Electrochemical Impedance Spectroscopy:

Basics of EIS

GAMRY INSTRUMENTS

Impedance

- The term *impedance* refers to the frequency dependant resistance to current flow of a circuit element (resistor, capacitor, inductor,etc.)

- *Impedance* assumes an AC current of a specific frequency in Hertz (cycles/s).

- *Impedance*: $Z_\omega = E_\omega / I_\omega$

  - $E_\omega =$ Frequency-dependent potential
  - $I_\omega =$ Frequency-dependent current

- Ohm's Law: $R = E/I$

 - R = impedance at the limit of zero frequency

Reasons To Run EIS

- EIS is theoretically complex (and can be expensive) – why bother?
  - The information content of EIS is <u>much</u> higher than DC techniques.
  - If two or more electrochemical reactions are taking place, EIS may be able to distinguish between them.
  - EIS can identify diffusion-limited reactions, e.g., diffusion through a passive film.
  - EIS provides information on the capacitive behavior of the system. This is always useful, but particularly for coatings.

Making EIS Measurements

- Apply a small sinusoidal perturbation (potential or current) of fixed frequency

- Measure the response and compute the impedance at each frequency.

  - $Z_\omega = E_\omega / I_\omega$

    - $E_\omega =$ Frequency-dependent potential
    - $I_\omega =$ Frequency-dependent current

- Repeat for a wide range of frequencies

- Plot and analyze

# Excitation and Response in EIS
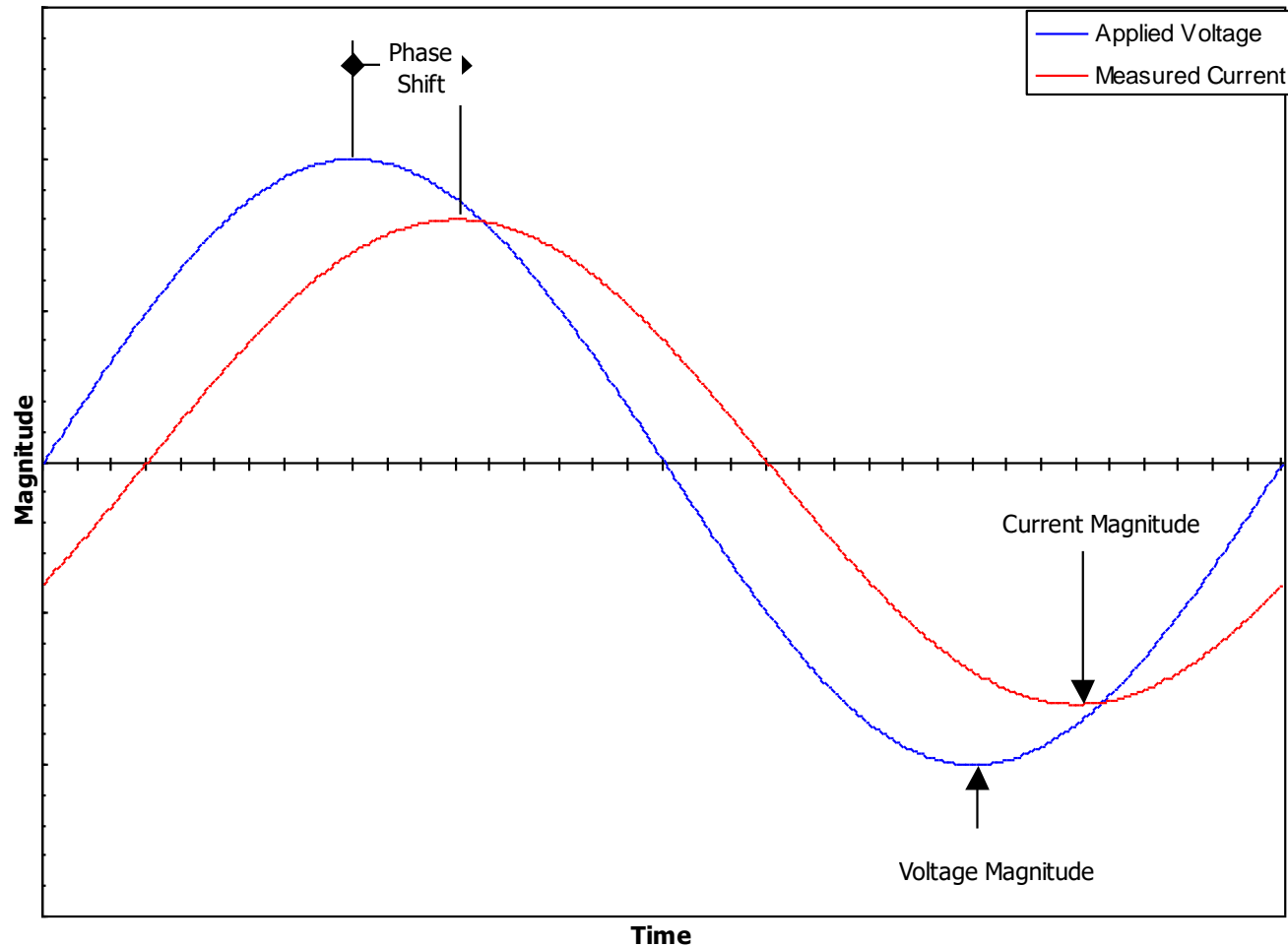
EIS Data Presentation

- EIS data may be displayed as either a vector or a complex quantity.

- A vector is defined by the impedance magnitude and the phase angle.

- As a complex quantity, $Z_{total} = Z_{real} + Z_{imag}$

- The vector and the complex quantity are different representations of the impedance and are mathematically equivalent.

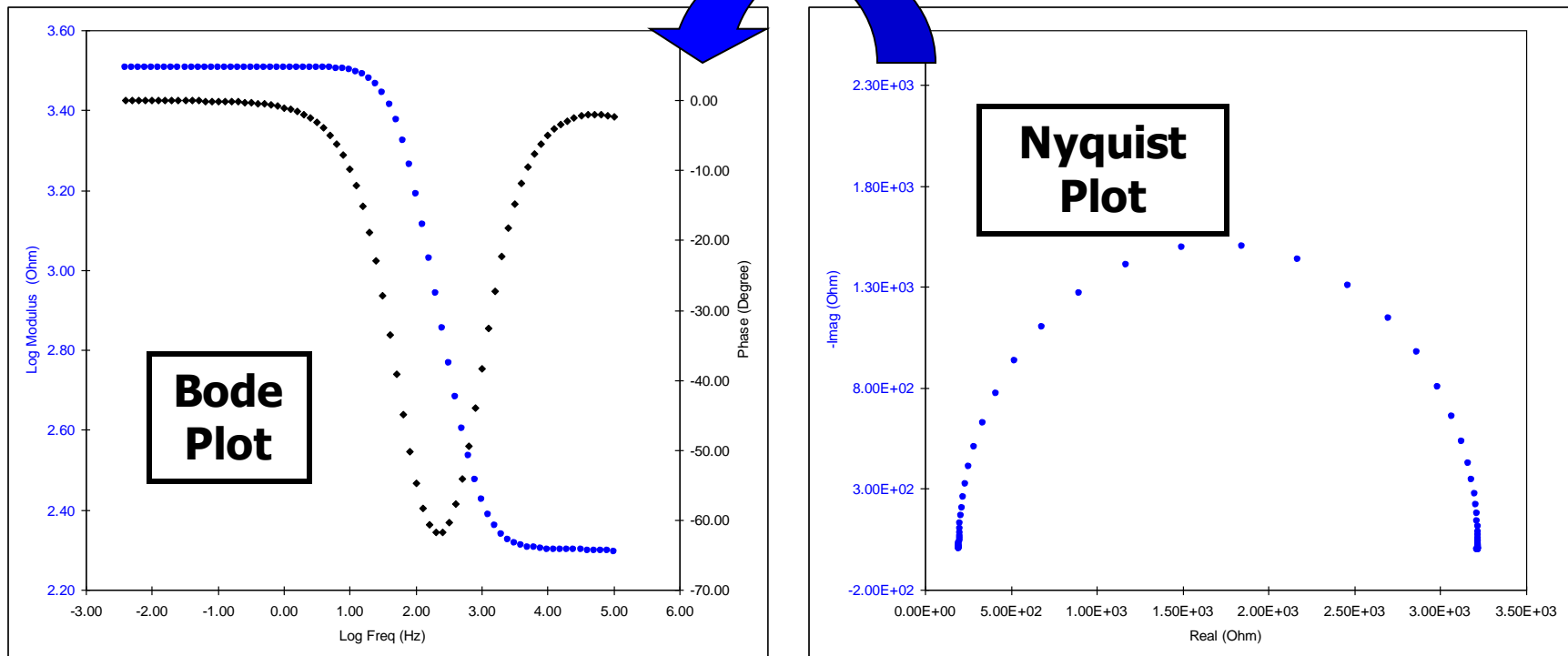# Vector and Complex Plane Representations

