Standard Operating Procedure

Task: Electrochemistry — Aqueous Silver Reference Electrodes
Date: October 8, 2021

Background:

- Reference electrodes enable the controlled regulation of the potential at the working electrode during electrochemical experiments.
- Effective reference electrodes involve a well-defined reversible reduction and have the ability to recover to their stable potential after current flows through the cell, typically by approaching unity activity for each component of the reference electrode reaction.
- A common reference electrode for aqueous electrochemistry utilizes the Ag/AgCl reaction.
- Ag/AgCl reference electrodes can be prepared or refreshed in a manner that ensures an accurate and consistent potential in your electrochemical data.
- Note that while many stable reference electrodes are available in water**,** nonaqueous reference electrodes are more prone to drifting, typically requiring the use of an internal reference such as ferrocene.

Training Requirements:

- Lab safety training
- Acids/bases Training Wheel
- Complete Training Modules 1–4 in Dempsey et al. *J. Chem. Educ*. **2018**, *95*, 197

Potential Hazards:

- Chemical hazards specific to concentrated HCl
- Electric shock

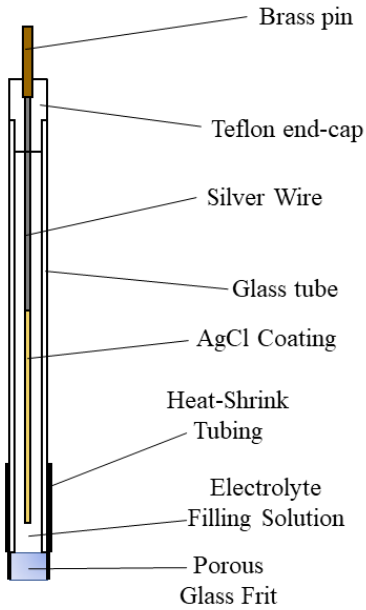
Special PPE Requirements:

- Oven mitts

Materials Needed:

- Glass tubing of diameter appropriate to fit into Ag wire electrode
- High-purity Ag wire electrode
- Vycor porous glass plugs
- Heat-shrink tubing
- Scissors
- Heat gun
- Fine sandpaper
- Potentiostat
- HCl for prepping 1M solution
- NaCl/KCl for prepping 3M solution
- HPLC (NERL) Water

Procedure:

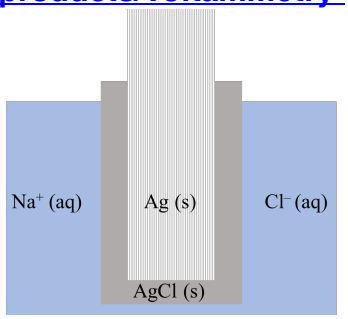


Locating necessary components. Reference electrodes consist of four primary parts—a body, a top seal, a junction, and an active component. Spare parts to assemble your own reference electrode can typically be found in the electrochemistry bench, but links for reordering these components are also included below:

- The **top seal** contains a Teflon end-cap and a brass pin soldered to a silver wire which sticks out of the top. The Teflon end-cap also contains a cavity which fits a glass tube. An airtight and leakproof seal between the glass tube and the end-cap is ideal, as it will ensure the stability, homogeneity, and lifetime of the electrode. **https://www.chinstruments.com/accessories.shtml** ***The part number used for fabricating your own aqueous reference electrode is CHI112, which comes with an empty glass tube of appropriate diameter to create a relatively airtight and leakproof seal. CHI111 is a premade Ag/AgCl reference electrode not covered in this SOP. In the Miller Lab, it is heavily preferred that you fabricate your own aqueous silver reference electrode.**
- The **body** of the electrode is a glass tube vital for isolating the active component from the rest of the electrochemical cell. The glass tube must have the appropriate diameter to snugly fit into the end-cap is the primary piece constituting the electrode body.
    - Again, **CHI112** (see above) comes with glass tubing appropriate for construction of the body of your electrode and should lead to a good fit with the Teflon end-cap.
- The **junction** of the electrode separates the filling solution from the rest of the electrochemical cell while allowing similar ionic mobilities on either side of it. A good junction is a Vycor frit affixed to the bottom of a glass tube with heat-shrink tubing.
    - **Vycor frits**: **https://orders.gamry.com/porous-glass-tips-pkg5.html** Note that while the material on these tips is not specified, Gamry has confirmed that the material is Vycor (**as of Spring 2021**). If some time has passed since the last time these frits were ordered, it may be necessary to call and re-inquire regarding this. For more information regarding frit material selection, refer to the following paper:

        Mousavi, M. P. S.; Saba, S. A.; Anderson, E. L.; Hillmyer, M. A.; Bühlmann, P. Avoiding Errors in Electrochemical Measurements: Effect of Frit Material on the Performance of Reference Electrodes with Porous Frit Junctions. *Anal. Chem.* **2016**, *88*, 8706–8713.

