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Electrochemical Impedance Spectroscopy and Its Applications

Camila Pía Canales

Abstract

Electrochemistry has become an important and recognized field for the future since many of its approaches contemplate the establishment of stable energy supplies and the minimization of our impact on the environment. In this regard, electrochemistry can face both objectives by studying the electrode/solution interface. As a result, different electrochemical techniques can be used to study the interface to understand the electron transfer phenomena in different reactions. Considering this, one of the most useful techniques to understand the electrode/solution interface is electrochemical impedance spectroscopy. This technique allows us to describe the electrode behavior in the presence of a certain electrolyte in terms of electrical parameters such as resistances and capacitances, among others. With this information, we can infer the electrochemical behavior toward a specific reaction and the capacity of the electrode to carry on the electron transfer depending on its resistance (impedance) values. The aim of this chapter is to go from the theory, based on Ohm's Law and its derivations, to actual applications. This will lead us to characterize the solution, electrode, and the interface between these two phases based on their electrical components by using an equivalent electrical circuit, such as the Randles equivalent circuit.

Keywords: electrochemical impedance spectroscopy, Randles equivalent circuit, electron transfer, Ohm's law, interface, electrocatalysis

1. Introduction

Electrochemistry is a branch of chemistry, which is focused on the study of chemical processes that cause the movement of electrons. This phenomenon is called electricity and can be generated by the movements of electrons from one elements to another in a reaction known as an oxidation–reduction (“redox”) reaction. This kind of reaction involves a change in the oxidation state of one or more elements or atoms. For instance, when an atom loses an electron, its oxidation state increases; thus, it is oxidized. On the other hand, when an atom gains an electron, its oxidation state decreases, and it is said to be reduced.

Many electrochemical techniques exist to study the movement of electrons in a redox reaction. Most of these reactions require the application of an external potential (E) since there is a gap in energy that the electrons need to move from one species to another, according to their Fermi levels. In this regard, most of the

electrochemical techniques require the application of a certain potential to reach this energy gap and generate a current response (I). This external potential, which is “away” from the equilibrium between the involved species, is called “overpotential” [1]. With this information, we can correlate this potential with the amount of energy necessary for the redox reaction to occur. Nevertheless, there are other techniques in which a current is applied, and, for instance, the potential is measured. The selection of the technique will depend on the objective of the study.

Electrocatalysis is one of the most important fields within electrochemistry. This field aims to find materials (called electrodes) that can serve as electrocatalysts, by means that a certain redox reaction can occur as close as the equilibrium potential of a specific specie and its redox couple. For example, many researchers are focused on studying the capacity of different materials to improve the performance toward reactions of environmental and energetic interest. One of the main reactions that are studied is the hydrogen evolution reaction (HER), which implies the reduction of two protons by gaining two electrons and resulting in one mol of hydrogen gas. Another reaction that is highly studied in electrocatalysis is the oxygen reduction reaction (ORR), where one mol of the oxygen molecule is converted into hydrogen peroxide if it gains two electrons, or a water molecule if the material is good enough to go further and be able to give four electrons instead. In this latter case, hydrogen peroxide can be an intermediate of the whole reaction. Both HER and ORR are involved in proton exchange fuel cells, where hydrogen gas serves as fuel, and it is oxidized to protons in the anode. Then, these protons diffuse through a proton exchange membrane to the cathodic chamber and are part of the ORR in the cathode [2].

For these studies, electrochemical techniques such as voltammetries (linear, cyclic, square wave, and differential pulse) are highly used as starting studies, where a potential scan is applied in a certain range and the current response is measured. Then, other techniques such as chronoamperometry and chronopotentiometry are used as well, where a specific potential and a specific current are fixed over time, correspondingly. However, these techniques are focused on obtaining the desired product by either oxidizing or reducing the reactant. To be able to use these techniques, the following is required: (i) a working electrode (WE), which is where the target reaction occurs, (ii) a reference electrode (RE), which has a known potential, and every potential acquired in the WE are described as “versus” the RE, and (iii) a counter electrode (CE), where the opposite reaction is occurring. In this case, if a reduction process is occurring onto the WE, an oxidation process occurs in the CE. Then, the same if it was the opposite way. This setup of three electrodes is called the “electrochemical cell” (**Figure 1**) and it is connected to an external equipment called potentiostat in which the operator can control the parameters of the techniques and measure the results.

Then, the reactant is mostly found in an aqueous phase that contains a supporting electrolyte. A supporting electrolyte is commonly a salt dissolved in the aqueous phase and gives conductivity to the solution, but it is inert to react with the WE, by means that it does not interfere in the selectivity of the electrode toward the reactant. Then, if the electrode is polarized toward negative potentials, the WE is referred to as a cathode, while if it is polarized toward positive potentials, it is called an anode. In any case, the electron movement from the electrode to the reactant or *vice versa* occurs in the proximities of the electrode surface (**Figure 2**), or interface electrode/solution, and it is known as the “double layer.”

To understand this, many models of the interface or double layer have been studied, where the closest layer corresponds to the Stern layer (region I), while other layers come afterward, such as the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) that are located further (regions II and III, respectively)

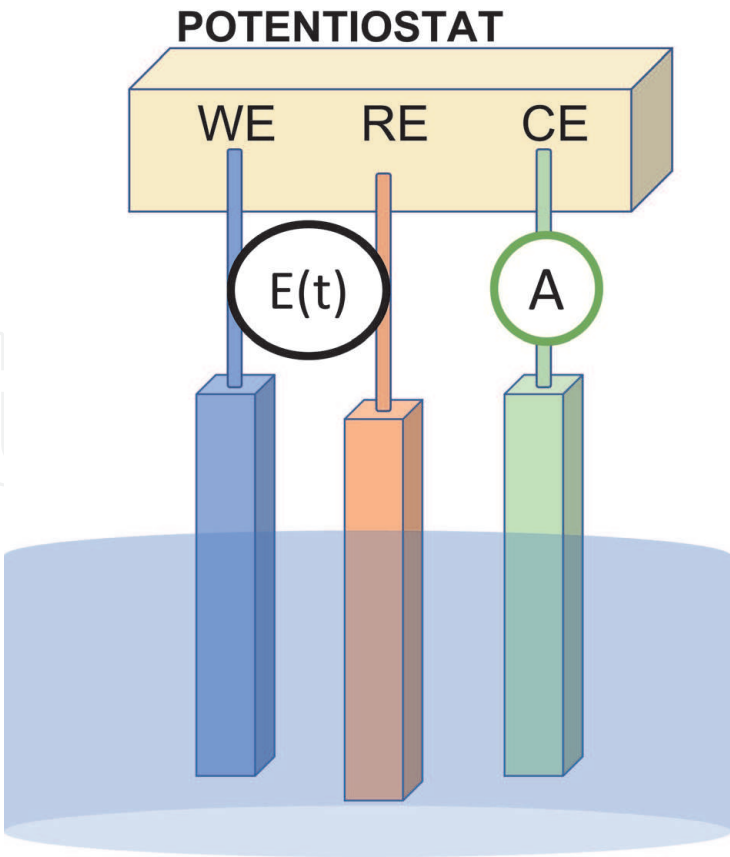


Figure 1.
An electrochemical system with a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). The potential $E(t)$ is applied between the working and reference electrode, and the resulting current is measured at location (A).

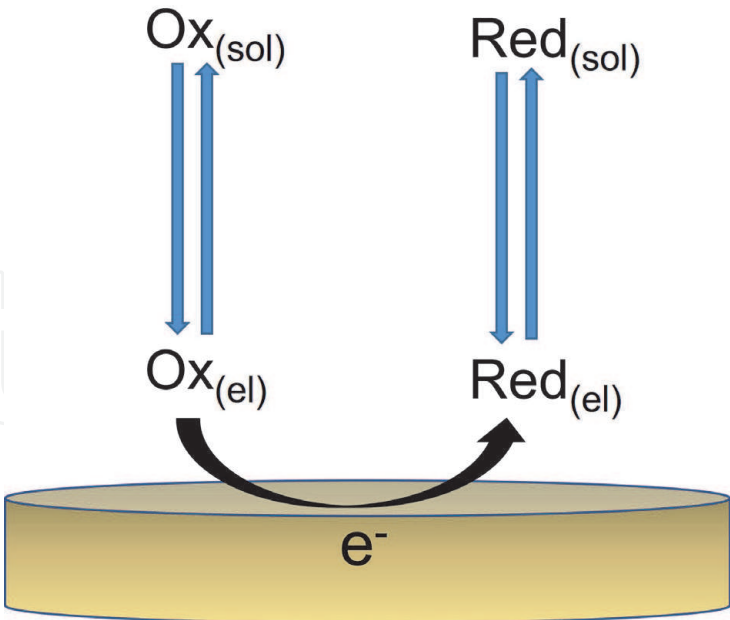


Figure 2.
Representation of a mass transfer controlled electrochemical reaction involving an oxidized species (ox) and a reduced species (red).

until we find the bulk solution (**Figure 3**). Once the WE is being polarized, the reactant diffuses toward the proximities of the electrode surface, forming the double layer; afterward, the electron transfer occurs.

