An Introduction to Electrochemical Impedance Spectroscopy (EIS)

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Outline

• A Little about Electrochemistry
  • without scaring you!
• A Little about EIS
  • without scaring you more!
  • EIS Data Plots
• Some Applications of EIS
• Equivalent Circuit Modeling
• EIS Applications
  • Some examples
What is Electrochemistry?

• Interaction of electrons with atoms, ions, or molecules.
  – Oxidation or Reduction
• Exchange of electrons between an atom, ion, or molecule and an electrode.
  – What does this have to do with anything?
    • Rudy Marcus (Nobel 1996)
    • Study electrode + A; electrode + B
    • Predict rxn   A + B
**Basics of Electrochemistry**

- Primary variables:
  - **Current (ampere, \( \text{A} \))**
    - Rate – electrons / second
    - \( 1 \text{ A} = 6 \times 10^{18} \text{ electrons} / \text{second} \)
  - **Voltage (volt, \( \text{V} \))**
    - Voltage = Energy
    - \( 1 \text{ V} = 1 \text{ joule} / \text{coulomb} \)
    - \( 1 \text{ V} = 1 \text{ joule} / 6 \times 10^{18} \text{ electrons} \)
    - \( 1 \text{ eV} = 0.16 \times 10^{-18} \text{ J} \)
Basics of Electrochemistry

• Variables and units
  – Charge (coulomb, $C$)
    • Number of electrons
    • 1 coulomb = 1 ampere for 1 second
      \[ = 6 \times 10^{18} \text{ electrons} \]
    • 1 mole of electrons = $6 \times 10^{23}$ e$^-$
    • 1 mole of e$^-$ = 1 faraday (F) = 96,485 C
    • 1 faraday = 1 A for 96,485 s (28.6 hr!)
Basics of Electrochemistry

• What controls the current?
  – Voltage
    • Energy of the electrons
  – Rate of supply of reactant
    • Reactions happen ONLY at the surface of the electrode! (Michael Faraday)
    • Diffusion
    • Stirring
    • Rotated electrodes
An Electrochemical Experiment

- Current and voltage are measured by and voltage is controlled by a **Potentiostat**
Electrochemical Impedance Spectroscopy (EIS)

- Small perturbation
- Nominally non-destructive
- Many variations on the experiment
  - Sine wave perturbation
  - Many sine waves (Multisine)
  - Small steps
  - Random noise
  - Hardware / Software implementations
- All give the same results
EIS Theory

- If the perturbation is small:
  - Current-voltage curve appears linear
  - Sine wave voltage perturbation gives *sine-wave-ish* current response
EIS Theory

- Sine wave *voltage perturbation*
- *Shifted* sine wave *current response*
- **Two** parameters characterize this response:
  - Time/*phase shift*
  - **Magnitude**: Ratio of voltage to current (E/I)
**EIS Theory**

- **Magnitude**
  - AC components only
  - voltage/current
  - Unit: ohm (Ω)
  - $1 \, \Omega = 1 \, \text{V} / 1 \, \text{A}$

- **Phase angle** (shift)
  - Degrees
  - $\Theta$ or $\phi$
EIS Theory

• Magnitude and phase together are impedance (Z)
• Magnitude = |Z|
  – Ohms, Ω
**Presenting EIS Data**

- “Bode Plot” - shows magnitude and phase
  - Bode Magnitude: log Magnitude vs log frequency
    - Magnitude and frequency both change over MANY decades
      - Frequency: $10^{-5}$ to $10^{+6}$ Hz
      - Magnitude: $10^{-5}$ to $10^{+14}$ ohm
    - Bode Phase: phase vs log frequency
      - Phase: $-180^\circ$ to $+180^\circ$
  - Frequency: $f$: Hz (cycles/s), $\omega$: rad/s, $\omega = 2 \pi f$
A Bode Plot

• Phase is sometimes plotted the other way
**Polar vs. Cartesian**

- Two parameters specify a point in a plane
- Use Polar coordinates: Magnitude, phase
- Use Cartesian coordinates: X, Y
Polar vs. Cartesian

- Polar: Bode plot
- Cartesian: Complex plane plot, Nyquist plot
  - Label axes: "real", "imaginary"; $Z', Z''$
**Nyquist Plot**

- Pretty pictures!
- Frequency is not shown on the plot
- Should use same scale on $X, Y$ ($Z_{\text{real}}, Z_{\text{imag}}$)
Which Plot is Right?

