Impedance Tutorial
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UV-Vis Spectroscopy

Input

\[ h\nu \]

Sample

\[ I_0 \]

Output

\[ I \]

• Scan Frequency: \(~ 3-8 \times 10^{14}\) Hz
• Change in Amplitude of signal- Related to the Transmittance(\(\nu\))
• Gain Information about the effect of frequency on the sample
**Impedance Spectroscopy**

- **Input Voltage Signal**
- **Sample Cell**
- **Output Current Signal**

- Scan Frequency: $\sim 0.01 - 1 \text{ MHz}$
- Change in Amplitude and phase related to the Impedance($\nu$)
- Difference elements respond differently to different Frequencies
Dependence of Resistor

**Resistor**

**Ohms Law**

\[ R = \frac{V}{I} \]

\[ Z = \frac{V(t)}{I(t)} \]

**Input Voltage**

\[ V(t) = \sin(\omega t) \]

**Output Current**

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

**Phase Angle**

\[ \phi = 0^\circ \]
Dependance of a Capacitor

\[ Q = CV \]
\[ \frac{dQ}{dt} = C \frac{dV}{dt} \]

\[ V(t) = \sin(\omega t) \]
\[ I(t) = C \omega \cos(\omega t) \]
\[ I(t) = C \omega \sin(\omega t + 90^\circ) \]

\[ Z = \frac{V(t)}{I(t)} \]

\[ Z_{\text{Capacitor}} = \frac{1}{\omega C} \]

Phase \( \phi = 90^\circ \)
How to Visualize the Data?

Magnitude, $Z_0$  Phase Angle, $\phi$

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$

Nyquist Plot (Complex Plane)

Bode Plots

Phase Angle $\phi = -51.7^\circ$
Common Electrode-Electrolyte System

- Faradaic Current
  \[ e^- + \rightarrow \]

- Nonfaradaic Current (Capacitive Charging)
  \[ C_{dl} \]
The diagram illustrates a frequency-dependent circuit with the following components:

- **R<sub>s</sub>**
- **R<sub>ct</sub>**
- **C<sub>dl</sub>**

The impedance of the capacitor at high frequency is given by:

\[ Z_{\text{capacitor}} = \frac{1}{i\omega C} \]

And the impedance of the resistor is:

\[ Z_{\text{resistor}} = R \]

At high frequency (**ω → ∞**), the capacitor impedance approaches zero:

\[ Z_{\text{capacitor}} \rightarrow 0 \]

At low frequency (**ω → 0**), the capacitor impedance approaches infinity:

\[ Z_{\text{capacitor}} \rightarrow \infty \]

The Bode plots show the magnitude (IZI) and phase (ϕ) of the circuit components over frequency. The plots indicate a phase shift of **-90°** at low frequencies and **0°** at high frequencies, with the overall resistance (**R<sub>1</sub> + R<sub>2</sub>**) remaining constant.
**Frequency Dependent Circuit**

\[ Z_{\text{Capacitor}} = \frac{1}{i\omega C} \quad Z_{\text{resistor}} = R \]

**High Frequency**  
\( \omega \rightarrow \infty \)  
"Looks like" \( R_s \)

**Low Frequency**  
\( \omega \rightarrow 0 \)  
"Looks like" \( R_s \parallel R_{ct} \)

**Bode Plots**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>( I_Z I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 )</td>
<td>( 0^\circ )</td>
</tr>
<tr>
<td>( R_1 + R_2 )</td>
<td>( \sim -90^\circ )</td>
</tr>
</tbody>
</table>

**Frequency**
Frequency Dependent Circuit

Nyquist Plot

High Frequency \( \omega \rightarrow \infty \)
\[
Z_{\text{Capacitor}} \rightarrow 0
\]

Low Frequency \( \omega \rightarrow 0 \)
\[
Z_{\text{Capacitor}} \rightarrow \infty
\]

\[
\tau = R_{\text{ct}} \cdot C_{\text{dl}}
\]

\[
R_{\text{ct}} = \frac{1}{i \omega C}
\]

\[
Z_{\text{resistor}} = R
\]

\[
\omega = \frac{1}{\tau}
\]

\[
\mathcal{R} = R_{\text{ct}}
\]

\[
\mathcal{L} = R_{\text{s}}
\]

\[
Z_{\text{Real}}
\]

\[
Z_{\text{im}}
\]
Running The Experiment

DEMO

\[ R_u \quad 2.95 \text{k}\Omega \quad - \quad 3.07 \text{k}\Omega \]
\[ R_1 \quad 196 \text{\Omega} \quad - \quad 204 \text{\Omega} \]
\[ C_1 \quad 0.9 \mu\text{F} \quad - \quad 1.10 \mu\text{F} \]
**Impedance Applications**

- **A** = region of high frequencies (MHz – KHz)
- **B** = region of low frequencies (Hz – µHz)

Impedance Applications

Butler-Volmer Equation

\[ i = i_0 \exp(\alpha \frac{nF}{RT} \eta) - \exp(-(1 - \alpha) \frac{nF}{RT} \eta) \]

Low Overpotential

\[ e^x \rightarrow (1 + x) \]

\[ R_{ct} = \frac{RT}{nF i_0} \]

Used to calculate \( i_0 \) (exchange current density)

Good Representation of catalytic activity of the electrode surface toward a specific redox couple