

Standard Operating Procedure

Task: Controlled Potential Electrolysis (a.k.a. Bulk Electrolysis)

Created by: Yang group (UC Irvine) Miller group (UNC)

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Background

- Controlled potential electrolysis (CPE) is an experiment where a specific potential is held for a period of time.
- CPE is usually conducted on a preparative scale, and is often called bulk electrolysis because the bulk of the material in the cell undergoes reaction. Note that there are other modes of bulk electrolysis, such as controlled or constant current electrolysis.
- CPE experiments may be conducted with a variety of goals in mind. Quantification of the amount of charge passed and the yield of product(s) can be used to determine the number of electrons transferred in a reduction reaction, the Faradaic efficiency and selectivity of a stoichiometric or catalytic reaction, to probe catalyst stability, and more.
- Electrolysis is usually performed in a cell which has separate compartments for the working and counter electrodes, often separated by a fine glass frit (or sometimes an ion-transporting membrane such as Nafion). The frit or membrane provides a charge-carrying salt bridge, while nominally separating the products formed at the anode and cathode to minimize unwanted product-product or product-electrode reactions.
- In order to pass enough charge in a reasonable amount of time, typically electrodes with higher surface areas than those used for cyclic voltammetry (CV) studies are used.
- If gaseous products are expected, the cell can be sealed during electrolysis and the post-electrolysis headspace can be sampled with a gas-tight syringe and analyzed by gas chromatography (GC).

Training Requirements:

- Glovebox or Schlenk line training
- CV training

Potential Hazards:

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

Special PPE Requirements:

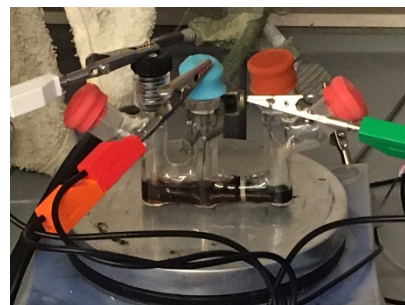
- Gloves, safety glasses, lab coat

- Other special PPE requirements should be checked based on the reagents/materials you are using

Materials Needed:

A wide variety of electrolysis cells are available, either commercially or custom-designed and prepared by a skilled glassblower. A typical 4 mL electrolysis cell used in our group is shown here. For the H-cell pictured, the following materials are needed.

- Electrolysis cell
- Reagent(s) of interest
- High purity electrolyte
- High purity solvent
- Working electrode. A common electrode material with high surface area (60 ppi) is reticulated vitreous carbon (RVC), which is prepared as described below using:
 - RVC foam block
 - Graphite rod
 - Razor blade
 - Copper thread
 - Wire cutter
- Counter electrode. A common electrode material is platinum (mesh or coil is preferred to ensure that the counter compartment reaction passes sufficient current to match the working compartment reaction). Consider having a counter electrode with substantially larger surface area than the working electrode.
- Reference electrode (the electrode should have its own junction, such as a glass frit)
- #7 Ace-Thread (fits reference electrode)
- Septa of appropriate size (consider whether they need to be punctured by electrode or GC needle)
- Stir bars for each compartment
- Potentiostat
- Volumetric glassware for preparing solutions



Procedure:

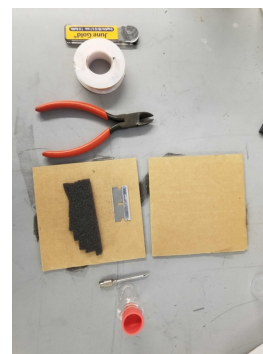
Planning

- Plan ahead. What is the goal of the experiment? What electrochemical data (e.g. current, charge) and analytical data (e.g. headspace GC, NMR spectra, ion chromatography) will be utilized before, during, and after electrolysis to characterize and quantify the reaction of interest?
 - Consider subsequent analytical experiments needed and their limits of detection
 - Consider the actual amount of solution needed and the headspace that results

