Standard Operating Procedure

Task: Cyclic Voltammetry
Date: 10/30/2020
Revision Date: 11/19/2021 (Alex Miller)

Background

- Cyclic Voltammetry (CV) is an essential electrochemical technique in which an applied potential is changed as a function of time, and the resulting current is monitored. From the resulting data, information such as redox potentials, diffusion coefficients, association/dissociation rate constants, and catalytic rate constants can be obtained.
- CV is incredibly sensitive to redox-active species, and care must be taken to purify all reagents and solvents before use

Training Requirements:

- Glovebox or Schlenk line training
- Complete Training Modules 1–4 in Dempsey et al. *J. Chem. Educ*. **2018**, *95*, 197

Potential Hazards:

- Chemical hazards specific to reagent(s) of interest
- Electric shock

Special PPE Requirements:

- Gloves, safety glasses, lab coat
- Any additional PPE as dictated by the particular chemicals of the experiment

Materials Needed:

- Chemical reagent(s) of interest
- High-purity electrolyte
- High-purity (and anhydrous, if needed) solvent
- High-purity internal standard if using organic solvent (e.g. $FeCp_2$, $FeCp^*_2$)
- Electrodes
    - Working Electrode (W.E.): glassy carbon (GC) disks of various sizes, Au disks of various sizes,
    - Counter Electrode (C.E.): usually a Pt wire
    - Reference Electrode (R.E.): usually Ag wire pseudoreference in a fritted compartment (containing $AgNO_3$ and the same electrolyte solution as bulk cell) in organic solvents, Ag/AgCl in 3 M KCl for aqueous solvents
- CV glassware such as vial or H-cell
- Teflon CV cap (vial) or screw caps (H-cell)
- Solvent bubbler (if on the line)
- Polishing pads

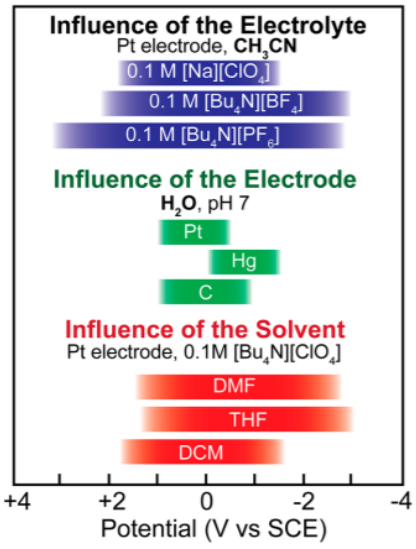
- Potentiostat capable of iR compensation (WaveDrivers, Wireless WaveNow, CHI)

Procedure:

Planning Experiments

- Design the experiment you want to run. As with any experiment: What do you want to learn? What is your hypothesis? Walk through the experiment before you run it: What scan rate or scan rate range? What sweep direction and sweep width? What data do you want to collect before and after adding certain reagents? What do you expect the data to look like? Preparation will guide the planning choices below, and will provide a basis for making adjustments on-the-fly during the experiment, thereby reducing the chance of having to repeat the experiment again later.
    - **See below for more detailed guidance on the questions posed here!**

- Select your solvent and electrolyte of interest based on the solubility of species and electrochemical window (most common examples are shown to the right; reproduced with permission from *J. Chem. Educ*. **2018**, *95*, 197, https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361, further permissions related to the material excerpted should be directed to the ACS.).
    - Organic solvents should be pure and dry. Water should be high-purity high-resistance (e.g. >18 MΩ/cm) grade. Do NOT use DI water from the sink taps!
    - [TBA][PF_6] should be triply recrystallized and then dried under heat and high vacuum before use



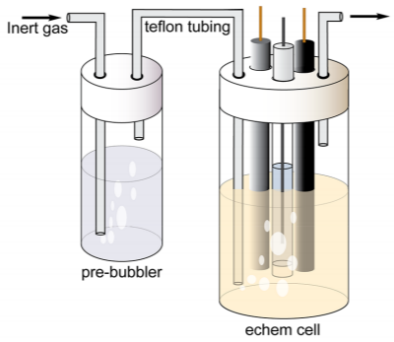
- Determine concentrations of reagents needed for experiment
    - A typical concentration of an organometallic species is ~1 mM, but current response can vary based on the complex and conditions, so it is possible to use concentrations in the range from 0.1 mM to 10 mM or higher. For quantitative analysis, be sure to weigh out at least 10.0 mg of sample, using stock solutions if needed to assure mass accuracy.
    - Concentration of electrolyte should be at least 100 mM to minimize effects of migration. Larger concentrations of electrolyte may be used to help improve solution resistance. For low polarity solvents such as THF, a minimum of 200 mM is recommended.
    - Concentrations of additional species such as acids, bases, or salts will be dependent on the system of interest

        - Stock solutions are often the most accurate way to introduce small amounts of additives in a controlled manner. Stock solutions for these titrations should contain the same concentration of electrolyte, reference compound, and compound of interest
        - If high concentrations of charged species are being added, the overall ionic strength will be changing. This may influence experimental design considerations.
    - The volume of solution will be dependent on the cell of choice, in which the volume must be high enough for all electrode surfaces to be submerged.
        - For 20 mL single-compartment cells equipped with a GC disc W.E., 6 mL of electrolyte solution is often sufficient
- Select electrochemical cell
    - CVs can be performed in either single or multi-compartment cells. Single compartment cells are generally easier to obtain, easier to clean, and have lower resistance. Multi-compartment cells (such as H-cells) provide separation between anodic and cathodic reactions. Because only very small amounts of reactive species should be generated during CV experiments, anode/cathode separation is not generally important, so single-compartment cells are often favored.
- Select electrodes
    - Glassy carbon (GC), boron-doped diamond, and gold disc electrodes are available.
        - We usually start with GC for routine experiments
        - Disc electrodes are available in a range of diameters
            - We typically use 3 mm planar disc electrodes
            - 1 mm disc electrodes are often needed to achieve scan rates above ca. 50 V/s in CV experiments
        - Rectangular planar electrodes, such as GC plate or transparent conducting oxide (TCO) slides such as tin-doped indium oxide (ITO) or fluorine-doped tin oxide (FTO) can also be used.
            - The electrode geometry impacts the shape of the voltammogram, and the edges and corners present in rectangular slides are not ideal for CV.
    - The reference electrode is typically a silver wire
        - For organic solutions, the silver wire may be contained in a fritted capillary containing the electrolyte solution containing a Ag^+ salt such as $AgNO_3$.
        - A bare silver wire (without $AgNO_3$ in solution) is called a “Ag pseudoreference” and may also be used for organic solutions; however, Ag pseudoreference electrodes generally drift in potential over the course of an experiment, so an internal standard (e.g. Cp_2Fe or Cp^*_2Fe) is required during each voltammogram.

