Reference Electrode Storage and Master Reference Electrodes

A Guide for Expert Reference Electrode Storage and Use

Pine Research Instrumentation offers various types of reference electrodes, many suitable for use as master reference electrodes. To aid in the proper use of a master reference electrode, Pine Research offers two reference electrode storange solutions. A master reference electrode with a well-known, stable equilibrium electrode potential is essential to test the performance of other laboratory active reference electrodes. Periodically testing all reference electrodes against the master reference electrode ensures that each reference electrode is working properly and in ideal condition. The article herein aims to introduce the purpose of reference and master reference electrodes, and then provides instructions on how to create, store, and test a master reference electrode.

1. Background

1.1 Reference Electrode

Many electrochemical techniques employ a three-electrode cell. 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 the *reference electrode* provides a stable potential against which the working electrode is poised. 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 potential difference 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. 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.

INFO:

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

https://www.pineresearch.com/shop/electrodes/reference-electrodes/standard

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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 developed a *Master Reference Electrode* to evaluate the stability of laboratory active reference electrodes. A master reference electrode is never used experimentally, rather it is kept in pristine working order by storing in electrode filling solution. Thus, a master reference electrode serves as the ultimate reference electrode in the lab, to which all others of same construction can be compared.

By comparing the potential difference across two of the same type of reference electrode, scientists determine the validity of a laboratory active reference electrode function. Due to the nature of a reference electrode, the reference potential is not directly measured. Rather, it is determined relative to the master. With both reference electrodes immersed in the same high electrolyte filling solution (*e.g.*, saturated KCl for the single junction Ag/AgCl reference electrode from Pine Research), the voltage difference (measured by open circuit potential) is ideally zero. $\Delta E = 0\,mV$ indicates that the internal redox reaction of both the master and laboratory active reference electrodes are at the same equilibrium and that the ceramic frits are clear and porous as expected. A small shift in open circuit potential ($-5\,mV < \Delta E < 5\,mV$) may be considered tolerable for the laboratory. The physical world often interferes with perfectly ideal reference electrode behavior, thus the lab must determine their own acceptable deviation between laboratory active vs. master reference electrodes.

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 must never be used in actual experiments to ensure its function, condition, and potential difference remain constant.

2. Electrode Storage Preparation

2.1 Products and Instrumentation

Pine Research Instrumentation offers two reference electrode storage cells (part #: AKREFHUT1, 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.

The reference electrode storage cells are ideal for permanently storing the master reference electrode as well as storing laboratory active reference electrodes between experiments. Never allow a reference electrode filling solution to completely dry. Doing so may cause crystallization build up inside the electrode and within the frit. While soluble, these crystals may interfere with a reliable reference potential.

INFO:

Never allow the filling solution in a reference electrode to completely dry. Always store an unused reference electrode in an adequate volume of filling/storage solution.

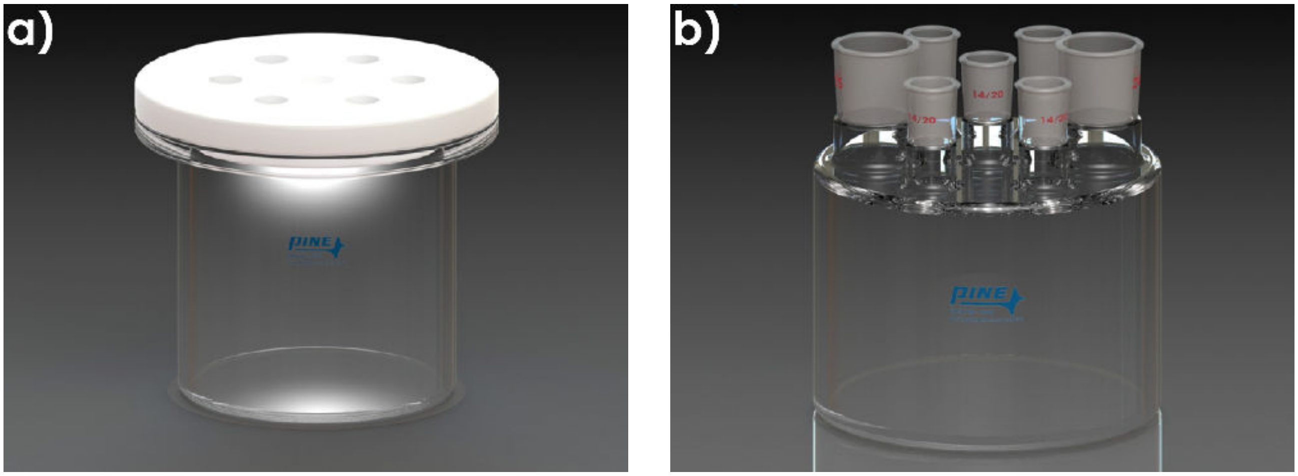

Figure 1. Reference Electrode Storage Containers a) AKREFHUT1 and b) AKREFHUT2

2.2 Typical Reference Electrode Solutions

Reference electrodes are filled with an electrolyte solution, whose composition depends on the redox reaction of interest within the electrode. For reference electrode storage, the same solution should be prepared and used in the storage cells. Pine Research recommends that a separate storage cell is used for each type of reference electrode, to minimize contamination across different electrolyte solutions. For the reference electrodes offered from Pine Research, a table has been provided to inform your electrode storage solution choices (see: Table 2-1).

