Overview: Three-electrode setup

The following electrodes are used in a three-electrode setup:

- **Working electrode (WE, red wire)**
  - ***Purpose***: The potential at the working electrode is either scanned or held constant to perform electrochemical transformations in the analyte solution.
  - ***What is used***: For analytical scale applications, the working electrode is most commonly a **glassy carbon (GC) disk**. Metallic disks (Pt, Au, Ag, Cu, Ni), boron doped diamond (BDD) or edge plane pyrolytic graphite (EPPG) disks can also be used as alternatives to glassy carbon in niche situations where different electrode-specific reactivity is desired.
  - Working electrodes may be purchased either from Pine Research (Catalog number AFE1B030GC for a 3 mm diameter glassy carbon disk, https://pineresearch.com/shop/products/electrodes/working-electrodes/e1b/) or CH Instruments (Catalog number CHI104 for a 3 mm diameter glassy carbon disk, http://www.chinstruments.com/accessories.shtml).
- **Reference electrode (RE, white wire)**
  - ***Purpose***: The reference electrode provides a well-defined redox couple that electrochemical processes occurring at the working and counter electrodes can be compared against.
  - ***What is used (non-aqueous)****:* In non-aqueous conditions, **Ag/Ag^+ reference electrodes** are typically used, with $AgNO_3$ as the Ag^+ salt.
  - ***What is used (aqueous)****:* In aqueous conditions, a saturated calomel electrode (SCE), standard/normal hydrogen electrode (SHE/NHE), or Ag/AgCl electrode can be used.
  - High quality non-aqueous Ag reference electrodes may be purchased from Pine Research (Catalog number RREF0153L2, https://pineresearch.com/shop/products/electrodes/reference-electrodes/lowprofile-35mmod/rref0153l2-miniature-ag-pseudo-ptfe-60-mm-long/) and perform better than those available from other vendors.
- **Counter electrode (CE, blue wire)**
  - ***Purpose***: The counter electrode (CE) performs an opposite electrochemical process to what is happening at the working electrode; oxidation/reduction at the WE means reduction/oxidation is taking place at the CE. In this way, the CE completes the circuit within the full electrochemical cell.
  - ***What is used***: For analytical scale applications, the counter electrode is almost always a **platinum wire.**
  - Platinum wire counter electrodes may be purchased from either Pine Research (Catalog number RRPG257PT, https://pineresearch.com/shop/electrodes/counter-electrodes/lowprofile/ or CH Instruments (Catalog number CHI115, http://www.chinstruments.com/accessories.shtml)

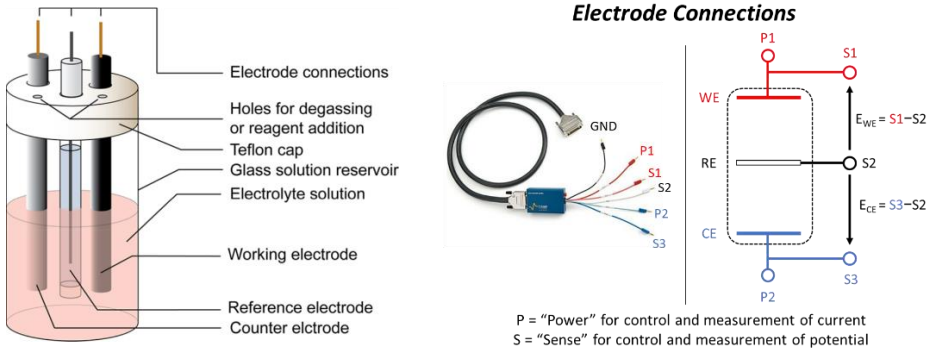
Assembly: Electrochemical cell and electronic connections

- All three electrodes are fit with correspondingly sized O-rings so they can rest upon a Teflon cap set into a glass electrochemical cell. All electrodes should be submerged in analyte/electrolyte solution and should ideally be level with each other.
- Electrical leads from the potentiostat should be assembled such that power pins are plugged into sensor pins of the same color (e.g. red power pin P1 is plugged into red sensor pin S1, blue power pin P2 is plugged into blue sensor pin S3). Each sensor pin is then plugged into an alligator clip

of the same color which connects to the corresponding electrode lead. The black ground lead (GND) should always be plugged into its own cap.

- The red wire connects to the working electrode, the white wire to the reference electrode, and the blue wire to the counter electrode.

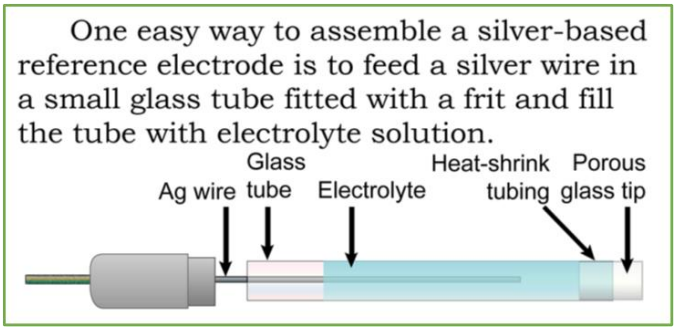
Basic assembly and electrical connections should be made according to the figures below.



Left: Three-electrode setup, taken from Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206.
Right: Electrode connections and electronics schematic, adapted from Installation and Configuration Manual for VMP-300-based Instruments and Boosters, Biologic Science Instruments, pages 44-45.

Assembly: non-aqueous Ag/Ag^+ reference electrode

- The non-aqueous Ag/Ag^+ reference electrode consists of two parts: a thick silver wire set into a Teflon electrode housing and a glass electrode capillary with a porous Vycor tip.
- The glass capillary should be filled about half to two-thirds of the way full of reference electrode solution (10 mM $AgNO_3$ and 100 mM electrolyte in desired solvent). To avoid getting gas bubbles in the capillary, it is best to use a long glass pipette in this step, slowly filling the capillary from the bottom and moving the pipette tip upwards while filling.
- Once the capillary is filled, it can then be snugly fit into the Teflon electrode housing. When the reference electrode is fully assembled, carefully and thoroughly wipe down the outside of the glass capillary and dab the Vycor tip with a Kimwipe to minimize $AgNO_3$ contamination of the analyte/electrolyte solution in main electrochemical cell.

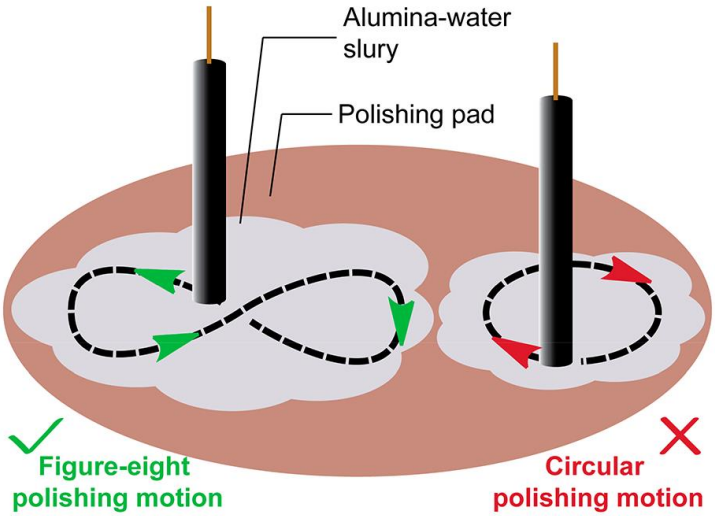


Non-aqueous Ag/Ag^+ reference electrode assembly, taken from Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206.