        - For aqueous solutions, the silver wire should be coated in AgCl (the wire will look dark and less shiny compared to a plain Ag wire). A capillary, containing a known concentration of an inert Cl^- salt such as 3 M KCl, is necessary for aqueous electrochemistry. The AgCl coating can be created by placing a freshly polished Ag wire in 0.1 M KCl and, as the working electrode, performing a constant current electrolysis at 0.4 mA/cm^2 for 30 minutes (see *Handbook of Electrochemistry* by Zoski or Electrochemistry — Aqueous Reference Electrodes SOP).
        - Reference capillaries can be prepared according to *A Practical Beginner's Guide to Cyclic Voltammetry* (*J. Chem. Educ.* **2018***, 95,* 197). Once the capillary is prepared, the porous glass frit (Vycor) must be soaked in the electrolyte solution for at least 24 hrs before use in order to equilibrate species across the frit. Once a capillary frit has been soaked in electrolyte, the frit should NEVER be allowed to dry out, as this will cause the high concentrations of electrolyte to precipitate and crack the frit. Thus, a capillary containing electrolyte should not be pumped into the glovebox without thoroughly rinsing and soaking the frit for several days in pure solvent to remove all electrolyte.
            - Vycor frits can become contaminated over time (turn yellow/brown). The frits can be cleaned by disassembling the capillary and soaking the frit in a cleaning solution such as a solubilizing solvent or HNO_3. See Zoski Table 4.11 on page 104. Note that it says can be cleaned with H_2O_2 *or* HNO_3, DO NOT MIX these.
            - Vycor frits are not in widescale production as of 2021, but a replacement product called "Coralpor" is available. Coralpor may be used interchangeably with Vycor to make reference capillaries.
            - $AgNO_3$ solutions should be made fresh before each series of experiments due to light sensitivity of the Ag salt.
    - The counter electrode is typically a Pt wire, although glassy carbon is occasionally used as well. If a GC electrode is used, ensure it is the same surface area or larger than the W.E.
- Determine if the experiment will take place in the glovebox or on the benchtop
    - The glovebox ensures that all species are air- and moisture-free for the entirety of the experiment and is necessary if any starting materials are air sensitive. Electrode polishing is more difficult in the glovebox, and electrical noise and vibrations can be complicating factors. All of our gloveboxes are equipped to perform electrochemistry experiments.
    - Benchtop electrochemistry is also possible, however redox-active O_2 must be removed (via sparging) from solution prior to data collection. See below for more details.

CVs on the Benchtop

- Turn off nearby vacuum pumps if possible: this will prevent vibrations interfering with your results. Unplug nearby equipment if possible: this will minimize interference from electrical noise.
- The solution should be sparged with a dry, oxygen-free gas prior to experiments, most commonly N_2 or Ar, although gases such as CO_2 or H_2 may be used. Anytime a new reagent is added or the WE is removed to polish, the solution should be re-sparged.
- A solvent pre-bubbler should be used for organic solvents to prevent evaporation by using solvent-saturated gas while sparging. Often times, we use dry solvents from the glovebox or solvent system stored over sieves in round bottom flasks sealed with septa. See right figure (reproduced with permission from *J. Chem. Educ*. **2018**, *95*, 197, https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361, further permissions related to the material excerpted should be directed to the ACS.).
- To sparge the solution: dip the PTFE tubing below the surface of the solution and let degas for an appropriate amount of time (dependent on cell geometry and solution volume). Once ready to perform the experiment, pull the tubing above the surface of the solution, but still within the headspace of the cell, which will create a "blanket" of gas above the solution.



General CV Procedures on the Benchtop

- Set up the CV cell (the following procedure uses a 20 mL scintillation vial as a single-compartment cell):
    - Polish W.E. and gather all necessary electrodes.
    - Set up your pre-bubbler with appropriate solvent and your Schlenk line with appropriate gas, and begin degassing the pre-bubbler.
    - Inside a glovebox, prepare electrolyte solution and transfer to scintillation vial and cap. Weigh out any sensitive reagents inside glovebox into scintillation vials and cap. Take all necessary materials out of glovebox.
    - Remove the cap from the scintillation vial containing the electrolyte solution and replace with the machined Teflon cap containing holes for each electrode and tubing.
    - Insert W.E., C.E., and R.E. into the cap and ensure that they are all in the electrolyte solution *and* that they are all at a similar solution depth. Place WE and RE as close together is practically possible. Place the outgoing Teflon tubing from your pre-bubbler into the cap.
    - Add a magnetic stir bar, if using.
    - Attach the alligator clips to the proper electrodes (For Pine Instruments: Red&Orange = WE, Green = CE, White = RE, Black/Grey = ground). Make sure that the alligator clips are not touching each other or any metal

surfaces besides the electrodes themselves, except for the black ground lead, which should be clipped to a grounded metal surface. Make sure that the alligator clips are not putting strain on the electrodes or the set-up. Ensure that all of the electrodes are submersed in the electrolyte solution.