• Both!
EIS Experiment

Diagram:
- Waveform Generator
- Potentiostat
- Analyzer
- Computer
- Electrochemical Cell
- Counter Electrode
- Reference Electrode
- Working Electrode

Connections:
- E from Potentiostat to Analyzer
- I from Potentiostat to Computer
- Connections to Electrochemical Cell
Electrochemical Impedance Spectroscopy (EIS)

- Many variations on the experiment
  - Sine wave perturbation
  - Many sine waves (Multisine)
  - Small steps
  - Random noise
  - Hardware / Software implementations
- All give the same results
- System cost: $10K-$35K
Applications of EIS

• Corrosion measurement
  – Understanding the corrosion process
• Coatings evaluation
  – How to tell (this week) if a coating will last 5 years or 10 years
• Fuel Cell “state of health”
  – Batteries, Supercapacitors
• Sensors - “Impedimetric”
  – Milk; Motor oil
How Do **Wizards** Model EIS Data?

- Propose a physical model
  - Fuel Cell
    - Gas flow, porosity of anode, cathode
    - Reaction rates at anode, cathode
    - Diffusion of H⁺ through Nafion membrane
    - Resistance of current collectors
  - Write differential equations for all processes & solve $I(E, f, \ldots)$
  - Linearize and write $Z = E_{AC} / I_{AC}$
How Do We Model EIS Data?

- Borrow from electrical engineers
  - “What circuit would give the same response as my fuel cell?”
  - Equivalent circuit model
    - Resistors, capacitors, inductors
    - Some special elements for echem
      - Diffusion
        » Warburg: W
        » Bounded Warburg: O, T
        » Diffusion with competing rxn
          Gerischer: G
Equivalent Circuit Models

- What do these circuit elements mean?
  - $R$ – resistor (resistance, $R$, $\Omega$)
    - $|Z|$ is constant, $\Theta = 0^\circ$
    - Physical meaning?
      - $R_s$: Resistance of conducting electrolyte
      - $R_p$: “Polarization Resistance” $\propto 1$/corrosion rate
Equivalent Circuit Models

• What do these circuit elements mean?
  – C – Capacitor (C, capacitance, farad)
    • \(| Z | = \frac{1}{\omega C}, \Theta = -90^\circ\)
    • Physical meaning?
      – Cdl: Double layer capacitance
Equivalent Circuit Models

• What do these circuit elements mean?
  – L – Inductor (inductance, L, henry)
    • \(| Z | = \omega L, \Theta = +90^\circ\)
    • Physical meaning?
      – Adsorption – appears @ low frequency
      – Artifact – appears @ high frequency
        » Interactions between wires!
PEM Fuel Cell Model -1
Equivalent Circuit Models

- Constant Phase Element (CPE)
  - $|Z| = \frac{1}{\omega^n Y}$, $\Theta = -90^\circ \times n$ (0 < $n$ < 1)
Equivalent Circuit Models

- Constant Phase Element (CPE)
  - $|Z| = \frac{1}{\omega^n Y}$, $\Theta = -90^\circ \times n$ (0 < n < 1)

- Physical meaning?
  - Rough surface
  - Inhomogeneous surface
  - Distribution of some physical process
    - Distribution of reactivity
PEM Fuel Cell Model -2

[Diagram of PEM Fuel Cell Model]

- R.E.
- Lstray
- HFR
- Ri-cathode
- Yo-cathode
- a-cathode
- Ri-anode
- Yo-anode
- a-anode
- W.E.