Preparation and maintenance of electrodes

Polishing the working electrode:

- Place 2-3 drops of an alumina-water slurry on the coarser (gray colored) polishing pad. While holding the working electrode upright, lightly press it down onto the drops of alumina-water slurry and trace a figure-eight pattern on the polishing pad for approximately 30 seconds. Repeat this procedure on the smoother (white colored) polishing pad.
- After mechanical polishing, thoroughly rinse the electrode surface with deionized or MilliQ water to remove alumina particles and then rinse with methanol to ensure the electrode surface dries. Sonication in deionized water can also be helpful in removing stubborn particles adsorbed to the electrode surface, but is not always necessary.
- Consider running a few scans in simple electrolyte solution over a wide potential window to "pretreat" the electrode and remove stubborn particles adsorbed to its surface, looking for successive scans to perfectly map onto each other. This is not always necessary but can be helpful in instances where substantial electrode fouling is known to occur.



Procedure for polishing the working electrode surface, taken from Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206.

Polishing the Ag reference electrode:

- Prior to use, lightly polish the surface of the Ag reference electrode with 600 grit sandpaper to remove tarnish.
- Afterwards, wipe the electrode with a methanol-wetted Kimwipe to remove particulates.

Cleaning the reference electrode capillary:

- To remove metallic silver and metal complexes adsorbed to the Vycor frit, soak the capillary in a vial of dilute nitric acid overnight.
- Thoroughly rinse the capillary with deionized or MilliQ water and soak the capillary in acetonitrile, or whatever solvent is being used for analysis, overnight. This will aid in minimizing junction potential and drift in potential measurements during the experiment.

Polishing the counter electrode:

- Any surface corrosion of a Pt wire counter electrode can be removed with brief exposure to acid.
- Afterwards, thoroughly rinse the counter electrode with deionized or MilliQ water, and then wipe with a methanol wetted Kimwipe.

Chemical Considerations:

Preparation of analyte solution

Prepare at least **5 mL** of solution according to the following specifications:

- **Analyte (compound of interest) in ~ 1 mM concentration is typical**. The exact concentration can vary, but for analytical scale techniques such as cyclic voltammetry this should be at least 0.1 mM and not exceed 2.0 mM.
- **Electrolyte in 100 mM concentration**. A sufficient electrolyte concentration is necessary for efficient charge transport in solution. Solutions with less than 100 mM electrolyte have greater electrical resistance, which in cyclic voltammetry will manifest as broadened signals with increased peak-to-peak separation. Solutions with greater than 100 mM electrolyte are sometimes albeit rarely used when efficient electron transport (ET) kinetics are particularly crucial to the experiment.

Preparation of reference electrode solution

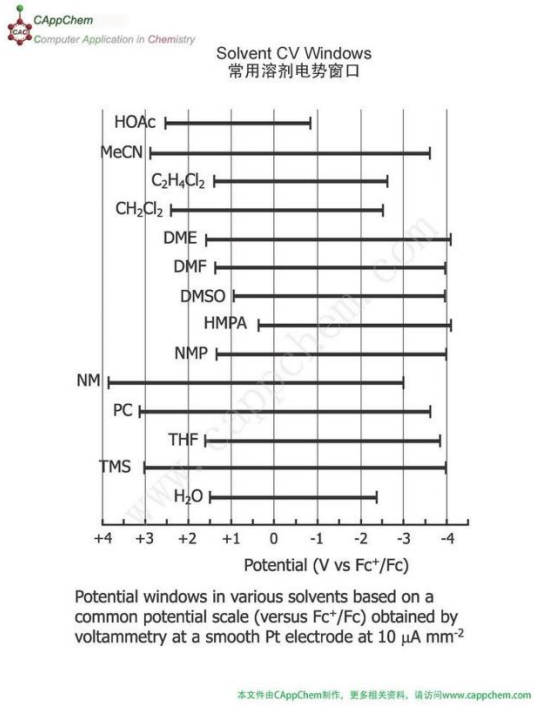
Prepare at least 10 mL of solution according to the following specifications:

- **$AgNO_3$ in 10 mM concentration.**
- **Electrolyte in 100 mM concentration.**

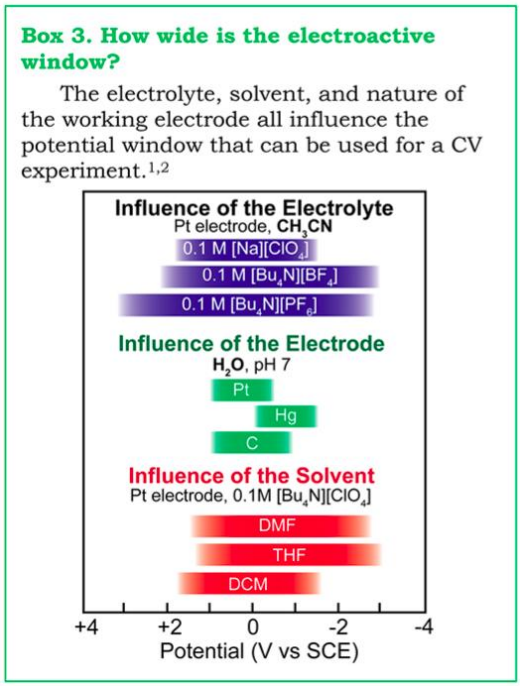
NOTE: $AgNO_3$ is light-sensitive. This solution should be stored in an opaque container and kept in a dark location to prevent photoreduction to metallic silver particles.
NOTE: If possible, aim to use the same solvent when preparing the analyte and reference electrode solutions, as this will minimize the junction potential between these components and assist in accurate measurements of potential. However, also realize that this is not strictly *essential*, as the use of an internal reference such as ferrocene allows for accurate comparison to other systems regardless of potential drift arising from different junction potentials.

Solvent and electrolyte considerations:

Solvent should be chosen according to the solubility of analyte and electrolyte and such that electrochemical processes of interest occur at potentials within the "electrochemical window," bounded by potentials where the solvent itself undergoes significant reduction or oxidation. Electrochemical windows of commonly used electrochemical solvents are given in the figure below.



Electrode and electrolyte identity can similarly impact the range of electrochemically accessible potentials. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) is a commonly used electrolyte due to its high solubility and very wide electroactive window.



Electroactive windows dictated by electrolyte, electrode, and solvent identities, taken from Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206.