- Obtain a background CV:
    - Sparge the solution for an appropriate amount of time to remove O_2. This time will vary based on cell volume and configuration. Residual O_2 is often visible as an irreversible or quasi-reversible reduction at around -400 to -800 mV vs $Ag^{+/0}$ (dependent on solvent and O_2 concentration).
    - With only the electrolyte solution present, take a CV. Ensure that your sweep width goes to the solvent window or covers all of the electrochemical window you plan on investigating. This will allow assignment of very negative or oxidizing features being caused by the solvent window. Will also identify any electrochemically active impurities or any issues with electrodes, including the surface of the W.E.
    - Note that more than one "background" is sometimes needed. For example, in addition to electrolyte background obtained before every experiment, it is important to obtain at least one representative background of any reagents (acids, CO_2, redox mediators, etc) in the absence of the complex or catalyst for comparison.
- Add reagents one at a time and get a CV between each reagent addition. This will help to determine the source of any impurities present. Remember to sparge every time you add a new reagent or polish the working electrode.
    - The easiest way to add reagents is to take electrolyte solution out of the CV cell and use it to dissolve your reagent. The reagent-containing solution is then added back to the CV cell and mixed through either sparging or stirring.
- The open circuit potential (OCP) should be measured after changing anything in the experiment (i.e. adding reagents, changing electrode configuration, etc). Start your scan at this OCP. This will ensure that you are not starting your scan in the middle of a peak. Additionally, it will allow assignment of peaks as oxidation or reductions of the analyte of interest.
    - Occasionally, the OCP is very close to a reduction or oxidation peak. In these instances, it is okay to shift the OCP, just ensure that you are not inadvertently shifting the OCP past any of the redox features.
- The cell resistance (iR comp) should be measured after changing anything in the experiment (i.e. adding reagents, changing electrode configuration, etc). See **iR compensation** section below for further details.
- The WE should ideally be polished in between every scan. See Electrode polishing section below for details.
- Refresh the solution at the surface of the electrode in between scans in order to prevent localized concentration changes. This can be accomplished via stirring, shaking, or sparging the cell for a few seconds. Stop movement and let the solution settle before taking the next scan to prevent convective interference.

- Clean the setup
    - Glass electrochemical cells should be cleaned with aqua regia after use, if possible.
    - The WE should be polished to clean.
    - The CE and RE should be rinsed and wiped down with a KimWipe.
    - The RE capillary should be rinsed and returned to the storage electrolyte solution.

CVs in the Glovebox

- Glassware should be oven- or flame-dried before bringing into glovebox. Electrodes and Teflon caps can be put in the warming oven before bringing into the glovebox, or pumped in overnight to ensure dryness.
- Unplug or turn off nearby equipment if possible, including equipment in the glovebox itself. Do not unplug anything that is vital to glovebox functioning or that will disrupt others' experiments
- Positioning the alligator clips properly is more difficult in the glovebox. Make use of multiple clamps if necessary.

General CV Procedures in the Glovebox

- Set up the CV cell (the following procedure uses a 20 mL scintillation vial as a single-compartment cell):
    - Polish W.E. and move all electrodes into the glovebox. Do not dry or pump in a R.E fritted capillary that has already been soaked in electrolyte, as this will cause electrolyte to crash out and crack the frit.
    - Prepare electrolyte solution and transfer to scintillation vial. Add the Teflon cap.
    - Insert W.E., C.E., and R.E. into the cap and ensure that they are all in the electrolyte solution *and* that they are all at a similar solution depth. Place WE and RE as close together is practically possible.
    - Insert a stir bar, if using
    - Attach the alligator clips to the proper electrodes (For Pine Instruments: Red&Orange = WE, Green = CE, White = RE, Black/Grey = ground). Make sure that the alligator clips are not touching each other or any metal surfaces besides the electrodes themselves, except for the black ground lead, which should be clipped to a grounded metal surface. Make sure that the alligator clips are not putting strain on the electrodes or the set-up. Ensure the electrodes are in the electrolyte solution.
- Obtain a background CV:
    - With only the electrolyte solution present, take a CV. Ensure that your sweep width goes to the solvent window or covers all of the electrochemical window you plan on investigating. This will allow assignment of very negative or oxidizing features being caused by the

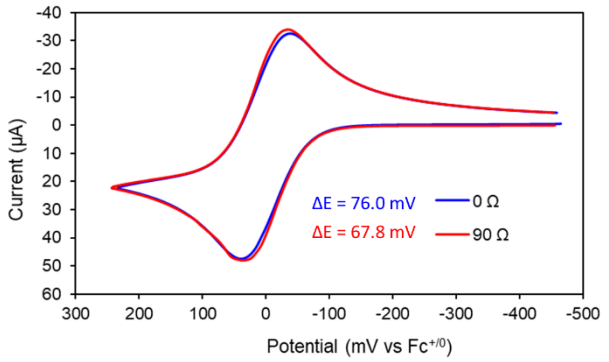
solvent window. Will also identify any electrochemically active impurities or any issues with electrodes, including the surface of the W.E.
    - Note that more than one “background” is sometimes needed. For example, in addition to electrolyte background obtained before every experiment, it is important to obtain at least one representative background of any reagents (acids, CO_2, redox mediators, etc) in the absence of the complex or catalyst for comparison.
- Add reagents one at a time and get a CV between each reagent addition. This will help to determine the source of any impurities present.
    - The easiest way to add reagents is to take electrolyte solution out of the CV cell and use it to dissolve your reagent. The reagent-containing solution is then added back to the CV cell and mixed through either sparging or stirring.
- The open circuit potential (OCP) should be measured after changing anything in the experiment (i.e. adding reagents, changing electrode configuration, etc). Start your scan at this OCP. This will ensure that you are not starting your scan in the middle of a peak. Additionally, it will allow assignment of peaks as oxidation or reductions of the analyte of interest.
    - Occasionally, the OCP is very close to a reduction or oxidation peak. In these instances, it is okay to shift the OCP, just ensure that you are not inadvertently shifting the OCP past any of the redox features.
- The cell internal resistance (iR) should be measured and corrected for after changing anything in the experiment (i.e. adding reagents, changing electrode configuration, etc). See **iR compensation** section below for further details.
- Refresh the solution at the surface of the electrode in between scans in order to prevent localized concentration changes. This can be accomplished via stirring orshaking the cell for a few seconds. Stop movement and let the solution settle before taking the next scan.
- Clean the setup
    - Glass electrochemical cells should be cleaned with aqua regia after use, if possible.
    - The WE should be polished to clean.
    - The CE and RE should be rinsed and wiped down with a KimWipe.
    - The RE capillary should be rinsed and returned to the storage electrolyte solution. Due to the difficulties of bringing RE capillaries into the glovebox, the capillary and electrolyte storage solution may be left in the glovebox for long-term storage in an appropriately-sized vial or bottle.