[Graph of PEM Fuel Cell]

Zreal (ohm)

- 0.000 ohm
- 10.000 mohm
- 20.000 mohm
- 30.000 mohm

Zimag (ohm)

- -10.000 mohm
- 0.000 ohm
- 10.000 mohm
- 20.000 mohm
- 30.000 mohm

Range:
- 0.000 ohm to 80.000 mohm

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PEM Fuel Cell Model -2
Applications of EIS

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• Coatings evaluation
  – How to tell (this week) if a coating will last 5 years or 10 years

• **Fuel Cell “state of health”**
  – Batteries, Supercapacitors

• Sensors - “Impedimetric”
  – Milk; Motor oil
Another Fuel Cell Study

• PEM Fuel Cell
  – Authors looked at three operating conditions
    • Dry, Normal, Flooded
    • Fit to model below

Fig. 4. Randles cell.

Another Fuel Cell Study

- $R_m$: membrane, $R_p$: $e^-$ xfr, $R_d$: diffusion
- Normal, Flooded, Dry

Fig. 4. Randles cell.

Fig. 12. Evolution of the fuel cell state of health as a function of time.

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Understanding Corrosion

- Titanium in fluoride containing saliva
  - Examined three alloys

*Fig. 14. Impedance spectra of: ○, Ti; □, Ti7Al4.5V; and △, Ti5Al2.5Fe in Fusayama-Mayer +0.1% weight F− solution at 200 mV vs. SCE. Dotted line—the fitted spectra.*

*Fig. 15. The equivalent circuit proposed to fit the impedance data in artificial saliva containing fluoride ions. DE, distributed element accounting for the double layer capacitance; Rct, charge transfer resistance; Lad, Rad, inductance and resistance, respectively associated with the presence of the adsorbed species on the electrode surface; Cox, Rox, capacitance and resistance of the oxide film.*

**Ti in saliva**

- Rct (Charge transfer resistance) not affected

### Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>Ti7Al4.5V</th>
<th>Ti5Al2.5Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{el} 10^5 T_{dl}/\Omega^{-1} s^n \text{ cm}^2$</td>
<td>4.94 ± 0.19</td>
<td>6.22 ± 0.25</td>
<td>3.82 ± 0.19</td>
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<tr>
<td>$n$</td>
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<td>$R_{ct}/\Omega \text{ cm}^2$</td>
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<td>$L_{ad}/\text{H cm}^2$</td>
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<td>$R_{ad}/\Omega \text{ cm}^2$</td>
<td>20.6 ± 0.65</td>
<td>21.6 ± 0.6</td>
<td>26.4 ± 0.77</td>
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<td>$C_{ox}/\text{mF cm}^2$</td>
<td>14.5 ± 0.13</td>
<td>13.8 ± 0.09</td>
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<td>$R_{ox}/\text{k\Omega cm}^2$</td>
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<td>$C_{dl}/\mu\text{F cm}^2$</td>
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**Ti in saliva**

- Rox (oxide film resistance) varies considerably

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**Table 3**
The parameters of the equivalent circuit from Fig. 15 after fitting the impedance spectra in artificial saliva containing fluoride ions

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EIS Applied to Coatings

• 3 Articles in JCT, available through:
  – www.ConsultRSR.com
  – www.gamry.com
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Sensing Motor Oil Quality

• Motor oil IS conducting (a little)
  – **IF** electrodes are closely spaced!
• Oil degrades by oxidation over time
  – 80 hr * 60 mi/hr = 4800 miles!
  – Trucks, 40 quarts, > $150/oil change

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Sensing Motor Oil Quality

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• www.gamry.com - good introduction
• www.consultrsr.com
• Books
  – Orazem, Tribollet, “Electrochemical Impedance Spectroscopy”
  – Barsoukov, Macdonald, “Impedance Spectroscopy” 2nd ed.
Thanks for your Attention!
And I hope I didn't scare you too much!