Introduction to Electrochemical Impedance Spectroscopy

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_ω = Frequency-dependent potential
    - I_ω = Frequency-dependent current
- Ohm's Law: R = E/I
    - R = impedance at the limit of zero frequency

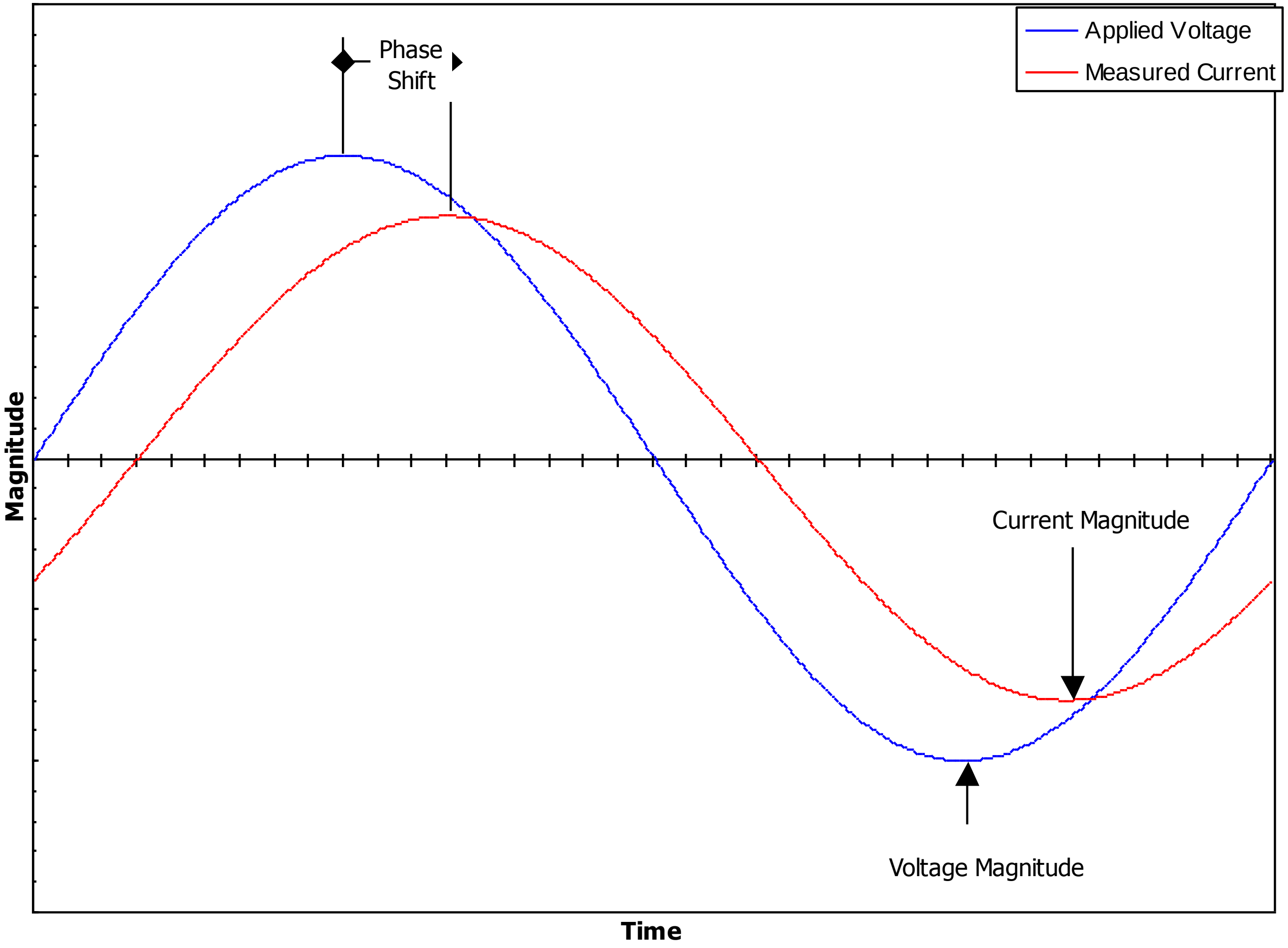
Reasons To Run EIS

- EIS is theoretically complex (and can be expensive) – why bother?
  - The information content of EIS is <u>much</u> higher than DC techniques or single frequency measurements.
  - EIS may be able to distinguish between two or more electrochemical reactions taking place.
  - EIS can identify diffusion-limited reactions, e.g., diffusion through a passive film.
  - EIS provides information on the capacitive behavior of the system.
  - EIS can test components within an assembled device using the device’s own electrodes.