Vector

Magnitude

Θ

Θ = Phase Angle

Complex Plane

Imaginary Impedance, Z"
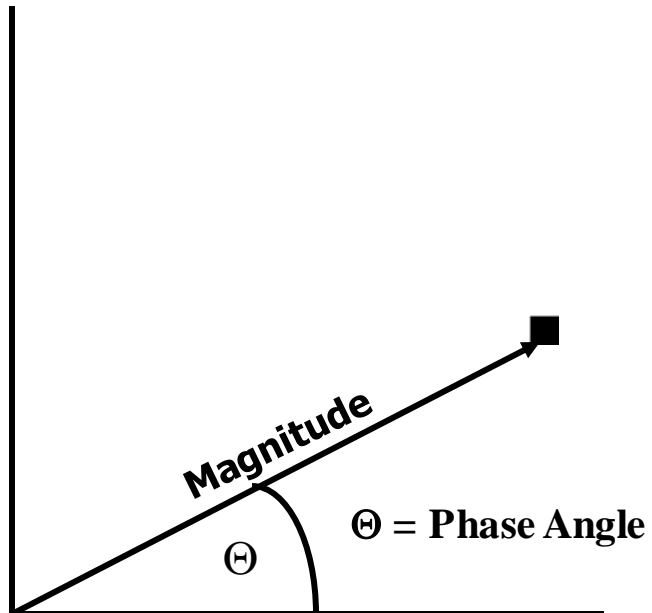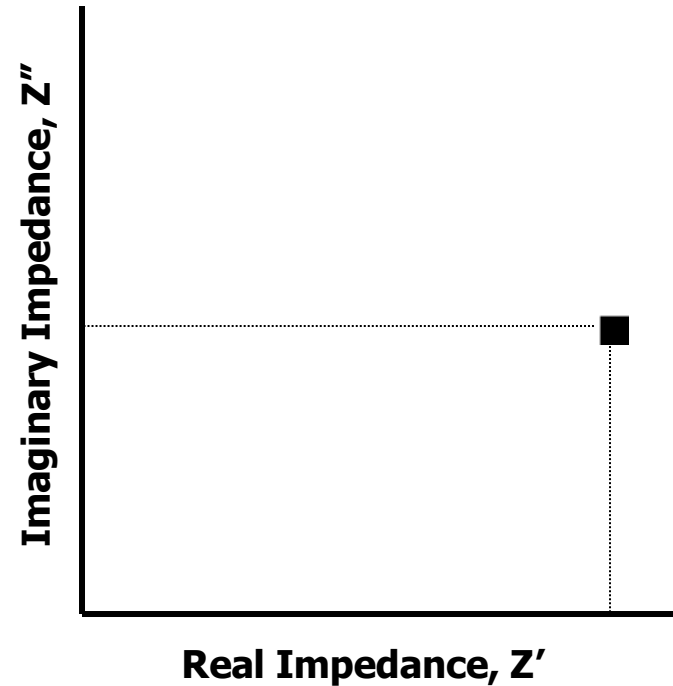
Real Impedance, Z'

EIS data may be presented as a Bode Plot or a Complex Plane (Nyquist) Plot

# Nyquist vs. Bode Plot

Bode Plot

- Individual charge transfer processes are resolvable.

- Frequency is explicit.

- Small impedances in presence of large impedances can be identified easily.
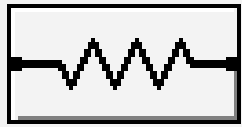
Nyquist Plot

- Individual charge transfer processes are resolvable.

- Frequency is not obvious.

- Small impedances can be swamped by large impedances.

Analyzing EIS: Modeling

- Electrochemical cells can be modeled as a network of passive electrical circuit elements.

- A network is called an "equivalent circuit".

- The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.
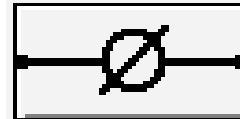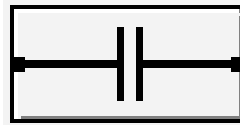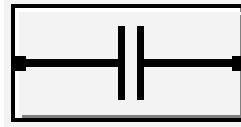
Frequency Response of Electrical Circuit Elements

Resistor

Capacitor

Inductor
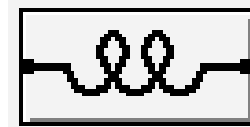
$Z = R$ (Ohms)

$Z = -j/\omega C$ (Farads)

$Z = j\omega L$ (Henrys)

0° Phase Shift

-90° Phase Shift
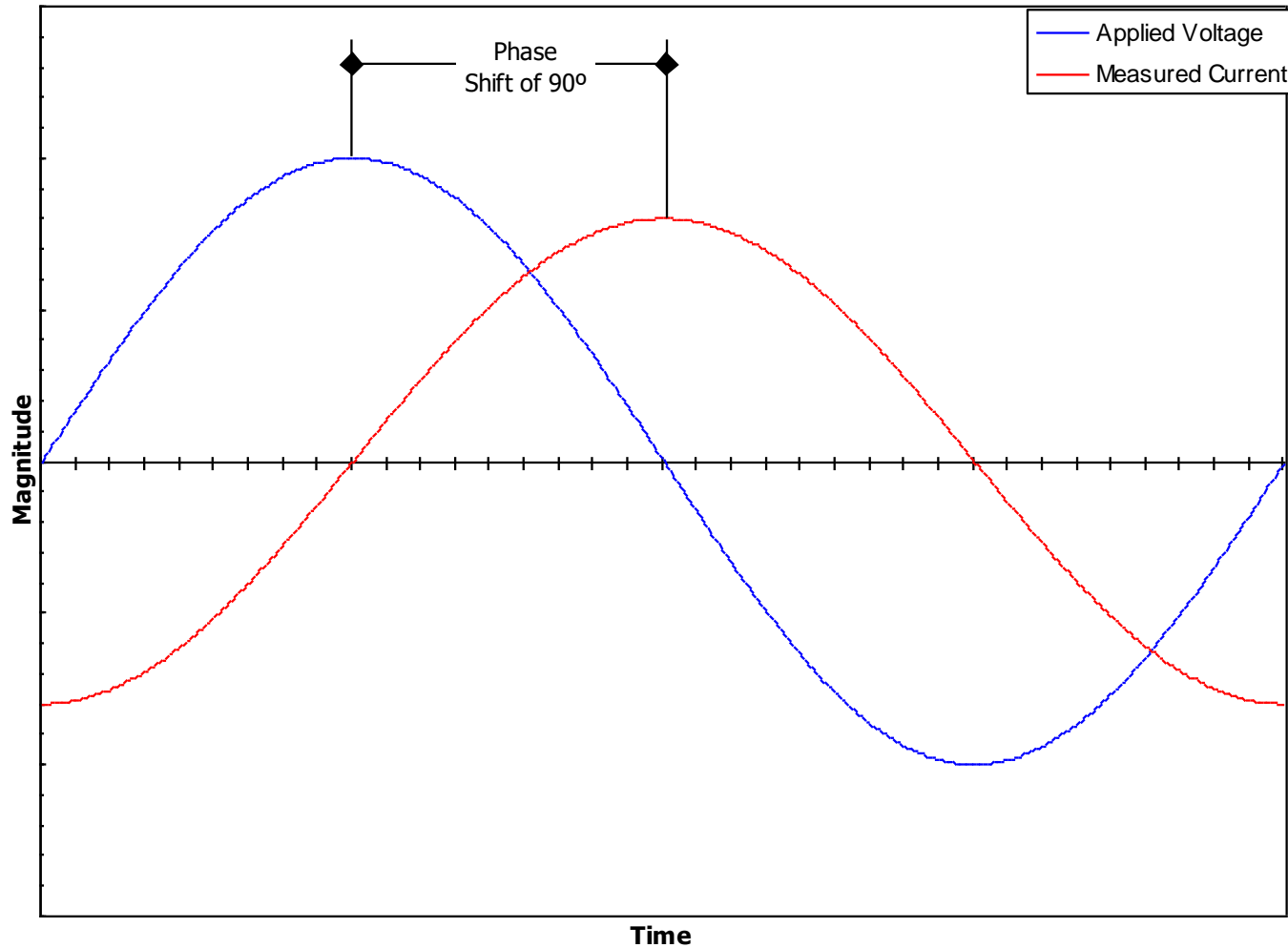
90° Phase Shift

- $j = \sqrt{-1}$

- $\omega = 2\pi f$ radians/s, f = frequency (Hz or cycles/s)

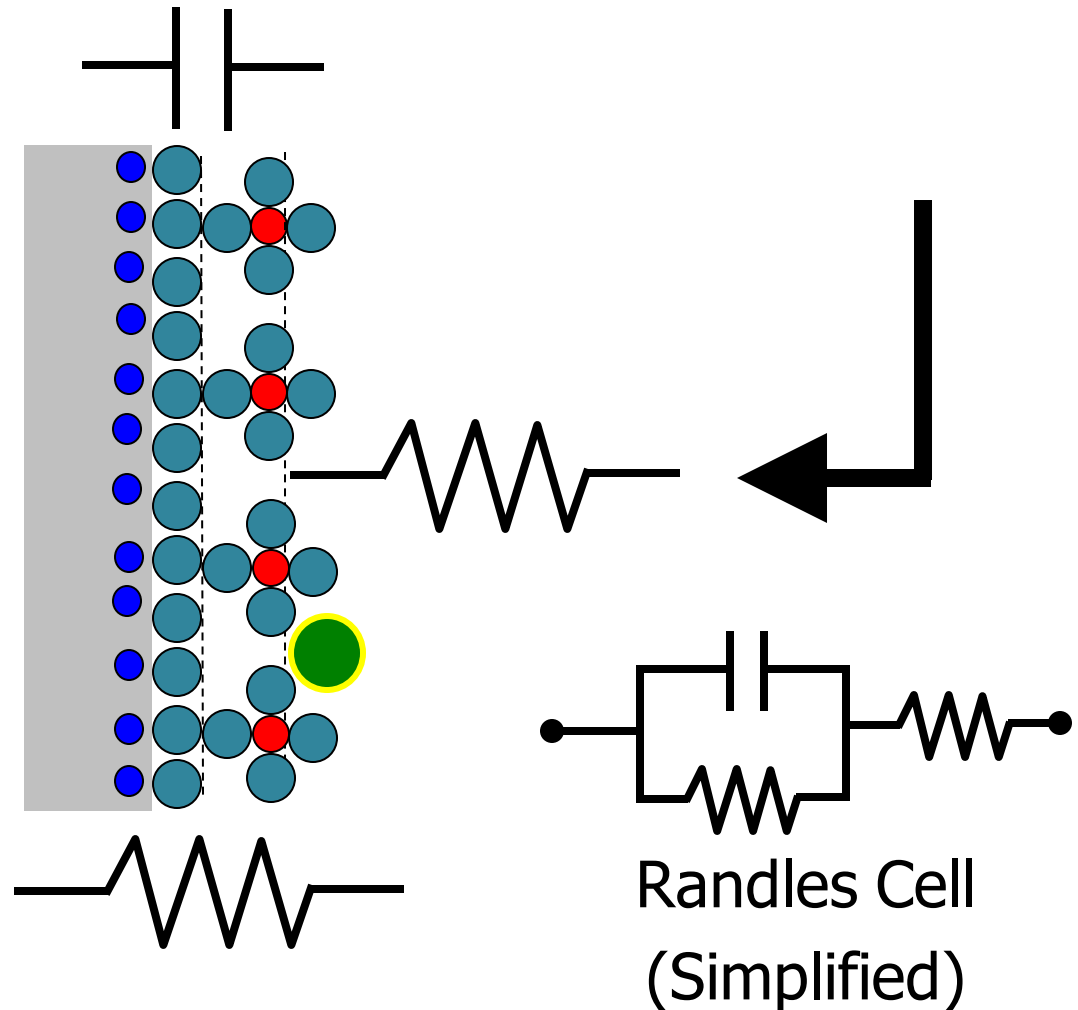- A real response is in-phase (0°) with the excitation. An imaginary response is ±90° out-of-phase.