- **Heat-shrink tubing**: **https://www.prosense.net/en/products/voltammetry-basi/reference-electrodes/qvmf2027/**



- The **active component** defines the potential the constructed electrode references to. In aqueous cells, the active component is typically a filling solution of KCl or NaCl in high purity H_2O and a silver wire coated with AgCl. It is important to note that the concentration of the filling solution will affect how to convert to other reference electrodes from the potentials measured using your aqueous silver reference electrode. A table summarizing this conversion is shown below.

Converting Between Aqueous Reference Electrodes

Target Reference Electrode	*From*	Saturated KCl/NaCl AgCl electrode	3M KCl/NaCl AgCl electrode
SHE		+0.197 V	+0.209 V
SCE		-0.044 V	-0.032
SSCE		-0.039 V	-0.027 V
NCE		-0.083 V	-0.071 V
MSRE		-0.443 V	-0.431 V

SHE: Standard Hydrogen Electrode; SCE: Saturated Calomel Electrode (saturated KCl); SSCE: Saturated Salt Calomel Electrode (saturated NaCl); NCE: Normal Calomel Electrode (1M KCl); MSRE: Mercury(I) Sulfate Reference Electrode (saturated K_2SO_4)

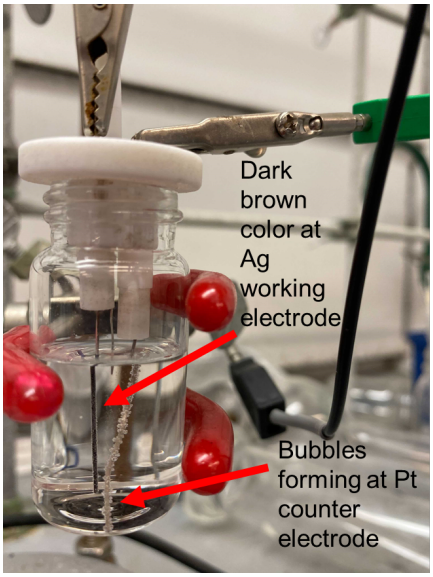
Preparing the AgCl-coated wire. AgCl-coated wires necessary for aqueous reference electrodes can be easily prepared via the following procedure adapted from a method reported by Zoski, Smith, and Stevenson in the *Handbook of Electrochemistry* (pp 73-110):

1. Obtain a silver wire electrode (CHI112).

2. The high purity silver wire important for this experiment will initially be coated with a passivating oxide layer undesirable for reference electrode purposes. To remove this layer, abrade the wire carefully using fine sandpaper. Then dip the wire in concentrated HNO_3 for a few seconds before soaking the wire with HPLC (NERL) water for 30 seconds and wiping with a Kimwipe. The wire should be noticeably shinier after this step.

3. Next, the metallic Ag layer of the electrode is chloridized electrochemically. A solution containing 1M HCl should be prepared before constructing a three-electrode cell with the polished Ag wire serving as the working electrode, a platinum wire serving as the counter electrode, and a Ag wire serving as the (pseudo)reference electrode.

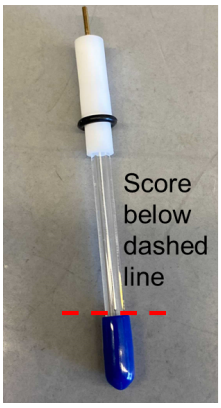
4. Perform a controlled potential using the setup from step 3. The potential selected for this experiment should be well anodic of the Ag/Ag^+ couple; +500 mV (vs. Ag/Ag^+) tends to work well. Electrolyze for 30 minutes. You will know if you have selected an appropriate potential based on the formation of bubbles at your counter electrode (H_2 from proton reduction) and discoloration of the polished Ag electrode to brown or tan (formation of AgCl). A picture of this setup is shown to the right.



5. The newly AgCl-coated wire should be rinsed with HPLC (NERL) water and soaked for at least 1 day. After washing, the wire will be range from pink to purple-brown.

Assembling Your New Aqueous Reference Electrode. Now that we have our AgCl-coated wire, we can assemble the reference electrode.

1. To prepare a glass tube of appropriate length for the electrode, start with the part CHI112 (Ag/Ag^+ reference electrode), which already includes a glass tube of appropriate diameter. Cut off the end of the glass tube just below where the Ag/AgCl wire ends to yield a tube ready to accommodate the attachment of the Vycor frit that will serve as your junction. The picture to the right shows where to cut.



2. Next you should prepare the body of the electrode by affixing a Vycor frit to the end of the glass tube using heat shrink tubing. To do this slide the unheated heat shrink tubing onto the frit and glass tube. It is only necessary to push about 1-2 cm past the frit connection to the tube. Trim the excess tubing off of the bottom with scissors.

3. Heat-shrink the tubing carefully using a heat gun. **Make sure that no flammable material is near the heat gun while doing this and be aware of other materials that may melt under excessive heat**. Successfully completing this step will be apparent once the tubing has tightened around the tube/frit connection, ensuring it is waterproof.

4. Prepare the electrode filling solution of 3M NaCl or KCl solution in HPLC (NERL) water. It is critical that you know the concentration of this solution and the ions present in it as this will affect the electrode's reference potential. (See the table at the end of this document for more information.)