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

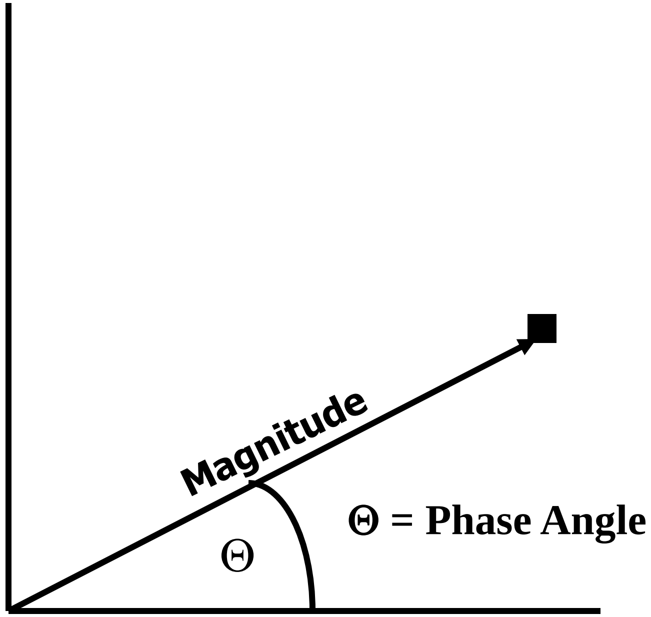
Excitation and Response in EIS

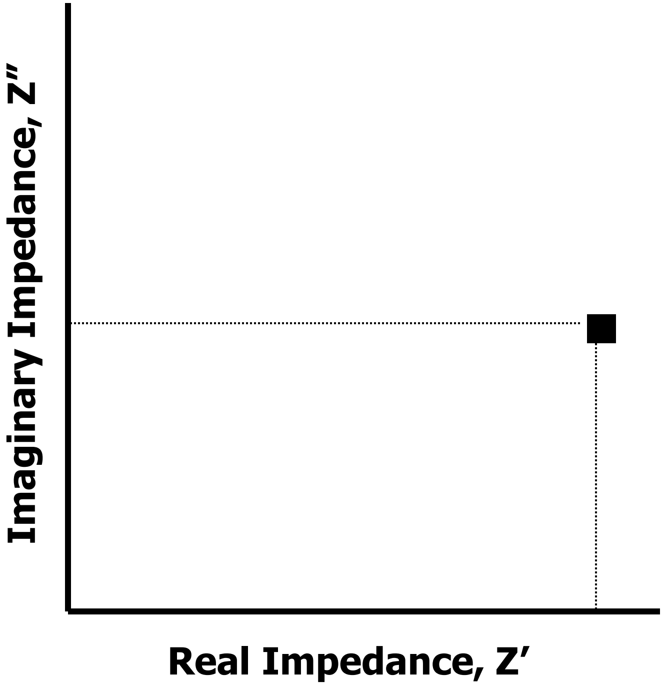


EIS Data Presentation

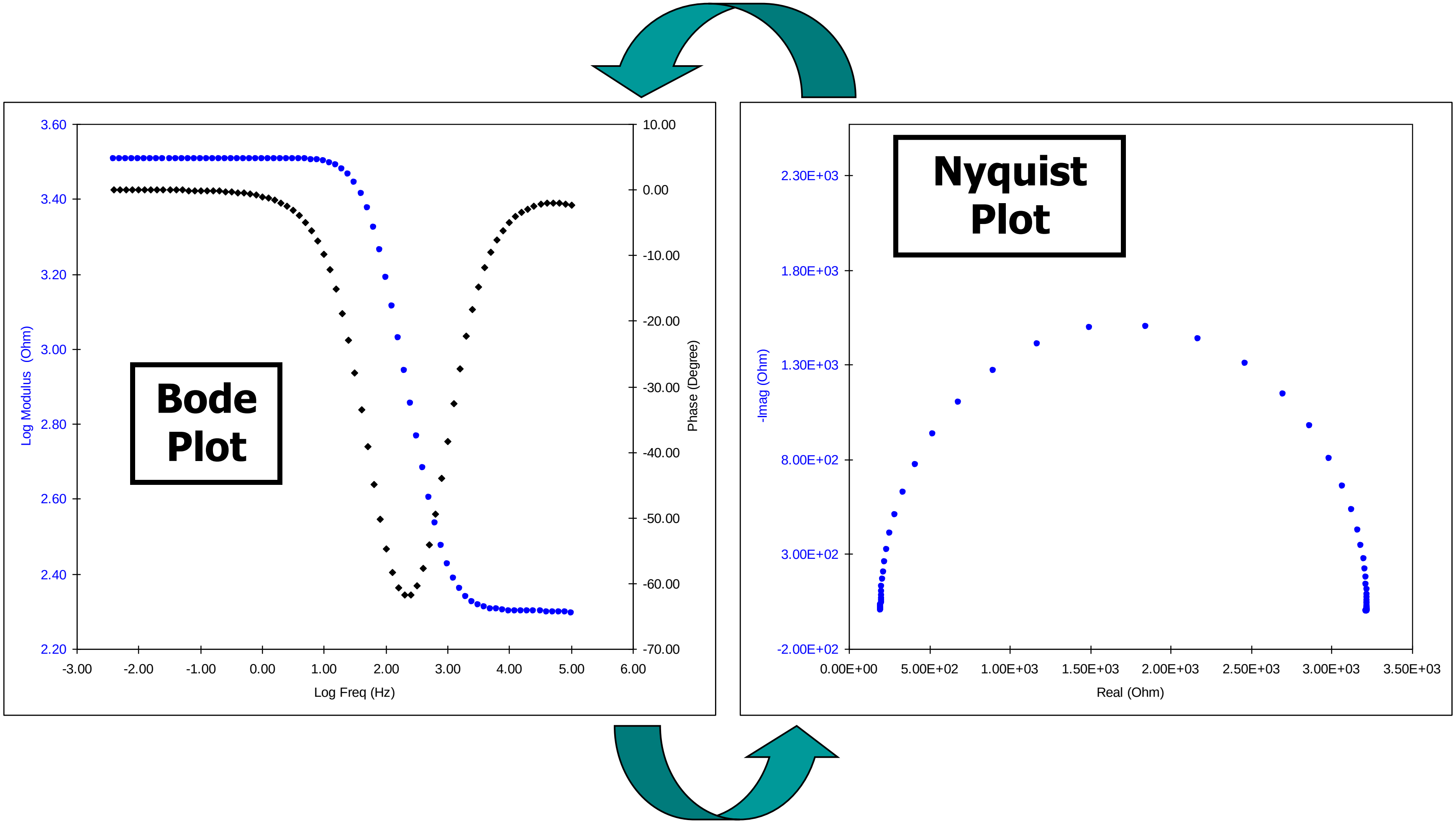
- EIS data may be displayed as either a vector or a complex quantity.
- A vector is defined by the impedance magnitude and the phase angle.
- As a complex quantity, $Z_{total} = Z_{real} + Z_{imag}$
- The vector and the complex quantity are different representations of the impedance and are mathematically equivalent.

Vector and Complex Plane Representations of EIS





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



Nyquist vs. Bode Plot

Bode Plot

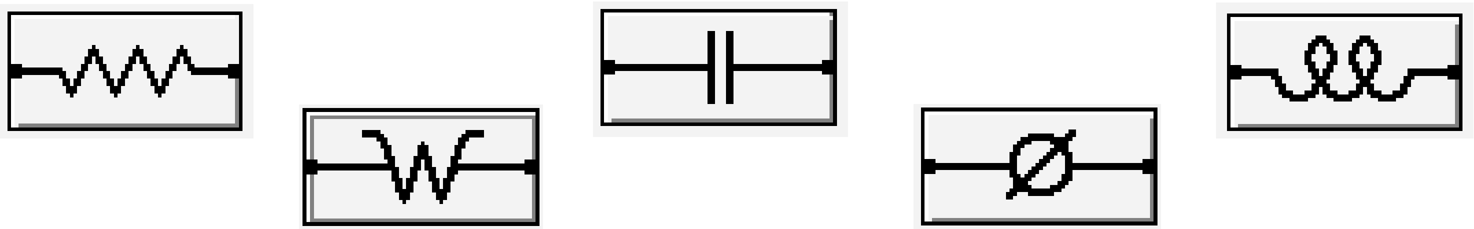
- Individual charge transfer processes are resolvable.
- Frequency is explicit.
- Small impedances in presence of large impedances can be identified easily.

Nyquist Plot

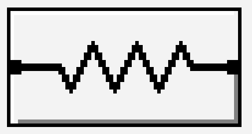
- Individual charge transfer processes are resolvable.
- Frequency is not obvious.
- Small impedances can be swamped by large impedances.

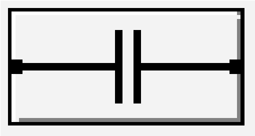
Analyzing EIS: Modeling

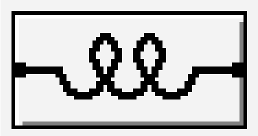
- Electrochemical cells can be modeled as a network of passive electrical circuit elements.
- A network is called an “equivalent circuit”.
- The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.