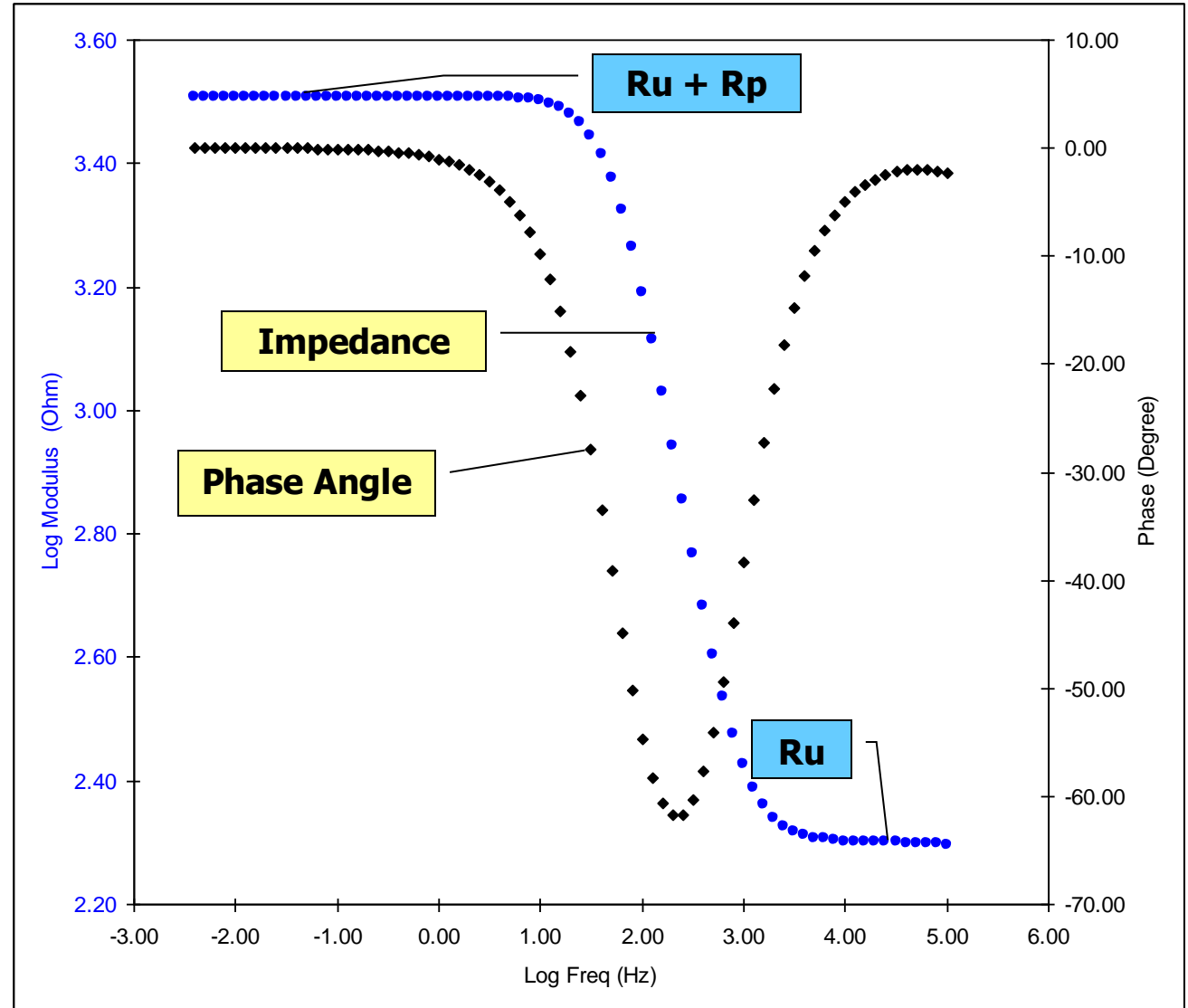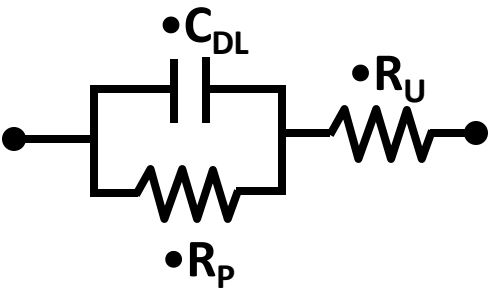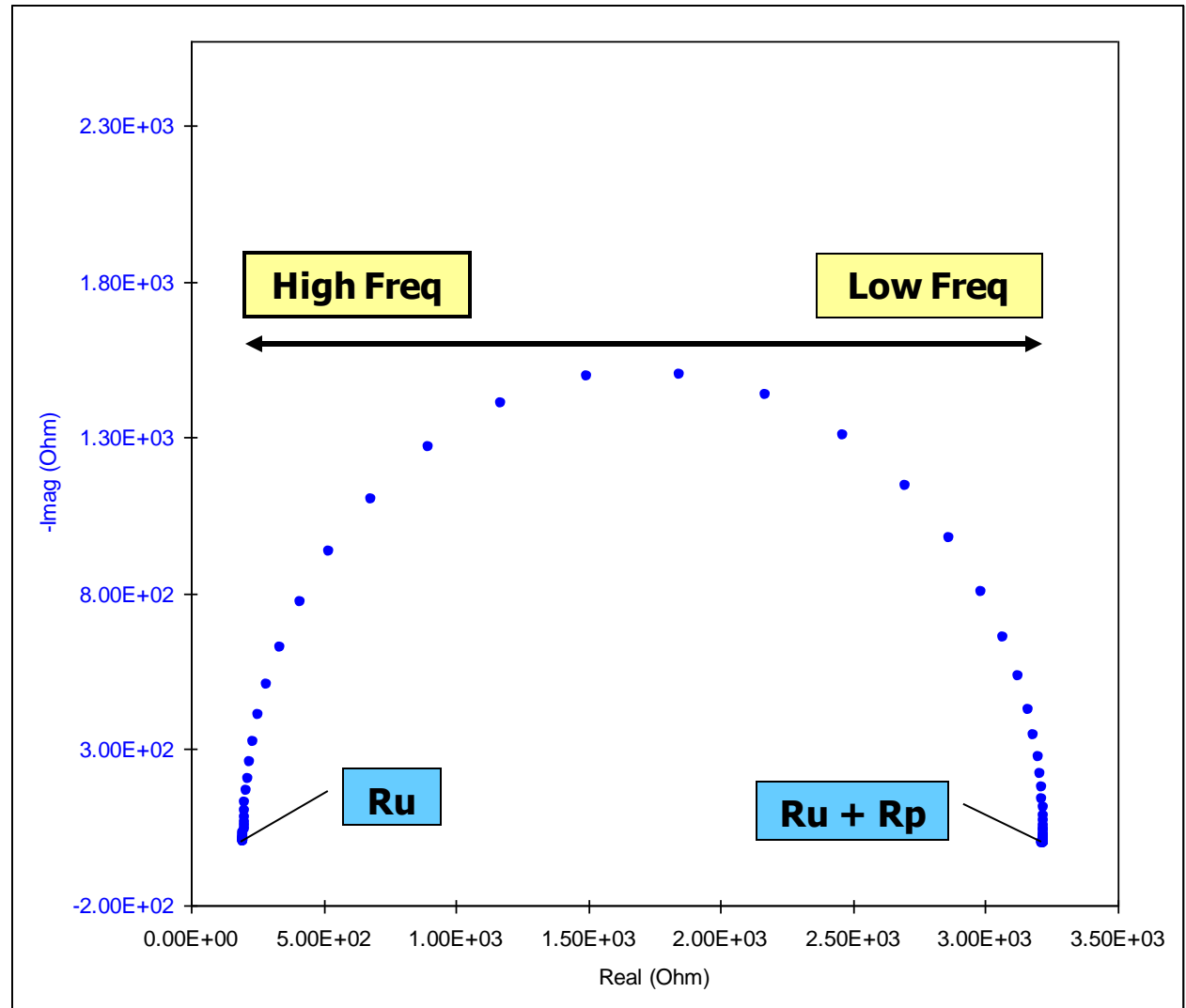# EIS of a Resistor
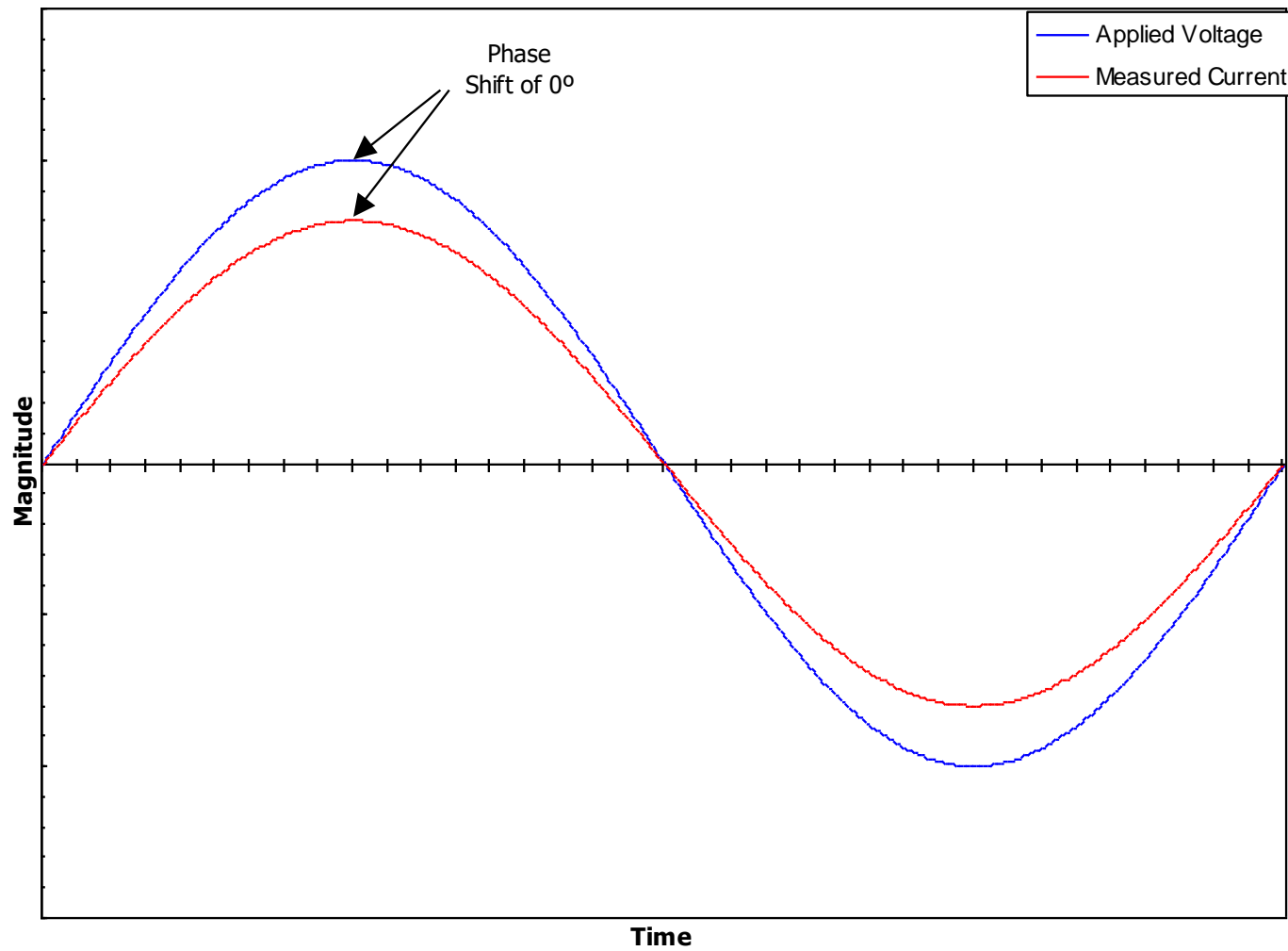
EIS of a Capacitor

