

Implementation of an Impedance Spectroscopy Equipment for the Measurement of Electrochemical Parameters

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Abstract—A device for the measurement of electrochemical parameters was designed and built using the NI USB 6250 card and the LabView 2010 software. The implemented technique, Electrochemical Impedance Spectroscopy (EIS), requires the measurement of the impedance in a wide scan of frequency, as well as the generation of its corresponding Nyquist diagram. The developed equipment, allows to recognize the type of interfaces in the layers between metals and electrolytes in order to measure corrosion parameters such as the electrical resistance of the layers, together with their capacitance and the physical model of the interface.

Keyword - LabView; Nyquist; EIS; electrochemistry; Lock-in amplifier.

I. INTRODUCTION

When a metal is immersed in an aqueous solution and this solution has electrolytes, they form on the surface an interface where they are organized on its surface; From here a first model named double layer of Helmholtz-Perrin arises in 1879 which is based on the accumulation of charges forming an equivalent capacitor and an electric resistance [1].

Subsequently, this layer was studied by (Gouy and Chapman 1910-1913) from where it is diffuse behavior was deduced in terms of the physicochemical variables of the electrolyte [2]. Currently the model are adopted between the electrolyte-metal is the Gouy-Chapman-Stern [3] that combines the two previous models as shown in Fig. 1.

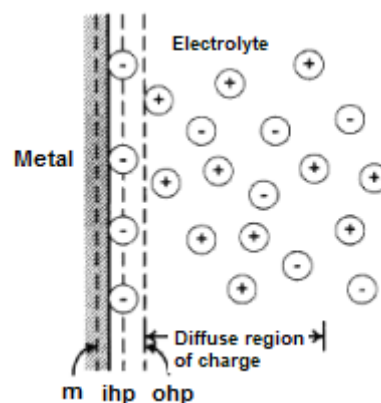


Fig. 1. Helmholtz-Perrin model+Gouy-Chapman model = Gouy-Chapman-Stern model [3].

The Helmholtz model [4] is supported as if on the surface there is a parallel plate capacitor, in the region inside the capacitor applies the Laplace equation given by

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho}{\epsilon} = 0 \rightarrow \frac{\partial \phi}{\partial x} = Ct \quad (1)$$

where ϕ is the potential between the metal and the outer layer of ions (ohp), x is the frontier distance of the interface, ρ is the charge density and ϵ is the electrical permittivity within the layer.

The charge density is considered to be zero in the same way as the internal layer of Helmholtz (ihp), causing the behavior of the potential in this region to vary linearly with the distance as Eq. (2):

$$\phi_{(x)} = \phi_e \left(1 - \frac{x}{d} \right) \quad (2)$$

This model does not take into account the electrolyte ions and excludes their contribution to the behavior of potential and capacitance in the double layer. Gouy and Chapman proposed a model taking into account the ions immersed in the electrolyte, based on the charge density that depends on the ionic concentration and the charge density of these ions can be written as

$$\rho = \sum_i Z_i F C_i \quad (3)$$

where Z_i is the net charge of each ion, F is the Faraday constant (96352C/mol), C_i is the concentration (mol/L) of the i th species of the electrolyte.

Considering that the charge density depends on the concentration as well as the energy of the ions immersed in the solution, they respond to the Boltzman distribution [5] as shown in Eq. (4):

$$C_i = C_{i(x=\infty)} e^{\left(\frac{-Z_i F \phi}{RT} \right)} \quad (4)$$

where R is the gas constant (8.3144 J/K mol), e is the charge of the electron (-1.6×10^{-19} C).

Using both equations 3&4 and in turn in the Poisson equation Eq. (1), is obtained the model based on the Poisson-Boltzman equation given by [6]

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{1}{\epsilon} \sum_i Z_i F C_{\infty} e^{\left(\frac{-Z_i F \phi}{RT} \right)} \quad (5)$$

The solution of the Eq. (5), results in (replacing the variable surface charge density $\sigma = -(\epsilon/4\pi)(\partial\phi/\partial x)_{x=0}$) Eq. (6):

$$\sigma = \pm \left(\frac{RT\epsilon}{2\pi} \right)^{1/2} \left[\sum_i C_i \left[e^{\left(\frac{-Z_i F \phi}{RT} \right)} - 1 \right] \right]^{1/2} \quad (6)$$

If the ion distribution is homogeneous and symmetrical on its surface, the charge distribution behaves as follows

$$\sigma = \left(\frac{2RT\epsilon}{\pi} \right)^{1/2} \sqrt{C} \text{Sinh} \left(\frac{-Z_i F \phi}{2RT} \right) \quad (7)$$

This model predicts a capacitance in the double layer of Helmholtz but takes into account the diffuse contribution of the ions inside the electrolyte since this capacitance per unit area is $C_G = \left(\frac{\partial\sigma}{\partial\phi} \right)$ as shown in Eq. (8):

$$C_G = \left(\frac{Z^2 F^2 \epsilon}{2\pi RT} \right)^{1/2} \sqrt{C} \text{Cosh} \left(\frac{Z_i F \phi}{2RT} \right) \quad (8)$$