Frequency Response of Electrical Circuit Elements



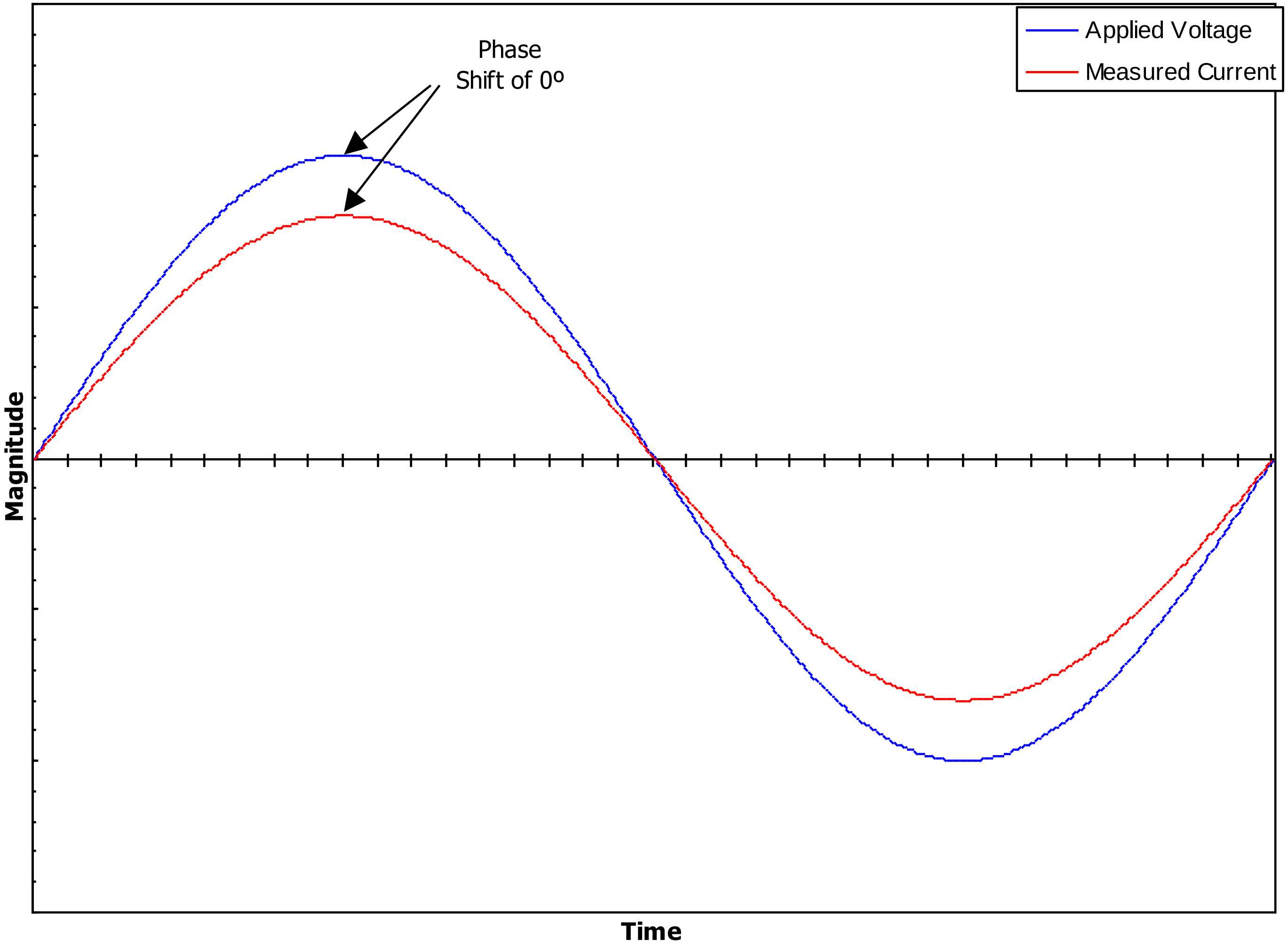




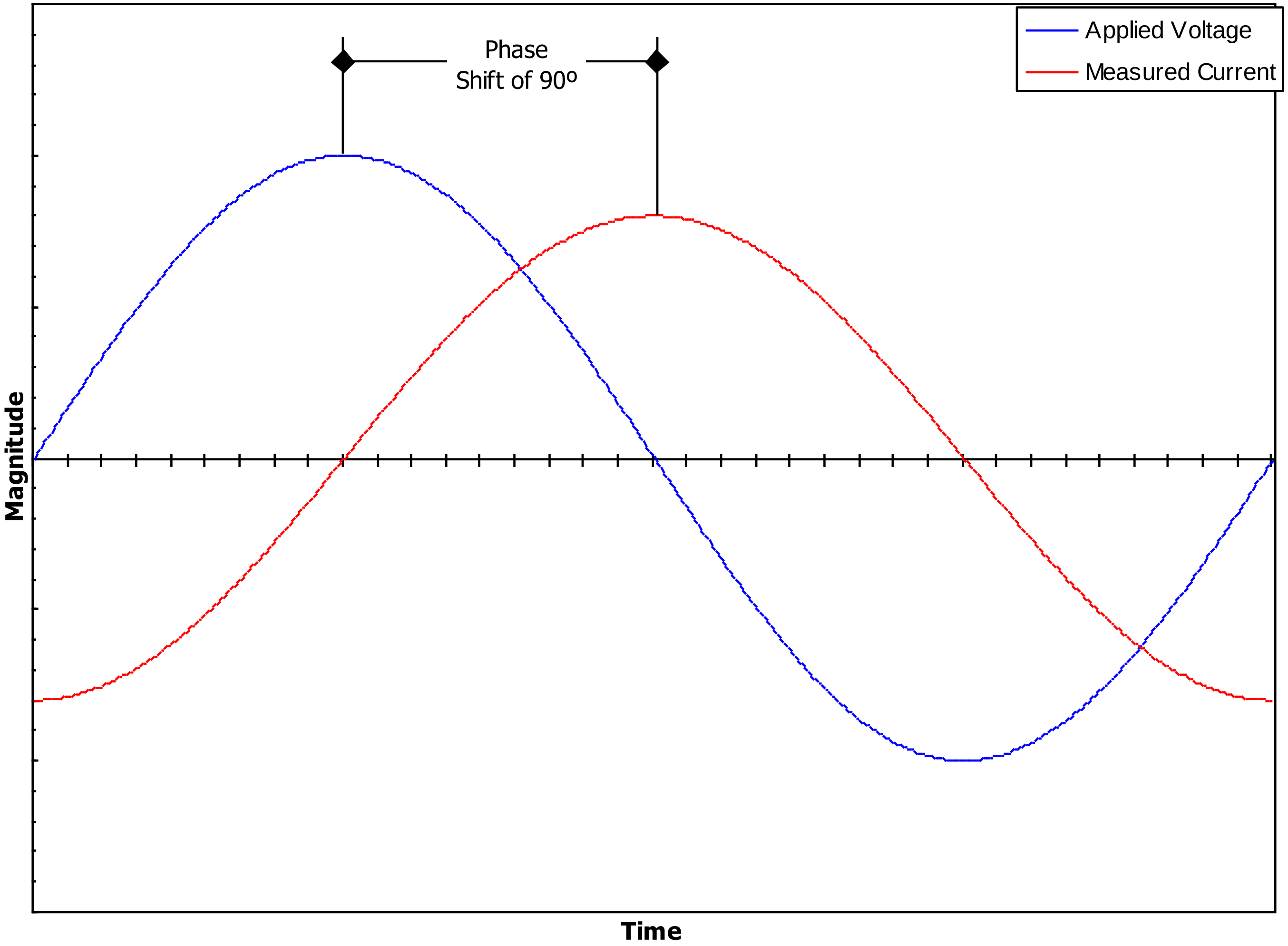
Resistor	Capacitor	Inductor
Z = R (Ohms)	Z = -j/ωC (Farads)	Z = jωL (Henrys)
0° Phase Shift	-90° Phase Shift	90° Phase Shift

