EIS of Difficult Samples

Overview

- **Goal: Learn how to get the best answer possible from your EIS system.**

- What are “Difficult Samples”?
- What limits measurement of those systems?
- Quick refresher on instrumentation
- EIS performance – Accuracy Counter Plots and Open Lead and Shorted Lead Spectra
- Ways to make bad measurements
- Ways to improve measurement results

Difficult Samples

- High impedance (Z)
  - GΩ+, Coatings, Small (μm) Electrodes
- Low Z
  - < 1 mΩ, Batteries, EDLCs, Fuel Cells, Large/Porous Electrodes
- Unstable samples
  - Batteries, Corrosion, Biological [fouling]
- Other
  - Autoclaves/Grounding, Curved surfaces, Reference Path/Impedance Issues

Sources of Limitatioions

- The Cell Cable
  - Configuration can improve
- Low current measurement capability
  - Faraday Cage blocks external noise sources
  - Low current range puts a hard limit on Imeasure
- Low Voltage measurement/control ability
  - Low noise system improves limits
  - Large CMRR better limits

Potentiostat

- Reference electrode/path
- Setup challenges
- The actual sample

Cell

Electrochemical Instrumentation

- Potentiostat definition

  An electronic instrument that measures and controls the voltage difference between a working electrode and a reference electrode. Generally measures the current flow between the working and counter electrodes.

- Galvanostat definition

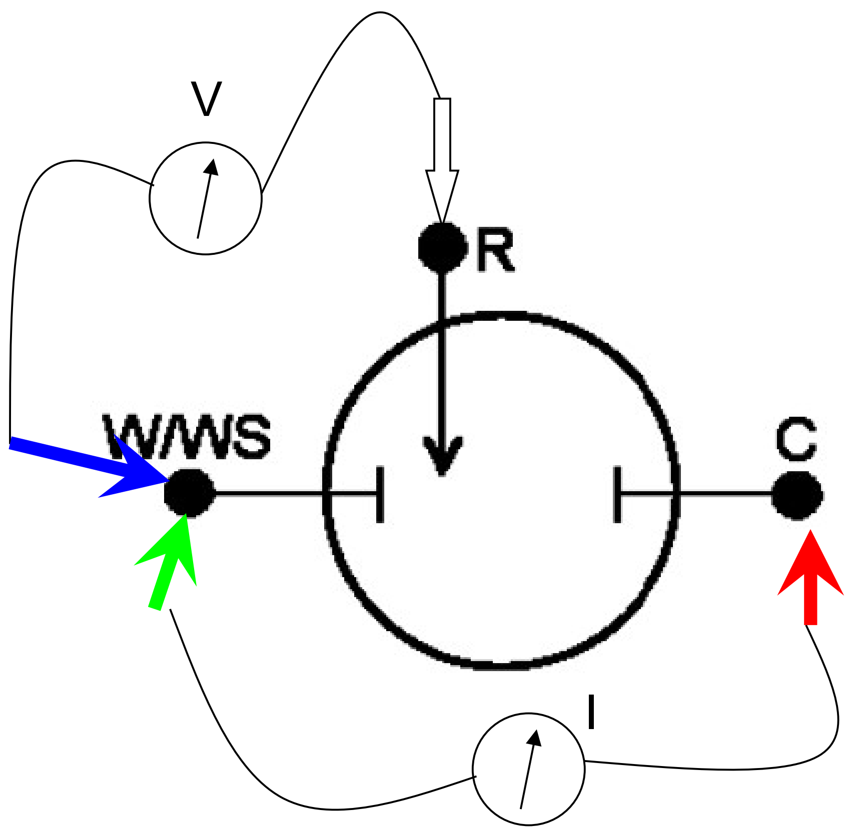
  An electronic device that controls and measures the current flow between a working and a counter electrode. Generally measures the potential between the working electrode and a reference electrode.

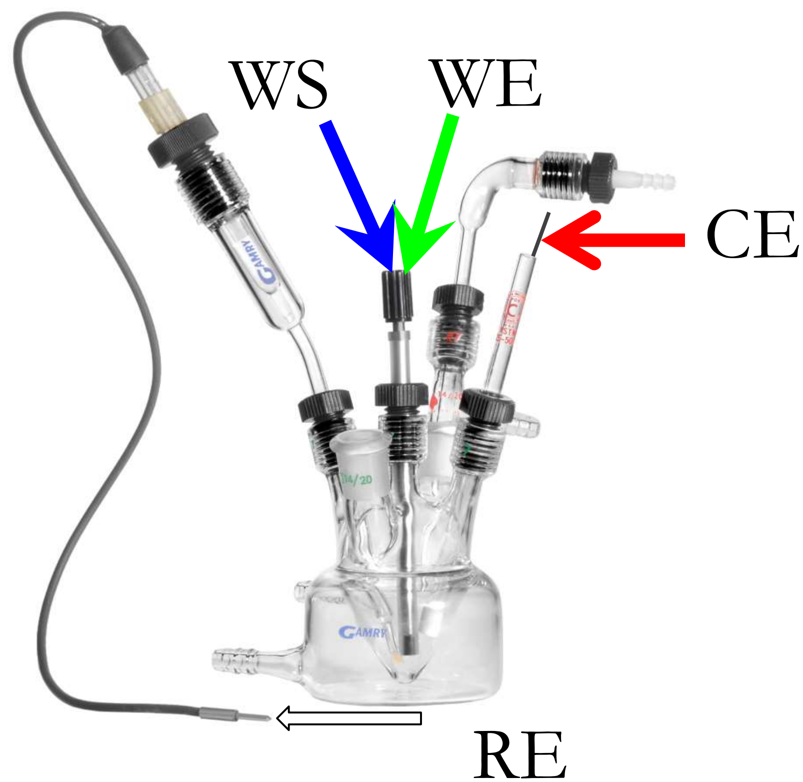
- Modern electrochemical instruments work as both a potentiostat and a galvanostat (and a ZRA and an FRA)

Potentiostat Force and Sense Terminals

- High performance potentiostats are always 4-Terminal Devices:
  - The Reference and Work Sense leads are **Sense** terminals which measure the cell voltage
  - The Counter and Working leads are **Force** terminals that carry the cell current

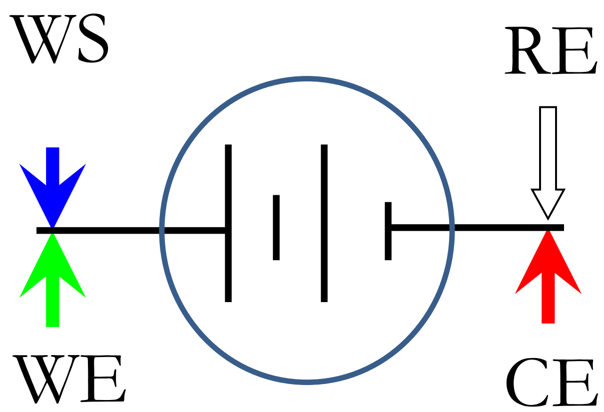
Three Electrode Cell





Note that potential is only measured through ½ of the cell.

2-Electrode Connections

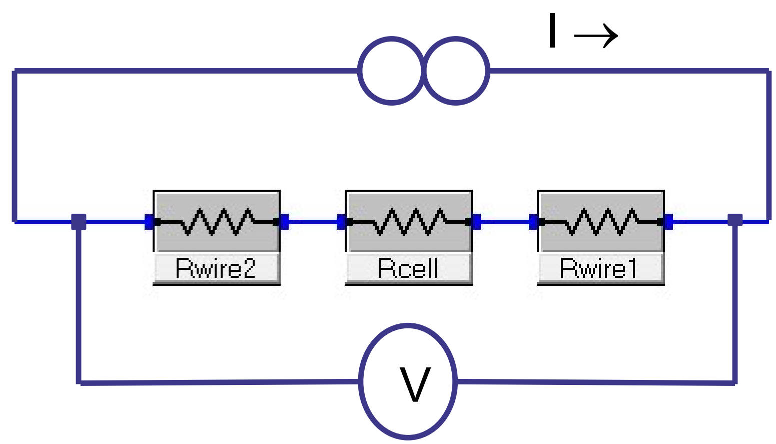


- 2-electrode devices (e.g. batteries) are not a problem for a 3-electrode potentiostat.
- The working and work sense leads connect to one electrode and the counter and reference leads connect to the other.

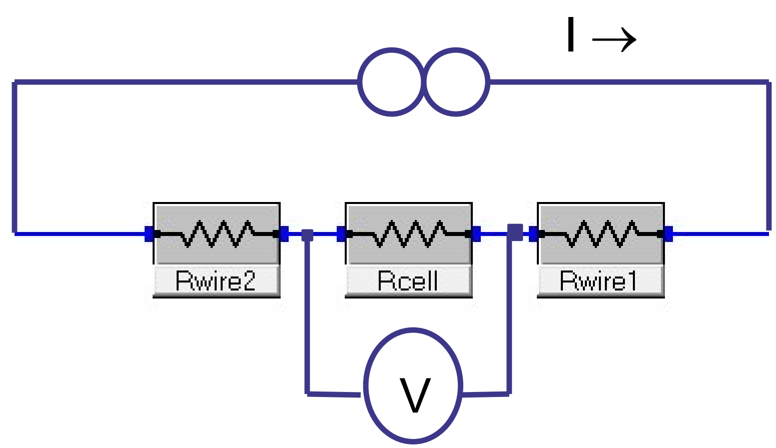
4-Terminal Connections

Research grade potentiostats use 4-terminal (or Kelvin) connections.
Force terminals carry the current and sense terminals measure voltage.

<u>2-Terminal</u>
These connections measure both the cell impedance and the wire resistance



