Electrochemical Impedance Spectroscopy

May 2012

Designing the Solution for Electrochemistry
Potentiostat/Galvanostat | Battery Cycler | Fuel Cell Test Station
+82-2-578-6516 | sales@wonatech.com
Nomenclature: EIS

- **Electrochemical?**
  - In electrochemistry, everything of interest takes place at the interface between electrode & electrolyte!
  - Controlling REDOX by Potentiostat/galvanostat

- **Impedance?**
  - AC circuit theory describes the response of a circuit to an alternating current or voltage as a function of frequency
  - Impedance is a totally complex resistance encountered when a current flows through a circuit made of resistors, capacitors, or inductors, or any combination of these
  - Ohm’s Law, $V = R \cdot I \rightarrow V = Z \cdot I$ (complex number $Z$)

- **Spectroscopy?**
  - No Quantum Process
  - Small Perturbation → Response
Excitations used in E’chem Techniques

1. DC
2. Sweep
   - LSV, Tafel, PD, LPR
   - CV
   - Cyclic Polarization
3. Pulse
   - DPV
   - NPV
   - RNPV
   - SWV
4. Sine
   - PEIS, GEIS

Potentiostatic

CA, CC, CP
 Electrochemical Interface and Electrochemical Process
Electrochemical Interface

- **Everything** happens at the interface
- Charge Transfer $\Rightarrow R_{ct}$
  - $R_{ct} \sim 1/i_0$
  - Butler-Volmer Equation
- Diffusion Layer $\Rightarrow W$
- Bulk Electrolyte $\Rightarrow R_{ser}, R_\Omega$
- Double Layer $\Rightarrow C_{dl}$
  - Non-Faradaic Process
Randles’ Circuit
**Process of Energy Storage in Electrochemical System**

**Common Steps**

- Ionic charge conduction through electrolyte in pores of active layer
- Electronic charge conduction through conductive part of active layer
- Electrochemical reaction on the interface of active material particles including electron transfer
- Diffusion of ions or neutral species into or out of electrochemical reaction zone.

**EIS**

\[ Z(SOC, SOH, T; \omega) \]

- Discharge Process
- Polarization Curve
- CV

**Study of Mechanism**

- Evaluation & Diagnosis
  - CO poisoning
  - Water flooding in FC

**Performance Simulation**

- Arbitrary Load
- DC/AC/Transient
- Power/Energy

Ex) \( R_s, R_{ct}, C_{dl}, W \ ... \)
Impedance Spectra of a Li-ion battery

Impedance Spectra upon cycling

Nyquist Plot vs. level of discharge

CF) Discharge curve upon cycling

Effect of temperature
A. PEMFC Under Dead End
   (H₂O outlet in cathode closed)

B. PEMFC Under CO Poisoning
   (H₂ + 100ppm CO as fuel gas)

Ref. Zahner elektrik-Kronach Impedance Day 2012
Circuit Elements (1)
# Basic Circuit Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Equation</th>
<th>Impedance (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resistor</strong></td>
<td>$E = RI$</td>
<td>$Z = R$</td>
</tr>
<tr>
<td></td>
<td>$I(t) = I_0 e^{j\omega t}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E = Z \times I$</td>
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</tr>
<tr>
<td><strong>Inductor</strong></td>
<td>$E = L \frac{dI}{dt}$</td>
<td>$Z = j\omega L$</td>
</tr>
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<td></td>
<td>$I(t) = I_0 e^{j\omega t}$</td>
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</tr>
<tr>
<td></td>
<td>$E = Z \times I$</td>
<td></td>
</tr>
<tr>
<td><strong>Capacitor</strong></td>
<td>$E = \frac{Q}{C} = \frac{1}{C} \int I dt$</td>
<td>$Z = -j \frac{1}{\omega C}$</td>
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AC Current, Voltage, and Impedance

Voltage \[ E(\omega) = E_0 \cos(\omega t) \]
\[ = E_0 e^{j\omega t}, \text{ where } j = \sqrt{-1} \text{ and } \omega = 2\pi f \]

Current \[ I(\omega) = I_0 \cos(\omega t - \varphi) \]
\[ = I_0 e^{j(\omega t - \varphi)} \]

Impedance \[ Z(\omega) = \frac{E(\omega)}{I(\omega)} \quad \text{← Ohm’s Law} \]
\[ = Z_0(\omega)e^{j\varphi(\omega)}, \text{ where } Z_0 = \frac{E_0}{I_0} \]
\[ = Z_0(\cos \varphi + j \sin \varphi) \quad \rightarrow \text{Modulus & Phase (Bode Plot)} \]
\[ = Z' + jZ'' \]
\[ \rightarrow \text{Real & Imaginary part (Nyquist Plot)} \]
Presentation of Impedance Spectrum

- **Nyquist Plot**
  - Vectors of length $|Z|$
  - Individual charge transfer processes are resolvable.
  - Frequency is not shown.
  - Small Z can be hidden by large Z.

