Reference Electrode Storage and Master Reference Electrodes

A Guide Detailing the Advantages and Setup of Master Reference Electrodes

Pine Research Instrumentation offers reference electrodes of several types. The importance of a stable reference potential is essential for comparing day to day experiments and ensuring that the desired potentials are actually applied during an experiments. A good practice it so keep a reference electrode in the lab that is never used in an experiment, called a master reference electrode. All experimental reference electrodes of the same type can be tested against the master to ensure the expected potential set point is used for all experiments. Pine Research offers two cells (e.g. Pine Research Part #: AKREFHUT1 and AKREFHUT2) suitable for reference electrode storage. Periodically testing all reference electrodes against the master reference electrode ensures that each reference electrode is working properly. The article aims to introduce the purpose of reference and master reference electrodes and how to create, store, and test a master reference electrode.

1. Background

1.1 Reference Electrode

In most traditional electrochemical techniques, a three-electrode cell is used. The three electrodes (working, counter, and reference) each have a specific function during the electrode reaction; the *working electrode* facilitates electron transfer to the analyte of interest, the *counter electrode* maintains electroneutrality by participating in a reaction of opposite sign and finally, the *reference electrode* provides a stable potential to which the working electrode potential can be compared. The stability of the reference electrode is crucial in all electrochemical experiments because individually measuring the absolute potential of each electrode is not possible. Rather, a known voltage is applied to the working electrode as a difference of potential between the reference electrode and working electrode. Therefore, if the potential of the reference electrode varies, the measured potential applied to the working electrode also varies, skewing experimental results.

Obtaining a stable reference electrode potential is accomplished by utilizing a reversible redox pair at equilibrium. In practice, there are very few redox pairs that can act as reference redox pairs. The silver chloride reference electrode, whose shorthand electrochemical reaction is written as $Ag|AgCl|KCl\ (saturated)$, is the most widely used reference electrode for aqueous systems. It is as stable and reliable as the saturated calomel reference electrode (SCE, whose shorthand electrochemical reaction is written as $Hg|Hg_2Cl_2\ |KCl\ (saturated)$), but not as toxic.[1] The silver/silver nitrate reference electrode, whose shorthand electrochemical reaction is written as $Ag|AgNO_3\ in\ CH_3CN$ |frit, is often used as an alternative reference electrode for non-aqueous solutions.[2]

With proper storage and cleaning techniques, most reference electrodes can be used repeatedly to save construction time and cost. However, if the reference electrode frit becomes clogged with analyte or electrolyte material, a significant rise in impedance across the frit can occur, leading to errors in the potential measured between the reference and working electrodes.[3] Often, this error propagates from experiment to experiment until the reference electrode condition worsens to the point that data is visibly incorrect to the scientist.

1.2 Master Reference Electrode

It is clear that only looking for inconsistencies in data to determine if a reference electrode is malfunctioning is a poor scientific method. Instead, electrochemists have proposed a *Master Reference Electrode* to evaluate the stability of laboratory active reference electrodes. A master reference electrode utilizes a saturated electrolyte solution of the same reversible redox pair as the test reference electrode. Because the redox pairs are the same and both electrodes are in the same solution at equilibrium, the voltage difference between the master electrode

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and test reference electrode should be zero. It is important to test all reference electrodes periodically with respect to the master electrode (if possible, before each experiment, see Section 3). Frequent comparison of laboratory active reference electrodes to the master reference electrode prevents error propagation discussed in Section 1.1. The master electrode is never used in an actual experiment, and so its frit is less likely to become clogged or otherwise to malfunction.

2. Master Reference Electrode Construction

2.1 Products and Instrumentation

Pine Research Instrumentation offers two reference electrode storage units for your needs (Pine Research Part #: AKREFHUT1 and AKREFHUT2, see Figure 1). Both storage units are equipped with multiple 14/20 ports to vertically orient and mount a standard size reference electrode (9.5 $mm\ OD$), as well as a center 14/20 port to store and distinguish the master reference electrode. AKREFHUT1 features a removable polytetrafluoroethylene (PTFE) lid for solution addition while AKREFHUT2 features larger side ports (24/25) for solution addition and removal. A set of PTFE stoppers for all ports is included for both.