<u>4-Terminal</u>
These connections measure only the cell impedance



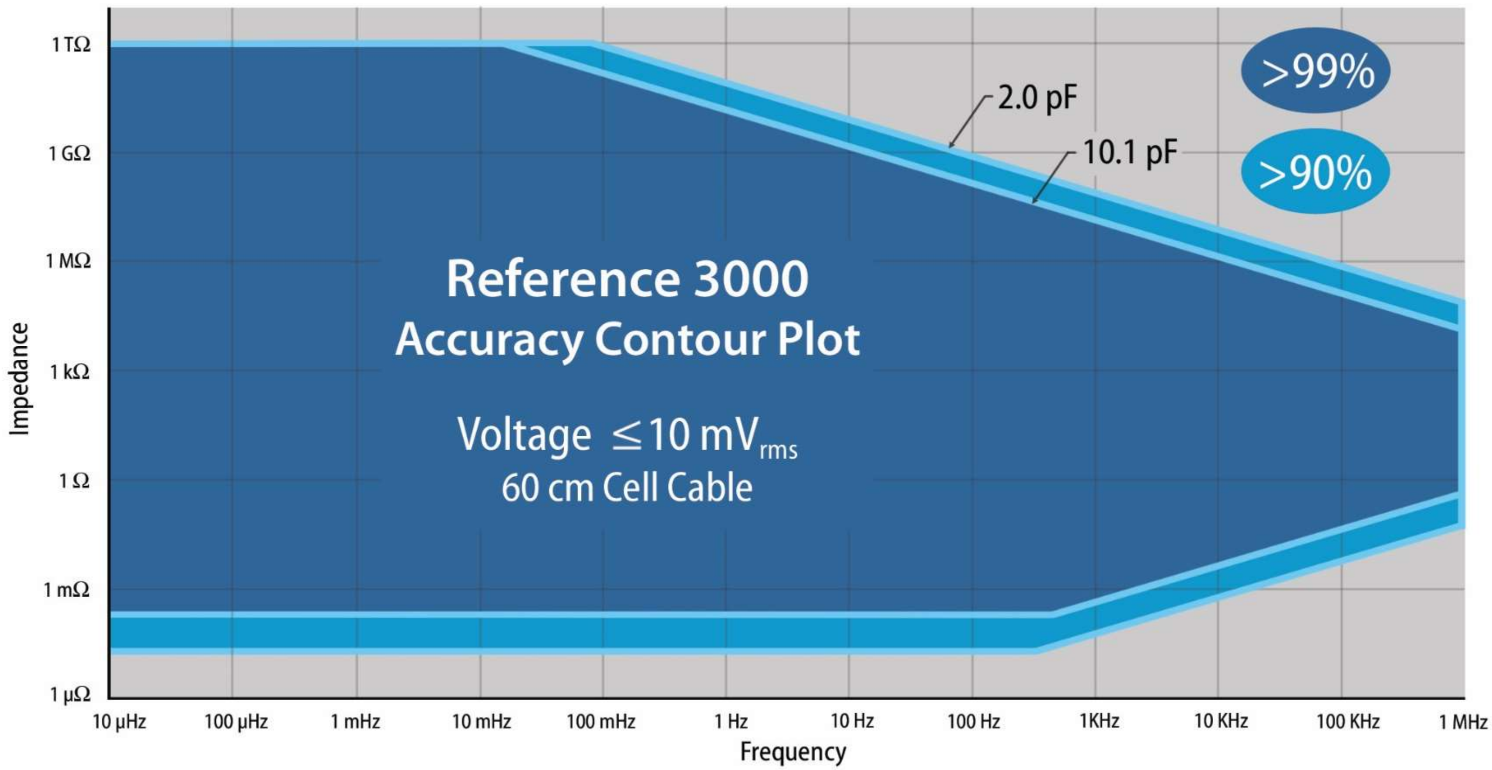
EIS System Performance

- Its important to understand your system's limitations. These are for ideal conditions. Real world situations could reduce instrument performance.

Accuracy Contour Plot

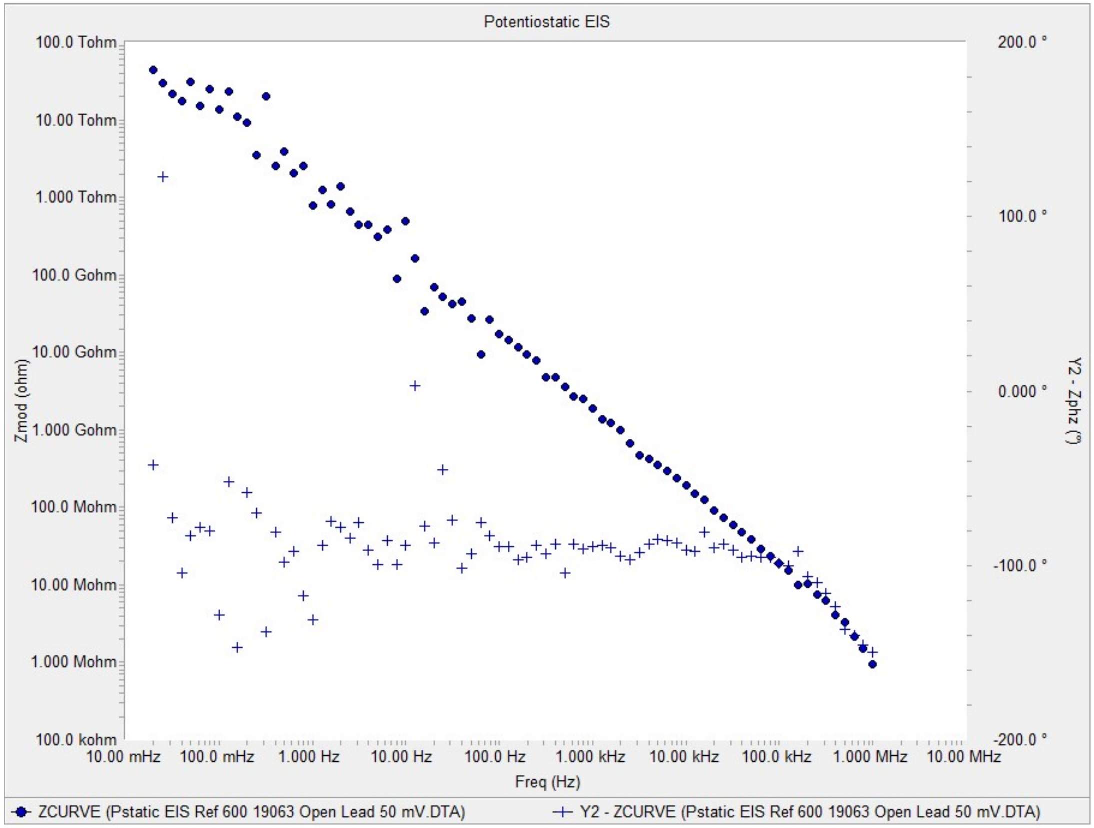
The ACP shows system performance under a given set of conditions (see below)

- Collected using normal operating parameters (e.g. potentiostatic or galvanostatic with voltage amplitudes <= 10 mV rms)



Open Lead Curve – High Impedance Limit

- Infinite resistance. Must use a Faraday Cage. W/WS in one, C/RE in a different Faraday Cage.
- Spectrum looks like a capacitor with -90° phase.
- At very low frequency, Z will tend toward horizontal line because of noise or finite printed circuit board resistance.
- $10^{14}\,\Omega$ with 50 mV V_{AC} gives an i_{AC} of 0.5 fA !

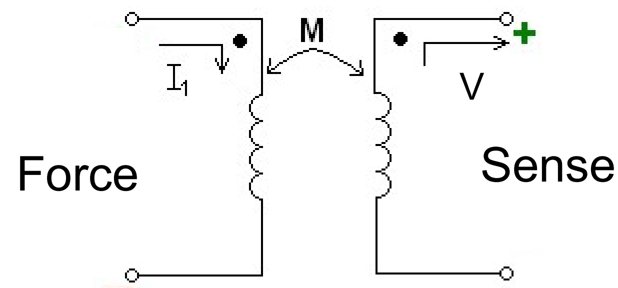


Measuring Low Impedance

- Resistance in energy storage and conversion devices:
  - Causes efficiency losses (power dissipated as heat)
  - Complicates thermal management of multiple device packs.
- Engineers strive for the lowest resistance possible.
- Low resistance devices are hard to test potentiostatically because applying small potentials is prone to errors and drift. **Measuring small potentials is easier than applying small potentials**.
- Always recommend **Galvanostatic EIS** for large batteries and capacitors.
- **Hybrid EIS** can be used to avoid non-linearity as the cell impedance changes. The cell is polarized galvanostatically and the excitation current is varied to maintain a constant AC voltage.

Mutual Inductance

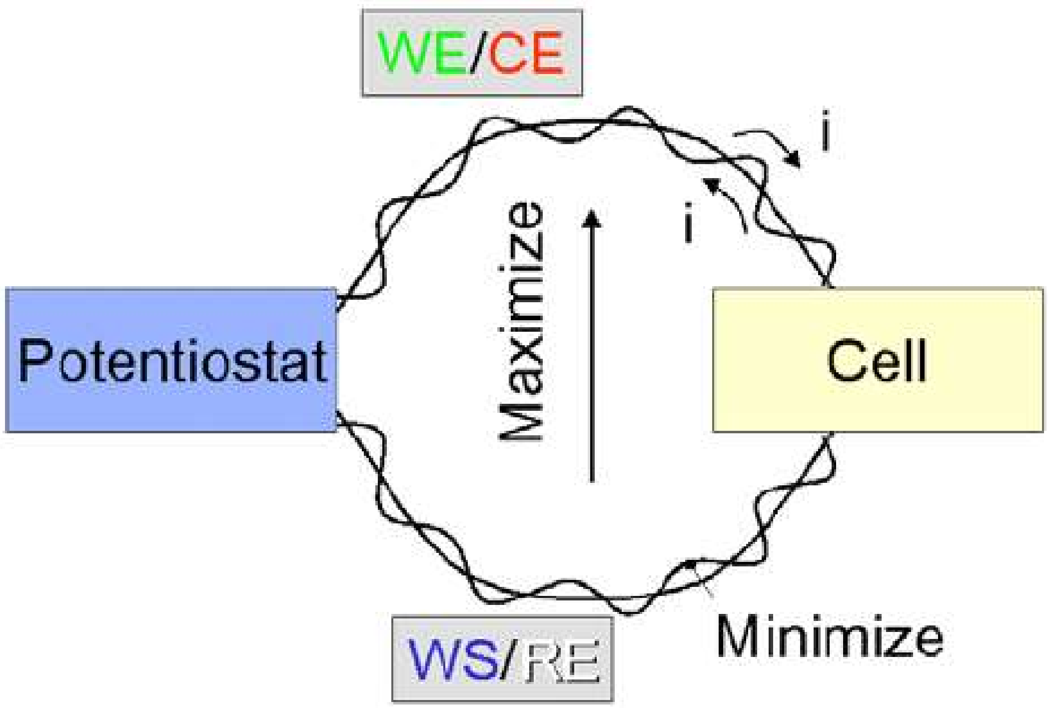
- Mutual inductance creates an apparent inductor in series with your electrochemical cell.
- The cell current creates a magnetic field in the working and counter leads. Think back to your undergraduate physics courses.



This magnetic field couples into the sense leads. In essence the cell leads form a transformer. The force leads are the primary and the sense leads are the secondary.

Mutual inductance is an artifact created by the measurement system. Note that the inductance value can be negative!

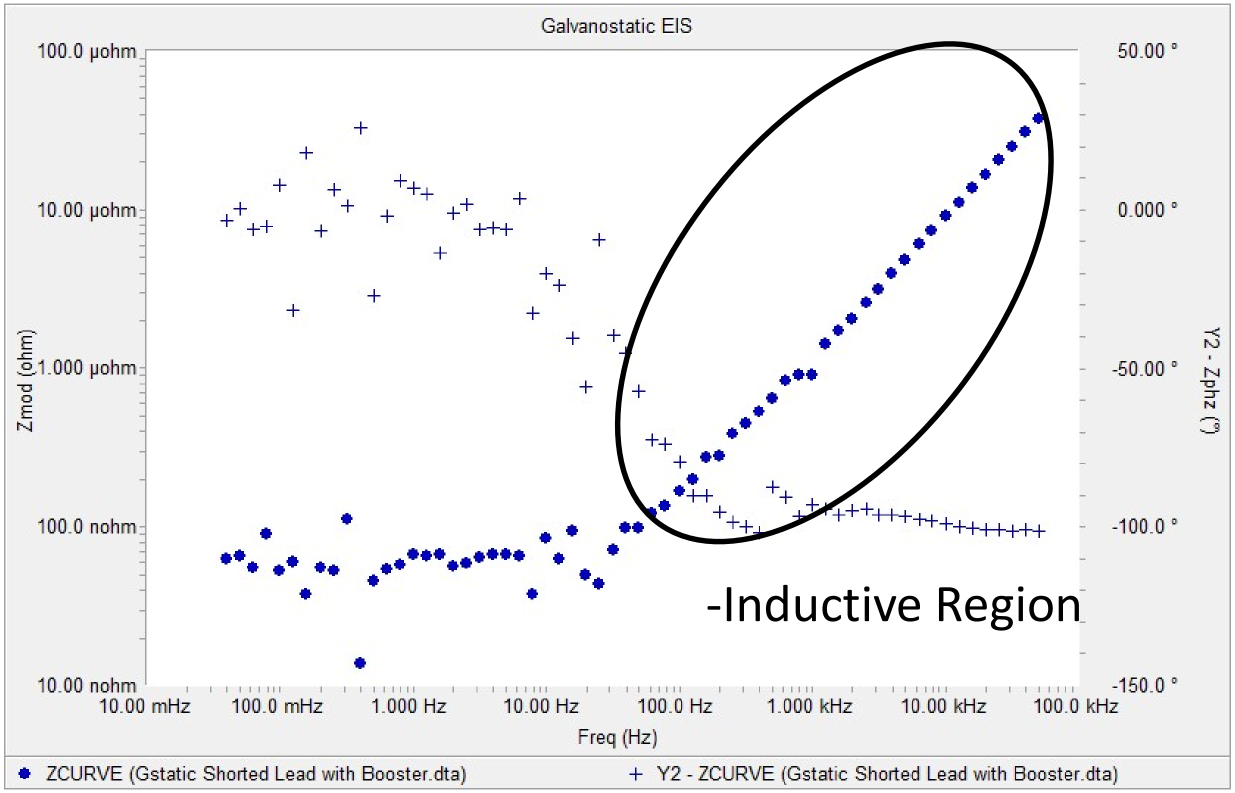
Preferred Cell/Cable Configuration for Low Impedance Devices



[Booster] Shorted Lead Curve

The inductance is again negative but at a gaudy -162 pH.

