Technical Note 200

Subject: Getting to Know Your Potentiostat: Potentiostat Stability Considerations

INTRODUCTION

When a company sells corrosion and impedance measurement instrumentation to customers that use the equipment to explore a wide variety of test cells and environments, there is always a chance that the equipment will be used in situations that will compromise the performance. One such situation has been observed more and more. This problem is a result of using a differential electrometer in the 263A, 273A and PARSTATs.

In the old days, the 173 and similar instruments used a single-ended electrometer design to control the potential of the electrode (see Figure 1). This design was possible due to the fact that the I/E converter was such that the working electrode was held at virtual ground. This style electrometer slowed down the response of the potentiostat and masked many of the problems encountered when using real cells.

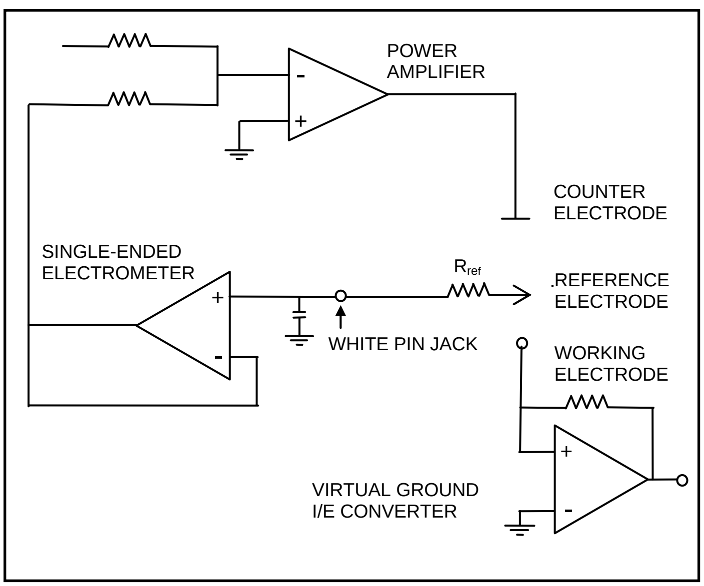

FIGURE 1: Simplified schematic of a 173 potentiostat.

In moving to the design of the current follower, used in more recent vintages of the potentiostats, the I/E converter is such that the ground electrode is no longer held at virtual ground. This requires that a differential electrometer be used to control the potential. Figure 2 shows the design employed in the 273A. The differential electrometer requires potential input not only from the reference electrode, but also from the working electrode. One benefit from this particular electrometer design is that during periods of overload of the current, potential control of the cell is maintained.

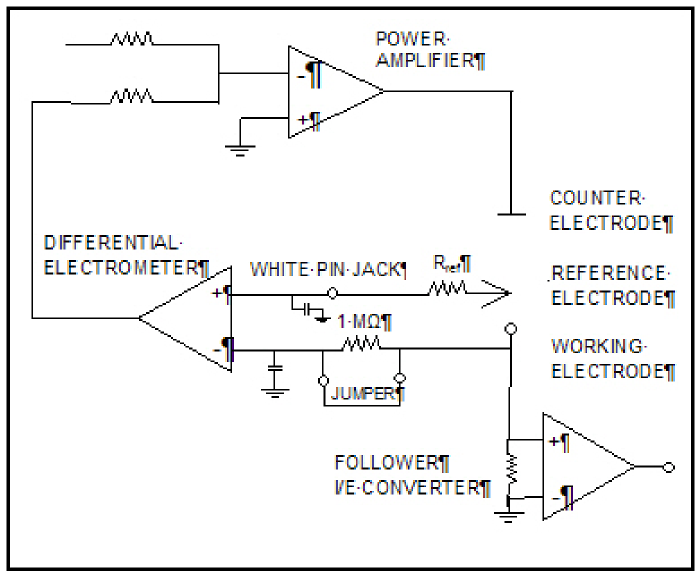

FIGURE 2: Simplified schematic of the 273A potentiostat.

The PARSTATs and Model 263A potentiostats also have differential electrometers despite the fact that they have virtual ground I/E converters.

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PROBLEM

One condition that could cause severe problems for a differential electrometer is when the reference impedance (R_{ref}) becomes very large, on the order of 50,000 Ω or more. Some of the situations where this can result are when Vycor frits used on the reference electrode and the bridge tube are dried out and reused, when the solution resistance is extremely high, when the bridge tube filling solution is highly resistive or when a luggin capillary arrangement for the reference is employed. In these instances, the reference circuit impedance could be increased to a value greater that the 50,000 Ω believed to be required for this problem to occur. This increased impedance, coupled with the stray capacitance of the reference circuit, slows down the negative feedback (stability generating) side of the electrometer operational amplifier. The positive feedback (stability destroying) side of this electrometer is not similarly slowed. When this occurs, oscillation of the potentiostat is likely to result.