Reference Electrode Name	Chemistry	Filling/Storage Solution
Silver/Silver Chloride (single junction)	$AgCl_{(s)} + e \rightleftharpoons Ag_{(s)} + Cl^-$	$4\ M\ KCl$ (saturated)
Silver/Silver Chloride (double junction)	$AgCl_{(s)} + e \rightleftharpoons Ag_{(s)} + Cl^-$	$10\%\ KNO_3$
Saturated Calomel (SCE)	$Hg_2Cl_{2(s)} + 2e \rightleftharpoons 2Hg_{(l)} + 2Cl^-$	$4\ M\ KCl$ (saturated)
Mercury/Mercury Sulfate (single junction)	$Hg_2SO_{4(s)} + 2e \rightleftharpoons 2Hg_{(l)} + SO_4^{2-}$	$\sim 0.7\ M\ K_2SO_4$ (saturated)
Mercury/Mercury Sulfate (double junction)	$Hg_2SO_{4(s)} + 2e \rightleftharpoons 2Hg_{(l)} + SO_4^{2-}$	$\sim 0.7\ M\ K_2SO_4$ (saturated)
Mercury/Mercury Oxide	$HgO_{(s)} + 2e + 2H_2O \rightleftharpoons Hg_{(\ell)} + 2OH^-$	$4.24\ M\ KOH$

Table 2-1. Reference Electrode Types, Chemistry, and Filling/Storage Solutions

2.3 Prepare the Master Reference Electrode Storage

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

1. Prepare $500\ mL$ filling/storage solution. Refer to Table 2-1 for the appropriate filling/storage solution.
2. Pour the saturated electrolyte solution into the reference electrode storage cell. A layer of electrolyte crystals may be visible at the bottom of the container for saturated solutions (see: Figure 2).
3. Ensure the master reference electrode is filled with filling solution. If needed, use a pipette to add electrolyte solution to the master electrode. Ensure that the master electrode tube is free from bubbles and does not contain electrolyte crystal deposits (see: Figure 2).
4. Place the master reference electrode in the saturated electrolyte solution. Pine Research recommends storage of the master reference electrode in the center $14/20$ port of the cell.

Figure 2. Steps to Prepare a Master Reference Electrode and Storage Cell

2.4 Storage and Maintenance

The master reference electrode should be stored in filling/storage solution in a cell like those available from Pine Research (part #: AKREFHUT1 or AKREFHUT2). These storage cells should not be used for experimental use. 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 and solvent evaporation (see: Figure 3).

Periodically, the electrolyte solution should be refreshed. Prepare excess fresh, filling/storage solution in a separate container. Divide the filling/storage solution into two containers. Thoroughly rinse the outside and inside of the master reference electrode with the fresh filling/storage solution before filling it with fresh filling/storage solution. 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 cell. 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 Master Reference Electrodes

The master reference electrode can be used to test if another 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 test 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 and are in electrical contact by high electrolyte concentration. 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 laboratory active reference electrode under study 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, relative to the master (which again, has never been used in an experiment). 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 laboratory active reference electrode is suspect and should be reconditioned or discarded (refer to the reference electrode product information for refreshing instructions).

Figure 4. Reference Electrode Test with a Multimeter

3.2 Using a Potentiostat

A potentiostat 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 test reference electrode and master reference electrode with a potentiostat, short the counter (green lead on Pine Research WaveNow and WaveDriver series potentiostats) and reference (white lead on Pine Research WaveNow and WaveDriver series potentiostats) cell cable leads together and connect them to the master reference electrode by using an alligator clip. In addition, the working drive (red lead on Pine Research WaveNow and WaveDriver series potentiostats) and working sense (orange lead on Pine Research WaveNow and WaveDriver series potentiostats) cell cable leads should be shorted together and connected to the laboratory active reference electrode being tested (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 (Pine Research potentiostat control software) 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, try changing the number of intervals to a larger number in the experimental parameters pane.