Considering this, the electrocatalytic reactions should be highly focused on understanding what happens in the electrode/solution interface as an addition to

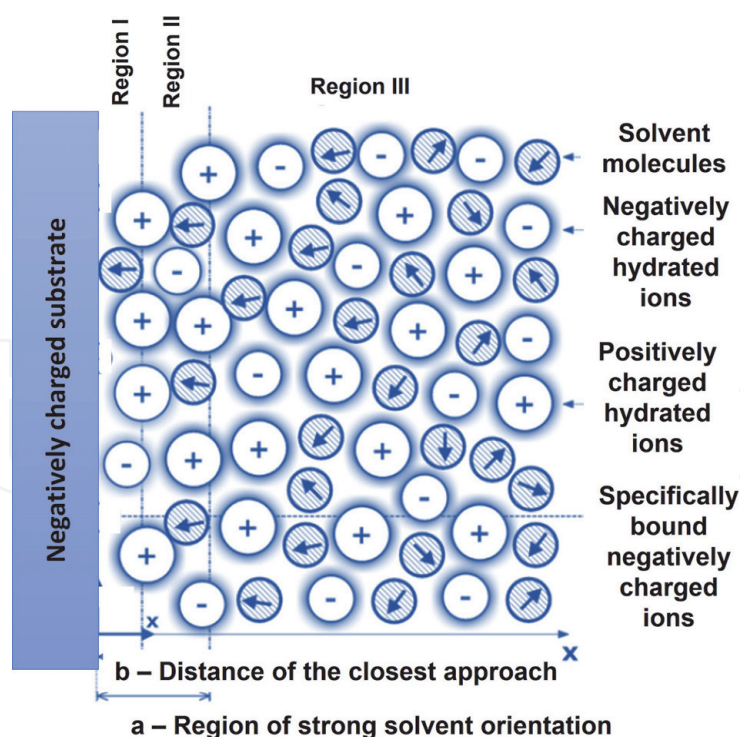


Figure 3.

Charge distribution in the generalized Stern model, where the interval $0 < x < a$ is the region of strong water orientation and b is the distance of closest approach [3].

the current or potential responses toward a particular redox reaction. The electrochemical impedance spectroscopy (EIS) is a very powerful tool that allows us to study the double layer or interface in more detail and describes it as a function of an electrical circuit. Based on this, when the double layer is formed, we can refer to it as a capacitor (C_{dl}) and calculate its value in Farads (F). The double layer is the heart of electrochemistry: All electrochemical reactions occur in this region, and it determines one of the basic macroscopic relations of electrochemistry that between the electrode charge and the potential, or equivalently its interfacial capacitance [4]. Then, when the electrochemical reaction occurs, we can correlate this process in terms of the resistance of the charge transfer (R_{ct}) or impedance (Z), both in Ohms (Ω). Other parameters can also be obtained by analyzing two main graphs: (i) Nyquist plots, which correlate with the imaginary impedance (Z'') *versus* the real impedance (Z'), and (ii) Bode plots, which show the correlation between the total impedance of the cell (Z) and the phase shift ($^\circ$) *versus* the frequency of an applied potential. To understand this technique, we must follow the derivation of Ohm's law and its components until we can find the actual applications in different known processes.

2. Electrochemical impedance spectroscopy: a theoretical review

The electrochemical impedance spectroscopy (EIS) technique is an electrochemical method used in many electrochemical studies, which is based on the use of an alternating current (AC) signal that is applied to the working electrode, WE, and determining the corresponding response. In the most common experimental procedures, a potential signal (E) is applied to the WE and its current response (I) is determined at different frequencies. However, in other cases, it is possible to apply a certain current signal and determine the potential response of the system. Thus, the potentiostat used processes the measurements of potential *vs.* time and current *vs.* time, resulting in a series of impedance values corresponding to each frequency

analyzed. This relationship of impedance and frequency values is called the “impedance spectrum.” In studies using the EIS technique, the impedance spectra obtained are usually analyzed using electrical circuits, made up of components such as resistors (R), capacitances (C), inductances (L), combined in such a way as to reproduce the measured impedance spectra. These electrical circuits are called “equivalent electrical circuits.”

Impedance is a term that describes electrical resistance (R), used in alternating current (AC) circuits. In a direct current (DC) circuit, the relationship is between current (I) and potential (E) is given by Ohm’s law Equation. (1), where E is in volts (V), I is amperes (A), and R is Ohms (Ω):

$$I(A) = \frac{E(V)}{R(\Omega)}. \quad (1)$$

In the case of an alternate signal, the equivalent expression is as follows:

$$I(A) = \frac{E(V)}{Z(\Omega)}. \quad (2)$$

In Eq. (2), Z represents the impedance of the circuit, in units of Ohms. It is necessary to note that, unlike resistance, the impedance of an AC circuit depends on the frequency of the signal that is applied. The frequency (f) of an AC system is expressed in units of hertz (Hz) or the number of cycles per second (s^{-1}). In this way, it is possible to define the admittance (Y) of an AC circuit. Admittance is the reciprocal of impedance and is an important parameter in mathematical calculations involving the technique and on the other hand, the equipment used in EIS studies measures admittance.

The impedance of a system at each frequency is defined by the ratio between the amplitude of the alternating current signal and the amplitude of the alternating potential signal and the phase angle. A list of these parameters at different frequencies constitutes the “impedance spectrum” (**Figure 4**). The mathematical development of the theory underlying the EIS technique allows describing the impedance of a system in terms of a real component and an imaginary component (associated with the square root of -1).

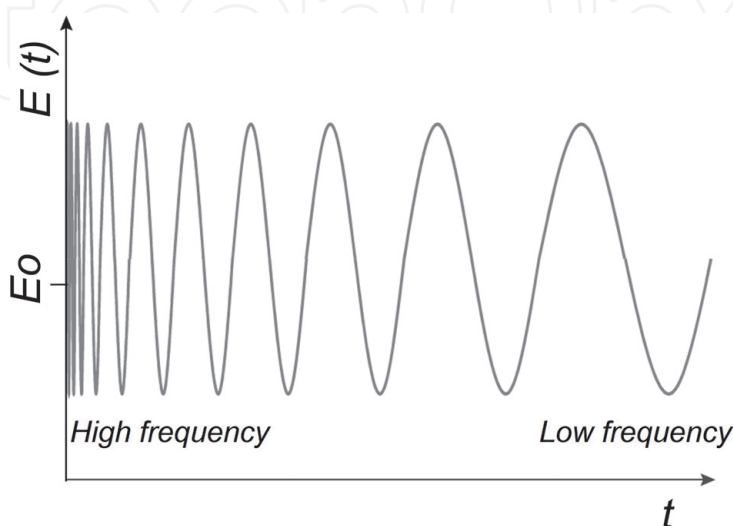


Figure 4.
 Periodic perturbation signal with amplitude (ΔE) is applied between the WE and RE from high to low frequencies.

Since the EIS technique is based on the study of electrical networks, there is a great deal of information in the literature regarding electrical circuits. Thus, in understanding the theory that supports the EIS technique, it is convenient to describe current and voltage as rotating vectors or “phasor,” which can be represented in a complex plane or “Argand Diagram.” For instance, a sinusoidal voltage can be represented by the following expression.

$$E(V) = \Delta E(V) \text{ sen } \omega t. \tag{3}$$

where E is the instantaneous value of the potential, ΔE is the maximum amplitude, and ω is the angular frequency, which is related to the frequency f according to

$$\omega = 2\pi f. \tag{4}$$

In this case, ΔE can be understood as the projection, on axis 0 of phasor E in a polar diagram, as shown in **Figure 5**.

In most cases, the current (I) associated with a sinusoidal potential signal is also sinusoidal, with the same frequency (ω) but with a different amplitude and phase than the potential. This can be represented according to Eq. (5).

$$I(A) = \Delta I(A) \text{ sen } (\omega t + \varnothing). \tag{5}$$

This means that, in terms of phasors, the rotating vectors are separated in the polar diagram by an angle \varnothing in degrees ($^\circ$). This can be illustrated as shown in **Figure 6**.

The response to a potential E , of a simple circuit with a pure resistance R , can be described by Ohm’s law Equation (1). This, in terms of phasors, corresponds to a situation where the phase angle is equal to zero.