This predicts a capacitance (minimum capacitance) at a potential ϕ called Guouy-Champan capacity, this originates in the charge accumulation of all the electrolyte up to the surface of the metal given by [9]

$$C_{G(\min)} = ZF \left(\frac{\epsilon}{2\pi RT} \right)^{1/2} \sqrt{C} \quad (9)$$

The Stern model [7] adjusts these two models so that it is condensed assuming a net capacitance in the interface Metal-Solution which is defined as follows

$$\frac{1}{C_d} = \frac{1}{C_{m-2}} + \frac{1}{C_{2-s}} = \frac{1}{C_H} + \frac{1}{C_G} \quad (10)$$

where C_d is the capacitance in the double layer.

Finally, the interface behaves as a capacitor which allows predicting parameters in the double layer as seen in Fig. 2.

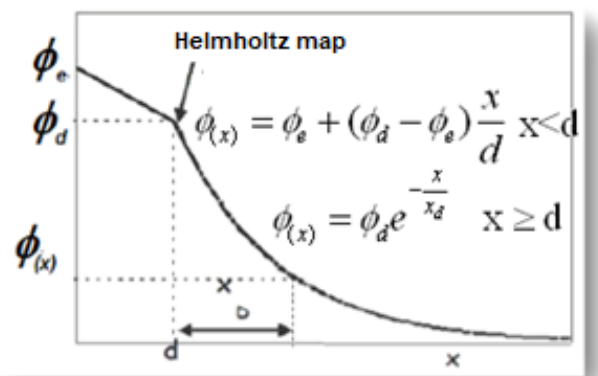


Fig. 2. Potential ϕ in the Stern=Gouy-Chapman+Helmholtz model.

II. EXPERIMENTAL DEVELOPMENT

The equipment was developed in two stages, the first focused on the hardware which consists of the analog circuit as shown in figure 3, and the second stage was developed around data acquisition and software development, taking as a reference to the National Instruments NI-USB-6250 card in charge of supplying the signal in the electrochemical cell, measuring the current signals and measuring the applied voltage. The software designed in Labview 2010 is responsible for processing the signals in order to extract the necessary data for the electrochemical characterization.

A. Potentiostat Analog Circuit

This circuit was designed based on the model commonly used in this type of equipment [3], in the plane of the circuit shown in Fig. 3.

The equipment works as follows; an AC signal from the DA₁ (Digital Analogue 1) port of the NI-USB6250 card is supplied on R₃; the amplifier A₁ is responsible for supplying the current demanded by the cell through the counter electrode; the signal of R₃ is brought by R₂ to the voltage tracker A₂ which is responsible for driving the reference electrode (R₁ fulfills the function of increasing the impedance of this amplifier).

By means of amplifier A₅, the voltage signal of the reference electrode is fed into the AD₂ (Digital Analog 2) port of the card; the excitation current of the cell passes through the working electrode (E. work) through the amplifier A₃ which performs the function of the current-to-voltage converter; R₅ fulfills the function of converting the current into voltage; R₅ is a resistor that is selected by a mini relay where there are resistors that have the following value according to their selection 10 Ω , 100 Ω , 1k Ω , 10k Ω , 100k Ω and 1M Ω ; R₄ fulfills the function of increasing the impedance of A₃ in order to avoid deviations of the current to be measured according to the Eq. (11):

