GROUNDING ELECTRODE CORROSION DIAGNOSING - SIGNAL ANALYSIS

Cleberson L. do Nascimento [a], Alysson N. Diógenes[b], Haroldo A. Ponte[c]

Abstract

The reliability of a power system depends on the perfect functioning of the electrical grounding materials. In this context, the reliability of a grounding coppered electrode is the time period that elapses from the actual installation in the ground until the corrosion of its coating layer, which will provide an electrical discontinuity and a consequent increase in electrode ohmic resistance. This resistance, on the other hand, increases due to surface accumulation of both corrosion products and carbonates deposition. Its value, however, is difficult to be determined both due to the buried and energized electrodes. During this research it was evaluated the electrical parameters of copper in different surface states: polished (active) and oxidized (passivated) aiming to model their equivalent electrical circuit design at the different states using the electrochemical impedance technique. At this research it was analyzed the electrochemical impedance signal. The results indicate the possibility to build a sensor that can be used to measure low alterations at the ohmic resistance with the electrode still connected to the ground and energized, exposing only a small portion of it, which only had to be partially cleaned, but required no further preparation. This procedure is adequate to field applications.

Keywords: Grounding electrode, electrochemical impedance, corrosion monitoring, electrochemical techniques

Introduction

During the 2000s, there were several technological innovations arising from power electronics, microelectronics and telecommunications. Even before, but even more so, after these innovations, electrical grounding plays a key role in the protection, reliability, and quality of electrical systems, whether residential, commercial or industrial, given their importance in the safety of people and lives -more. It is spoken about buildings and smart cities [1].

By definition, in the technical context, grounding is an intentional connection with low impedance to ground. This grounding circuit provides a suitable way of current circulation, which is necessary to ensure the best performance of the electrical installation. Since the connection is buried and its visual inspection is difficult, grounding systems tend to be overlooked and only noticed when problems arise due to increased ground resistance. These

---

[a] Mestre, Engenheiro Eletricista – UFPR
[b] Dr, Engenheiro Eletricista – Universidade Positivo
[c] Dr, Engenheiro Mecânico – UFPR

problems can damage equipment, cause unexpected electrical shock, failures of control operation and failures of protective devices, etc.

The increase in the grounding resistance tends to happen due to corrosion, more specifically due to carbonate deposition at the grounding electrode surface. Corrosion refers to the natural process wherein a metal has to return to its original state, meaning its gradual destruction over time and the degradation of metal properties to the action of environment [2]. In this context a functional electrical grounding system must have, as an essential parameter of functionality, a low ohmic resistance value. This resistance, otherwise, increases due to surface accumulation of corrosive products and have its value difficult to be determined due to be buried electrodes [3].

It has been tried to avoid corrosion in a number of ways, such as increasing the number of conductors and modifying their arrangement [4], which, according to Nahman and Salamon [5], can cause great risks, if these modifications are not well planned. It has also been attempted to replace the grounding of metallic materials by alternative materials, such as carbon fiber doped concrete [6]. On the other hand, the monitoring of grounding electrodes connected to the network is still little studied.

Aiming to investigate this phenomenon, it was analyzed characteristics electrical parameters related to different surface states of the copper electrode by applying oscillating electrical signal [7] as shown in the block diagram shown in figure 1. In order to model the carbonate deposition it was generated an oxide with controlled conditions. After this, it was designed a system in which the electrochemical boundary conditions were well established by applying traditional electrochemical techniques such as linear sweep voltammetry and electrochemical impedance spectroscopy - EIS [7].

Figure 1 Block diagram of the electrical parameters for the electrochemical system proposed: (a) copper electrode polished state and (b) copper electrode on passivation film

The results indicate that the technique can be applied to measure a system's resistance variation without disconnecting the electrode from the power system or unburying it.

Metodology

The electrochemical system assembled for this study was composed by an electrochemistry cell consisting of three stationary electrodes and an electrolyte to provide the passivation of the copper electrode, Cu_2O or CuO. The experiment was held at a temperature of 21ºC and relative humidity set at around 50%. The pH of the electrolyte was maintained constant during all the experiment. The electrolyte was a sodium bicarbonate solution - $NaHCO_3$, with a pH

8.3. That was designed according to the Pourbaix diagram for the copper [10], in deionized water with a concentration of 84.01 g/L or 1M. All the potential results were related to a saturated Calomel (SCE) reference electrode. The Working electrode was a copper rod with purity ≥ 99,96%, and a diameter of 4 mm imbibed epoxy resin with a exposed surface area of 0,1256 cm². The Auxiliary electrode was a platinum wire.

In order to characterize the electrical parameters they were used the following traditional electrochemical techniques [11]-[13]:

- Linear potential voltammetry: It was used a potentiostat/galvanostat Automation system from Microquimica Ltd. , model MQPG - 01 coupled to an interface and an application software MQI12/8PC-C MQPG - EXE ;
- Electrochemical impedance spectroscopy (EIS): It was used a potentiostat/galvanostat and ZRA (Zero Resistance Ammeter) from Gamry Instruments , Reference Model 600 with the PC via USB interface coupled to ESA software application 410 .
- Signal generator ICEL 2005. It was used to emulate the power network.