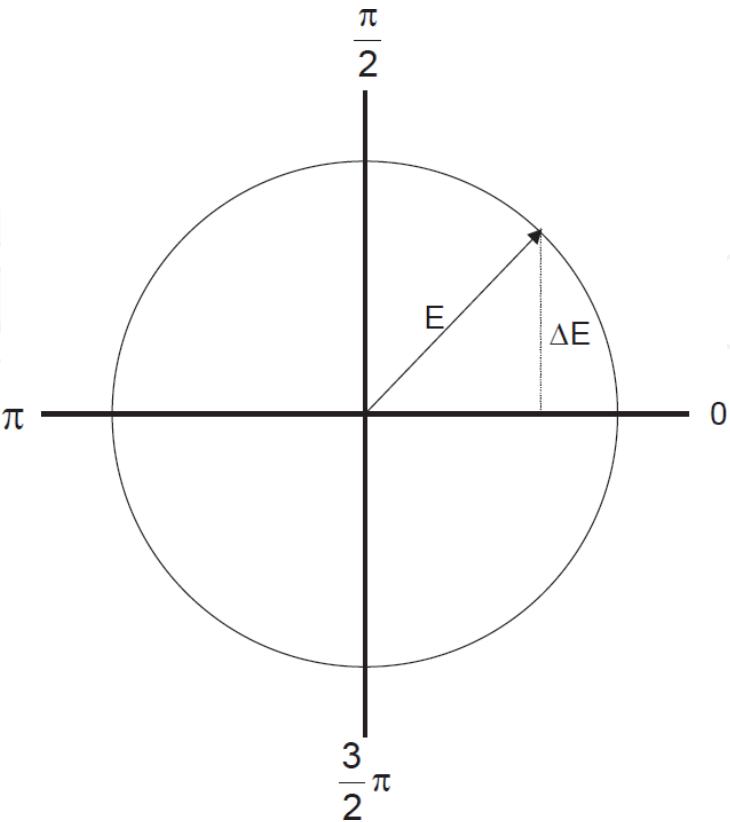


Figure 5.
Phasor diagram corresponding to the alternating potential of Eq. (3).

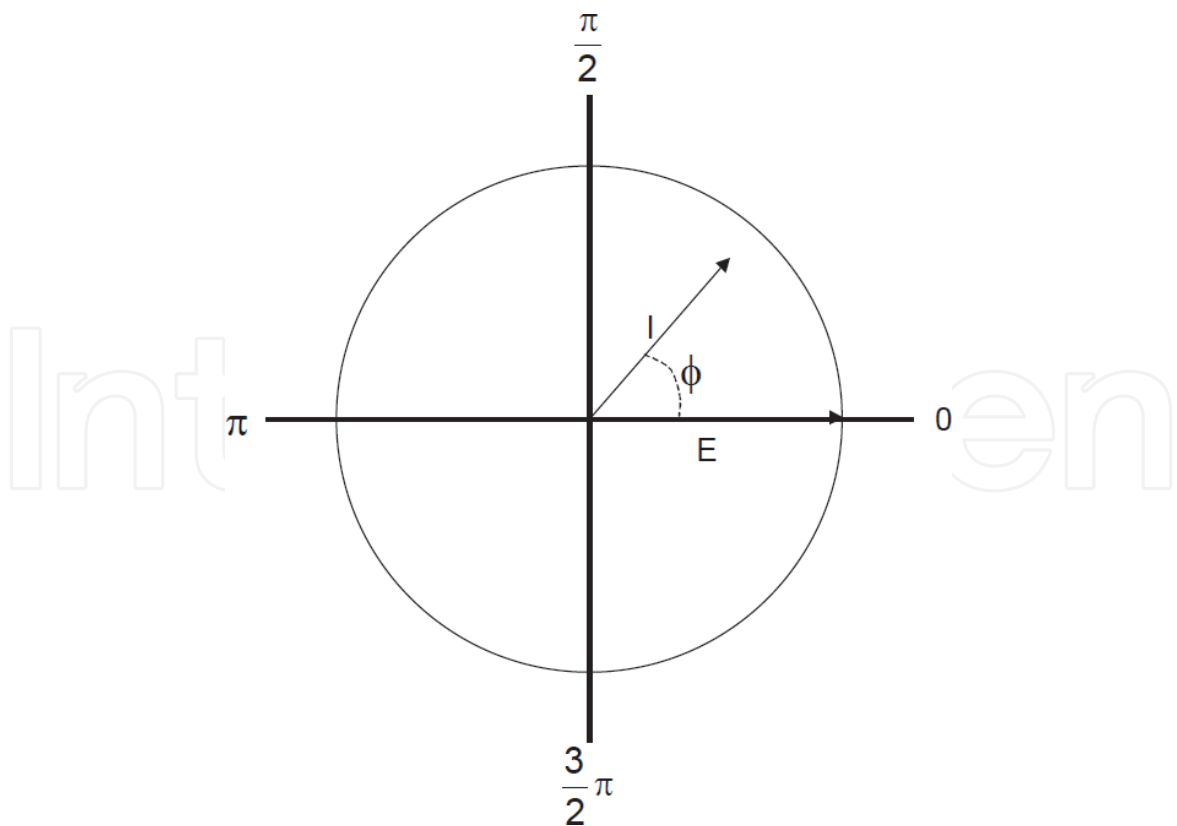


Figure 6.
Phasors of current (I) and potential (E) separated by a phase angle ϕ .

When a capacitor is considered in the electrical circuit, different aspects must be known. The concept of “capacitance” (C) can be defined as the relationship between the potential applied (between the capacitor plates) and the total charge (q), according to Eq. (6):

$$q = CE. \tag{6}$$

Considering the current $I(A)$ flowing through the capacitor, the current can be expressed as

$$I(A) = \frac{dq}{dt} = C \frac{dE}{dt}. \tag{7}$$

Thus, considering that current is obtained as a sinusoidal response, we can describe it in terms of the potential, capacitance, and angular frequency, as shown in Eq. (8):

$$I(A) = \omega C \Delta E(V) \cos \omega t. \tag{8}$$

As Ohm’s equation described in Eq. (1), it is possible to rewrite the equation in terms of Eqs. (3) and (5), giving the following expression:

$$Z(\Omega) = \frac{\Delta E(V) \sin \omega t}{\Delta I(A) \sin (\omega t + \phi)}. \tag{9}$$

In mathematical terms, the real and imaginary components of phasor E and phasor I can be represented in an Argand diagram, with the abscissa corresponding to the real component and the ordinate axis referring to the imaginary component.

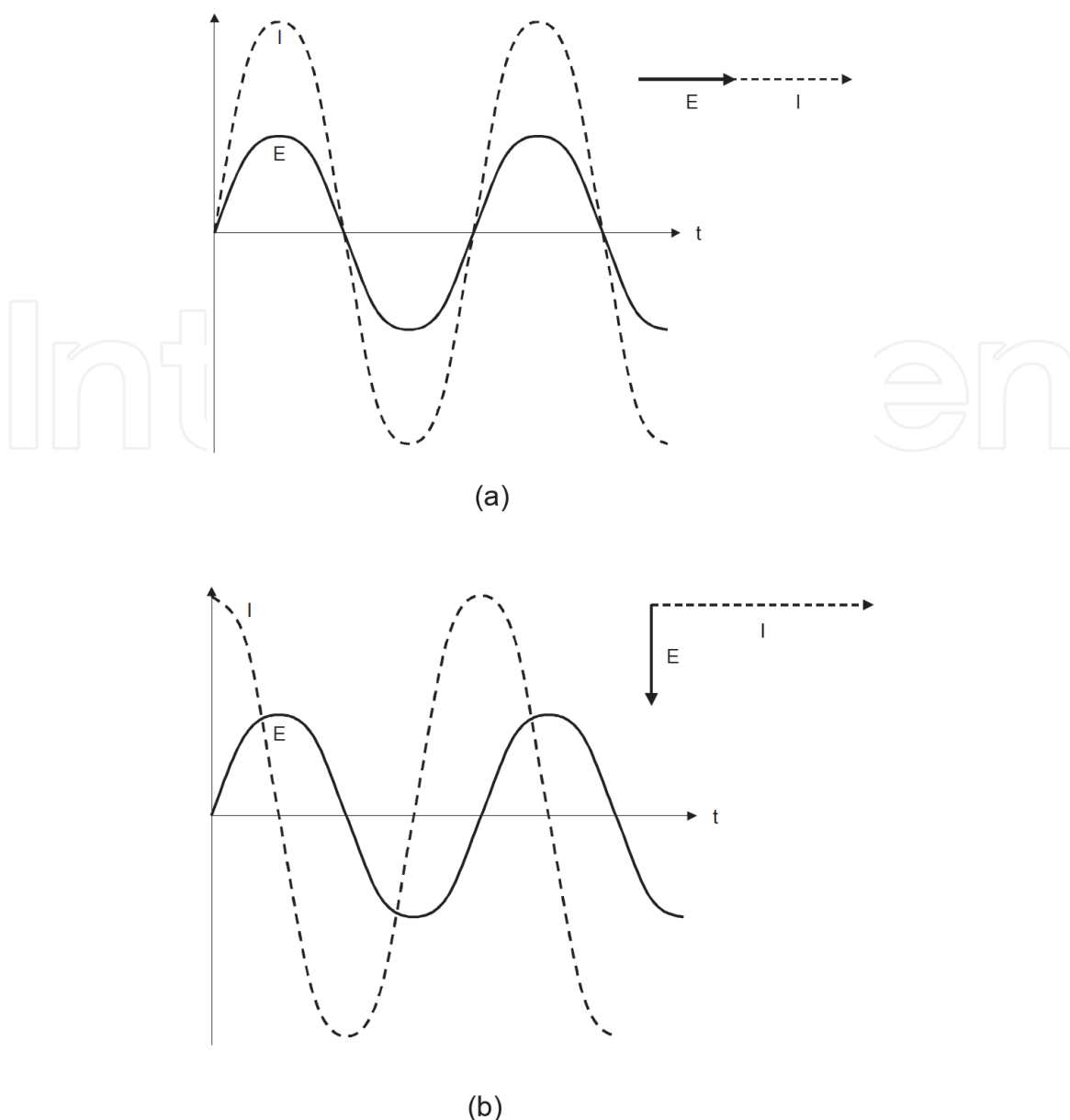


Figure 7.

