Potentiostat Fundamentals

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GAMRY INSTRUMENTS

Outline

- What is a Potentiostat?
- What is a Galvanostat?
- What kind of trouble will you encounter?
- What additional resources are available for you?

What is a Potentiostat?

- A potentiostat is an instrument that measures and controls the potential difference between a Working Electrode and a Reference Electrode.
- Measures the current flow between the Working and Counter Electrodes.

What is Potential?

Voltage or Potential (V, E, U):

- The Potential is the driving force for the electrochemical reaction and is related to the thermodynamics of the system:

  $$E_{rev} = -\Delta G / n\mathbf{F}$$

  (negative ΔG is spontaneous)
- Unit: **Volt**
- Potential is always measured versus a Reference Electrode.
- An applied potential positive of Eoc (open-circuit) is oxidizing
- An applied potential negative of Eoc is reducing
- 0 Volts is not nothing! 0 Volts simply means that the voltage of the working electrode is at the same potential as the reference electrode.

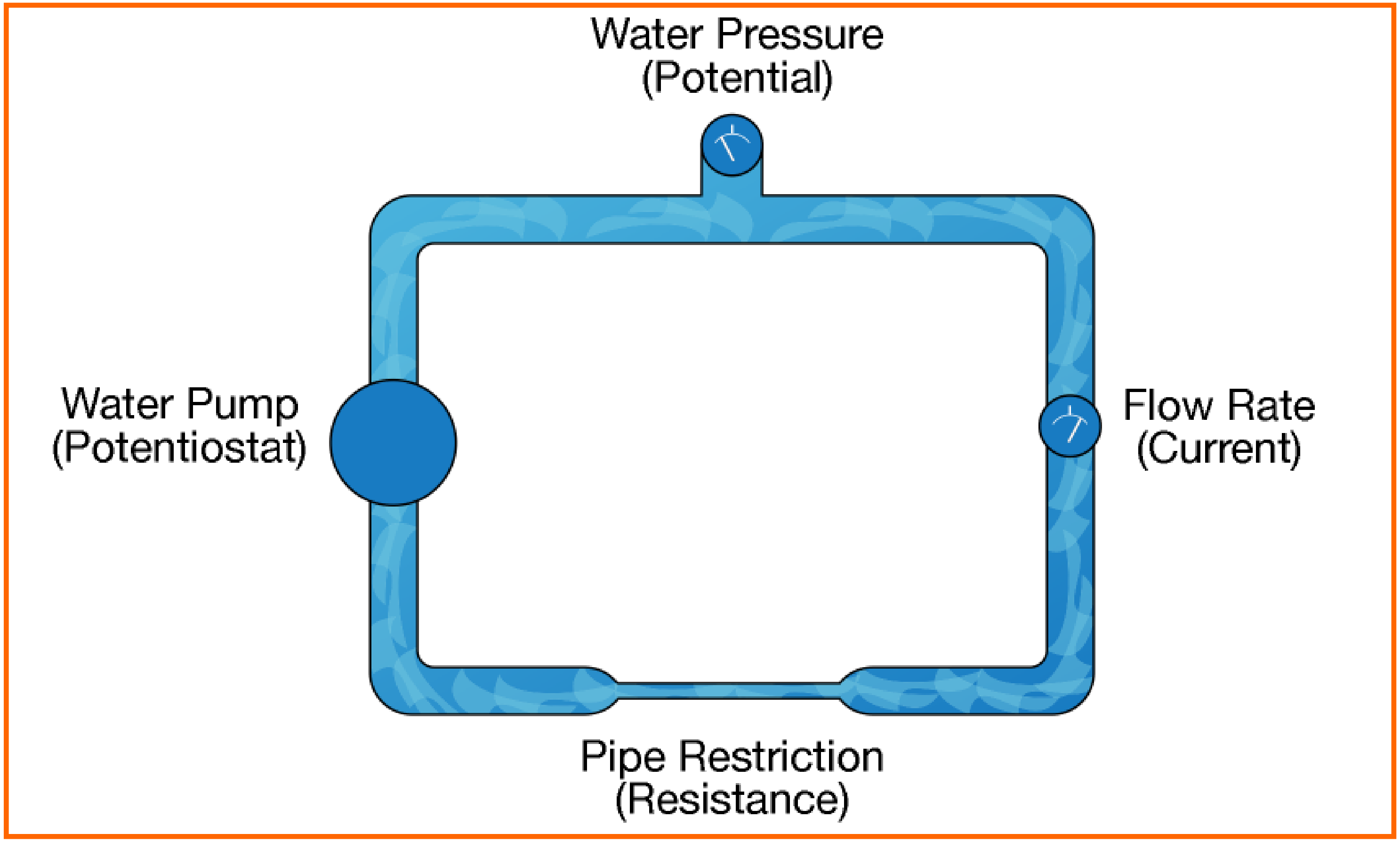
There is no correlation between the thermodynamics of the chemical system and the kinetics (rate) of the reaction.

What is Current?

Current (i):

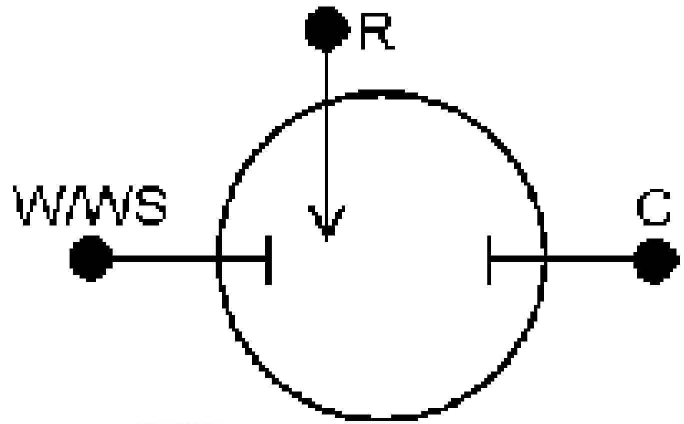
- Current is the flow of electrons.
- Electron flow is the result of an electrochemical reaction.
- Unit: **Ampere**
- Zero current is nothing, i.e., if the current is zero, there is no net flow of electrons within the system. It is possible that anodic and cathodic reactions are occurring at the same rate, producing no net current.
- Anodic (oxidation) and cathodic (reduction) currents have different polarity (signs).
- Current may be expressed as current or current density.

Potentiostat, Potential, and Current Illustrated as Water Flow



Electrodes

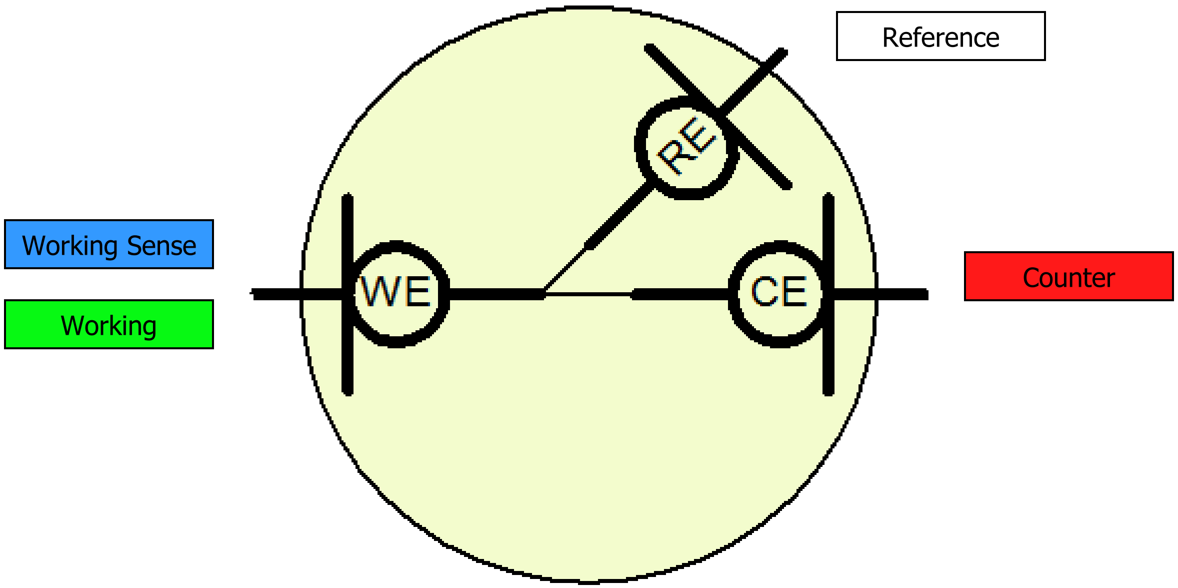
Typical 3-Electrode Setup:



1) Working Electrode
   A sample of the corroding metal being tested.
2) Reference Electrode
   An electrode with a constant electrochemical potential.
3) Counter Electrode
   A current-carrying electrode that completes the cell circuit.

Why Three Electrodes?

- In order to isolate the study to the working electrode.



Pay Special Attention to the Reference Electrode!

– A Potentiostat needs a low impedance Reference Electrode!
  - Use large diameter reference electrodes
  - Replace isolation frits when needed
  - Avoid narrow Luggin Capillaries
  - Typical values would be less than a few thousand Ohms

