FABRICATING ELECTRODES AND USING A POTENTIOSTAT TO PERFORM CYCLIC VOLTAMMETRY

General Schedule and Comments

In general, the format for this "discussion" session will be the same every week and is as follows:

1. Present brief outline of experiments, goals, and updates
2. Break into groups of two or three, set-up work space, and connect to the BioLogic potentiostat using the EC-Lab software on a PC laptop
3. Perform experimental procedure(s), while being assisted by the Instructor
4. If time permits, as a class provide feedback on the activity and recommend other activities
5. Clean-up work space, return items, and store electrodes for subsequent weeks. *(You are not dismissed from the discussion section until this is complete.)*

Since your discussion sessions are short (110 minutes) and we want to get as much out of them as possible, please use your time wisely by getting started promptly and working efficiently. *It is recommended that you save or print procedures and reference publications/files before you watch the experiment video and attend the hands-on discussion sections. This will help you to become acquainted with the experiment, formulate questions to ask during the discussion session, and will allow you to stay connected to the potentiostat as you run the experiments, because there are sometimes issues when the Internet and the potentiostat are used simultaneously.* This week there is an additional pre-lab assignment consisting of a short (~5 min) survey via a link that was emailed to you through Canvas Announcements; please complete it.

Introduction

Last week you learned how to control the potential (voltage) and current of electrodes and plot and analyze data using a software program that is freely available online, EC-Lab. EC-Lab controls a potentiostat from BioLogic, the instrument that allows us to perform electrochemical measurements. This week, you will be introduced to the potentiostat, you will fabricate the materials needed to perform basic electrochemical measurements – namely the electrodes – and you will test their activity. Notably, you will construct working electrodes – based on inert carbon and platinum materials, reference electrodes – based on silver, and a counter electrode – based on carbon. These electrodes will be used throughout the course, so it is important to learn best practices to take care of them and how to fix them when necessary.

Purpose

The purpose of this hands-on discussion activity is to learn how to construct and use electrodes that are central to this course. You will prepare one of each of the following electrodes: platinum ultramicroelectrode (UME), carbon button electrode, carbon cloth electrode, and two silver | silver

chloride (Ag/AgCl) reference electrodes. After you are finished constructing your electrodes, you will use them to perform cyclic voltammetry experiments using an aqueous redox shuttle. This will provide you with hands-on experience using the software, potentiostat, and the electrodes, as well as visualizing, manipulating, and analyzing actual electrochemical data.

Safety

As a pre-lab assignment, watch the safety video titled "Lab Techniques & Safety: Crash Course Chemistry #21" located at https://youtu.be/VRWRmIEHr3A. For each hands-on discussion session you must bring personal protective equipment consisting of a lab coat and safety glasses/goggles. In addition, at a minimum you must wear closed-toe shoes, pants, and a tee-shirt that covers your entire torso. Attendance at these hands-on discussion sessions are mandatory so please do not get a grade of a zero due to improper lab attire. While in lab you will need to wear gloves, which we will supply as nitrile gloves. In addition, to reduce the possibility of electric shock to you and your labmates be sure to control the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment. Lastly, the soldering iron and liquid solder are hot and can easily burn. Thus, please use care and take caution when soldering. Melt solder and mix epoxy only in a well-ventilated area (i.e. fume hood) and wash your hands after use.

Procedures

Part A: Connecting to the potentiostat (Windows PC only)

These directions have been adapted from page 15 in the "VSP Installation and Configuration Manual" found under **Help** in the main tool bar of EC-Lab (the potentiostat software).

(1) Go to your network and or adapter settings page. In most Windows operating systems, go to Network and Internet, Network Connections (either by searching or through the control panel). Then, right click and select Properties for your Ethernet connection. A new window will open.

(2) In the middle of the new window, under "This connection uses the following items:" double click "Internet protocol version 4 (TCP/IP4)" or click the "Properties" button. A new window will open.

(3) Select the radio button for "Use the following IP address:". Then, under "IP address:", input the following IP address 192.109.209.XXX, where XXX is a number assigned to you. The group using potentiostat channel 1 will use XXX = 111, for channel 2 use XXX = 121, for channel 3 use XXX = 131, and so on. Channels are numbered down each column as 1, 2 and then 3, 4, 5. You may have to enter a "Subnet mask:" as "255.255.255.0", but those numbers should populate automatically, if necessary.

(4) Open the EC-Lab software. In the "Devices" box, you should not see any online devices. If you see any with a red signal before the name of the device, select the device and press the red "–" to delete the device.

(5) Click on the blue "+" to add the VSP device with IP address ending in ".128."