Results and discussion

The first part of the experiment was to determine the open circuit potential (OCP) for a previously polished copper electrode in a 1,0 M sodium bicarbonate solution. The obtained OCP was -179 mV. The second experimental step was a linear sweep voltammetry ranging from -1 V to 1.2 V with scanning rate of 50 mV/s. This procedure was performed in accordance to [13]. The adopted equipment is exposed in Figure 2.
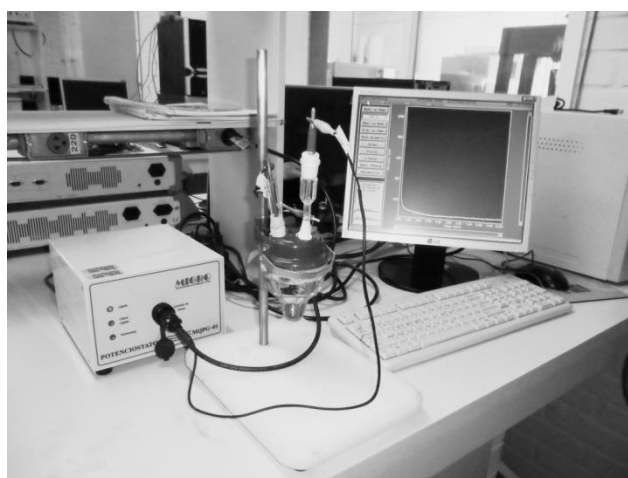

Figure 2 Electrochemical system considered for modeling

The voltammogram presented in figure 3 defines the transition between the cathodic and anodic behavior for copper at -179 mV. It is observed a passivation step, that could be held until 1.220 mV, been followed by a transpassivity process. During the passivation process it is formed a very adherent oxide film at the copper surface.
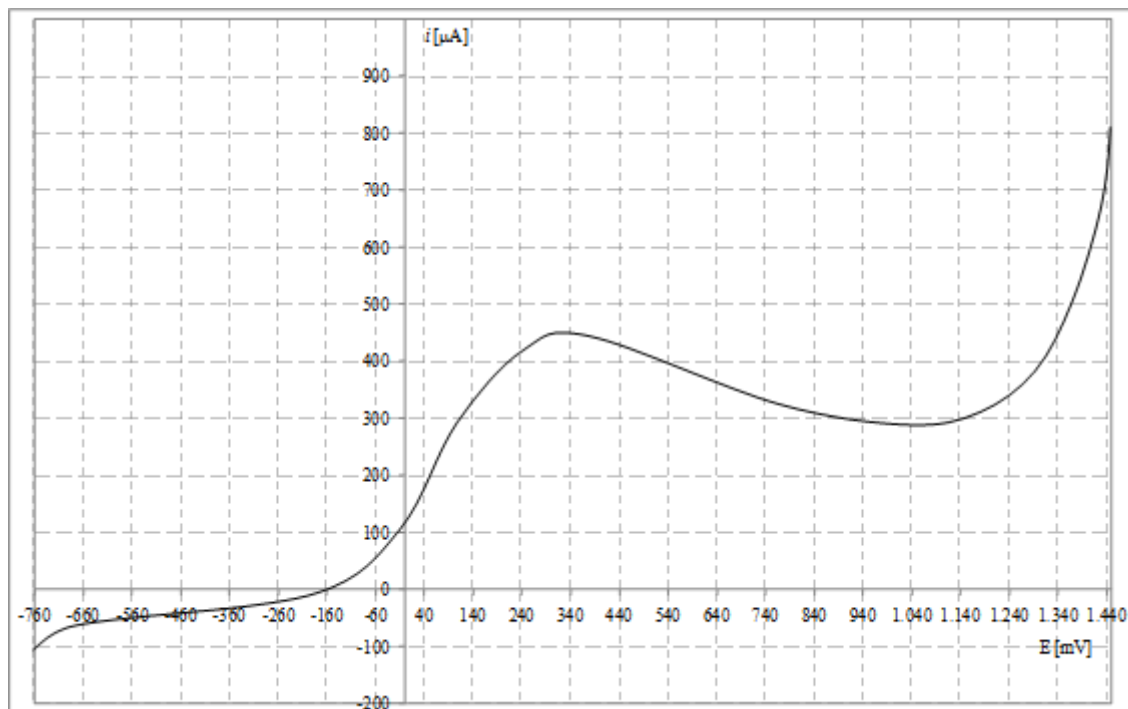
Figure 3 Potentiodynamic voltammogram of copper electrode in aqueous 1M sodium bicarbonate with potential sweep rate of 50 mV/s. E vs SCE

The use of the technique of electrochemical impedance spectroscopy (EIS) [5, [14] requires determining the resistance and reactive elements for modeling circuits proposed by the block diagram in figure 1.

To study the behavior of the polished copper electrode a frequency sweep potential was performed at the open circuit potential (OCP) of -179 mV. This potential was use as off-set potential during scanning frequencies in the range of 0.01 Hz to 10000 Hz.