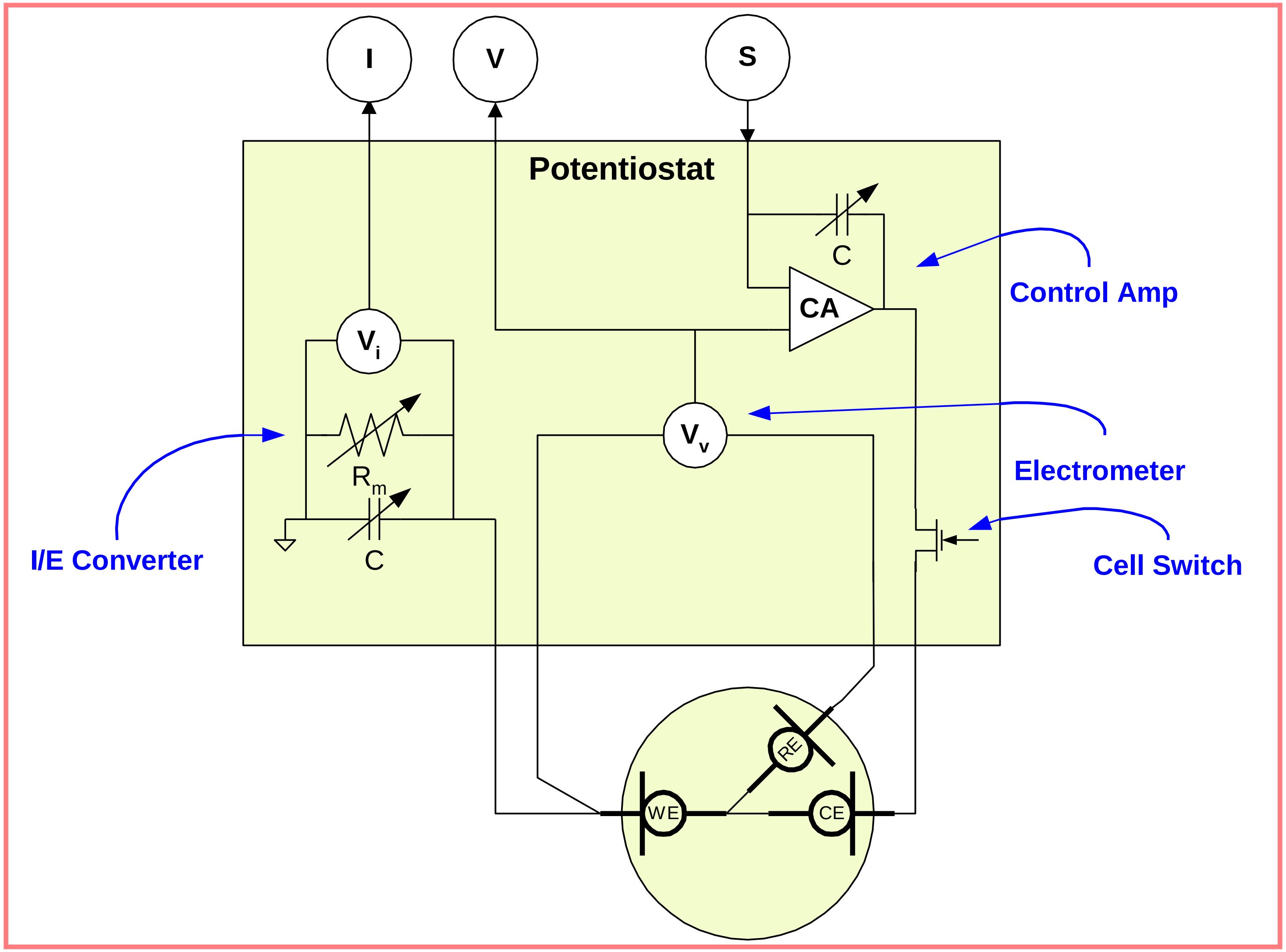
– If there's a problem with the *cell*, it's almost always the Reference Electrode. This is observed through oscillations or instabilities.

–Easiest way to check is by switching to 2-electrode mode. Remove the RE from the system and connect the reference lead to the counter electrode.

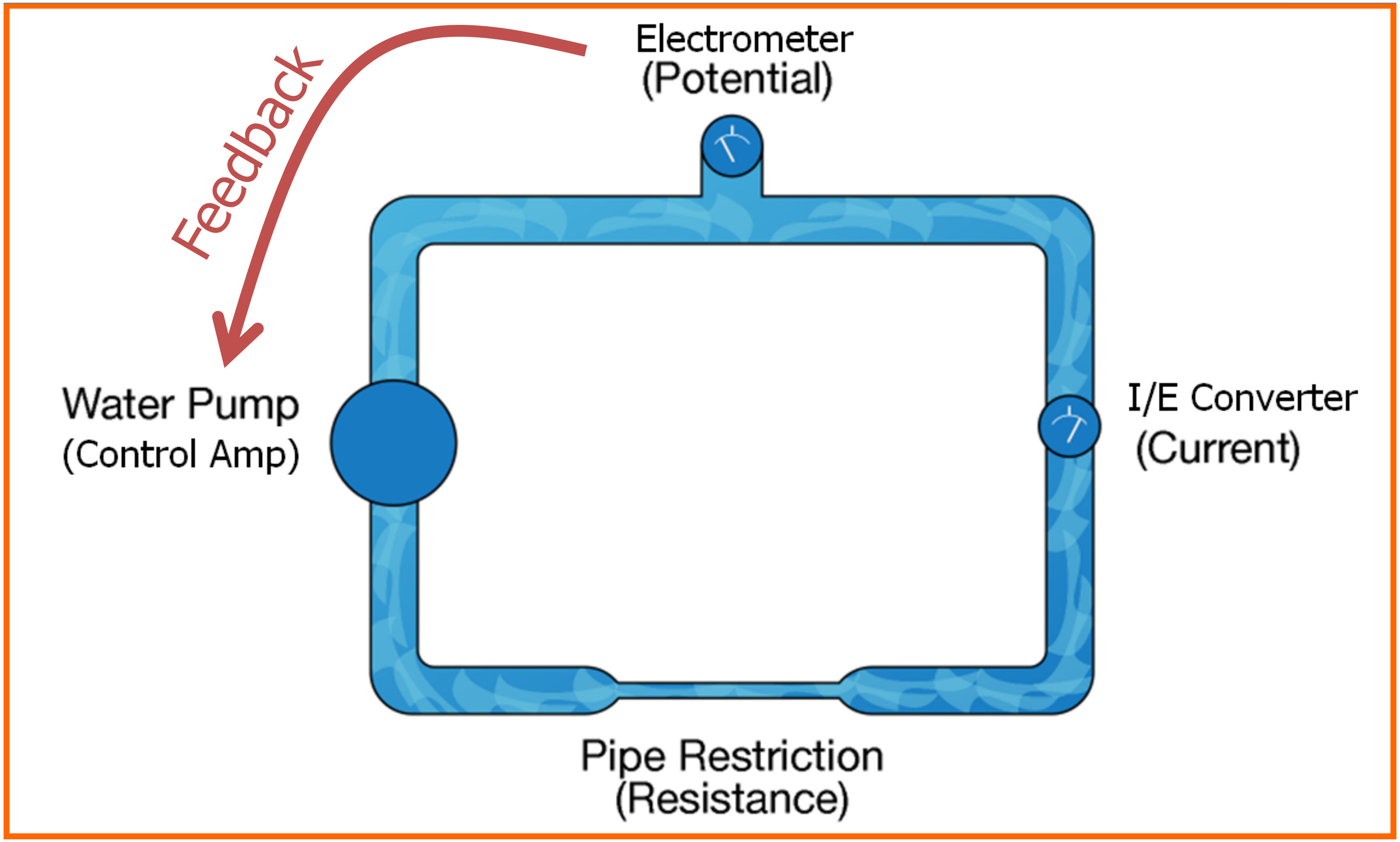
Let’s go inside a potentiostat

The Analog Potentiostat

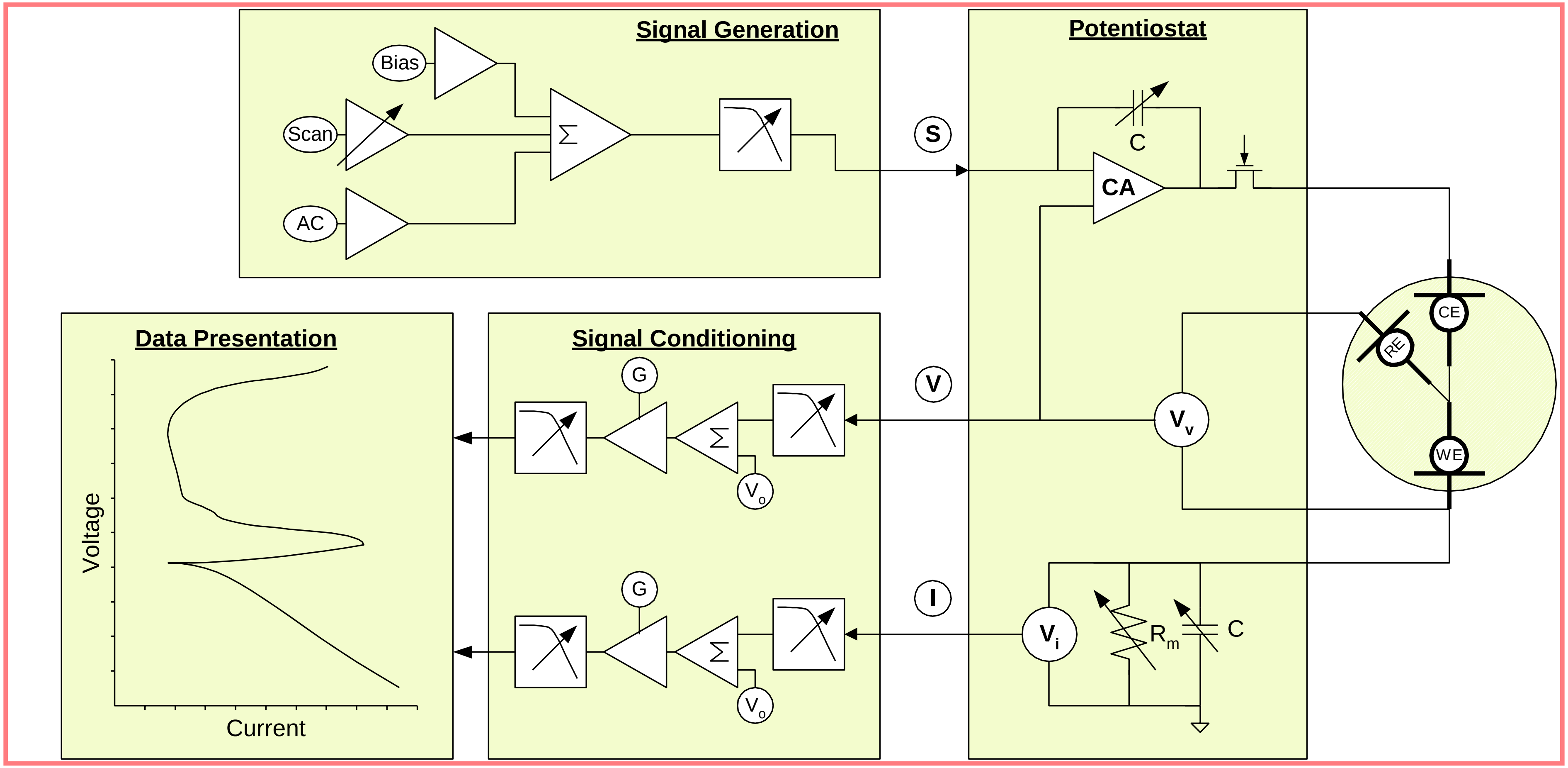
(Control Section)