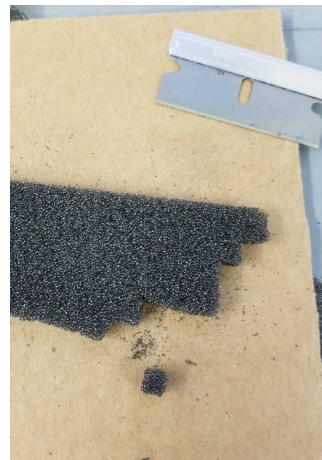
- Consider all products being made, including those being made at the cathode and the anode
- It is often useful to quickly setup a mock CPE with the exact electrodes, septa/caps, and stir bars and fill with a solvent such as acetone to get a rough idea of volumes and length/width of electrodes
- Precise cell volumes for gas analysis can be determined by recording the mass of water that fills each compartment of the cell
- If aliquots are being taken, prepare the solutions and measurements such that less than 10% of the reaction mixture will be removed during the reaction.
- Obtain “time zero” spectroscopic or analytical measurements to confirm that no product is present before electrolysis as a control.
- Prepare the solutions for electrolysis
 - Concentrations of electroactive species will be dictated by the application, but 5–15 mM is typically sufficient.
 - Volumetric glassware is strongly recommended for solution preparation when precision in concentration is needed for post-electrolysis analysis. Keep in mind that three sig figs can be achieved for masses >10 mg on our balances. For quantitative applications, always weigh out more than 10 mg of material, and use stock solutions and dilution if needed.
- Acquire CVs under the desired conditions before carrying out a CPE experiment, except with a normal working electrode, such as a glassy carbon. This will provide insight into the applied potential required for the reaction of interest, as well as appropriate electrochemical conditions (solvent, electrolyte, reference electrode, electrode materials)

RVC Working Electrode Assembly

- Carbon foam dust/residue is abrasive and a skin irritant. Wear chemical-resistant gloves while handling. Clean up the bench area with a wet paper towel to avoid spreading particles.
- Before cutting off the RVC electrode needed; first prepare the graphite rod/copper wire connection
 - Take a 0.7 mm or greater graphite pencil lead rod and cut to the appropriate length (usually about half way). Cut off a piece of copper thread about 6” long.
 - Wind the copper thread tightly around one end of the graphite rod making a strong graphite-copper contact. Do not coat too much of the graphite rod (< 0.5 cm) as you do not want any copper wire to touch/be submerged within the solution.
 - After forming a tight graphite-copper connection; take the remaining copper thread and loop back upon itself several times to create a thicker, braided copper wire.

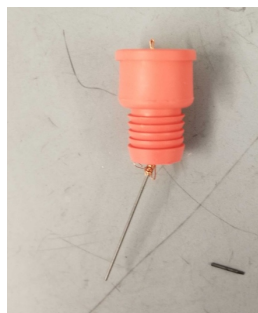


- Before making electrodes, determine the size needed. Then cut off the amount of RVC needed using a razor blade (usually a cube/rectangular prism). Attach to the copper thread/graphite rod by inserting the graphite into the RVC electrode. If the RVC electrode is too thin, at this point it will often fall off the end of the graphite rod. Check that the RVC is not too thick to fit through the neck of the cell
- Take a wide-gauge needle (18 gauge) and pierce a septum. Then feed the braided copper wire through the needle. Remove the needle, leaving the copper wire embedded in the septa.
- Place in the warming oven for at least 12 hours to remove any traces of water.



Experimental Setup

1. Bring all the necessary materials properly into a glovebox.
 - a. If possible, pre-assemble as much of the setup prior to bringing to glovebox (e.g. puncture electrodes through septa and adjust for proper height in electrolysis cell)
 - b. Reference capillaries that have already been soaked in electrolyte on the bench top should NOT be pumped into the glovebox, as the electrolyte will