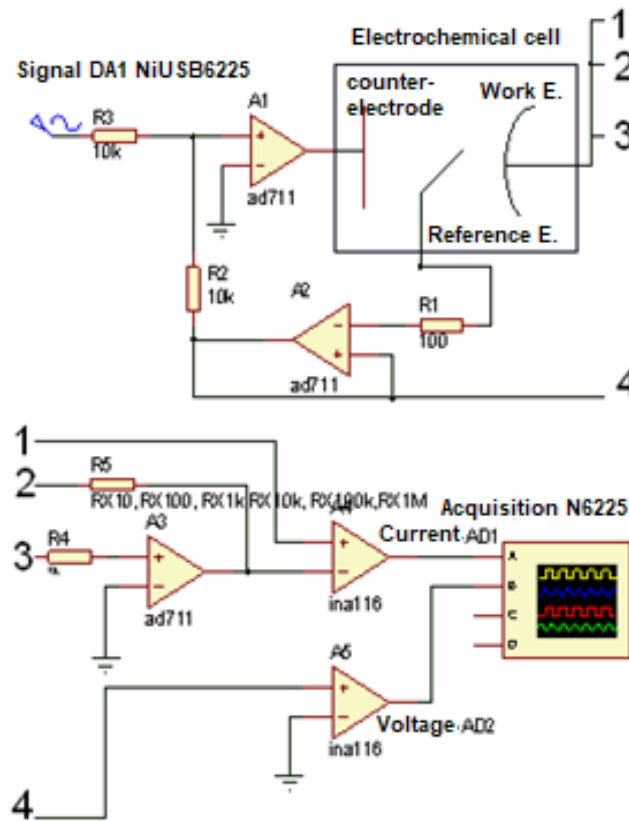


Fig. 3. EIS potentiostat analog circuit

$$\begin{aligned}
 I_{DCx} &= I_{Input} \cos(\omega t + \phi_i) \cos(\omega t) \Rightarrow \overline{I_{DCx}} = \frac{1}{2} I_{Input} \cos(\phi_i) \\
 I_{DCy} &= I_{Input} \cos(\omega t + \phi_i) \sin(\omega t) \Rightarrow \overline{I_{DCy}} = \frac{1}{2} I_{Input} \sin(\phi_i) \\
 V_{DCx} &= V_{Input} \cos(\omega t + \phi_i) \cos(\omega t) \Rightarrow \overline{V_{DCx}} = \frac{1}{2} V_{Input} \cos(\phi_i) \\
 V_{DCy} &= V_{Input} \cos(\omega t + \phi_i) \sin(\omega t) \Rightarrow \overline{V_{DCy}} = \frac{1}{2} V_{Input} \sin(\phi_i)
 \end{aligned}
 \tag{11}$$

Once the AD₁ and AD₂ voltages have been acquired, the measure of the amplitude and phase from the electrochemical cell is made by the subVI (lock-in) where they are each multiplied by two reference signals having the same amplitude and frequency at the excitation but phase-shifted 90°, between them according to Fig. 4.

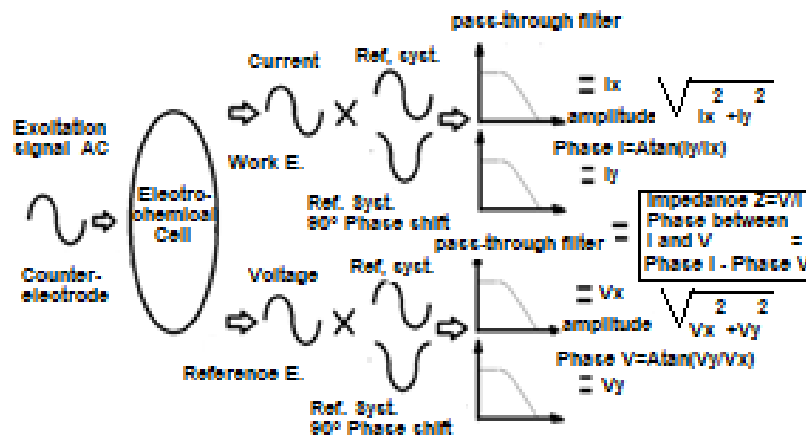


Fig. 4. Lock-In technique (phase-sensitive detection)

After being multiplied by the reference signal each one goes through a low-pass filter to obtain a *DC* signal (I_{DCx} , I_{DCy} , V_{DCx} , V_{DCy}) representing the amplitude of the measured signal; since the original signal was multiplied by two out-of-phase signals each one is used to obtain the phase with respect to the reference signal [8-10].

From Eq. (11) the components of the current and voltage as well as the phases of each are obtained with respect to the reference signal as shown in Eq. (12):

$$\begin{aligned} I_{Input} &= \sqrt{2} \sqrt{I_{DCx}^2 + I_{DCy}^2}; & \phi_i &= A \tan\left(\frac{I_{DCy}}{I_{DCx}}\right) \\ V_{Input} &= \sqrt{2} \sqrt{V_{DCx}^2 + V_{DCy}^2}; & \phi_v &= A \tan\left(\frac{V_{DCy}}{V_{DCx}}\right) \end{aligned} \quad (12)$$

Using Eq. (12) gives the Eq. (13) and Eq. (14) to implement the impedance spectra.

$$Z_{(\omega)} = \frac{V_{input}}{I_{input}} \quad (13)$$

$$\phi_{i-v} = \phi_i - \phi_v \quad (14)$$

III. RESULTS

The verification of the correct functioning of the equipment was performed by measuring different spectra in emulated conditions (dummy circuits) and simulated (with Zsimpwin). For the validation of the data we analyzed the theoretical models realized in the program Zsimpwin version 3.20 developed by Ph.D. Bruno Yeum [11], this version of the software was used thanks to its precision in the analysis of electrochemical models.