- j = √-1
- ω = 2πf 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

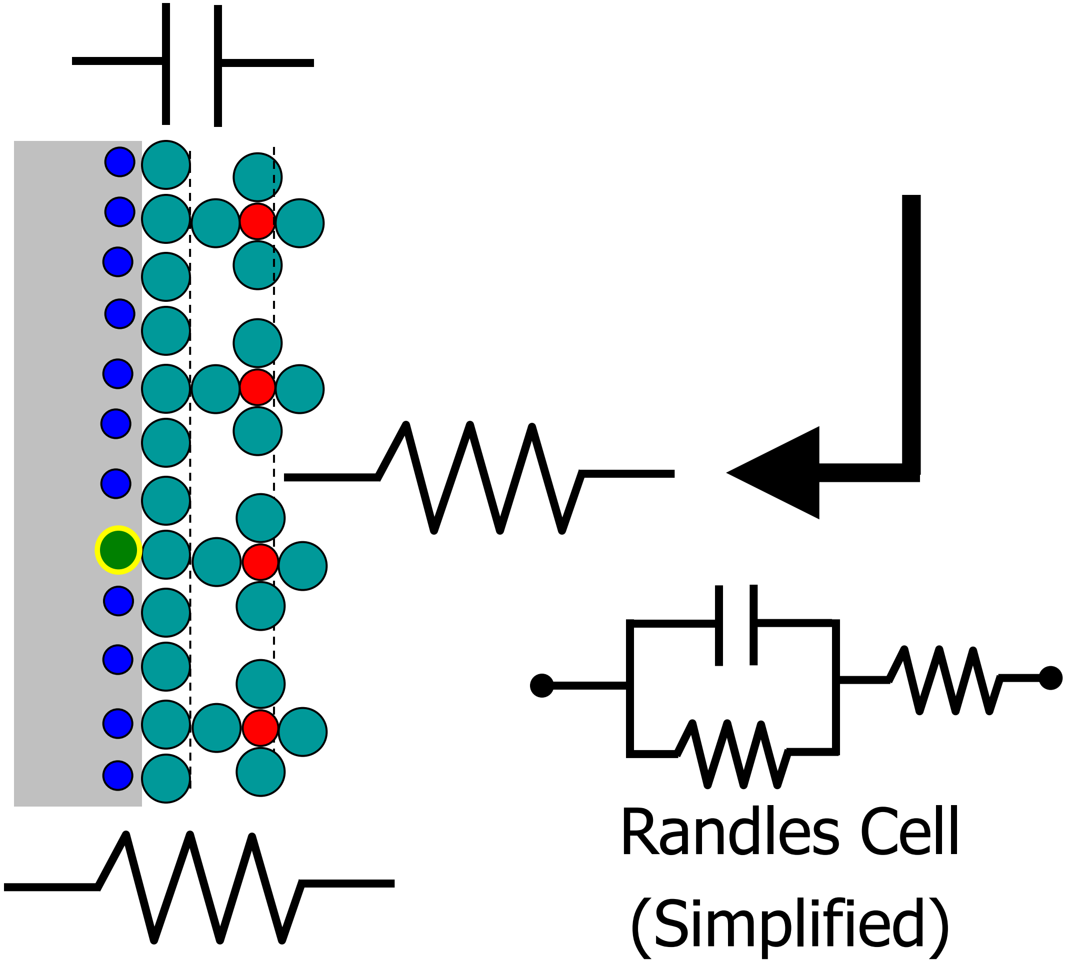


EIS of a Capacitor



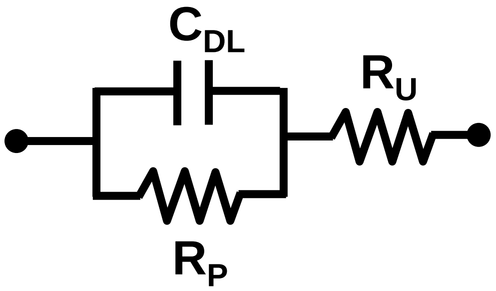
Electrochemistry as a Circuit

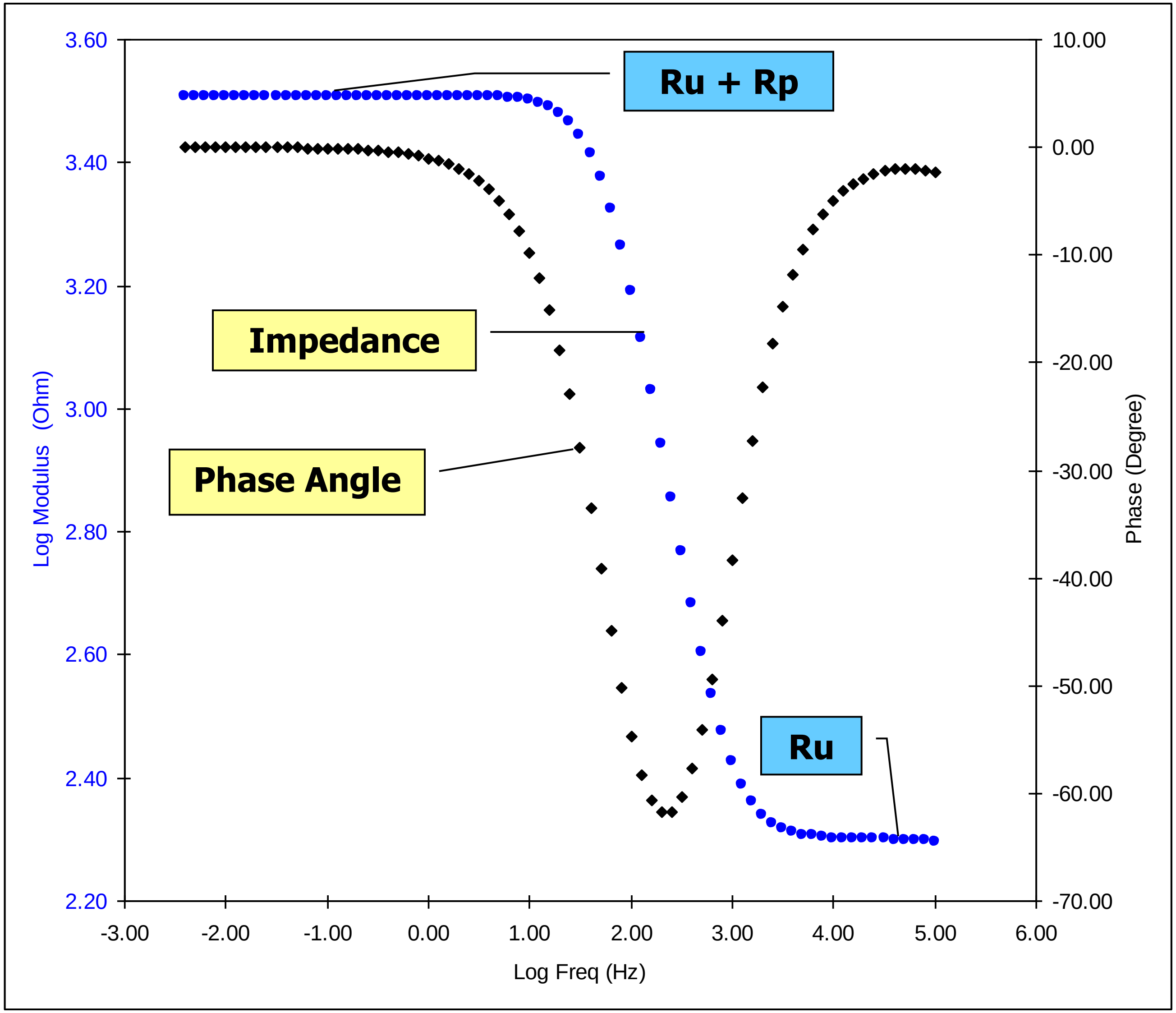
- Double Layer Capacitance
- Electron Transfer Resistance
- Uncompensated (electrolyte) Resistance



