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A study on electrochemical impedance spectroscopy

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Abstract
Electrochemical impedance spectroscopy (EIS) is an electrochemical technique which is used for determining various electrochemical processes occurs on electrode. This is also used for making batteries, to study corrosion etc. It is measured as opposition voltage when current is applied. EIS is interpreted by Nyquist and Bode plots. Many types of resistance, double layer phenomenon, zeta potentials etc. are studied by this process.

Keywords: Electrochemical impedance spectroscopy, Nyquist plots, Bode plots

Introduction
In electrochemical systems, Electrochemical Impedance spectroscopy (EIS) is one of the main technique. Electrochemical impedance spectroscopy has been widely used for a long time in the field of electrochemistry, e.g., electrodes kinetics, double layer studies, study of mechanisms of interfacial processes, evaluation of parameters like rate constants and double layer capacitance. This method is also used extensively in applied systems like batteries, corrosion, bio-electrochemistry, etc. In contrast to other electrochemical techniques, it is noninvasive and can be used for studying bulk as well as interfacial processes connected with time constants ranging from minutes down to microseconds. It is a nondestructive method to differentiate time constants related to the processes occurring at the electrolyte/electrode interfaces.

Electrical impedance is the measure of the opposition that a circuit presents to a current when a voltage is applied. In quantitative terms, it is the complex ratio of the voltage to the current in an alternating current (AC) circuit. Impedance extends the concept of resistance to AC circuits, and possesses both magnitude and phase, unlike resistance, which has only magnitude. In this paper, it is discussed that Electrochemical Impedance spectroscopy (EIS) is one of electrochemical method which is used for various phenomenon such as double layer studies, electrode kinetics and study of resistance in AC circuit etc.

The impedance is measured as a function of the frequency of the AC source. The technique where the cell or electrode impedance is plotted vs. frequency is called electrochemical impedance spectroscopy (EIS).

Impedance assumes an AC current of a specific frequency in Hertz (cycles/s).

Impedance: $Z = E/I$

Where E = Frequency-dependent potential

I = Frequency-dependent current

This equation is used only the ideal resistor. An ideal resistor is which follow:

- Ohm's Law at all current and voltage levels.
- Its resistance value is independent of frequency.
- AC current and voltage signals though a resistor should be in phase with each other

A purely sinusoidal voltage can be expressed as

$E = E_o \sin\omega t$ ------- (1)

where w is the angular frequency.

We have to consider the relationship between two related sinusoidal signals, such as the current, I, and the voltage, E. Each is then represented as a separate phasor, I or E, rotating at the same frequency.

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As shown in Figure 1, they generally will not be in phase; thus their phasors will be separated by a phase angle, φ. One of the phasors, usually E, is taken as a reference signal, and φ is measured with respect to it. It can be expressed generally as

$$I = I_o \sin(wt + \phi) \qquad \text{------(2)}$$

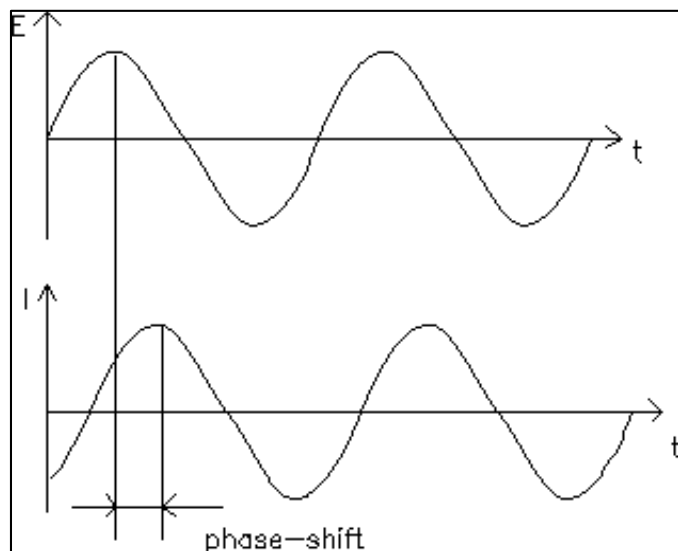where φ is a signed quantity, which is negative in this case.