A. Circuit 1

The circuit of Fig. 5, emulates double layer behavior with passivating oxide coating (typical characteristic values according to bibliography) [12], the measured spectrum is observed in the Fig. 6 and the simulation in Zsimpwin is represented in the Fig. 7

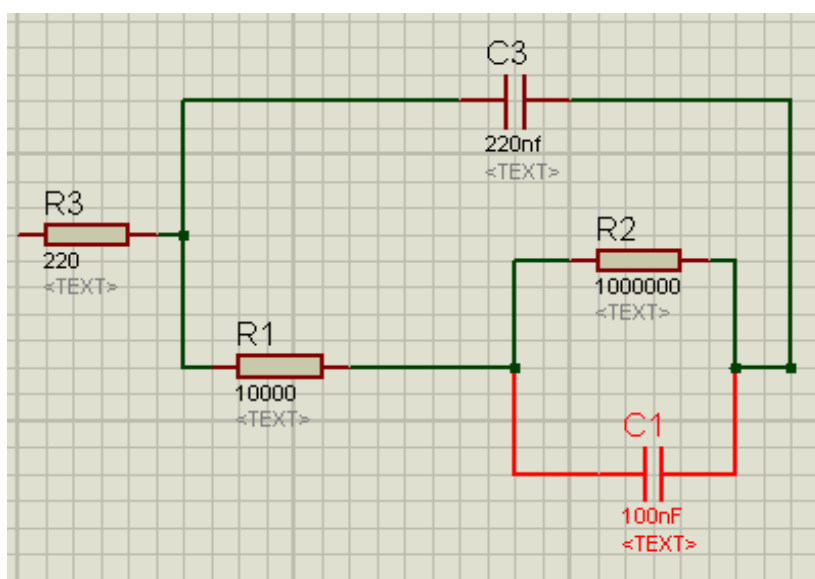


Fig. 5. Dummy circuits 1

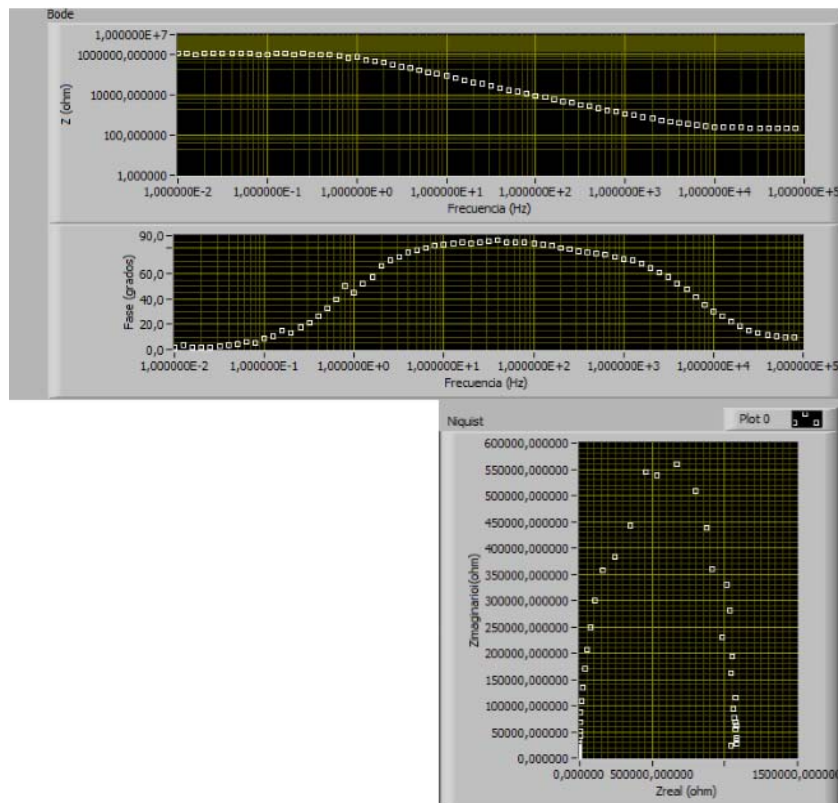


Fig. 6. Circuit spectrum dummy 1 taken by the equipment

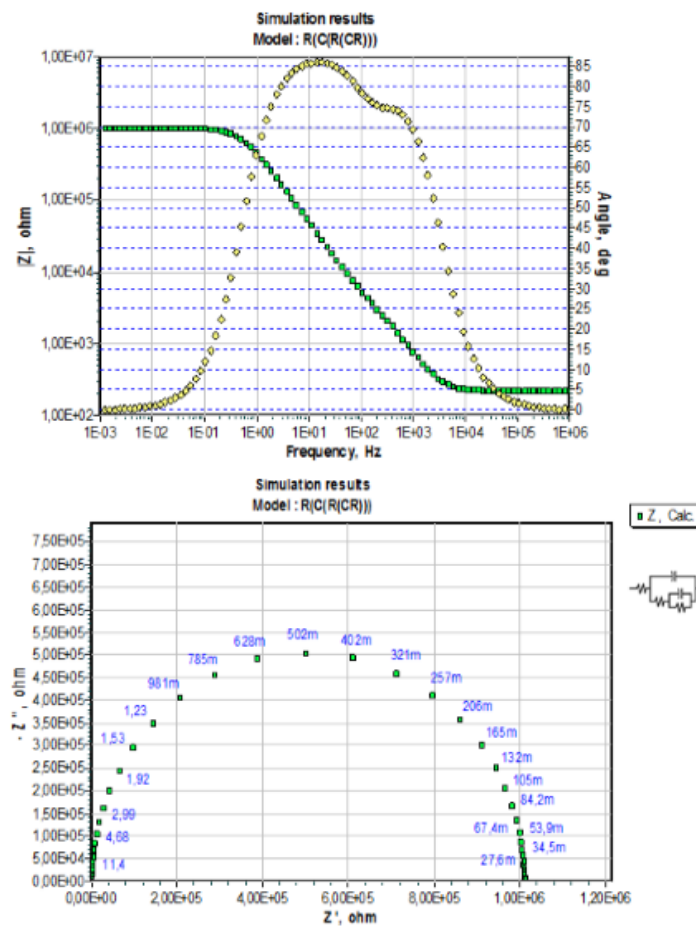


Fig. 7. Circuit spectrum dummy 1 simulated in Zsimpwin

B. Circuit II

The dummy circuit 2 shown in Fig. 8 which does not emulate specific electrochemical surface condition was tested and measured as shown in Fig. 9 in order to compare its impedance spectrum and the simulation in Zsimpwin shown in Fig. 10.

