Electrochemical Impedance Spectroscopy

When used to study electrochemical systems, electrochemical impedance spectroscopy (EIS) can give you kinetic and mechanistic information in the study of corrosion, batteries, electroplating, and electro-organic synthesis.

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. Assume that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal.

The main advantage of EIS is that you can use a purely electronic model to represent an electrochemical cell. An electrode interface undergoing an electrochemical reaction is typically analogous to an electronic circuit (or equivalent circuit) consisting of a specific combination of resistors and capacitors.

In practice, you can correlate an impedance plot obtained for a given electrochemical system with one or more equivalent circuits. You can use this information to verify a mechanistic model for the system. Once you choose a particular model, you can correlate physical or chemical properties with circuit elements and extract numerical values by fitting the date to the circuit model.
Linearity of Electrochemistry Systems

A linear system ... is one that possesses the important property of superposition: If the input consists of the weighted sum of several signals, then the output is simply the superposition, that is, the weighted sum, of the responses of the system to each of the signals. Mathematically, let $y_1(t)$ be the response of a continuous time system to $x_1(t)$ and let $y_2(t)$ be the output corresponding to the input $x_2(t)$. Then the system is linear if:
1) The response to $x_1(t) + x_2(t)$ is $y_1(t) + y_2(t)$
2) The response to $x_1(t)$ is $y_1(t)$ ...

For a potentiostated electrochemical cell, the input is the potential and the output is the current. Electrochemical cells are not linear! Doubling the voltage will not necessarily double the current. However, electrochemical systems can be pseudo-linear. If you look at a small enough portion of a cell's current versus voltage curve, it appears to be linear. In normal EIS practice, a small (1 to 10 mV) AC signal is applied to the cell. With such a small potential signal, the system is pseudo-linear.

Current versus Voltage Curve Showing Pseudo-Linearity
**Electrochemical Impedance Spectroscopy**

Electrochemical impedance theory is a well-developed branch of ac theory that describes the response of a circuit to an alternating current or voltage as a function of frequency.

In dc theory (a special case of ac theory where the frequency equals 0 Hz), resistance is defined by Ohm's Law:

\[ E = I R \]

Using Ohm's law, you can apply a dc potential \( E \) to a circuit, measure the resulting current \( I \), and compute the resistance \( R \). Potential values are measured in volts \( (V) \), current in amperes or amps \( (A) \), and resistance in ohms \( (\Omega) \). A resistor is the only element that impedes the flow of electrons in a dc circuit.

In ac theory, where the frequency is non-zero, the analogous equation is:

\[ E = I Z \]

\( E \) and \( I \) are here defined as potential and current, respectively.

\( Z \) is defined as impedance, the ac equivalent of resistance.

Impedance values are also measured in ohms \( (\Omega) \). In addition to resistors, capacitors and inductors impede the flow of electrons in ac circuits.
Electrochemical Impedance Spectroscopy

In an electrochemical cell, slow electrode kinetics, slow preceding chemical reactions, and diffusion can all impede electron flow, and can be considered analogous to the resistors, capacitors, and inductors that impede the flow of electrons in an ac circuit.

The terms resistance and impedance both denote an opposition to the flow of electrons or current. In direct current circuits, only resistors produce this effect. However, in alternation current (ac) circuits, two other circuit elements, capacitors and inductors, impede the flow of electrons. Impedance can be expressed as a complex number.

The total impedance in a circuit is the combined opposition of all its resistors, capacitors, and inductors to the flow of electrons. The opposition of capacitors and inductors is given the same name reactance, symbolized by X and measured in ohms (Ω).
Since the symbol for capacitance is C, capacitive reactance is symbolized by $X_C$. Similarly, since the symbol for inductance is L, inductive reactance is symbolized by $X_L$. 
Electrochemical Impedance Spectroscopy

The current sine wave can be described by the equation:
\[ I(t) = A \sin (wt + \theta) \]
where
- \( I(t) = \) instantaneous current
- \( A = \) maximum amplitude
- \( w = \) frequency in radians per second = \( 2\pi f \) (where \( f = \) frequency in Hertz)
- \( t = \) time
- \( \theta = \) phase shift in radians

