Physical Electrochemistry & Electrocatalysis

Viktoriia Saveleva
Methods to Measure Electrode Reactions
Electrochemical Impedance Spectroscopy
Electrochemical Impedance Spectroscopy (EIS) or Impedance Spectroscopy or AC Impedance Spectroscopy

EIS is used to study dielectric and electric properties of materials, components and cells
Often used in corrosion studies, batteries, fuel cells
EIS helps to determine Ohmic, Charge Transfer, Mass-Transfer Resistances as well as Capacitances and Inductances
AC Circuit Theory

Ohm's law defines resistance in terms of the ratio between voltage $E$ and current $I$.

$$R = \frac{E(t)}{I(t)}$$

The relationship is limited to only one circuit element -- the ideal resistor. An ideal resistor has several simplifying properties:

- It follows Ohm’s Law at all current and voltage levels
- Its resistance value is independent of frequency.
- AC current and voltage signals though a resistor are in phase with each other
AC Circuit Theory….in reality

- Circuit elements typically exhibit much more complex behavior.
- These elements force us to abandon the simple concept of resistance.
- In its place we use impedance, which is a more general circuit parameter.
- Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current (not being limited by the simplifying properties of an ideal resistor)
- Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell.
AC Circuit Theory….in reality

- Application of a sinusoidal potential excitation.
- The response to this potential is an AC current signal, containing the excitation frequency (and its harmonics).
- This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).
- Electrochemical Impedance is normally measured using a small excitation signal in order to get a pseudo-linear response.
- In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.
Excitation function

\[ E(t) = E_0 \cos(\omega t) \]

Response function

\[ I(t) = I_0 \cos(\omega t - \varphi) \]

- \( E(t) \): potential at time \( t \)
- \( E_0 \): amplitude of the signal
- \( \omega \): radial frequency (in rad/s)
- \( I(t) \): current at time \( t \)
- \( I_0 \): amplitude of response signal
- \( \varphi \): phase shift
- \( f \): frequency in Hz=1/s

\[ \omega = 2\pi f \]
\[ E(t) = E_0 \cos(\omega t) \]

\[ I(t) = I_0 \cos(\omega t - \varphi) \]
\[ E(t) = E_0 \cos(\omega t) \]

\[ I(t) = I_0 \cos(\omega t - \varphi) \]
Change in amplitude

Phase shift

$E(t)$
Ohm’s Law

\[ R = \frac{E(t)}{I(t)} \]

A similar expression can be defined for the Impedance

\[ Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \varphi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \varphi)} \]

The impedance is expressed in terms of a magnitude, \( Z_0 \), and a phase shift, \( \varphi \).
Physical Electrochemistry & Electrocatalysis

\[ E + \Delta E \]

\[ I + \Delta I \]

\[ \eta \text{ [mV]} \]

\[ j \text{ [mA/cm}^2\]
Impedance as Complex Number

\[ Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t + \varphi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \varphi)} \]

With Euler’s definition of \( \cos(z) \) expressed as complex number
(and neglecting the complex conjugate \( \square \)--this is the fast and sloppy way*)

\[ \cos(\omega t) = \frac{\exp(i\omega t) - \exp(-i\omega t)}{2} \]

with \( i^2 = -1 \)

\[ Z(\omega) = \frac{E(t)}{I(t)} = Z_0 \exp(i\varphi) = Z_0 (\cos(\varphi) - i\sin(\varphi)) \]

*for details: see M. Orazem, Electrochemical Impedance Spectroscopy, Wiley-VCH)
Impedance as Complex Number

\[ Z(\omega) = \frac{E(t)}{I(t)} = Z_0 \exp(i\varphi) = Z_0 (\cos(\varphi) - i\sin(\varphi)) \]

\[ Z(\omega) = \text{Re}(Z) - i \cdot \text{Im}(Z) \]
\[ |Z(\omega)| = \left[ \text{Re}(Z)^2 + \text{Im}(Z)^2 \right]^{1/2} \]

*for details: see M. Orazem, Electrochemical Impedance Spectroscopy, Wiley-VCH*
Circuit Elements

- **Resistor**
  \[ Z_R = R \]

- **Capacitor**
  \[ Z_C = -\frac{i}{\omega C} \]

- **Inductance**
  \[ Z_{In} = i\omega L \]

- **Warburg Element** (diffusion resistance)
  \[ Z_W = \frac{\sigma}{\omega^{1/2}} - i \frac{\sigma}{\omega^{1/2}} \]

\[
\sigma = \frac{RT}{(nF)^2 \sqrt{2}} \left[ \frac{1}{c_{b,ox} \cdot D_{ox}^{1/2}} + \frac{1}{c_{b,red} \cdot D_{red}^{1/2}} \right]
\]
Graphical representation

\[ Z = Z_1 + Z_2 \quad \text{for serial connection} \]