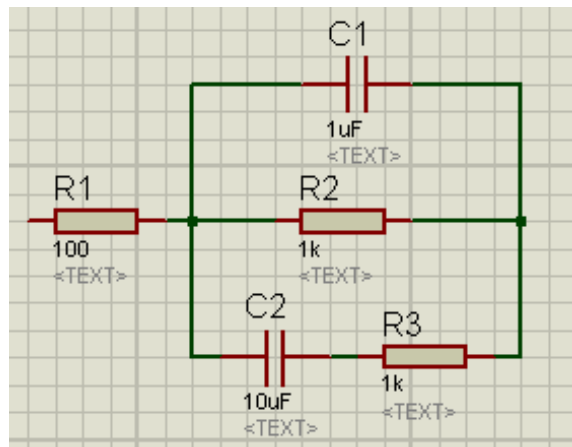


Fig. 8. Circuit dummy 2

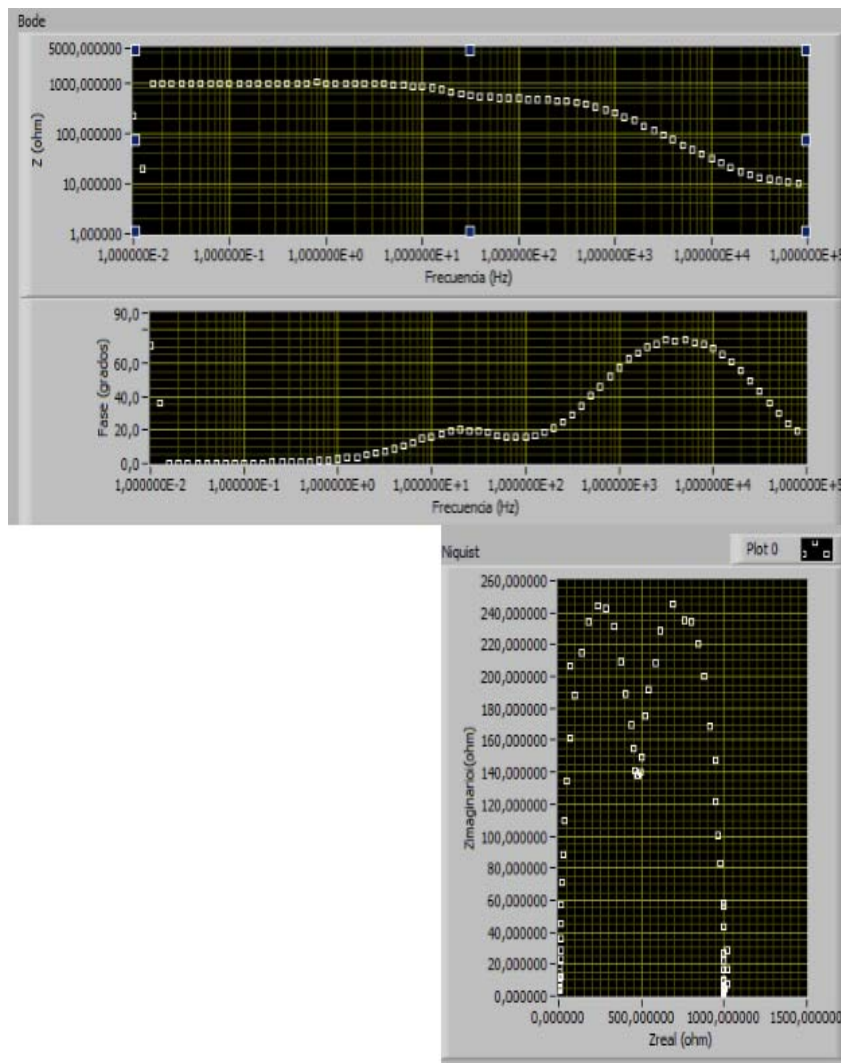


Fig. 9. Circuit spectrum dummy 2 taken by the equipment

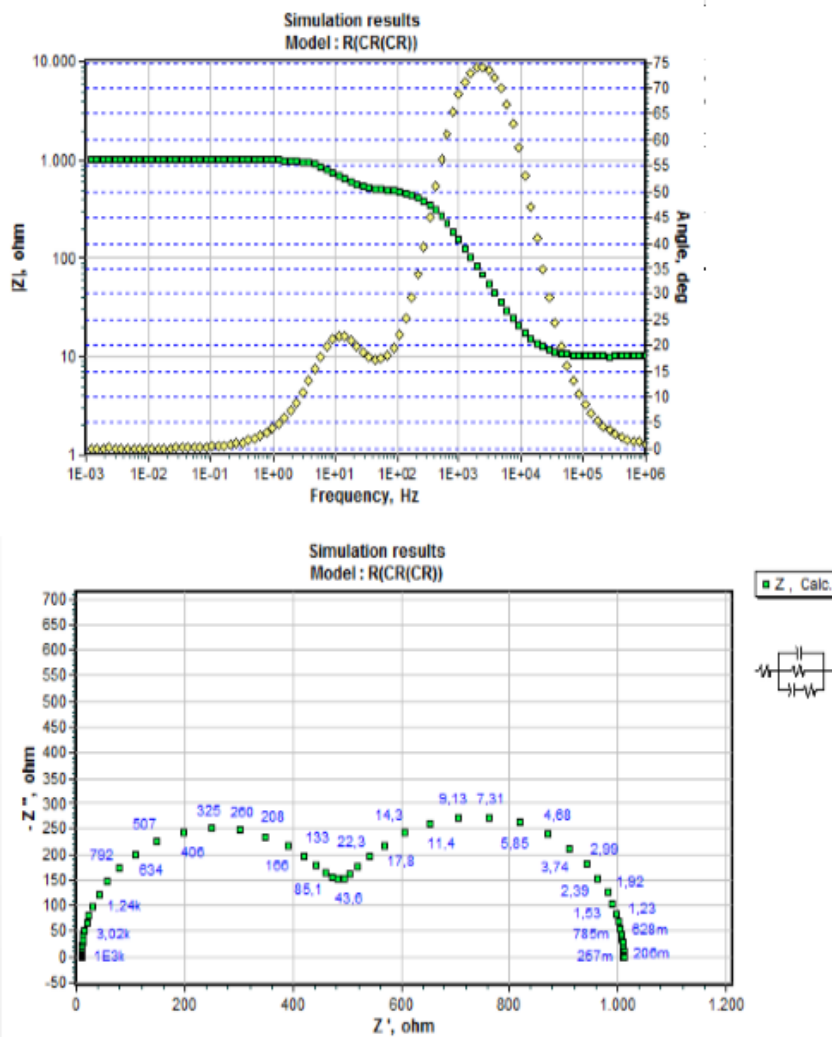


Fig. 10. Spectrum circuit dummy 2 simulated in Zsimpwin

C. Electrochemical Cell

In the electrochemical cell, 316L steel and 10% sulfuric acid were used as the electrolyte; the measurement parameters were: $V_{offset} = 0$ V, reference electrode $V = 10$ mV, $f_{initial} = 0.01$ Hz, $f_{final} = 100$ kHz, frequency resolution = 10 data per decade. In the spectrum observed on the cell, electric noise is pronounced, especially at low frequencies, as shown in Fig. 11.

The spectrum measured by the equipment coincides with the typical double layer model [8] where the resistance of the measured solution (R_s) was 240 Ω , this is justified in the fact that the sulfuric acid used in this concentration has a high ionic conductivity.

A double layer formation with a capacitance formed by the passive layer (C_p) generated by the chromium (Cr_2O_3) oxides as well as the Helmholtz (Ch) capacitance on the surface was also observed, the passive layer obtained measured approximately 0.8 μF and the Helmholtz layer showed an approximate capacity of 4.5 nF, resulting in a medium accumulation of protons in the Helmholtz layer and in the polarization of the passive layer.