The impedance and phase displacement results obtained during the test are presented as a Bode diagram in figure 4, in which it can be obtained the circuit parameters. At this point of the experiment, a signal generator was attached to the system and a sinusoidal function in the frequency of 60Hz and 220V of amplitude was inserted in the experiment.
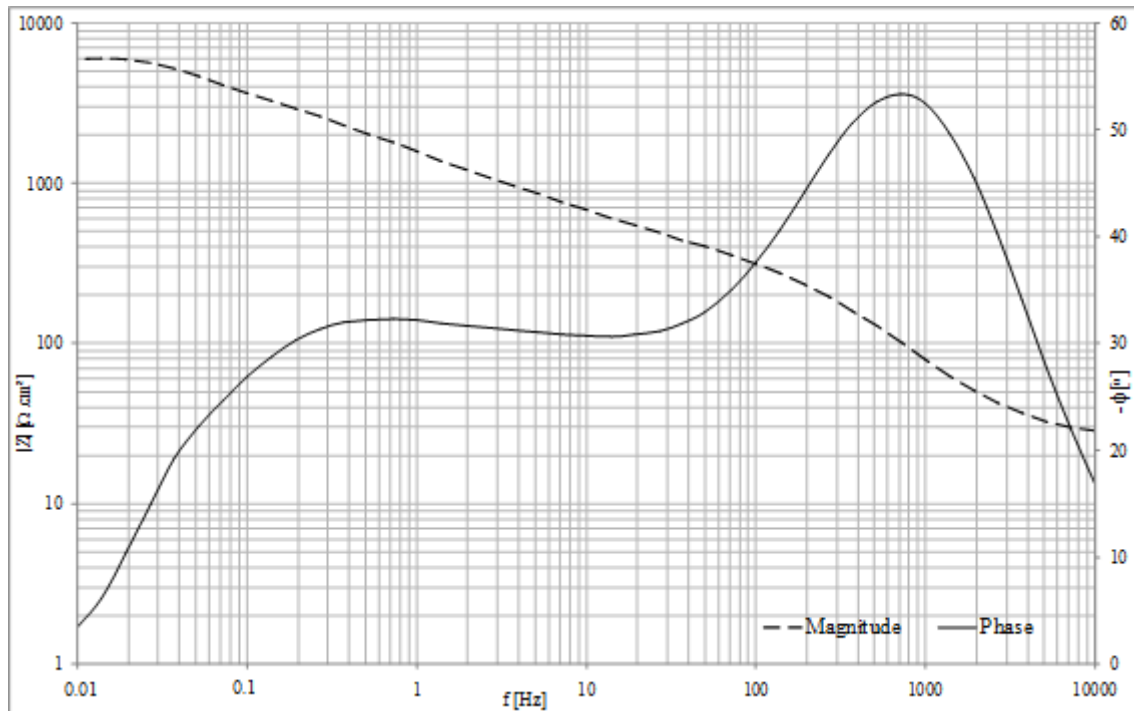
Figure 4 Bode plot of impedance magnitude and phase displacement versus frequency for active copper electrode in aqueous 1M sodium bicarbonate

Through the Bode plot of the impedance scanning frequency magnitude it is observed that the value of the electrolyte Ohmic resistance of 27 Ω.cm² is obtained at very high frequencies of 10000 Hz. The phase displacement presents a bow with more pronounced peak at higher frequencies indicating a capacitive behavior.

Its value is given by the mathematical expression shown below for the maximum point.

