BRIEF SURVEY ON ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY EVALUATION AND ITS APPLICATION ON NICKEL CORROSION IN CHLORIDE SOLUTIONS

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ABSTRACT
A short review on the use of the electrochemical impedance spectroscopy for evaluation of the corrosion behaviour of the metallic materials and the practical illustrations for the nickel behaviour in chloride solutions (artificial seawater) are shown in this paper. One step in developing sustainability could be to place electrochemistry in the energy strategies. Many new experimental researches are using EIS for investigation on pipelines corrosion occurrence in the field of power plants and/or urban distribution grids.

Keywords: electrochemical method, corrosion rate, nickel, seawater

INTRODUCTION
The electrochemical impedance spectroscopy (EIS) has matured over the past 20 years as a tool in corrosion protection research and has provided to be one of the most useful electrochemical characterization technique presently available [1]. EIS uses small periodic signal to perturb an electrode surface and measure an electrochemical response that can be analyzed to gain information on corrosion mechanism and corrosion kinetics [1-11]. The EIS method permits the analysis of the alternating current (AC) impedance data, which is based on the modelling a corrosion process by an equivalent electrical circuit. Many new experimental researches are using EIS for investigation on pipelines corrosion occurrence in the field of power plants and/or urban distribution grids, as following: near-neutral pH stress corrosion cracking (SCC) of pipelines, occurs in a dilute, deaerated bicarbonate environment, with pH ranging from 6 to 7, depending on the microcrystalline structure of the metallic material [5], influence of microbial Gordonia-iron oxidizing bacteria, from sewage treatment plants on corrosion of carbon steel [6], anti-corrosive coatings used as preventive measures in corrosion of metal artifacts [7], corrosion of transportation infrastructure for fuel grade, ethanol and ethanol fuel blends [8], effects of chloride ions and hydrogen-charging on the passivity and pitting corrosion behavior of X80 pipeline steel in a bicarbonate-carbonate solution[10], corrosion resistance titanium and cobalt alloys, or stainless steels frequently used as biomaterials [11]. The aim of this paper is to present the use of the EIS methods for analysis to an electrochemical interface undergoing corrosion, including the determination of the resistance polarization (R_p), the corrosion current (i_corr) and corrosion rate (r_corr).

MATERIALS AND METHODS
1. Theoretical considerations
1.1. Equivalent circuits and impedance parameters of the electrode/ electrolyte interface
The simplest equivalent circuits [1] used to represent an electrochemical interface undergoing corrosion and associated parameters are shown in figure 1.
**Fig. 1. Electrical equivalent circuits used to represent an electrochemical interface undergoing corrosion [1]**

$R_s$ is the solution resistance, $R_p$ – the polarization resistance, $C_{dl}$ – the double layer capacitance, $R_{ct}$ – the charge transfer resistance in absence of mass transport and reaction intermediates, $Z_w$ – the diffusion or Warburg resistance.

(a): $R_p = R_{ct}$ when there are no mass transport limitations and electrochemical reactions involve no adsorbed intermediates and nearly instantaneous charge transfer control prevails;

(b): $R_p = R_{ct} + Z_w$ in the case of mass transport limitations.

**1.2. Solution resistance**

Solution resistance is often a significant factor in the impedance of an electrochemical cell. The solution resistance between the reference electrode and the working electrode must be considered. 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:

$$R_s = \rho \frac{l}{A} \quad (1)$$

where:

$\rho$ is the solution resistivity.

The conductivity of the solution, $\lambda$, is more commonly used in the solution resistance calculations. Its relationship with solution resistance is:

$$R_s = \frac{1}{\lambda} \frac{l}{A} \quad (2)$$

Most electrochemical cells do not have uniform current distribution through a definite electrolyte area and solution resistance calculation is difficult. Using EIS method, the solution resistance is found when it fit a model to experimental EIS data.

**1.3. Double layer capacitance, $C_{dl}$**

An electrical double layer exists at the interface between an electrode and its surrounding electrolyte, characterized by existence of a charge excess on metal that attract ions of opposite charges from solution. The simplest model of the electrolyte region is that of a line charges at a fixed distance from electrode surface (Helmholtz model) similar to a simple parallel-plate capacitor.
On a bare metal immersed in an electrolyte, it can estimate that there will be approximately 30 µF of capacitance for every cm$^2$ of electrode area.