Fig 1: Sinusoidal Current Response in a Linear System

The relationship between two phasors at the same frequency remains constant as they rotate; hence the phase angle is constant. Consequently, we can usually drop the references to rotation in the phasor diagrams and study the relationships between phasors simply by plotting them as vectors having a common origin and separated by the appropriate angles.
Let us apply these concepts to the analysis of some simple circuits.

Eis of A Resistance: Let's take a pure resistance, R, across which a sinusoidal voltage, e = Esinωt, is applied. Since Ohm's law always holds, the current is
(E/R)sinωt or, in phasor notation,

$$E = IR \qquad \text{------(3)}$$

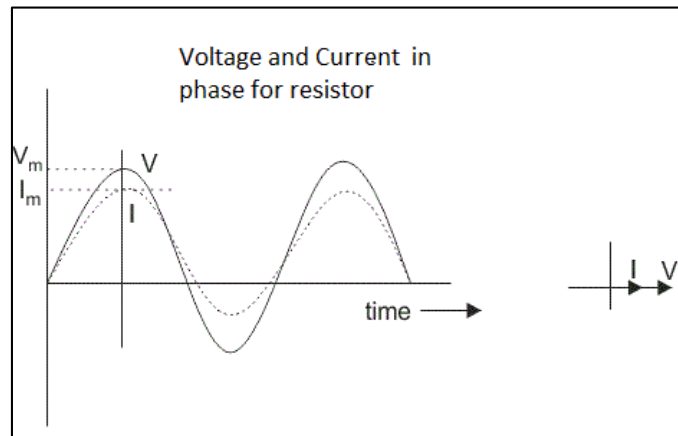The phase angle is zero, and the vector diagram is that of Figure 2.

Fig 2: Relationship between the voltage across a resistor and current through the resistor.

Eis Of A Capacitor: Consider first a pure capacitance, C. The fundamental relation is q = Ce, or i = C (de/dt) thus
i=wCE cos wt

$$i = E/Xc \sin (wt+\pi/2) \qquad \text{------(4)}$$

where Xc is the capacitive reactance, l/wC. The phase angle is π/2, and the current leads the voltage, as shown in Figure 3.
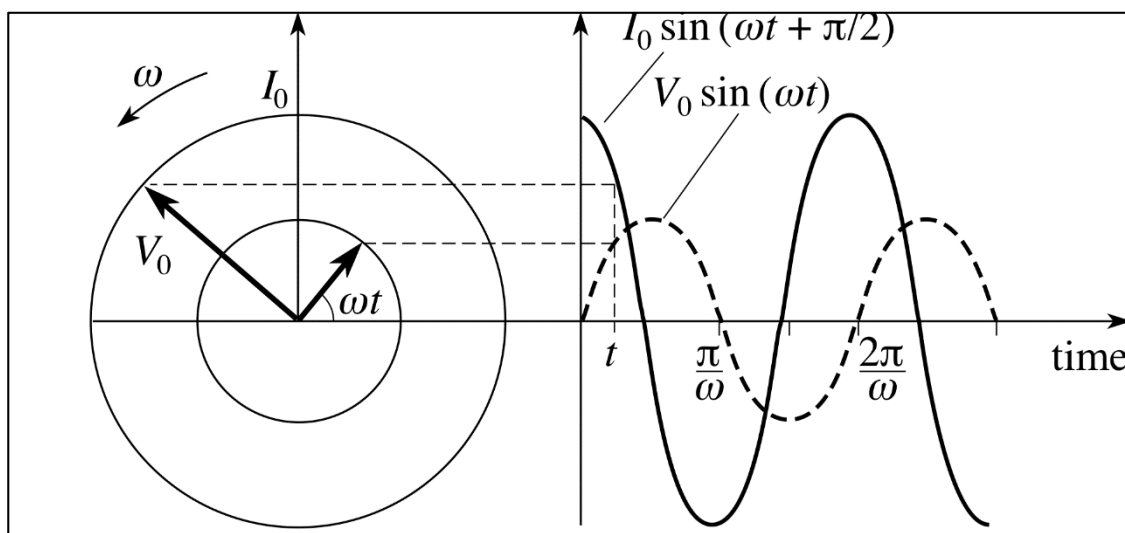

Fig 3: Relationship between an alternating voltage across a capacitor and the alternating current through the capacitor.