Vector analysis provides a convenient method of characterizing an ac waveform. It lets you describe the wave in terms of its amplitude and phase characteristics.
Electrochemical Impedance Spectroscopy

\[ Z_{\text{Total}} = \frac{E' + E''j}{I' + I''j} \]

\[ E_{\text{total}} = E' + E''j \]
\[ I_{\text{total}} = I' + I''j \]
\[ |Z| = \sqrt{Z'^2 + Z''^2} \]
\[ \tan \theta = \frac{Z''}{Z'} \]
\[ Z = Z' - Z''j \text{ (제 4 상한)} \]
Electrochemical Impedance Spectroscopy

In an electrochemical cell, slow electrode kinetics, slow preceding chemical reactions, and diffusion can all impede electron flow, and can be considered analogous to the resistors, capacitors, and inductors that impede the flow of electrons in an ac circuit.

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Electrochemical Impedance Spectroscopy

Impedance expressions for some simple electrical circuits.

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<tr>
<th>Circuit Element</th>
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<tr>
<td><img src="Image" alt="Resistor" /></td>
<td>$Z = R + j\omega C$</td>
</tr>
<tr>
<td><img src="Image" alt="Capacitor" /></td>
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Impedance of a resistor has no imaginary component at all. The phase shift is zero degrees - that is, the current is in phase with the voltage. Both current and impedance are independent of the frequency.

The impedance of a capacitor has no real component. Its imaginary component is a function of both capacitance and frequency. The current through a capacitor is always 90 degrees out of phase with the voltage across it, with current leading the voltage. Because the impedance of a capacitor varies inversely with frequency, at high frequencies a capacitor acts as a short circuit - it's impedance tends toward zero. At low frequencies (approaching dc) a capacitor acts as an open circuit, and the impedance tends toward infinite.
Electrochemical Impedance Spectroscopy

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<tr>
<td></td>
<td>$Z = 0 - j/\omega C$</td>
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<tr>
<td></td>
<td>$Z = \frac{R}{1 + \omega^2 CR^2} - \frac{j\omega CR^2}{1 + \omega^2 CR^2}$</td>
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The third simple electrical component is the inductor. Like a capacitor, the current through an inductor is always 90 degrees out of phase with the voltage drop across it. However, the phase shift is in the opposite direction - the current lags behind the voltage. Also, as the frequency increases, the impedance of an inductor increases. It acts as a short circuit at low frequencies and as a large impedance at high frequencies.
## Electrochemical Impedance Spectroscopy

Impedance expressions for some simple electrical circuits.

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![Impedance Diagram]
Impedance Plot Analysis

You can study an equivalent circuit by deriving its impedance equation. However, it’s simpler to perform a measurement on the circuit and analyze the resulting plot.

Equivalent Circuit for a Single Electrochemical Cell

Equivalent Circuit for a Metal Coated with a Porous, Non-conductive Film
Impedance Analysis

Impedances in Series

\[ Z_{eq} = Z_1 + Z_2 + Z_3 \]

Impedances in Parallel

\[ \frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3} \]
**Impedance Plot Analysis**

![Equivalent Circuit for a Single Electrochemical Cell](image)

The impedance of a capacitor diminishes as the frequency increases, while the impedance of a resistor is constant. Thus, above a certain frequency, the impedance of the capacitor, $C_{DL}$, becomes much smaller than the impedance of the resistor, $R_p$. Since $C_{DL}$ is in parallel with $R_p$, the capacitor acts as a short and effectively removes the resistor from the circuit.

**At the highest frequencies**, the impedance of the capacitor will also become much smaller than $R_\Omega$. Thus, the high frequency behavior of the Randles cell is controlled almost entirely by $R_\Omega$. However, **at the lowest frequencies**, the capacitor acts as an open circuit and is effectively removed from the circuit. The impedance of the Randles cell is then the combined resistance values of the two series resistors $R_\Omega$ and $R_p$.