The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

**1.4. Charge transfer resistance, $R_{ct}$**

Considering a metal substrate in contact with an electrolyte, the metal can electrochemical dissolves into the electrolyte, according to the reaction:

$$\text{M} \leftrightarrow \text{M}^{n+} + nz$$

(3)

A charge transfer takes place at the interface; in the direct reaction, electrons enter in the metal and metal ions diffuse into the electrolyte. If we neglect diffusion, the rate of this charge transfer is given by the Butler-Volmer relation [12]:

$$i = i_0 \left[ e^{\frac{\alpha zF \eta}{RT}} - e^{-(1-\alpha) \frac{zF \eta}{RT}} \right]$$

(4)

where:
- $i_0$ is exchange current density;
- $F$ – Faraday’s constant;
- $T$ – temperature;
- $R$ = gas constant;
- $z$ = number of electrons involved in reaction;
- $\eta$ – overpotential;
- $\eta = E - E_0$ ($E$ – electrode potential under current and $E_0$ - equilibrium potential electrode).

When the overpotential, $\eta$, is very small, the equation (4) becomes:

$$\eta = \frac{RT i_{app}}{zFi_0} = R_{ct} i_{app}$$

(5)

where:
- $R_{ct}$ is the charge transfer resistance that characterized the electrochemical system at equilibrium;
- $R_{ct}$ is a resistance that opposes to the charge transfer.

From $R_{ct}$ expression the exchange current density can be calculated:

$$R_{ct} = \frac{RT}{zF \ i_0}$$

(6)

**1.5. Polarization resistance, $R_p$**

When an electrode undergoes uniform corrosion at open circuit, the open circuit potential (OCP), the mixt potential or the corrosion potential ($E_{corr}$) is controlled by the equilibrium between two different electrochemical reactions: anodic metal dissolution and cathodic reduction of an oxidant from solution. At corrosion potential, the cathodic and anodic currents are equal and equal with the corrosion current, $i_{corr}$. 
According to the Stern-Geary method [12], the corrosion current, \( i_{\text{corr}} \) (A/cm\(^2\)) can be calculated by relation:

\[
    i_{\text{corr}} = \frac{1}{2.3} \cdot \frac{b_a b_c}{b_a + b_c} \left( \frac{\Delta I_{\text{app}}}{\Delta E} \right)_{E_{\text{corr}}} = \frac{B}{R_p}
\]

(7)

where:

\[
    B = \frac{1}{2.3} \cdot \frac{b_a b_c}{b_a + b_c},
\]

\[
    R_p = \left( \frac{\Delta E}{\Delta I_{\text{app}}} \right)_{(E - E_{\text{corr}})^\infty}
\]

is the polarisation resistance given by the slope of linear part \((dE / di)\) at \(t = \infty\), \(\Delta E = 0\) [ohm-cm\(^2\)].

\(b_a\) and \(b_c\) are the Tafel slopes for anodic and cathodic reaction, respectively, \((\text{V/decade})\), obtained from the polarization measurements.

As shown anterior [12], the determination of \(R_p\) by the linear polarisation method can give errors. The complications and sources of error associated with the polarisation resistance method [1,12,13] can be avoid using EIS method that introduced equivalent circuit parameters to represent and simulate the corroding electrochemical interface [14,15]. In absence of the mass transport limitations, \(R_p = R_{\text{ct}}\).

2. **Diffusion impedance, \(Z_W\)**

When a corrosion process is controlled by diffusion or film adsorption, the corroding interface can be modelled using the equivalent circuit shown in figure 1b. In this case, diffusion impedance \((Z_W)\), known as the Warburg impedance, is included in circuit. Notice that \(Z_W\) and \(R_{\text{ct}}\) are connected in series. In the case of mass transport limitations: \(R_p = R_{\text{ct}} + Z_W\).

3. **Correlations between the impedance parameters and characteristic diagrams**

The impedance of the electrode/solution interface is described [1, 2] by the following expression:

\[
    Z(\omega) = R_s + \frac{R_p}{1 + j\omega R_p C_{\text{dl}}}
    = \left[ R_s + \frac{R_p}{(1 + \omega^2 R_p^2 C_{\text{dl}}^2)} \right] - j \left[ \frac{j\omega C_{\text{dl}} R_p^2}{(1 + \omega^2 R_p^2 C_{\text{dl}}^2)} \right]
    = Z'(\omega) + jZ''(\omega)
\]

(8)

where:

\(\omega = 2\pi f\), the frequency of the applied signal in rad \(s^{-1}\);

\(f\) – the frequency of the applied signal in Hz;

\(C_{\text{dl}}\) – the interfacial capacity, F cm\(^2\).

Therefore, the impedance of the interface consists of two parts, a real number \(Z'(\omega)\) and imaginary number \(Z''(\omega)\) with a complex representation \(Z(\omega) = Z'(\omega) + jZ''(\omega)\) and with phase angle \((\theta) = \tan^{-1} Z''(\omega) / Z'(\omega)\).
$R_p$ is a function of potential applied to the electrode; at $\eta = 0$, it becomes the charge transfer resistance, $R_{ct}$.