$$Z_i = \frac{1}{\omega_{max}.C_{dc}} = \frac{1}{2.\pi.f_{max}.C_{dc}}$$

$$C_{dc} = \frac{1}{2.\pi.725.80,97} \cong 2,71\,\mu F.cm^{-2}$$

Analyzing the Nyquist diagram exposed in Figure 5, it is obtained a ohmic resistance of 780 Ω.cm² by extrapolating the semicircle of the first maximum point. The polarization resistance is 754 Ω.cm². The considered electrical equivalent circuit for the active copper electrode is shown in figure 6.
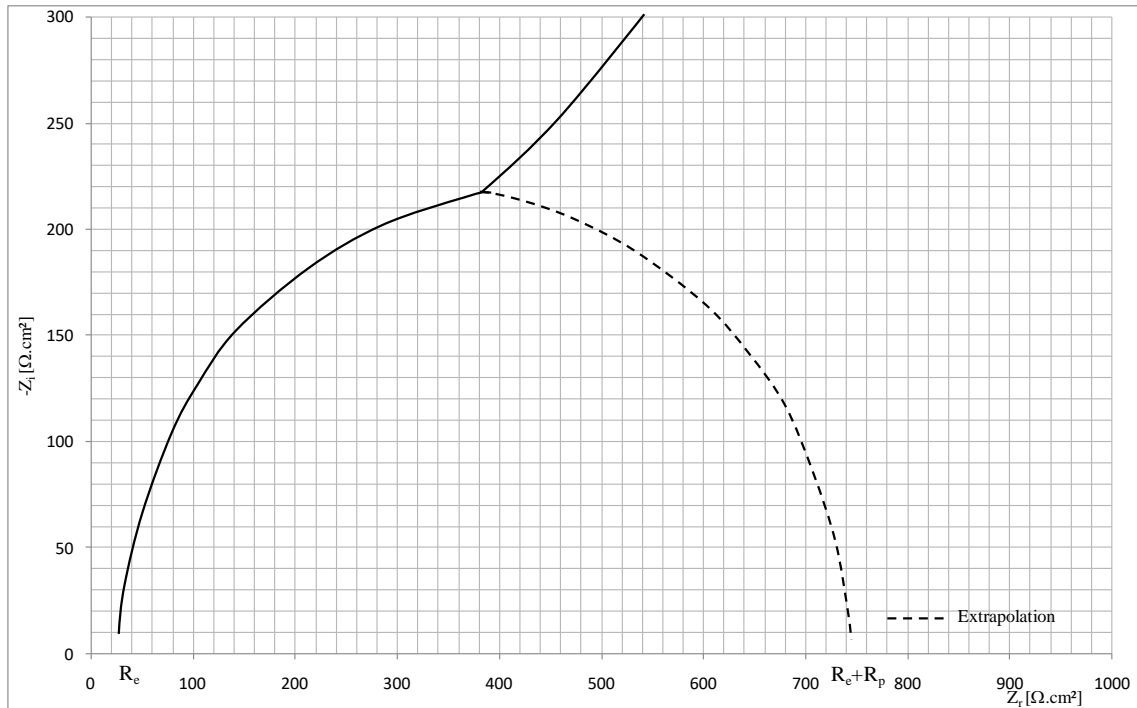
Figure 5 Nyquist diagram extrapolated for active copper electrode in 1M aqueous sodium bicarbonate
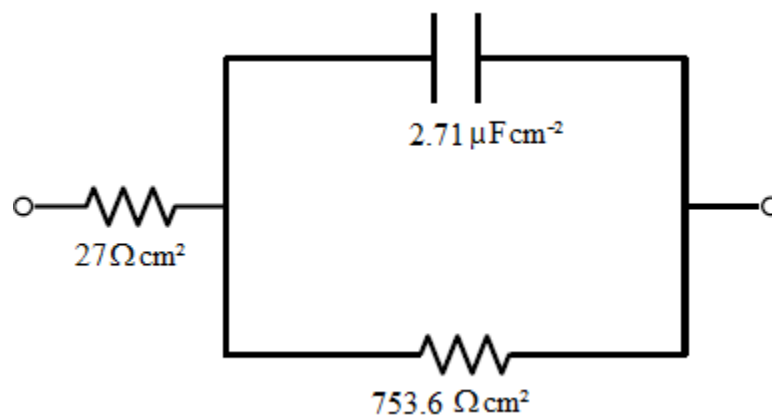

Figure 6 Equivalent circuit for the electrochemical cell with the working electrode surface in active copper

To study the behavior of the copper electrode at the passivation condition it was first polarized the electrode at a potential of 620 mV for 30 minutes. Subsequently, the electrode was held at the open circuit potential (OCP) for a period of 60 minutes, yielding a value of -171 mV. This OCP value was adopted as a potential off-set during scanning frequencies in the range 0.01 Hz to 10000 Hz. The Bode diagram for this experimente is exposed in Figure 7.
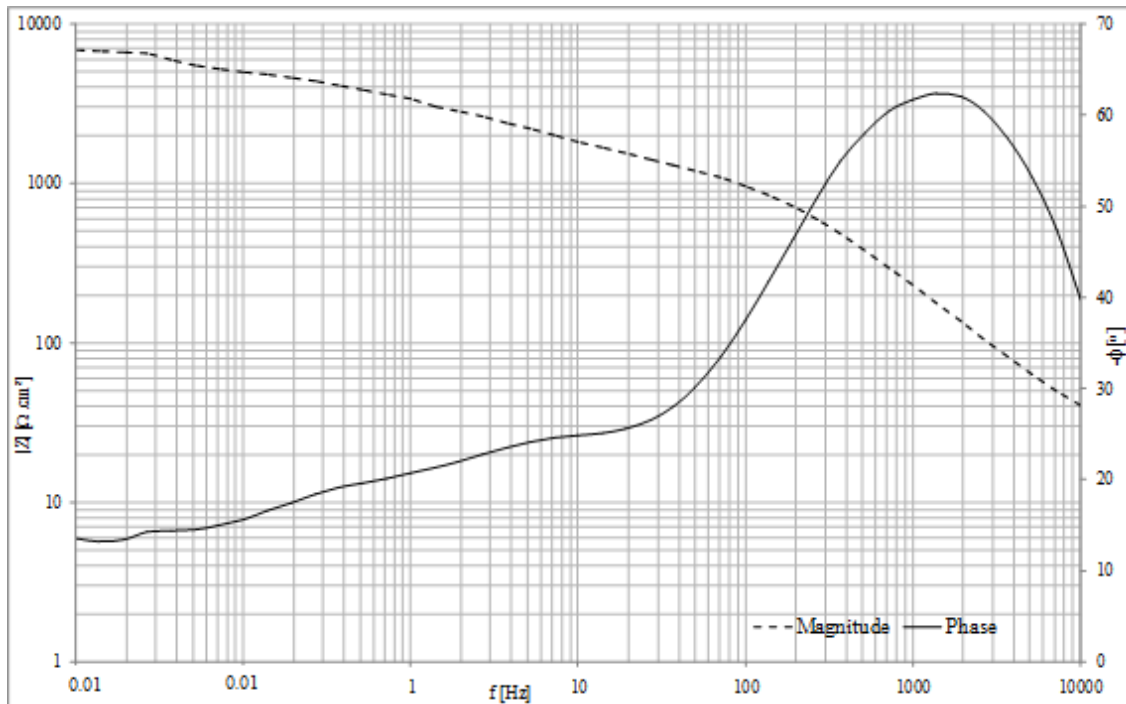
Figure 7 Bode plots of impedance magnitude and phase displacement versus frequency for passivated copper electrode in 1M aqueous sodium bicarbonate