Purification of Bu_4NPF_6 electrolyte

Since electrolyte is used is very high concentrations for electrochemical analysis, it is essential that the solid material is extremely pure. Bu_4NPF_6 can be isolated as a clean, crystalline solid according to the following procedure:

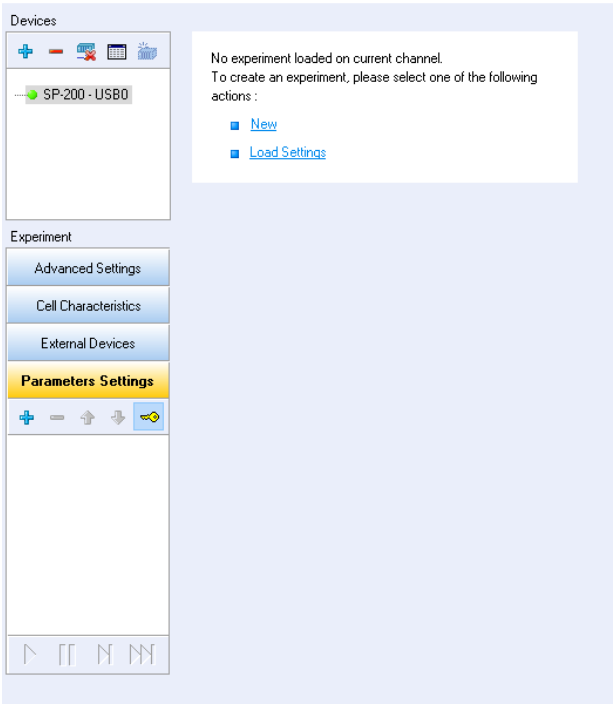
- Perform a thermal recyrstallization of Bu_4NPF_6 solid from EtOAc, using approximately 100 mL of EtOAc, heated just below its boiling point (77 ºC), per every 25 g of Bu_4NPF_6.
    - When the solid has fully dissolved, filter the solution through a medium or fine frit into a 250 mL filter flask. It is important that both the frit and the filter flask are oven dried and still warm during this step to prevent premature precipitation of Bu_4NPF_6 out of solution. When starting directly from commercially available material, it is not unusual to see light orange residue collected on the frit.
    - Allow ample time to let the contents of the filter flask cool to room temperature. Bu_4NPF_6 solid should crystallize as long white needles during this time.
    - Collect the crystallized Bu_4NPF_6 on a filter flask and wash with chilled EtOAc.
    - Perform this recrystallization procedure two more times to obtain triply recrystallized product.
- After recrystallizing Bu_4NPF_6 for a total of three times, dry the crystals under dynamic vacuum at 85ºC for *at least* 24 hours. Be aware that it can be difficult to fully dry the electrolyte to the extent that residual solvent does not interfere with electrochemical analysis.
- Test the purity of electrolyte by cyclic voltammetry, sweeping from -2 V to +2 V on a 100 mM solution of Bu_4NPF_6 in acetonitrile (CH_3CN). A pure sample should show a fairly narrow and flat waveform except at the curved ends of the voltammogram. A sample that still contains residual solvent and needs further drying will likely show an irreversible anodic feature at approximately +0.5 V to +0.6 V vs $Ag/AgNO_3$.

Bu_4NPF_6 solid obtained from thermal recrystallization with EtOAc.

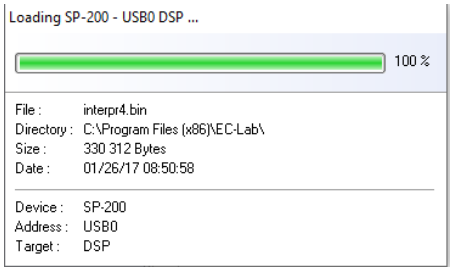
Instrument Operation

Connecting the potentiostat

- Turn on the potentiostat and wait for approximately ten seconds as it boots up. Then open EC-Lab from the computer desktop or taskbar.
- Typically, the instrument automatically connects to the computer and gives the following window:



- If the computer displays an error message and/or the potentiostat does not automatically connect, perform the following troubleshooting steps:
    - If "SP-200 – USB0" is listed as a device but has a red dot next to it, click the  button in the toolbar directly above to connect it. If successful, the following pop-up and loading bar will appear and the device will be connected.

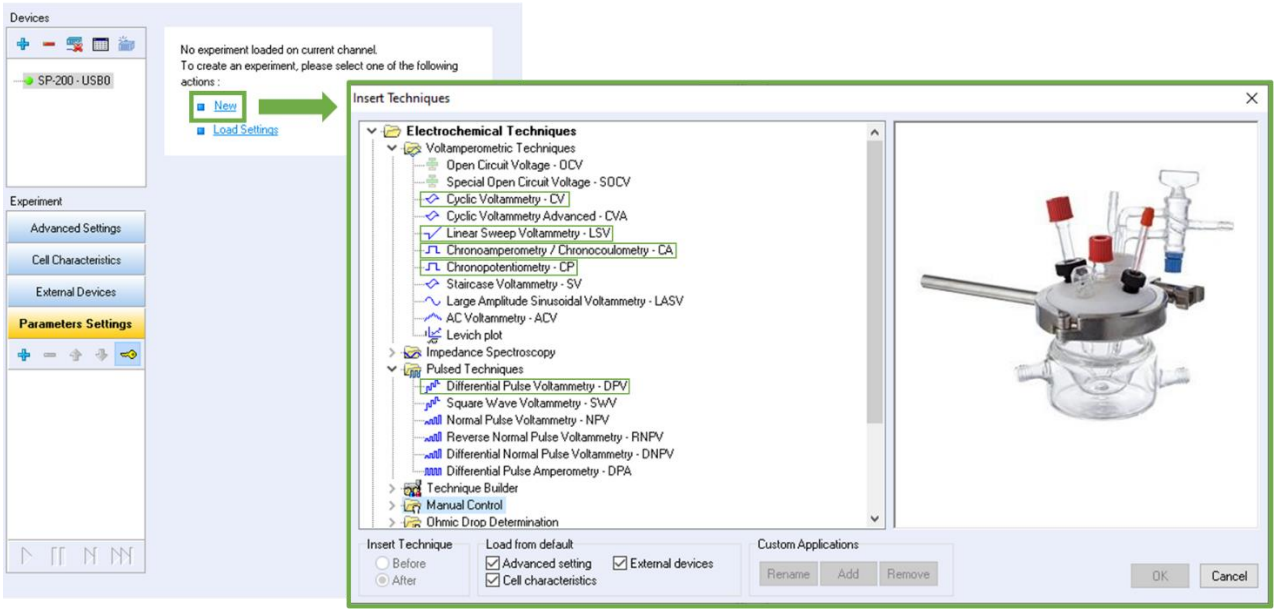


    - If this does not resolve the issue, exit EC-Lab and manually turn off the potentiostat. *Wait for at least 10 seconds* and then turn on the potentiostat again. Wait to hear a beep as the potentiostat reboots and then open EC-Lab again. Repeat these steps as necessary until the potentiostat connects and "SP-200 – USB0" is listed under the device column with a green dot to its left.