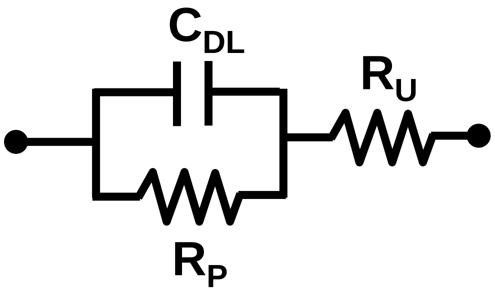
Randles Cell (Simplified)

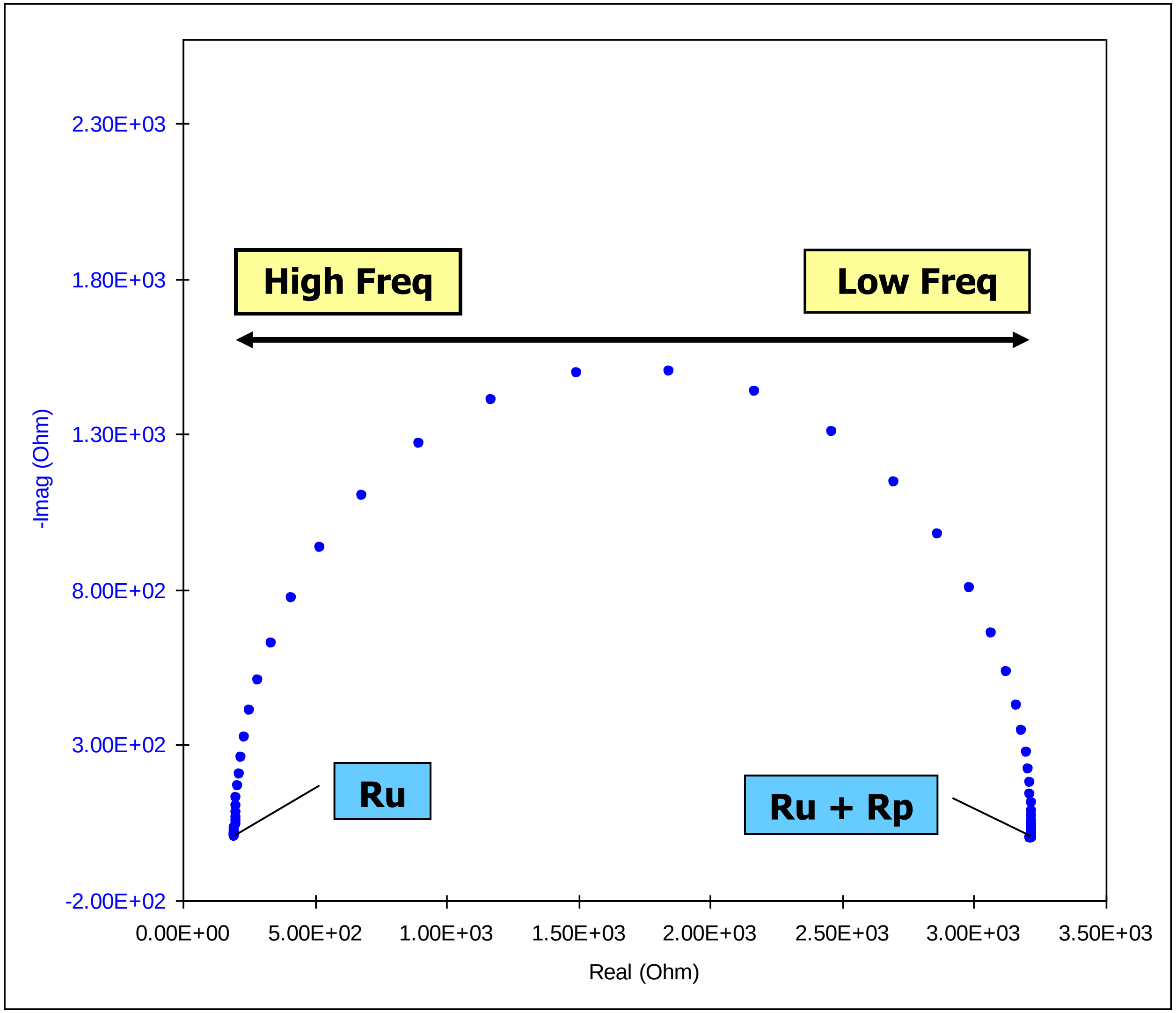
Bode Plot


C_{DL}
R_U
R_P

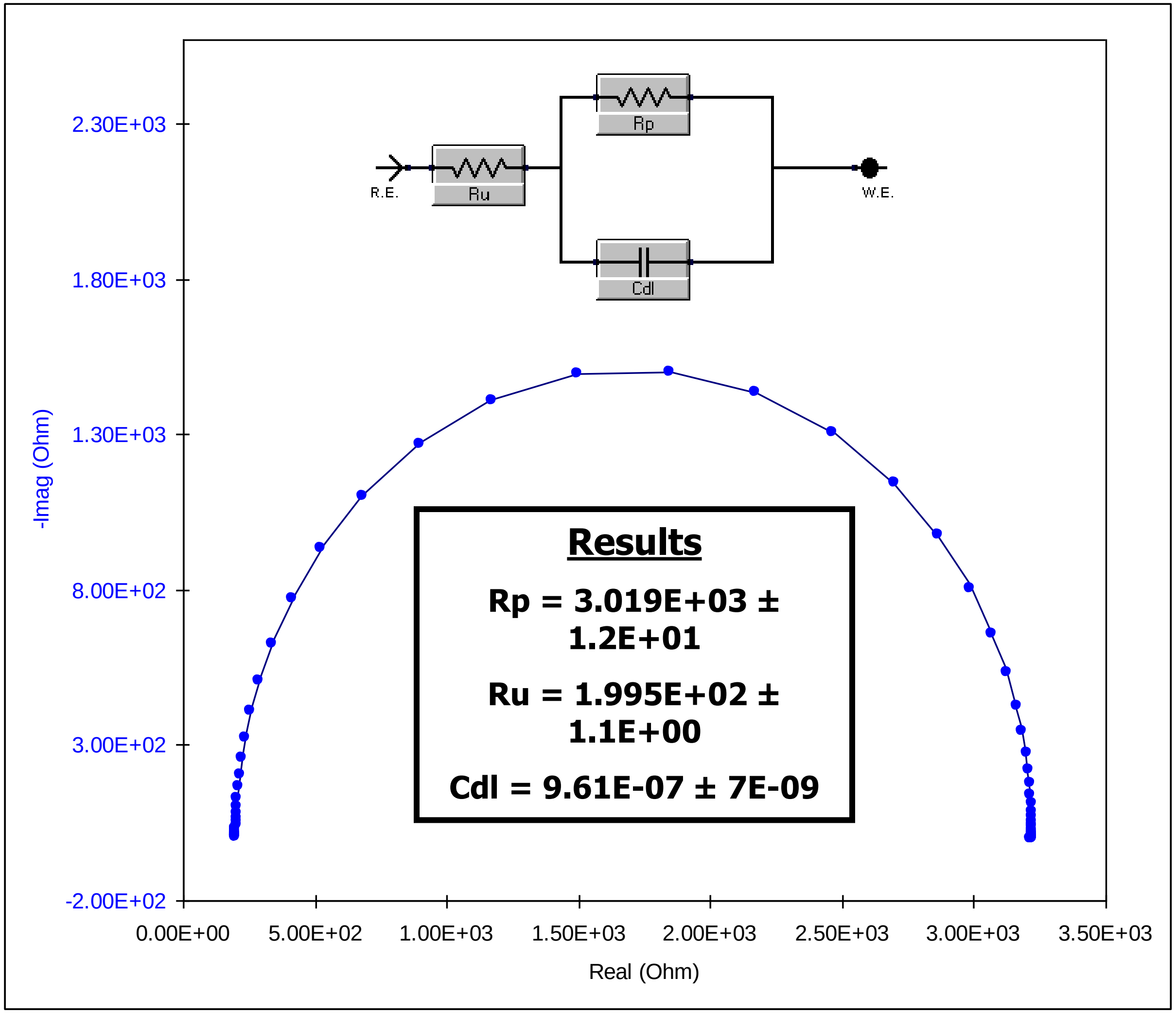

Ru + Rp
Impedance
Phase Angle
Ru
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
Log Modulus (Ohm)
10.00
0.00
-10.00
-20.00
-30.00
-40.00
-50.00
-60.00
-70.00
Phase (Degree)
-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
Log Freq (Hz)

Complex Plane (Nyquist) Plot





Nyquist Plot with Fit



Results

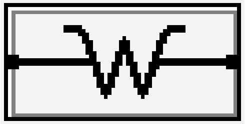