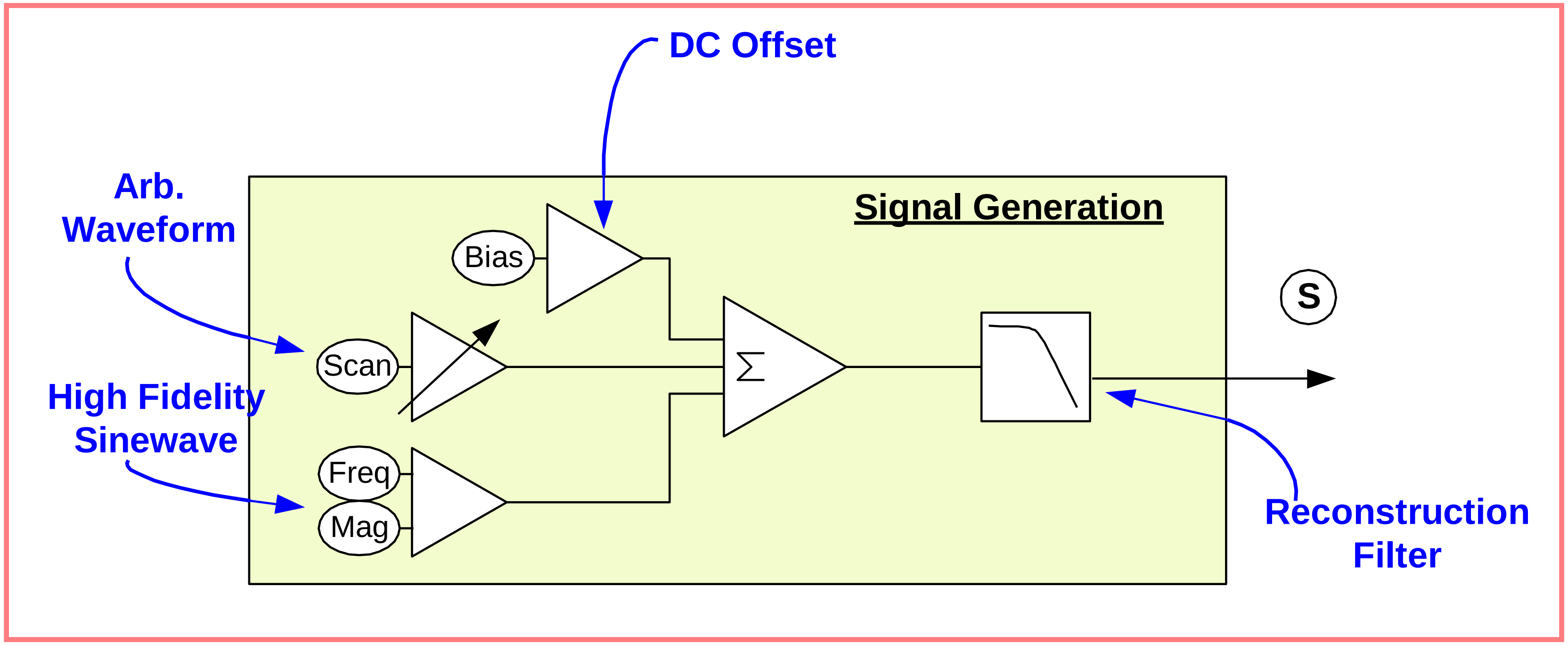
Water Circuit with Feedback



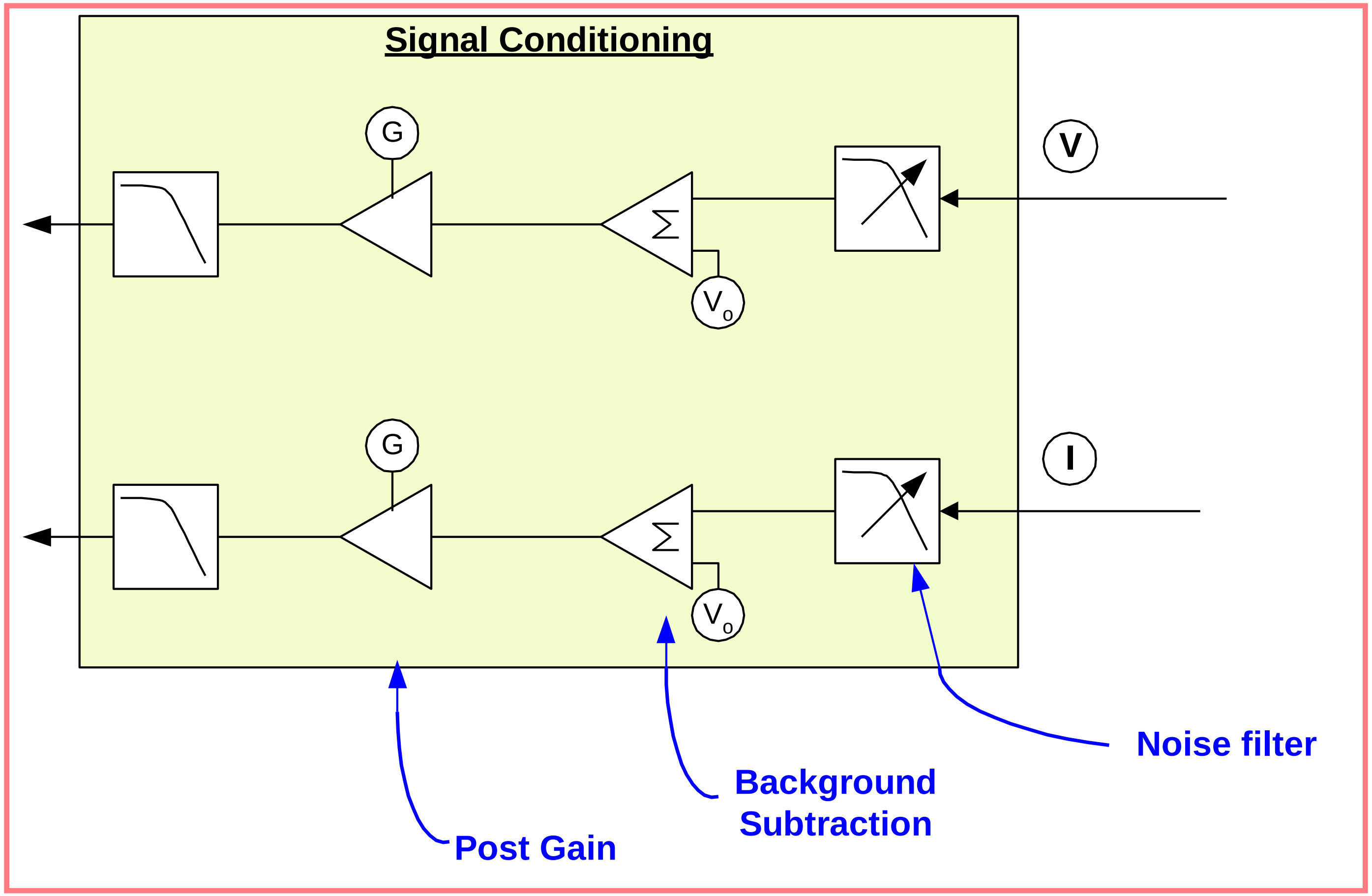
Need to have signal input and measurement output