- **X-axis**: ohmic resistance, \( \text{Re}Z \)
- **Y-axis**: \(-\text{Im}Z\), here \(-i/\omega C\)

\[ |Z(\omega)| = \left[ \text{Re}(Z)^2 + \text{Im}(Z)^2 \right]^{1/2} \]

\[ \tan \phi = \frac{\text{Im}(Z)}{\text{Re}(Z)} \]
Graphical representation

\[ \frac{1}{Z(\omega)} = \frac{1}{R_{CT}} - \frac{\omega C_{DL}}{i} \]

for parallel connection

\[ \frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} \]

\[ C_{dl} = 10 \mu F \]

\[ R_F = 100 \Omega \]

\[ \text{ImZ} / \Omega \]

\[ \text{ReZ} / \Omega \]
Graphical representation

Randles Circuit
Represents the electrochemical cell

\[ Z(\omega) = R_S + \frac{1}{R_{CT} \omega C_{DL}} = R_S + \frac{R_{CT}}{1 + i\omega C_{DL} R_{CT}} \]

Separation of real from complex part:

\[ Z(\omega) = R_S + \frac{R_{CT}}{1 + i\omega C_{DL} R_{CT}} \cdot \frac{1 - iC_{DL} R_{CT}}{1 - iC_{DL} R_{CT}} \]

\[ Z(\omega) = R_S + \frac{R_{CT}}{1 + (\omega C_{DL} R_{CT})^2} - i \cdot \frac{\omega C_{DL} R_{CT}}{1 + (\omega C_{DL} R_{CT})^2} \]
Graphical representation

\[ Z(\omega) = R_S + \frac{1}{\frac{1}{R_{CT}} - \frac{\omega C_{DL}}{i}} = R_S + \frac{R_{CT}}{1 + i\omega C_{DL}R_{CT}} \]
Graphical representation. Other Plots

RC\text{CT}  
R_S  
C_{DL}  

Admittance \quad Y = \frac{1}{Z}

\[
\begin{align*}
C_{\text{dl}} &= 20 \mu F \\
R_F &= 10 k\Omega \\
R_S &= 1 k\Omega
\end{align*}
\]
Warburg Impedance – Diffusion Limitation

\[ Z_W = \frac{\sigma}{\omega^{1/2}} - i \frac{\sigma}{\omega^{1/2}} \]

\[ \sigma = \frac{RT}{(nF)^2} \frac{1}{\sqrt{2}} \left[ \frac{1}{c_{b,ox} \cdot Dox^{1/2}} + \frac{1}{c_{b,red} \cdot Dred^{1/2}} \right] \]

\[ \sigma = \frac{RT}{(nF)^2} \frac{\sqrt{2}}{c_b D^{1/2}} \quad \text{for identical c and D} \]

\[ R_S = 1 \Omega \text{cm}^2; \quad R_F = 5 \Omega \text{cm}^2; \quad C_{dl} = 20 \mu\text{F cm}^{-2} \]

\[ c_{b,ox} = c_{b,red} = 10 \text{mM}; \quad D = 1 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}, \quad k_{sh} = 5 \times 10^{-3} \text{ cm s}^{-1}. \]
Warburg Impedance: Changing concentrations

\begin{align*}
a & \quad c = 100 \text{ mM} \quad j_0 = 26 \text{ mA cm}^{-2} \\
b & \quad c = 10 \text{ mM} \quad j_0 = 2.6 \text{ mA cm}^{-2} \\
c & \quad c = 1 \text{ mM} \quad j_0 = 0.26 \text{ mA cm}^{-2} \\
d & \quad c = 0.1 \text{ mM} \quad j_0 = 26 \mu\text{A cm}^{-2}
\end{align*}
Example from Redox Flow Cell Research

- Electrolyte storage
- Current collector Electrode (carbon felt) (Nafion117®)
- Membrane flow field
Reaction on VRB

Oxidation (-)

\[ V^{2+} \rightarrow V^{3+} + e^- \]

Discharge

Reduction (+)

\[ VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \]
**Ideal Nernstian behaviour**

\[
\Delta E_p = E_{p,a} - E_{p,c} = \frac{59}{n} \text{ mV}
\]

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(\Delta E_p), mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated GC</td>
<td>710</td>
</tr>
<tr>
<td>Heat GC</td>
<td>700</td>
</tr>
<tr>
<td>Acid GC</td>
<td>510</td>
</tr>
<tr>
<td>EC oxidised GC</td>
<td>186</td>
</tr>
<tr>
<td>Rough GC</td>
<td>184</td>
</tr>
<tr>
<td>Rough+EC oxidised GC</td>
<td>165</td>
</tr>
</tbody>
</table>

Most active for V(V) reduction
Impedance Spectroscopy

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_{CT}$ $\Omega\text{cm}^2$</th>
<th>$\Delta E_p$ mV</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated GC</td>
<td>30.2</td>
<td>710</td>
<td>$24.77 \times 10^{-3}$</td>
</tr>
<tr>
<td>EC oxidised GC</td>
<td>9.2</td>
<td>186</td>
<td>$3.019 \times 10^{-3}$</td>
</tr>
<tr>
<td>Rough GC</td>
<td>8.7</td>
<td>184</td>
<td>$3.06 \times 10^{-3}$</td>
</tr>
<tr>
<td>Rough+EC oxidised GC</td>
<td>5.4</td>
<td>165</td>
<td>$13.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$\eta = 10$ mV

Equivalent Electrical circuit

\[ R_{\text{E}} \quad \text{R}_{\text{CT}} \quad C_{\text{DL}} \]