Thus, at both the high and the low frequency limits, the Randles cell behaves primarily as a resistor. The imaginary component is very small, the phase angle is close to 0 degrees, and the impedance does not change with frequency. **At intermediate frequencies**, the capacitor's impedance begins to have an effect and the cell becomes more capacitive. The imaginary component becomes significant, the phase angle can start to approach 90 degrees, and the cell impedance becomes frequency dependent.
Impedance Plot Analysis

To determine which equivalent circuit best describes the behavior of an electrochemical system, you must measure the impedance over a range of frequencies. The standard technique is to apply an ac voltage or current over a wide range of frequencies and measure the current or voltage response of the electrochemical system. You can then calculate the system's impedance by analyzing the response signal at each frequency. To completely describe the behavior of an electrochemical system, you must know the values of both the in-phase and out-of-phase impedance components at a number of frequencies across the range of interest. You can characterize most electrochemical systems quite well by gathering impedance data in the 0.001 Hz to 1 x 10^4 Hz frequency range.
At high frequencies, the impedance of the Randles cell was almost entirely created by the ohmic resistance, $R_\Omega$. The frequency reaches its high limit at the leftmost end of the semicircle, where the semicircle touches the x axis. At the low frequency limit, the Randles cell also approximates a pure resistance, but now the value is $(R_\Omega + R_p)$. The frequency reaches its low limit at the rightmost end of the semicircle.

The Nyquist plot has several advantages. The primary one is that the plot format makes it easy to see the effects of the ohmic resistance. If you take data at sufficiently high frequencies, it is easy to extrapolate the semicircle toward the left, down to the x axis to read the ohmic resistance. The shape of the curve (often a semicircle) does not change when the ohmic resistance changes. Consequently, it is possible to compare the results of two separate experiments that differ only in the position of the reference electrode! Another advantage of this plot format is that it emphasizes circuit components that are in series with $R_\Omega$. 
Nyquist Plot

The Nyquist plot format also has some disadvantages. For example, frequency does not appear explicitly. Secondly, although the ohmic resistance and polarization resistance can be easily read directly from the Nyquist plot, the electrode capacitance can be calculated only after the frequency information is known. The frequency corresponding to the top of the semicircle, $\omega_{\text{max}}$, can be used to calculate the capacitance if $R_p$ is known. Although the Nyquist format emphasizes series circuit elements, if high and low impedance networks are in series, you will probably not see the low impedance circuit, since the larger impedance controls plot scaling.
**Bode Plot**

The Bode plot format lets you examine the absolute impedance, |Z|, and the phase shift, θ, of the impedance, each as a function of log (frequency). The Bode plot has some distinct advantages over the Nyquist plot. Since frequency appears as one of the axes, it’s easy to understand from the plot how the impedance depends on the frequency. The plot uses the logarithm of frequency to allow a very wide frequency range to be plotted on one graph, but with each decade given equal weight. The Bode plot also shows the impedance magnitude, |Z|, on a log axis.

This can be an advantage when the impedance depends strongly on the frequency, as is the case with a capacitor. The log |Z| vs. log w curve can yield values of $R_p$ and $R_Ω$. At the highest frequencies, the ohmic resistance dominates the impedance and log $(R_Ω)$ can be read from the high frequency horizontal plateau. At the lowest frequencies, polarization resistance also contributes, and log $(R_Ω + R_p)$ can be read from the low frequency horizontal plateau. At intermediate frequencies, this curve should be a straight line with a slope of -1. Extrapolating this line to the log |Z| axis at w = 1 (log w = 0, f = 0.16 Hz) yields the value of $C_{DL}$ from the relationship: $|Z| = 1/C_{DL}$, where $w = 2πf$. 

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**Diagram Notes:**
- $C_{DL}$: Double layer capacitance
- $R_Ω$: Uncompensated resistance
- $R_p$: Polarization resistance
- $R$: Total resistance
Bode Plot

The Bode plot format also shows the phase angle, $\theta$. At the high and low frequency limits, where the behavior of the Randles cell is resistor-like, the phase angle is nearly zero. At intermediate frequencies, $\theta$ increases as the imaginary component of the impedance increases. The $\theta$ vs. log $w$ plot yields a peak at $w_{\theta_{\text{max}}}$, the frequency, in radians, at which the phase shift of the response is maximum. The double-layer capacitance, $C_{\text{DL}}$, can be calculated from the following equation.