Technique selection

- Open the pop-up menu for Electrochemical Techniques by clicking on “New” in the start window. Alternatively, click “Load Settings” to use the same parameters from a previous experiment.
- Select the desired technique or previous experiment from the pop-up menu. From the Electrochemical Techniques menu, the following techniques are most commonly used in our laboratory:
    - Under “Voltammetric Techniques”
        - Cyclic Voltammetry – CV
        - Linear Sweep Voltammetry – LSV
        - Chronoamperometry/Chronocoulometry – CA
        - Chronopotentiometry – CP
    - Under “Pulsed Techniques”
        - Differential Pulse Voltammetry – DPV

Technique selection from the Electrochemical Techniques menu is outlined in the figure below.



Cyclic Voltammetry

From an initial value E_i, potential applied at the working electrode is adjusted at a constant scan rate υ to a first vertex potential E_1. Potential is then adjusted at a constant rate in the opposite direction to a second vertex potential E_2. This “cycle” can then be repeated as current is measured as a function of applied potential.

The current versus potential relationship (i vs E) is informative of many salient points, including redox potentials for electrochemical processes, the chemical and electrochemical reversibility of these processes, and in some cases can be used to infer the mechanism of sequential chemical and electrochemical steps within a process.

Main uses:

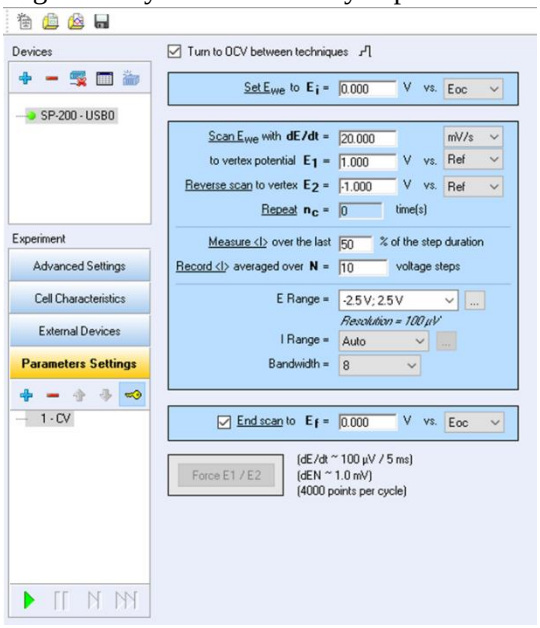
- Determining redox potentials
- Determining chemical and electrochemical reversibility
- Mechanistic insights into combined chemical and electrochemical processes

Tips for data collection:

- The analyte/electrolyte solution should be sparged with an inert gas for about one minute beforehand (if performing the experiment outside a glovebox) but should not be sparged or stirred during data collection.
- Collect a wide sweep voltammogram within the range of the electroactive window dictated by your solvent, electrolyte, and electrode material first. Then adjust vertex potentials E_1 and E_2 to collect data on individual redox events.
- It is a good idea to perform multiple cycles for each experiment (set n_c to at least 1).
    - Unless you are using advanced techniques to hold a certain applied potential prior to data collection, the first cycle will likely show currents arising from abruptly polarizing electrodes at the start of the experiment rather than true electrochemical phenomena. Reporting Scan 2 is usually a good way to avoid this issue.
- It is often worth it to collect voltammograms over a wide range of scan rates (try υ = 20, 50, 100, 250, and 500 mV/s).
    - Examining the peak current and peak separation versus square root of scan rate relationship can help determine the electrochemical reversibility of a process or identify cases where materials have adsorbed onto the electrode surface.
- When you are satisfied with data collection, use the tip of a glass pipette to add in a small amount of solid ferrocene to the analyte solution and mix well. Then collect another voltammogram, noting the redox potential of the ferrocene internal standard versus your Ag/Ag^+ reference electrode. Use this difference to report your data with respect to the Fc/Fc^+ redox couple.

Data acquisition parameters:

Default parameters upon selecting a new cyclic voltammetry experiment are shown in the figure below.



- E_i is initial potential at the working electrode. It can be set in reference to open circuit potential E_{oc} (the potential for which no current flows in the circuit) or Ref (the potential versus the Ag/Ag^+ reference electrode, and x-axis of the voltammogram that's directly shown in the user interface).
- dE/dt is the scan rate υ. Most commonly, 100 mV/s is used in reported cyclic voltammograms. This is still worth playing around with to get a sense for chemical/electrochemical reversibility in your sample and seeing how the waveform changes at different scan rates.
- Vertex potentials E_1 and E_2 dictate the window and scanning direction of the voltammogram. They can also be set versus E_{oc} or, more commonly, Ref.
- n_C is the number of times the cycle is repeated (for example, n_C=1 repeats once for a total of 2 scans). n_C of 1 or 2 is advisable.
- Parameters for measuring current over the last 50% of potential step duration and averaged over the last 10 voltage steps are typically reasonable and do not need to be adjusted from their default values.
- E Range marks the range of potentials that the potentiostat should consider for a given experiment. This can also affect the resolution of the voltammogram. Select a range that is appropriate for the experiment being performed.
- I Range determines how the potentiostat's amplifier behaves based on the expected current response. "Auto" can be functional, particularly when the expected current is not immediately known. This can be adjusted after collecting preliminary data to resolve "saw-tooth" signals.
- Bandwidth should be adjusted in niche cases where saw-tooth signals persist even after adjusting electrode configurations and I Range settings. Refer to page 57 of the Installation and Configuration Manual for VMP-300-based Instruments and Boosters, Biologic Science Instruments for further details.

Understanding the shape of the voltammogram

This is a brief, simplified explanation. See Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206 for further details.

An initial increase in (magnitude of) current can be understood from the Nernst equation. Considering the reduction from oxidized analyte (Ox) to reduced analyte (Red), this is:

$$E = E^{\circ} + 2.303\frac{RT}{nF}log\frac{[Ox]}{[Red]}$$

Notice E is being actively changed by the potentiostat throughout the experiment, so the ratio of [Ox] and [Red] located at the electrode surface also changes accordingly. The flow of electrons involved in the transformation of Ox to Red creates a measurable current, the magnitude of which increases dramatically as applied potential E approaches the constant, standard redox potential E^o.

Soon afterward, the continued passage of current requires that additional oxidized material freely diffuses from bulk solution to the electrode surface. This mass transport becomes slower over the course of the scan, so the measured current peaks and then decreases in magnitude. Once the vertex potential is reached, the same process occurs for the oxidation of reduced analyte Red to oxidized analyte Ox.

Realize that this is occurring at an extremely small scale localized to the electrode surfaces; cyclic voltammetry is an analytical scale technique rather than bulk scale process. Also realize that there are often exceptions to the classic "duck" shape when chemical reactions involving electrochemically-generated species occur on the time scale of the cyclic voltammetry experiment. Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206 also describes these situations in more detail.

