

Reference Electrode Effects on Potentiostat Performance

Background

This Application Note presumes that you have a basic understanding of potentiostat operation.

If you are not that knowledgeable concerning electrochemical instrumentation you can find a Primer on Potentiostats on Gamry's Homepage. Experienced potentiostat users may skip the primer and read on.

It's only natural that electrochemists concentrate on the working electrode. After all, reactions at the working electrode are what they study.

However, the reference electrode shouldn't be ignored. Its characteristics can greatly influence electrochemical measurements. In some cases, an apparently "good" reference electrode can cause a complete failure of the system.

For reliable Reference Electrode performance, you should assign a Lab Master Electrode and treat it very, very carefully so it can serve as a standard for your other Reference Electrodes.

The photo below is from Dr. Barbara Shaw's lab at Penn State. The Reference Electrode in the container on the bench with the white top is the Lab Master; it's NEVER used in an actual experiment. The only purpose of the Lab Master is to serve as a check for the other Reference Electrodes, which are on the shelf in the photo.



If a Reference Electrode is suspected to be bad, the potential is measured versus the Lab Master. You can do that with a voltmeter, as in the photo, or with your Gamry Potentiostat. If the potential difference is less than 2-3 mV, it's OK. If it's higher than 5 mV, it needs to be refreshed or discarded.

The Ideal Reference Electrode

Everyone agrees that an ideal reference electrode has a stable, well-defined electrochemical potential. Common reference electrodes (SCE, Ag/AgCl, Cu/CuSO₄) meet this criterion when they are functioning properly. Many workers do not realize how often reference electrodes fail, causing drastic changes in their potential. Many complaints of potentiostat failures turn out to be reference electrode failures.

Testing Reference Electrode Potential

The simplest way to test an unknown reference electrode is to compare its potential with a known good reference electrode. Place the known good and unknown electrodes in a beaker containing an electrolyte. Momentarily connect the two electrodes to the inputs of a good quality voltmeter. Ideally the voltmeter's input impedance should be 100 MΩ or greater. Try not to leave the voltmeter connected for a long period of time.

If the voltmeter reads less than 3 mV difference between the electrodes, the unknown reference is good enough for routine lab use.

If you do not have a known good reference electrode, get four or five electrodes of the same type. Check each electrode's potential versus one electrode chosen as the "standard". Good electrodes should all have the same potential versus the standard. Any electrode different from the rest is probably bad.

If you do not have a high quality voltmeter, you can use your potentiostat to make the voltage measurement. Connect one reference electrode to the working electrode terminal of your potentiostat. Hook up the working sense wire if you have one. Connect the second reference in the normal fashion. Do not connect the counter electrode to anything and do not turn the cell on.

Immerse the reference electrodes in electrolyte. Read the open circuit voltage of the system. This is a measure of the potential difference between the two reference electrodes.

In a Gamry Instruments' system, you can do this test using the Eoc vs. Time experiment, or by running any experiment and using its Initial Delay step.

An ideal reference electrode should also have zero impedance. As discussed below, a reference electrode's impedance can strongly affect the performance of a potentiostat.

Impedance of Laboratory Reference Electrodes

The impedance of a standard laboratory reference electrode is usually determined by the resistance of its isolation junction. This junction separates the reference electrode's internal filling solution from the test electrolyte. A variety of junction types have been used, including ceramic frits, unfired Vycor™ frits, and asbestos threads. A slow flow of the filling solution through this junction is necessary for proper electrode operation. This flow can have the unwanted effect of altering the test solution composition, so the flow rate is kept to a minimum.

Unfortunately, slower flows require a more restricted flow path, and restrictions raise the resistance of electrolyte in the path. There is a fundamental tradeoff between electrode impedance and leakage rate. An SCE with a Vycor™ frit (for

example Gamry Instruments' P/N 930-03) will typically have an impedance of about 1 k Ω . Ceramic junctions can have lower impedance than this while asbestos thread junctions have much higher impedance.

Reference Electrode Impedance Check

The following procedure can be used to quickly estimate the impedance of your reference electrode. You must have EIS capability in your electrochemistry system to perform this test.