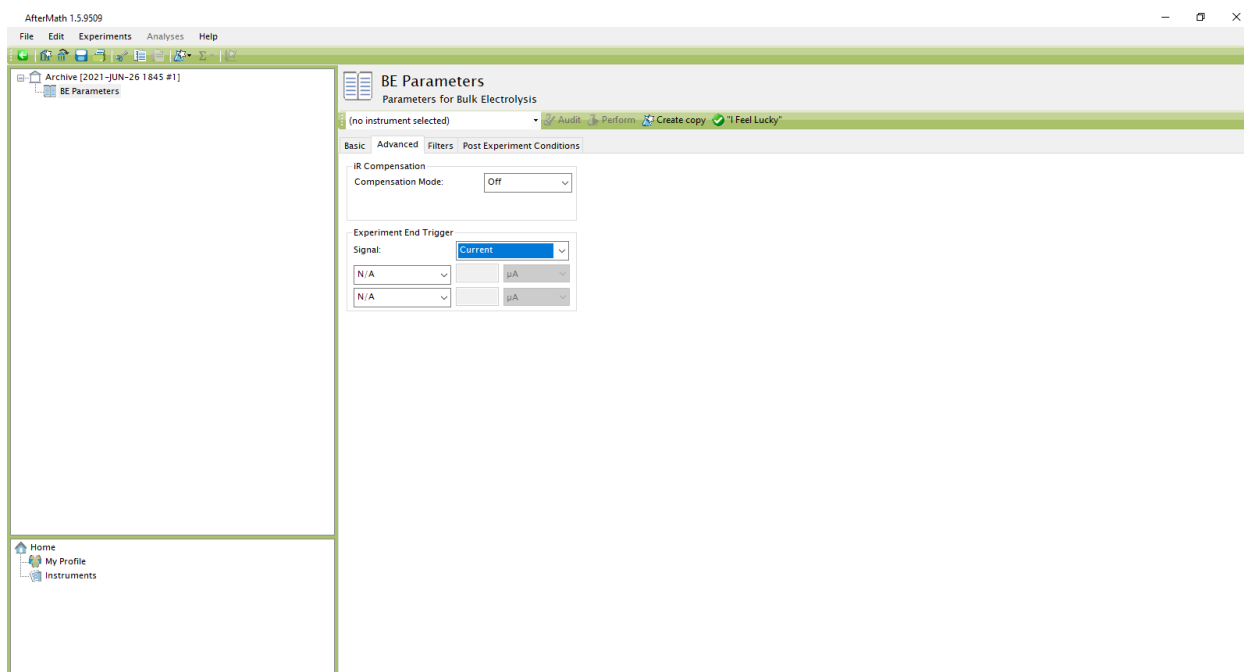
crack the frit as it dries out. Prepare and store your reference capillaries in the glovebox.

- c. Note: these steps can also be carried out on the bench or on a Schlenk line and can be dried as needed under nitrogen. Make sure solvents are degassed prior to use by sparging with nitrogen.
2. The electrodes should be on opposite sides of the frit in the cell. Adjust the height of the wire on top to make sure they fit properly then take them back off (electrodes should be out of the way of stirring)
 3. Add the precise volume of solution containing electrolyte and reagent(s) into working compartment.
 4. Add electrolyte solution to counter compartment.