There are two conventional modes of treating the impedance data: the Nyquist diagrams, in which the imaginary component, $Z''(\omega)$, is represented a function of real component $Z'(\omega)$, and the Bode diagrams, in which the absolute values of impedance, $|Z(\omega)|$ or the phase angle $\theta$ are represented as function of frequency.

In figure 2 are shown the ideal Nyquist diagrams that correspond to the equivalent circuits shown in figure 1.

\[ Z'(\omega)_{\text{react}} = -1/\omega C_{dl} \]

\[ Z'(\omega)_{\text{max}} = -1/\omega C_{dl} \]

At low and high frequencies, equation (8) yields:

\[ Z(\omega)_{\omega \to 0} = R_s + R_p \tag{9} \]

which is an intercept on the $Z'(\omega)$ axis on the low frequency side.

\[ Z(\omega)_{\omega \to \infty} = R_s \tag{10} \]

which is an intercept on the $Z'(\omega)$ axis on the high frequency side ($Z''(\omega) = 0$).

Combining equations (9) and (10) yields the polarization resistance as:

\[ R_p = Z(\omega)_{\omega \to 0} - R_s = Z(\omega)_{\omega \to 0} - Z(\omega)_{\omega \to \infty} \tag{11} \]
In Nyquist plot $R_p$, is equal with the semicircle diameter. Replacing $R_p$ in equation (7) it yields the corrosion current density in terms of impedance:

$$i_{corr} = \frac{B}{Z'(\omega)_{\omega \rightarrow 0} - Z'(\omega)_{\omega \rightarrow \infty}}$$

(12)

Using Faraday’s law, the corrosion rate can be calculated as rate of loss weight (eq. 13) or as rate of penetration (eq. 14):

$$r = \frac{A_w i_{corr}}{zF}, \text{[g/cm}^2\text{s]} \text{ or}$$

$$r = \frac{A_w i_{corr}}{zFd}, \text{[cm/s]}$$

(13)

(14)

where:
- $r$ is corrosion rate;
- $A_w$ – atomic mass of metal, g/mol;
- $z$ – valence of metal;
- $d$ – metal density, g/cm$^3$.

The obtained values with the above relations can be easily transformed in the common units to the engineers and designers, respectively in g/m$^2$·h and mm/y.

The presence of diffusion controlled corrosion processes does not invalidate the EIS method. The mass transfer impedance is a vector containing real and imaginary components which are identical, that is the phase angle $\theta = a \tan \left[ Z''(\omega)/Z'(\omega) \right] = a \tan(-1) = -45^\circ$. On complex plane plot it is a straight line with slope of 1 (figure 2b). Also, extrapolating the semicircle (dashed line) to intercept the real impedance axis $Z'(\omega)$ graphically defines the polarization resistance $R_p$.

At low frequencies, the diffusion impedance is frequency independent[3] and given by relation:

$$Z_w(\omega)_{\omega \rightarrow 0} = \sigma \delta \frac{\sqrt{2}}{\sqrt{D}}$$

(15)

where:
- $\sigma = RT / (zFAC_x \sqrt{2D})$ is the Warburg impedance coefficient;
- $\delta$ = thickness of the diffusion layer;
- $C_x$ = concentration of the specie in the diffusion layer;
- $D$ = diffusion coefficient of the reactant specie and $A$ = exposed area.

Therefore, the low frequency limit of the electrode impedance equals:

$$Z(\omega) = R_s + R_a + \sigma \delta \frac{\sqrt{2}}{\sqrt{D}}$$

(16)

and $R_p$ defined in eq. (7) as $[\Delta E / \Delta i_{app}]$ as $\omega \rightarrow 0$, becomes the sum of the charge transfer resistance and diffusion impedance:
From the Bode plots (figure 3) can be obtained similar information. $R_s$ and $R_s + R_p$ are obtained from $|Z(\omega)|$ versus log $\omega$ at high and low frequencies from the same argument as the Nyquest plot. In the intermediate frequencies region, an almost straight line with slope of -1.0 can be seen. The equation for this line is obtained by ignoring the frequency independent terms, $R_s$ and 1 in the denominator, of equation (8) and taking the logarithm it yields:

$$\log|Z(\omega)| = -\log \omega - \log C_{dl}$$  

(18)

where the angular frequency is $\omega = 2\pi f$. For $\omega = 1$, $f = 0.16$ Hz, $|Z(\omega)|$ becomes equal to $1/C_{dl}$.