Common issues and how to resolve them

Error: "E(WE) Overload on Channel 1"

- The measured potential difference between pins S1 and S2 lies outside the bounds set by the experiment

Solution:

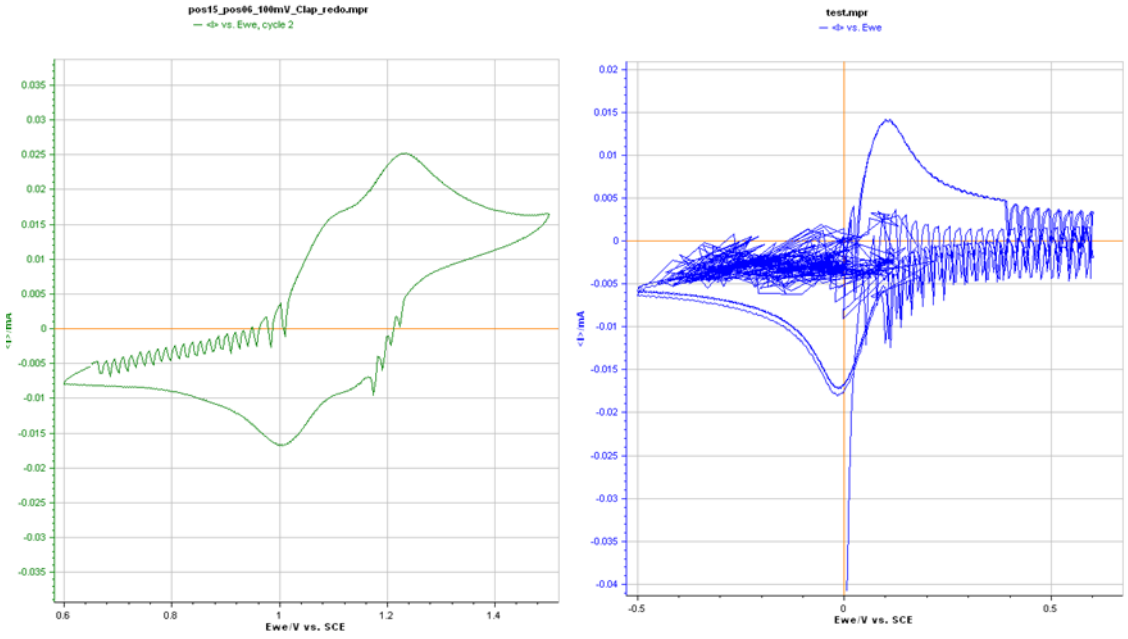
- Check that "E Range" is appropriately set on the user interface
- Physically adjust the working and reference electrodes, checking for the following:
    - Good electrical contact between pins, alligator clips, and electrode leads
    - Electrodes are submerged in solution
    - Electrodes are not touching each other or the counter electrode
    - Reference electrode capillary is filled, without gas bubbles, and the Vycor tip is clean (may require replacement of the capillary if issue persists)

Error: "I Overload on Channel 1," or a saw-tooth pattern on the voltammogram.

- There is either a connection issue or the settings chosen to measure current are inappropriate.

Solution:

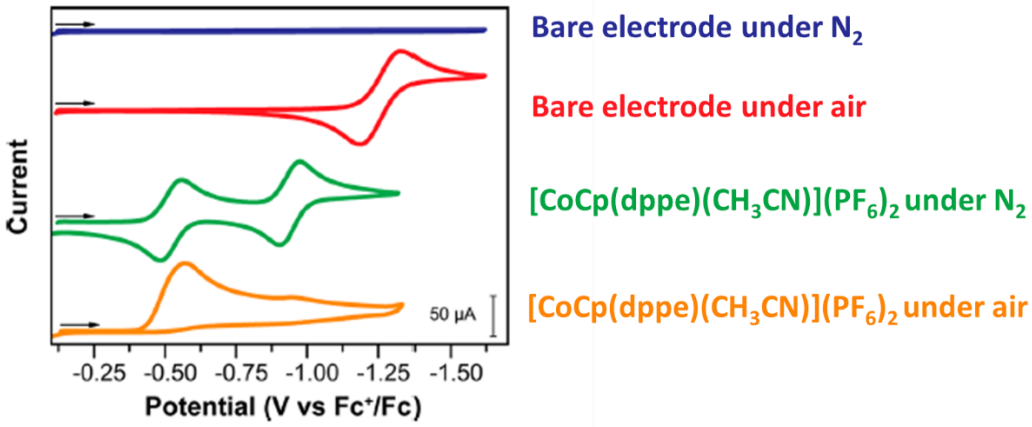
- Physically adjust the working and reference electrodes as stated "E(WE) Overload on Channel 1" solution.
- On the program's user interface, select a different I Range setting appropriate for the expected current response.
- If the other solutions do not work, change the Bandwidth setting from its default value of 8, testing other values to see if this resolves the issue. Refer to page 57 of the Installation and Configuration Manual for VMP-300-based Instruments and Boosters, Biologic Science Instruments for more details.
- If the issue persists, it may be an indication that something is wrong with the circuitry of the potentiostat. Consult with Rob McClain to test for this.



Examples of saw-tooth patterns in current responses, resolvable by changing the I Range from the default Auto setting in the program's user interface.

Error: Anomalous peak at ~ –1.2 V vs Fc/Fc^+ in CH_3CN (and similar potentials in other solvents)

- This peak arises from the reduction of ambient oxygen to the superoxide radical anion as part of the $O_2^{\bullet -}/O_2$ redox couple.

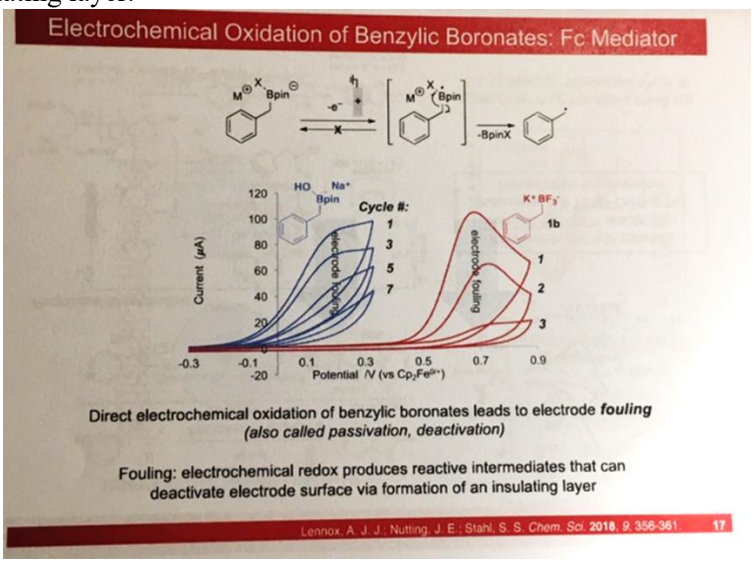


Example voltammograms demonstrating issues arising from air contamination, adapted from Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206.