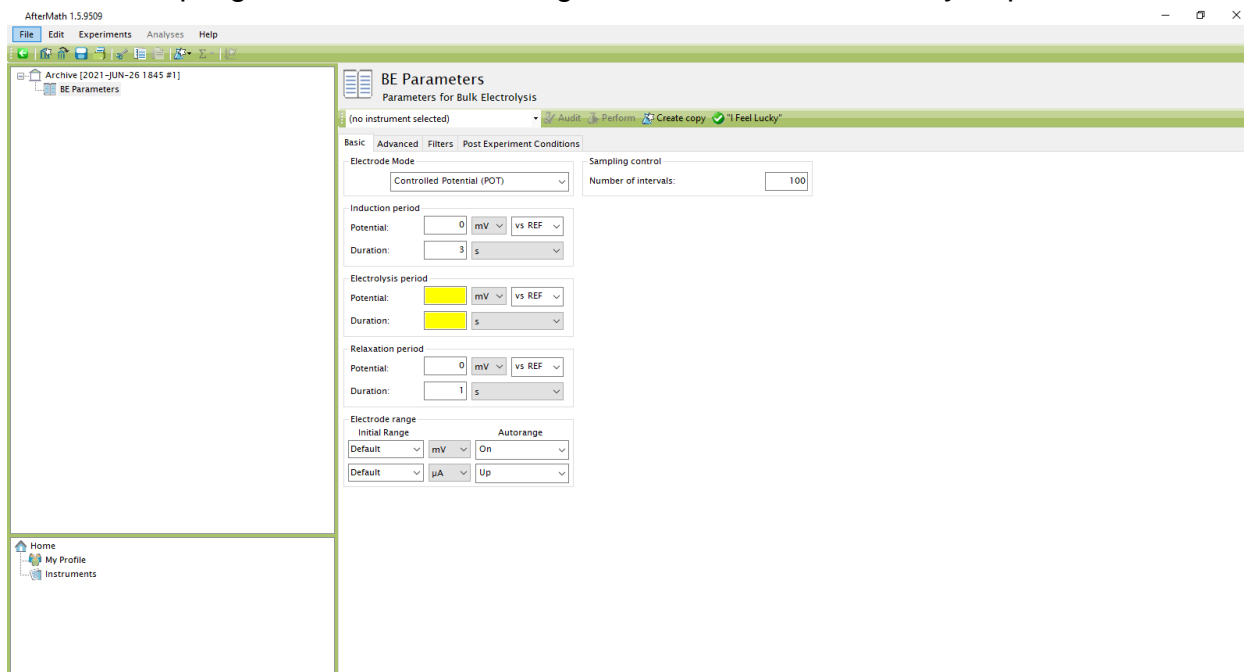
5. Mark the solution height in the working compartment with a marker or tape. This helps track down potential issues pertaining to the solutions migrating to another compartment due to pressure differentials.
 - a. This is often exacerbated when the solvent lines in both compartments are wildly different. Aim for the solvents to be the same height
 - b. When gas products are produced, the pressure differential will typically cause the solution levels to shift. Consider using a cell with a pressure bridge if gaseous products are to be analyzed.
6. Place the reference and counter electrodes on top of their corresponding ports, but do not seal them. If you are worried about pressure buildup **and** are not going to analyze gaseous products, a vent needle can be used.
7. At this point, it may be possible to run the experiment in the glovebox. If running on a Schlenk line outside of the box, seal all ports with septa or threaded electrodes.

Running the Experiment

1. Carefully clip on the electrical leads and run all necessary CVs to determine the choice of potential for the CPE.
2. After deciding on potential, run a test 30-second electrolysis at this potential with stirring. Using the average current from the test electrolysis, calculate how long you will need to run the actual electrolysis in order to pass the amount of charge needed (Hint: consider what you're trying to show with this experiment. See "Data Workup" section below for additional help). Current drops over time, so the actual electrolysis should be set for at least double the calculated time. Alternatively, you can set the experiment to finish if a certain amount of current is passed before the time is finished under the Advanced tab.



3. Select the number of data points you want. The default is 100 points which means no matter how long your electrolysis is, you only get 100 data points (Example: 100 points of a 100-minute electrolysis means that it records the current being passed once a minute). This is entered as the “Number of Intervals” in the “Sampling Control” box on the right side of the Bulk Electrolysis parameters tab.



4. Double check that stirring is still on and stable (not bouncing around or hitting anything, especially the fragile frit)

5. Seal all ports. If performing gas sampling of headspace, all septa should be sealed with grease and electrical tape and screw caps should be used with o-ring seals.
6. Start the electrolysis and regularly monitor the solvent level and stirring. Stirring should be stable and consistent and not touching the electrodes or the frit, as that disrupts the experiment.
7. At the end of the electrolysis, measure the solvent volume in each compartment. This measurement is critical for quantitative analysis of either solutes or gaseous products, as the solvent volume and headspace volume may be changing over the course of the experiment.
8. Proceed with characterization and analysis as desired. If doing gas headspace analysis, draw aliquot using gas-tight syringe through a septum in the working compartment before opening the cell. If doing liquid product analysis, open a port on the working compartment and remove solution using syringe or pipet. Note: removing headspace gas from a tightly sealed and closed cell will cause a pressure differential between the compartments, leading to solution transfer. Keep this in mind if doing both gas and liquid product analysis