- **Bode Plot**
  - $C$ may be determined graphically.
  - Small Zs in presence of large Zs are usually easy to identify.
Basic Circuit Elements

**Resistor**

\[ Z = R \]

**Inductor**

\[ Z = j\omega L \]

**Capacitor**

\[ Z = \frac{1}{j\omega C} = -j\frac{1}{\omega C} \]
Combinations of Elements

- Serial Combination
  \[ Z = Z_1 + Z_2 \]

- Parallel Combination
  \[ \frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} \]
Combinations of Circuit Elements

\[ R-C \]
\[ Z = R + \frac{1}{j\omega C} \]

\[ R|C \]
\[ \frac{1}{Z} = \frac{1}{R} + j\omega C \]

\[ R-R|C \]
\[ Z = R_s + \frac{1}{\frac{1}{R} + j\omega C} \]
\[ Z = R_s + \frac{1}{\frac{1}{R} + j\omega C} = \left[ R_s + \frac{R}{1 + \omega^2 R^2 C^2} \right] - j \left[ \frac{R \times \omega RC}{1 + \omega^2 R^2 C^2} \right] \]

\[ \equiv Z' + jZ'' \]

1. \( \omega \to 0, \ Z = R_s + R \)
2. \( \omega \to \infty, \ Z = R_s \)
3. \( Z' = R_s + \frac{R}{1 + \omega^2 R^2 C^2}, \quad Z'' = -\frac{R \times \omega RC}{1 + \omega^2 R^2 C^2} \quad \therefore \left\{ Z - (R_s + \frac{R}{2}) \right\}^2 + Z''^2 = \left( \frac{R}{2} \right)^2 \)
4. \( Z' = R_s + \frac{R}{2} \Rightarrow \frac{R \times \omega_{\max} RC}{1 + \omega_{\max}^2 R^2 C^2} = \frac{R}{2} \)

\[ \therefore \omega_{\max} = \frac{1}{RC} \quad \Rightarrow \quad -Z'' = -Z''_{\max}, \quad \text{phase} = \varphi_{\min} \]
\[ R_S - R|C \]

\[ \omega_{\text{max}} = 2\pi f_{\text{max}} = \frac{1}{RC} \]

\[ \omega \rightarrow \infty \]
\[ \omega \rightarrow 0 \]

\[ -Z'' \]

\[ Z' \]

\[ \text{Phase } \phi \]

\[ \log \omega \]
Coating Capacitance

- Ideal Coating
  \[ C_{coat} = \varepsilon \frac{A}{d} \]

- Imperfect Coating
Uniqueness of Models

- There is not a unique equivalent circuit that describes a spectrum.
- Measuring Z is simple and easy, but analyzing it is difficult.
- Physically relevant model is important.
  - It can be tested by altering physical parameters.
- Be cautious in handling empirical models even if you get a good looking fit.
  - Use the fewest elements
  - Test it by T-test
Disadvantages of EIS

• Ambiguities in interpretation
  – All cells have intrinsically distributed properties
  – Ideal circuit elements may be inadequate to describe real electrical response
  – Use of distributed elements (e.g. CPE)

• There is not a unique equivalent circuit describes measured impedance spectrum
Advantages of EIS

- Relatively simple electrical measurement
- But analysis of complex material variables: mass transport, rates of chemical reactions, corrosion...
- Predictable aspects of the performance of chemical sensors and fuel cells
- Providing empirical quality control procedure

![Diagram showing the process of Electrochemical System EIS Experiment Ze(ω) Theory Physically Relevant Model Mathematical Model Ztheory(ω) Empirical Circuit Zem(ω) Curve Fitting System Characterization.](Modified figure shown in page 10, IS(2nd ed.))
Circuit Elements and Electrochemical Meanings
Physical Electrochemistry & Equivalent Circuit Elements

- Electrolyte Resistance
  - 3 electrode: between WE and RE
  - 2 electrode: all series R in the cell are measured incl. R of contacts, electrodes, solution, and battery separators
  - Depends on ionic concentration, type of ions, temperature, and geometry
• **Charge Transfer Resistance**
  – Echem charge transfer reactions are generally modeled as resistances.
  – When an EIS spectrum is measured on a corrosion cell at $E_{corr}$, the resistance at low-frequency is identical to the polarization resistance.

