking the "Open" button, followed by in the "Variables" region at the right, making sure that the "Same selection for all files" checkbox is checked and then setting the "Representation:" drop-down box to "I vs. Ewe" and clicking the "OK" button. *You will have to do this step, or something like it that you may discover is faster, after simulating and saving every dataset.*

(6) Navigate back to "Analysis", "General Electrochemistry", and "CV Sim…". In the "Setup" tab, change "R_Ω" from "1" to "10,000" *to simulate a 10^4 times smaller concentration of supporting inert electrolyte or a 10^4 times larger distance between the working and reference electrode*. Click the "Calculate" button and then click the "Close" button, and then right click on the plot and choose "Save Data File As…" and enter a meaningful filename for the dataset and then click the "Save" button. *Then repeat Step 5.*

(7) Change "R_Ω" back to "1", and change "Double layer capacitance" from "1" to "30" *to simulate a 30 times larger electrochemically active surface area (ECSA)*. Again, "Calculate", "Close", and "Save Data File As…". This plot should look much wider vertically. *Then repeat Step 5.*

(8) Change "Double layer capacitance" back to "1", and change "Scan rate" from "100" to "1000" "mV/s" (use these units). Again, "Calculate", "Close", and "Save Data File As…". *Then repeat Step 5.*

(9) It is likely that the units for "Scan rate" will have changed to "V/s", so now change "Scan rate" back to "100" "mV/s", and change "Radius" to 10 µm (in mm, of course). Again, "Calculate", "Close", and "Save Data File As…". This plot should look much thinner vertically. *Then repeat Step 5.*

(10) Re-enter the "Radius" of 10 µm (at times this value may change by orders-of-magnitude for no apparent reason; if it changes by less than a factor of 2 then it is fine), and change the "Geometry" drop-down box from "Linear Semi-infinite" to "Hemispherical Semi-infinite" *to more accurately simulate an ultramicroelectrode*. Again, "Calculate", "Close", and "Save Data File As…". This plot should look similar to the last one, and is your 6th and final CV dataset.

Part E: Manipulating plots, Part 1

(1) Read the PowerPoint file, slides 19 – 20 (through the end), that was included with this activity to get acquainted with the features and the settings for plotting; try some of these on your own to better understand the capabilities and how to make your figures as professional as possible, *after doing the steps below to obtain figures that you will submit for this assignment*.

(2) Right click on the graph, which should contain 6 plots, and choose "Graph Properties" (which is also "Alt+P"). (If the graph does not contain 6 plots, right click on the graph and choose "Load Files…", select all 6 files while holding down the "Shift" key, and click the "Open" button. In the "Variables" region at the right, make sure that the "Same selection for all files" checkbox is checked and then set the "Representation:" drop-down box to "I vs. Ewe vs" and click the "OK" button. If you had to do this step, do not forget to then choose "Graph Properties".)

(3) In the "Custom Graph Style" region choose the "Units" tab and set the "Current" to "µA" by first checking the checkbox. (To make any edits in this and the following steps, first you will have to check the appropriate checkbox.) Also, make sure that the "Potential" is set to "V", which it already should be. Then click the "OK" button to set this change.

(4) Go back to "Graph Properties" and in the "Custom Graph Style" region choose the "Axes" tab and set the "X-axis" sub-tab "Scale:" to -0.5 to +0.7 V and the "Y1-axis" sub-tab "Scale:" to -15 to +15 µA. If you did not change the current units to "µA" as per the previous step, this would set the range to a different unit and your graphs would not show up clearly.

(5) Before clicking the "OK" button, also change the "Y1-axis" sub-tab "Title:" to "I, uA" and the "X-axis" sub-tab "Title:" to "Ewe, V vs. Ag/AgCl (KCl sat'd)". To ensure that the legend is shown, also choose the "Graph" tab and make sure that the "Legend" checkbox is checked. Then click the "OK" button to set these changes.

(6) Save your graph of the 6 plots (only 4 should be visible on this scale, meaning that 2 of them will look like horizontal lines) by choosing from the menu bar at the top left "Edit", "Copy Graph Advanced…" (at the bottom), "as Metafile", and then click the "Save…" button, enter a meaningful filename for the figure, making sure the file type is "Enhanced Metafiles (*.emf)", and then click the "Save" button, followed by the "Close" button.

(7) Remove the first 4 datasets by clicking on the "Selector" button located in the toolbar at the top middle (logo of a white piece of paper with I and E on it and check marks), and selecting each dataset and clicking the "Remove" button, four times in total, followed by clicking the "OK" button.

(8) Zoom in on the anodic current branch by using the "Zoom +" button located in the toolbar at the top (logo of a magnifying glass and a plus on it) until the current is small enough to see differences between the final 2 simulations.

(9) Re-set the x-axis range to the values from the step above.

(10) Save your graph of the 2 plots (both should be visible in one range; if they are not, try simulating them again by re-entering the value for the electrode "Radius") by choosing from the menu bar at the top left "Edit", "Copy Graph Advanced…" (at the bottom), "as Metafile", and then click the "Save…" button, enter a meaningful filename for the figure, making sure the file type is "Enhanced Metafiles (*.emf)", and then click the "Save" button, followed by the "Close" button.

(11) Save your entire workspace by choosing from the menu bar at the top far left "Experiment", "Save Settings As…", enter a meaningful filename for the workspace, making sure the file type is "EC-Lab settings file (*.MPS)", and then click the "Save" button.

Part F: Simulating data – Electrochemical Impedance Spectroscopy

(1) Go to the "Analysis" menu bar at the top and choose "Electrochemical Impedance Spectroscopy", "Z Sim…".