It is remarkable to note that in the range of higher frequencies the impedance magnitude diagram of the scanning frequency gives the value of the ohmic resistance of the electrolyte, which showed values closed to those found during the test with the active copper electrode surface, as shown in figure 5. The obtained value for the ohmic resistance of the electrolyte was obtained at very high frequencies, in 10.000 Hz, yielding a value close to 27Ω.cm ². Similarly, the capacitive arc at high frequencies presents the capacitance value of film formed, given by the following expression.

$$Z_i = \frac{1}{\omega_{max}.C_{filme}} = \frac{1}{2.\pi.f_{max}.C_{film}}$$

$$C_{film} = \frac{1}{2.\pi.1600.85,02} \cong 1,17 \ \mu F.cm^{-2}$$

The Nyquist diagram exposed in Figure 8, after the extrapolation of the semicircle, gives a value of 2100 Ω.cm ², referring to the sum of portions of the ohmic resistance of the electrolyte and passivated oxide film formed. It is observed, therefore, that the value of the ohmic resistance for the copper with a passive oxide film is 2073Ω. cm². This value is about three times larger in magnitude than the value of ohmic resistance obtained for the active electrode surface.
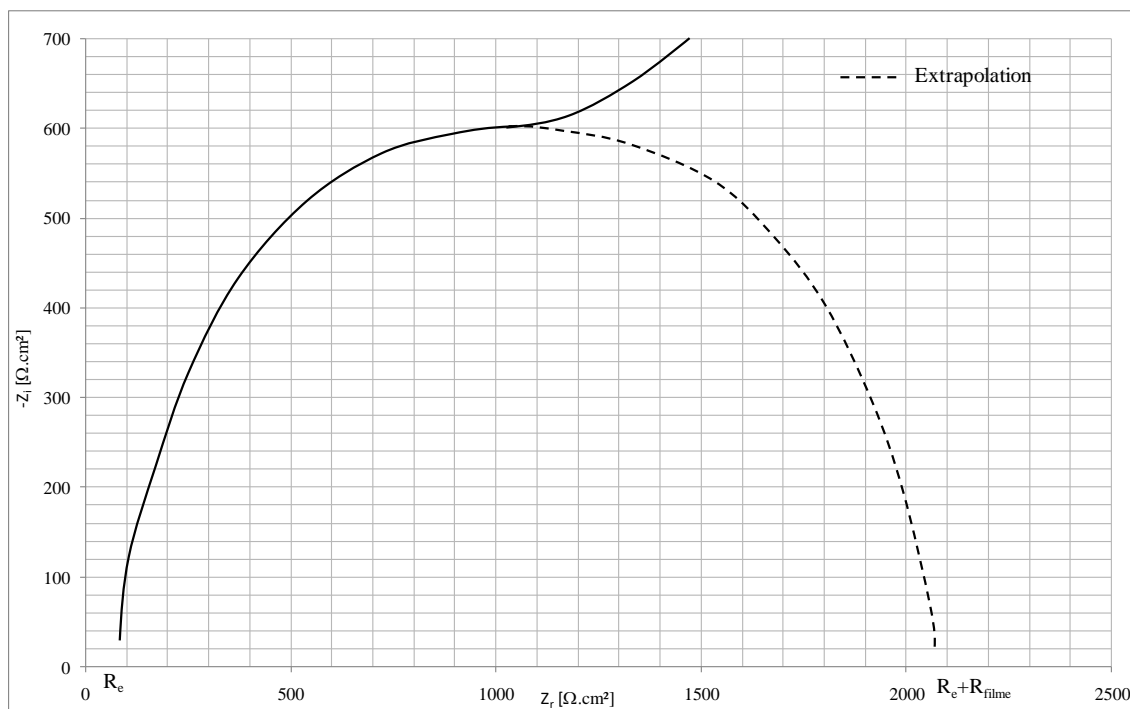
Figure 8 Nyquist diagram extrapolated for the copper electrode passivation film in 1M aqueous sodium bicarbonate

The proposed electrical circuit to the oxidized copper electrode surface is presented in Figure 9.
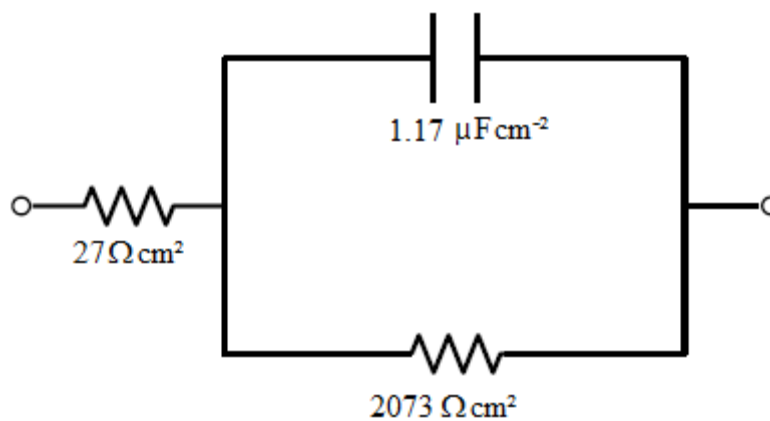