For a one step, multi-electron process, $O + ne \rightleftharpoons R$ small overpotential is given by

$$\eta = \frac{RT}{nF} \left[ \frac{C_O(0,t)}{C^*_O} - \frac{C_R(0,t)}{C^*_R} + \frac{i}{i_o} \right]$$

$$R_{ct} = \frac{\partial E}{\partial i} \bigg|_{C_O(0,t),C_R(0,t)}$$

$$= \frac{RT}{nFi_0}$$
**Double Layer Capacitance**

- A electrical double layer forms as ions from the solution “stick on” the electrode. There is an Å-wide separation between charge in the electrode and ionic charges in the solution.
- Charges separated by an insulator form a capacity. On a bare metal, estimate 20 to 40 μF of C for every cm² of electrode area.
- Depends on electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

From A. J. Bard & L. R. Faulkner, “Electrochemical Methods”
Physical Electrochemistry 
& Equivalent Circuit Elements

- Constant Phase Element (CPE)
  - The CPE is basically an imperfect capacitor.
  - It’s phase shift is less than 90°.

\[ Z_{CPE} = \frac{1}{A \times (j\omega)^\alpha} \]

- Unlike C, a CPE has 2 parameters
  - \( \alpha \) is generally between 0.9 and 1.0
  - A is similar to C
- Possible Explanations
  - Surface roughness → Fractal Dimension, \( D=1+1/\alpha \)
  - Distribution of reaction rates on a surface
  - Varying thickness or composition of a coating
Physical Electrochemistry & Equivalent Circuit Elements

- **Diffusion**
  - Diffusion processes can create an impedance, which is small at high frequency and increases as frequency decreases.
  - **Warburg Impedance**
    - Warburg looks like a special CPE with $A=1/s$ and $\alpha=1/2$.
    - However, remember that Warburg is derived from electrochemical kinetics. Parameters you obtain with Warburg have physical meanings. It is only partly true for CPE.
    - You can get a good fit, but how to interpret the resulting parameters?

\[
Z_W = \frac{\sigma}{\sqrt{\omega}} (1 - j) = \frac{\sigma}{\sqrt{\omega}} e^{-\frac{\pi}{4} j} = \frac{\sigma}{(j \omega)^{1/2}}
\]

\[
\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{D_o^{1/2} C_o^*} + \frac{1}{D_R^{1/2} C_R^*} \right)
\]

For a one-step, multi-electron process.
Physical Electrochemistry & Equivalent Circuit Elements

• Diffusion
  – Nernstian & Finite Diffusion Impedance

\[ Z = \frac{\sigma}{\sqrt{\omega}} (1 - j) \tanh(\delta \sqrt{\frac{j \omega}{D}}) \]
\[ Z = \frac{\sigma}{\sqrt{\omega}} (1 - j) \coth(\delta \sqrt{\frac{j \omega}{D}}) \]

  – Homogeneous reaction (Gerischer)
  
\[ Z = \frac{1}{A \sqrt{B} + j \omega} \]

  – Spherical Diffusion

\[ Z = \frac{1}{A \sqrt{B} + \sqrt{j \omega}} \]
Physical Electrochemistry & Equivalent Circuit Elements

- Diffusion ← Transmission Line Model

Warburg

\[ Z = \frac{\sigma}{\sqrt{\omega}}(1 - j) \]

Nernstian Impedance: Diffusion by Constant Concentration

\[ Z = \frac{\sigma}{\sqrt{\omega}}(1 - j) \tanh(\delta \sqrt{j\omega/D}) \]

Finite Diffusion Impedance: Diffusion by Phase Boundary

\[ Z = \frac{\sigma}{\sqrt{\omega}}(1 - j) \coth(\delta \sqrt{j\omega/D}) \]
Nernstian Impedance

$R: 100\, \Omega$

$C: 0.001\, F$
Nernstian Impedance

\[ R: 100\Omega \]
\[ C: 0.001F \]
Finite Diffusion Impedance

R: 100Ω
C: 0.001F
Finite Diffusion Impedance

R: 100Ω  
C: 0.001F
Validation of Impedance Data
Kramers-Kronig Relation
Validation of Impedance Data

• Ideal impedance data must fulfill:
  – **Causality**: The output must be exclusively a result of the input
  – **Linearity**: The response must be a linear fn. of the perturbation
  – **Stability**: The system must not be changing during measurement
    → a serious problem for corroding systems
  – **Finite-Valued**: Impedance must be finite value at any frequency

• Kramers-Kronig Relation:
  – Validation Test
  – Low Frequency Extrapolation
    \[ Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_{0}^{\infty} \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx \]
  – The integration range includes the frequencies zero and infinity
  – Note pure capacitor cannot be calculated

  a. \( Z'' \rightarrow Z' \)
  b. \( Z' \rightarrow Z'' \)
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.

E’chem: A Stationary System?