iR Compensation

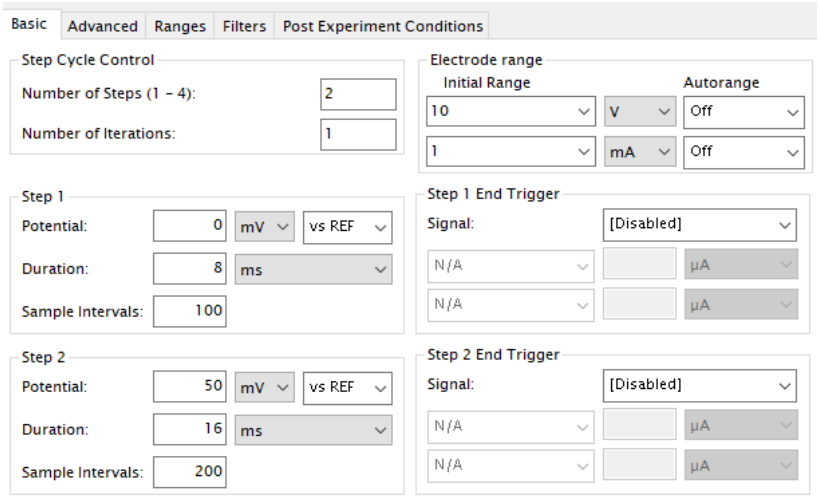
- Ohm’s Law states: V = iR (voltage equals current times resistance)
- In an electrochemical cell, the solution resistance, R_s, is defined as the resistance measured between the WE and CE. This resistance can be minimized

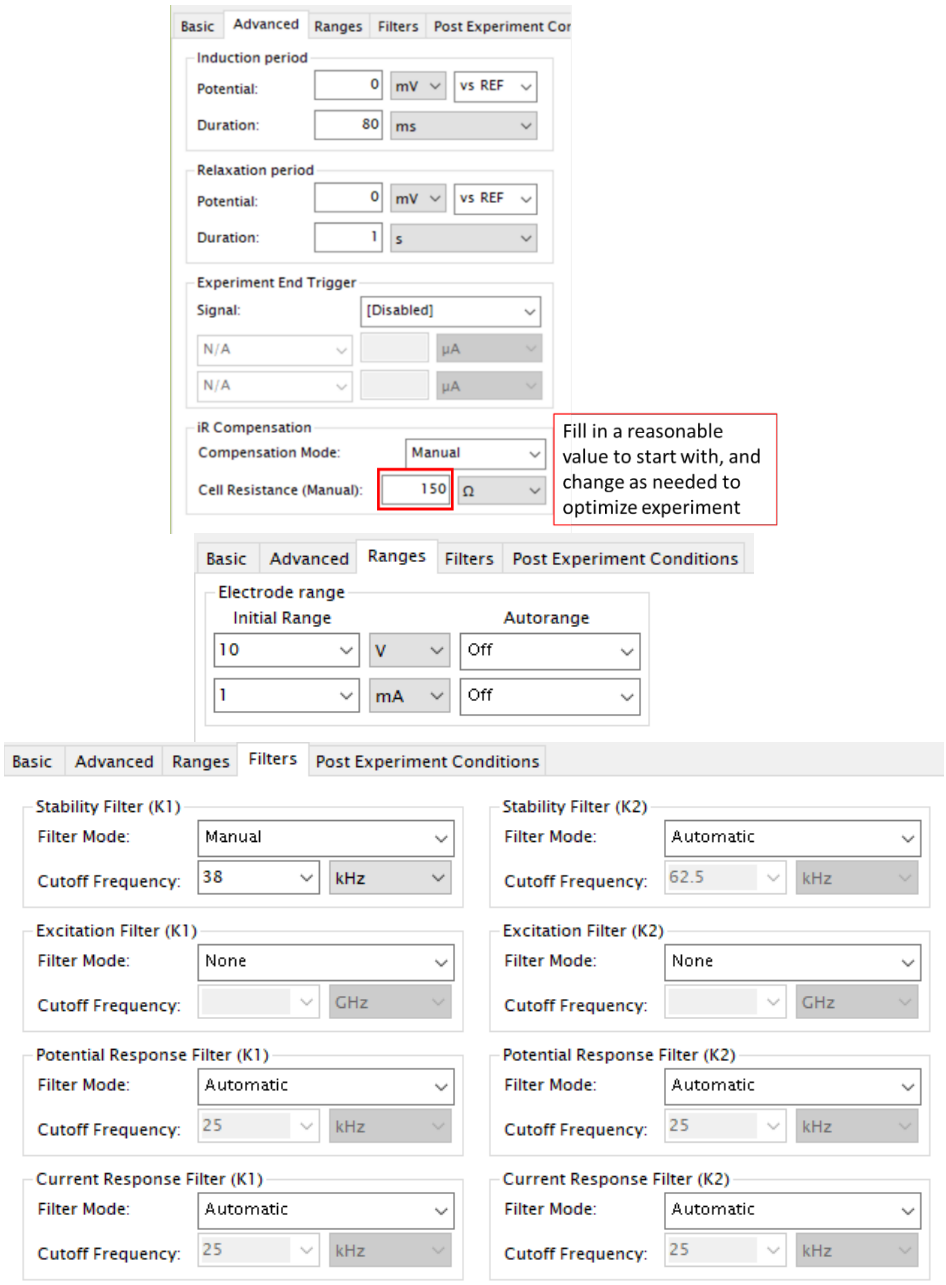
by utilize the typical three-electrode setup that places the RE in close proximity to the WE. Based on that WE–RE distance, there will still be some uncompensated solution resistance, R_u.