The $\theta$ versus log $\omega$ show that impedance responses are resistive primarily at high and low frequencies as indicated by practically no phase shift, while as at intermediate frequencies, they are mostly capacitive as their phase shift get closer to 90°. On a Bode plot, the Warburg impedance exhibits a phase shift of 45°.

The maximum applied frequency allowed obtaining $R_s + R_p$ from the low frequency plateau can be approximated by relation [1]:

$$f_{max} < f_{top} = \frac{1}{2\pi C_{dl}(R_s + R_p)}$$

(19)

where:

\[ f_{top} = \text{approximation of the lower breakpoint frequency (Hz)} \quad \text{and} \quad f_{max} = \text{the maximum test frequency (Hz)}. \]

Thus it can be seen from eq. (16) that increasing values of $C_{dl}$, $R_s$ or $R_p$ dictate that a lower $f_{max}$ is required to obtain $R_s + R_p$ at $Z(\omega)_{\omega \rightarrow 0}$ accurately. The capacitance may become larger than that expected double layer capacitance alone, in the presence of adsorption – pseudo-capacitance [1,12]. Such a pseudo-capacitance may be caused by an adsorbed intermediate with some fractional monolayer coverage [1], by the dielectric compound capacitance of the electrode surface [16] or is
related to the porosity of the electrode [17]. One way that \( R_p \) may be increased is by passivity [1]. Another is by diffusion control corrosion such that \( R_p = R_{ct} + Z_w \).

A frequency of 1 mHz is typically chosen as a reasonable initial choice of \( f_{\text{max}} \), but it is obvious from eq. (16) that either lower or higher frequencies may be required depending upon the circumstances.

Similarly, a frequency above the high-frequency breakpoint [1] must be applied to obtain \( R_s \):

\[
f_{\text{hf}} = \frac{1}{2\pi C_{dl} R_s}
\]

(20)

Typically, \( f_{\text{app}} \) must be in the kHz range to determine \( R_s \).

4. Practical Illustrations

The Electrochemical spectra in the complex plane as Nyquist and Bode plots for Ni electrode at open circuit potential (OCP-measured after 10 minutes from cathodic activation of the electrode surface) in solutions containing chloride ions - artificial seawater [18,19] are given in Fig.4.

![Fig. 4. Nyquist and Bode plots for the Ni electrode at open circuit potential in artificial seawater at 25°C](image)

The impedance data do not have a shape of semicircle in the Nyquist plot (Fig.4a) suggesting a high corrosion resistance of Ni in the seawater. The Bode plot also suggests a capacitive behaviour of the Ni electrode at OCP. The logarithm modulus of impedance (\( \log|Z| \)) varies linearly with logarithm frequency (\( \log(f) \)) with a slope of \(-0.82\), which is close to the theoretical value of \(-1\) for a pure capacitor. Under these conditions, \( |Z| \) is related to the double – layer capacitance, \( C_{dl} \), by relation (15). The value of \( C_{dl} \) obtained from Fig. 4b for the Ni electrode at OCP of 0.31 mF.cm\(^2\) is much higher than \( C_{dl} \) for the Hg/solution interface (about 20 µF.cm\(^2\)). It is assumed that these high values of \( C_{dl} \) are due to a pseudo-capacitance, which arises due to adsorption of \( O_2 \), \( OH^- \) or intermediates of corrosion and passivation reactions at the solid electrode/electrolyte interface.

The faze angle (\( \theta \)) is about \(-75^\circ\) over a wide frequency range that corresponds to the behaviour of metals on which it forms barrier layers, such as passive films. The experimental impedance spectra show that the nickel is corrosion resistant in seawater due to the formation of the
passive film on its surface. However, if the corrosion potential becomes sufficiently noble, the chloride ions contained in seawater can induce the pitting corrosion [19, 20].

CONCLUSIONS

The use of the EIS methods for analysis to an electrochemical interface undergoing corrosion permits the determination of the resistance polarization ($R_p$), the corrosion current ($i_{corr}$) and corrosion rate ($r_{corr}$). The EIS nickel behaviour in artificial seawater shows a high corrosion resistance due to the spontaneous passivity. David A.J. Rand invites researchers from every field to a fascinating journey on the electrochemical road to sustainability: as the nations of the world develop their industrialization and populations, they will require increasing amounts of energy. Yet, global energy consumption, even at present levels, has already given rise to major concerns over the security of future supplies, together with the attendant twin problems of environmental degradation and climate change. Accordingly, countries are examining a whole range of new policies and technology issues to make their energy futures “sustainable”, that is, to maintain economic growth and cultural values, and in the same time providing energy security and environmental protection. One step in the right direction is to place electrochemistry and clean technology—at the cutting edge of energy strategies [9].

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