We set a different IP address for each device connecting to the potentiostat because no two devices (computers and/or potentiostat) may have the same IP address. (You may also have to disable your Wi-Fi while using the instrument.) Since we set the IP address of your computer to a local area connection you will most likely be unable to access the Internet while using the potentiostat. After you are finished in lab, return your Ethernet connection to "Obtain an IP address automatically" instead of "Use the following IP address" to access the Internet as you normally do.

Part B: Constructing a Platinum (Pt) Electrode

Tools/materials needed: high-purity water, platinum wire, tinned copper wire, metal tweezers, helping hands, solder, flux, soldering iron, wire cutters, epoxy, wooden rod, disposable weigh boat

(1) Strip ~1 cm of plastic insulating coating from each end of the tinned copper wire (~11 cm in length) using a wire cutter/stripper. Stripping the coat allows you to make an electrical connection to the wire and to solder the wire to something else.
(2) Have a lab partner or a helping hands hold the wire. In another hand/helping hands clamp the thin platinum wire (~2 cm in length; ~0.3 mm in diameter) and bring it into contact with the exposed tinned copper wire. There should be a minimal amount of overlap (~2 mm). *(You will be given one piece of expensive platinum wire so please do not lose it.)*
(3) Place the hot soldering iron adjacent to the overlapped material, making sure not to place it too close to the plastic coating because it will melt and burn. Hold in place for a few seconds and then bring the solder to the hot overlapped section. Allow the solder to melt and join the materials. If the solder is not wetting well, dab some flux onto the wire and try again.
(4) Allow the solder to cool in place for about 10 seconds. Then, using tweezers, tug the platinum wire gently to determine whether it is bonded to the wire. If the platinum comes off then you must repeat the soldering step until it holds.
(5) At the end of the lab we will cut off most of the platinum wire and return the excess to your Instructor. Then you will apply epoxy over all exposed portions of the tinned copper wire, solder, and platinum so that it is fully covered and hang the wire with tape to allow the epoxy to cure/dry.

Part C: Constructing a Carbon (C) Rod Electrode

Tools/materials needed: carbon rod, ruler, sandpaper, epoxy, wooden rod, disposable weigh boat

(1) Take a carbon rod (3 mm in diameter) and break off a 6 cm piece using gloved hands. You will use this as one of your carbon electrodes.
(2) Sand the ends until they are flat.
(3) At the end of the lab you will apply epoxy over the length of the rod leaving only the circular-face free from epoxy and hang the rod with tape to allow the epoxy to cure/dry.

Part D: Constructing a Carbon Cloth (CC) Electrode

Tools/materials needed: high-purity water, carbon cloth, scissors, tinned copper wire, needle-nose pliers, wire cutters, epoxy, wooden rod, disposable weigh boat

(1) Prepare a piece of tinned copper wire like you did for construction of the platinum electrode.
(2) Cut a ~1 cm by ~3 cm piece of carbon cloth using scissors.
(3) Push the exposed tip of the tinned copper wire through the short side of the carbon cloth electrode and bend it with needle-nose pliers to hook the carbon cloth. Squeeze the hook with the pliers to flatten it and more firmly hold the carbon cloth in place.
(4) If possible, carefully solder the junction of the tinned copper wire and the carbon cloth.
(5) At the end of the lab you will apply epoxy over all exposed portions of the tinned copper wire, including the top of the carbon cloth, and hang the wire with tape to allow the epoxy to cure/dry.

Part E: Constructing Silver – Silver Chloride (Ag/AgCl) Reference Electrodes

Tools/materials needed: high-purity water, 1 M NaCl (aq) or household bleach, silver wire, sandpaper, wire cutters, another electrode from above, cleaned scintillation vial, 1 mL plastic syringe, small cork, agarose, 250 mL Erlenmeyer flask, 250 mL beaker

(1) Prepare two (2) Ag/AgCl reference electrodes per the following procedure, which is similar to those reported here:

Electrode preparation (Figure 4.15)
High-purity silver wire (>99.999% Ag) preparation. High-purity silver wire will have an oxide on its surface that must be removed before use. This can be accomplished by dipping (41) the wire in 0.1 M HNO_3 for a few seconds. The wire should be rinsed with 18 MΩ cm water prior to use in subsequent steps.

Anodic AgCl coating (42). The freshly cleaned silver wire can be chloridized by placing it in a compartmentalized cell containing 0.1–1 M HCl or KCl and applying 0.4 mA/cm^2 current for 30 min. The coated wire should be washed with 18 MΩ cm water and soaked for 1–2 days in 18 MΩ cm water. The color of the AgCl should be sepia (dark brown with a reddish tint) if chloridized in the absence of light or pale tan to brown if chloridized while exposed to a light source. After washing, the coating color will range from pink to a shade of plum.