Fig. 10 Equivalent circuit for the electrochemical cell with the working electrode surface in passivated copper

Electrochemical system response to the application signals in oscillating frequency was used in modeling and parameterization of the different copper surface states at the electrochemical system. The system response on pre-established surface conditions was obtained. The applied input sinusoidal signal had a peak potential of 1 V rms and 0.707 V at 50 Hz and 100 Hz frequencies. It was evaluated other frequencies; however the ones with a greater impedance difference were the mentioned.

The obtained values for the current density of different copper surface states are shown in table 1 and at the graphs of the figures 11 and 12.

Table 1 – Values of current density for the complex electrochemical system with distinct surface state of copper electrode under excitation voltage 0.707 Vrms.

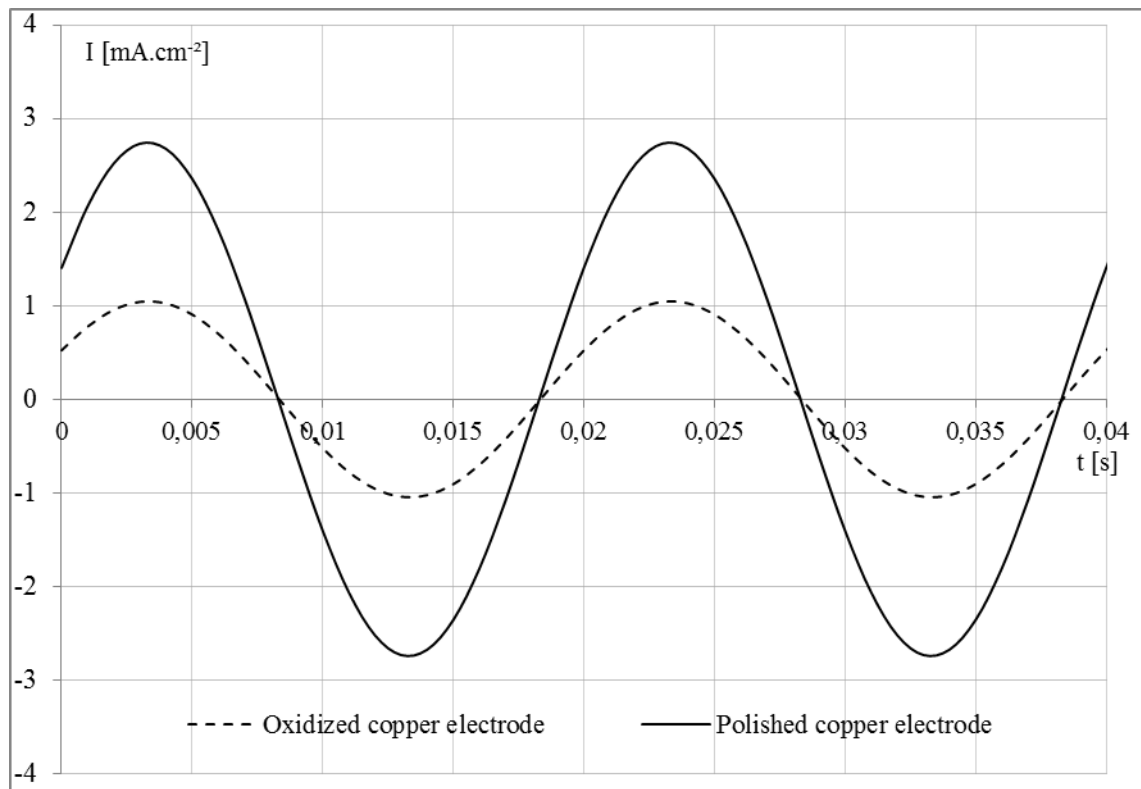| Frequency	active Cu electrode		passivated Cu electrode	
[Hz]	$Z[\Omega \cdot cm^2]$	$I [mA \cdot cm^{-2}]$	$Z [\Omega \cdot cm^2]$	$I [mA \cdot cm^{-2}]$
50	$365 \angle -30.80°$	$1.94 \angle 30.80°$	$1200 \angle -30.00°$	$0.59 \angle 30.00°$
100	$290 \angle -34.60°$	$2.44 \angle 34.60°$	$955 \angle -37.40°$	$0.74 \angle 37.40°$