Since the vector diagram has now expanded to a plane, it is convenient to represent phasors in terms of complex notation. Components along the ordinate are assigned as imaginary and are multiplied by $j = \sqrt{-1}$. Components along the abscissa are real.
It is clear that,
E = -jXcI

A comparison of equations for resistor and capacitor shows that Xc must carry dimensions of resistance, but, unlike R, its magnitude falls with increasing frequency.

Eis of Series Combination Of Resistance And Capacitance: Consider a resistance, R, and a capacitance, C, in series. A voltage, E, is applied across them, and at all times

it must equal the sum of the individual voltage drops across the resistor and the capacitor; thus

$E = E_R + E_c$

$E = I(R - jX_c)$ ----- (5)

$E = IZ$

We find that the voltage is linked to the current through a vector $Z = R - jX_c$ called the impedance. In general the impedance can be represented as

$Z(\omega) = Zre - j\ Zim$ ----- (6)

where Zre and Zim are the real and imaginary parts of the impedance. For the example here, $Zre = R$ and $Zim = Xc = l/\omega C$. The magnitude of Z, written |Z |or Z, is given by

$|Z|^2 = R^2 + Xc^2 = (Zre)^2 + (Zim)^2$ ----- (7)

and the phase angle, ϕ, is given by

$\tan \phi = Zim/Zre = Xc/R = 1/\omega RC$ ----- (8)

The impedance is a kind of generalized resistance. The phase angle expresses the balance between capacitive and resistive components in the series circuit. For a pure resistance, $\phi = 0$; for a pure capacitance, $\phi = \pi/2$; and for mixtures, intermediate phase angles are observed.

Impedance

An expression according to Ohm's Law gave the impedance of the system as:

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

So, impedance is expressed in terms of a magnitude, Z_o, and a phase shift, Φ

If we plot the applied sinusoidal signal E(t) on the X-axis of a graph and the sinusoidal response signal I(t) on the Y-axis, the result is an oval. This oval is known as a "Lissajous Figure" shown below-
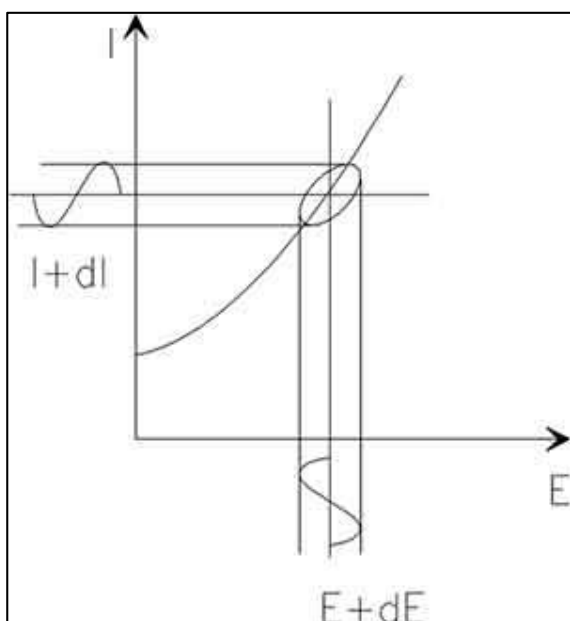

Fig 4: Lissajous Figure

Data interpretation

The impedance is represented as a complex number and can be written as follows:

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)$$

----- (9)

EIS data may be displayed as either a vector or a complex quantity.

The expression for $Z(\omega)$ is composed of a real and an imaginary part. EIS data may be presented as a Bode Plot or a Complex Plane (Nyquist) Plot.

Nyquist Plot: If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a "Nyquist Plot".

It displays Z_{im} vs. Z_{Re} for different values of ω.