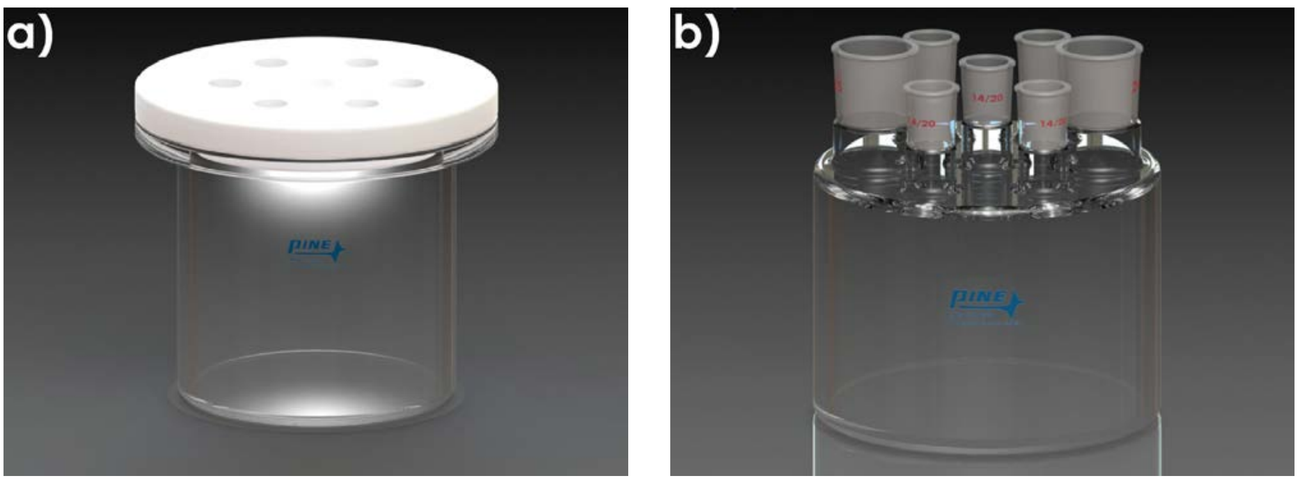


Figure 1. Reference Electrode Storage Containers a) AKREFHUT1 and b) AKREFHUT2

INFO:

Pine Research Instrumentation also offers a variety of standard reference electrodes. For more information, shop on our website:

https://www.pineresearch.com/shop/

2.2 Constructing the Reference Electrode Storage System

To construct the reference electrode storage system, follow the instructions outlined below:

1. Prepare a saturated electrolyte solution (common examples are saturated KCl in water or saturated $AgNO_3$ in acetonitrile, see Figure 2).
2. Pour the saturated electrolyte solution into the reference electrode storage container. A layer of electrolyte crystals should be visible at the bottom of the container (see Figure 2).
3. Place the master reference electrode in the saturated electrolyte solution.

Figure 2. Steps to Construct a Master Reference Electrode

> **INFO:**
>
> **It is recommended that the master reference electrode, the electrode that has never been used in an actual experiment, is stored in the center port of the storage cell. This way, experimental reference electrodes are stored in a port around the outside of the cell to differentiate them as experimental electrodes.**

2.3 Storage and Maintenance

The master reference electrode should be stored in a saturated electrolyte solution (e.g. KCl in water) in a container like AKREFHUT1 or AKREFHUT2 that has not been used in experiments. The master reference electrode should never be used in conjunction with chemicals other than the electrolyte. Other reference electrodes utilizing the same electrolyte solution may be stored alongside the master reference electrode. Any ports or openings that are not used on the reference electrode storage container should be sealed with PTFE stoppers to prevent solution contamination (see Figure 3).

Periodically, the electrolyte solution needs to be changed. Prepare excess fresh, saturated electrolyte in a separate container. Divide the electrolyte into two containers. Thoroughly rinse the outside and inside of the master reference electrode with the fresh electrolyte before filling it with fresh electrolyte. To prevent the frit from drying, rest the master reference electrode in one of the electrolyte solution containers. Repeat this procedure for any other reference electrodes stored in the reference electrode storage container. Pour the old electrolyte solution from the reference electrode storage container into a proper waste container and then rinse it with fresh electrolyte solution before filling it completely with the fresh solution. Remount the master reference electrode and any other reference electrodes in the 14/20 port of the storage container. Seal off any open ports with PTFE stoppers.