1. Partially fill a beaker with electrolyte. If you normally use a Luggin capillary, the concentration of this electrolyte should be approximately the same as that of your test solution.
2. Immerse the tip of your reference electrode into the solution. If you will be using a Luggin capillary place the tip of the Luggin capillary in the solution and place your reference in the Luggin. Make sure you have an unbroken electrolyte path from the tip of the reference to the tip of the Luggin capillary.
3. Add a high surface area platinum wire or graphite rod counter electrode to the solution.
4. Connect the reference electrode to the working (and working sense) leads of your potentiostat. Yes, we said the working electrode!
5. Connect the graphite rod to the reference and counter electrode (and counter sense if applicable) leads.
6. Set up an EIS scan starting from 5 kHz (or higher) and scanning towards lower frequencies. Make sure that the applied DC potential is zero versus the open circuit potential (E_{oc}). A 5 mV AC amplitude should be sufficient.
7. Start the scan. Make sure that the DC current is less than 10 mA. If it isn't, shut off the potentiostat as soon as possible.

CAUTION: Do not allow the test to run if significant DC currents are flowing. Your reference electrode could be damaged if this occurs.

8. Let the scan run for about a decade in frequency, then halt the scan and turn off the cell. Note the magnitude and phase of the measured impedance.

The measured impedance at high frequency should be resistive (the phase angle should be near zero).

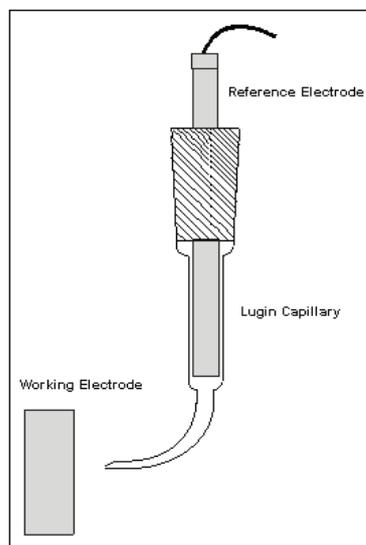
If it is, the impedance magnitude is a good estimate of your reference electrode's resistance. If the phase angle isn't near zero, the impedance cannot be trusted.

We have used this test on several electrodes in our lab. It gives reasonable results on our P/N 930-03 SCE with a Vycor frit.

Reference electrode junctions can become clogged, often without causing any significant shift in the reference's DC potential. Adsorption of organic materials or precipitation of insoluble salts in the junction can both cause clogging. The resistance of a clogged junction can exceed 1 M Ω .

A double junction reference electrode is used to minimize filling solution contamination of the test electrolyte. A double junction is often required when chloride ion contamination is a concern. The resistance of a double junction reference electrode is generally more than twice that of a single junction electrode.

Electrochemists often use a Luggin Capillary to control the placement of the reference electrode relative to the working electrode. The Luggin capillary is filled with electrolyte. The resistance of this electrolyte adds to the reference electrode impedance. Larger diameter, shorter Luggin capillaries have lower impedance than narrow bore, longer capillaries.



Corrosion chemists often use a pseudo-reference electrode in electrochemical corrosion testing. The pseudo-reference is a second piece of the working electrode material immersed in the same solution. If both the working electrode and pseudo-reference corrode similarly, they should have similar potentials. In most cases, the impedance of a pseudo-reference electrode is smaller than that of standard reference electrodes.

Bubbles and Reference Electrode Impedance

A reference electrode with a gas bubble interrupting its electrolyte path has a very high impedance. The bubble can be produced by electrolysis, from deaeration gas, outgassing of a heated electrolyte, or from trapped air. You should always check that your electrochemical setup has an unbroken electrolyte path from the working electrode to the sensing element within the reference electrode.

Be especially careful if your reference electrode has a flat isolation frit. If this flat surface is horizontal within the cell, it can easily trap a gas bubble. A 45 degree angle on this surface allows natural convection to remove any bubble that tries to stick on this surface.

Luggin capillaries are also notorious for problems with bubble entrapment.

Reference Electrode Impedance and DC Errors

High impedance reference electrodes can cause DC errors. At DC, the electrometer input current of most modern potentiostats is less than 50 pA. Ohm's Law tells you that a reference electrode with a 20 k Ω resistance causes a DC voltage measurement error of less than one microvolt. Reference electrode potentials are typically only reproducible to about one millivolt, so a one microvolt error is inconsequential. Reference electrode impedance must get quite high before DC errors become significant.