Nyquist Plots have one major shortcoming. When we look at any data point on the plot, we cannot tell what frequency was used to record that point.
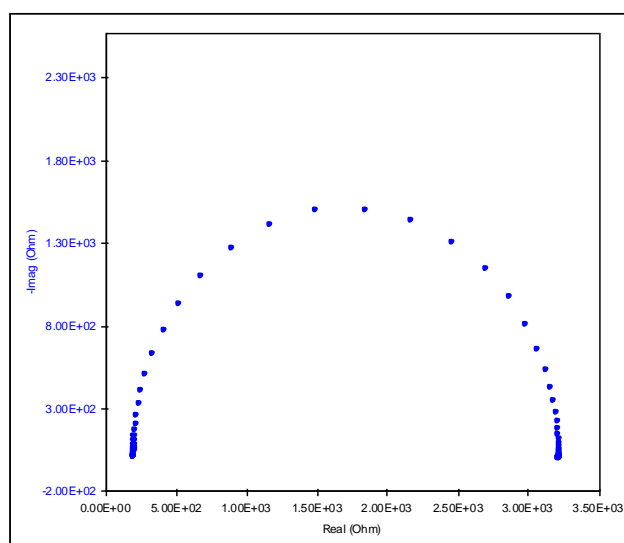

Fig 5: Nyquist Plot

Bode Plot: In a Bode plot, log |Z| and ϕ are both plotted against log ω.

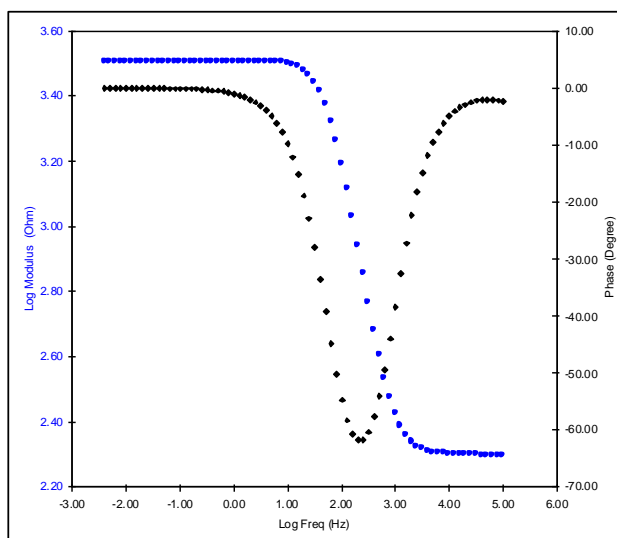Unlike the Nyquist Plot, the Bode Plot does show frequency information.

Fig 6: Bode Plot

Table 1: Nyquist vs. Bode Plot

Nyquist Plot	Bode Plot
Individual charge transfer processes are resolvable	Individual charge transfer processes are resolvable
Frequency is not obvious	Frequency is explicit
Small impedance cannot be identified in presence of large impedance	Small impedance can be calculated even in presence of large impedance

Admittance: Sometimes it is easy to analyze ac circuit in terms of admittance, represented as Y which is the inverse impedance, 1/Z, and therefore represents a kind of conductance. The generalized form of Ohm's law can then be rewritten as

I= EY

These concepts are especially useful in the analysis of parallel circuits, because the overall admittance of parallel elements is simply the sum of the individual admittances.
Vector relationship between Z and Y can be given as follows:
If Z is written in its polar form.

$Z = Z\exp(j\varphi)$

then the admittance is

$Y = 1/Z \exp(-j\varphi)$ ---- (10)