$$\Omega_{(\theta = \text{MAX})} = \sqrt{\frac{1}{C_{\text{DL}}} R_p (1 + R_p/R_{\Omega})}$$

Note that both $R_p$ and $R_{\Omega}$ appear in this equation. It is important to remember that this frequency will not be the same as the frequency at which the Nyquist plot reaches its maximum.
The Bode plot is a useful alternative to the Nyquist plot. It lets you avoid the longer measurement times associated with low frequency \( R_p \) determinations. Furthermore, the log |\( Z \)| vs. log \( w \) plot sometimes allows a more effective extrapolation of data from higher frequencies. The Bode format is also desirable when data scatter prevents adequate fitting of the Nyquist semicircle.

At intermediate frequencies, the impedance of the capacitor \( C \), can control the total impedance of the Randles cell. The capacitor becomes the controlling component whenever \( R_{\Omega} \) and \( R_p \) differ by more than a factor of 100 or so. Under these conditions:

\[
Z_C = -j \omega C, \quad \text{and log } |Z| = \log \left( \frac{1}{\omega C} \right)
\]

\[
= -\log (\omega C) = -\log (w) - \log (C) = -\log (2\pi f) - \log (C) = -\log (2\pi) - \log (f) - \log (C)
\]

Note that the Bode plot of log |\( Z \)| vs log \( f \) or log \( w \) has a slope of \(-1\) in this region.

At this point \( f = 0.16 \text{ Hz}, \omega = 2\pi f = 1 \text{ and } \log (2\pi f) = 0. \)

Therefore: Log (|\( Z \)|) = -log (C) (when \( f = 0.16 \text{ Hz} \)) or |\( Z \) (\( f = 0.16 \text{ Hz} \)) | = 1/C
Bode Plot

Simple Equivalent Circuit with One Time Constant

Bode Plot with One Time Constant
On some electrochemical processes, there is more than one rate-determining step. Each step represents a system impedance component and contributes to the overall reaction rate constant. The electrochemical impedance experiment can often distinguish among these steps and provide information on their respective rates or relaxation times. This figure is typical of multiple time-constant Nyquist plots. While close inspection reveals two semicircles, one of the semi-circles is much smaller than the other, making it difficult to recognize multiple time constants.
These figures show Bode plots for the same data shown in the Nyquist plot. The Bode plot format lets you easily identify the frequency break points associated with each limiting step.
The Bode plot also has some disadvantages. The greatest one is that the shape of the curves can change if the circuit values change. The only differences are the values of the uncompensated resistance $R_\Omega$. Note that the location (θ= MAX) and height of the phase maximum depend on the value of $R_\Omega$. Also note that the slope of the central portion of the log $|Z|$ plot is influenced by the value of $R_\Omega$ as well.
Circuit Elements

Electrolyte Resistance

Solution resistance is often a significant factor in the impedance of an electrochemical cell. Any solution resistance between the reference electrode and the working electrode must be considered when you model your cell. The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature, and the geometry of the area in which current is carried. In a bounded area with area, A, and length, l, carrying a uniform current, the resistance is defined as,

\[ R = \rho \left( \frac{l}{A} \right) \]

\( \rho \) is the solution resistivity. The reciprocal of \( \rho \), conductivity (\( \kappa \)), is more commonly used. \( \kappa \) is called the conductivity of the solution.

\[ R = \frac{1}{\kappa \cdot \frac{l}{A}} \Rightarrow \kappa = \frac{l}{RA} \]
Circuit Elements

Double Layer Capacitance

An electrical double layer exists on the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution "stick on" the electrode surface. The charged electrode is separated from the charged ions. The separation is very small, often on the order of angstroms. Charges separated by an insulator form a capacitor. On a bare metal immersed in an electrolyte, you can estimate that there will be 20 to 60 μF of capacitance for every 1 cm² of electrode area. The value of the double layer capacitance depends on many variables. Electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc. are all factors.
Circuit Elements

Charge Transfer Resistance

As an example of a single reaction at equilibrium, consider a metal substrate in contact with an electrolyte. The metal can electrolytically dissolve into the electrolyte, according to,

\[ M \leftrightarrow M^{n+} + ne^- \]

or more generally

\[ \text{Red} \leftrightarrow \text{Ox} + ne^- \]

In the forward reaction in the first equation, electrons enter the metal and metal ions diffuse into the electrolyte. Charge is being transferred. This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.

\[
i = i_0 \left( \frac{C_0}{C_{0}^*} \exp\left(\frac{\alpha nF \eta}{RT}\right) - \left(\frac{C_R}{C_{R}^*}\right) \exp\left(-\left(1 - \alpha\right)\frac{nF \eta}{RT}\right) \right)\]

When the concentration in the bulk is the same as at the electrode surface, \( C_0 = C_{0}^* \) and \( C_R = C_{R}^* \).