Rp = 3.019E+03 ± 1.2E+01

Ru = 1.995E+02 ± 1.1E+00

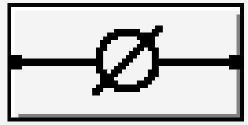
Cdl = 9.61E-07 ± 7E-09

Other Modeling Elements

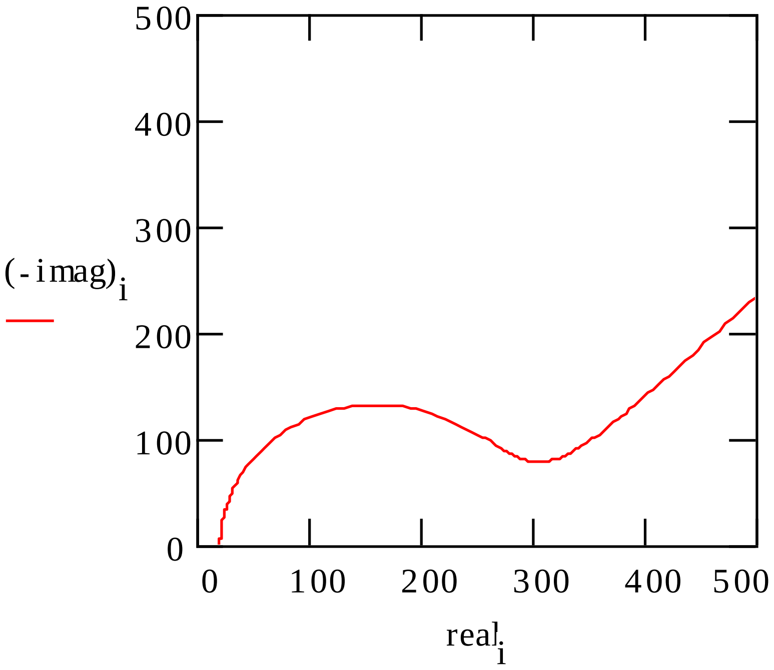
- Warburg Impedance: General impedance which represents a resistance to mass transfer, i.e., diffusion control. A Warburg typically exhibits a 45° phase shift.
  - Open, Bound, Porous Bound

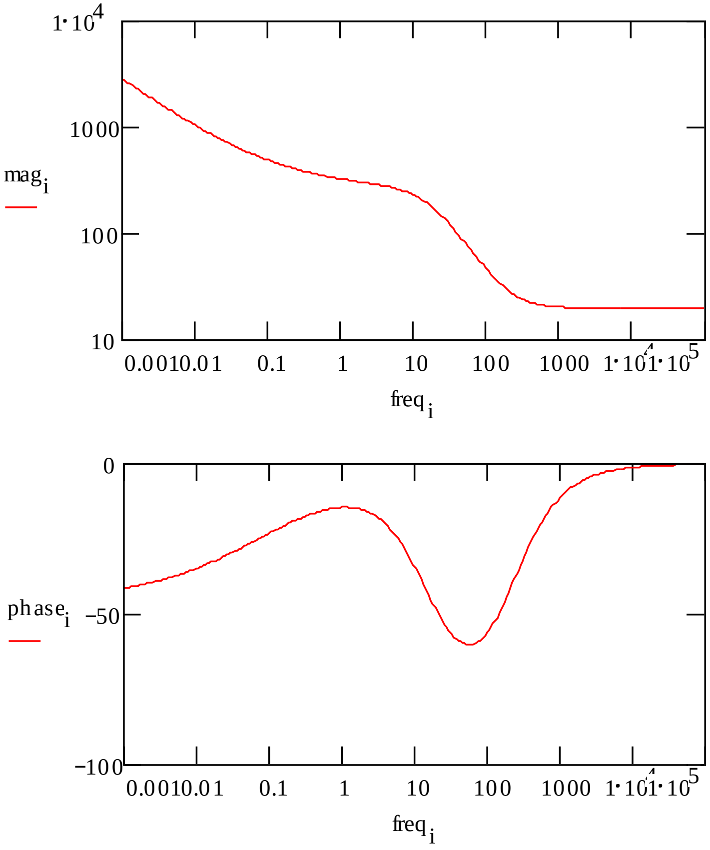


- Constant Phase Element: A very general element used to model “imperfect” capacitors. CPE’s normally exhibit a 80-90° phase shift.