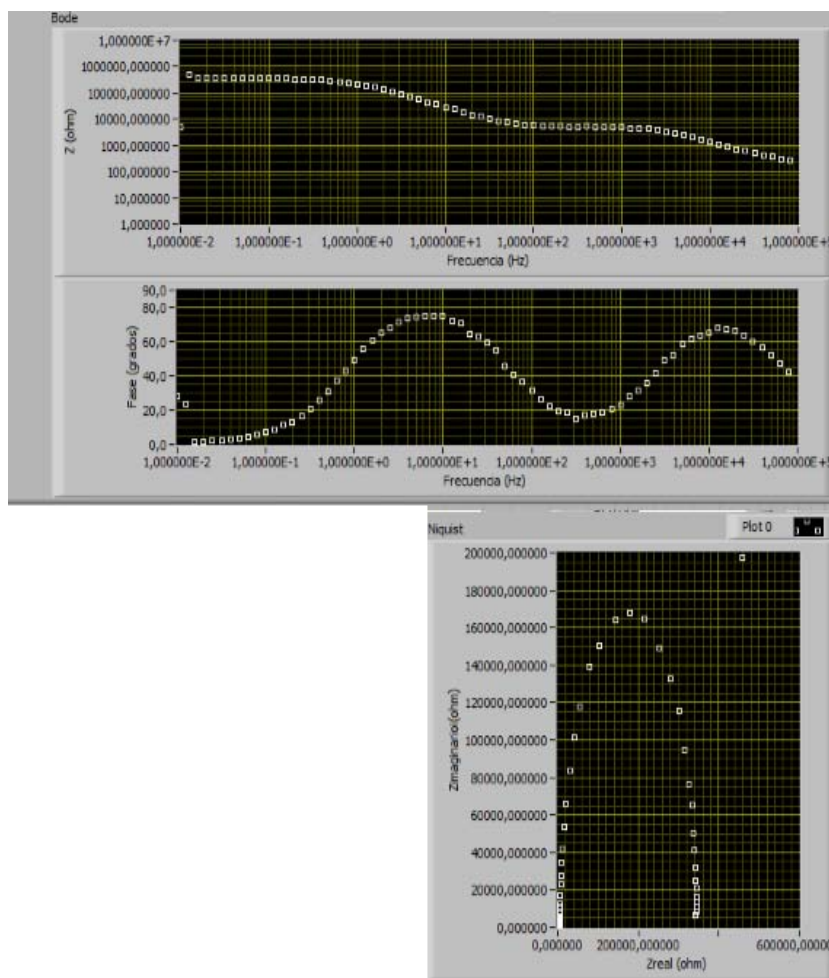


Figure 11. Spectrum of the electrochemical cell Steel 316L, in 10% H₂SO₄

The impedance of the passive layer (R_p) was approximately 340 k Ω while the impedance of the Helmholtz (R_h) layer was in the order of 4700 Ω coinciding with the fact that it was a stainless steel. This layer generated on the steel surface coincides of being highly insulating (almost impenetrable by the ions). Although this layer is not indestructible it is restored to continue to protect the metal each time it is broken [10; 13-15]. The typical model of this layer are shown in Fig. 12, which was simulated in Zsimpwin and is observed in Fig. 13.

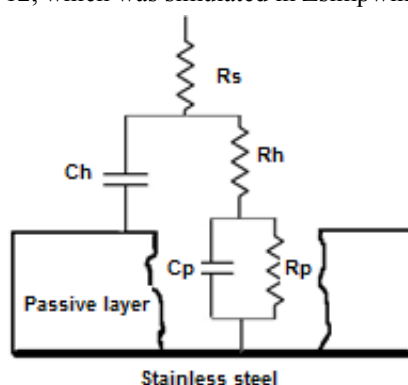


Fig. 12. Double-layer model in 316L stainless Steel

The electrical resistance values of the bilayer were obtained from the impedance measurement in the frequency spectrum of Fig. 11. For frequencies below 0.1 Hz the impedance is approximately constant and is maintained at a value of 340 k Ω , in the range of 100 Hz to 1 kHz the value returns to approximately constant of 4700 Ω , from 2 kHz the impedance falls again until it reaches a nearly constant value near 90 k Ω ; these three constant impedances are the impedances of the first layer R_p , the second layer R_h and the resistance of the solution R_s according to the model of Fig. 12.