The low frequency resistance fit is 67 nΩ.   Note that in this case the value is positive.



Ways To Make Bad Measurements

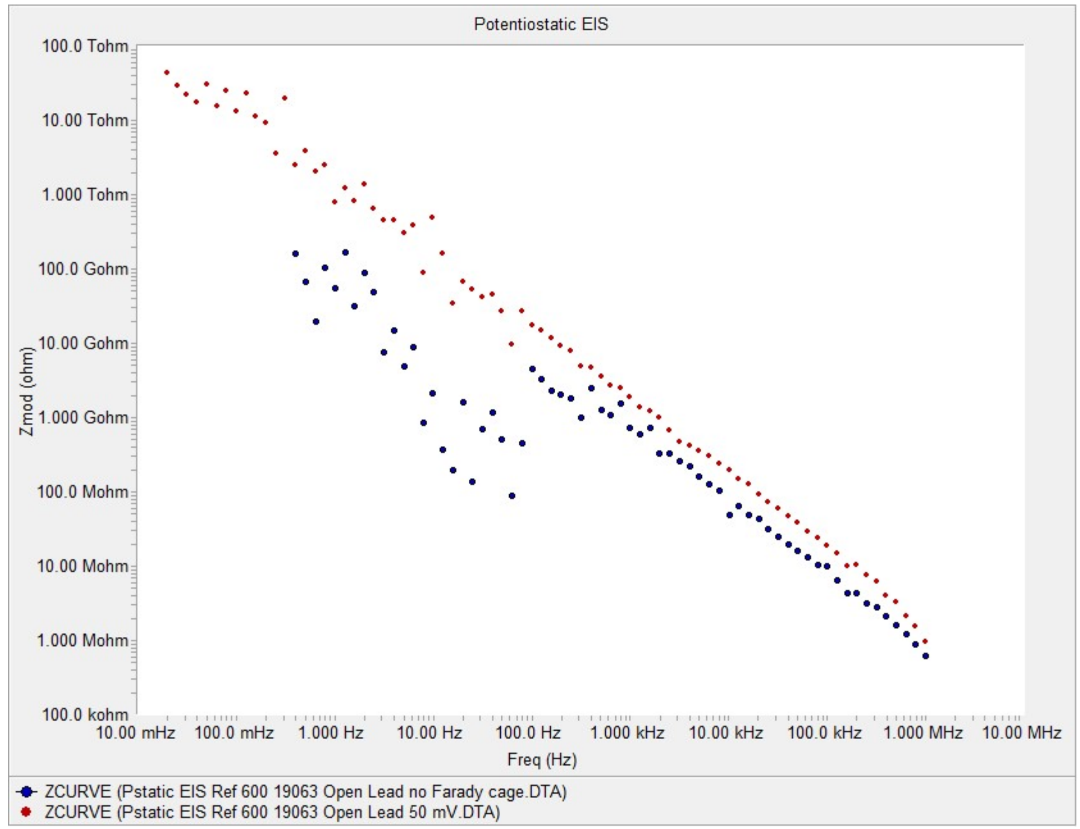
- There are many, but some happen more than others…

Low I/High Z Measurements: Faraday Cage

This figure shows magnitude only Bode plots for **two open lead curves.**

The red spectrum was measured with the cell leads in a Faraday cage. The blue spectrum was recorded outside the Faraday cage.

Impedances above 100 MΩ should <u>always</u> be made in a Faraday cage.



Low I/High Z Measurements: Grounding

- All Gamry Potentiostats are Floating, i.e. isolated from earth ground.
  - Required for
    - Experiments with grounded electrodes
    - Experiments in an autoclave
    - Experiments with multiple systems connected in the same cell
- The black lead is a float ground, and must be connected to a Faraday cage if one is being used
- Earth grounding the system can further reduce noise if floating not required
  - Only use one point of earth ground (Faraday cage itself or ground lug on potentiostat chassis)

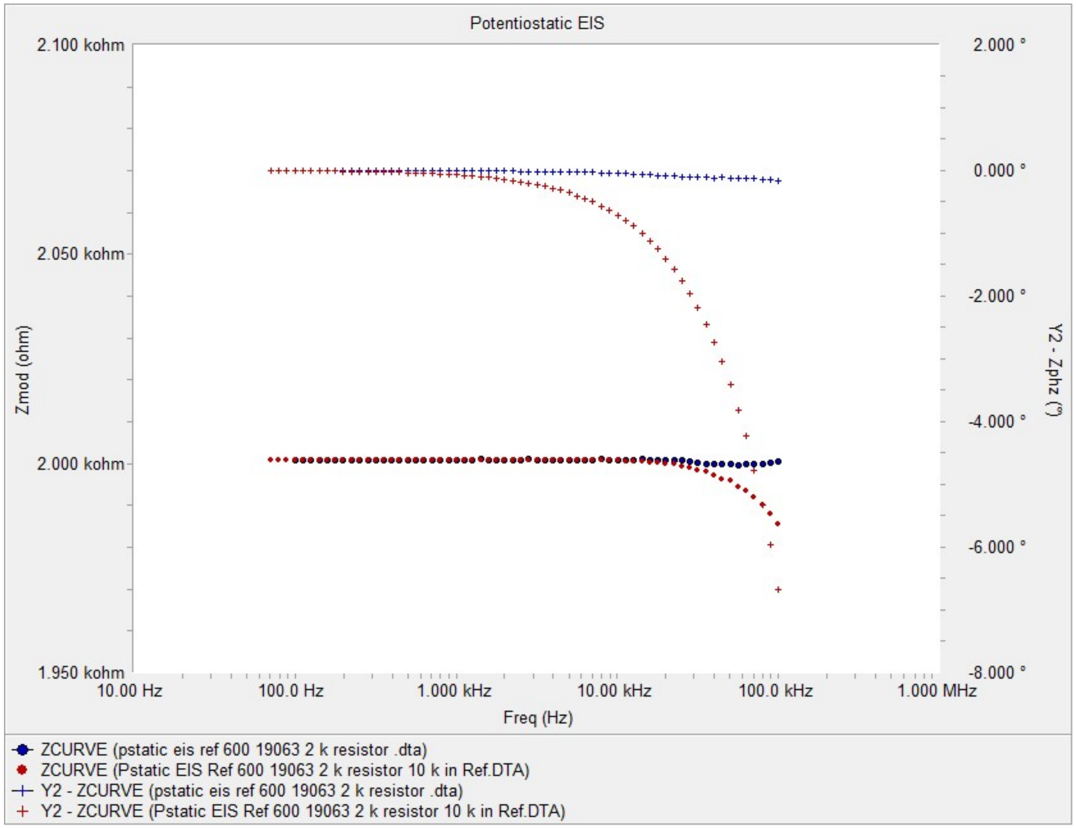
High Impedance Reference Electrodes

This figure shows EIS spectra recorded on a 2 kΩ resistor. Upper frequency is only 100 kHz.

The blue spectrum is the normal flat response.

The red spectrum had a 10 kΩ resistor in its Reference lead.

All reference electrodes have non-zero resistance. 10 kΩ is a “typical” value for a reference electrode in a Luggin capillary or a semi-clogged frit.

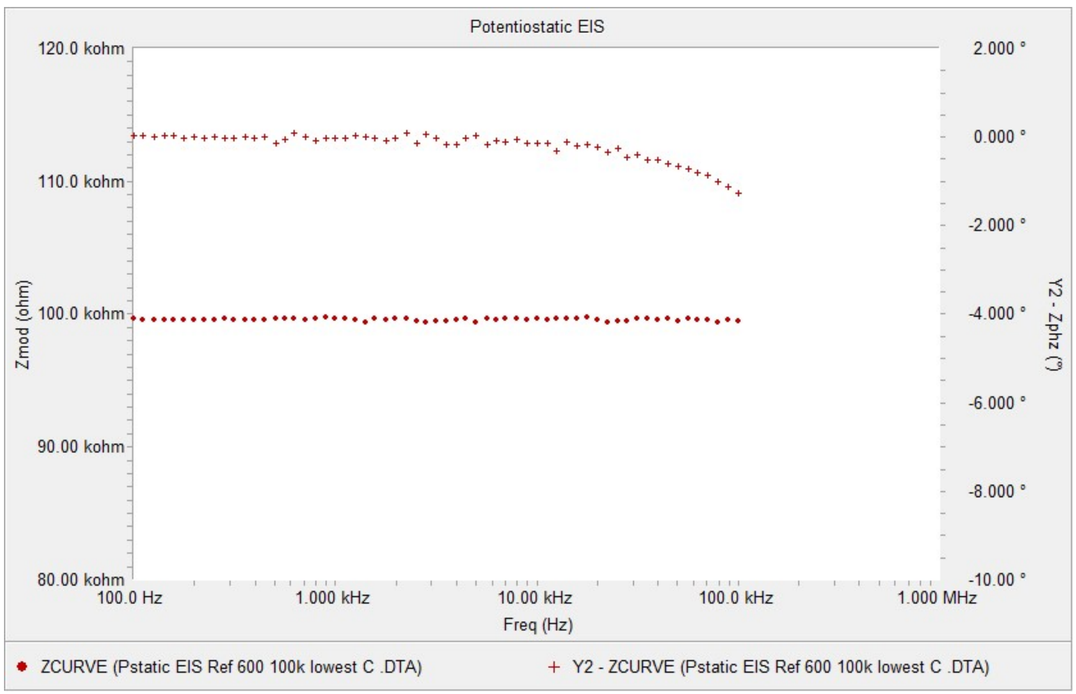


Ignoring Capacitance in Connections

Spectrum of a 100 kΩ resistor connected as shown.