Here we see that Y is a vector with magnitude 1/Z and a phase angle equal to that of Z, but opposite in sign.
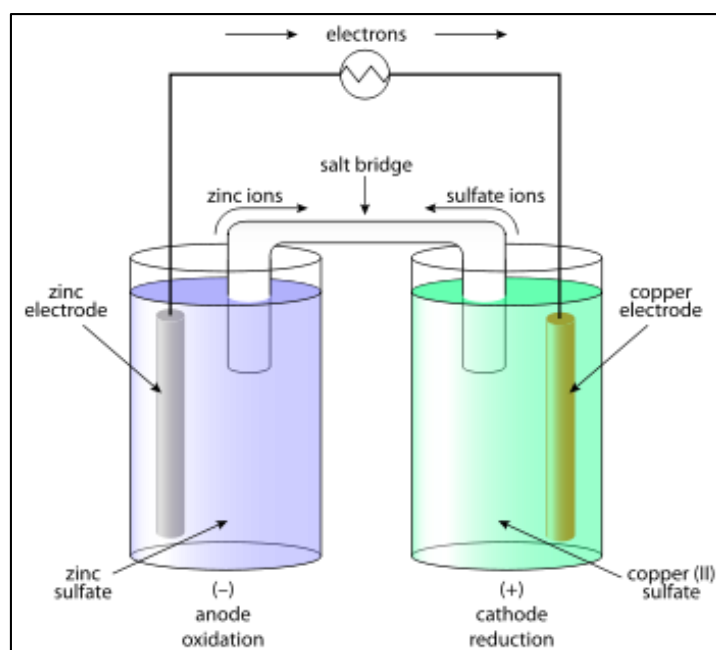
Electrochemical Cell
An electrochemical cell is a device which convert electrical energy to chemical energy or chemical energy to electrical energy. It is of two types:
Galvanic cell which converts chemical energy to electrical energy and electrolytic cell which converts electrical energy to chemical energy.
It is made up of two half-cells. Each half-cell consists of an electrode and an electrolyte. The two electrodes are cathode and anode on anode there occurs oxidation and at cathode reduction occurs. Sign convention differs in both type of electrochemical cells. The two half-cells may use the same electrolyte, or they may use different electrolytes. A salt bridge (mainly made up of $KNO3$ in agar-agar, $NaCl$, or some other electrolyte) is often employed to provide ionic contact between two half-cells with different electrolytes and prevent the solutions from direct mixing which may cause side reactions.
Each half-cell has a characteristic voltage. Various choices of substances for each half-cell give different potential differences. Each reaction is undergoing an equilibrium reaction between different oxidation states of the ions.

Fig 7: Cu-Zn galvanic cell

Equivalent Circuit Elements (Analysis of Eis)
Electrochemical cells can be modeled as a network of passive electrical circuit elements. A network is called an "equivalent circuit". In a general sense, an electrochemical cell can be considered simply an impedance to a small sinusoidal excitation; hence we ought to be able to represent its performance by an equivalent circuit of resistors and capacitors that pass current with the same amplitude and phase angle that the real cell does under a given excitation.
The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.

Different equivalent circuit elements are described below
Electrolyte Resistance
Solution resistance is often a significant factor in the impedance of an electrochemical cell**.** Resistance is which oppose the current flow and according to ohm's law given as
V=IR
Here, V is potential and I is current and R is resistance.
SI unit of resistance is Ohm.
Resistance is measured with the help of Wheatstone bridge, it is an electrical circuit used to measure an unknown electrical resistance by balancing two legs of a bridge circuit, one leg of which includes the unknown component.
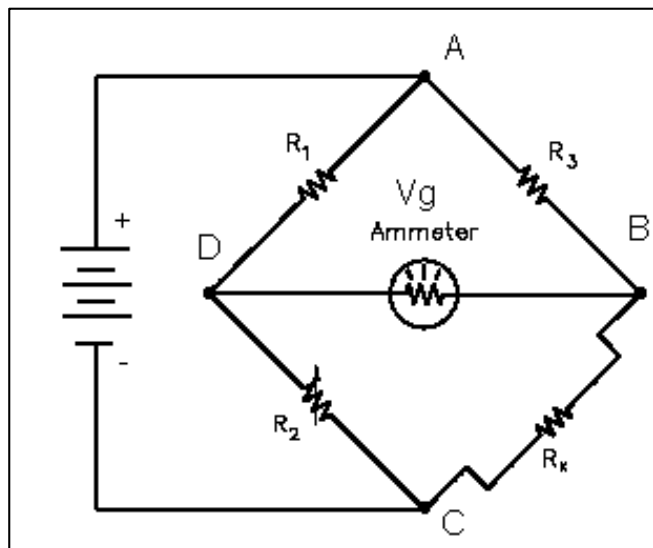
Fig 8: A Wheatstone Bridge