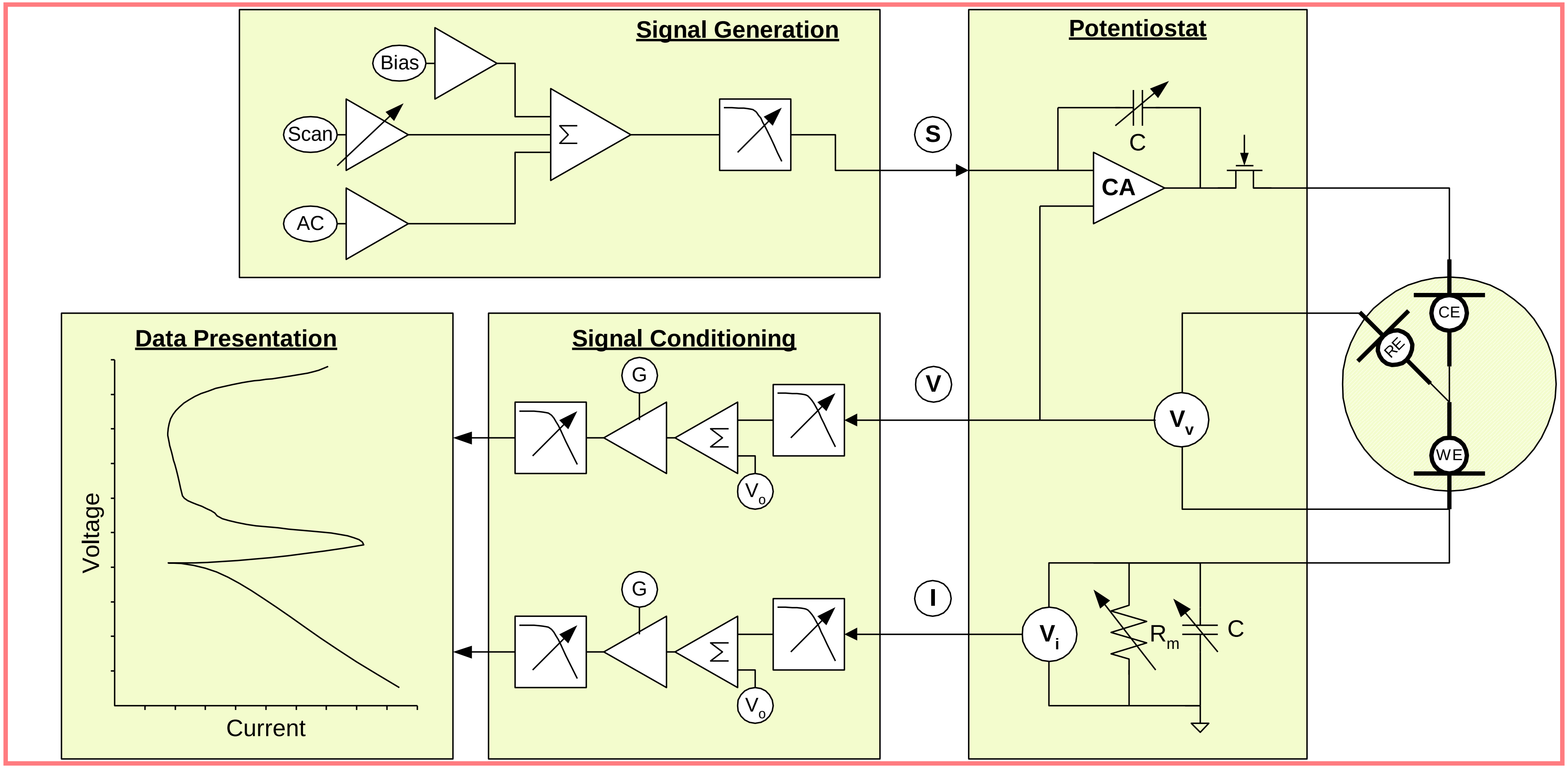
Signal Generation



Signal Conditioning

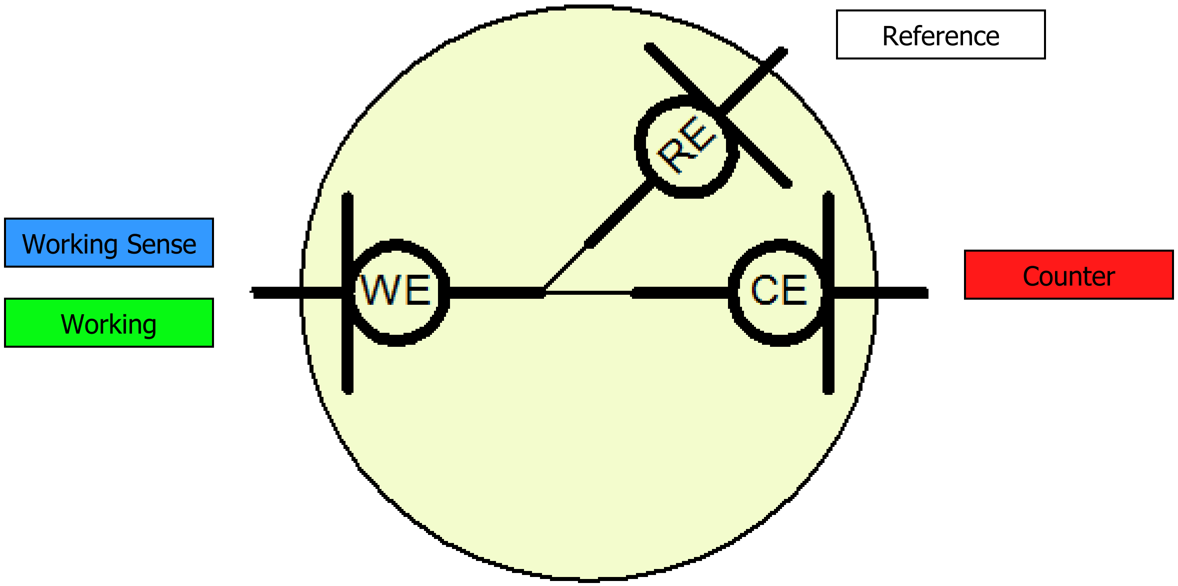


Putting It Back Together

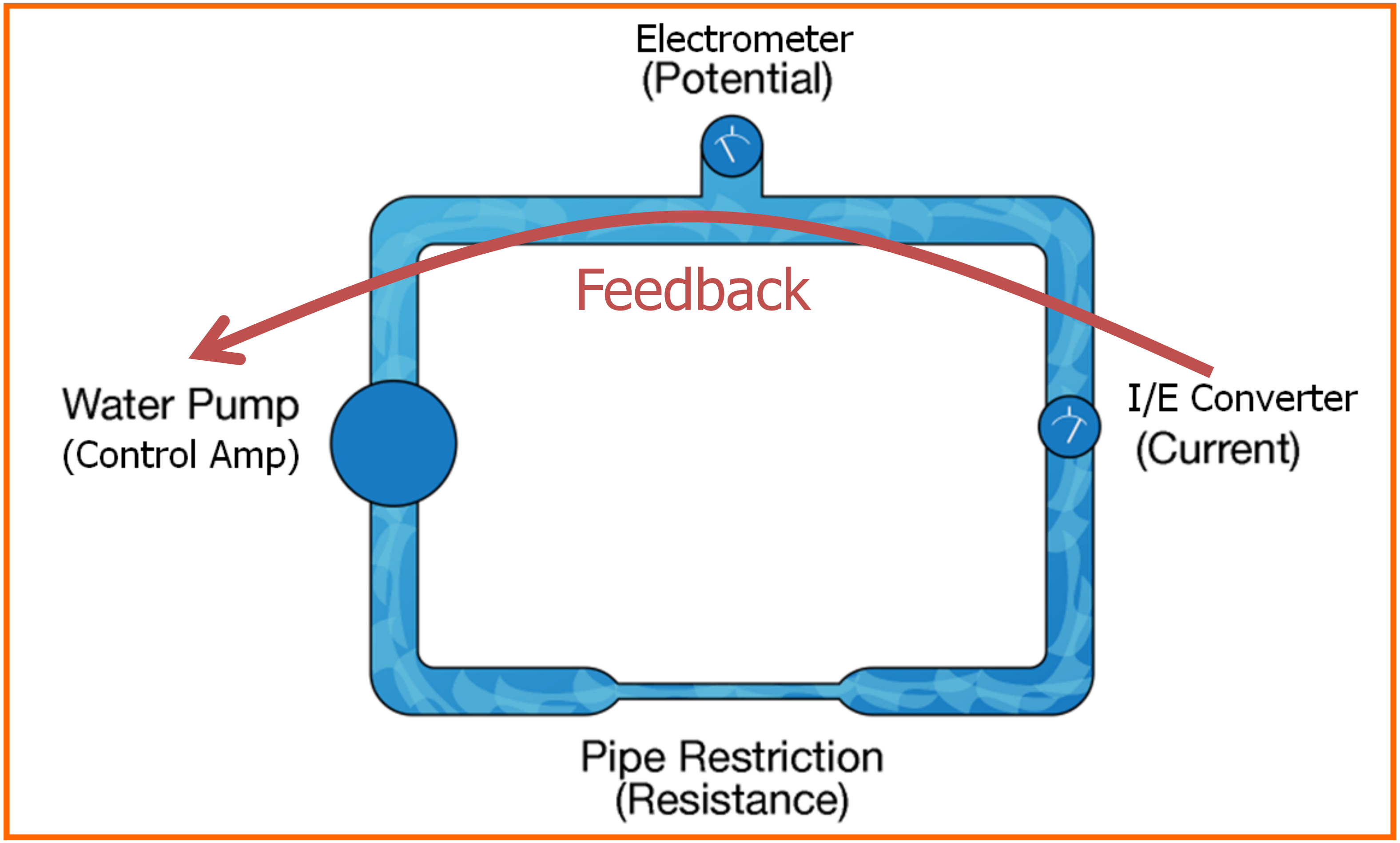


Galvanostat

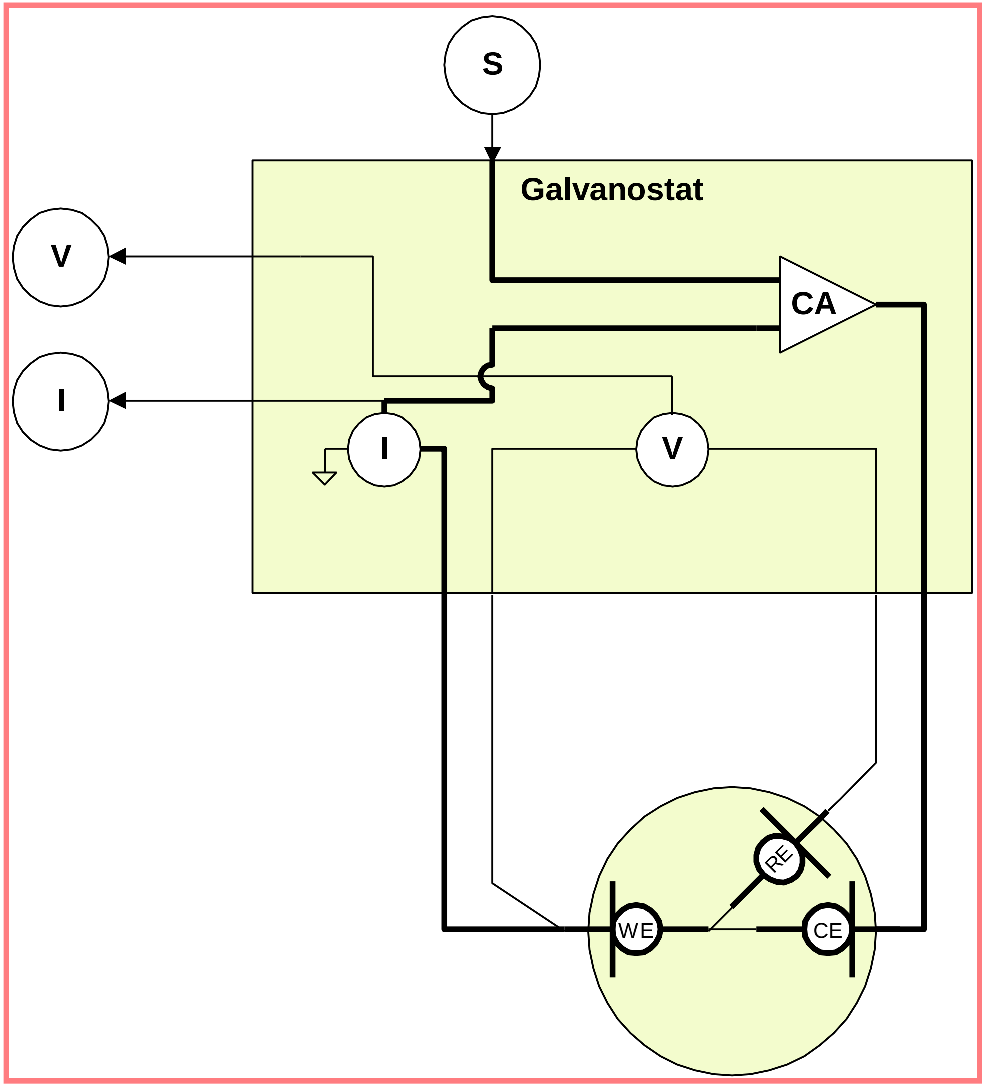
- A galvanostat applies and measures a current between the counter and working while measuring the potential between the reference and working.



Going back to the Analogy



Galvanostat Schematic



- **Do you need to know how a Potentiostat works?**
- **No.**

- **Do you need to be able to recognize when something is wrong?**
- **Yes!**

- **Why would something go wrong?**
- **Because the performance of the Potentiostat is affected by the electrical characteristics of the sample…or something in the cell is causing a problem…or the Potentiostat is busted!**

<u>To Evaluate Your Electrochemical Data…
Look At It!</u>

- Electrochemical data is <u>always</u> a collection of individual data points…one followed smoothly by another.

- Noisy data is bad.

- Flat-lined data is bad.

- Overloads are bad.

- Good data <u>looks</u> good, but bad data can also look good.