Figure 3. Example Reference Electrode Storage Container with Proper Sealing

3. Testing Reference Electrodes

The master reference electrode can be used to test if another experimental reference electrode is working properly. As discussed in Section 1.1, a properly functioning reference electrode relies on a well-defined and constant equilibrium of redox pairs. This stable equilibrium gives rise to a constant potential. Therefore, if both the master reference electrode and experimental electrode are functioning properly, the voltage difference measured between them should be less than $5\ mV$ because they are governed by the same reversible redox reaction at equilibrium. This test can be performed easily with a multimeter or potentiostat. The following sections will describe how to use both techniques.

3.1 Using a Multimeter

A multimeter has special electronic circuitry that enables it to measure several electronic signals including voltage. To test the potential difference between a reference electrode and the master reference electrode with a multimeter, simply connect one lead of the multimeter to the test reference electrode and the other lead to the master reference electrode (see Figure 4). Ensure that the leads do not touch and that both electrodes are allowed to equilibrate in the same electrolyte solution (at least 10-15 minutes). Turn the selection dial on the multimeter to mV or V to measure the potential difference. The value should be less than $5\ mV$ if the test reference electrode is working properly. If the value is changing rapidly on the display, allow the electrodes to equilibrate longer with the solution. If the potential difference is greater than $5\ mV$, the experimental reference electrode must be refreshed or replaced.

Figure 4. Reference Electrode Test with a Multimeter

3.2 Using a Potentiostat

A potentiostat (such as the WaveNow or WaveDriver) can perform an experiment called Open Circuit Potential that utilizes similar circuitry as the multimeter to find the potential difference between two electrodes. To test the potential difference between the experimental reference electrode and master reference electrode with a potentiostat, short the counter (green for Pine Research USB-based potentiostats) and reference (white) banana posts together and connect them to the master reference electrode. In addition, the working drive (red for Pine Research USB-based potentiostats) and working sense (orange for Pine Research USB-based potentiostats) banana posts should be shorted together and connected to the experimental reference electrode (see Figure 5). Ensure that the leads do not touch and that both electrodes are allowed to equilibrate in the same electrolyte solution (at least 10-15 minutes). Open AfterMath and select **Open Circuit Potential** from the **Experiments** menu. Click "I Feel Lucky" in the upper right corner to set default parameters for the experiment (see Figure 6). Click perform to run the experiment. The resulting chronopotentiogram should be relatively flat (without a slope) and have values between $\pm 5\ mV$ (see Figure 7).

TIP:

If a smoother chronopotentiogram is desired, change the number of intervals to a larger number in the experimental parameters pane.