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

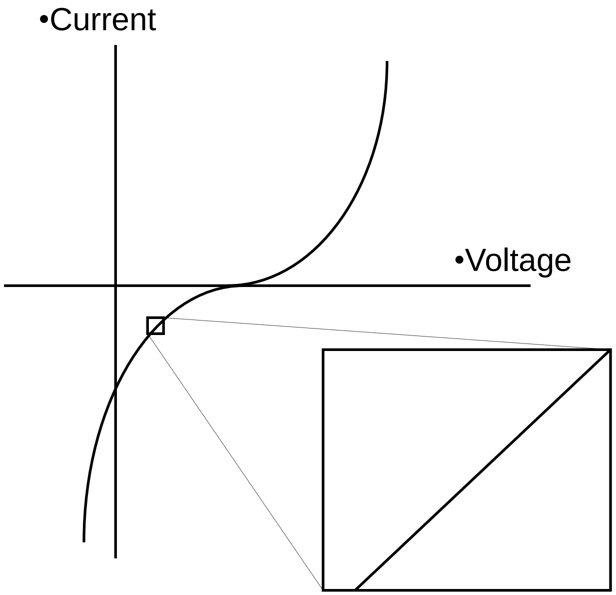
- Linear: The system obeys Ohm’s Law, E = iZ. The value of Z is independent of the magnitude of the perturbation. If linear, no harmonics are generated during the experiment.

- 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).



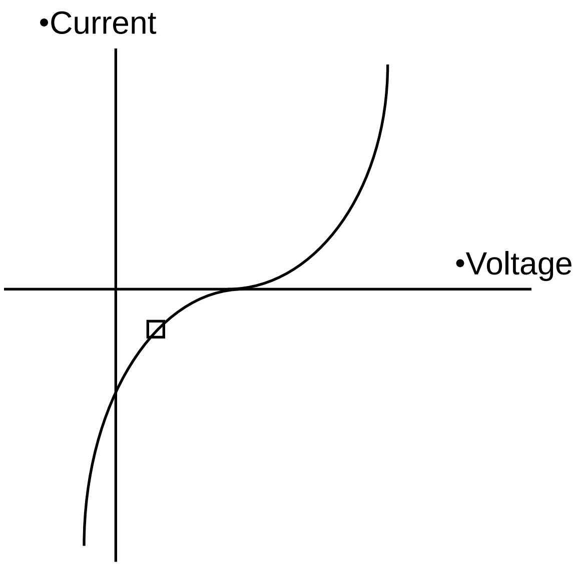
Look at a small enough region of a current versus voltage curve and it becomes linear.

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).



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

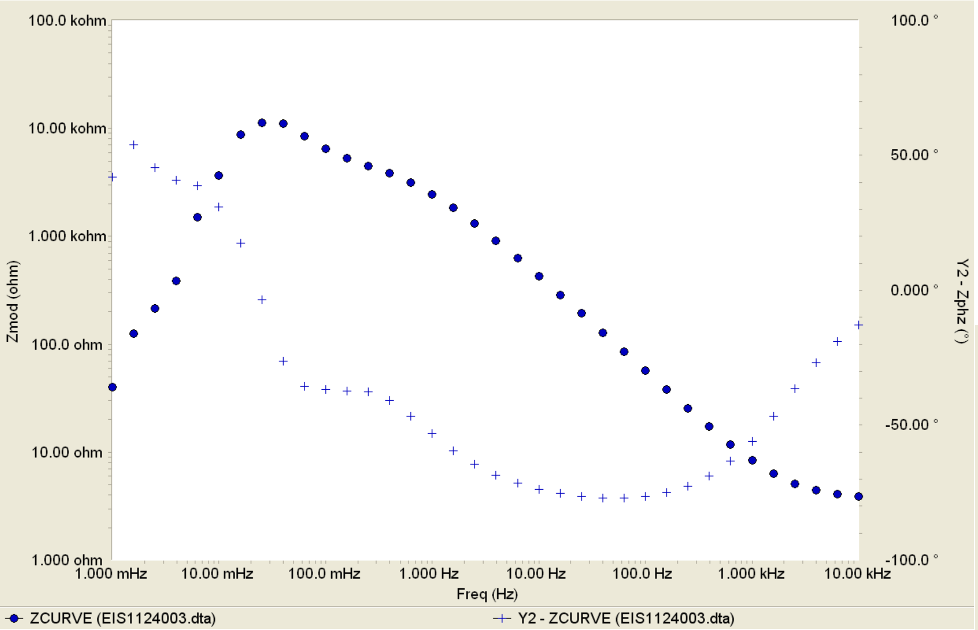
- The K-K Transform states that the phase and magnitude in a real (linear, stable, and causal) system are related.

- 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.

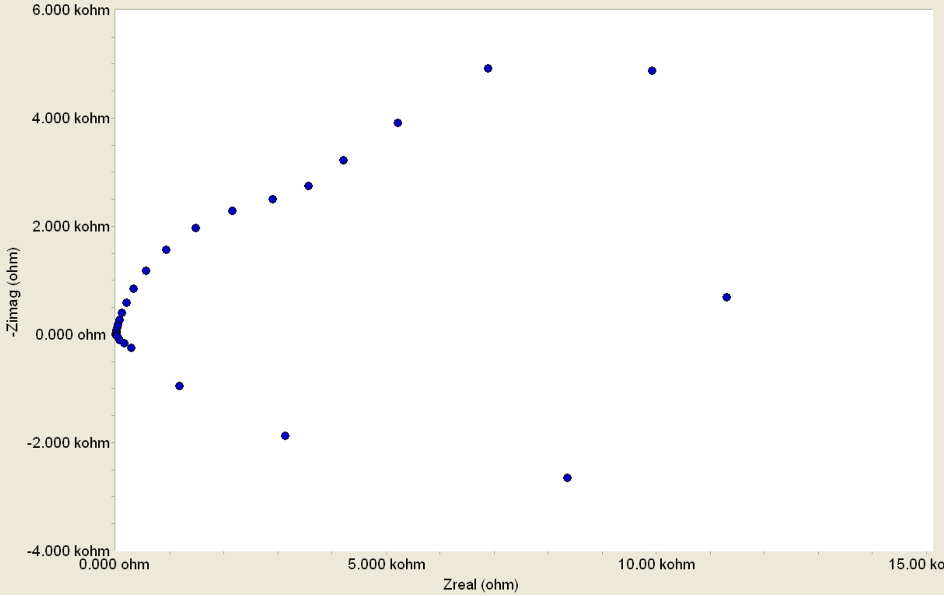
- If the values do not match, then the probability is high that your system is not linear, not stable, or not causal.