(2) If it is not already selected, set the "Equivalent circuit selection" drop-down box to the typical Randles circuit, which consists of a resistor in series with a parallel capacitor and resistor titled "R1+C2/R2". *Click the "Edit" button to access the "Equivalent Circuit Edition", which allows you to see the equivalent circuit model as well as diagrams of how each circuit element is manifest in the Nyquist plot; play around! Then click the "OK" or "Cancel" button at the bottom to close the editor and return to ZSim.* If you cannot see those buttons, maximize the window, or close it using the "X" in the upper right.

(3) In the "Set Sampling" region at the bottom, set "f_i" to 1 "MHz" and "f_f" to 0.01 "Hz" with "10" points "per decade" in "Logarithm" spacing, for a total of ~80 points. The screenshot to the right shows the EIS simulation dialog box.

(4) Create Nyquist plots for the 4 specific circuit conditions indicated in the table below, by typing the values into the table, clicking the "Calculate" button, and then clicking the "Close" button. If you do not see the result of your simulation in the plot at the right,
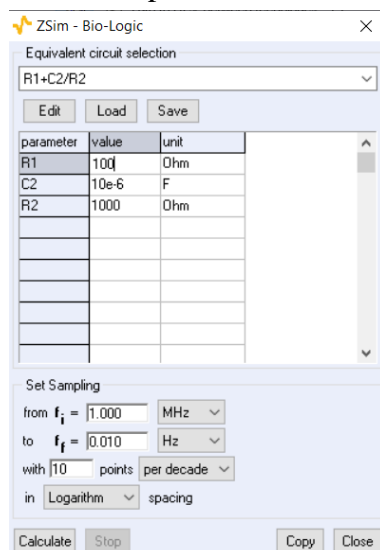
remove the last 2 CV datasets by clicking on the "Selector" button located in the toolbar at the top middle (logo of a white piece of paper with I and E on it and check marks), and selecting each dataset and clicking the "Remove" button, two times in total, followed by in the "Variables" region at the right, making sure that the "Same selection for all files" checkbox is checked and then setting the "Representation:" drop-down box to "Nyquist Impedance" and clicking the "OK" button.

(5) Right click on the plot and choose "Save Data File As…" and enter a meaningful filename for the dataset, making sure the file type is "EC-Lab text files (*.MPT)", and then click the "Save" button. (If this step does not work, click on the name of the dataset in the legend at the top of the plot, likely in blue and named "-Im(Z) vs. Re(Z)". Although there will be no indication that this did anything, it makes that dataset active and should fix any problems with saving the file; when you have more than one dataset in your plot, a "#" will appear to the right of the name of the selected dataset in the legend.)

(6) Again, because the software is a bit buggy and/or I am a bit novice at using it, you must remove that single dataset by right clicking on the plot and choosing "Remove Trace" (which is also "Alt+R"). *Oddly, this cannot be performed using the "Selector" button located in the toolbar at the top middle (logo of a white piece of paper with I and E on it and check marks).*

(7) Repeat Step 1 for the next entry in the table below.

EIS Experiment Name	R1	C2	R2
F1) Standard conditions	100 Ohm	10 μF	1000 Ohm
F2) Entry F1, *modified with a 2 times faster rate of interfacial charge transfer*	100 Ohm	10 μF	500 Ohm
F3) Entry F2, *modified with a 5 times larger ECSA*	100 Ohm	50 μF	100 Ohm
F4) Entry F3, *modified with a 10 times smaller concentration of supporting inert electrolyte*	1000 Ohm	50 μF	100 Ohm

Part G: Manipulating plots, Part 2

(1) Plot another graph showing all 4 Nyquist plots by right clicking on the graph and choosing "Load Files…", selecting all 4 files while holding down the "Shift" key, and clicking the "Open" button. In the "Variables" region at the right, make sure that the "Same selection for all files" checkbox is checked and then set the "Representation:" drop-down box to "Nyquist Impedance" and click the "OK" button.

(2) Right click on the graph, which should contain 4 plots, and choose "Graph Properties". If not already the case, label each plot with a different color and make sure that the legend is shown on the graph.

(3) Save your graph of the 4 Nyquist plots using the procedure in Part E, Steps 10 and 11.

Assignment 1 – e-Lab 1 *(due on Monday, October 16, 2023 at noon (extended deadline))*

Because this is not a laboratory 101 class, and our roster contains students who are not graduate students in the Department of Chemistry, Prof. Ardo does not require that your assignment include a formal lab report. Instead, simply turn in a Word document that contains your name, the name(s) of anyone you worked with on this assignment, and the three figures that you saved above (one with 6 CV plots where only 4 were clearly visible, one with 2 CV plots, and one with 4 Nyquist plots). Also, answer the following question:

1. The standard alkaline primary battery undergoes solid-phase reactions (i.e. there are few soluble redox species). Answer the following questions based on the main redox chemistry that occurs in these batteries, i.e. $Zn^{2+/0}$ and $Mn^{4+/3+}$ (and where the oxidized form of the ions are $ZnO(s)$ and $MnO_2(s)$).
   a. Use the Pourbaix diagram from class to identify the main Mn redox species present <u>under alkaline conditions</u> and then balance the overall cell reaction. Show work.
   b. Write the cell reactions using line notation. (Recall that the anode is on the left, and assume a salt bridge is present between the anolyte and the catholyte.)
   c. Calculate $E°_{cell}$ (V) and $\Delta G°$ (J), using the CRC Standard Reduction Potentials table for the Zn redox potential and the Pourbaix diagram for the Mn redox potential.
   d. Identify the reducing agent and oxidizing agent, during galvanic discharge.
   e. Over what pH values will oxidation of $MnO_2(s)$ result in an aqueous reaction product?