Electrochemistry as a Circuit

- Double Layer Capacitance

- Electron Transfer Resistance

- Uncompensated (electrolyte) Resistance

Randles Cell
(Simplified)

Bode Plot

Complex Plane (Nyquist) Plot
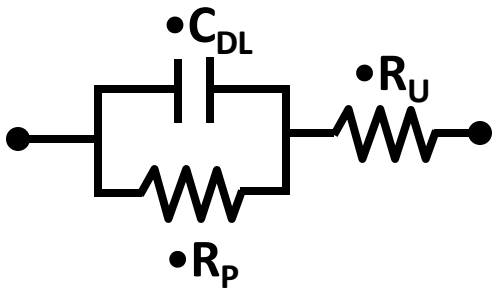
Complex Plane Plot with Fit
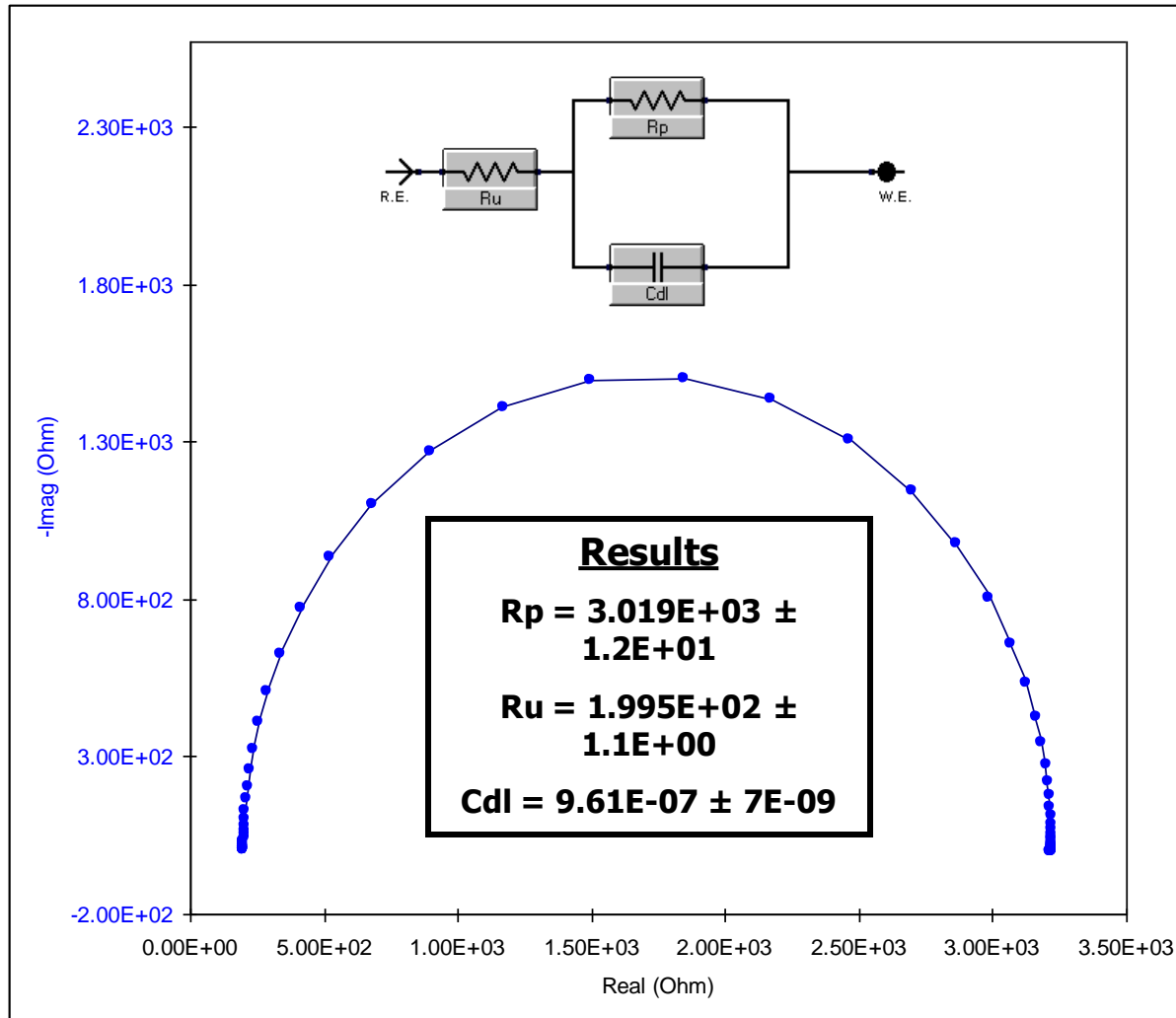
Other Modeling Elements

- Warburg Impedance: General impedance which represents a resistance to mass transfer, i.e., diffusion control. A Warburg typically exhibits a 45° phase shift.