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

Bad K-K

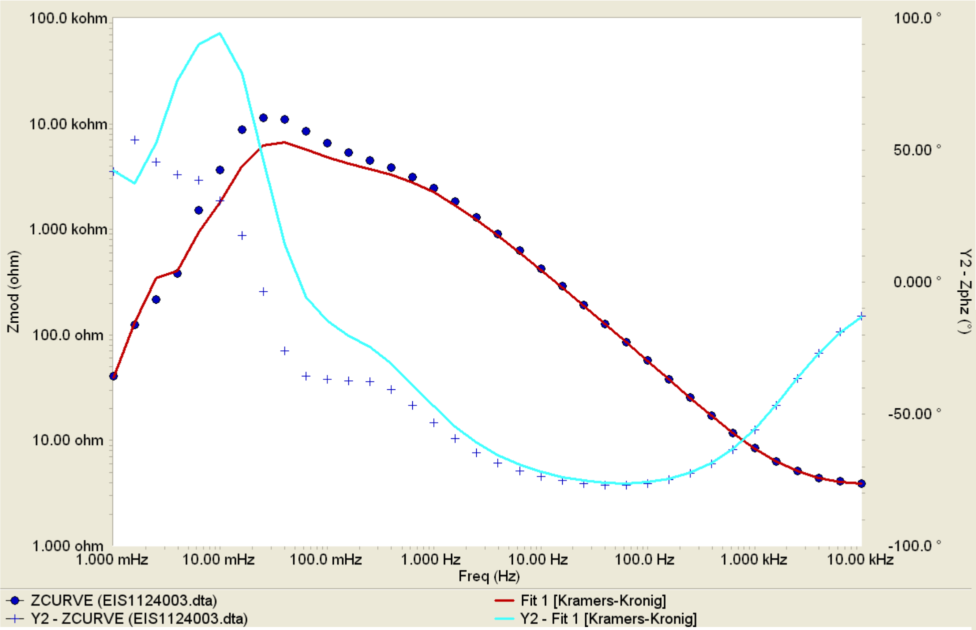


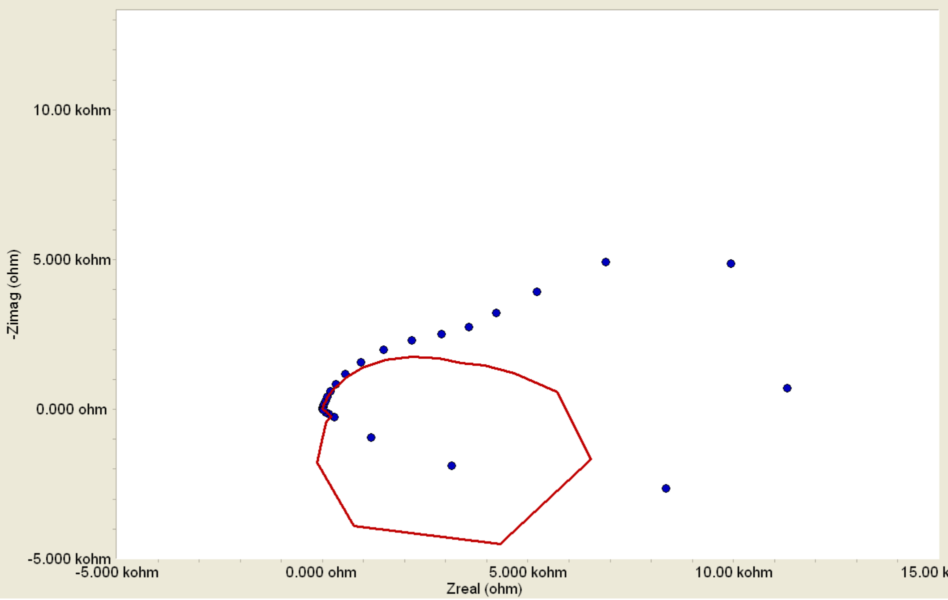
100.0 kohm
10.00 kohm
1.000 kohm
100.0 ohm
10.00 ohm
1.000 ohm
Zmod (ohm)
100.0 °
50.00 °
0.000 °
-50.00 °
-100.0 °
Y2 - Zphz (°)
1.000 mHz
10.00 mHz
100.0 mHz
1.000 Hz
10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
Freq (Hz)
ZCURVE (EIS1124003.dta)
Y2 - ZCURVE (EIS1124003.dta)



6.000 kohm
4.000 kohm
2.000 kohm
0.000 ohm
-2.000 kohm
-4.000 kohm
-Zimag (ohm)
0.000 ohm
5.000 kohm
10.00 kohm
15.00 ko
Zreal (ohm)

Bad K-K


100.0 kohm
10.00 kohm
1.000 kohm
100.0 ohm
10.00 ohm
1.000 ohm
Zmod (ohm)
100.0 °
50.00 °
0.000 °
-50.00 °
-100.0 °
Y2 - Zphz (°)
1.000 mHz
10.00 mHz
100.0 mHz
1.000 Hz
10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
Freq (Hz)
ZCURVE (EIS1124003.dta)
Y2 - ZCURVE (EIS1124003.dta)
Fit 1 [Kramers-Kronig]
Y2 - Fit 1 [Kramers-Kronig]


10.00 kohm
5.000 kohm
0.000 ohm
-5.000 kohm
-Zimag (ohm)
-5.000 kohm
0.000 ohm
5.000 kohm
10.00 kohm
15.00 k
Zreal (ohm)

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

- Potentiostat/Galvanostat
- Sine wave generator
- Time synchronization (phase locking)
- All-in-ones, Portable & Floating Systems

Things to be aware of…

- Software – Control & Analysis
- Accuracy
- Performance limitations

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

  An excellent tutorial that is highly recommended.
- Electrochemical Techniques in Corrosion Engineering, 1986, NACE International

  Proceedings from a Symposium held in 1986. 36 papers. Covers the basics of the various electrochemical techniques and a wide variety of papers on the application of these techniques. Includes impedance spectroscopy.
- Electrochemical Impedance: Analysis and Interpretation, STP 1188, Edited by Scully, Silverman, and Kendig, ASTM, ISBN 0-8031-1861-9.

  26 papers covering modeling, corrosion, inhibitors, soil, concrete, and coatings.
- EIS Primer, Gamry Instruments website, www.gamry.com