Reference Electrode Impedance and AC Errors

The situation for AC signals is quite different. A typical reference input has a capacitance of 5 pF. A 20 k Ω reference electrode connected to this input forms an RC low pass filter with a 100 nsec time constant. This filter will severely attenuate sine waves with frequencies greater than 1.5 MHz. It will also cause a phase shift of close to 4° at 100 kHz.

The effects become worse as the reference electrode impedance rises. Mansfeld, Lin, Chen, and Shih (1) have shown that EIS phase data can be severely distorted through this effect. They recommend use of a reference electrode combined with a capacitively coupled platinum wire to minimize these errors. See below for a further discussion of this combination.

Capacitive Cells and Potentiostat Stability

High impedance reference electrodes also degrade potentiostat stability.

All potentiostats can become unstable when connected to capacitive cells. The capacitive cell adds phase shift to the potentiostat's already phase shifted feedback signal. The additional phase shift can convert the potentiostat's power amplifier into a power oscillator. Unfortunately, almost all electrochemical cells are capacitive at high frequency.

Potentiostat oscillation is an AC phenomenon. However, it can affect both AC and DC measurements. Oscillation often causes excessive noise or sharp DC shifts seen on the system's graphical output. A potentiostat is often stable on less sensitive current ranges and unstable on more sensitive current ranges. This effect is induced by phase shifts in the cell voltage caused by the current measurement circuit. These phase shifts increase as current sensitivity increases.

The Gamry Instruments' PCI4 Potentiostat has been tested for stability with cell capacitors between 10 pF and 750 F. In all but its fastest control amp speed setting, it is stable on any capacitor in this range - as long as the impedance in the reference electrode lead does not exceed 20 k Ω . With reference electrode impedances greater than 20 k Ω , the PC4 may oscillate. The RC filter formed by the reference electrode impedance and the potentiostat's input capacitance causes yet more phase shift in the feedback needed for potentiostat stability.

Longer cell cables make the problem worse by increasing the reference terminal's effective input capacitance.

Most waveforms applied to the cell are digital approximations to a linear waveform. There are steps in this waveform. Even when the system is stable (not oscillating), it may exhibit ringing whenever there is a voltage step applied to the cell. While this ringing is not a problem with slow DC measurements, it can interfere with faster measurements. The steps taken to eliminate potentiostat oscillation also help to minimize ringing.

Improving Potentiostat Stability

There are a number of things that you can do to improve an unstable or marginally stable potentiostat/cell/reference electrode system. This list is not in any particular order. Any or all of these steps may help.

Lower the reference electrode impedance

Make sure that you don't have a clogged reference electrode junction. Avoid asbestos fiber reference electrodes and double junction electrodes. Avoid small diameter Luggin capillaries. If you do have a Luggin capillary, make sure that the capillaries' contents are as conductive as possible.

Slow down the potentiostat's control amplifier

The Gamry Instruments' PCI4 has 4 control amplifier speed settings which can be selected in software. Slower settings are generally more stable. Simple software changes allow user control of these settings.

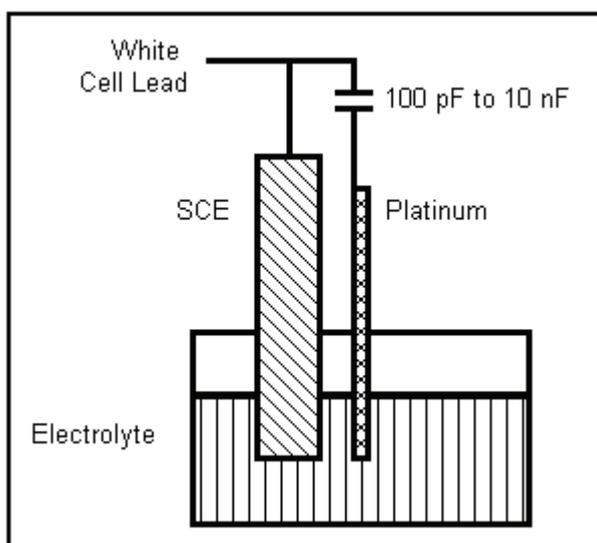
Increase the PCI4's I/E stability setting

The PCI4 includes 2 capacitors that can be paralleled with its current measurement resistors. These capacitors are connected to relays that are under software control. Switching in these capacitors improves system stability by minimizing phase shifts caused by current measurement circuit.