■ **PREPARATION OF THE ELECTRODE**

Electrode Body and the Salt Bridge

The electrode is housed in an autopipettor tip. The salt bridge consists of an agarose gel with predissolved inert electrolyte. The gel composition consists of 7 g of agarose, 500 mL of water, and 25 g of KNO_3. This mixture is heated and stirred to dissolve the agarose. The hot mixture is transferred to a large beaker; the depth of the solution in the beaker is 1−2 cm. The autopipettor tips are placed upright in the beaker and the mixture is allowed to cool and gel for a minimum of 24 h. Hundreds of autopipettor tips containing agarose are prepared prior to the laboratory session and made available to students.

The chemical deposition of AgCl(s) onto Ag(s) by use of laundry bleach has been described.[7,8] In a small beaker, equal volumes of the laundry bleach and $AgNO_3$(aq) are mixed. Silver wires (5−6 cm in length and about 1 mm in diameter) are placed vertically into this solution, which is in contact with about $^2/_3$ of the bottom of each wire. Chemical deposition takes approximately 30−50 s to give a coating of AgCl (s). The AgCl(s)|Ag (s) wire is placed into the autopipettor tip with ~1 mL of 3.0 M (aq) KCl, so that the wire is in contact with the KCl(aq) but not the agarose gel; see Figure 1. A small cork is fitted into the autopipettor tip to keep the wire in a fixed position and to allow easy connection to the voltmeter.

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(2) *If not already prepared by your Instructor*, as a class prepare fitted reference electrode tubes.

a. Into a clean 250 mL Erlenmeyer flask pour ~50 mL of high-purity water and add 1 g of agarose (~2% w/w).
b. Dissolve the agarose by microwaving the mixture for 1 min on a high setting.
c. Remove the plungers and cut off the top "wings" from 20 plastic syringes (1 mL).
d. In a clean 250 mL beaker place the plastic syringes in an upright position so that the tips of the syringes are touching the base of the beaker.
e. Pour the 2% agarose solution into the beaker containing the syringes, so that all syringes are filled to the 0.2 mL mark with the agarose solution.
f. Wait approximately 20 min for the agarose solution to turn into a gel, which serves as the salt bridge for ion transport.

(3) Take the silver wire (~6 cm in length) and clean it by sanding lightly. Then, rinse the electrode with water. (Try not to contaminate the silver with dirty gloves (e.g. oils or grease) or by placing it on surfaces (i.e. dust) as it can impede the chloridizing reaction.)
(4) Set-up a two-electrode electrochemical cell in the pre-rinsed vial to chloridize the silver wire using one of the other electrodes that you made and a chloride-containing solution (either 1 M NaCl (aq) or 1 M KCl (aq) or 5% hypochlorite (aq)). Apply a potential bias sufficiently large to chloridize the electrode (90 sec at 4 V should suffice).
(5) Take one fritted plastic syringe prepared above and fill it with 1 M NaCl (aq) or 1 M KCl (aq) solution.
(6) Place the visibly chloridized Ag wire in the solution, such that the chloridized end is in contact with the solution and uncoated Ag end is sticking out from the top of the syringe. (This end will be used to make electrical contact with the potentiostat reference electrode lead.)
(7) Plug the top of the syringe with a small cork or rubber septum to prevent electrolyte from leaking, but allow the Ag wire to stick out at the edge.
(8) If you have time at the end of the lab session, prepare another reference electrode by repeating the above steps. It will be useful for a future activity held during another class.

<u>Part F: Cyclic Voltammetry of Ferricyanide/Ferrocyanide</u>

The goals of this portion of the experiments are to determine the potential ranges necessary to observe redox behavior, to obtain a good quality cyclic voltammogram, to compare behavior at different scan rates and with/without forced convection (i.e. stirring). The reported standard reduction potential for the ferricyanide/ferrocyanide redox couple is approximately +0.45 V *vs* SHE.

Tools/materials needed: high-purity water, aqueous solution containing redox couple and K_2SO_4 electrolyte, cleaned scintillation vial or ~50 mL beaker, vial cap with *predrilled* holes or septum and small gauge (large opening) needle, stir plate, stir bar

(1) *If not already prepared by your Instructor*, as a class prepare a ~100 mL aqueous solution containing 10 mM ferricyanide ($[Fe^{III}(CN)_6]^{3-}$) salt, 10 mM ferrocyanide ($[Fe^{II}(CN)_6]^{4-}$) salt, and 0.5 M K_2SO_4.