Phasor representation of current (I) and potential (E) with time (t), for a relationship between current and potential in a circuit with a capacitive reactance of (a) phase angle (ϕ) = 0, and (b) phase angle (ϕ) = 90° .

Figure 7a shows the representation of phasor E and I for a purely resistive circuit and **Figure 7b** shows a circuit with a reactive capacitance.

In this regard, when an electrode is highly conductive, it is expected that the phase angle tends to zero, due to limited resistivity for the electron transfer to occur. However, in practice, the electrodes present a delay in the current response, which in this technique is represented by the phase angle (phase shift). This means that the system presents a certain resistivity toward the electron transfer, or in actual terms, impedance.

In **Figure 8**, we can observe the final representation of the terms explained in this section.

Therefore, to understand the practical applications, it is important to consider the following. Assume that we apply a sinusoidal potential excitation. The response to this potential is an AC signal. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series). Concisely, a conventional electrochemical impedance experimental setup involves an electrochemical cell, a potentiostat, and a frequency response analyzer (FRA). The FRA applies the sine wave and examines the response of the system to determine its impedance. The quality of the

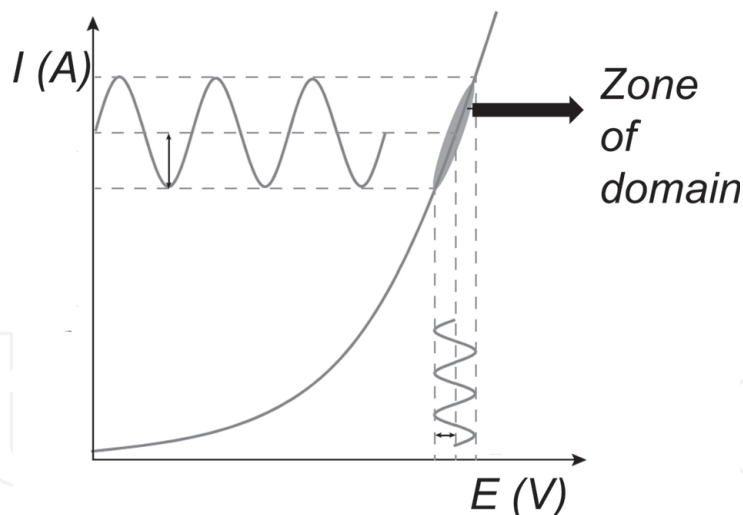


Figure 8.
Electrochemical response to the potential perturbation measured in the linear domain.

impedance measurement is controlled by a series of parameters, including the selection of potentiostatic or galvanostatic modulation, the perturbation amplitude, the frequency range, and the number of cycles used to measure each frequency. The parameters used are highly dependent on the experimental setup and are influenced by factors such as material type, electrolyte, and electrolyte concentration. According to Gamry Instruments [5], a simple explanation of these parameters is described below:

- i. Initial frequency: It defines the frequency of the first AC signal applied during data acquisition. The frequency is entered in Hertz. It is generally recommended to start at high frequency (e.g., 100,000 Hz) and sweep to low frequencies.
- ii. Final frequency: It is specified as the frequency of the last AC signal applied during data acquisition (usually 0.1 Hz).
- iii. Points per decade: It corresponds to the number of measurements that will take place within one decade of frequency. Each data point corresponds to a different frequency of the applied AC signal.

Therefore, the initial frequency, final frequency, and points per decade parameters can help us to calculate the total number of data points acquired. It is recommended that the frequency range used is as wide as possible. Preferably, this implies a range of 6–7 decades (e.g., 10^{-2} – 10^5 Hz), if mathematical tool such as Kramers–Kroning (KK) analysis is used. However, many systems do not allow analysis over a wide frequency range, without obtaining a significant amount of noise.

- iv. AC voltage: It determines the amplitude of the AC signal applied to the cell. The units are RMS (root mean square) millivolts. The resolution of the AC voltage and its range differs from system to system. They vary on both the frequency response analyzer (FRA) and the potentiostat. Generally, you can enter values from 1 mV to around 2 V, depending on the sensitivity of the equipment.
- v. DC voltage: This is specified as the constant potential offset that is applied to the cell throughout the data acquisition. This potential is chosen based on

the study at hand. There are some studies where the DC voltage is set up at the open circuit potential (OCP), which is the potential where the total current in the system is zero. Other potentials can be chosen from the voltammetric profiles obtained from the initial studies, where the capacitive and faradaic zones can be recognized. The AC voltage is summed with the DC voltage.

- vi. Estimated Z: It corresponds to a user-entered estimate of the cell's impedance at high frequencies. It is used to limit the number of trials required while the system optimizes the potentiostat settings for improvement, current range, offset, etc. Before taking the first data point, the system chooses the potentiostat settings that are ideal for the estimated Z value. If the estimate is precise, the first (or the following one) attempt to determine the impedance will succeed. Nevertheless, if the estimate lacks accuracy, the system will take a few trials while it optimizes the potentiostat settings.

2.1 Graphical representations of impedance measurements

As mentioned before, data obtained in electrochemical impedance spectroscopy tests are reported by the potentiostat equipment in the following two ways:

- a. Real component of total impedance (Z_{real}) and imaginary component of total impedance ($Z_{\text{imaginary}}$), as shown in **Figure 9**.

Although the International Union of Pure and Applied Chemistry (IUPAC) conventions hold that the real part should be represented by Z' and the imaginary part denoted by Z'' , the use of this notation can also be found as Z with a subscript notation of "r" for the real part and "j" for the imaginary part.

- b. Impedance modulus ($|Z|$) and phase shift (angle) ($^\circ$) versus the frequency (f), as shown in **Figure 10**.

These two methods of describing impedance measurements are the basis for two common ways of presenting data, called Nyquist and Bode plots, respectively.

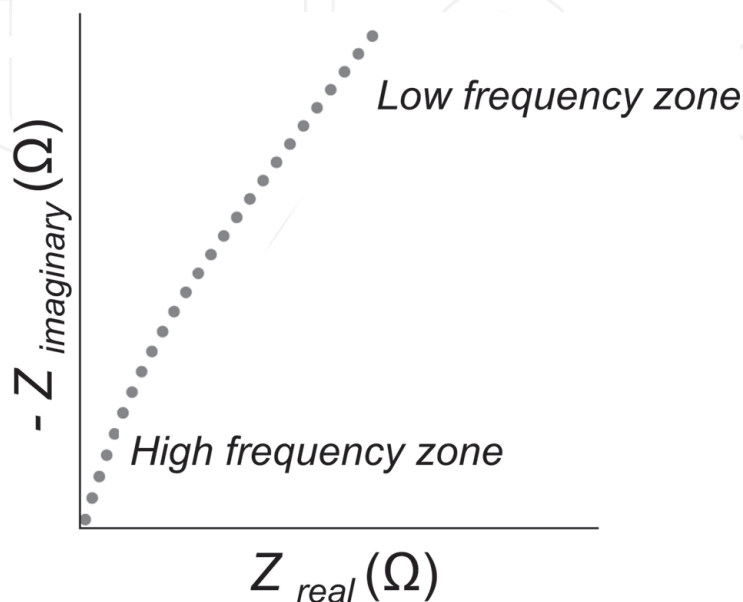


Figure 9.
Impedance data presented in $-Z_{\text{imaginary}}$ (Z'') versus Z_{real} (Z') representation.