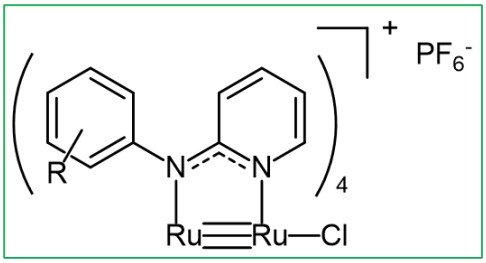
Solution: Sparge the analyte/electrolyte solution with an inert gas, either N_2 or Ar, to remove oxygen gas. The peak should then disappear. It is also possible to perform electrochemistry under an inert atmosphere in a glovebox.

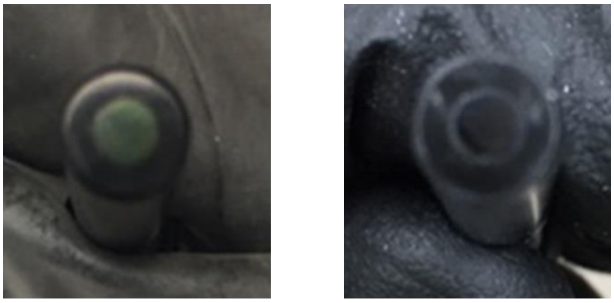
Error: Current decreases dramatically in successive scans

- This is often an indication of electrode "fouling," where "electrochemical redox produces reactive intermediates that can deactivate [the] electrode surface via formation of an insulating layer."



Stahl lab Electrochemistry short course, page 17. Adapted from Lennox, A. J. J.; Nutting, J. E.; Stahl, S. S. *Chem. Sci.* **2018**, *9*, 356-361.





R=H ***R=CH$_3$***

Examples of electrode fouling following oxidation of $[Ru_2(p\text{-}R\text{-}ap)_4Cl]^+$ species at highly anodic (positive) applied potentials.

Solution: Carefully wipe the electrode surface with a Kimwipe, or preferably polish the electrode if possible, after seeing evidence of fouling. Although it cannot be avoided altogether, be cognizant of potential ranges where electrode fouling becomes problematic and plan accordingly.

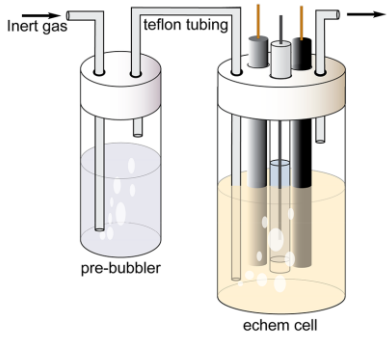
Error: Analyte solution evaporates over the course of the experiment

- This can change the concentration of solution over time and make direct comparisons between different samples difficult.

Solution: Use a pre-bubbler to saturate inert gas with solvent vapors to reduce the loss of solvent in the electrochemical cell. This can be especially helpful for experiments done in more volatile solvents like CH_2Cl_2.

Box 7. How to sparge a solution with minimal concentration changes

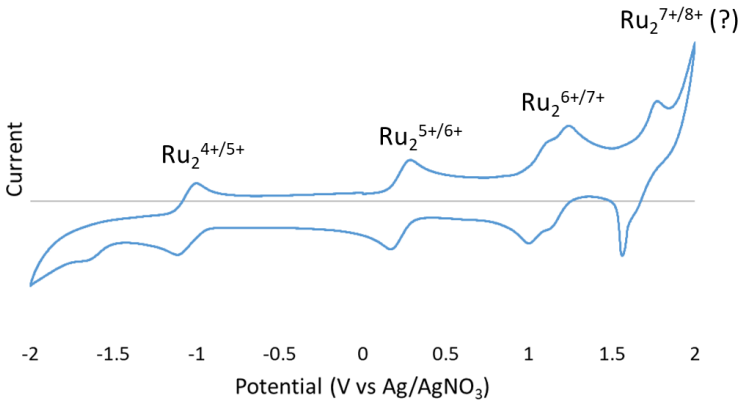
Using a pre-bubbler to saturate the inert gas with solvent vapors helps reduce the loss of solvent in the electrochemical cell due to evaporation during the sparge process.



Pre-bubbler schematic, taken from Dempsey, et al. *J. Chem. Educ.* **2018**, *95*, 197−206.

Error: Voltammogram appears with extremely sharp, narrow peaks.

- This is likely due to electrodeposition and stripping on the electrode surface, as opposed to diffusion-limited redox couples.



1.0 mM $[Ru_2(p\text{-}Clap)_4Cl][PF_6]$, 100 mM $[Bu_4N][PF_6]$ in CH_2Cl_2

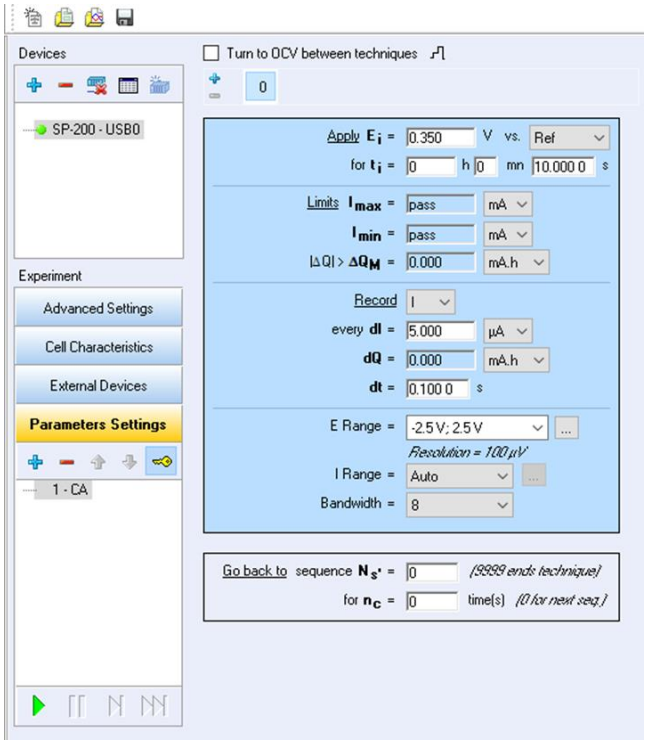
Solution: This behavior itself isn't necessarily problematic unless it results in electrode fouling, and unavoidable except by not scanning at the corresponding potentials. However, electrodeposition/stripping behavior can be more accurately diagnosed.

- Collect voltammograms of the feature at varied scan rates, plotting current against the square root of scan rate, which shows a linear relationship for diffusion-controlled redox events, and current against scan rate itself, which shows a linear relationship for instances where material is adsorbed onto the electrode surface.
- Check peak to peak separation at various scan rates. Varied peak to peak separation across scan rate is indicative of a diffusion-controlled event, while constant peak to peak separation may be indicative of an event with material adsorbed onto the electrode surface.