(2) Set-up a three-electrode electrochemical cell using a pre-rinsed vial or small beaker half-filled with the ferricyanide/ferrocyanide solution as the electrolyte. Think about which electrodes from above make the most sense to be used in this experiment and write this information down, in addition to all other information that is not recorded by the software during the experiment. Carefully place the electrodes through a vial cap with *predrilled* holes for the electrodes, including one large hole for the reference electrode and carbon rod, or a rubber septum where electrodes and wires are threaded through the septum, and attach the alligator clips from the potentiostat to the electrodes making sure they are not in electrical contact with one another.

(3) Set-up EC-Lab to perform a two-step experiment consisting of an OCV followed by a CV. Determine the parameters and potential range necessary to observe the complete redox behavior for the redox couple during the CV. This can be done in a "quick and dirty" run where you change the potential window in real time to capture its complete behavior. Before starting the experiment, triple check all wire connections. Also, the first time you perform an electrochemical measurement on a specific cell setup, be prepared to stop the experiment quickly if unexpectedly large currents result or if the system overloads, likely due to bubbles present in the reference electrode tip. **Also, don't forget to click the key image to edit the options in real-time.**

(4) Using these parameters, or adjusted ones, perform a 1 min long OCV, followed by 2 cycles of CV at each of the following scan rates: 1000 mV/s, 100 mV/s, and 20 mV/s. If the OCV reading seems odd, stop the experiment and troubleshoot the cause of the behavior with your labmates and Instructor. For your report *(due in two weeks)*, plot these CVs as *I vs E*, *I vs* time, and *E vs* time.

(5) While stirring vigorously on a stir plate, with the stir bar close to the WE, repeat the previous experiments. For your report *(due in two weeks)*, plot these CVs as *I vs E*, *I vs* time, and *E vs* time.

Part G: Finishing Electrode Construction

(1) Mix the two-part epoxy (e.g. LOCTITE Hysol 1C) in amounts recommend by the manufacturer (ideally by mass: 44:100 (beige:white), but otherwise by length/volume: 1:2.5 (beige:white)) using a disposable weigh boat to hold the epoxy and a toothpick to mix it *thoroughly*. Mix this in the hood as small amounts of fumes are given off during the mixing process.

(2) As noted above, apply the epoxy to dry electrodes making sure to cover all exposed wires that should not contact electrolyte.

(3) Using tape, affix the electrodes to a ledge of the Instructor's cart so that they can cure over the week.

(4) The tip of the reference electrode should always be immersed in an aqueous solution of the electrolyte used to make the reference electrode. Take a centrifuge tube and fill it with 5 mL of the electrolyte solution. Always store the reference electrode in this tube with the tip immersed into the solution.

(5) Between classes, all electrodes can be stored in one of the drawers in the lab. Get a lock from the stockroom for the drawer that you plan to store your electrodes. As you (might) know, it is best to store the reference electrodes in the dark. (*Why?*)

Assignment 2 – Lab 2 *(combined with next week's activity; due on Monday, October 23, 2023 at noon)* (You must show your work for credit on all problems.)

1. Using the data provided to you for Lab #2, do the following. Assume that the concentration of ferrocyanide ($Fe^{II}(CN_6)^{4-}$) was 10 mM, ferricyanide ($Fe^{III}(CN_6)^{3-}$) was 10 mM, and K_2SO_4 was 500 mM, and that you used the button electrode (i.e. epoxied and polished carbon rod) for your measurements, with a well-defined geometric area of 7 mm^2.

a. Submit *three plots* displaying the CV data in the absence of stirring (as *I vs E* (plot 1), *E vs* time (plot 2), and *I vs* time (plot 3)), where each plot includes the data taken for the various scan rates. If possible, use the EC-Lab software to generate the plots.

b. Repeat part a but with the CV data in the presence of stirring.

c. Diffusion coefficients can be calculated from the peak currents measured in a cyclic voltammogram. Plot the peak current *vs* the square root of the scan rate for the anodic *and* cathodic processes of each cyclic voltammogram *and* use the Randles–Sevcik equation *(Google it)* and the slope of the data to calculate the diffusion coefficient for $Fe^{II}(CN_6)^{4-}$ *and* $Fe^{III}(CN_6)^{3-}$. Submit the plots as part of your answer.

d. Explain what stirring did to mass transport of the redox-active species *and* in your answer indicate what terms dominated the flux *toward* the electrode (i.e. outside of the boundary layer) *and at* the electrode surface (i.e. within the boundary layer).