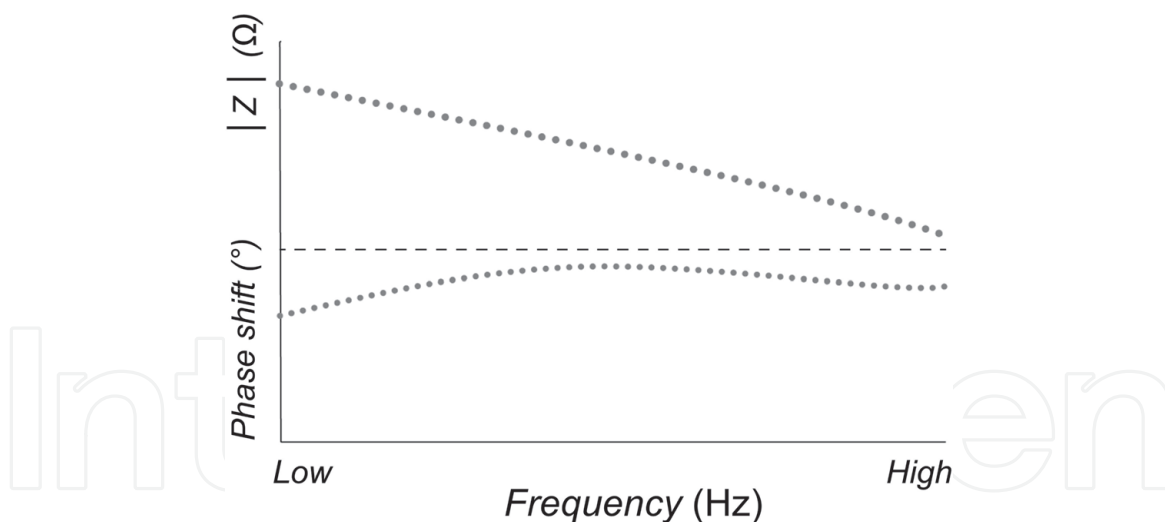


Figure 10.
 Impedance data presented in phase shift and total impedance versus f representation.

Nyquist plots show the correlation between the real and imaginary parts of the impedance when the frequency varies. The difficulty of Nyquist plots is that frequency information cannot be directly shown. However, Bode plots show how the magnitude and phase angle of impedance change as a function of the frequency [6]. Because of this, it is important to have a complete understanding of both Nyquist and Bode plots, when analyzing impedance data.

The impedance modulus $|Z|$, the phase shift, \varnothing ($^{\circ}$), and the real and imaginary components of the total impedance are related to each other according to the following expressions.

$$|Z|^2 = Z'^2 + Z''^2. \quad (10)$$

$$\tan \varnothing = \frac{Z''}{Z'}. \quad (11)$$

$$Z' = |Z| \cos \varnothing. \quad (12)$$

$$Z'' = |Z| \sin \varnothing. \quad (13)$$

The previous analysis has not considered the fact that all electrodes show a capacitance, called “double layer capacitance” (C_{dl}), which is independent of Faradaic reactions. On the other hand, an electrical resistance, associated with the resistance of the electrolyte (R_{sol}), exists between the point at which the potential is measured (usually the tip of the Luggin capillary) and the working electrode. This resistance will also manifest itself in the total impedance of the system.

2.2 EIS data manipulation and fitting

All Kramers–Kronig-consistent impedance spectra may be fitted to an equivalent circuit, which is the point of using a measurement model. The effects of C_{dl} and R_{sol} can be considered in impedance analysis if their magnitudes are known. They can also be determined by measurements in the absence of the pair of electroactive species. However, determining the C_{dl} and R_{sol} values separately increases the complexity of experimentation and information analysis. An analysis method that avoids the need to separate measurements is derived from a process widely used in other areas, such as electrical engineering, and adapted for electrochemical applications. This method is called “complex plane impedance analysis.”

Considering a simple series circuit of resistance and capacitance, the total impedance is equal to

$$Z = R + \frac{1}{j\omega C}, \tag{14}$$

where the real part of Z is simply R and the corresponding imaginary part is $\frac{1}{j\omega C}$.

If the behavior described by Eq. (14) is represented in a diagram of $Z = Z' + Z''$ (Argand diagram), where Z' = real component of total impedance and Z'' = imaginary component of total impedance, the graph of **Figure 11** will be obtained. In this case, the corresponding graph is a series of points at different values of ω , where the value of the imaginary impedance component (Z'') tends to zero as the frequency tends to infinity. Here, the capacitance can be considered as short-circuited. Additionally, it is necessary to mention that, in electrochemical studies, the imaginary component of the total impedance (Z'') is usually multiplied by -1 . This is because, in strict mathematical rigor, in most of these systems, Z'' has negative a value (as shown in **Figure 9**).

The ohmic resistance-adjusted phase angle has an asymptotic value of -90° at high frequency when an electrode is considered “ideally polarizable.” If there is a constant-phase element (CPE), the asymptotic value at high frequency would be lower than 90° . Thus, plots of the ohmic resistance-adjusted phase angle present a direct demonstration of a capacitive behavior or frequency dispersion behavior.

The constant-phase element (CPE) is frequently used to improve the fit of models of impedance data. Then, a capacitance may be obtained from a distribution of time constants along the electrode surface. However, not all time-constant distributions lead to a CPE. The ohmic resistance-corrected phase angle gives a useful method to establish whether a time-constant distribution is represented by a CPE or a C_{dl} .

Every graphical result can be described in an equivalent circuit. For the results shown in **Figure 11**, two main elements appear: (i) R_{sol} , which corresponds to the resistivity of the electrolyte, and (ii) a capacitor in series to the R_{sol} , which assumes

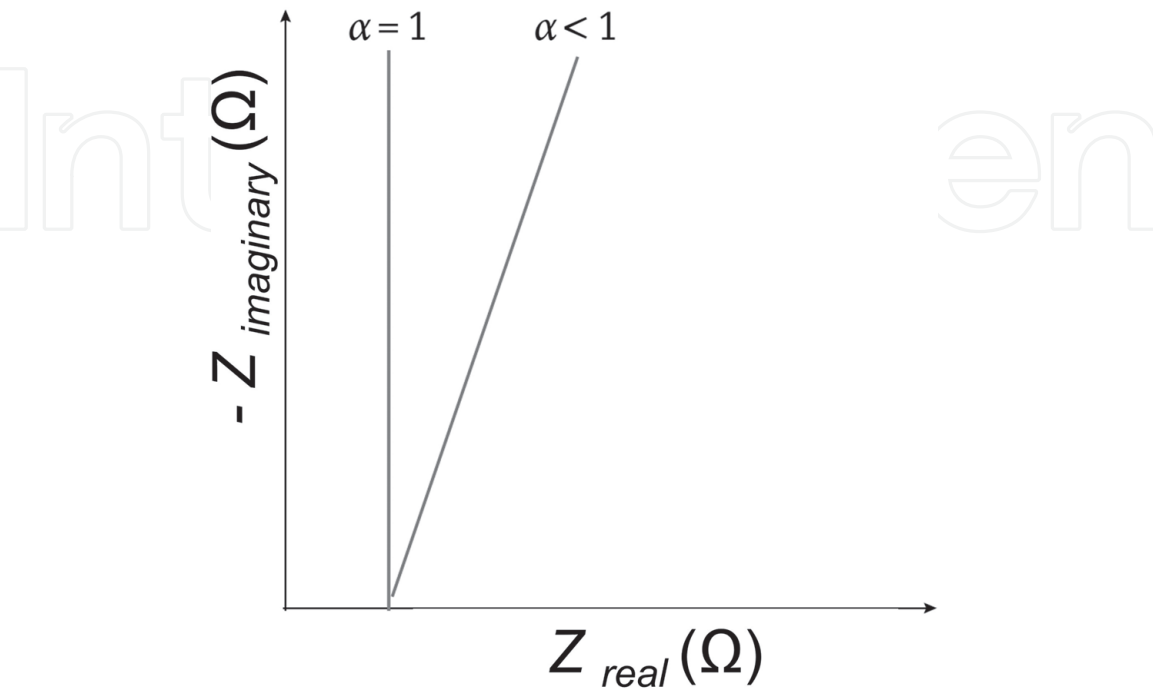


Figure 11.
Representation of Eq. (14).

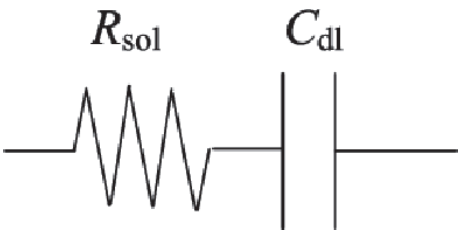


Figure 12.
Electrical equivalent circuit consisting of R_{sol} in series to a capacitor (C_{dl}).

the formation of the double layer or the deposition of charged species over the electrode surface. The equivalent circuit is shown in **Figure 12**.

In other cases, the real and imaginary components of the total impedance can behave as parallel combinations of resistors and capacitors. Thus, the response is characterized by the presence of a semicircle. At low frequencies, the impedance is purely resistive because the reactance of the capacitor is very large. The diagram in **Figure 13** corresponds to the simplest analogy of a Faradaic reaction on an electrode with an interfacial capacitance, C_{dl} . Graphically, in a Nyquist plot, the initial point of the semicircle corresponds to the R_{sol} , while the final point that reaches the x -axis minus the value of the R_{sol} , corresponds to an R_{ct} . Here, it is important to consider that, for a redox reaction to occur, the species must be close enough to allow the electron transfer. Then, a capacitor (C_{dl}) or CPE in parallel will always be used in this circuit model.