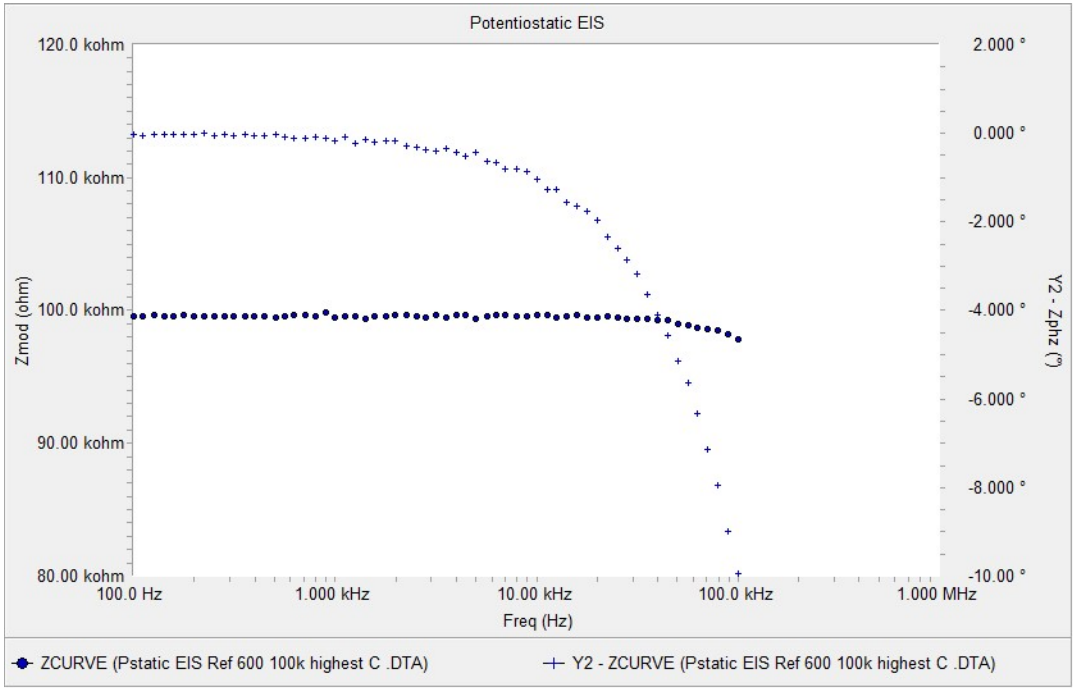
C/R

W/WS



Same Resistor Different Connections

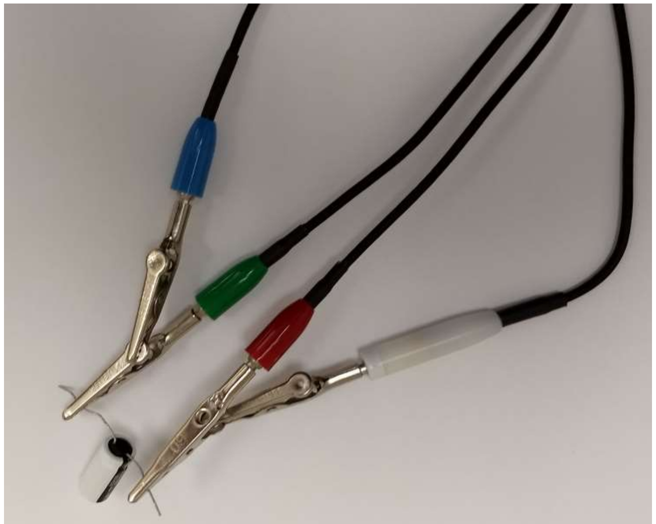
Spectrum of a 100 kΩ resistor connected badly



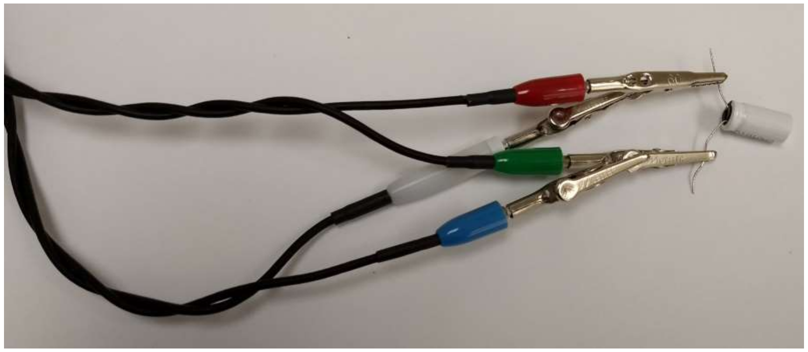
Make Poor Cell Connections

- These pictures show three ways to connect to a 5 F EDL capacitor.

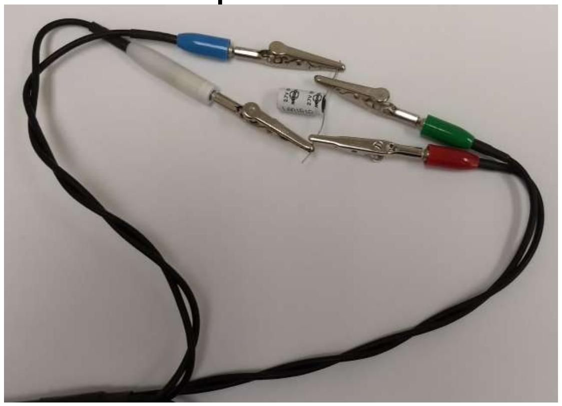
Bad – Two Terminal, Wires not Twisted



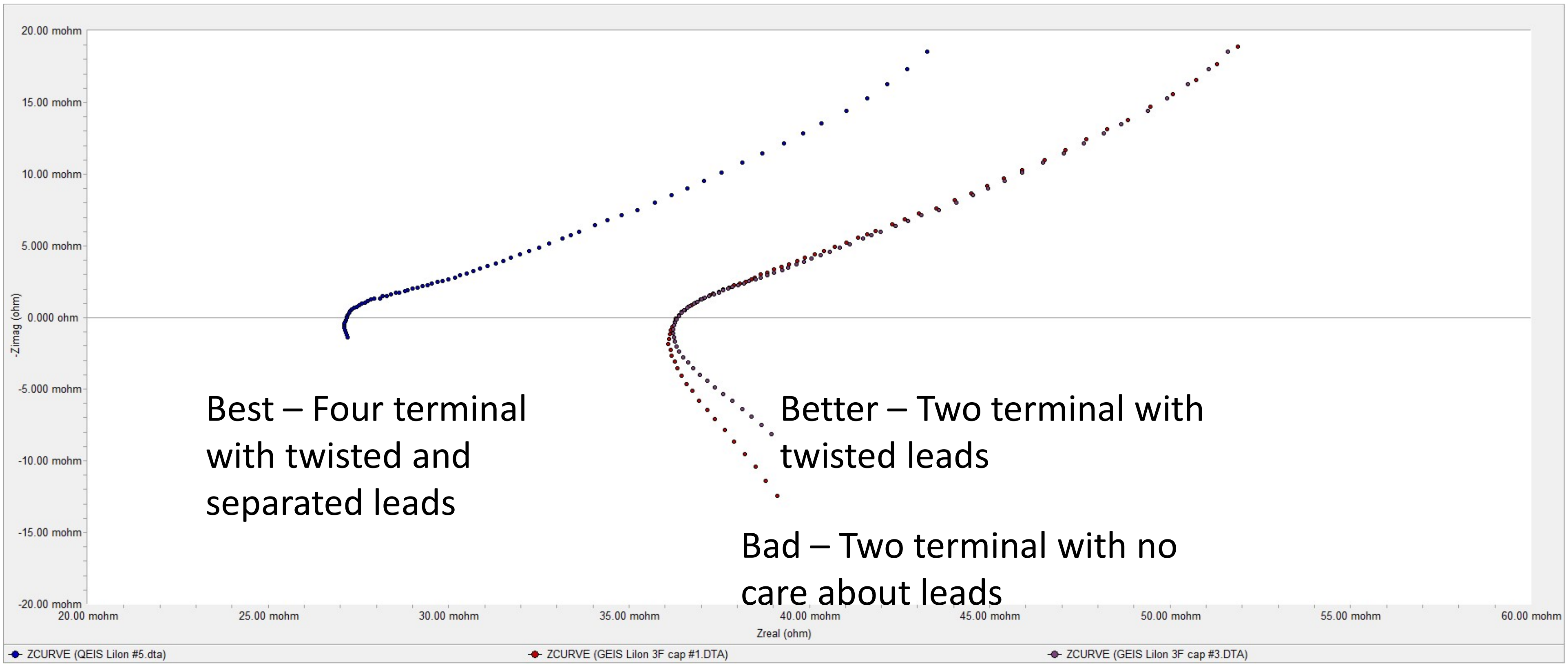
Better – Two Terminal but Wires Twisted



Best – Four terminal, wires twisted and separated



5 F EDL Cap Spectra



Note on Low Z vs. High Z connections

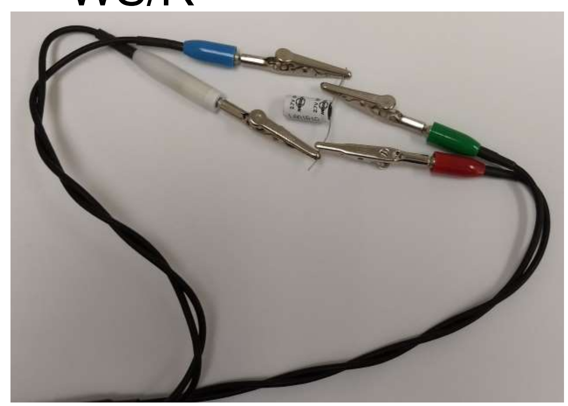
- Ideal cable setup for a Low Z system is the bad for a High Z system and vise versa.
- High Z – minimize capacitance
- Low Z – minimize inductance

C/R

W/WS

High Z

WS/R

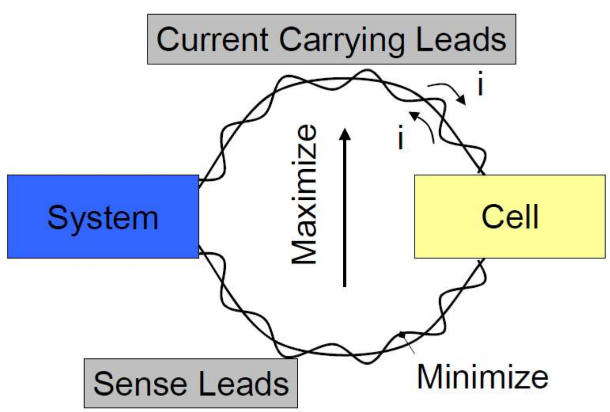


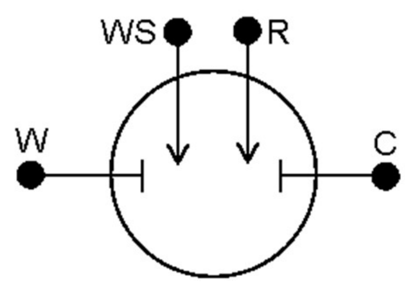
W/C

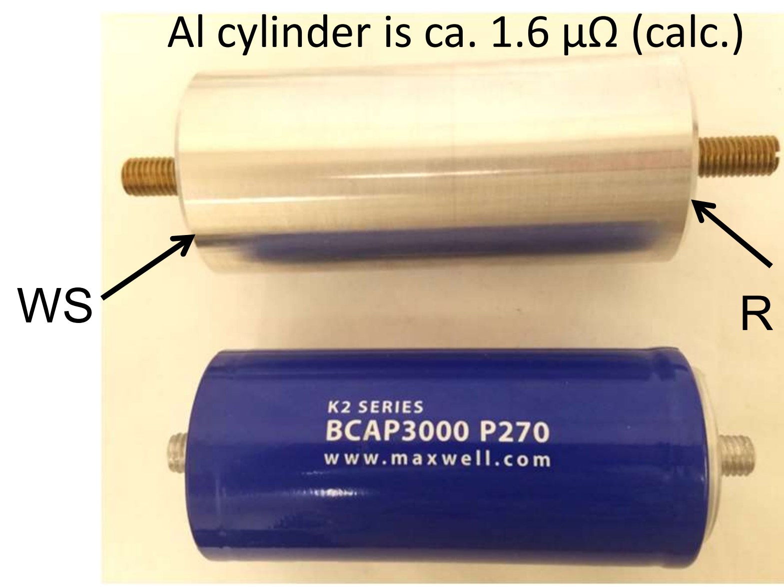
Low Z

Measuring Ultra Low impedance

- Minimize cable inductance
- Utilize 4-probe design
- Measure background with low Z surrogate