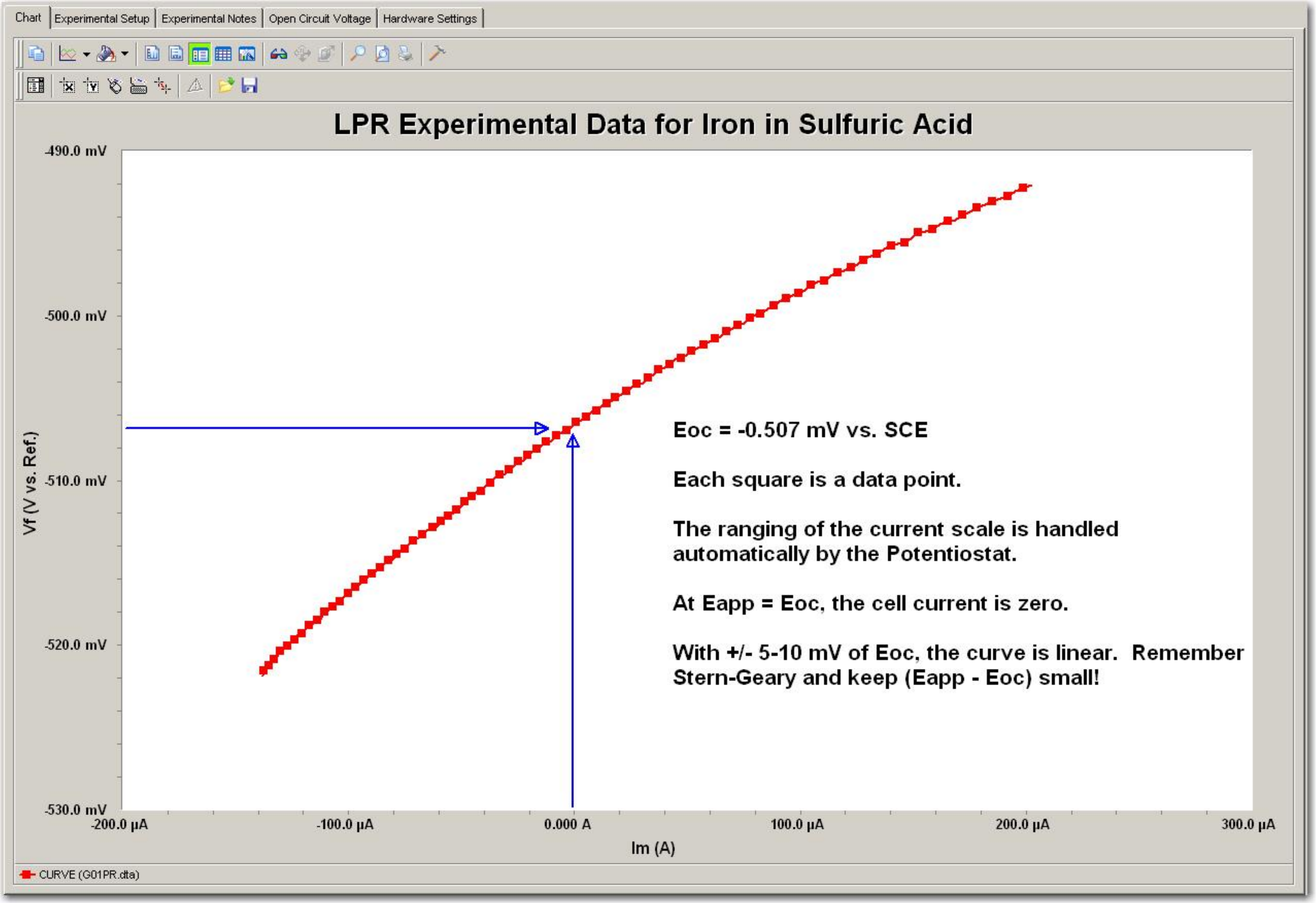


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
LPR Experimental Data for Iron in Sulfuric Acid
-490.0 mV
-500.0 mV
-510.0 mV
-520.0 mV
-530.0 mV
Vf (V vs. Ref.)
-200.0 µA
-100.0 µA
0.000 A
100.0 µA
200.0 µA
300.0 µA
Im (A)
Eoc = -0.507 mV vs. SCE
Each square is a data point.
The ranging of the current scale is handled automatically by the Potentiostat.
At Eapp = Eoc, the cell current is zero.
With +/- 5-10 mV of Eoc, the curve is linear. Remember Stern-Geary and keep (Eapp - Eoc) small!
CURVE (G01PR.dta)

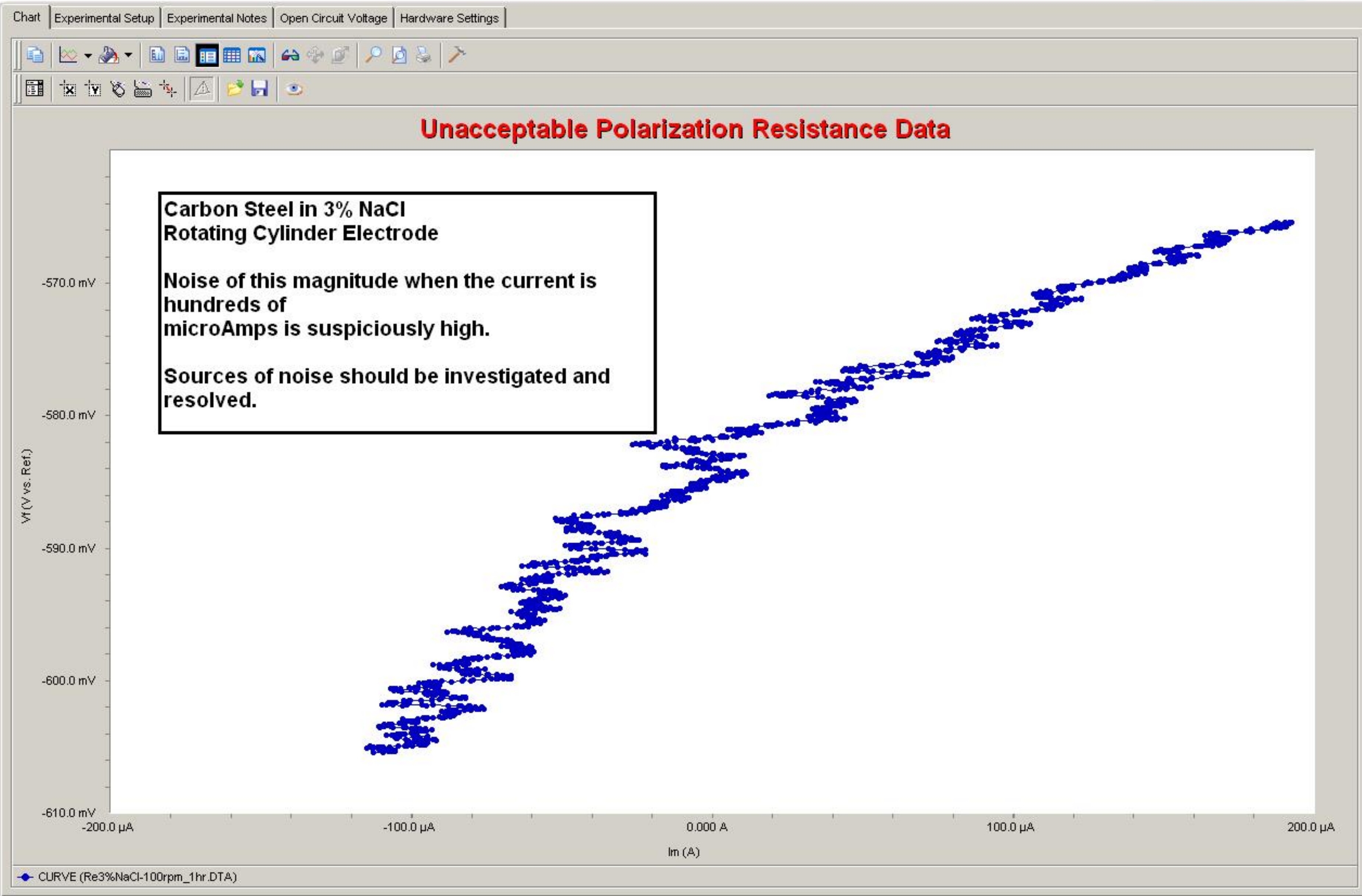


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
Unacceptable Polarization Resistance Data
Carbon Steel in 3% NaCl
Rotating Cylinder Electrode
Noise of this magnitude when the current is hundreds of
microAmps is suspiciously high.
Sources of noise should be investigated and resolved.
-570.0 mV
-580.0 mV
-590.0 mV
-600.0 mV
-610.0 mV
Vf (V vs. Ref.)
-200.0 µA
-100.0 µA
0.000 A
100.0 µA
200.0 µA
Im (A)
CURVE (Re3%NaCl-100rpm_1hr.DTA)

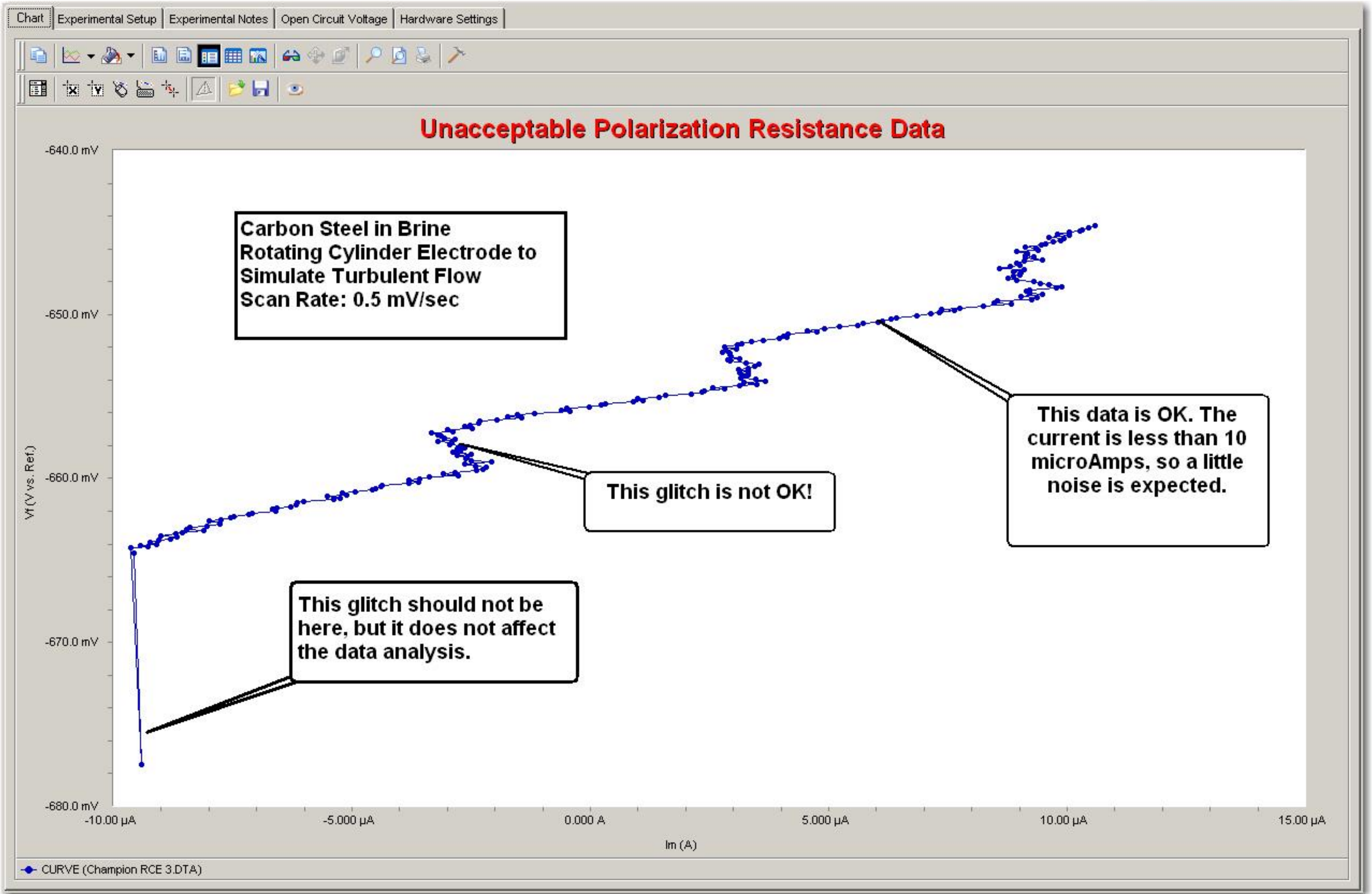


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
Unacceptable Polarization Resistance Data
Carbon Steel in Brine
Rotating Cylinder Electrode to
Simulate Turbulent Flow
Scan Rate: 0.5 mV/sec
This data is OK. The current is less than 10 microAmps, so a little noise is expected.
This glitch is not OK!
This glitch should not be here, but it does not affect the data analysis.
-640.0 mV
-650.0 mV
-660.0 mV
-670.0 mV
-680.0 mV
Vf (V vs. Ref.)
-10.00 µA
-5.000 µA
0.000 A
5.000 µA
10.00 µA
15.00 µA
Im (A)
CURVE (Champion RCE 3.DTA)