    - Open, Bound, Porous Bound

- Constant Phase Element: A very general element used to model "imperfect" capacitors. CPE's normally exhibit a 80-90° phase shift.
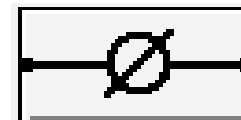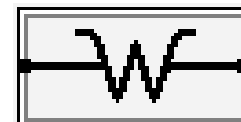
Mass Transfer and Kinetics - Spectra
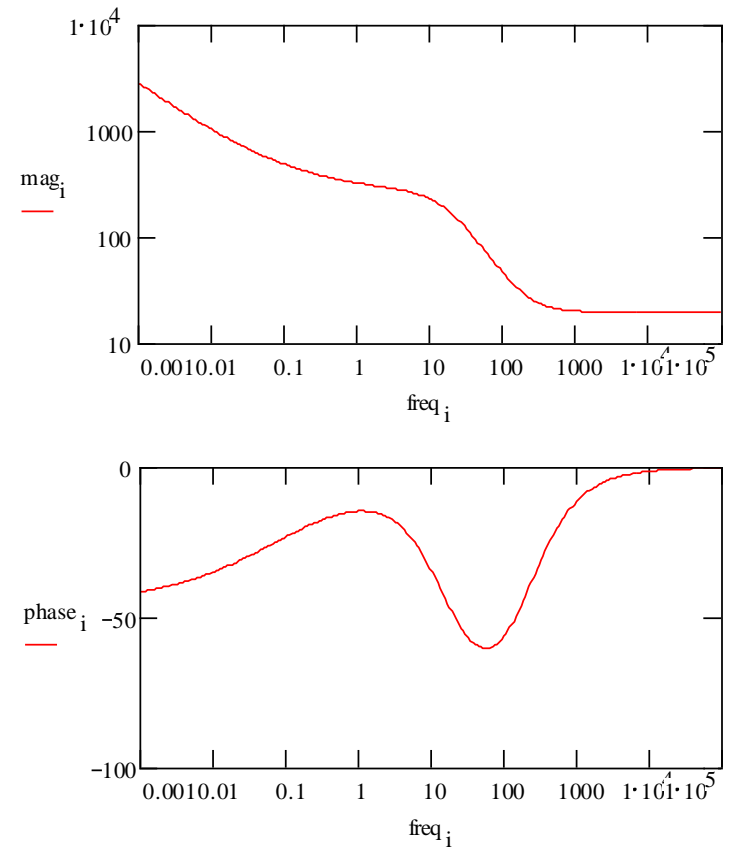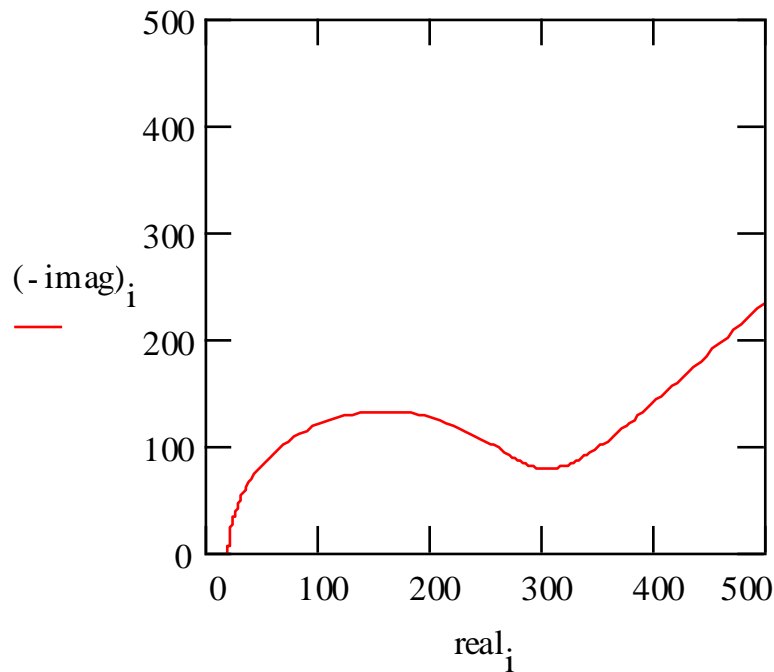
EIS Modeling

- Complex systems may require complex models.

- Each element in the equivalent circuit should correspond to some specific activity in the electrochemical cell.

- It is not acceptable to simply add elements until a good fit is obtained.

- Use the simplest model that fits the data.

Criteria For Valid EIS

Linear – Stable - Causal

- **Linear:** The system obeys Ohm's Law, $E = iZ$. The value of Z is independent of the magnitude of the perturbation. If linear, no harmonics are generated during the experiment.

- **Stable:** The system does not change with time and returns to its original state after the perturbation is removed.

- **Causal:** The response of the system is due only to the applied perturbation.

Electrochemistry: A Linear System?

Circuit theory is simplified when the system is "linear". Z in a linear system is independent of excitation amplitude. The response of a linear system is always at the excitation frequency (no harmonics are generated).
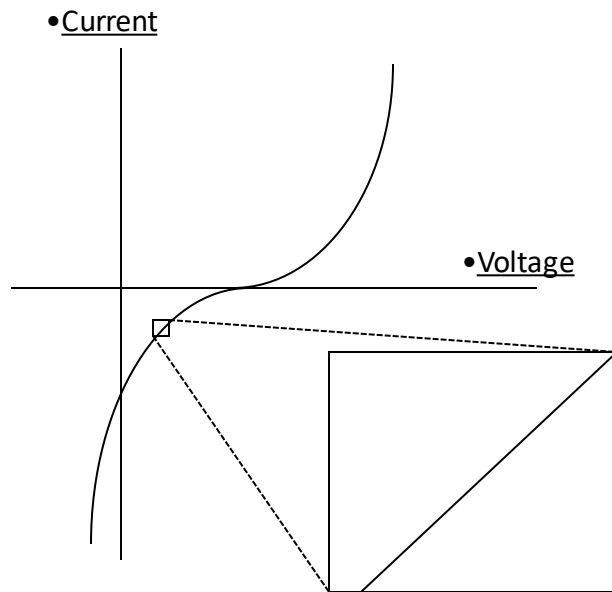
• Current

• Voltage

Look at a small enough region of a current versus voltage curve and it becomes linear.

If the excitation is too big, harmonics are generated and EIS modeling does not work.

The non-linear region can be utilized (EFM).

Electrochemistry: A Stable System?

Impedance analysis only works if the system being measured is stable (for the duration of the experiment).

• Current

• Voltage
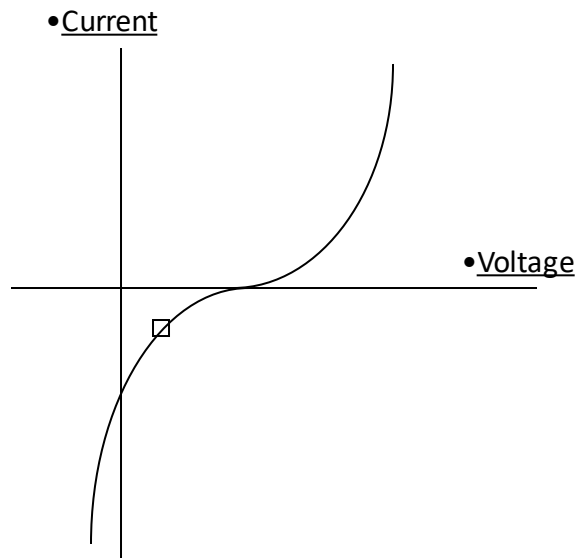
An EIS experiment may take up to several hours to run.

Electrochemical (Corroding) systems may exhibit drift.

Open circuit potential should be checked at the beginning and end of the experiment.

Kramers-Kronig may help.

Kramers-Kronig Transform

- The K-K Transform states that the phase and magnitude in a real (linear, stable, and causal) system are related.

- Apply the Transform to the EIS data. Calculate the magnitude from the experimental phase. If the calculated magnitudes match the experimental magnitudes, then you can have some confidence in the data. The converse is also true.

- If the values do not match, then the probability is high that your system is not linear, not stable, or not causal.

- The K-K Transform as a validator of the data is not accepted by all of the electrochemical community.