Figure 5. Reference Electrode Test with a Potentiostat

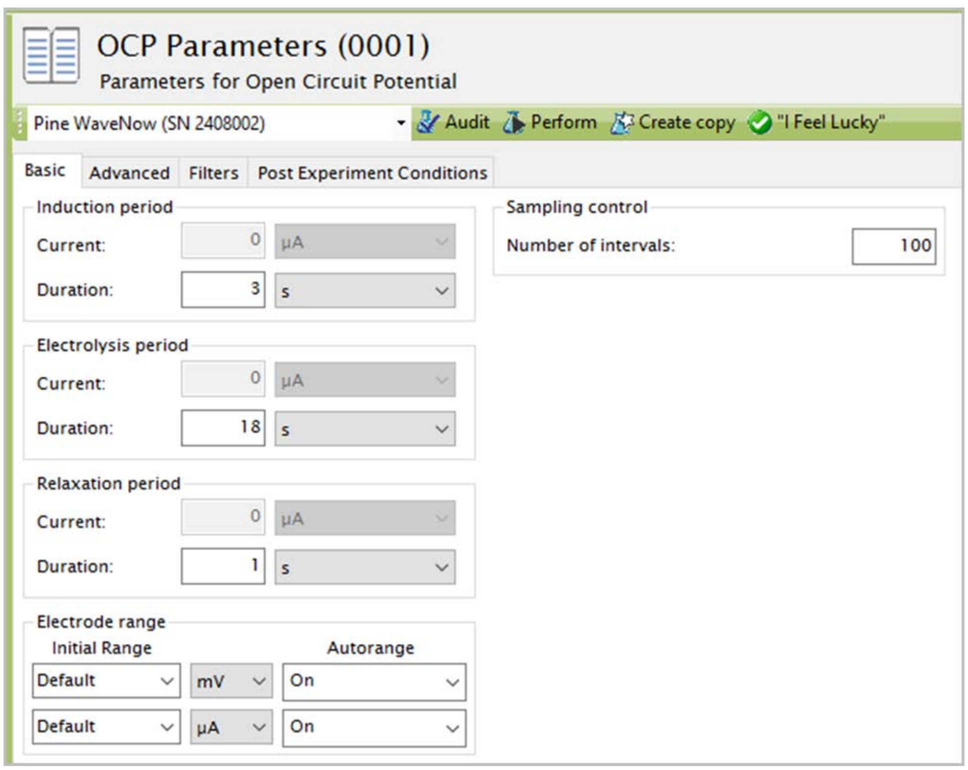


Figure 6. Open Circuit Potential Parameters

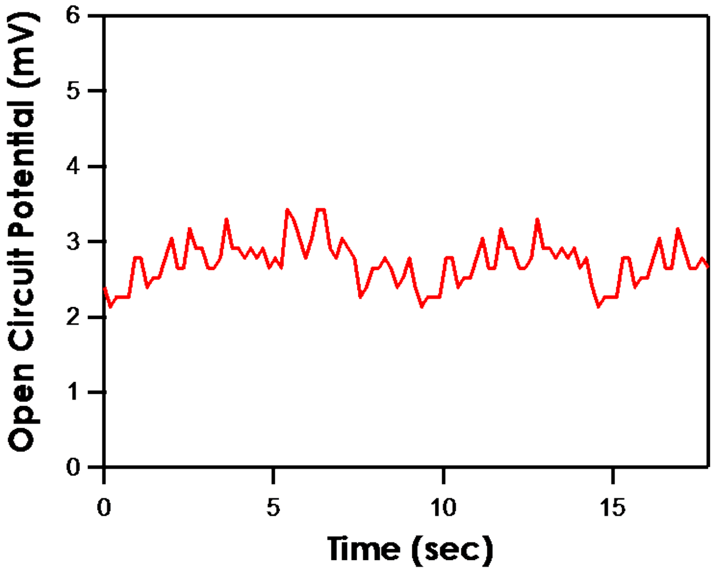


Figure 7. Typical Chronopotentiogram Acquired when Testing Reference Electrodes

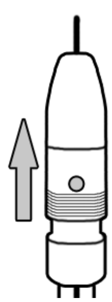
4. Refreshing Reference Electrodes

If an experimental reference electrode fails during testing against the master reference electrode, the reference electrode needs to be refreshed and tested again. Should it fail a second time, it is possible the reference electrode is damaged (significant current passed through the reference electrode, often by connecting the wrong leads to the electrode during use), or the frit has become blocked.

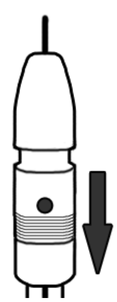
4.1 Refreshing a Reference Electrode

When the ceramic frit has been plugged (by precipitates or crystals), a higher than normal input impedance may cause problems such as potentiostat instability. To refresh the electrode, take the following steps:

1. Slide the access door down and drain the internal solution through the filling port.
2. Fill the glass electrode with distilled water (or 1 $M\ HCl$) and store the electrode in water (or 1 $M\ HCl$) instead of filling solution, for 24 – 48 hours.
3. After, drain the water (or 1 $M\ HCl$) through the filling port and replace with filling solution. Close the filling port and store as instructed for 24 hours before use. Check E° vs. the lab master reference electrode before use.



Slide access door (D) up to close the fill port for storage



Slide access door (D) down to open the fill port during use and to fill or drain

5. References

1. Zanello, P. *Inorganic Electrochemistry: Theory, Practice, and Application*; The Royal Society of Chemistry: Cambridge, UK, 2003.
2. Gritzner, G.; Kuta, J. Recommendations on Reporting Electrode Potentials in Nonaqueous Solvents. *Pure Appl. Chem.* **1984**, *29*, 869–873.
3. Faulkner, L. R. . A. J. B. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; John Wiley & Sons, Inc., 2001.

6. Contact Us

If you have any questions or would like to inquire about the availability of the reference electrode storage containers described in this document, please contact us via the means provided below:

6.1 By E-mail

Send an email to pinewire@pineresearch.com. This is the general sales email and our team will ensure your email is routed to the most appropriate technical support staff available. Our goal is to respond to emails within 24 hours of receipt.

6.2 By Website

There is a contact us form on our website. There may also be additional resources (such as YouTube videos) for some of the products mentioned here: http://www.pineresearch.com.

6.3 By Phone

Our offices are located in Durham, NC in the eastern US time zone. We are available by phone Monday through Friday from 9 AM EST to 5 PM EST. You can reach a live person by calling +1 (919) 782-8320.