This representation allows obtaining a simile of an electrochemical reaction and increases the complexity of the analysis. Then, if the R_{sol} or R_e value is high, the semicircle will be shifted to higher values of the x -axis of the graph. The corresponding electrical circuit is shown in **Figure 14**.

Another representation that is common to see in practice is a diffusional component in series to the R_{ct} . This diffusional component is called “Warburg element” (denoted as W) and it is shown as a 45° linear response right after the semicircle

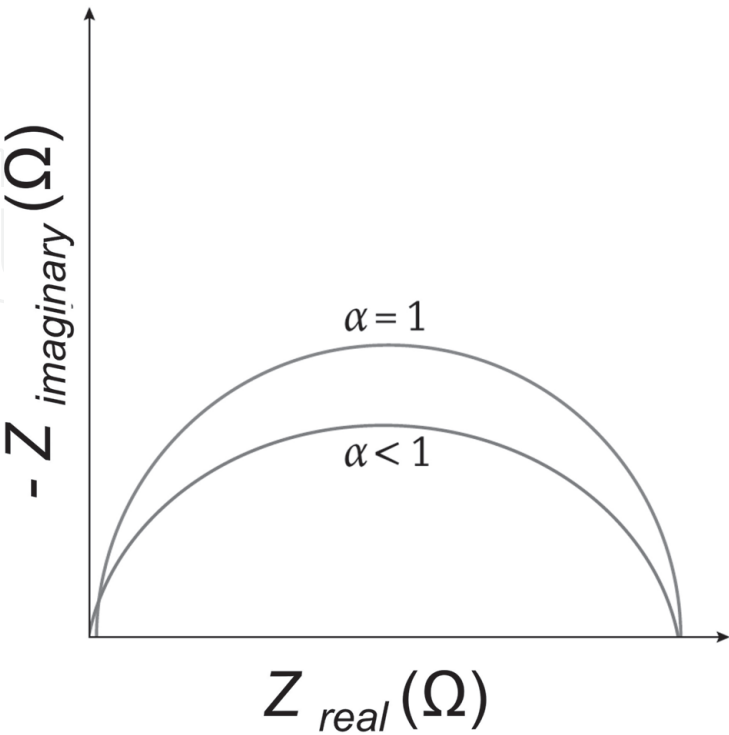


Figure 13.
Representation of the real and imaginary components of the total impedance of a parallel combination of a resistor and a capacitor. α , a parameter associated with the CPE.

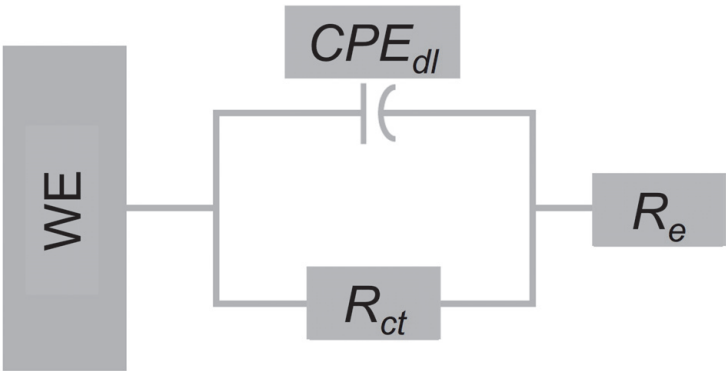


Figure 14. Equivalent circuit in which a mechanistic interpretation of the system under study is used to extract a meaning for the faradaic impedance, R_{ct} ; double-layer constant-phase element, CPE_{dl} ; and ohmic resistance of the solution, R_e .

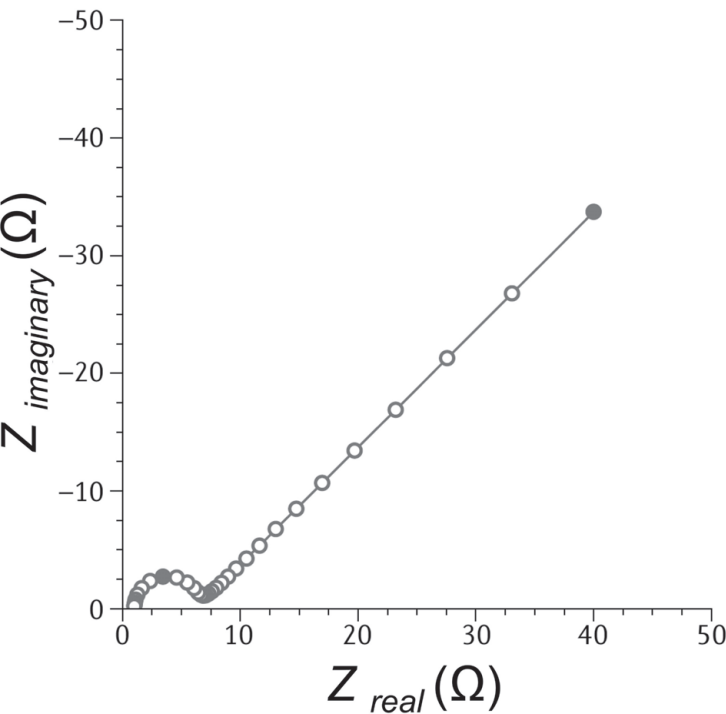


Figure 15. Equivalent circuit corresponding to the R_{sol} in series with a Warburg element, and a capacitor in parallel.

closes at the x -axis (**Figure 15**). Warburg semi-infinite diffusion is an impedance element, which describes the diffusion behavior of the electrolyte in the absence of convection with a diffusion layer that can spread to infinity.

When this electrical component is shown, the equivalent circuit is called the “Randles equivalent circuit” (**Figure 16**).

The circuit representation of the process model shown in **Figure 16** has a corresponding mathematical expression given as

$$Z = R_e + \frac{R_{ct} + W_o}{1 + (j\omega)^\alpha Q (R_{ct} + W_o)}, \tag{15}$$

where R_e is the ohmic resistance, R_{ct} is the charge-transfer resistance, W_o is the diffusion impedance, and α and Q are parameters for a CPE, that is, $Z = ((j\omega)^\alpha Q)^{-1}$. The diffusion impedance is expressed in terms of a diffusion resistance, R_d , and a dimensionless diffusion impedance, $-1/\theta'(0)$, as:

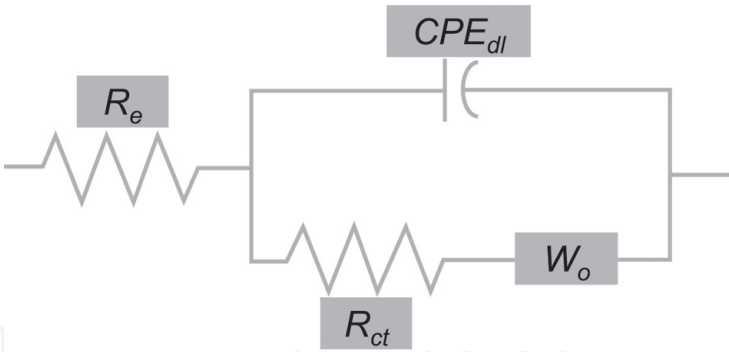


Figure 16. Electrical circuit corresponding to a high-frequency constant-phase element (CPE) behavior, which is associated with the double layer. R_e (R_{sol}) is the ohmic resistance; R_{ct} is the charge-transfer resistance associated with electrode kinetics; W_o , diffusion impedance is associated with the transport of reactive species to the electrode surface.

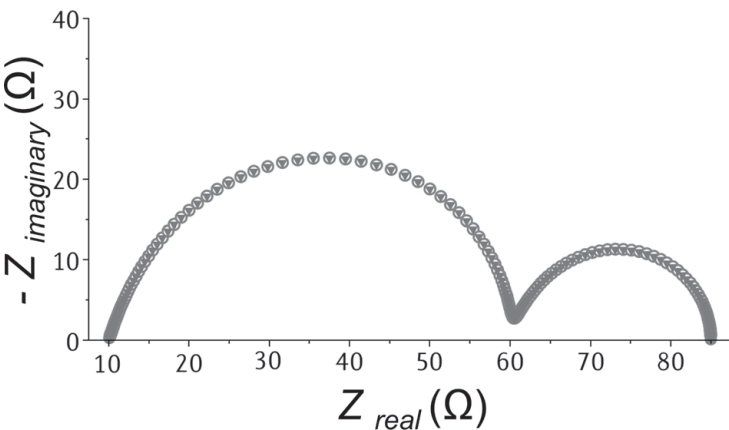


Figure 17. Nyquist plot with more than one R_{ct} denoted by semi-circles.

$$W_o = R_d \left(\frac{-1}{(\theta)'(0)} \right), \tag{16}$$

where θ is the dimensionless concentration phasor scaled to its value at the electrode surface, and $\theta'(0)$ is the derivative with respect to the position evaluated at the electrode surface [7].