• Measuring EIS spectrum takes time (often many hours).
• The sample can change during the time the spectrum is recorded.
• If this happens, modeling results may be wildly inaccurate.
• To shorten the measuring time of impedance spectrum, use FFT EIS method.

Non-Stationary Conditions result in non-stationary spectra!
K-K Relation

Ref. Scribner Associates Inc. – ZView K-K Transform Tutorial
Validation of Impedance Data

Z-HIT
Limitation of K-K Relation

- The integration range includes the frequencies zero and infinity
- $|Z|$ and Phase are measured independently with different accuracy and sensitivity, but in theory, they are correlated with each other.
Heating NTC, PTC

Phase is more stable than |Z|!

Ref. Zahner elektrik-Kronach Impedance Day 2012
Z-HIT Approximation

\[ \ln|Z(\omega_0)| \approx \text{const.} + \frac{2}{\pi} \int_{\omega_s}^{\omega_0} \varphi(\omega) d\ln \omega + \gamma \cdot \frac{d\varphi(\omega_0)}{d\ln \omega} \]

Local relationship between impedance and phase

=> Not affected by the limited bandwidth problem

=> Reliable detection of artifacts and instationarities (drift)

=> **Reconstruction (!!!)** of causal spectra

=> Reliable interpretation of spectra

Ref. Kronach Impedance Day 2012
Ex. Spectrum of a fuel cell under load

1. Z-HIT
2. FIT

Ref. Kronach Impedance Day 2012
Ex. Fuel cell under CO poisoning

**Raw data**

**Refined data**

Ref. Zahner elektrik- Kronach Impedance Day 2012
Other Methods to Measure EIS
Multi-Sine Wave Method

In Galvanostatic EIS,
Freq ↓ ⇒ |Z|↑ ⇒ |V|↑: Linear Region?
⇒ “Pseudo-Galvanostatic EIS”

Multi-Sine Method
Time Resolved EIS

1. Real Time-Drift Compensation

An EIS recorded at the PEMFC with **flooded cathode**, after 4450s of “dead end” operation at 2A. After pp501-505, IS (2nd ed.) & Schiller
Inductive Loop at High Frequency

• The effects of inductances are often seen at the high frequencies.

• The value of inductor is very small, however, this can be important if the electrode impedance is low.

• Possible Causes
  – Actual physical inductance of loop or coil of wire between electrode and potentiostat
  – Self inductance of the electrode itself: even a straight piece of rod has some self inductance ~ several nH
  – Some cylinder-type batteries also shows this effect ~ uH
  – Instrumental artifacts, notably capacitance associated with the current measuring resistor, however. Potentiostat manufacturers may have already made corrections for this effect.

\[ E = L \frac{dI}{dt} \rightarrow Z_L = j\omega L \]
Mutual Induction - Twisting Cables

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<th>C</th>
<th>D</th>
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<tr>
<td></td>
<td>Arbitrary</td>
<td>CE/RE &amp; WE/WS</td>
<td>CE/WS &amp; WE/RE</td>
<td>CE/WE &amp; RE/WS</td>
</tr>
</tbody>
</table>

Cell: 20 mΩ planar resistor

Ref. Zahner elektrik-Kronach Impedance Day 2012
Galvanostatic EIS is Better for Low Z

• Potentiostatic Mode
  – Vac is 1 mV Minimum!
  – $1 \text{ mV}_{\text{rms}} = 1.414 \text{ A}_{\text{rms}} \times Z$
  – $Z_{\text{min}} = 707 \mu\Omega$
  – These are Absolute Minimum Z Values!
    • Limitation is APPLIED E
    • Measured E is still Accurate!

• Galvanostatic Mode
  – Can Measure Smaller E Values! ~Microvolts
  – CMR of electrometer may limit the absolute minimum Z Values! -> 5 uΩ
  – Refer to “Shorted Lead Test”
How to Extract Model Parameters

- Building equivalent circuit model
  - Physically relevant model
    - Each component is postulated to come from a physical process in the EChem cell based on knowledge of the cell’s physical characteristics.
  - Empirical model

- Complex Nonlinear Least Square (CNLS) Fitting Algorithm
  - is used to find the model parameters that cause the best agreement between a model’s impedance spectrum and a measured spectrum.
  - starts with initial estimates of model parameters.
  - Iterations continue until the goodness of fit exceeds an acceptance criterion, or until the number of iterations reaches a limit.
  - Please check the change of $\chi^2$ after each iteration.
  - Sometimes, CNLS algorithm cannot converge on a useful fit because of
    - An incorrect model
    - Poor estimates for the initial values
    - Noise and etc.
  - Don’t care if the fit looks poor over a small section of the spectrum.