Most of the time, this problem can be addressed by examining your reference electrode. Making sure that the frits are new, using a bridge tube filling solution with higher conductivity and making sure there are no air bubbles in the reference electrode or the bridge tube will possibly eliminate the problem. However, sometimes these remedial actions are not sufficient to remove the problem.

How does one overcome this potentiostat or experimental design limitation? One way to gain some insight into the problem is to remove the black shorting plug that shorts the working and sense leads together on the front panel of the electrometer (Model 273A). This will incorporate a 1 MΩ resistor into the working input of the electrometer (see Figure 3) and may increase the time constant of the working input to match that of the reference. This should reduce or possibly eliminate the oscillations. However, by removing the shorting plug from the electrometer, you have compromised the capability of the electrometer and may produce errors in measurement. Thus, this is not a solution to the problem but should indicate the source of the problem. There are, however, a number of solutions to this problem.

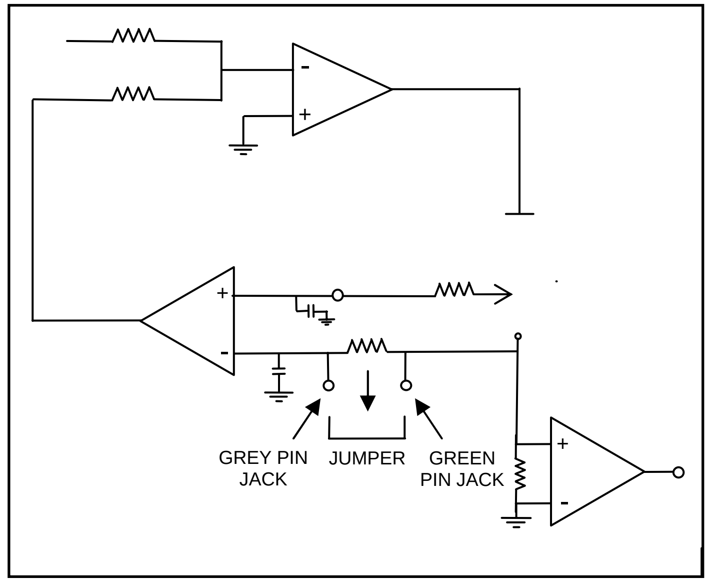

FIGURE 3: Effect of removing the shorting plug.

SOLUTIONS

If the problem occurs because of the restricted volume (poor conductance) of the luggin capillary, the solution may be as simple as placing a platinum wire inside of the capillary, beginning at the liquid junction of the reference electrode and terminating as close as possible to the luggin tip (see Figure 4).[1] This will short the high reference resistance. This will also attenuate the mains interference that may be present and reduce the need for Faraday shields. This method will also work when the wire is placed inside of the bridge tube that is sealed with a Vycor tip.

Perhaps one of the easiest ways of addressing this problem is to place a 0.1 µF capacitor between the counter electrode and the reference electrode (see Figure 5). This has the effect of slowing down the potential controlling op amp (summing amplifier) and does not allow the potential control to outrace the feedback response.

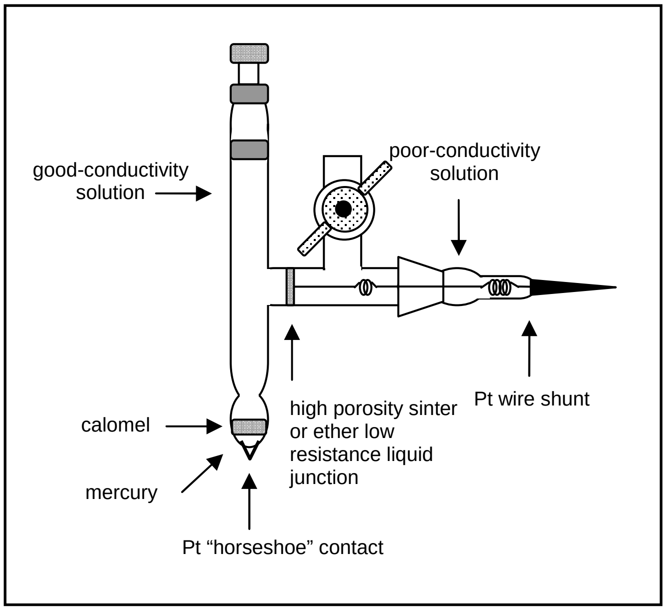

FIGURE 4: Placing Pt wire inside the reference bridge tube.