Once we obtain the measured data and the corresponding Nyquist and Bode plots, the data can be fitted with these corresponding electrical equivalent circuits. Most of the software that are in the potentiostats can fit the results by using common electrical circuits. Nevertheless, it is highly important to know what kind of materials we are using in practice to give the electrical circuit a physical meaning. The fitting software, such as ZView/ZPlot from Scribner Associates®, can approach the fit of the results by graphing an electrical circuit and getting the “theoretical” graph out of the model, in addition to the precision of the electrical circuit. The quality of the fit can be defined using a graphical comparison of the impedance data or by the weighted χ^2 statistic. Both simplex regression and Levenberg–Marquardt regression strategies are used [7, 8].

Finally, when two or more semicircles are shown, it is possible to modify the electrical equivalent circuit shown in **Figures 14** and **16**, by adding more R_{cts} in the fitting. Usually, the R_{cts} that are away from the R_{sol} are the charge transfers occurring on the proximities of the surface of the electrode and are in the low-frequency zone (**Figure 17**). Here, many possibilities appear as options for fitting the data as shown in **Figure 18**.

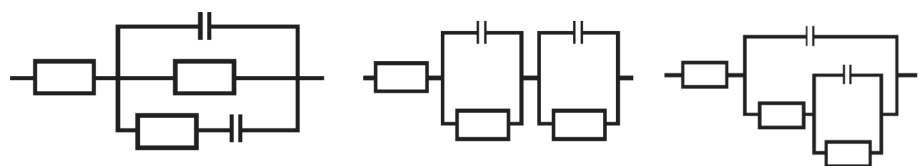


Figure 18.
Different examples of equivalent circuits when two charge transfers are involved plus the resistance of the electrolyte (in boxes).

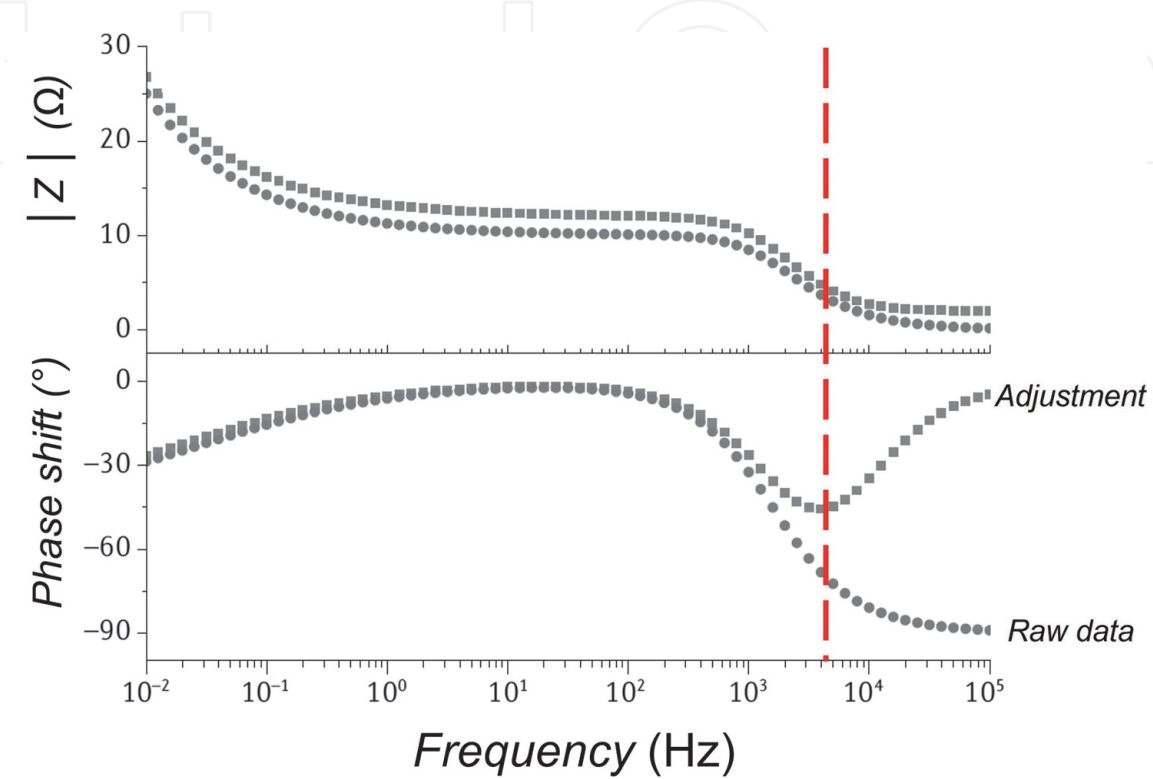


Figure 19.
Bode plot from circuit presented in Figure 14.

Regarding the Bode plots for these examples, **Figure 19** shows the expected diagram for the Randles equivalent circuit in **Figure 14**. As it is observed in **Figure 19**, a typical Bode plot is shown for a simplified Randles circuit (without the diffusional component). In this case, the frequency values go from the lowest to the highest, which means that the first points correspond to the impedance of the electrolyte if we analyze the graph from the right to the left. When a charge transfer occurs, the $|Z|$ vs. f graph shows a slope (red dashed line), while the phase shift vs. f shows a valley at the same frequency value. The flattened areas correspond to the rearrangements of the double layer until we observe another slope and a semi-valley. At these frequencies, the electrical behavior may be attributed to diffusional effects. In an ideal system, where no resistance or impedance is contributing to the electrochemical system, the phase shift tends to zero, but, as mentioned earlier, all electrodes present a resistance toward the charge transfer, as well as the electrolyte, where the reaction is taking place. For instance, neither of these parameters can be ignored.

2.3 Applications

Electrochemical impedance spectroscopy can be used in many areas, and its application is highly important when describing the interface electrode/solution. As the results are represented in equivalent circuits, it must be considered that this

electrical behavior occurs between the WE and the CE, where a differential in current is taking place.

2.3.1. Electrocatalysis

As mentioned earlier, electrocatalysis is one of the main fields within electrochemistry. Many electrocatalysts are built with the aim to electrocatalytic reactions that are involved, for example, in batteries or fuel cells. In these cases, the studies are more complex since it is important to consider the performance of the anode, cathode, and membrane. All these components contribute to the final impedance value in the electrochemical system.

Figure 20 shows an example of a Nyquist plot resulting from a solid oxide fuel cell.

In this example, three semicircles are observed, meaning that three electron transfers are taking place over the range of measurement. An ideal panorama for the performance of the electrodes is to have the impedance values as low as possible, meaning that the electrodes are highly conductive and the application of the potential is low.

Another example, in fuel cells, is presented in **Figure 21**, where four zones can be identified. From left to right, we observe proton conduction in electrolyte membrane, charge transfer at the electrode-electrolyte interphase, gas diffusion through gas diffusion layer, and water transport across membrane or relaxation of adsorbed intermediates.

In this case, where a polymer electrolyte fuel cell is studied, we can observe a fourth zone that is attributed to the adsorption of species onto the surface of the electrode. When fitting the results of this diagram, an inductor (L) must be added to the equivalent circuit. An inductor considers both a capacitive and a resistive behavior due to the formation of another double layer. Thus, every time the semicircles pass through the x -axis, it is considered that the system presents an inductance in its electrochemical performance. An inductive contribution is usually caused by the connecting wires in the high-frequency domain when low impedances are measured (for battery applications) or when a significant noise in the low-frequency range is found when measuring high impedance.

2.3.2. Corrosion

The number of equivalent circuits that can fulfill the behavior of a corrosion cell is practically infinite. However, there is an essential condition for the selection of an

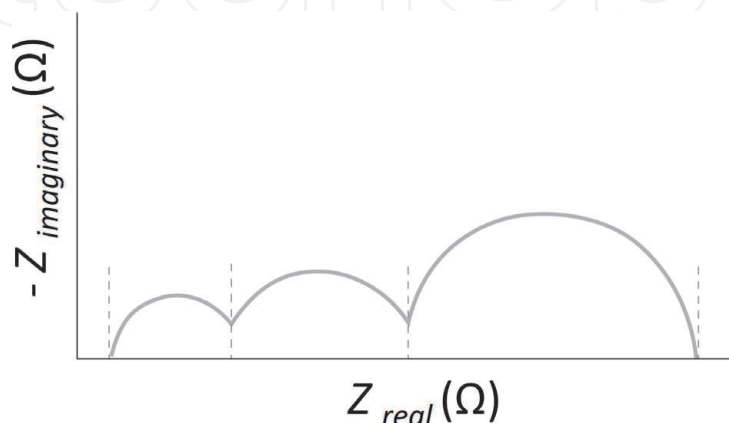


Figure 20.