Bad K-K
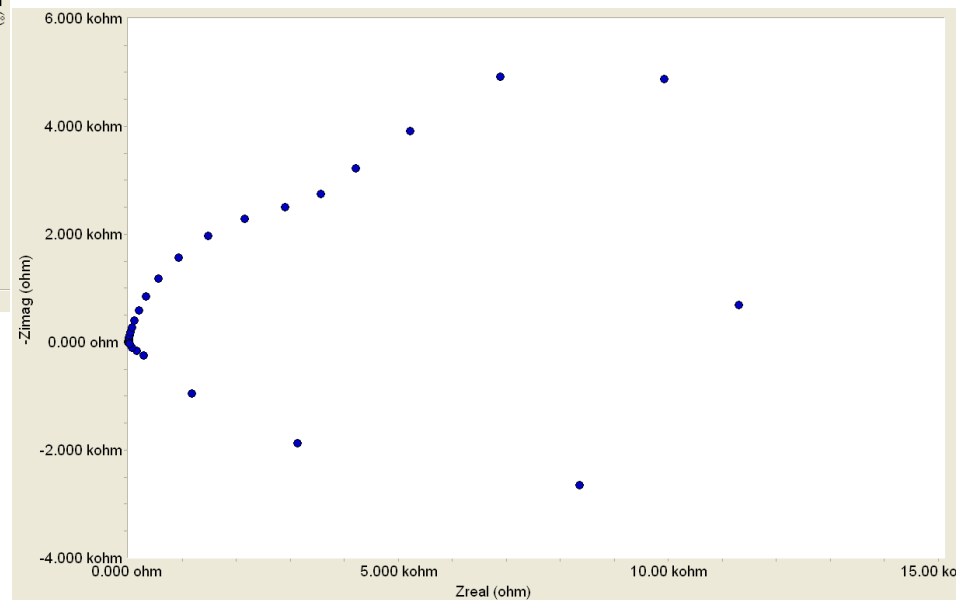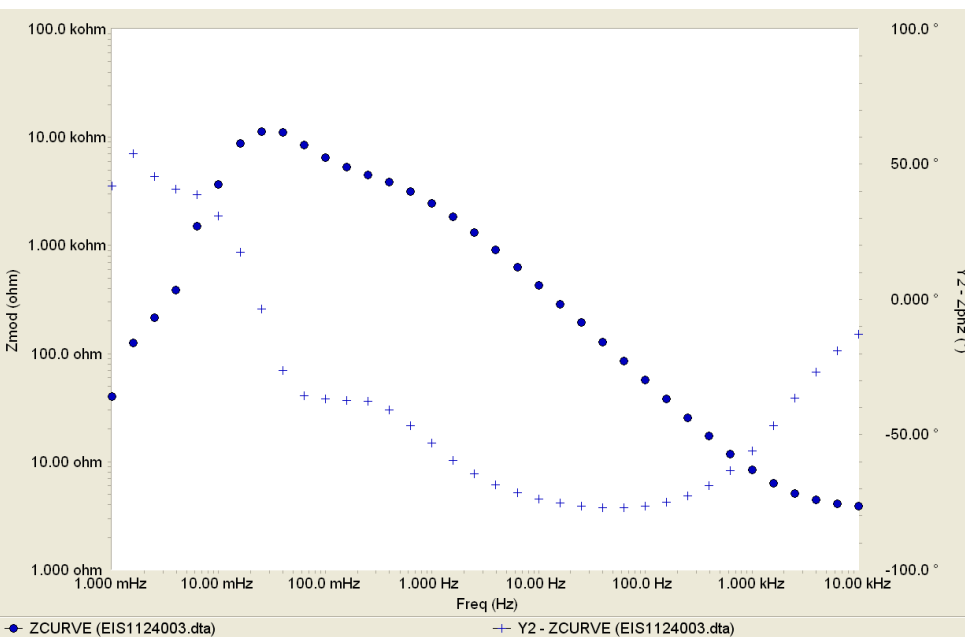
Bad K-K
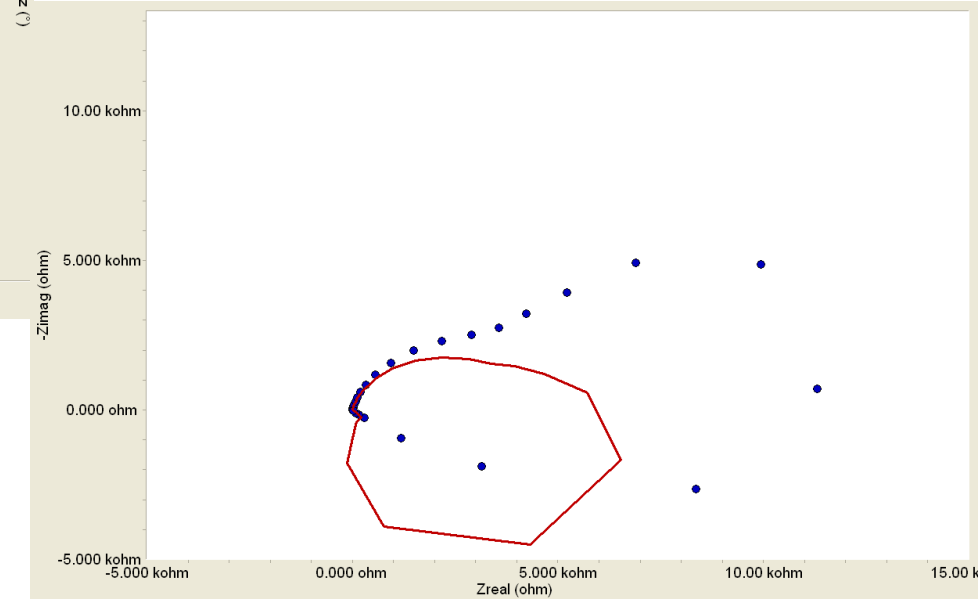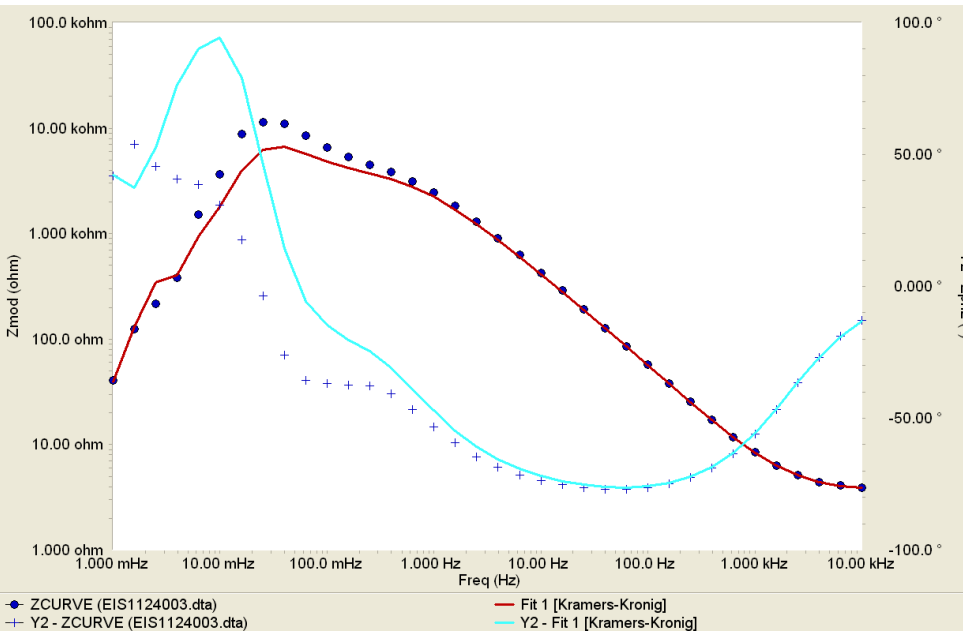
Steps to Doing Analysis

- Look at data
  - Run K-K
  - Determine number of RC loops
  - Figure whether L or W exists
    - If W determine boundary conditions
- Pick/design a model
- Fit it
  - Check to see if CPEs/Transmission Lines needed
- Repeat as necessary
- Extract data

EIS Instrumentation

- Sine wave generator
- Time synchronization (phase locking)
- Potentiostat/Galvanostat
- All-in-ones

Things to be aware of...

- Software
- Accuracy
- Performance limitations

The Virtual Grad Student

Optimizing the Single Sine (~1993)

Measure Z(f, Vdc, Vac)

Use last good measurment to estimate: Z(f), Iac, Idc Inoise Vnoise Gain(f)

Too many tries?

Pick IERange(f, peak levels)

Pick Ich Gain/Offset VchGain/Offset

Measure Z, Idc,Iac,Vdc,Vac

Adjust $Gain_{est}$

Adjust Z_{est}

Adjust Z_{est}, Idc_{est}

Adjust Etc.

Vac too big/small

Iac too big/small

Idc too big

Etc.

Report Unable to Measure

Done
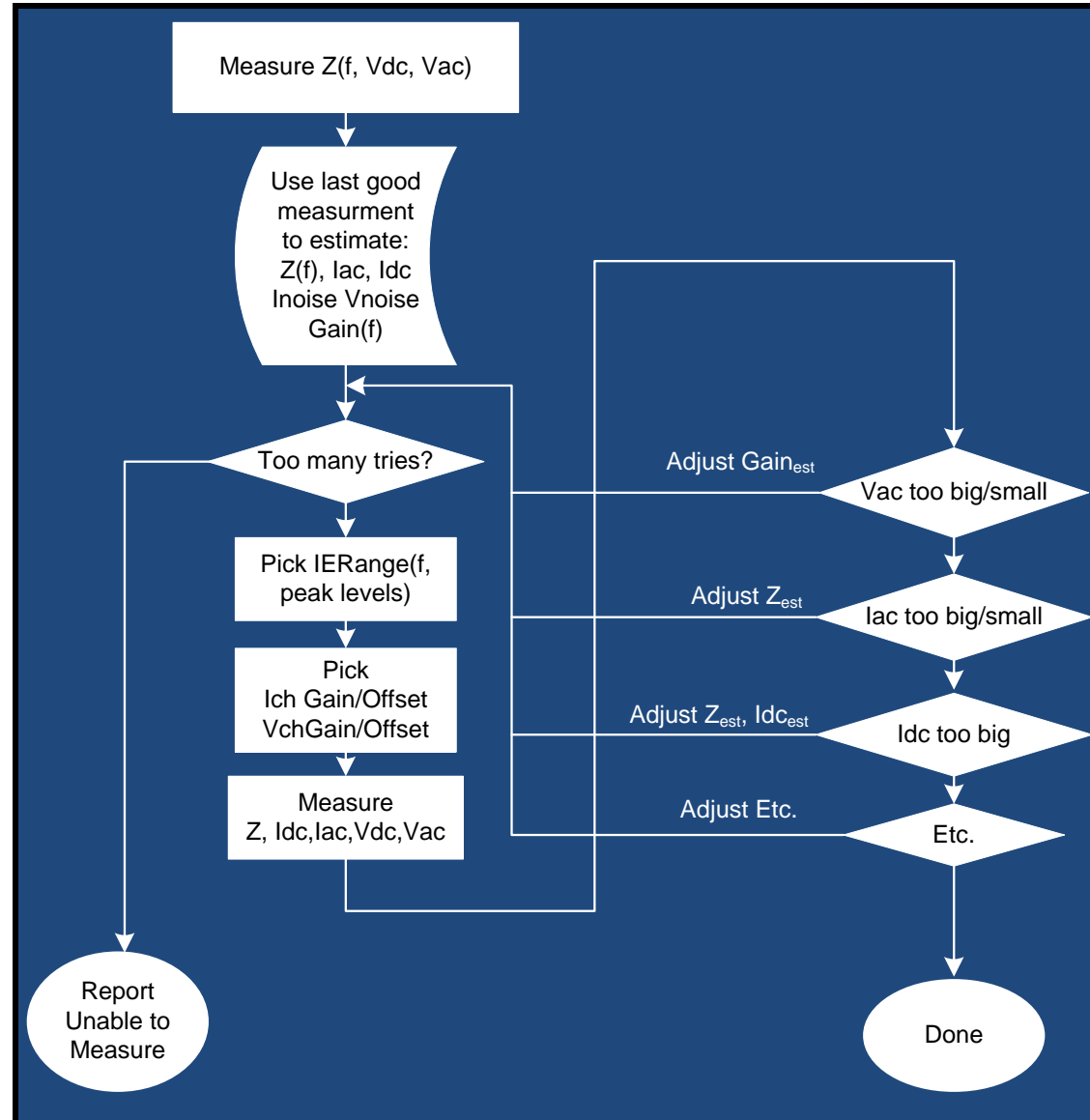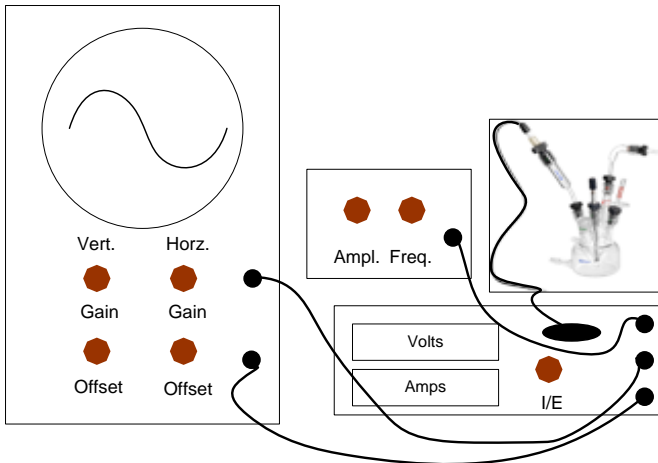
Accuracy and System Limits