Troubleshooting/Common Errors

- Rapid drop in current may be the result of stirring problems. If the stir bar is hitting the electrodes or the frit, or it gets stuck in a crevice of the cell, the slower mass transport leads to less current being passed.
- Complete loss of current may indicate an electrical problem. Stop the electrolysis and check that all electrodes are properly attached and connected to the correct leads. The RVC working electrode is quite delicate and it is not uncommon for it to break or become disconnected. Note: DO NOT touch electrodes/leads while the experiment is running, as this can lead to electric shock.
- Noisy current vs. time plots may be the result of gas bubbles produced at the electrode(s) during the electrolysis. The bubbles forming and releasing can lead to sudden surface area changes occurring due to changes in functional electrode surface area. This is normal and expected, and difficult to circumvent, though tapping the glass can help remove bubbles from the electrode.
- If the current response jumps between positive and negative values, this typically indicates an electrical issue with the potentiostat, and the experiment should be stopped to troubleshoot. In particular, check that electrode connections/wires are not touching. Also check that the applied potential selected is in the right units (V vs mV). This problem is most likely not caused by issues with stirring.
- Overreduction, decomposition, or unexpected product selectivity may indicate incorrect applied potential. Check that the parameters are correct and are set to the correct units. Confirm that there is NO iR compensation applied. iR compensation correlates with the surface area of the working electrode and the high surface area of WE used during CPE (such as RVC) results in such large

values of resistance that they cannot be appropriately compensated for, leading to different-than-intended applied potentials.

- During electrolyses last more than about 12 hours, typical problems encountered include potential drift of the reference electrode, solution crossover between the compartments, and loss of gaseous products. Using a Ag/AgNO₃ reference electrode with a new nanoporous glass membrane can help minimize drift and leakage from the reference electrode. Crossover can be minimized by using fine frits or specialized membranes, and special gas tight cells can be constructed to minimize gas leaks.
- Low current density is sometimes symptomatic of a clogged frit or membrane, or a cell having a frit/membrane that is too small. If a frit becomes clogged or is very small diameter, slow ion transport through the frit can limit the current density.

Cleanup

- The cell should be thoroughly cleaned and degreased. If needed, the whole cell can be cleaned with aqua regia (safety hazard: see aqua regia SOP for details). If cleaned using aqua regia, rinse with copious amounts of water and then consider adding a rinse with a basic solution at later stages to neutralize the glassware/frit. Also make sure to thoroughly degrease all the joints, using pipe cleaners with hydrocarbon solvent if needed. If grease remains and the cell is put in the oven, it will burn into a brown residue that is much more difficult to remove.

Data Workup

- The output of the CPE experiment will be a plot of charge (in Amps, which is Coulombs/second) vs. time (in seconds). To get the total amount of charge passed (in Coulombs), you therefore need to integrate the area under the curve. This can easily be done in Aftermath by right-clicking on the plot and selecting integrate.
- Once you know the Coulombs of charge passed, you can use Faraday's constant to calculate moles or charge passed in order to determine equivalents of charge passed with respect to moles of catalyst or product.
 - $\text{mol } e^- = \text{charge} / F$; $F = 96485 \text{ C}\cdot\text{mol}^{-1}$
- The Faradaic efficiency of a product is taken by the ratio of moles of product generated to the moles of electrons passed (adjusted for the equivalents of electrons needed for 1 equivalent of product). If generating multiple products, a Faradaic efficiency should be calculated for all products.
 - $\text{FE} = \text{mol product} / \text{mol } e^-$; make sure to correct for if the product formed requires multiple electrons (example: CO₂ to HCO₂H is a 2 e^- reduction, N₂ to 2NH₃ is a 6 e^- reduction)
- For gaseous products, you need to know the headspace volume of the cell in order to get from % gas (which you get from the GC calibration curve) to moles of gas.

References and Related SOPs

- Electrochemistry CV SOP
- Electrochemistry Troubleshooting SOP
- Aqua Regia SOP