Controlled potential and current techniques

Controlled potential electrolysis and chronoamperometry

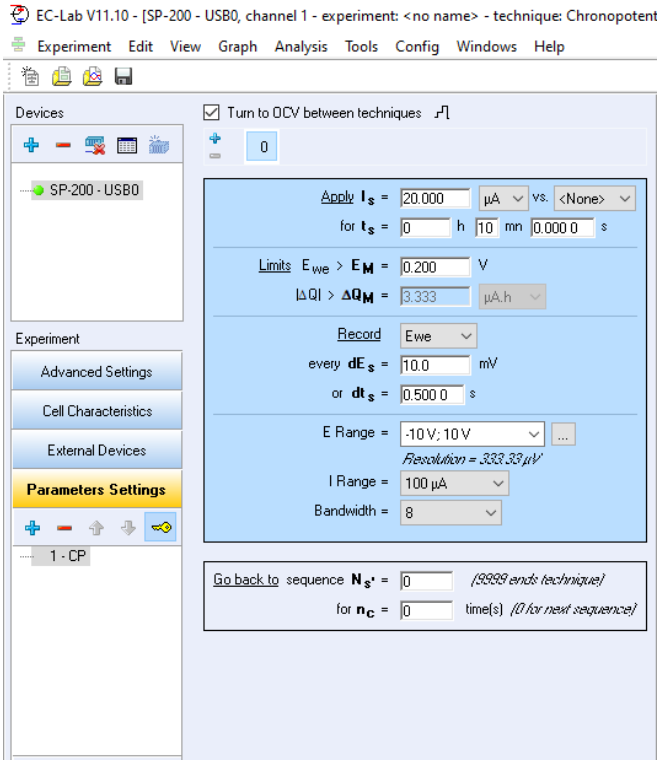
A constant potential is applied at the surface of the working electrode while current is measured as a function of time. Charge passed, equated by integrating current over time, can also be measured by this technique. This technique might be done in scenarios where multiple redox events are accessible for a sample but you only wish to target one event by keeping the applied potential constant. This can be done at either a bulk scale or an analytical scale, but different equipment is needed in both cases.



- E_i is the constant potential applied in the experiment. This potential is most commonly set versus a reference electrode (Ref), but can also be set in reference to open circuit potential E_{oc}.
- t_i is the time for which the potential E_i is applied, in hours, minutes, and seconds.
- I_{max}, I_{min}, and ΔQ_M respectively set limits for the maximum current, minimum current, and passed charge for the experiment. If measured values eventually go beyond the limits set here, the experiment will automatically end. By default, these limits are ignored, and the experiment will run to the full time set by t_i.
- The "Record" dropdown can be set to directly record either current or charge, although the two can be interconverted. It is recommended that current (I) be selected here.
    - Measurements can be made at intervals for difference in current, charge or time, respectively dI, dQ, or dt. Setting any value to 0 means that data is not collected in intervals of that variable. Usually, dI and dQ are set to 0 and dt is set to some number of seconds.
- E Range should be set appropriately such that E_i lies within this range. You will get an error if E Range and E_i are in conflict with each other.
- I Range and Bandwidth can typically be left in their default settings for this technique
- The  button can be used to build a more complicated technique where different constant potentials are sampled for different periods of time. Ns' and n_c values other than 0 can be used to repeat such sequences when constructing more complicated experiments.

Controlled current electrolysis and chronopotentiometry

A constant current (i.e. a constant rate of electron flow) is requested and the potential applied at the working electrode is adjusted to maintain that current over the course of the experiment. The necessary applied potential is recorded as a function of time. This technique might be done in cases where the rate of an electrochemical transformation must be precisely controlled. This can be done at either a bulk scale or an analytical scale, but different equipment is needed in both cases.



- I_s is the constant current maintained in the experiment. By default, select vs <None>. A positive value of I_s will perform electrochemical oxidation, and a negative value of I_s will perform electrochemical reduction.
- t_s is the time for which the potential E_i is applied, in hours, minutes, and seconds.
- E_M and ΔQ_M respectively set limits for the applied potential passed charge for the experiment. If measured values eventually go beyond the limits set here, the experiment will automatically end.
- The "Record" dropdown can be set to directly record applied potential at the working electrode.
    - Measurements can be made at intervals for difference in potential or time, respectively dE_s or dt_s. Setting any value to 0 means that data is not collected in intervals of that variable. Usually, dE_s is set to 0 and dt is set to some number of seconds.
- E Range should be set appropriately such that working electrode potential expected for the experiment falls within this range.
- I Range should be set appropriately such that the desired constant current value I_s falls within this range. You will receive an error if I Range and I_s are in conflict with each other.
- The  button can be used to build a more complicated technique where different constant potentials are sampled for different periods of time. Ns' and n_c values other than 0 can be used to repeat such sequences when constructing more complicated experiments.

Equipment for bulk electrolysis techniques

Electrodes

Bulk electrolysis techniques require high surface area working and counter electrodes.

- For a working electrode, use a sufficiently large block of reticulated vitreous carbon (RVC). A 1-2 cm^3 piece cut by scalpel is typically sufficient and can be stuck on the end of a conductive

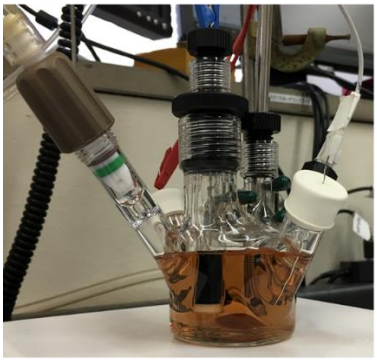
platinum wire. RVC should not be reused, and a fresh piece should be cut for each experiment. 80 PPI (pores per inch) RVC can be ordered from Ultramet at ~ $2.75 per in^3, although a minimum purchase of $750 is necessary. When possible, ask for free samples.

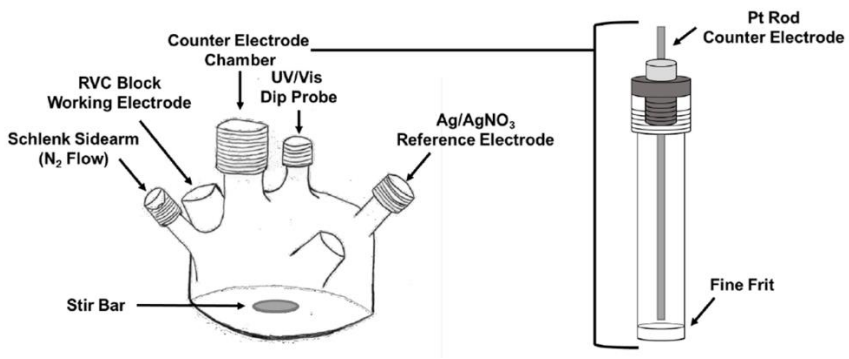
- For a counter electrode, we have typically used a platinum rod with additional platinum wire wrapped around it to grant more surface area. A similar RVC electrode could also be used, but might have a larger overpotential for a process like reducing proton equivalents to hydrogen gas.