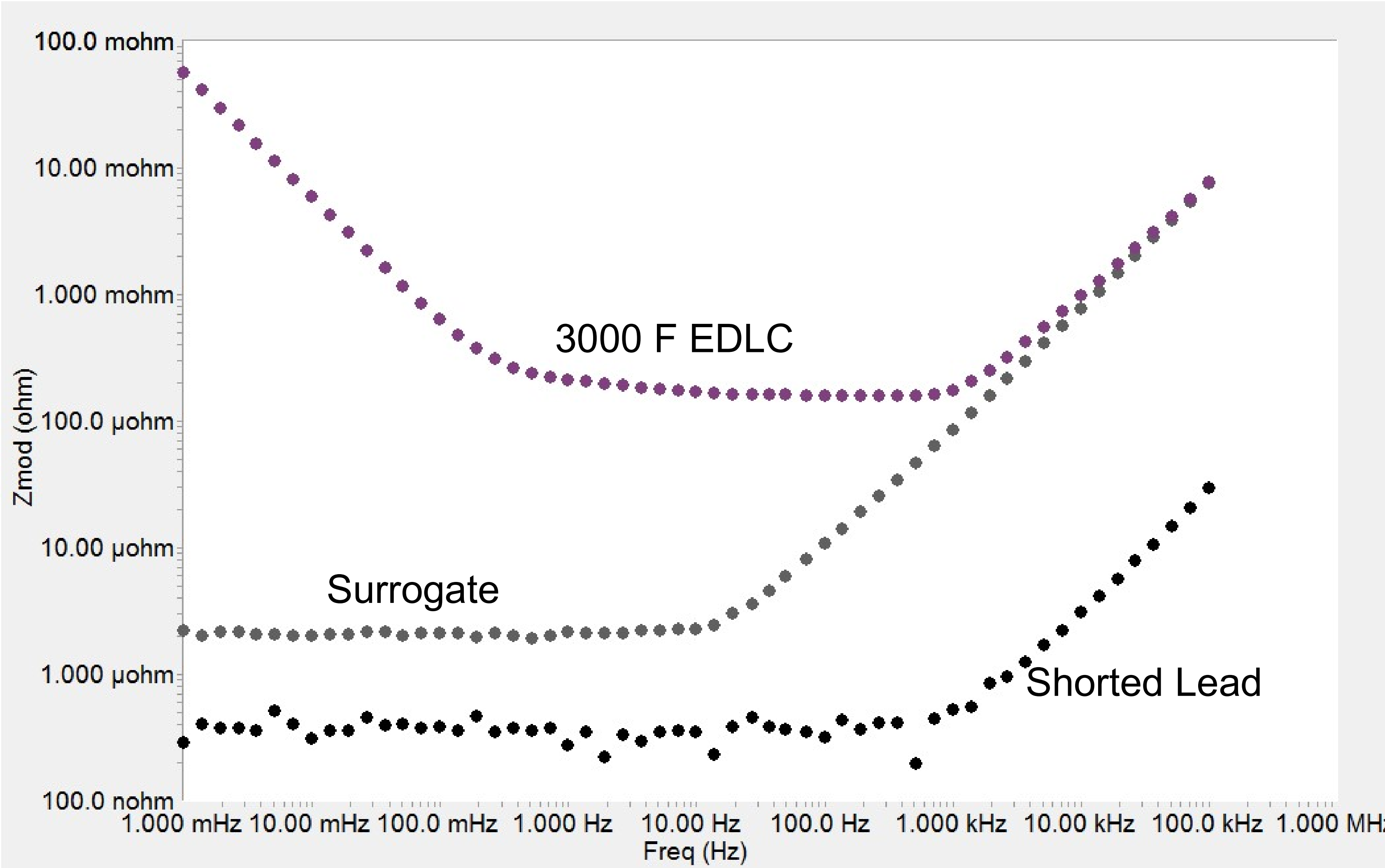
Measuring Background Using a Low Z Dummy

- Same size & shape as cell under study
- Same connections*
- Much lower impedance**

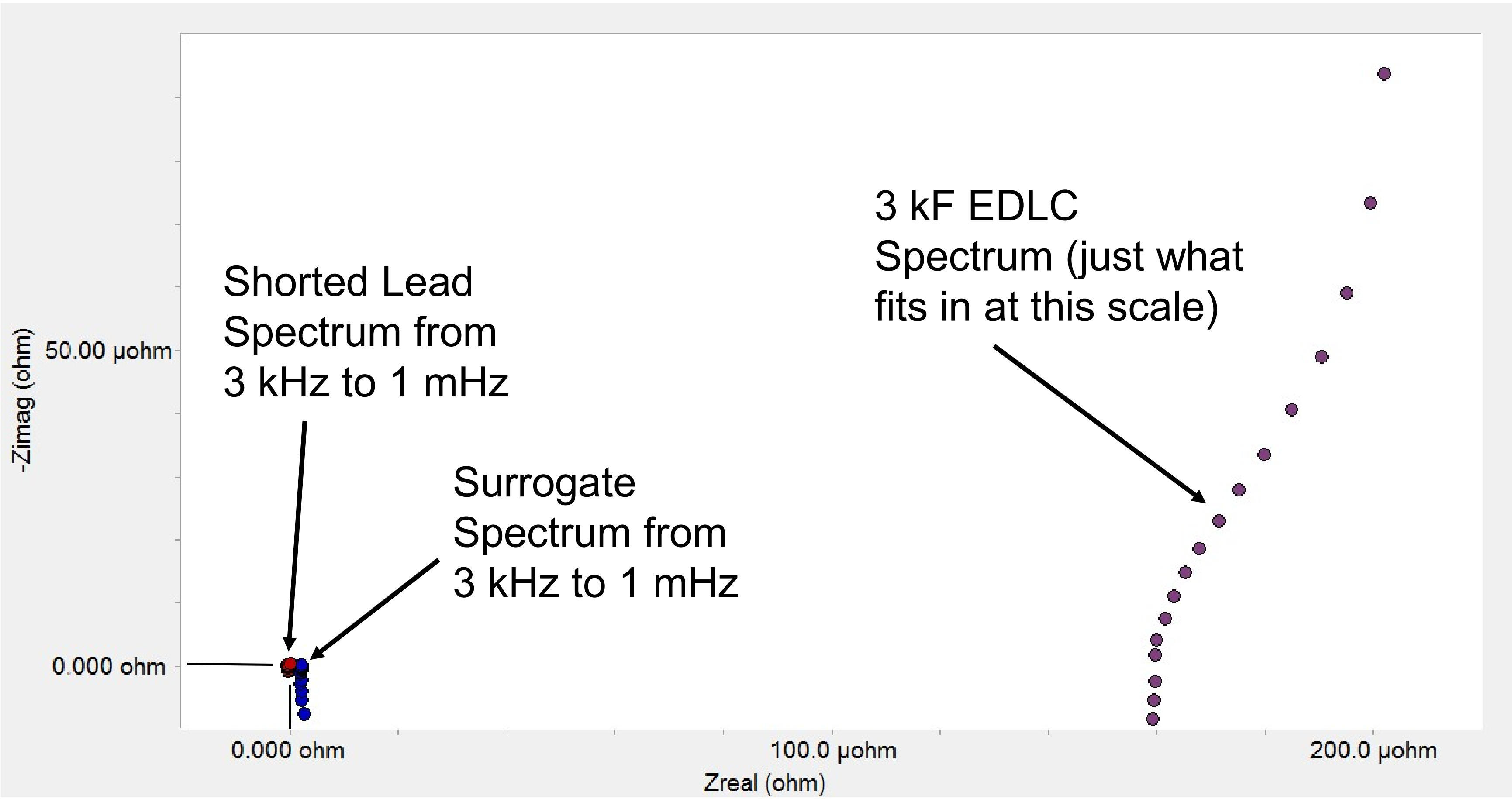
*note that the brass threads add contact resistance which is mitigated by not connecting sense lead to brass but is by connecting to the Al body

**calculated impedance of that diameter and length of Al is ~ 1.6 μΩ

Measuring Ultra Low Impedance



Measuring Ultra Low Impedance

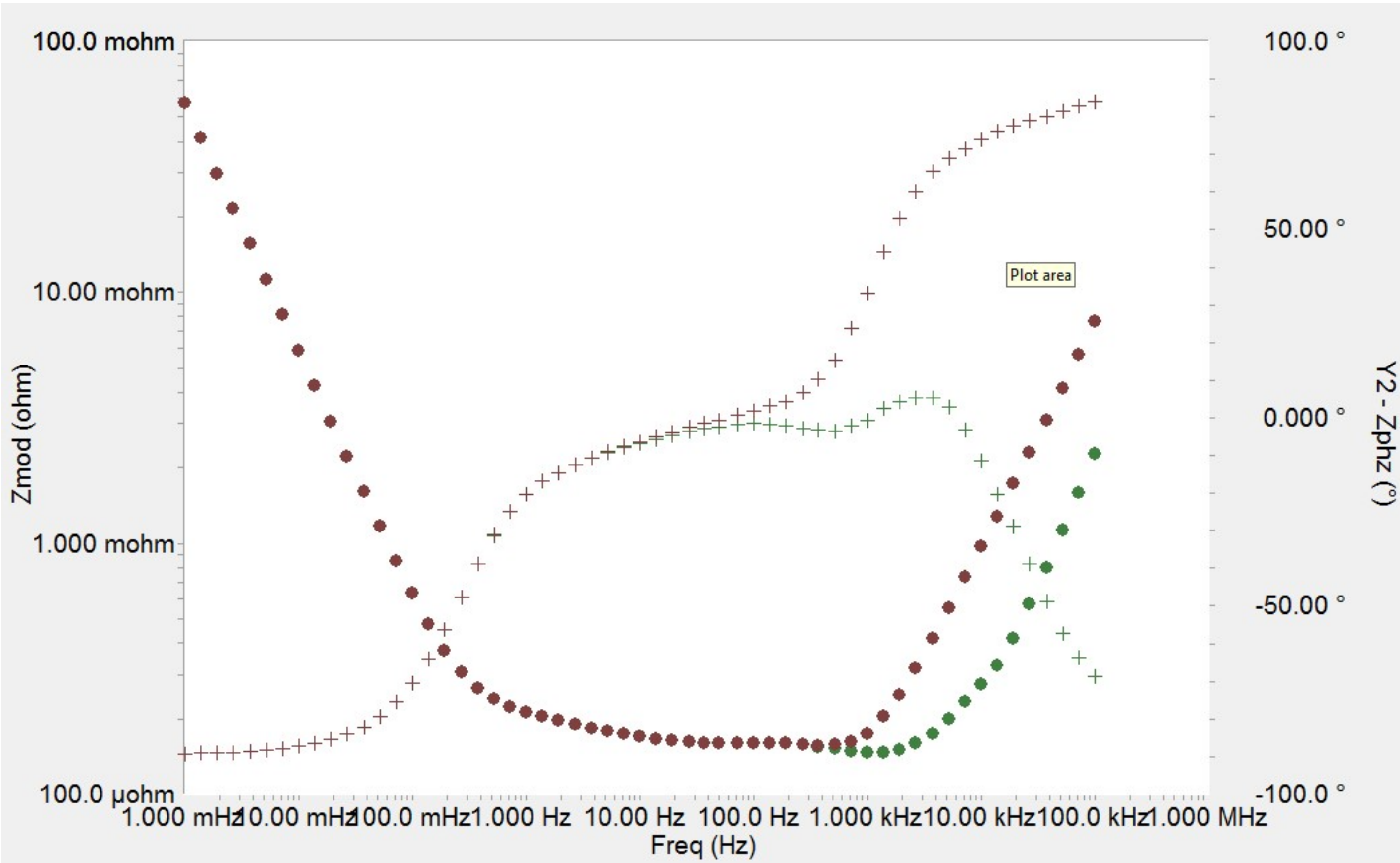


Comparison of Results

- High Performance System:
  - 2 electrode, 2 terminal 250 µΩ
  - 2 electrode, 4 terminal 165 µΩ
  - 4 terminal, minimized L 150 µΩ
  - Capacitance 2700 F