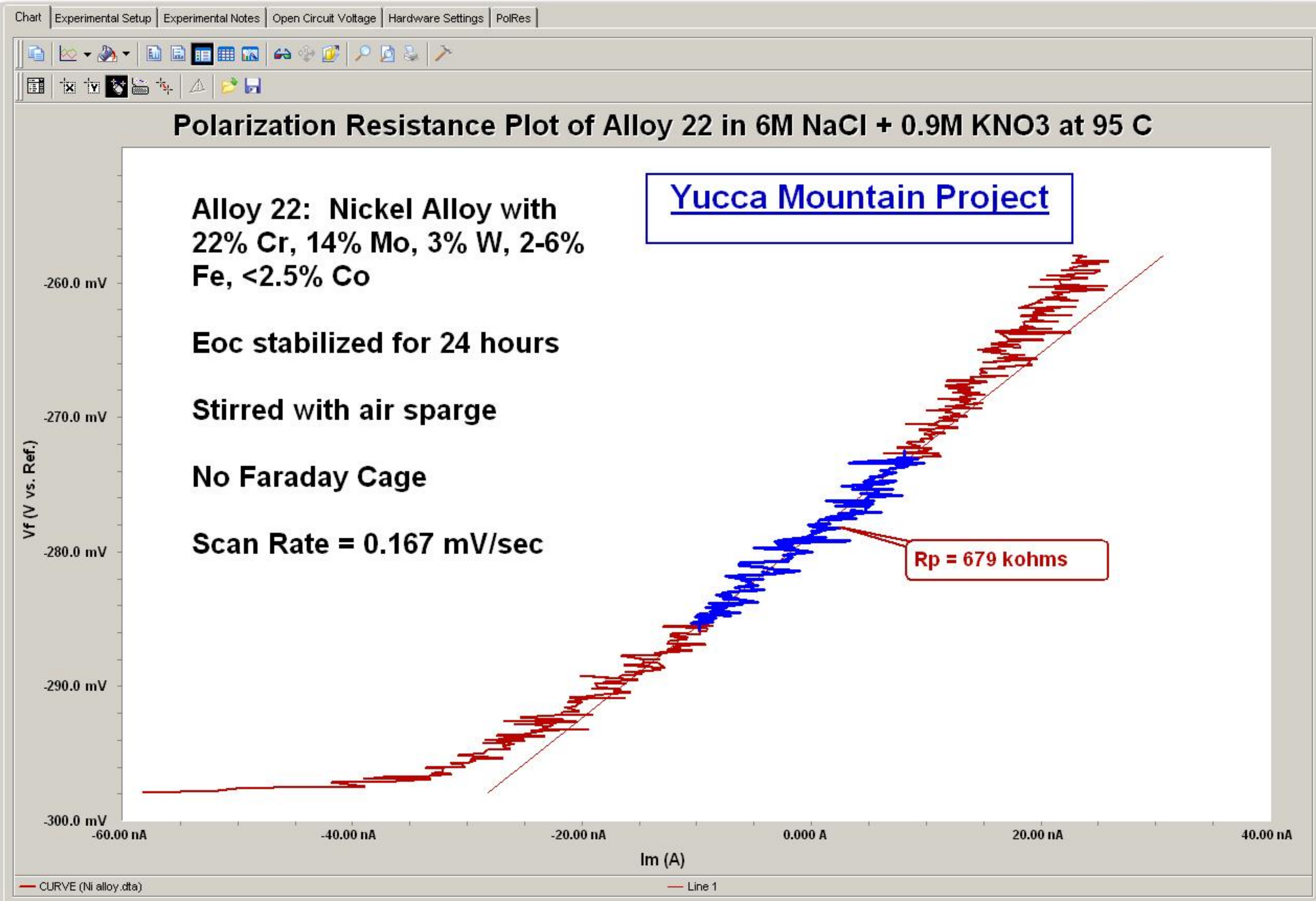
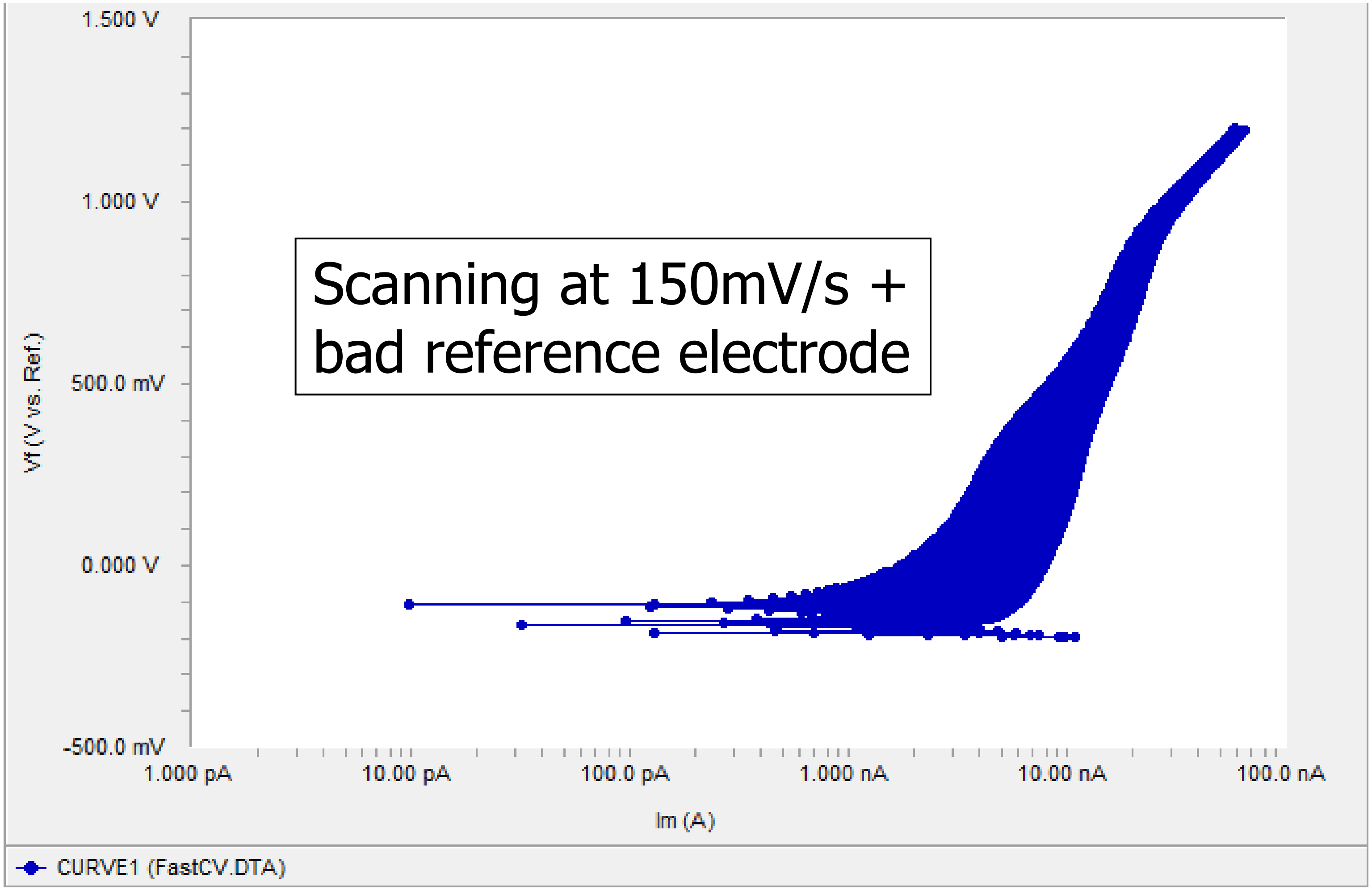


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
PolRes
Polarization Resistance Plot of Alloy 22 in 6M NaCl + 0.9M KNO3 at 95 C
Alloy 22: Nickel Alloy with 22% Cr, 14% Mo, 3% W, 2-6% Fe, <2.5% Co
Eoc stabilized for 24 hours
Stirred with air sparge
No Faraday Cage
Scan Rate = 0.167 mV/sec
Yucca Mountain Project
Rp = 679 kohms
-260.0 mV
-270.0 mV
-280.0 mV
-290.0 mV
-300.0 mV
Vf (V vs. Ref.)
-60.00 nA
-40.00 nA
-20.00 nA
0.000 A
20.00 nA
40.00 nA
Im (A)
CURVE (Ni alloy.dta)
Line 1

Bad Looking Bad Data



Potentiostat as a Feedback Device:

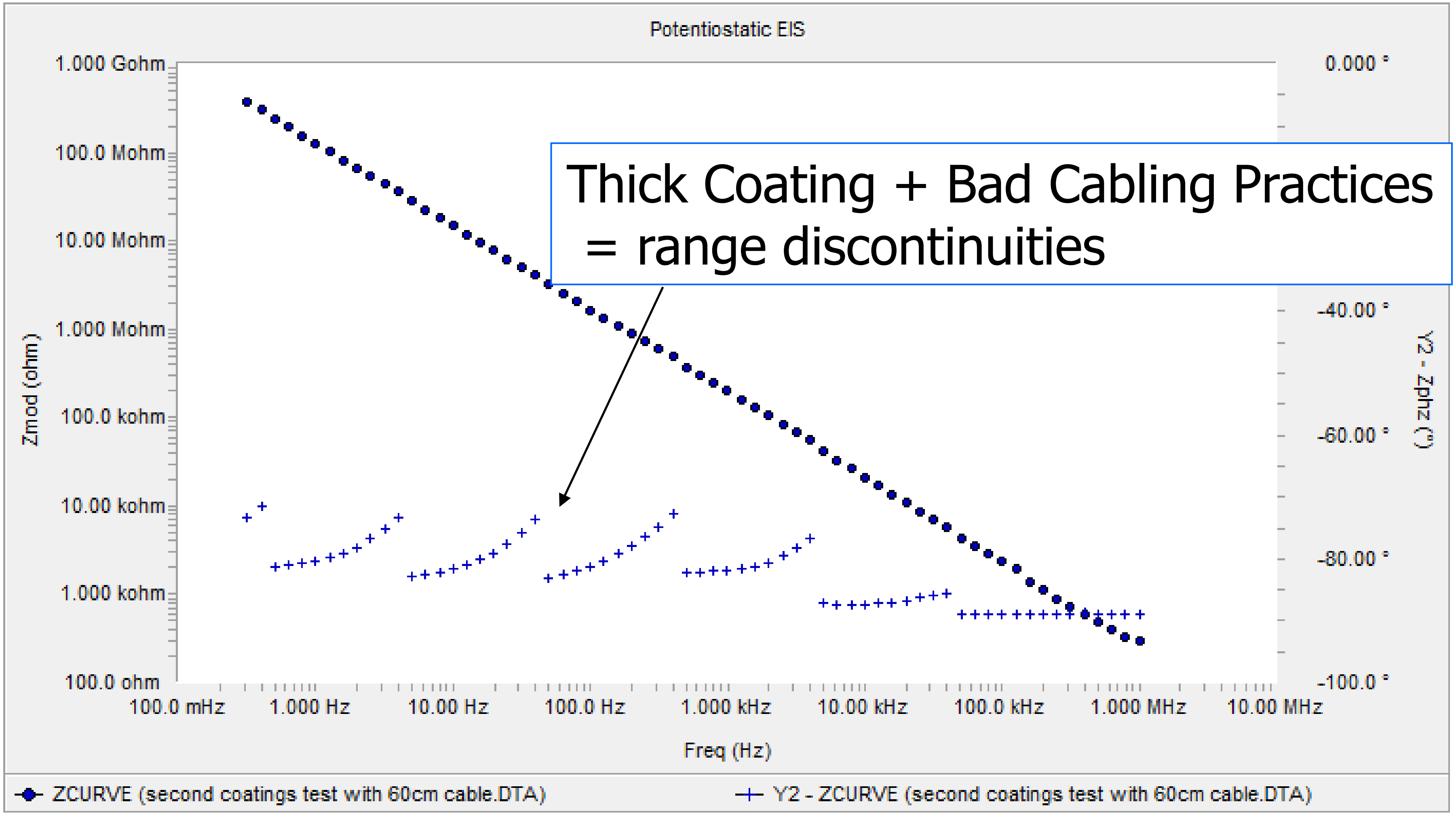
Another Water Analogy to Explain Oscillations

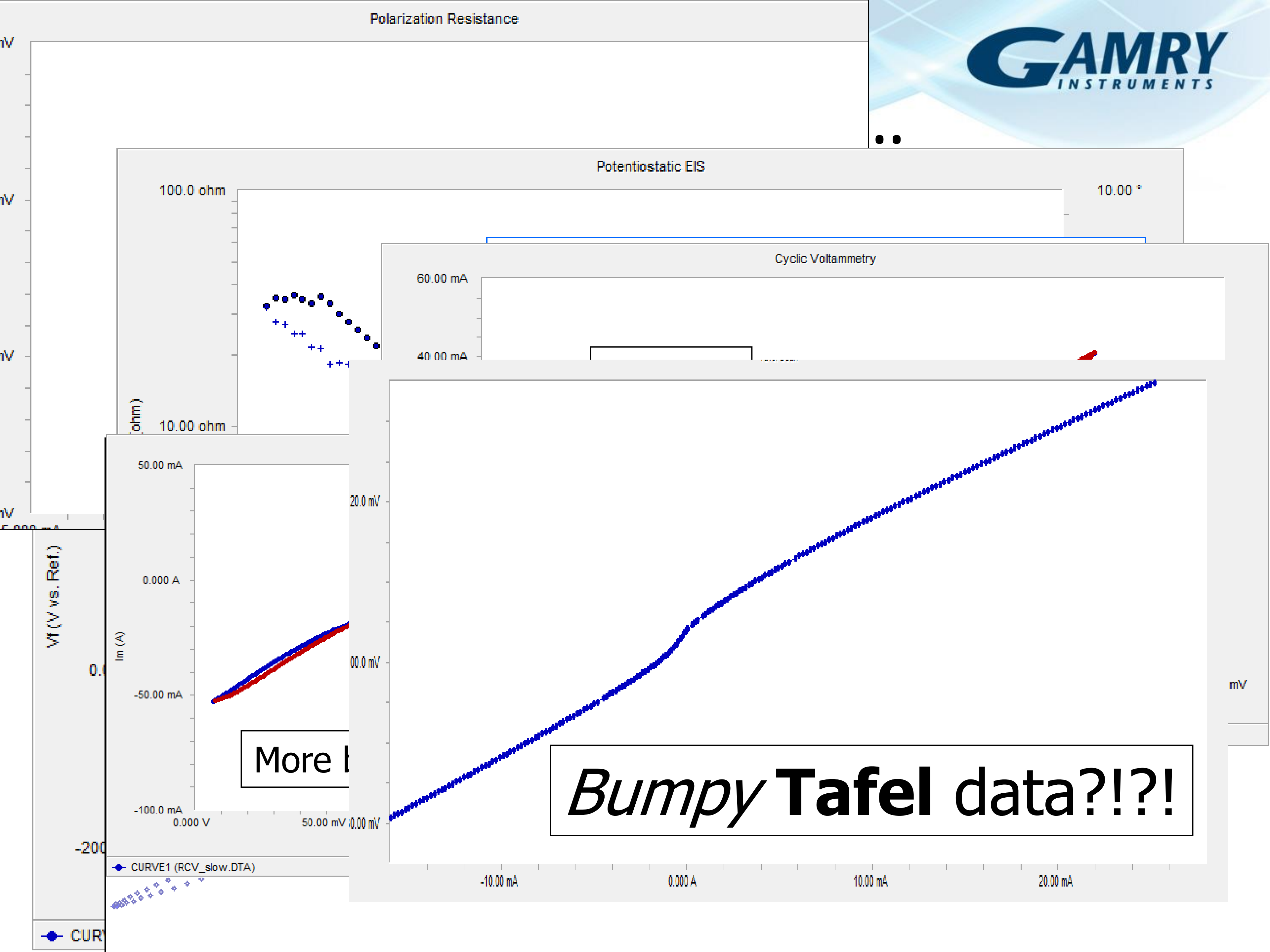
- Skin = Electrometer
- Hand = Control Amp
- Water is **too hot**
  - Turn the knob to **COLD**
  - 2 seconds later, you're **freezing** !
  - Turn the water to **HOT**
  - 2 seconds later, you're **scalded** !
  - Turn the knob to **COLD**
  - Repeat

SOMEONE FLUSHED THE TOILET!
Start Over!

Oscillations due to I/E range changes

Instrument Artifacts





Polarization Resistance
Potentiostatic EIS
100.0 ohm
10.00 ohm
10.00 °
Cyclic Voltammetry
60.00 mA
40.00 mA
50.00 mA
0.000 A
-50.00 mA
-100.0 mA
Im (A)
0.000 V
50.00 mV
Vf (V vs. Ref.)
CURVE1 (RCV_slow.DTA)
More b
20.0 mV
-10.00 mA
0.000 A
10.00 mA
20.00 mA
mV
Bumpy **Tafel** data?!?!

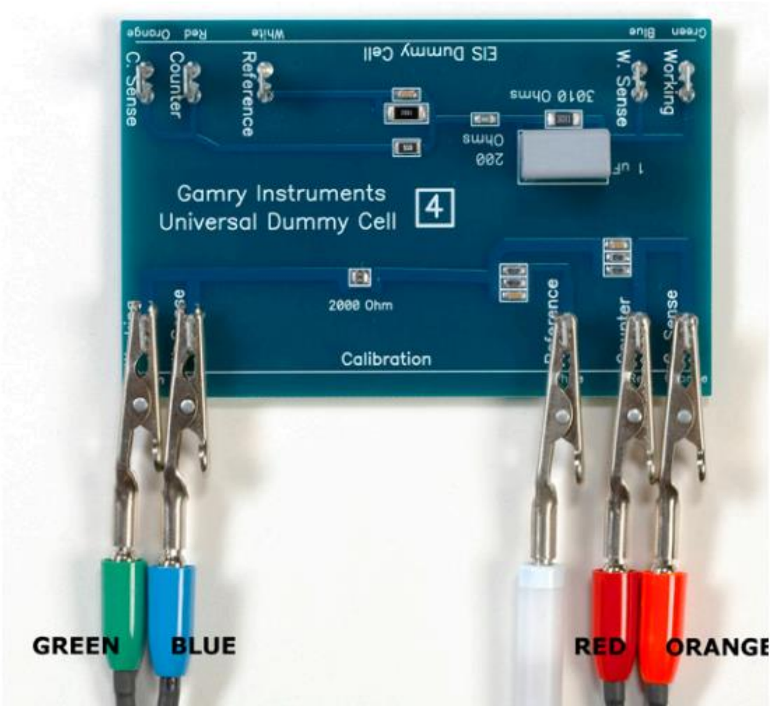
My Data Is Bad. Now What Do I Do?

Troubleshooting is the art of eliminating unknowns.