- The measured cell potential is comprised of the analyte potential (what we want to measure) and the product of current being passed and the uncompensated resistance iR_u. Depending on the magnitude of current passed, Ru can lead to Ep,c being shifted cathodically and Ep,a being shifted anodically. This leads to peaks that look “smeared out”
- Modern potentiostats have software protocols that attempt to compensate (correct for) the solution resistance, a process called *iR compensation*.



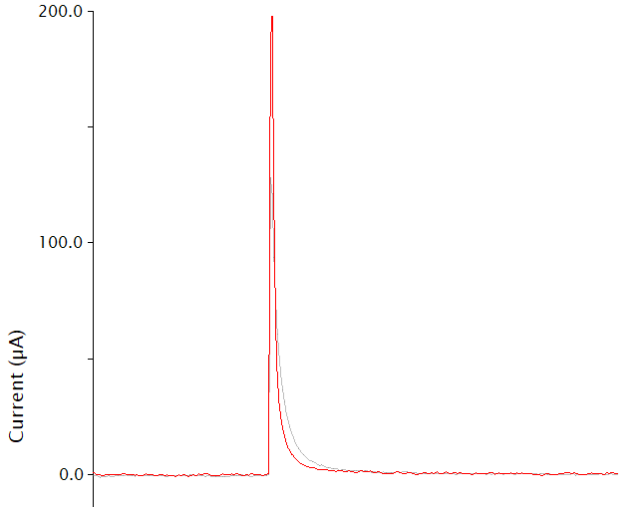
- The effects of uncompensated resistance can be mitigated by:
    - Decreasing current (*i*): using a smaller surface area electrode, or working at lower scan rates
    - Decreasing resistance (R): increasing electrolyte concentrations, changing electrolyte composition, changing solvents, moving RE closer to WE
- Wavedriver, wireless WaveNow, and CHI potentiostats are capable of iR comp
- Determining R_u on Pine Instruments potentiostats (Wavedriver, WaveNow)
    - Start CSCA (cyclic step chronoamperometry) experiment as shown below.
    - Under the “Advanced” tab, change the value in the red box.
    - Typical R_u values (good first guesses):
        - ~120 Ω for MeCN with a Ag/$AgNO_3$ reference capillary
        - ~50 Ω for MeCN with a Ag pseudo reference
        - ~50-200 for buffered H_2O with a Ag/AgCl reference capillary
        - ~1100 Ω for THF in 0.2 M electrolyte with reference capillary



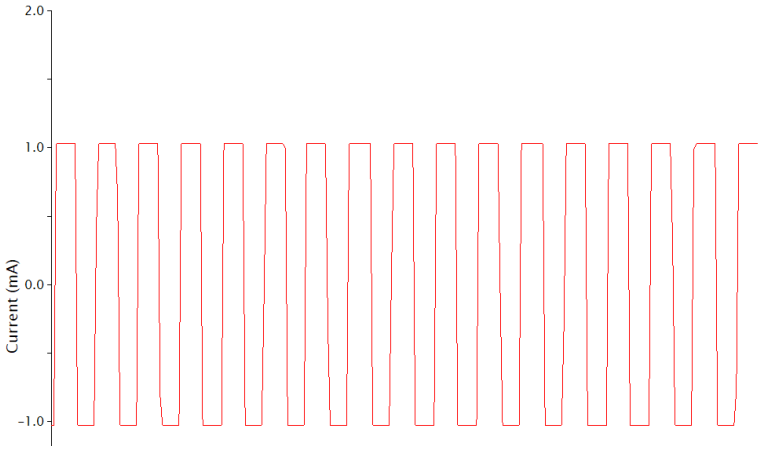


- When ready, click the “Perform” button (just like for any other electrochemistry experiment).

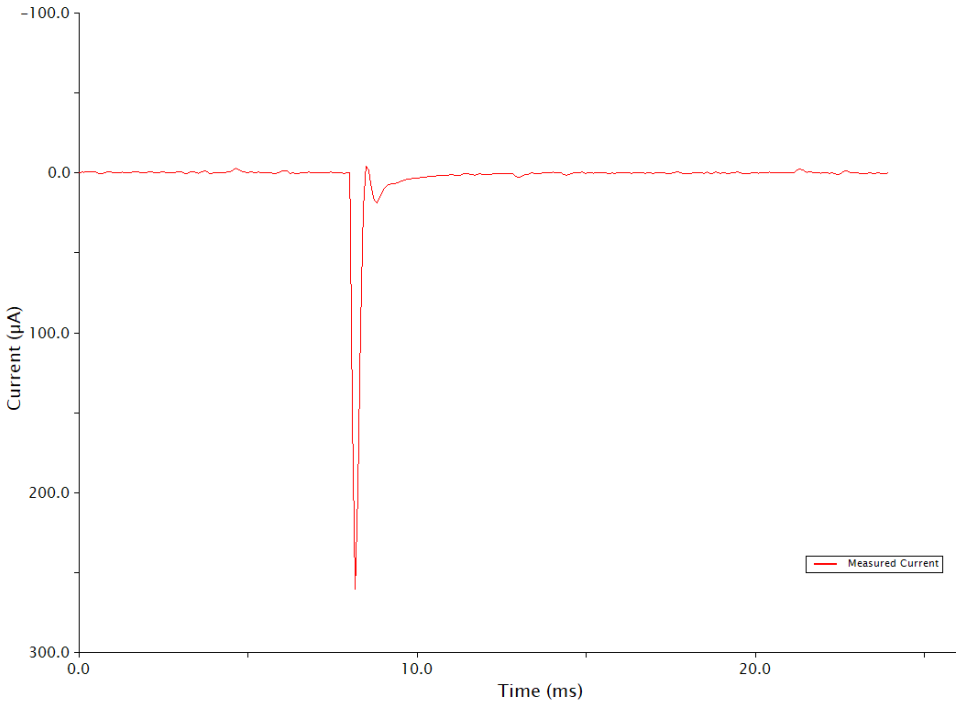
- An example of a chronoamperogram. A sharp peak followed by rapid and smooth decay back to baseline is expected. A sharper peak is better, as shown in the red trace. The grey trace is an example in which too little iR comp is being used. Note that during collection the y-axis may be inverted:



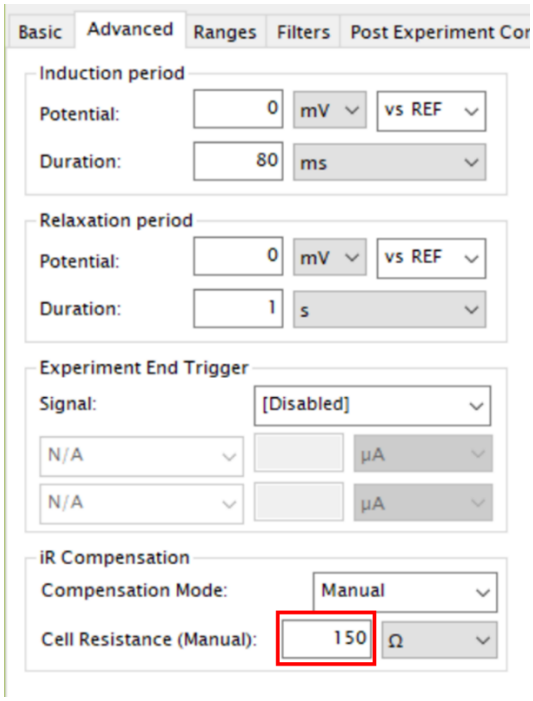
- Oscillations are a sign of too much iR comp:



- An example of slightly too much iR comp. Note that the current axis is inverted here, but is of similar magnitude to the previous example of a “good” iR comp value



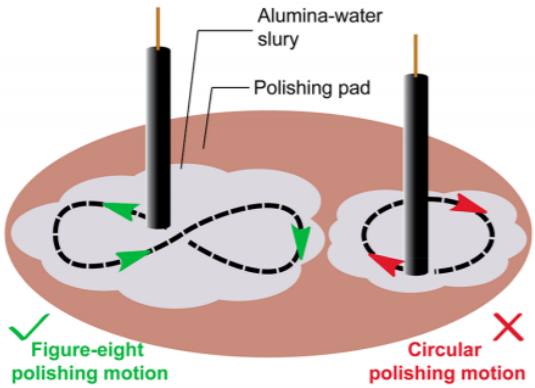
- Once the resistance has been measured in the CSCA experiment, the value of the resistance should be inserted into the cell resistance box for the CV experiment parameters, highlighted in the box in red. Note that for every type of electrochemical experiment performed/parameters input generated in AfterMath, you will need to manually set the iR compensation based on the value you determined.



- R_u should be re-measured (and iR compensation modified) when any changes are made to the system, such as adding reagents or changing electrode configuration. Even polishing electrodes and re-setting them in the cell changes the distance between WE and RE slightly, so R_u may change as well.

Polishing Electrodes (See also Electrochemistry — Electrode Polishing SOP)

- Electrode polishing helps to create a structurally consistent surface to facilitate the acquisition of reproducible data.
- Disc electrodes should be polished using 0.3 and 0.05 micron alumina according to this SOP before any electrochemical experiment (e.g. cyclic voltammetry, chronoamperometry, differential pulse voltammetry, controlled potential electrolysis)
- Disc electrodes should be polished *between every cyclic voltammetry scan* using 0.05 micron alumina whenever possible. Assume that some amount of deposition onto the electrode is occurring until proven otherwise. When working in the glovebox where polishing is cumbersome or impossible, bring multiple pre-polished disc electrodes into the glovebox for use in successive scans.
- To polish:
    - Before beginning an experiment, polish with 0.3 micron powder, followed by 0.05 micron alumina
    - Between CV or DPV scans or between CA experiments, polish with 0.05 micron alumina
    - Rinse the electrode with water. Note: Water for polishing and rinsing should be high-purity high-resistance (>18 MΩ) grade. **Do NOT use DI water from the sink taps!**
    - Keeping the plane of the disc electrode perpendicular to the pad, firmly (but not forcefully) and move the electrode in a figure 8 pattern for 20 seconds (See figure, reproduced with permission from *J. Chem. Educ.* **2018**, *95*, 197, https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361, further permissions related to the material excerpted should be directed to the ACS.)
    - Thoroughly rinse the electrode with water
    - Repeat with the other alumina powder, if necessary. **Note: If you are polishing between each scan, it is not necessary to add fresh alumina and water each time.**
    - Rinse the electrode with acetone to remove water. Blot with a KimWipe to



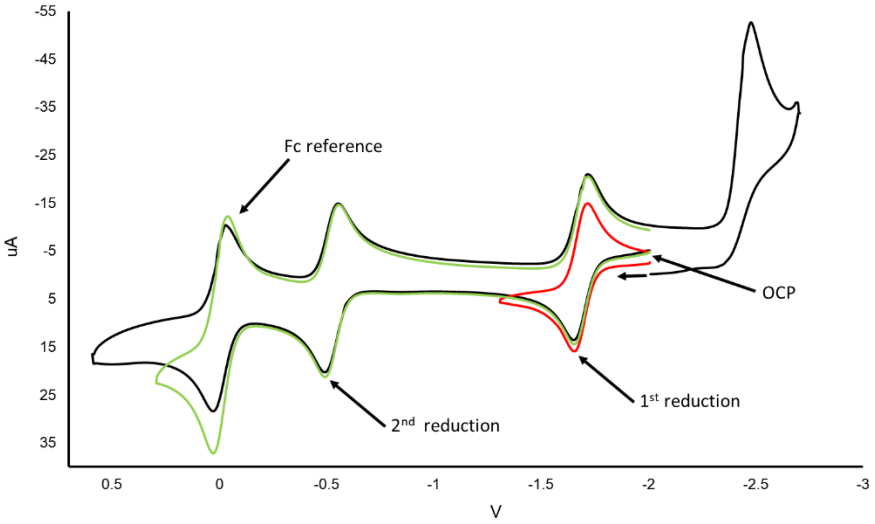
remove any solvent droplets. Do NOT apply pressure or "scrub" the electrode with the KimWipe, as this could scratch the electrode surface.
    - Inspect the electrode surface in the light to check for scratches or blemishes. If scratches are present, consult an experienced electrochemist.
    - Cover the polishing pads for storage after use, to keep away dust or particulates.