- Specified ESR: 290 µΩ (DC Measurement)
- Specified Capacitance: 3000 F (initial, DC measurement)

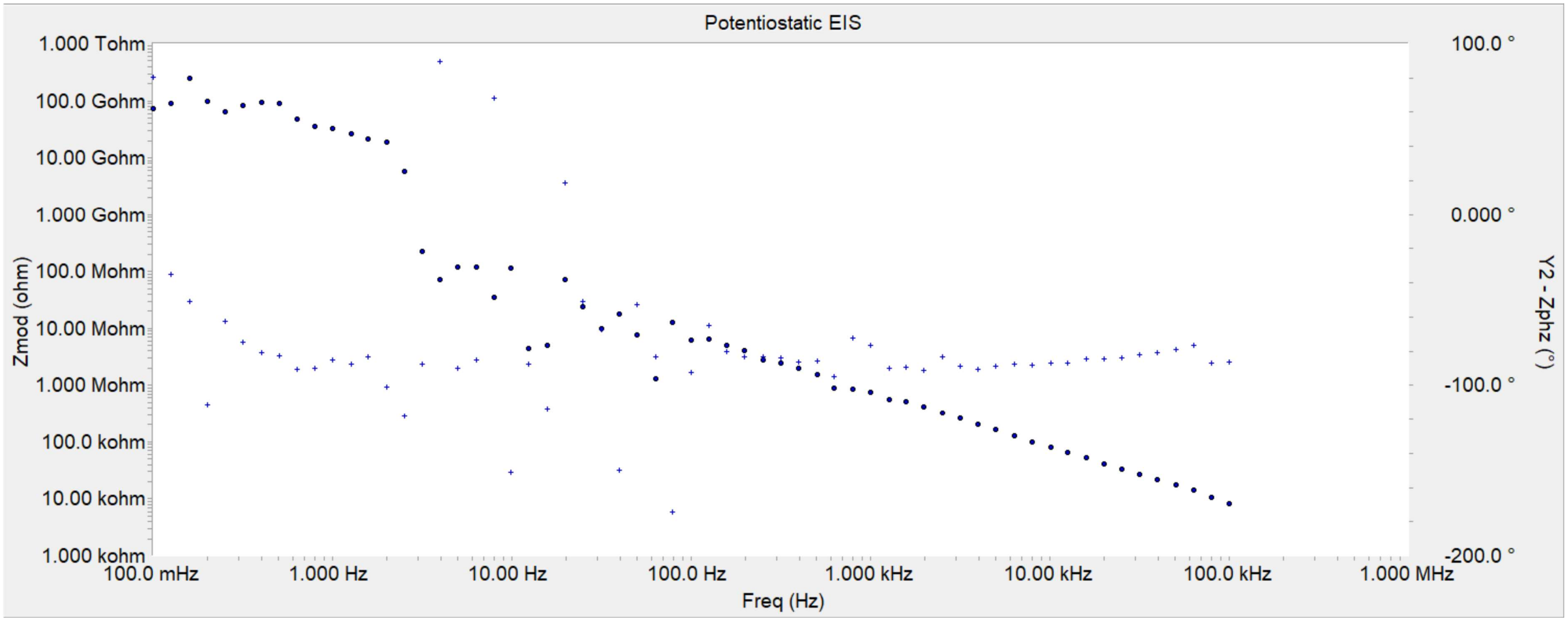
Background Subtracting
Low Z Dummy - Inductance



Baseline
L = 16 nH
ESR = 150 µΩ
C = 2700 F

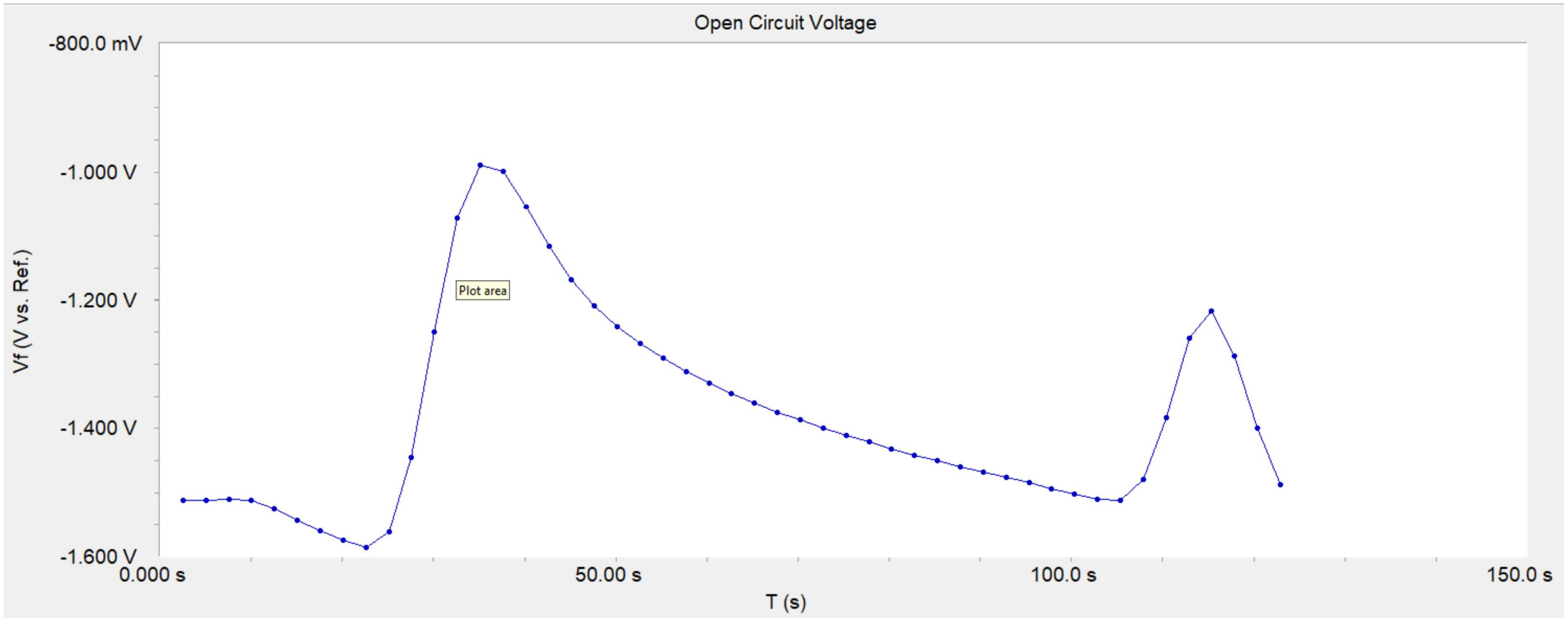
Surrogate
L = 15.5 nH
R = 2 µΩ

Stability



Sample is Al in “electrolyte”

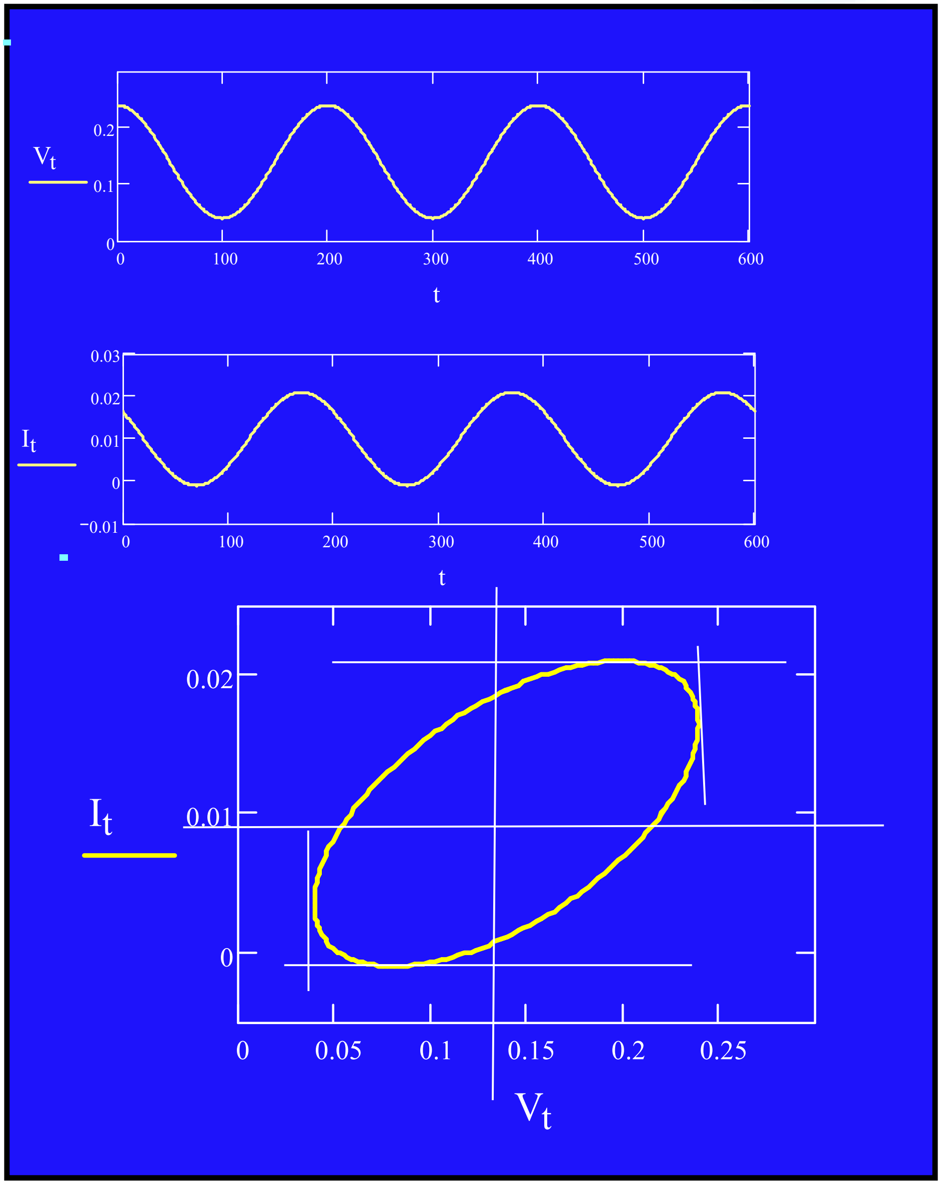
Stability



The electrolyte contained chloride, which will pit Al.
This sample is not stable.
Fix: change electrolyte to something more stable, use a smaller area electrode, speed up experiment* as much as possible, and you may still have to content yourself with only higher frequency data