Here R_1, R_2 (variable) and R_3 are known resistance and R_x is unknown resistance which is calculated by equation-

$R_1/R_2 = R_3/R_x$

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,

$$R = \rho \frac{l}{A}$$

where ρ is the solution resistivity. κ is called the conductivity of the solution and its relationship with solution resistance is:

$$R = \frac{1}{\kappa} \cdot \frac{l}{A} \Rightarrow \kappa = \frac{l}{RA}$$

$\qquad$ ---- (11)

The units of κ is Siemens per meter (S/m). The Siemen is the reciprocal of the ohm, so 1 S = 1/ohm.

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 adsorb onto the electrode surface. The charged electrode is separated from the charged ions by an insulating space, often on the order of angstroms. Charges separated by an insulator form a capacitor so a bare metal immersed in an electrolyte will be have like a capacitor. The value of the double layer capacitance depends on many variables like electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

Polarization Resistance

Whenever the potential of an electrode is forced away from its value at open-circuit, that is referred to as "polarizing" the electrode. When an electrode is polarized, it can cause current to flow through electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

In cells where an electrode undergoes uniform corrosion at open circuit, the open circuit potential is controlled by the equilibrium between two different electrochemical reactions. One of the reactions generates cathodic current and the other generates anodic current. The open circuit potential equilibrates at the potential where the cathodic and anodic currents are equal. It is referred to as a mixed potential.

Charge Transfer Resistance

Consider a metal substrate in contact with an electrolyte. The metal can electrolytically dissolve into the electrolyte, according to,

$$Me \Leftrightarrow Me^{n+} + ne^-$$

or more generally

$$Red \Leftrightarrow Ox + ne^-$$
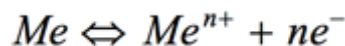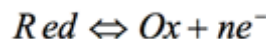
In the forward reaction in the first equation, electrons enter the metal and metal ions diffuse into the electrolyte. Charge is being transferred.

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.

The general relation between the potential and the current (which is directly related with the amount of electrons and so the charge transfer via Faradays law) is [1]

$$i = i_0 \left(\frac{C_O}{C^*_O} \exp\left(\frac{\alpha n F \eta}{RT}\right) - \left(\frac{C_R}{C^*_R} \exp\left(\frac{-(1-\alpha)nF\eta}{RT}\right) \right) \right)$$

$\qquad$ --(12)

Where

i_0 = exchange current density
C_O = concentration of oxidant at the electrode surface
C_O^* = concentration of oxidant in the bulk
C_R = concentration of reductant at the electrode surface
η = overpotential (Eapp – Eoc)
F = Faradays constant
T = temperature
R = gas constant
a = reaction order
n = number of electrons involved

When the concentration in the bulk is the same as at the electrode surface, $C_O = C_O^*$ and $C_R = C_R^*$. This simplifies above equation into:

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

$\qquad$ ---- (13)

This equation is called the Butler-Volmer equation. It is applicable when the polarization depends only on the charge-transfer kinetics. Stirring the solution to minimize the diffusion layer thickness can help minimize concentration polarization.

When the overpotential, η, is very small and the electrochemical system is at equilibrium, the expression for the charge-transfer resistance changes to:

$$R_{ct} = \frac{RT}{nFi_0}$$

---- (14)

From this equation the exchange current density can be calculated when Rct is known.

Conclusion
Electrochemical Impedance spectroscopy (EIS) is one of electrochemical method which is used for various phenomenon which is used for double layer studies, electrode kinetics and study of resistance in AC circuit. Nyquist Plots and Bode plots are used for data interpretation in this technique. Electrochemical cells are of two types galvanic and electrolytic cells. Different type of resistances are there such as electrolyte resistance depends upon concentration of electrolyte, charge transfer and polarization resistance.

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