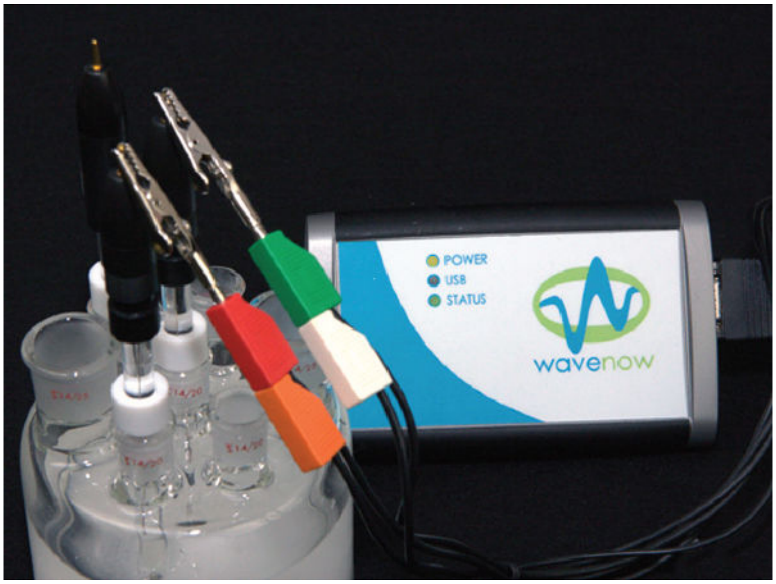

Figure 5. Reference Electrode Test with a Potentiostat

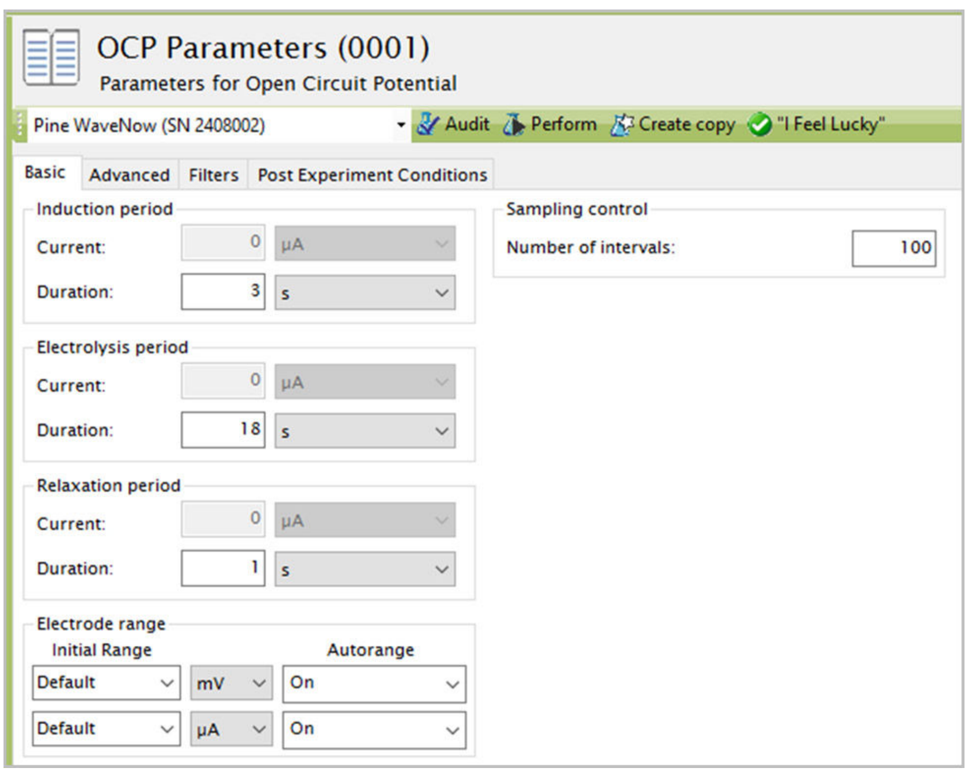

Figure 6. Open Circuit Potential Parameters

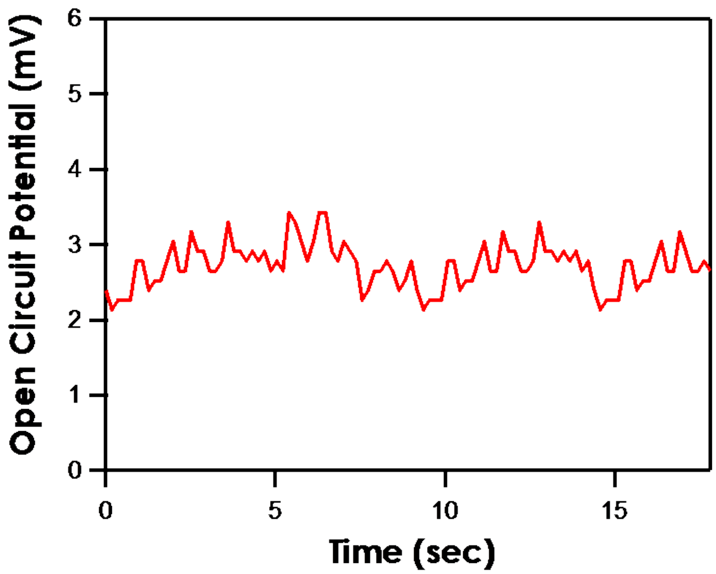

Figure 7. Typical Chronopotentiogram Acquired when Testing Reference Electrodes

4. 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.

5. 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:

5.1 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.

5.2 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.

5.3 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.