Figure 11 Response current density for the electrochemical system oscillating at a frequency of 50 Hz
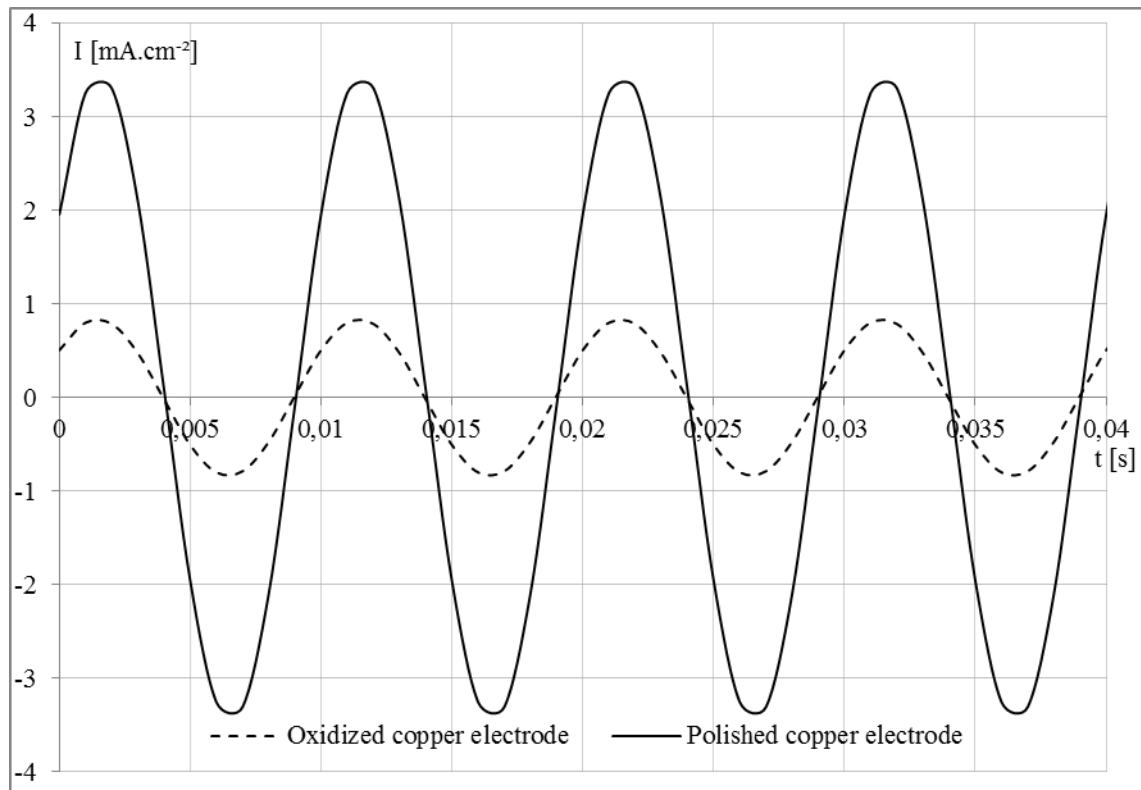
Figure 12 Response current density for the electrochemical system oscillating at a frequency of 100 Hz

As observed in the graphs of figures 11 and 12 it was found that the temporal response in current densities for the three applied frequencies does not present significant differences regarding the phase displacement between the magnitudes involved. Otherwise, it was observed a significant gain in signal amplitude at current density for the different electrode surface states (active and passivated condition) in the three frequency bands and that the response amplitude of current density presenting the greatest displacement is established in the frequency range of 100 Hz. This result shows an increase in signal amplitude of approximately three times between the different states of the copper electrode surface under study. The phase modification varied less than the magnitude. This was expected, since the copper oxide increases uniformly in both the capacitive and resistive layers.

Considering the principles already described by Ohm's law, it is observed that for a given constant RMS voltage value, it could be obtained a higher current density value to the active electrode surface than that for the electrode with a passivation film presenting the lowest value of ohmic resistance.

At this point of the experiment, the signal generator was attached to the system. A 220V and 60Hz sinusoidal signal wave was applied and the experiment was repeated. The result can be observed in figure 13.
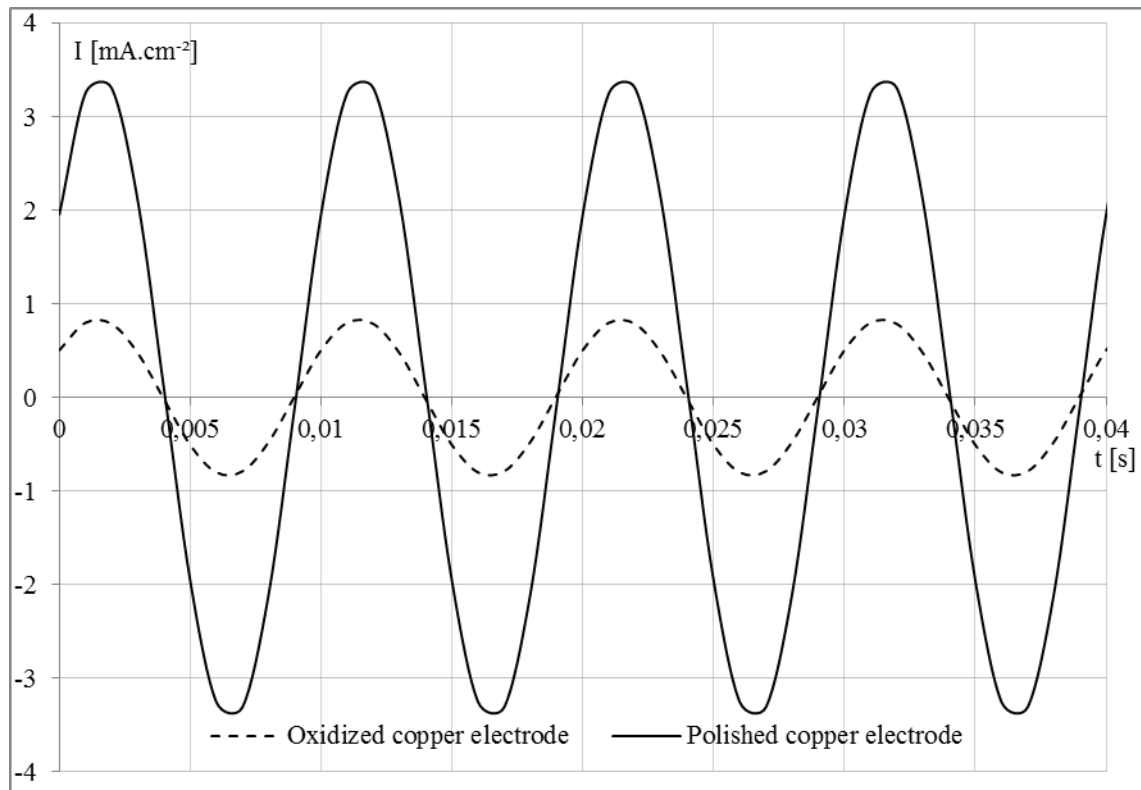
Figure 13 Response current density for the electrochemical system oscillating at a frequency of 100 Hz during a 220V and 60Hz wave application.