- Check Your Potentiostat…
  - To Understand a System and Its Limits
  - Comparison 2+ Different Systems
  - Manufacturer Specifications:
    - Are Not Standardized
    - Do Not Tell the Whole Story
  - For EIS: Setup Matters

EIS: Accuracy Contour Plot vs. Quick Check

- A complete ACP shows total, normal system performance (see right)
   - Generally collected using normal operating parameters (e.g. 10 mV potentiostatic EIS)
    - May also be optimized for each point/region
    - Takes a long time to measure and determine
    - (Open and Shorted Lead EIS spectra are *Not* the ACP)
- EIS Quick Check:
    - Simple test that will work across platforms
    - Gives a rough check of system performance
    - Establishes proper setup for making accurate measurements
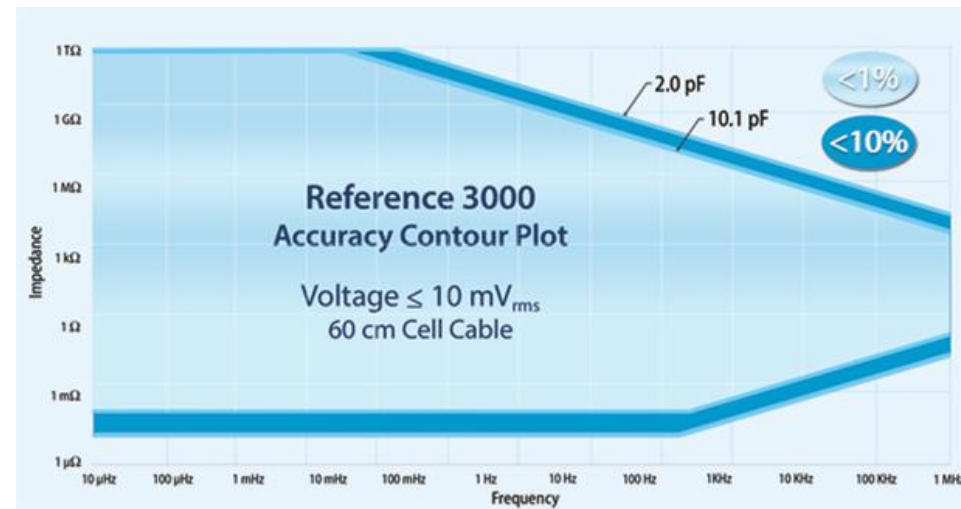
How to Run an EIS Quick Check

- **Run EIS on Some Precision Resistors**
  - Potentiostatic, 10 mV AC
  - $100\,\Omega$ 1 kΩ and 10 kΩ
  - Shows Real System Response

- **Run Shorted Lead EIS**
  - Galvanostatic, 100-400 mA AC
  - Shows Low Impedance Ability
  - Measure of Cable Inductance

- **[Optional] Run an Open Lead EIS**
  - Potentiostatic, 50 mV AC
  - Measure of Cable Capacitance, System Limit
 - Not Necessarily Useful for Accuracy

Cable Setup Matters

- For some impedance measures Cable positioning makes a big difference.

- 1 kΩ: Any should work

- 100 Ω and Shorted: minimize inductance by twisting cables (current pair together from one side, sense pair together from the other)

- 10 kΩ and Open: minimize capacitance by separating work leads from counter/ref leads as much as possible

    – (for Open connect work to work sense and counter to reference, place working pair inside Faraday cage)
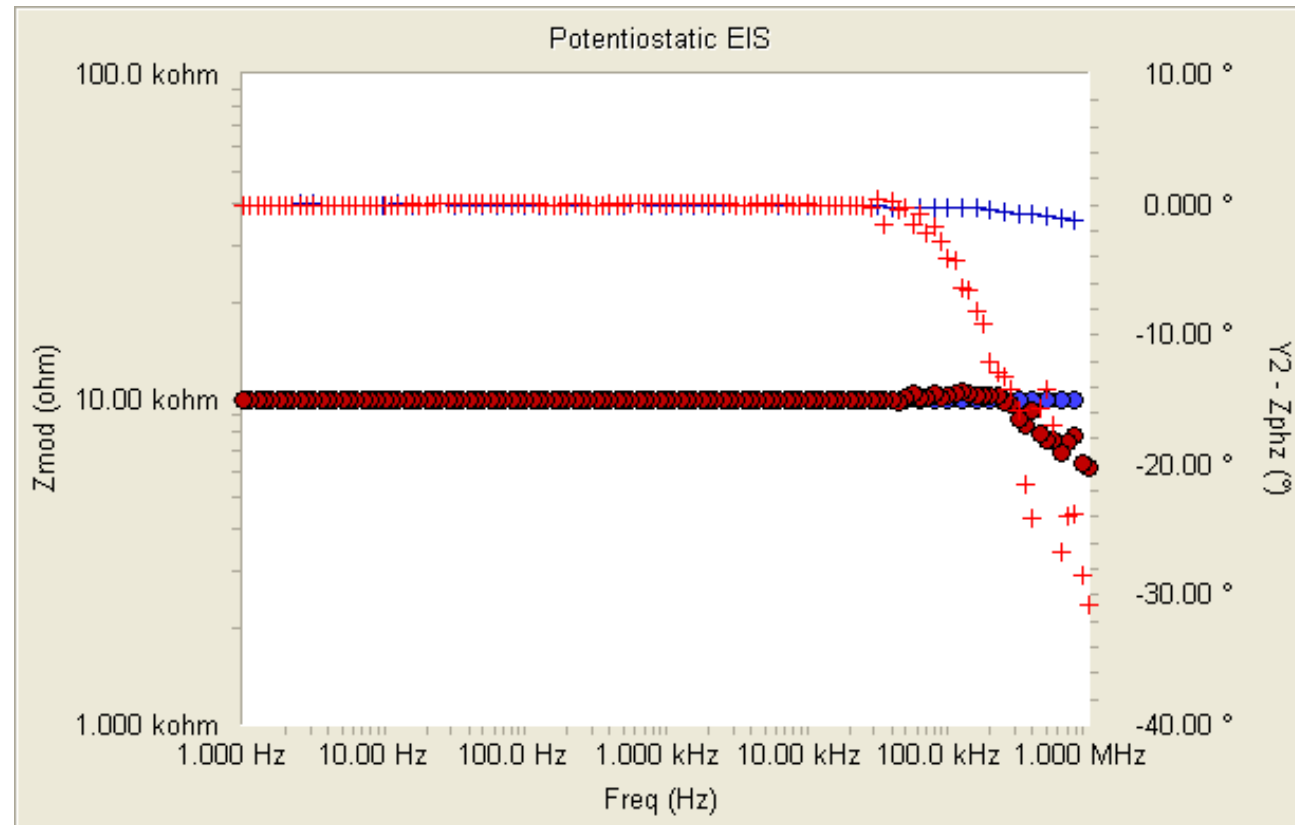
Good Resistor Response