Kraken cell

This is a spectroelectrochemical cell that enables air-free bulk electrolysis with simultaneous collection of UV-Vis absorption spectra. The cell includes 6 ports:

- A Schlenk sidearm
- 2 ports that can be plugged by 19/22 septa and secured with copper wire. One of these ports can be used to hold the RVC/Pt wire working electrode as it pierces the septum.
- 2 size #7 threaded glass ports. The upright port is intended for the UV-Vis dip probe, which can be secured in place with a correspondingly sized O-ring and black nylon bushing. The side port is intended for the Ag/Ag^+ reference electrode, which can also be secured in the same manner. The reference electrode's Teflon housing has been tightly wrapped with electrical tape to make it wide enough to make a proper seal.
- 1 size #15 threaded glass port. A counter electrode chamber can be secured in this port with a correspondingly sized O-ring and black Nylon bushing.





Assembly: Working electrode (main) chamber

- Prepare analyte solution in the glovebox if necessary and place it in the working electrode cell with a stir bar. 75-100 mL of solution are necessary to keep the counter electrode cell insert submerged.
- With a scalpel, cut an appropriately sized block of reticulated vitreous carbon (approximately 1.5 × 1.0 × 0.5 cm) and pierce it with a platinum wire. Carefully bend the end of the wire slightly to ensure the RVC block doesn't slide off.
- Seal the cell with the appropriate coverings as outlined below:
    - Place a Teflon Schlenk adapter in the Schlenk Sidearm
    - Place a prepared non-aqueous Ag/Ag^+ reference electrode in the reference electrode port and secure it in place with a correspondingly sized O-ring and black Nylon bushing. A reference electrode reserved for use in this setup has been wrapped in electrical tape to increase the thickness of its housing and appropriately seal this port.

- Seal the two non-threaded glass ports with 19/22 septa. Beforehand, pierce one of these septa with an 18 gauge (pink) needle and feed through the platinum wire affixed to the RVC block working electrode.
- Seal the UV/Vis port with either a glassy carbon working electrode or an identically sized plug. Secure it in place with a correspondingly sized O-ring and black Nylon bushing.
- Seal the counter electrode chamber port with a white Teflon screw and thick brown O-ring. These components are the same as what is used to seal pressurized reaction vessels.
- Remove the sealed vessel from the glovebox.

Assembly: Counter electrode chamber insert

- If using the platinum rod and coil counter electrode, feed the rod through its white Teflon housing such that approximately 1 cm of the rod is exposed at the top. Place an appropriately sized O-ring around the Teflon housing.
- Place the glass counter electrode chamber insert through an appropriately sized black Nylon bushing. Next, put an appropriately sized O-ring around the glass, moving it upwards to reach the bushing and hold it in place.
- While blowing nitrogen gas through the Schlenk side arm of the main chamber, remove the white Teflon screw cap and brown O-ring, and replace them with the counter electrode insert and its O-ring, securing it in place by tightening the bushing.
- While still blowing nitrogen gas through the Schlenk side arm of the main chamber, fill the counter electrode chamber insert with sacrificial oxidant/reductant solution by syringe until the solution level is even with that of the analyte solution in the main chamber. Place the assembled counter electrode, Teflon housing, and O-ring into the glass insert, securing it in place with an appropriately sized black Nylon bushing.

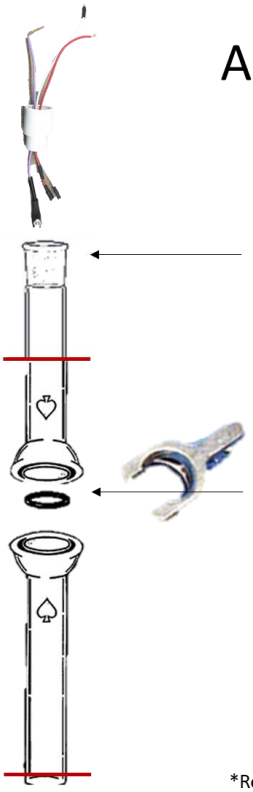
Assembly: UV-Vis setup

- Equip the dip probe with an appropriately sized tip and perform a blank measurement in solvent.
- While blowing nitrogen gas through the Schlenk side arm of the main chamber, remove the working electrode/plug and replace it with the dip probe, securing it in place with an appropriately sized O-ring and black Nylon bushing.
- To automatically collect spectra at regular intervals, use the program developed by Christian Wallen. It is named GUIUV.exe, and is accessible either via Desktop or Taskbar shortcut on the instrument computer.

Custom electrochemical cell designs:

Schematics on the following pages outline the necessary components for fabricating undivided and divided electrochemical cells for bulk electrolysis performed at the ~ 5-8 mL solution scale. Clamps, O-rings, and glass components are available via Ace Glass and all catalog numbers are provided.

Assembly: Single-chamber cell



19/22 rubber septum is punctured with proper electrode leads and sealed with epoxy.

The septum and **7585-34** joint is further sealed with Teflon tape prior to the experiment.

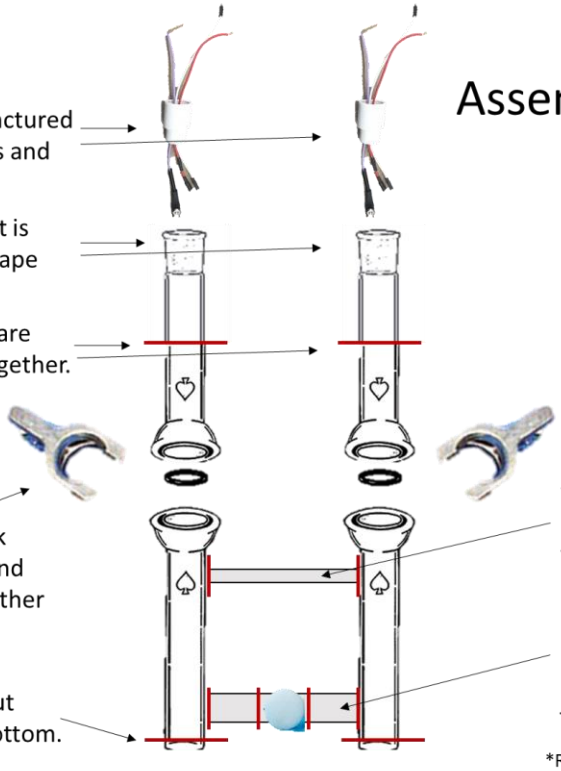
7585-34 and **7646-08** (top) are both cut short and fused together.

7669-12 28/15 SS screwlock pinchclamp holds the top and bottom **7646-08** joints together during experiment.

7646-08 (bottom) may be cut short and is sealed at the bottom.

*Red lines denote junctions where glassworking is necessary

Assembly: Two-chamber cell



19/22 rubber septa are punctured with proper electrode leads and sealed with epoxy.

The septa and **7585-34** joint is further sealed with Teflon tape prior to the experiment.

7585-34 and **7646-08** (top) are both cut short and fused together.

7669-12 28/15 SS screwlock pinchclamp holds the top and bottom **7646-08** joints together during experiment.

~2-5 mm ID glass tubing (for equalizing gas pressures between electrode chambers) fused between bottom **7646-08** joints

7176-36 12 mm E filter disc sealed within 15 mm ID glass tubing (for allowing ion exchange) fused between bottom **7646-08** joints

7646-08 (bottom) may be cut short and is sealed at the bottom.

*Red lines denote junctions where glassworking is necessary