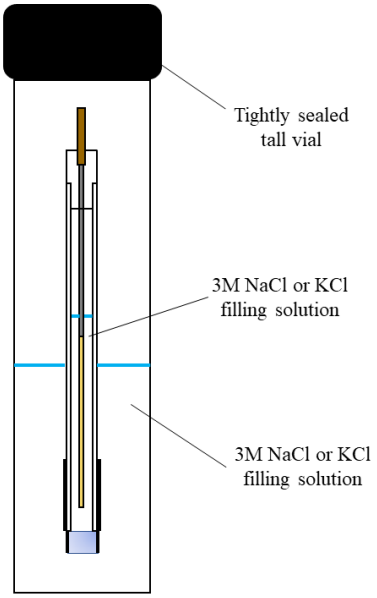
5. Carefully pipette the filling solution into the newly fabricated electrode body.

6. Slide the body onto the top seal containing the AgCl coated Ag wire. **This connection should be as secure as possible to minimize evaporation of the filling solution over**

time. If you are concerned about the secureness of this seal, you may add a layer of electrical tape, but make sure that this tape is not exposed to solution over time.

Storing Your New Aqueous Reference Electrode. Care should be taken to store your new electrode to ensure its longevity and minimal drift from the reference potential. Several best practices regarding storage are listed below:

- Prepare a 3M NaCl or KCl solution in HPLC (NERL) water identical to that used for the electrode filling solution. Find an airtight container to seal the electrode inside when not in use and fill it with this solution. Ideal containers will allow for easy storage of the electrode upright, a configuration which will keep the junction soaking in a solution of consistent ionic strength.
- Regularly check to make sure that storage and filling solutions are not escaping or evaporating. **If the frit is allowed to dry out, do NOT simply add more salt solution and re-soak. If the electrode dries out the junction/frit should be replaced, as salt crystals have likely formed in the pores of the frit.**



Testing and Troubleshooting the Electrode: Assuming the previous procedures have been followed, the electrode should now reference to the Ag/AgCl reaction in aqueous electrochemical cells. However, should you suspect any issues with your electrode, refer to this section for useful guidelines.

- **Testing the electrode reference potential**:
  1. Prepare a solution of potassium ferricyanide ($[K]_3[Fe(CN)_6]$) in HPLC water with a supporting electrolyte, such as 0.1 M sodium phosphate buffered to pH 7. The concentration of ferricyanide should be approximately 1 mM.
  2. Prepare a three-electrode cell consisting of a polished glassy carbon working electrode, a platinum counter electrode, and your Ag/AgCl reference electrode.
  3. Fill the cell with the ferricyanide solution and connect a potentiostat to the electrodes.
  4. Set up a cyclic voltammetry experiment scanning from -1000 mV to +1000 mV at a rate of 100 mV/s.
  5. You should be able to observe a redox couple corresponding to the ferricyanide ($[Fe(CN)_6]^{3-}$) to ferrocyanide ($[Fe(CN)_6]^{4-}$) couple. It is important to note that that the reversibility of this couple is heavily dependent upon the surface character of the glassy carbon electrode. If the couple you observe is only quasi-reversible, don't sweat it! However, the $E_{1/2}$ of the couple should be close to that expected for the couple. For pH 7 0.1 M sodium phosphate, this potential is approximately +436 mV, though the exact number depends on a number of factors such as the electrolyte being used, the concentration of salt in your filling solution, and the surface kinetics of the glassy carbon working electrode.
  6. If the $E_{1/2}$ you obtain is significantly different than the one you expect, it is time to try to troubleshoot your electrode.

- **Remedying Common Issues:**
  - **Replace the junction**. Some electrolyte mixtures are more prone to precipitating within the pores of the Vycor frit. If this occurs, it is typical for the frit to change colors from colorless to yellow or brown. If contamination is suspected, replace the frit.
  - **Replace the filling solution**. Because Vycor is porous, electrolyte from electrochemical experiments may diffuse into the body of the electrode, causing the reference to drift. This is normal and happens over time, especially to frequently used electrodes. To fix this, prepare a fresh filling solution of 3M NaCl or KCl in HPLC water. Dump the previous contaminated one out and rinse the empty electrode body and AgCl coated Ag wire 2-3 times with the new filling solution. Finally, refill the body and reattach it to the Teflon end-cap, being careful to avoid bubbles.
  - **If the previous two steps do not work, rechloridize the electrode**. To do this, refer back to the "Preparing the AgCl-coated Wire" section of this SOP. Remember to clean the wire thoroughly by sanding and rinsing before proceeding to the electrochemical chloridization!

References and Related SOPs:

- Zoski, C. G.; Smith, T. J.; Stevenson, K. J. In Handbook of Electrochemistry; Elsevier: Amsterdam, Netherlands, 2007; pp 73–110.
- Mousavi, M. P. S.; Saba, S. A.; Anderson, E. L.; Hillmyer, M. A.; Bühlmann, P. Avoiding Errors in Electrochemical Measurements: Effect of Frit Material on the Performance of Reference Electrodes with Porous Frit Junctions. *Anal. Chem.* **2016**, *88*, 8706–8713.