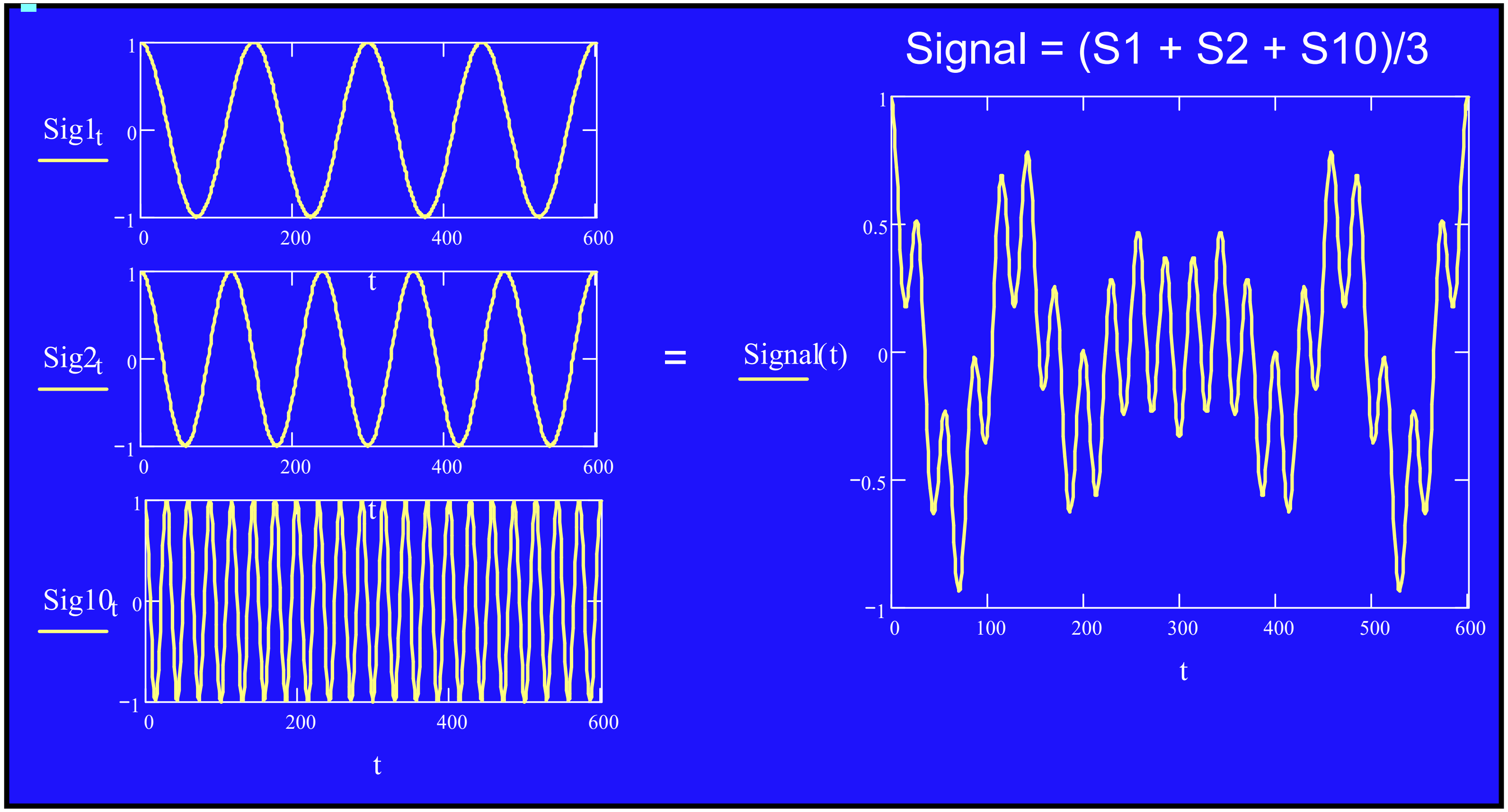
Single Sine EIS

- Apply a known sine wave + dc
- Measure V(t), I(t)
- Plot V(t) vs I(t)
- Fit V vs I to get V_{dc} I_{dc} V_{ac} I_{ac} Z
- Repeat for range of frequencies



Multi-Sine EIS: Measure Several Frequencies Simultaneously

developed by Don Smith (Northwestern U.)- Early '70s

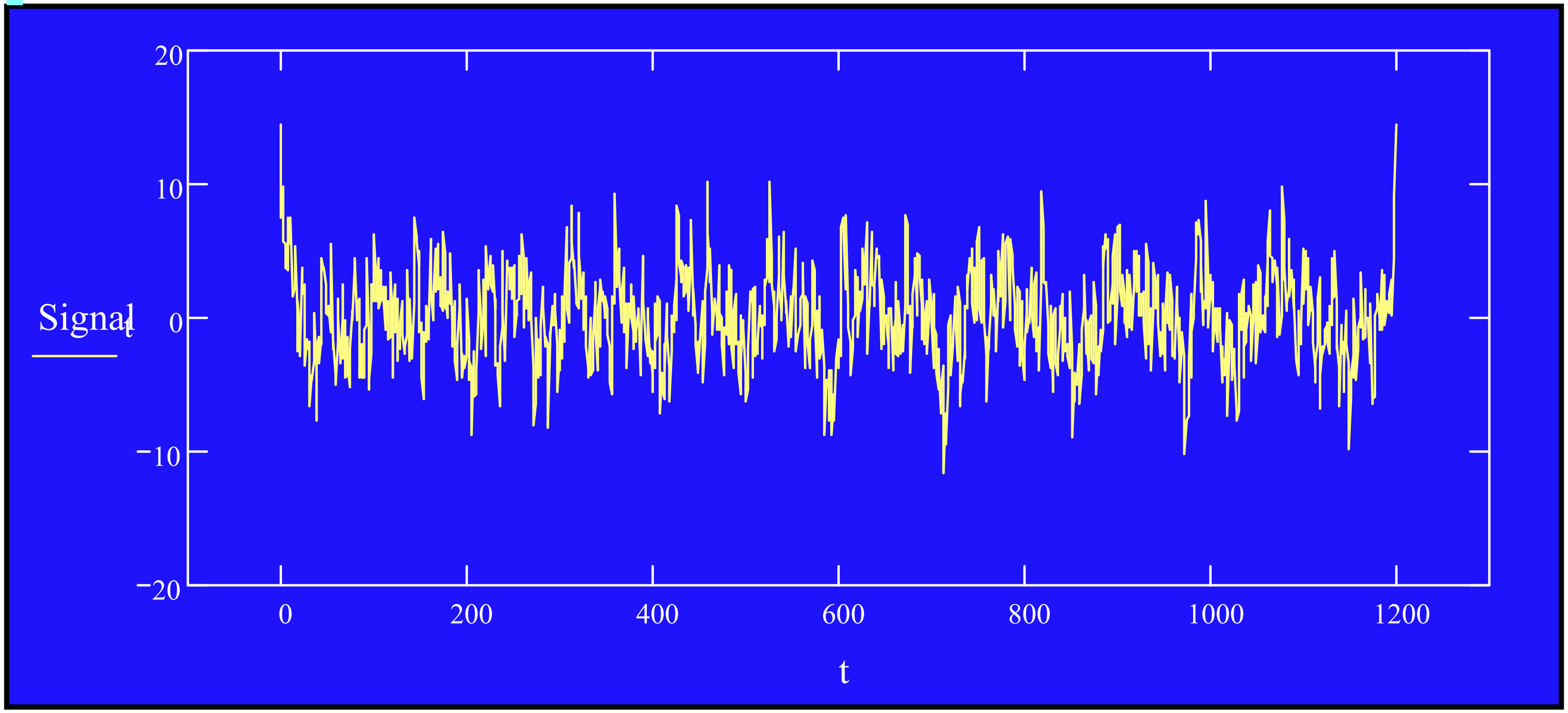


A 2 decade, 24 frequency, Multi-sine Signal

$$S[i] = \sum_{k=0}^{K-1} A_k \cdot \cos\left(2\pi\left(f_k \tau i + \varphi_k\right)\right)$$