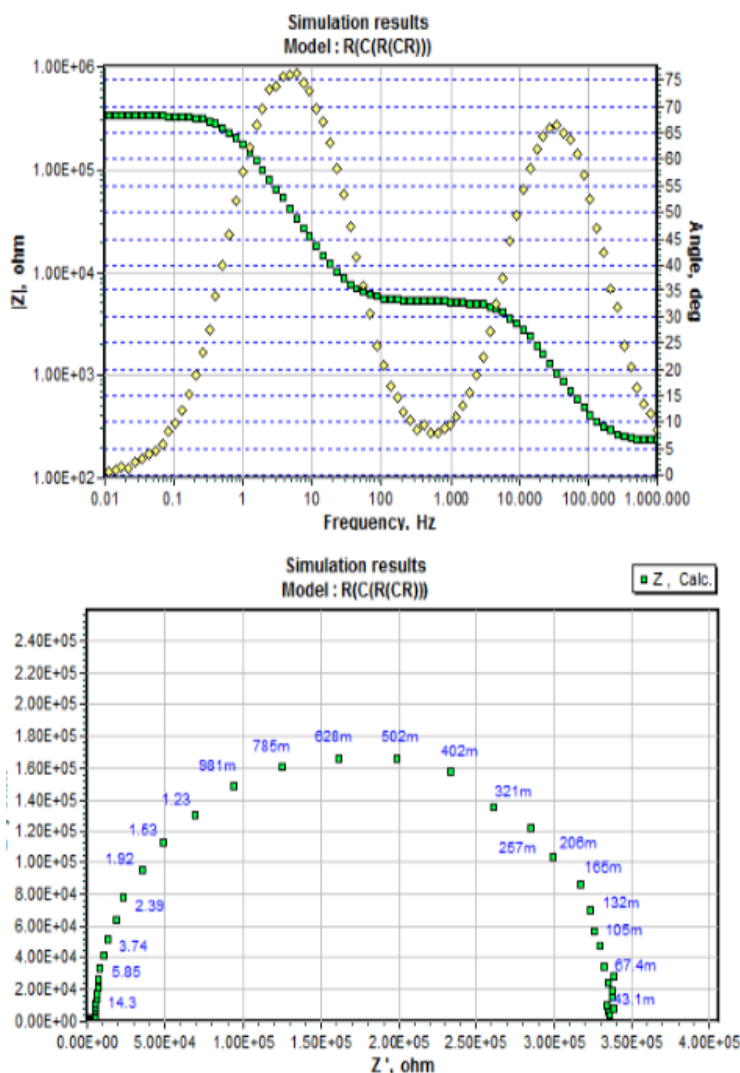


Fig. 13. Simulation of the model according to figure 12 of the electrochemical cell in Zsimpwin

Two capacitances were observed from the diagrams due to two notorious bumps in the phase versus frequency located at 7 Hz and 17 kHz approximately, these frequencies are determinant for the calculation of capacitances C_h and C_p of the model used which were calculated from the Following form.

For the calculation of C_p , a maximum of phase change at 17 kHz is observed for the complex impedance (capacitive); at this frequency the complex impedance has a value close to 2 k Ω ; these values allow to calculate the capacitance C_p according to the relation $C=(2\pi fZ)^{-1}$ [2], replacing these values results in an approximate value of 4.5 nF.

By performing the same procedure for the calculation of C_h , it is observed that the maximum phase change for this capacitance is around 7 Hz, having a complex impedance value close to 25 k Ω ; by replacing in the relation $C=(2\pi fZ)^{-1}$ results in a value of 0.8 μ F for C_h . The impedance values allow to appreciate the conductive tendency of the layer, as it is for the case of 316L stainless steel.

While the capacitance allows us to perceive the amount of charge accumulated in the interface allowing to postulate a model around the Bode and Nyquist diagrams. In order to validate the data in statistical form, the Zsimpwin 3.20 program was used, which has the option to load the data of frequency, real and complex impedance in any file with .txt extension and to perform the statistical procedure based on the transforms of Kramers-Kronig [16].

This program gives a result in terms of χ^2 which is the final validation parameter of the equipment; the calculation of the values of χ^2 for each dummy circuit and for the electrochemical cell yielded the following results, circuit 1 $\chi^2 = 3.4 \times 10^{-6}$, for circuit 2 $\chi^2 = 7.5 \times 10^{-7}$, for the cell electrochemistry $\chi^2 = 1.2 \times 10^{-5}$, and in other test circuits the values χ^2 gave similar results, to these data checked in a quantitative form using the Kramers-Kronig transforms [14], that measurements are in the range of acceptable and good.

IV. CONCLUSION

An electrochemical impedance spectroscopy equipment was designed and built based on the National Instruments NI 6250 data acquisition card and the Labview G-language program. The operation of the equipment was based on measurements made by commercial teams whose objective is to obtain the Bode and Nyquist diagrams for analysis. The equipment has a measurement range of 0.01 kHz up to 100 kHz in bandwidth, measures impedances from 0.1 Ω to 10 M Ω ; has the ability to vary voltages at the reference of electrode from 2 mV to 400 mV amplitude.

The measurements are performed using the Lock-in amplifier technique programmed in a subVI of the program which allow to obtain measurements of high precision in amplitude and phase shift in AC signals in the presence of electrical noise. The program consists of a general VI (virtual instrument) which is supported by several subVI's each with its corresponding function. The advantage of the equipment lies in the simplicity of its hardware and software, which can make viable its easy commercialization and debugging.

In order to verify the correct functioning of the equipment and the validation of its data, tests were carried out on different Dummy circuits characterized in real electrochemical interfaces and compared with the simulations made by the program Zsimpwin 3.20, a test was also carried out in an electrochemical cell with 316L steel immersed in H₂SO₄ obtaining consistent results.

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