Example of Data Collection Workflow for a New Compound

- Design the experiment. Set goals for what you want to learn, and make predictions about what you may or may not observe. Consider the time of the experiment accordingly, and reserve the appropriate amount of time on the instrumentation in advance.
- Set up the cell, electrodes, and potentiostat as described above
- With just the electrolyte solution in the cell, take an OCP measurement and perform iR compensation
- Take a background CV, ensuring the upper and lower potential limits are just within the solvent window. The baseline should be relatively flat, note any non-ideal behavior. If unexpected bumps are present, try sparging for longer and cleaning/repolishing the working electrode. If still present, make a fresh electrolyte solution. If this does not resolve unknown compounds in the background, then move in and dry fresh solvent and take an NMR of the electrolyte to confirm purity.
    - One known example is *o*-difluorobenzene, which has small, but reversible electrochemically active impurity at approximately –1.2 V vs $Ag^{0/+}$. Distillation, drying over CaH_2, and storing over sieves has no impact.
- Add your compound of interest, aiming for 1 mM solution.
- Take an OCP measurement and update iR compensation.
- Plug the resistance value into the CV experimental settings and then collect a "full sweep" CV of your compound of interest. A full sweep spans the region from the anodic solvent window to the cathodic solvent window in 3 segments. Start the sweep in either the rising (oxidative) or falling (reductive) direction at a scan rate of 100 mV/s.
    - Make note of any reversible features
    - Make note of any irreversible features: are they reductive or oxidative, do they appear after another feature, etc.
- Stir/agitate/sparge the solution afterwards and polish the electrode if necessary. Now take a full sweep in the opposite direction.
    - Compare the two full sweep CVs. Has the shape or reversibility of any peaks changed? Are there any features that appear or disappear depending on sweep direction?
- "Isolate" each redox feature, stirring/agitating/sparging between each scan and polishing the electrode if necessary. This means sweeping from the OCP past

the intended redox feature (oxidative or reductive) and then turning around. Complete a scan rate study (detailed below) and then move the turn-around potential to the next feature.

- If reversible, measure different scan rates between 25 and 1000 mV/s (e.g. 25, 50, 100, 250, 500, 750, 1000 mV/s). These will then be used to generate Randles-Sevcik plot.
- If the feature remains irreversible, or partially irreversible, increase the scan rate until reversibility is achieved, data quality degrades substantially, or the limit of the instrument is reached (ca. 200 V/s). This information can be used for kinetic analysis to investigate the rate of the chemical reaction occurring upon electron transfer. (Note: a 1 mm GC electrode should be used for scan rates above 2 V/s. If you need to switch electrodes, repeat slower scan rates with new electrode to enable comparisons across all scan rates)
- An example is included below. The full CV is in black and the first and second reduction features were isolated, as depicted by the red and green traces respectively.



- "Isolate" multiple features that may be coupled: A common situation involves an irreversible feature observed sweeping in one direction, followed by another irreversible feature observed on the return sweep. Set the segment parameters to include the two features of interest, then vary the scan rate systematically. If the first feature becomes reversible at faster scan rates, the second feature may disappear if it was a product formed by a chemical reaction that is no longer occurring on the timescale of the experiment.
- Perform a multi-sweep experiment if necessary: A common situation involves an irreversible feature observed sweeping in one direction, followed by another irreversible feature observed on the return sweep. If the feature on the return sweep is reversible, adding an additional segment to include a second sweep in the initial direction can lead to the appearance of new features. This is typical of ECE reactions, for example. Varying scan rate should alter the relative peak

currents of the features, which may be modeled using digital simulation to obtain kinetic information.

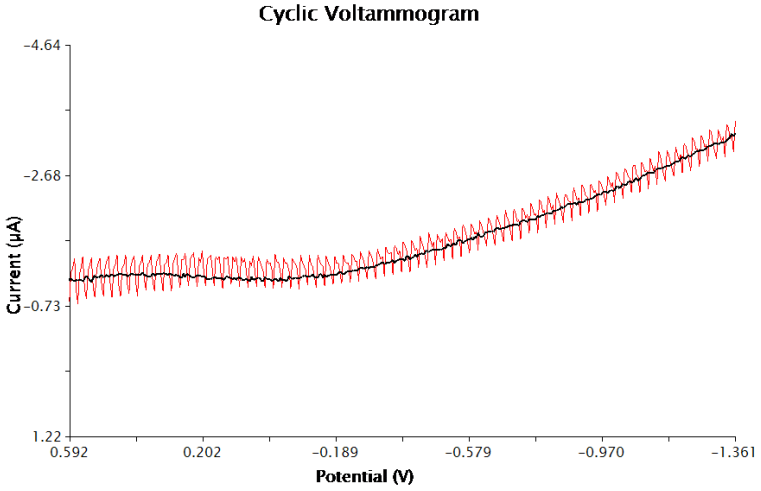
- At the end of your experiment, add a reference compound (Fc, Fc*, etc) and take a full width CV at 100 mV/s sweeping in both directions. This will allow you to determine whether the complex being studied is compatible with Fc. Once you have confirmed that your reference compound does not interfere with the electrochemical response of your compound of interest, repeat all CV scans of interest with the reference compound for the most accurate referencing. For future experiments, you can add it at the beginning of the experiment to save time.
- Fc is much more chemically reactive than Fc*. For example, halides react rapidly with Fc, leading to an irreversible wave that cannot be used for referencing. Thus, Fc* should be used whenever halides are present, and care should be taken to check that Fc is compatible with the reaction conditions.