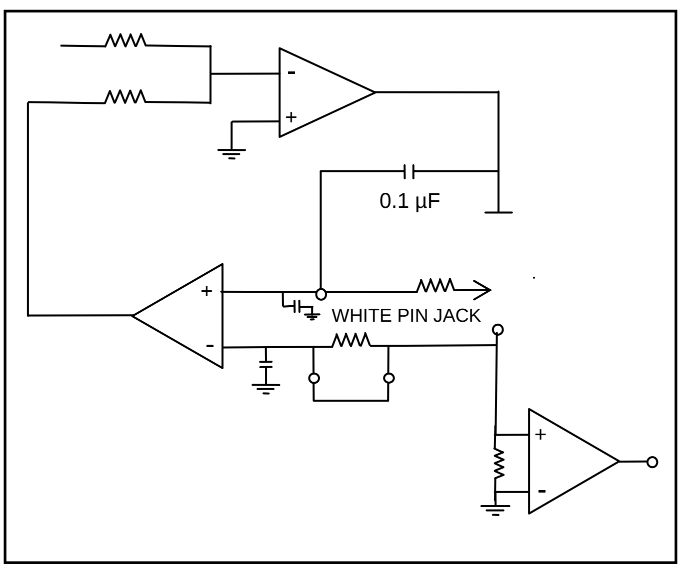

FIGURE 5: Shorting the reference and counter electrodes.

If the experiment that needs to be run is a corrosion type experiment, then placing a 0.1 -1 µF capacitor between the working and the ground leads will allow the high frequency ac signal causing the problem to bypass the current measuring resistors. This will tend to slow down the potentiostat's current measurement and would eliminate the oscillations. When using a large electrode and measuring small currents, this solution will have the additional benefit of removing unwanted ac current noise. However, this solution will not work for impedance experiments.

For impedance experiments, use a platinum wire in parallel with the reference electrode that is normally used. One end of the platinum wire should terminate close to the tip of the reference electrode or bride tube, whichever is closer to the specimen. The other end of the wire is connected to the input jack of the reference lead before it goes into the electrometer. The placement of a 0.1 -1 µF capacitor in series with this wire will allow the high frequency component of the signal to bypass the reference electrode (if a 1 µF capacitor is used, anything over 2 kHz will be shunted) while the dc component will be passed through the reference electrode.

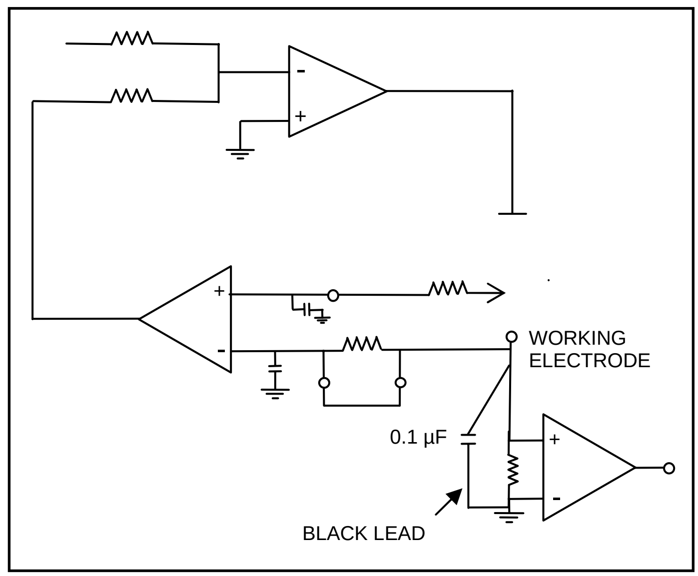

FIGURE 6: Shorting of the working and ground leads.

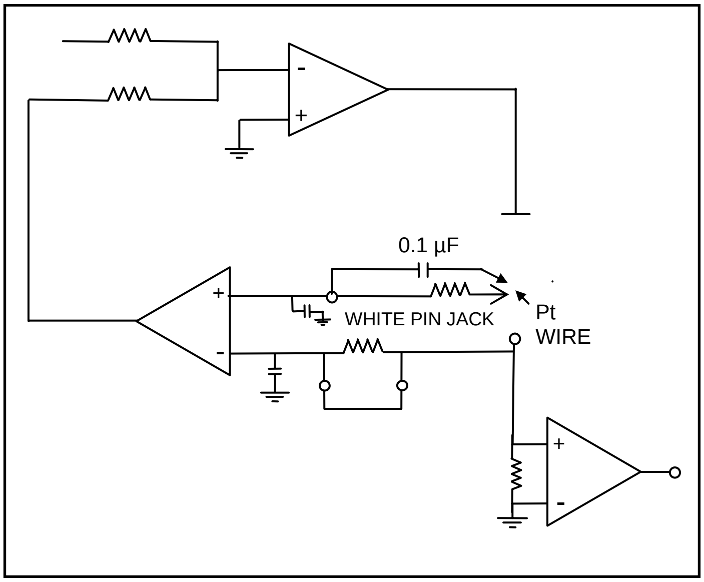

FIGURE 7: High frequency bypass of the reference.

These are a few of the suggestions that have been offered to improve the response of a differential electrometer in a cell environment that produces a high reference impedance. We are always open for new, improved ways of eliminating this problem. Of course, when all else fails, the use of a "pseudo-reference" electrode, like a platinum wire alone, will work but then the actual electrode potential is not known.

REFERENCES

1. Fletcher, S.; Horne, M. *J. Electroanal. Chem.*, 297 (1991), 297-299, Short Communication.