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:

\[ E_{rev} = -\Delta G / nF \]

(negative \( \Delta G \) 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

Water Pressure (Potential)

Water Pump (Potentiostat)

Flow Rate (Current)

Pipe Restriction (Resistance)
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

- Water Pump (Control Amp)
- Electrometer (Potential)
- Pipe Restriction (Resistance)
- I/E Converter (Current)
- Feedback arrow pointing from Electrometer to Water Pump
Need to have signal input and measurement output

**Signal Generation**
- Signal Generation
- Signal Conditioning
- Potentiostat

**Data Presentation**
- Voltage
- Current

**Bias**
- Scan
- AC
- CE
- WE
- RE
- CA
- V
- I
- Vv
- Vi
- Rm
- C
- G
- Vv
- Vi
- V
- S
- CA
- CE
- WE
- WB
Signal Generation

Arb. Waveform
High Fidelity Sinewave

Bias
Scan
Freq
Mag

DC Offset

Signal Generation

Reconstruction Filter
Signal Conditioning

- Noise filter
- Background Subtraction
- Post Gain
Putting It Back Together

Signal Generation

Signal Conditioning

Potentiostat

Data Presentation

Voltage vs. Current

Bias
Scan
AC

CE
WE
RE
CA

I
V
S

V
V_v

R_m
C

V_i

G

G

G

G
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

- Electrometer (Potential)
- Water Pump (Control Amp)
- Feedback
- Pipe Restriction (Resistance)
- I/E Converter (Current)
• 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!
To Evaluate Your Electrochemical Data...

Look At It!

- Electrochemical data is always 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 looks good, but bad data can also look good.
LPR Experimental Data for Iron in Sulfuric Acid

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 E_{app} = E_{oc}, the cell current is zero.

With +/- 5-10 mV of E_{oc}, the curve is linear. Remember Stern-Geary and keep (E_{app} - E_{oc}) small!
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.
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.
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

Rp = 679 kohms
Bad Looking Bad Data

Scanning at 150mV/s + bad reference electrode
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

Thick Coating + Bad Cabling Practices = range discontinuities
Electrode Experiment:

Concentric copper coils in CuSO₄

Just plain weird…

Non-linear PolRes

Nonsensical Impedance Spectrum

Distorted Lissajous Curves!

Bad CV

More badder slow CV

After 24 Hours

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


The slope of this curve is the “Polarization Resistance”. In this case, the measured $R_p = 2000$ ohms.

$E = -5.94$ mV. Calculated from Ohm’s Law, $i = 2.97$ microA, assuming $R = 2000$ ohms.
EIS on the AC Dummy Cell

Z = 3200 ohms

Phase

Impedance

Pstat Check-Out: EIS on a Dummy Cell
Help! I get **OVERLOADS** during my experiments!

- **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
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/](https://www.gamry.com/support/technical-support/troubleshooting/)
- General Technical Support
  - [https://www.gamry.com/support/technical-support/troubleshooting/](https://www.gamry.com/support/technical-support/troubleshooting/)
- techsupport@gamry.com
- Phone - 1 877 367 4267
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?