Troubleshooting of Common Errors

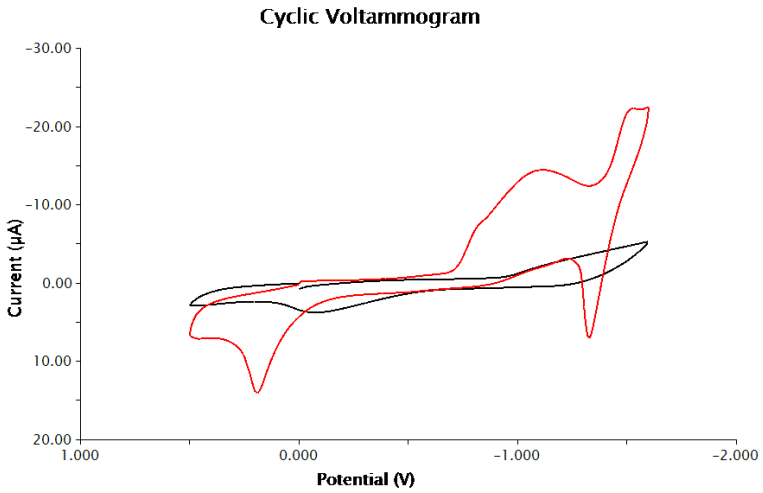
- Common problem: Noisy, distorted, or irreproducible scans
    - Ensure that all electronics are connected on the same circuit. Different outlets can be at different potentials leading to anomalous currents in the system. This has been noticed when the pH probe is used during electrochemical experiments.
    - Make sure the sparging tubing been pulled out of solution and that the solution is not being agitated or stirred
    - Ensure that the electrodes are connected to the correct lead:
        - Red/orange – working (1)
        - Purple/blue – working (2, WaveDriver only)
        - Green – counter
        - White – reference
        - Black – ground
    - Ensure that none of the electrodes or leads are touching each other or other conducting metals.
    - Ensure that all of the electrodes are submerged in the electrolyte solution.
    - Check the grounding wire or change where the ground is clipped.
    - Ensure that no motors are running on the same circuit or in the vicinity (fans, stirplates, vacuum pumps…).
    - Test each electrode separately.
        - Disconnect the alligator clip from the white banana clip and plug into the back of the green clip. Run the experiment. If the problem has disappeared, the problem is with the reference electrode.
            - Common reference electrode problems are bubbles in tube, dry vycor (particularly with new reference electrodes), and low solution level in the glass tube.
        - Polish glassy carbon (if using) and check to make sure that the electrode surface is shiny and reflective.

- If the surface is distorted, the configuration of the cell might be damaging the electrodes, seek help before proceeding.
- The brass pins at the top of the electrode can rust (especially if stored near solvent), which can lead to high resistance. The rust can be gently sanded off. Seek assistance before sanding any electrodes.

    - Check Pt counter electrode for cracks or deposited films.
- Disassemble and reassemble the circuit:
    - Disconnect USB from computer and potentiostat and reconnect.
    - Disconnect electrode leads from cell. Disassemble the cell. Take a break.
    - Approach the experiment again as though starting for the first time with fresh solutions, clean electrodes and new electrical connections.
- Common problem: erratic “spiderweb formations”
    - Typically caused by a disconnected working electrode, a short circuit or by a bubble in the reference electrode.
- Common problem: Regular, periodic noise
    - Grounding problem
    - 60 Hz noise caused by electronics in the vicinity
    - Figure shows linear sweep voltammogram with and without a fan operating inside the glovebox at the time of data collection

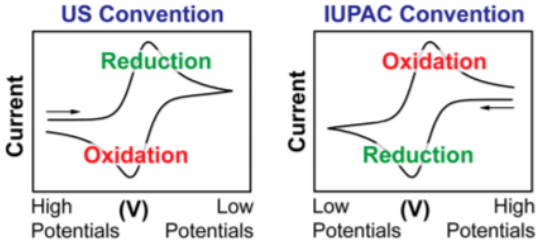


- Common problem: “Smeared-out” CV features
    - High solution resistance: add electrolyte or change cell configuration to move reference electrode closer to the working electrode.
    - Did you remeasure OCP and update iR compensation after changing something in the system?
    - The figure shows CVs of the same solution with working and reference electrodes separated by a frit (black) or in the same compartment (red).

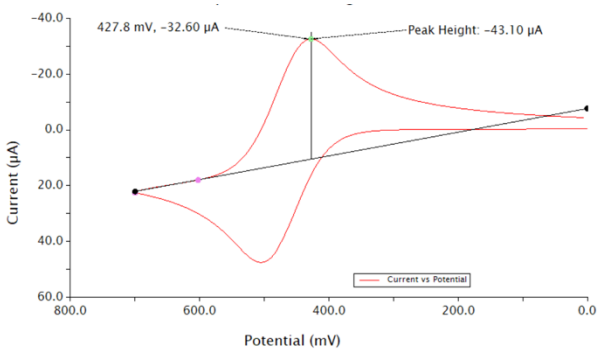


- Common problem: perfectly linear regions in CV and/or missing data points
  - Usually caused by “auto-ranging”, it is recommended to avoid errors due to software auto-ranging by turning this feature off.
- Common problem: broad features in background scans
  - Try sparging longer, in case oxygen is present. Oxygen will typically show up between -400 mV to -800 mV vs $Ag/AgNO_3$.

Data Analysis and Presentation — Quick Tips



- There are two conventions for plotting CVs. The Miller group currently uses the “US Convention” rather than the IUPAC convention (see figure, reproduced with permission from *J. Chem. Educ.* **2018**, *95*, 197, https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361, further permissions related to the material excerpted should be directed to the ACS.).
- Always report potential vs. a reference electrode.
  - In organic solvents, use $Cp_2Fe^{+/0}$ even if a different reference electrode (e.g. $Ag/AgNO_3$) or different internal reference (e.g. $Cp^*_2Fe^{+/0}$) was used.
  - This requires manually changing the measured potential vs the reference electrode based on the measured $E_{1/2}$ of Cp_2Fe.
- Peak heights should be measured vs baseline, not vs zero current, as shown in the figure.



- Always include full details on concentration of all species, electrolyte identity, solvent identity, atmosphere, scan rate(s), identity and geometry of all electrodes.

References and Related SOPs:

Dempsey *et al. J. Chem. Educ*. **2018**, *95*, 197
Bard and Faulkner *Electrochemical Methods: Fundamentals and Applications*
Saveant, *Elements of Molecular and Biomolecular Electrochemistry*
Zoski, *Handbook of Electrochemistry*