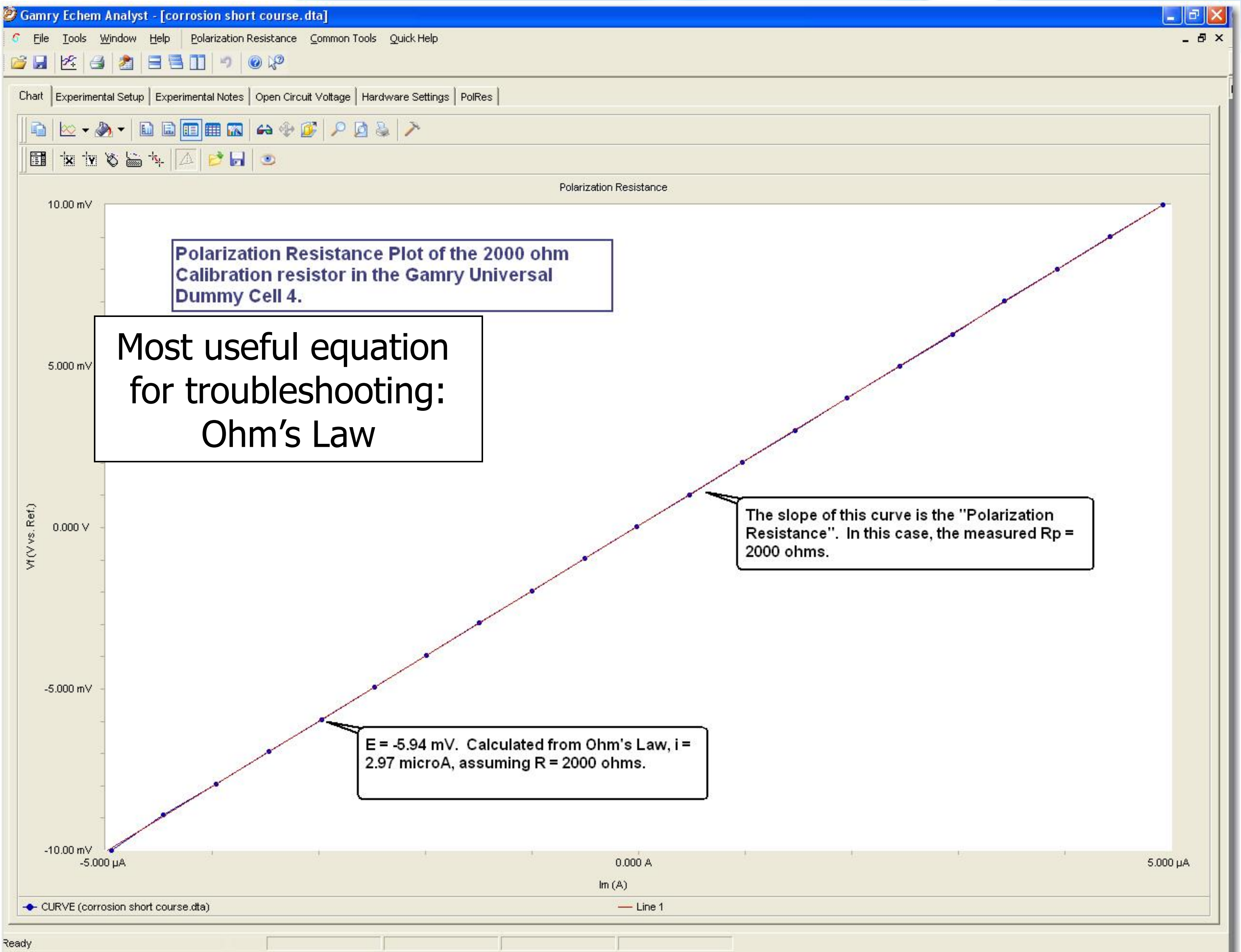
1. Calibrate the Potentiostat.
2. If calibration is successful, check the Potentiostat by running a dummy cell (a network of resistors/capacitors that give a known result).
3. If the instrument is OK, then check the cell. Check the Reference Electrode first!
4. If the cell is OK, then it's something in your sample chemistry, or you may need a Faraday Cage.
5. At some point, you should contact your Potentiostat supplier for technical support.

What does calibration do?

- Easiest way to rule out a potentiostat problem
- "Zeroes" all current measurement ranges to account for any offset
- Quickly checks continuity of cell cable by applying known voltage to dummy cell
- You may find non-critical errors

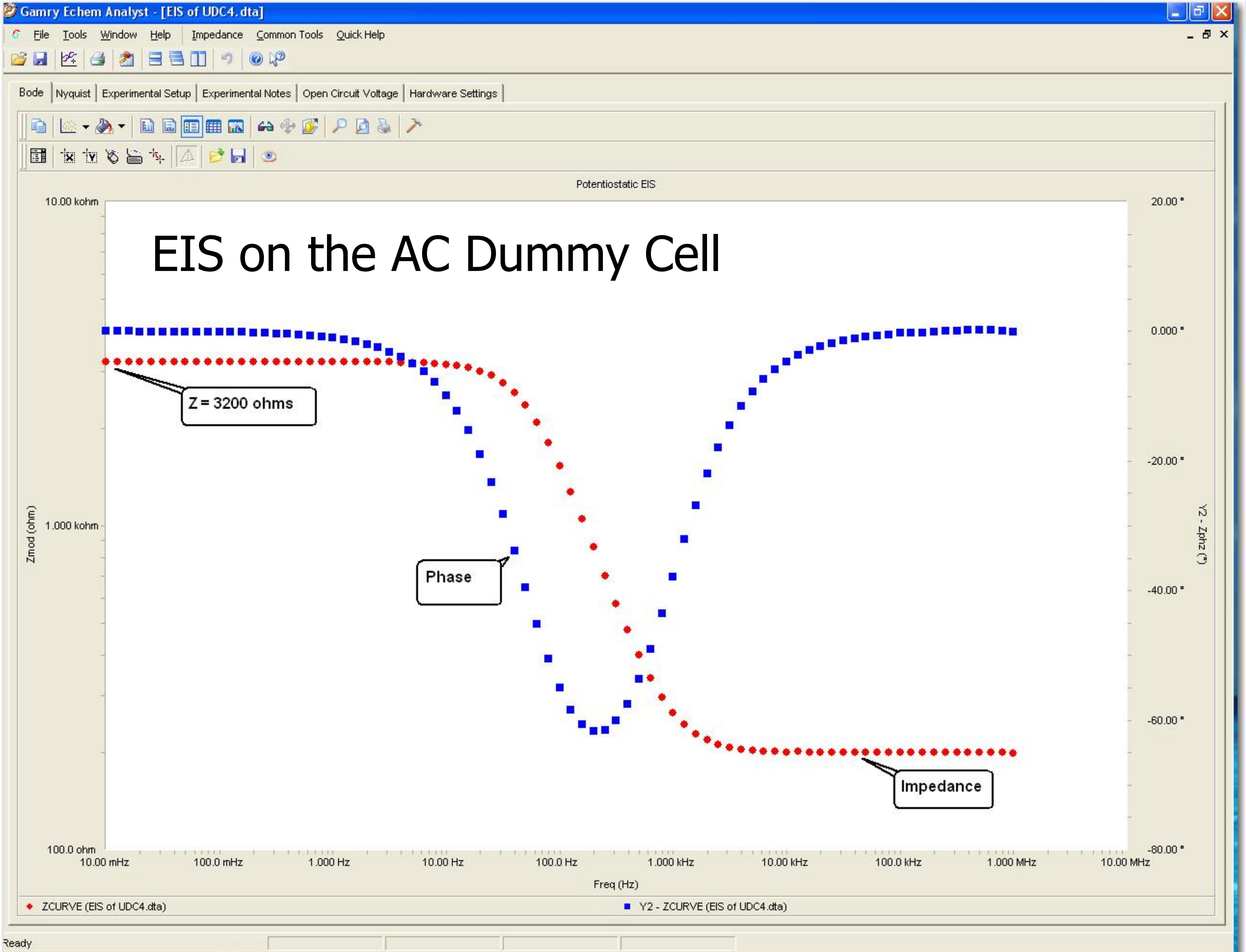


If Calibration is Successful, run tests on the dummy cell!



Most useful equation for troubleshooting: Ohm's Law

Pstat Check-Out: EIS on a Dummy Cell



Help! I get OVERLOADS during my experiments!

- The most common overloads are:
  - V Overload: overload of the Electrometer
    - Sense or Reference lead disconnected, bad reference electrode
    - Applying large current to highly resistive cell
  - I Overload: overload of the I/E Converter
    - Short between Working and Counter leads
    - Applying high potential to a low resistance sample
    - Exceeding the current limit of a particular current measurement range
  - CA Overload: overload of the Control Amplifier
    - Sense lead became disconnected or counter electrode is too small
    - Measurements in low conductivity solutions or counter electrode is far from working (Compliance Voltage exceeded)

Cable check

- Cables are a wear item and the second most common problem for potentiostats. Covered during calibration but this identifies what has failed.
- Run a cable integrity check – e.g. pin 1 to blue lead, pin 13 to green lead, pin 16 to white lead, pin 23 to red lead

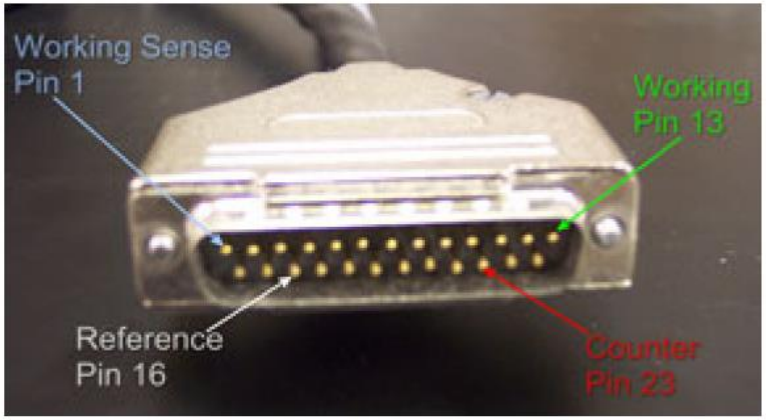


Figure 2. Pins in the Cell Cable for the Reference 600 Potentiostat.

Important Bits to Remember:

- Potentiostat performance is affected by the system it is measuring
- Reference Electrode is the most common source of experimental problems (try 2-electrode)
- Calibration provides a quick check of the hardware and the cell cable
- Effective troubleshooting will save you time and money (Gamry is here to help)

Where else can I get help?

- Interactive Troubleshooting Guide
  - https://www.gamry.com/support/technical-support/troubleshooting/
- General Technical Support
  - https://www.gamry.com/support/technical-support/troubleshooting/
- techsupport@gamry.com
- Phone - 1 877 367 4267

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Next week - Understanding Specifications

- What do all of these specifications mean?
- What do they tell you about performance limitations?
- Which ones are important to me for my application?

POTENTIOSTAT/GALVANOSTAT/ZRA

	Reference 3000/3000AE	Reference 600+	Interface 5000	Interface 1000
SYSTEM				
Cell Connections	2, 3, 4, 5 or 21*	2, 3, 4, or 5	2, 3, 4, or 5	2, 3, 4, or 5
Maximum Current	± 3 A @ 15 V or ± 1.5 A @32 V	± 600 mA	± 5 A	± 1 A
Current Ranges	11 (300 pA – 3 A)	11 (60 pA – 600 mA)	6 (50 μA - 5 A)	9 (10 nA to 1 A)
Current Ranges (including internal gain)	13	13	8	11
Minimum Current Resolution	92 aA	20 aA	150 pA	3.3 fA
Maximum Applied Potential	± 32 V	± 11 V	± 6 V	± 12 V
Rise Time	< 250 ns	< 250 ns	< 1 μs	< 1 μs
Minimum Timebase	3.333 μs	3.333 μs	10 μs	10 μs
Noise and Ripple (typical)	< 2 μV rms	< 2 μV rms	< 20 μV rms	< 20 μV rms