Add a capacitively coupled low impedance reference element in parallel with your existing reference electrode

The classic fast combination reference electrode is a platinum wire and a junction isolated SCE. The capacitor insures that DC potential comes from the SCE and AC potential from the platinum wire. The capacitor value is generally determined by trial and error.

Fast Combination Reference Electrode

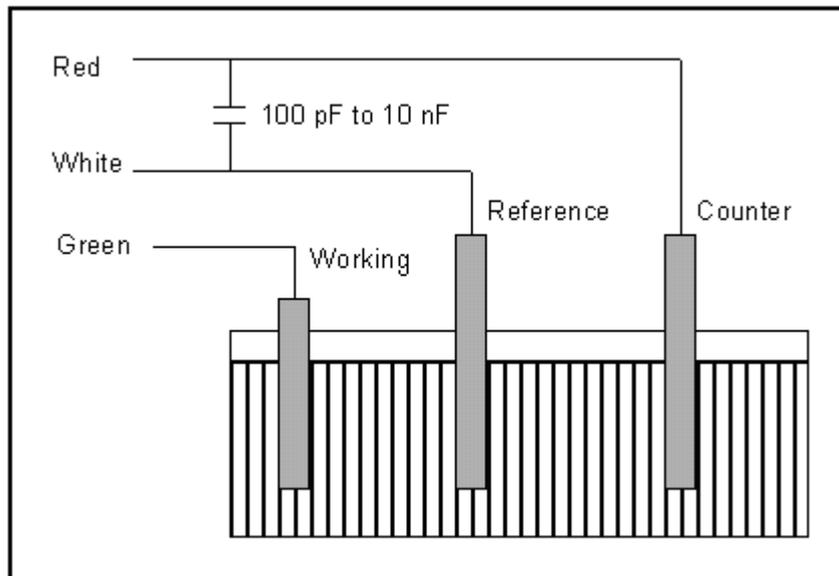


Provide a high frequency shunt around the cell

A small capacitor between the counter and reference cell leads allows high frequency feedback to bypass the cell. The capacitor value is generally determined by trial and error. One nanofarad is a good starting point.

In a sense, this is another form of an AC coupled low impedance reference electrode. The counter electrode is the low impedance electrode, eliminating the need for an additional electrode in the solution

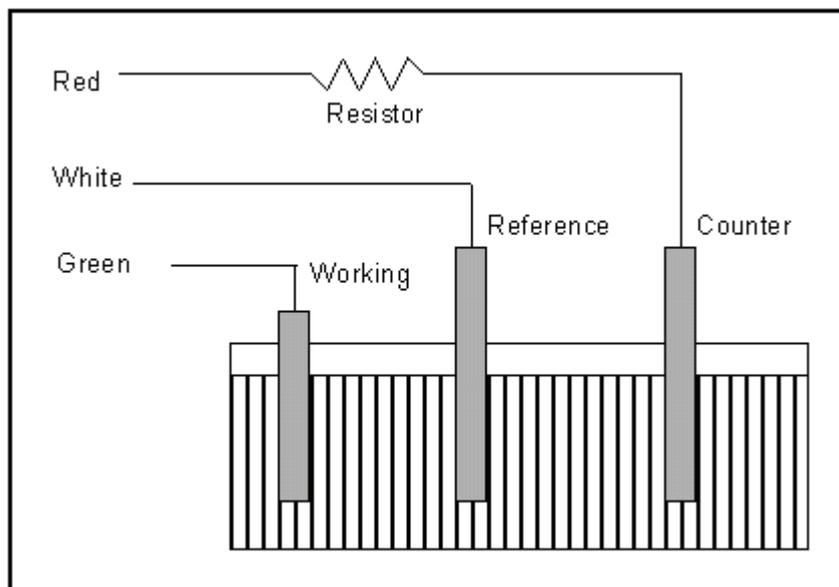
High Frequency Shunt



Add resistance to the counter electrode lead

This change lowers the effective gain bandwidth product of the control amplifier. As a rule of thumb, the resistor should be selected to give one volt of drop at the highest current expected during the experiment. For example, if you expect your highest current to be around 1 mA, you can add a 1 k Ω resistor.

Resistor Added for Stability



References

- (1) F. Mansfeld, S. Lin, Y.C. Chen and H. Shih, "Minimization of High-Frequency Phase Shifts in Impedance Measurements", JES 135, 906 (1988).