Electrochemical Impedance Spectroscopy: Theory and Application

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Electrochemical Impedance Spectroscopy: EIS

• Basics of EIS
  – What Impedance is
  – How to run EIS
  – Circuit Elements/Equivalent Circuits
  – EIS instrumentation

• EIS for Corrosion
  – General Corrosion
  – Coatings and Passive Films

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*: \( Z_0 = \frac{E_0}{I_0} \)
  - \( E_0 \) = Frequency-dependent potential
  - \( I_0 \) = Frequency-dependent current
• Ohm’s Law: \( R = \frac{E}{I} \)
  - \( R \) = impedance at the limit of zero frequency

Some Trigonometry

A voltage excitation has the form:
\[
E_t = E_0 \sin(\omega t)
\]
The resulting current has the form:
\[
I_t = I_0 \sin(\omega t + \phi)
\]
Ohm’s Law becomes:
\[
Z = \frac{E}{I} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}
\]
The impedance is expressed in terms of a magnitude, \( Z_0 \), and a phase shift, \( \phi \).
Making EIS Measurements

- Apply a small sinusoidal perturbation (potential or current) of fixed frequency
- Measure the response and compute the impedance at each frequency.
  - \( Z_\omega = \frac{E_\omega}{I_\omega} \)
- Repeat for a wide range of frequencies
- Plot and analyze

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, \( Z_{\text{total}} = Z_{\text{real}} + Z_{\text{imag}} \)
- The vector and the complex quantity are different representations of the impedance and are mathematically equivalent.
EIS data may be presented as a Bode Plot or a Complex Plane (Nyquist) Plot.

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.

Bode vs. Nyquist 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 may be more easily resolved.
  - Frequency is not obvious.
  - Small impedances can be swamped by large impedances.

Frequency Response of Electrical Circuit Elements

- **Resistor**
- **Capacitor**
- **Inductor**

\[
Z = R \text{ (Ohms)} \quad Z = -j/\omega C \text{ (Farads)} \quad Z = j\omega L \text{ (Henrys)}
\]

- $0^{\circ}$ Phase Shift
- $-90^{\circ}$ Phase Shift
- $90^{\circ}$ Phase Shift

- $j = \sqrt{-1}$
- $\omega = 2\pi f \text{ radians/s, } f = \text{ frequency (Hz or cycles/s)}$
- A real response is in-phase ($0^{\circ}$) with the excitation. An imaginary response is $\pm90^{\circ}$ out-of-phase.
EIS of a Resistor

EIS of a Capacitor

Electrochemistry as a Circuit

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

Bode Plot

- Impedance
- Phase Angle
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:** 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.

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.

Steps to Doing Analysis

- Look at data
  - (Run K-K)
  - Determine number of RC loops
  - Figure whether W exists
  - If so determine boundary conditions
- Pick/design a model
  - Randles as starting point
- Fit it
  - Check to see if CPEs needed
- Repeat as necessary
- Extract data

EIS Instrumentation

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

Things to be aware of...

- Software/Control
- Accuracy
- Performance limitations

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

- A complete ACP shows total, normal system performance (see right)
- Preferably 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

Reasons To Run EIS

- EIS is theoretically complex (and can be expensive) – why bother?
  - EIS is a non-destructive technique
  - The information content of EIS is much higher than DC techniques like polarization resistance.
  - 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.

EIS of Corrosion and Coatings

- Impedance from a tens of Ω to over several GΩ
- EIS of general corrosion looks to measure Rp (by itself)
- Corrosion events like pitting/passivation can be identified with EIS, but complicate analysis
- Insulating coatings model as (very) small capacitors
- EIS is often used in conjunction with to measure how coatings/ change/breakdown
- Systems can exhibit drift
- Diffusion related events may occur

430 SS in H2SO4, Randles Model

- Data from a 430 Stainless Steel sample

Leaders in Corrosion Control Technology
430 Stainless Steel, CPE Model

- Same Data Fit to CPE model

Randles versus CPE model

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<th>Parameter</th>
<th>Value</th>
<th>Δ Bppm</th>
<th>Units</th>
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<tr>
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<tr>
<td>Corrosion</td>
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</table>

Bode Plot of Carbon Steel in Aerated Water with 1000 ppm Cl⁻

Complex Plane Plot of Carbon Steel in Aerated Water with 1000 ppm Cl⁻

Warburg Impedance, evidence of diffusion control
EIS of Passive Films and Coatings

- Because of the barrier properties, a coated metal substrate may initially exhibit a very high impedance ($>10^{10} \, \Omega$).
- A high impedance sample will exhibit low cell currents which are more difficult to measure.
  - Use a system designed for low-current applications.
  - Use a Faraday Cage.
- It may be necessary to increase the AC amplitude to 30-50 mV to see a measurable current.
- Use of larger sample areas will improve results.

Capacitive Drift (Challenges of Very Good Barrier Coatings)

- An undamaged intact coating is a capacitor.
- The bias current of a system slowly charges this capacitor, causing what appears to be a drift in $E_{OC}$.
- Unless checked, the $E_{OC}$ will continue to increase, and can reach values over 5 volts.
- To obtain the “first” EIS measurement, use an applied DC voltage that is equal to the $E_{OC}$ of the metal substrate.
- As exposure time increases, a stable $E_{OC}$ may be observed.

Experimental Procedure

- EIS is a very sensitive detector of coating condition
- Only look at relative changes
- Need a stress mechanism to induce failure
- As EIS is non destructive, failure can be tracked with time

Description of Coated Surface
Evaluation of Coated samples

- Degradation can be described in 5 stages:
  - Capacitive
  - Water Uptake
  - Pore Resistance
  - Corrosion Initiation
  - Major Damage
Stage Two: Water Uptake

Stage Three: Pore Resistance

Stage Three: Pore Resistance

Stage Four: Corrosion Initiation
Stage Four: Corrosion Initiation

Stage Five: Major Damage

Example: Aluminum
Example: Aluminum

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

Experimental Methods Of Coating Evaluation

- Single Frequency Measurement (0.1 Hz)
- EIS and Cabinet Tests
- Thermal Cycling
- Rapid Electrochemical Assessment of Paint (REAP)
- AC-DC-AC
- Free standing films

References for EIS

- 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.
- EIS Primer, Gamry Instruments website, www.gamry.com
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