A's are a unity

φ's are random

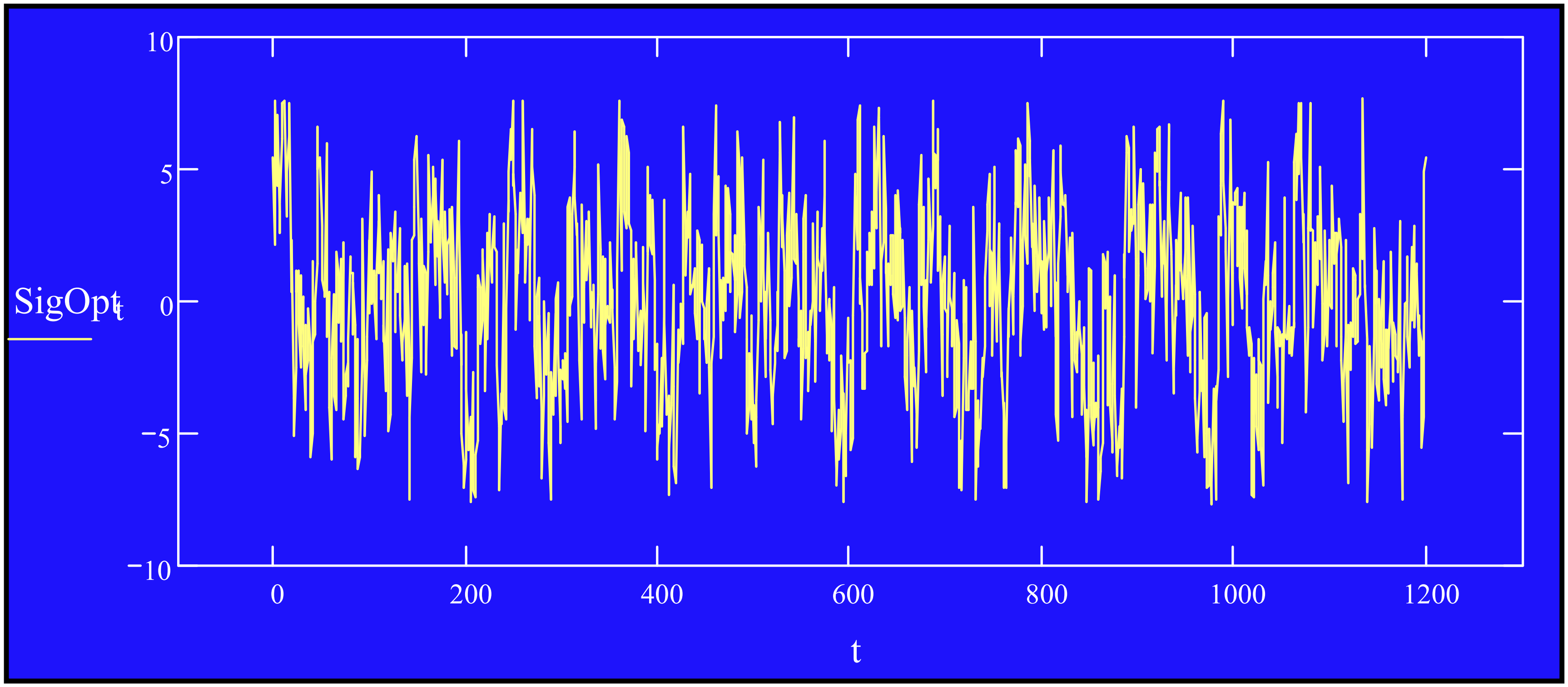


Whack-a-mole* Phase Optimization

Do for #iterations

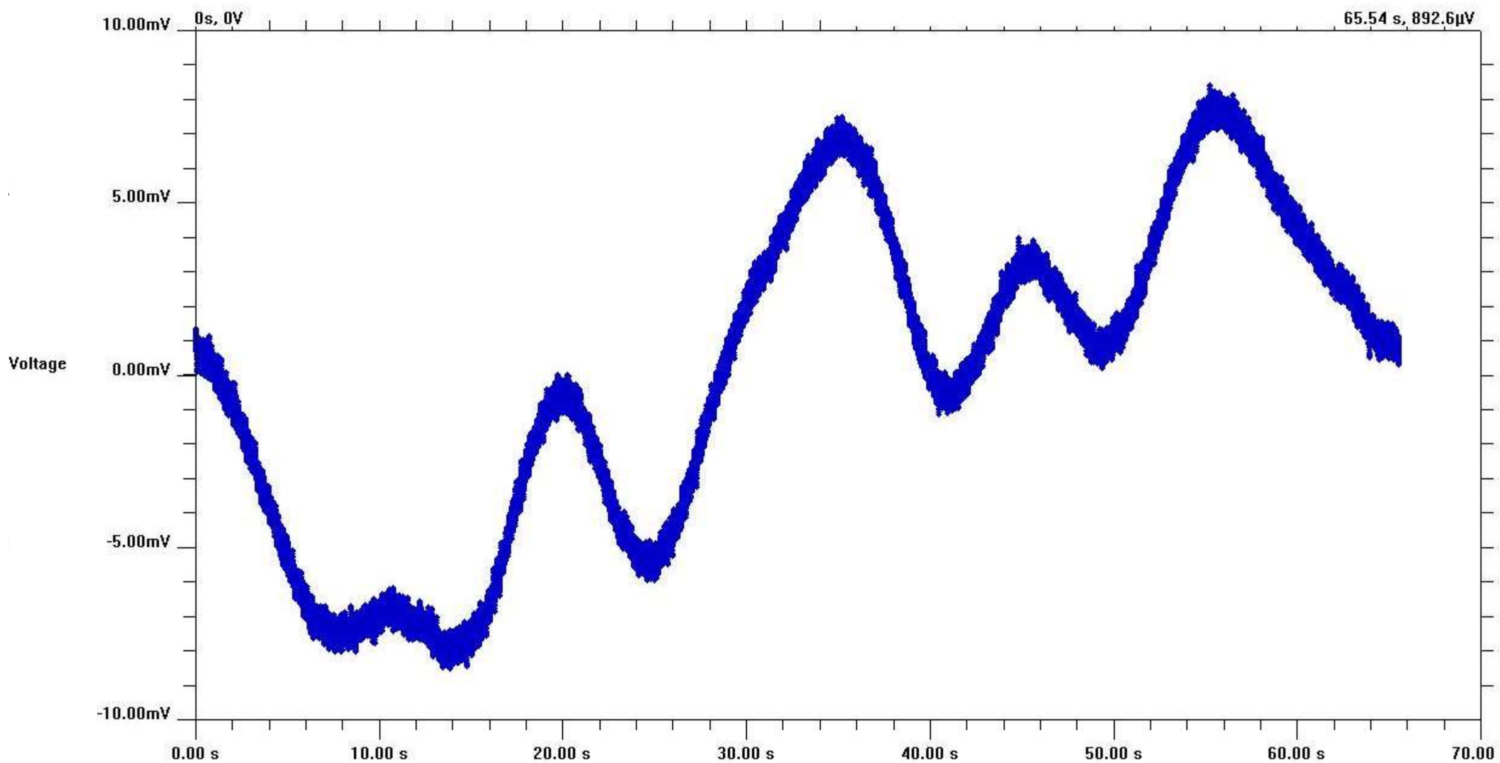
Find S_{max}=Max(Abs(S)) (Find what to whack)

Take a steepest descent step in ϕ_k (Take a good whack)

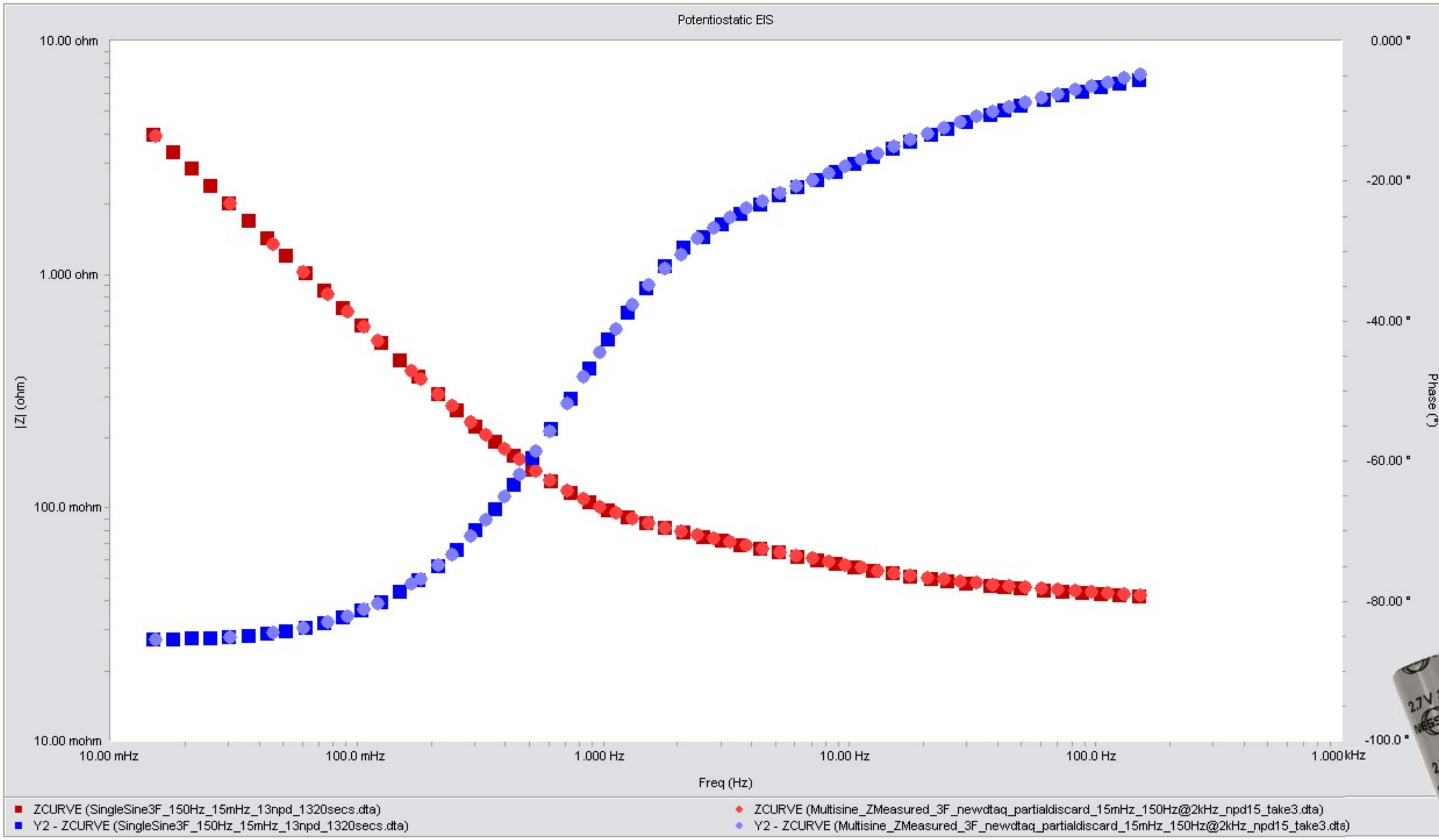


Farden, Leon, Tallman (NDSU) 1999
*Named by Ulgut, 2009

Amplitude Optimization

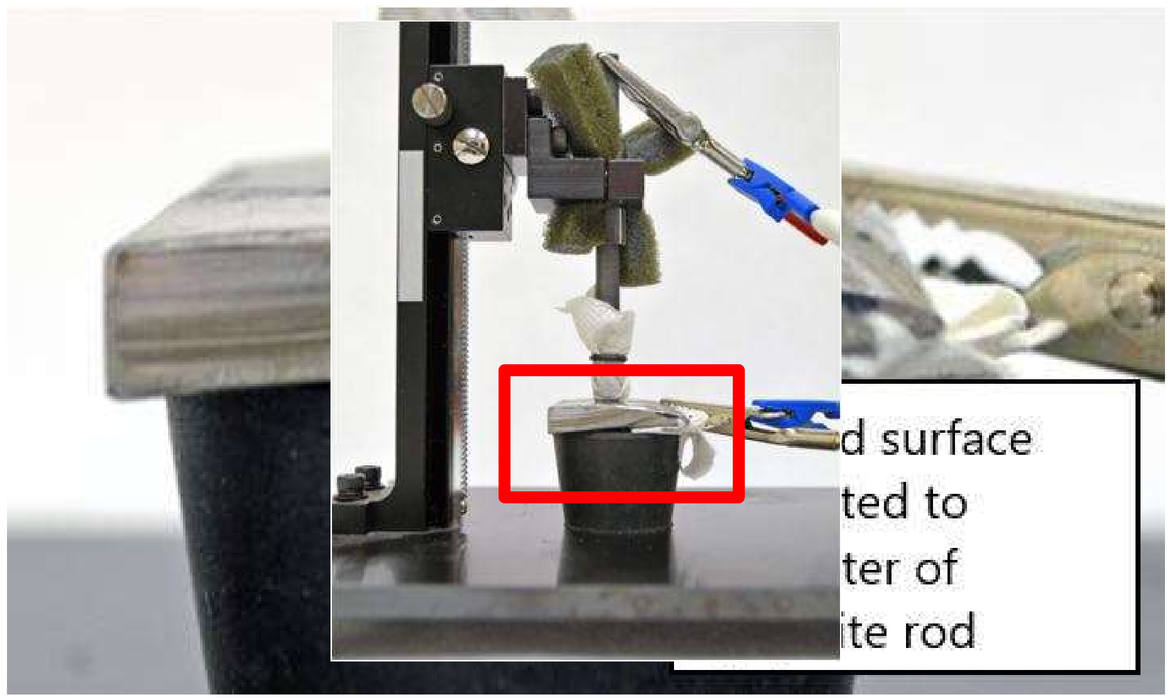


Single Sine and MultiSine Overlayed



Difficult Samples

- Some samples are just difficult to use with conventional cells.
- So long as you can control the active area, other means of collecting data can be used.
- For example:



Analysis of Difficult Systems

- Connections matter
- Cable layout matters
- Use a Faraday cage
- Reference electrodes can be a source of problems
- Think about cell setup

…Try to change things up