- 100 Ω: Green
- 1 kΩ: Blue
- 10 kΩ: Red

- Magnitude w/in 1%
- Phase w/in 2°
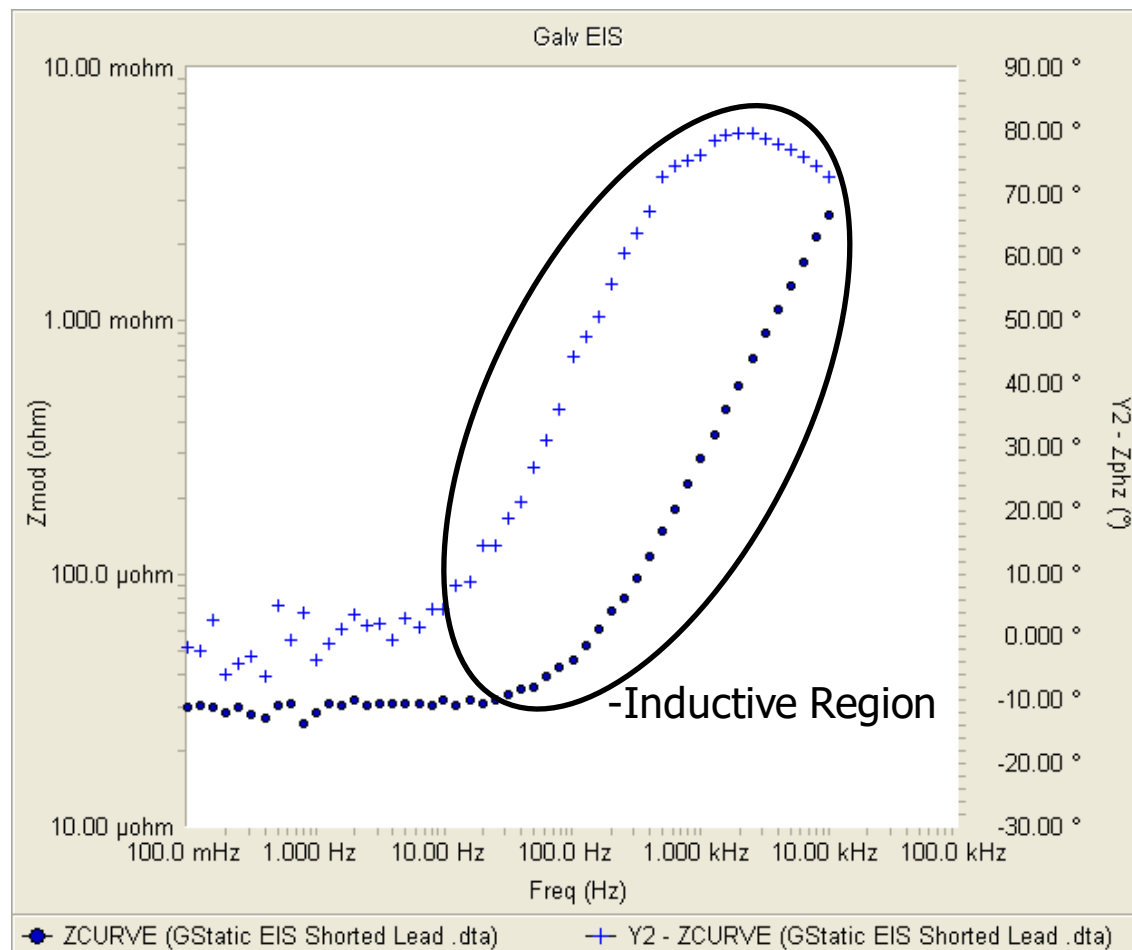 – Down capacitive
  – Up Inductive
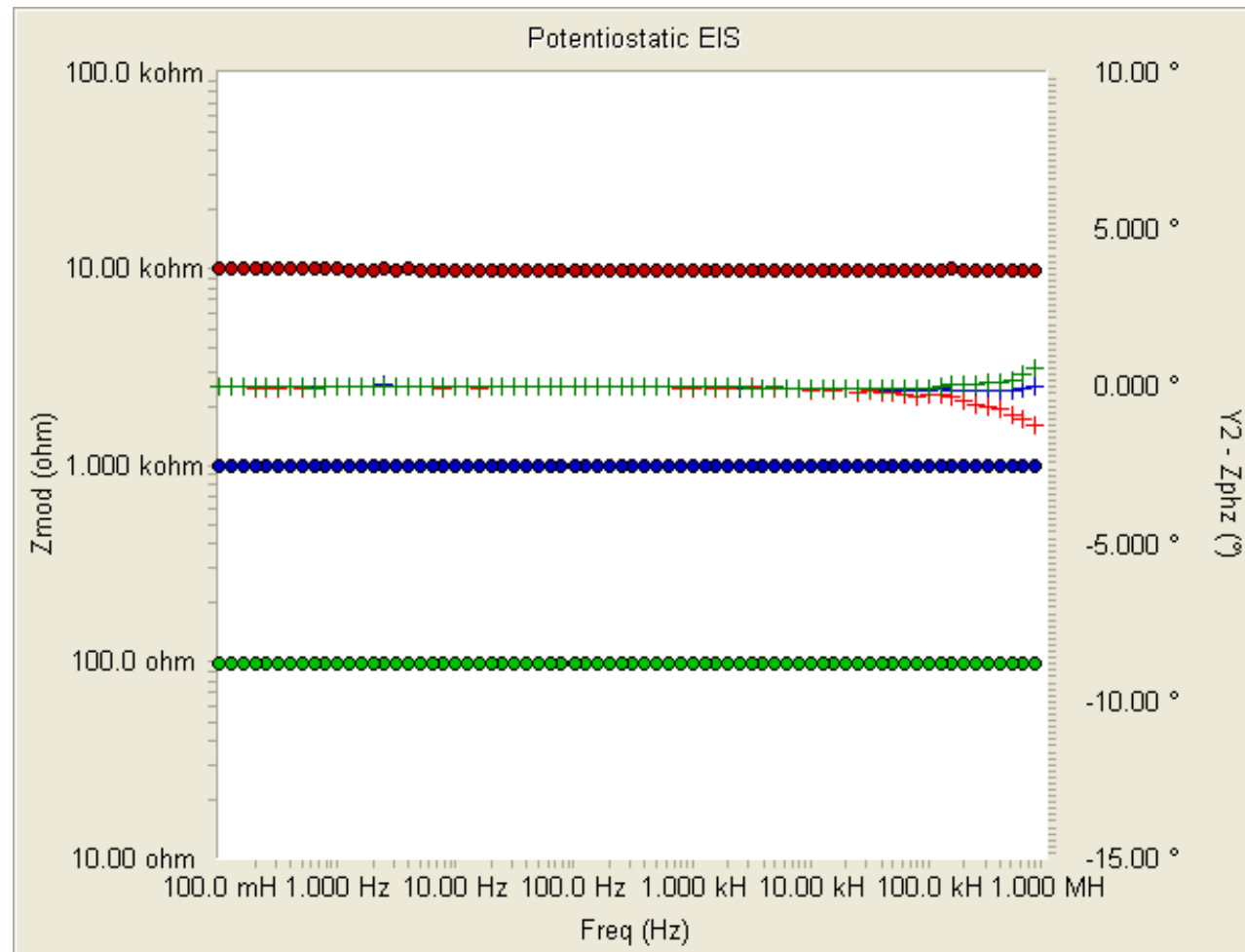
Bad Resistor Response

- Gamry: Blue

- *Other*: Red

- *Other* 1 MHz System
  - 40% Error in Z
  - 30° Phase Error
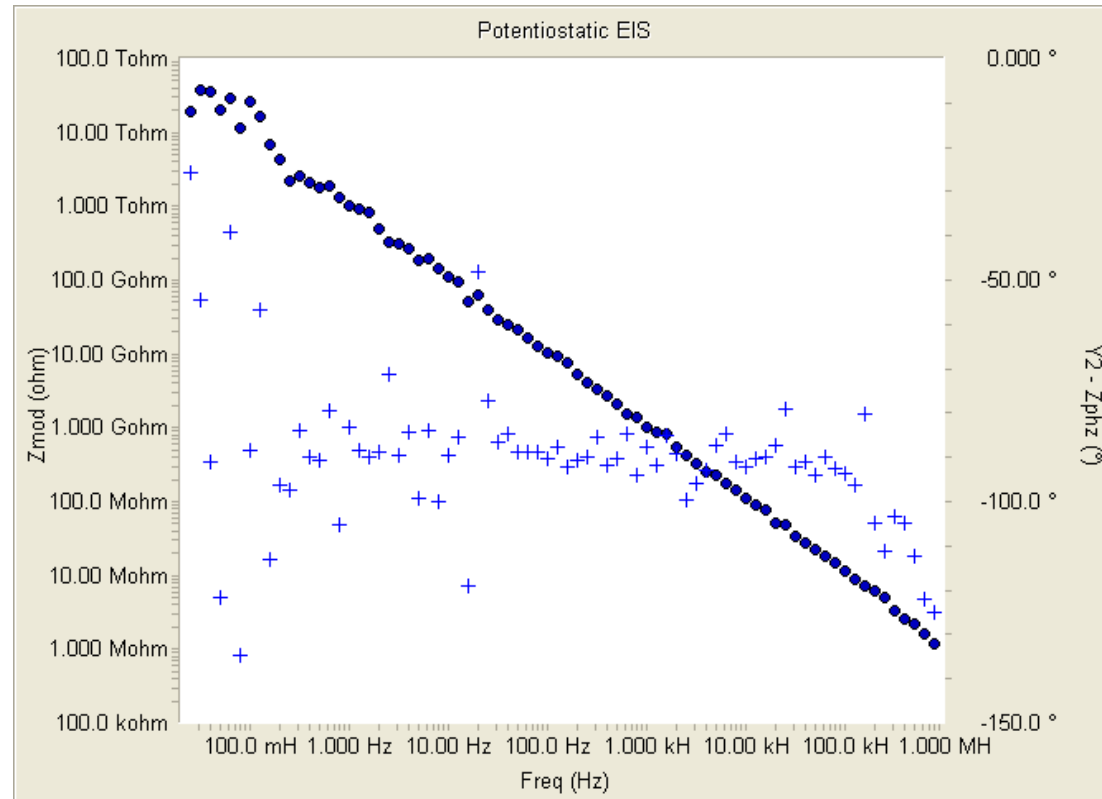 - System only accurate to ~50 kHz

Shorted Lead Curve

- Very small resistor
- Inductance will be present at higher f

- Note:
  - Calculated resistance of copper braid is 10 mW per mm, with 2-3 mm between leads (or about the measured 30 mW)

Open Lead Curve

- ## Should look like a capacitor
  - 90° phase
  - Capacitance based on cabling
  - Low f rolloff may be present on less sensitive systems

Quick Check Take Home

- Instruments have limits

- Setup matters

- Know where your system lies
  - High Impedance (Coatings)
  - Low Impedance (Energy Devices)
  - Other…(Corrosion, Sensors)

EIS Take Home

- EIS is a versatile technique
  - Non-destructive
  - High information content
- Running EIS is easy
- EIS modeling analysis is very powerful
  - Simplest working model is best
  - Complex system analysis is possible
  - User expertise can be helpful

References for EIS

- *Electrochemical Impedance Spectroscopy*, M. Orazem, B Tribollet. ISBN: 978-1118527399

- Electrochemical Impedance and Noise, R. Cottis and S. Turgoose, NACE International, 1999. ISBN 1-57590-093-9.

- Electrochemical Impedance: Analysis and Interpretation, STP 1188, Edited by Scully, Silverman, and Kendig, ASTM, ISBN 0-8031-1861-9.

- *Basics of EIS*, *Intro to EIS (part 2)*, and other applications notes, Gamry Instruments website, www.gamry.com