Typical EIS spectra and the corresponding physical processes in a solid oxide fuel cell, where the first semi-circle corresponds to ion conduction within grains; the second to ion conduction across or along grain boundaries; and the third, to the charge transfer at the electrode-electrolyte interface.

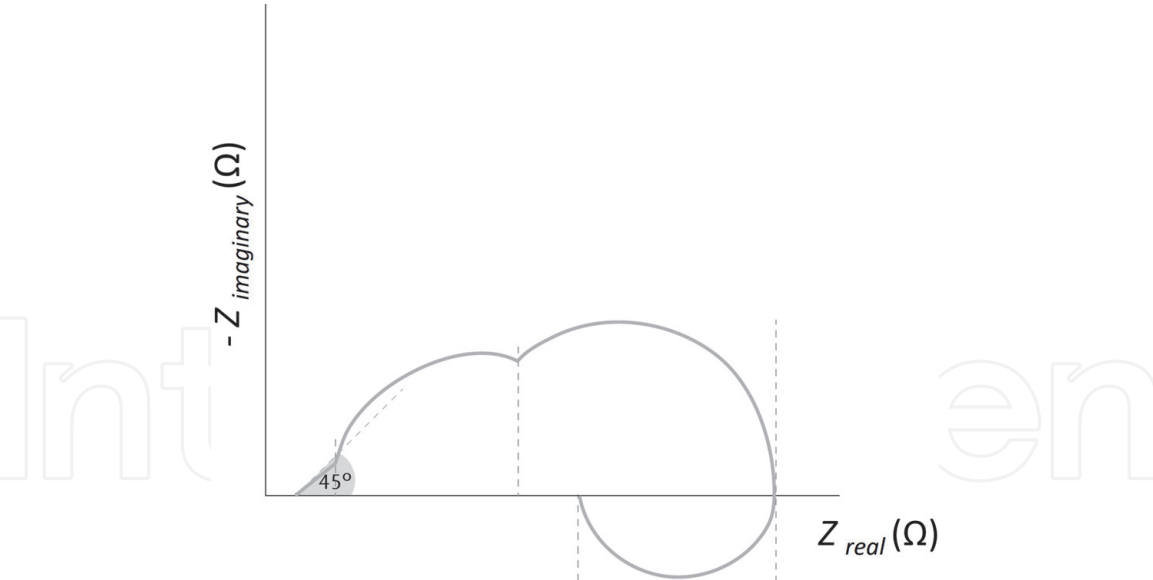


Figure 21.
Typical EIS spectra and the corresponding physical processes in a polymer electrolyte fuel cell.

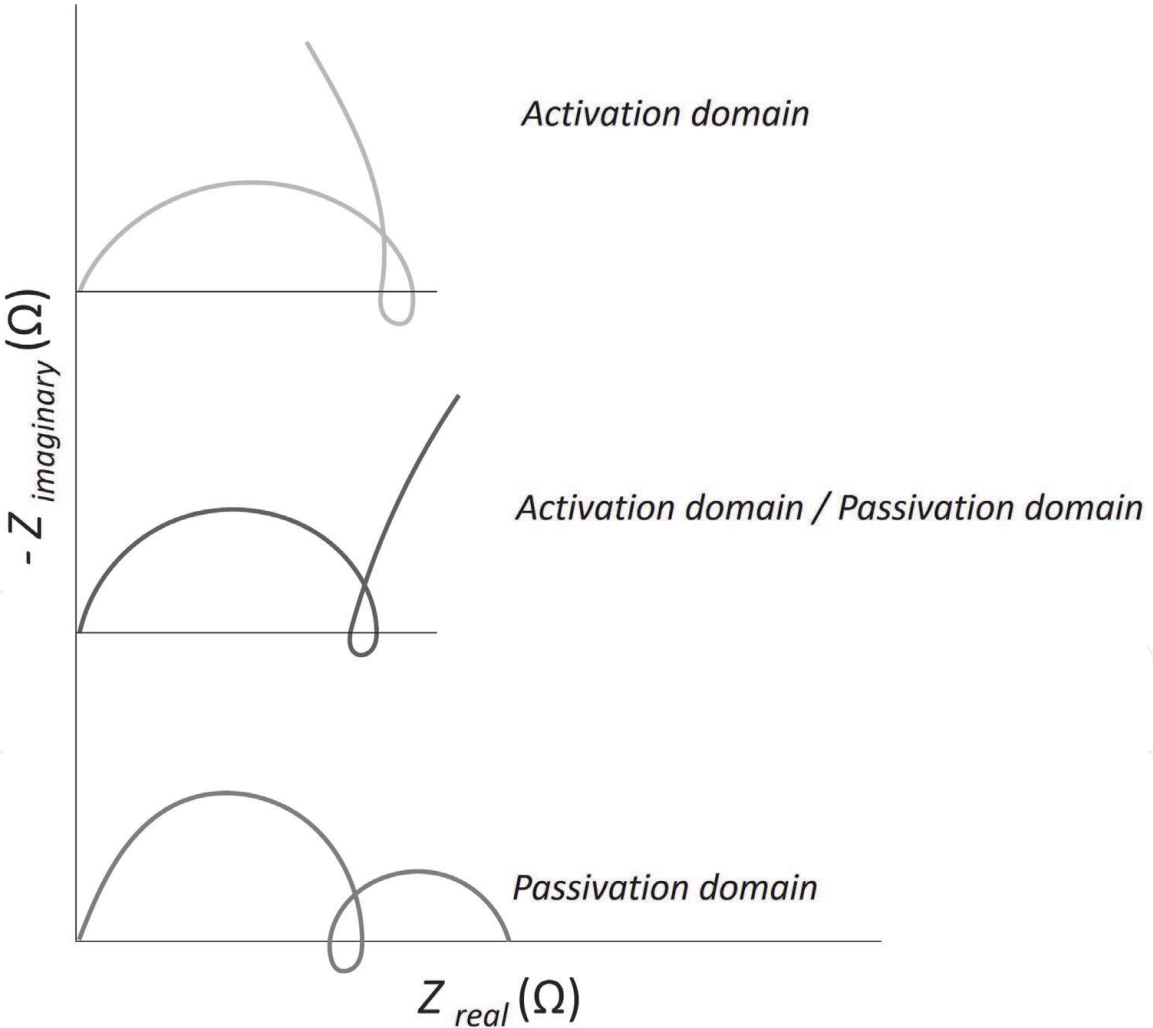


Figure 22.
Typical EIS of iron corrosion in sulfuric acid solution.

equivalent circuit: Both the components of the circuit, as well as the electrical circuit itself, must have a physical explanation. This is of particular importance since there can usually be several equivalent circuits that describe the experimental data with the same accuracy. Most of the EIS works related to corrosion processes are

complementary tools for the Tafel Slopes obtained in the materials. In this regard, the circuits can become very complex, but they can help to understand the phenomena occurring during the oxidation processes such as crevice and pitting corrosion.

In general, galvanostatic impedance is more suitable for non-invasive probing of metal corrosion at the open-circuit potential and for measuring most high-energy electrochemical devices, where the impedance is low and current levels are elevated. Inductive loops are commonly seen in corrosion processes. For example, the inductive loops for the corrosion of iron in sulfuric acid are attributed to the coupling of electrochemical reactions by three intermediate species (**Figure 22**). However, many examples can be given in these processes, and they will highly depend on the material and the electrolyte.

3. Conclusions

Electrochemical impedance spectroscopy (EIS) is a highly used technique in electrochemistry and helps to understand the phenomena occurring at the interface electrode/solution. Nevertheless, in the case of an electrochemical system, the main complication is that the system must remain in a stationary state during the measurement. EIS uses a small-amplitude potential or current perturbation to excite the electrochemical system at different frequencies, as illustrated in the figures presented in the chapter. By measuring the response in the current of the system to this perturbation, a transfer function is calculated known as the electrochemical impedance of the system. The data acquisition helps us to understand the processes that the system is performing, by means of resistances, capacitances, inductances, etc. In this regard, Nyquist and Bode plots can be fitted in commercial software to obtain the actual values of every electrical component, based on the equivalent circuit chosen. This technique is highly used in electrocatalysis and corrosion studies, two important fields within electrochemistry, and serves as a complementary tool to other electrochemical techniques, such as voltammetry.

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Conflict of interest

The author declares no conflict of interest.

Notes/thanks/other declarations

In honor of my Ph.D. advisor, Professor Thomas E. Mallouk, and my beloved husband, Dr. Arnar Már Búason.

Acronyms and abbreviations

EIS	Electrochemical impedance spectroscopy
Z	impedance


R	resistance
C	capacitance
WE	working electrode
RE	reference electrode
CE	counter electrode
R _{ct}	Charge transfer resistance
R _e or R _{sol}	Electrolyte resistance
C _{dl}	Capacitance of the double layer
CPE	Constant Phase Element
L	Inductance
q	charge
t	time
w	radial frequency
f	frequency
Q	variable of the CPE constant
α	variable of the CPE constant
W	Warburg element

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