The 220V wave was purposely omitted in Figure 13, due to the current amplitude caused by the signal generator, which is greater than the electrochemical impedance signal measured. Even so, it was possible to separate the signals and to measure only the 100Hz applied signal. Since the proposed methodology was able to measure independently the 60Hz and the 100Hz frequencies, the proposed methodology is adequate for field applications.

Conclusion

The value of the ohmic resistance of the electrolyte is sufficiently small compared to surface resistances encountered, namely polarization and passivated film not affecting the processes of electric charge transfer between the anodic and cathodic reactions for both surface states of the copper electrode (polished and passivated)
The oxide model for the carbonate deposition seems to provide an adequate system to measure the electrical resistance in copper electrodes.
In this context it was obtained the basis for the parameterization of the electrical surface condition of copper electrode providing necessary experimental set up for monitoring its ohmic resistance without the need to remove the grounding electrode. This technique make possible to evaluate the ground operating condition under an energized system

References

[1] P. KRÄUCHIA, DAHINDEN, D. JURT, V. WOUTERS, U. -P. MENTI, O. STEIGERA. Electricity consumption of building automation. Energy Procedia. Vol 122, pps 295-300 (2017)

[2] CAPELLI, A. (2007). **Energia Elétrica para Sistemas Automáticos da Produção**. 1st Ed., Érica Ed. Ltda, São Paulo

[3] GENTIL, V. (2003) **Corrosão**. Livros Técnicos e Científicos, 4th Ed, Rio de Janeiro.

[4] C. E. F. CAETANO, A. B. LIMA, J. O. S. PAULINO, W. C. BOAVENTURA, E. N. CARDOSO. A conductor arrangement that overcomes the effective length issue in transmission line grounding. Electric Power Systems Research. In Press. (2017)

[5] J. NAHMAN, D. SALAMON. Mutual interference of neighboring grounding systems and approximate formulation. Electric Power Systems Research. Vol 151. Pps 166-173. (2017)

[6] J. ZHANG, L. XU, Q. ZHAO. Investigation of carbon fillers modified electrically conductive concrete as grounding electrodes for transmission towers: Computational model and case study. Construction and Building Materials. Vol 145. Pps 347-353. (2017)

[7] KINDERMANN, G. and CAMPAGNOLO, J. M. (1995). **Aterramento Elétrico**.: 3ª Edição, Sagra DC Luzzato, Porto Alegre.

[8] STEIGERWALD, J.M., MURARKA, S.P., GUTMANN, R.J., DUQUETTE, D.J. Chemical Processes in the Chemical Mechanical Polishing of Copper. (1995) **Materials Chemistry and Physics**, Vol. 41. pp. 217-228.

[9] TICIANELLI, E. A. & GONZALEZ, E. R. (2005) **Eletroquímica**: Princípios e Aplicações. 2nd Ed. Edusp. São Paulo.

[10] POURBAIX, M. (1974) **Atlas of Electrochemical of Equilibria in Aqueous Solutions. Houston**: NACE,.

[11] WOLYNEC, S. (2003) **Técnicas Eletroquímicas em Corrosão**, Edusp, São Paulo.

[12] ASTM. **Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements**. G 59 – 97, 1997.

[13] ASTM. **Standard practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements**. G 102 – 89, 1989.

[14] HARUYAMA, S. & TSURU, T. (1981) **A Corrosion Monitor Based on Impedance Method**. In: STP 727: Progress in Electro-chemical Corrosion Testing. Pittsburg, ASTM, pp. 167-186.

[15] MANSFELD, F. (1993) Models for the impedance behavior of protective coatings and cases of localized corrosion. **Electrochimica Acta**, v. 38, n. 14, p. 1891 -1897.

ASTM - STP1188 - **Electrochemical impedance** – Analysis and interpretation, 1993.

* * *