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

When the overpotential, \( \eta \), is very small and the electrochemical system is at equilibrium,

\[
R_{ct} = \frac{RT}{nFi_0}\]
Circuit Elements

Coating Capacitance

A capacitor is formed when two conducting plates are separated by a non-conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is,

\[ C = \frac{\varepsilon_o \varepsilon_r A}{d} \]

\( \varepsilon_o \) = permittivity of free space
\( \varepsilon_r \) = dielectric constant (relative electrical permittivity)
\( A \) = surface of one plate
\( d \) = distances between two plates
Circuit Elements

Constant Phase Element

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element as defined below.

\[ Z_{CPE} = \frac{1}{(j\omega)^\alpha Y_0} \]

\[ Y_0 = C = \text{capacitance} \]
\[ \alpha = \text{generally 0.9-1.0 (}\alpha=1 \text{ for an ideal capacitor)} \]

For a constant phase element, the exponent \( \alpha \) is less than one. The "double layer capacitor" on real cells often behaves like a CPE, not a capacitor. While several theories (surface roughness, “leaky” capacitor, nonuniform current distribution, etc.) have been proposed to account for the non-ideal behavior of the double layer, it is probably best to treat \( \alpha \) as an empirical constant (fitting parameter) with no real physical basis.
Circuit Elements

Virtual Inductor

The impedance of an electrochemical cell sometimes also appears to be inductive. Some workers have ascribed inductive behavior to the formation of a surface adsorption layer, like a passive layer or fouling. Others have claimed that inductive behavior results from errors in the measurement.
**Circuit Elements**

**Diffusion (infinite Warburg impedance)**

Diffusion also can create an impedance called a Warburg impedance. The impedance depends on the frequency of the potential perturbation. At high frequencies, the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies, the reactants have to diffuse farther, increasing the Warburg-impedance.

The equation for the "infinite" Warburg impedance is:

\[ Z_w = \sigma (\omega)^{-\frac{1}{2}} (1-j) \]

On a Nyquist Plot the Warburg impedance appears as a diagonal line with an slope of 45°. On a Bode Plot, the Warburg impedance exhibits a phase shift of 45°.

\[ \sigma = \frac{RT}{n^2F^2A\sqrt{2}} \left( \frac{1}{C^{*o}\sqrt{D_O}} + \frac{1}{C^{*r}\sqrt{D_R}} \right) \]

\( \omega \) = radial frequency  
\( D_O \) = diffusion coefficient of the oxidant  
\( D_R \) = diffusion coefficient of the reductant  
\( A \) = surface area of the electrode  
\( n \) = number of electrons involved
Equivalent Circuit

Purely Capacitive Coating

A metal covered with an undamaged coating generally has a very high impedance. The model includes a resistor (due primarily to the electrolyte) and the coating capacitance in series.
Equivalent Circuit

Simplified Randles Cell

The Simplified Randles cell is one of most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer (or polarization resistance). The double layer capacitance is in parallel with the charge transfer resistance. In addition to being a useful model in its own right, the Simplified Randles Cell is the starting point for other more complex models.
Equivalent Circuit

Mixed Kinetic and Diffusion Control

First consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.
Equivalent Circuit

Mixed Kinetic and Diffusion Control

First consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.
Electrochemical Reaction

Equivalent Circuit

EIS of Coated Metals

The impedance behavior of a purely capacitive coating was discussed above. Most paint coatings degrade with time, resulting in more complex behavior. After a certain amount of time, water penetrates into the coating and forms a new liquid/metal interface under the coating. Corrosion phenomena can occur at this new interface.