
APPLICATION OF DYNAMIC ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TO THE EVALUATION OF THE CORROSION RESISTANCE OF A HISTORIC BRONZE OBJECT IN ARTIFICIAL ACID RAINWATER

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Abstract

Anodic potentiodynamic polarization curves (PPC) and dynamic electrochemical impedance spectroscopy (DEIS) measurements were carried out on a historic bronze object exposed to an artificial acid rain in order to assess its corrosion resistance. DEIS measurements were performed over a wide range of potentials covering the open circuit potential, passive, breakdown and dissolution ranges revealed in the potentiodynamic polarization curve. DEIS reveals the changes that occur in the structure of the passive layer due to increased anodic polarization. Impedance spectra determined in various potential regions were satisfactorily fitted to model electrical equivalent circuits, and conclusions regarding the layers formed on the surface of the materials at those polarizations were extracted. The surface morphology and composition of the bronze surface after different polarizations were characterized using scanning electron microscopy (SEM) combined with energy dispersive spectrometry (EDX) techniques.

Keywords: bronze, acid rain, linear anodic potentiodynamic polarization, DEIS, SEM

1. Introduction

Bronze is an alloy with a wide application both contemporary and historic [1-3]. Since bronze has good resistance against atmospheric corrosion, it is an alloy frequently employed in works of art (sculptures, monuments, bells, etc.)

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and in bronze ornaments for building constructions [4].

The corrosion destruction of a metal or alloy by its reaction with the environment is mainly an electrochemical oxidation process that usually produces soluble metal ions or precipitated metal oxides. The choice of corrosion test methods is made on the consideration of the extent and type of information desired for the system, and the environmental conditions expected in service for a given material. In general, electrochemical testing methods have been shown to be an efficient and convincing tool for the characterization of the corrosion behaviour of metallic materials in numerous studies.

Over the last three decades, electrochemical impedance spectroscopy (EIS) has proved to be advantageous for the characterization of the various oxide films developed on the surface of metallic materials. In the conventional EIS technique, the system is operated under stationary conditions, in which case the investigated process should remain mostly constant during the time required to record the complete impedance spectra. Dynamic electrochemical impedance spectroscopy (DEIS) is an impedance method that opens new opportunities for the investigation of corrosion processes while the impedance spectra are measured under potentiodynamic conditions (non-stationary condition).

In this contribution, dynamic electrochemical impedance spectroscopy (DEIS) was employed to characterize the passive regime and the corrosion behaviour of a historic bronze object subjected to electrical polarization during its immersion in simulated acid rainwater under ambient conditions.

2. Experimental part

2.1. Materials

The bronze sample was taken from a fissured church bell built approximately 150 years ago. The chemical composition of the bronze has already been reported elsewhere [4]. The bronze samples were abraded to a 4000 grit finish.

Table 1. Physicochemical parameters found in natural rainwater and composition of the artificial acid rainwater employed in this work.

Species	Typical natural rainwater (μM)*	Artificial rainwater (μM)
pH	3.5 – 5.5	4.3
SO_4^{2-}	1 – 150	55
Cl^-	0.5 – 1800	1800
$\text{CH}_3\text{COO}_2^-$	1 – 10	5
NO_3^-	0.3 – 50	50
NH_4^+	0.1 – 39	30
Na^+	4 – 2200	2200
Ca^{2+}	2 – 500	480
Mg^{2+}	2 – 160	120

* According to[5]

Electrochemical tests were performed in naturally-aerated artificial acid rainwater of the composition given in Table 1. For the sake of comparison, ranges for the characteristic physicochemical parameters typically found in natural rainwaters found in the scientific literature [5] are also listed in Table 1.

2.2. Electrochemical methods

A glass corrosion flow cell kit (C145/170, Radiometer, France) with a platinum counter-electrode and a freely adjustable Luggin capillary containing a saturated calomel reference electrode (SCE) was employed to perform the electrochemical measurements (Figure 1). The temperature of the electrochemical cell was kept at 25 ± 1 °C, and the solution was naturally aerated. All potentials in this work are referred to the SCE.

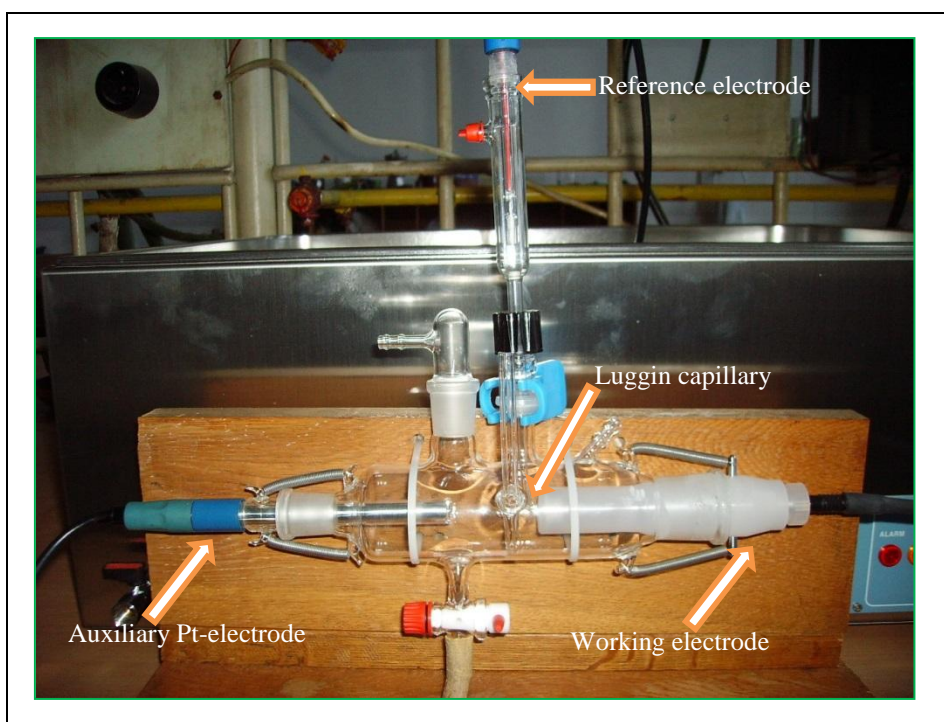


Figure 1. Glass corrosion flow electrochemical cell.

Electrochemical measurements were performed using a potentiostat manufactured by PAR (Model PARSTAT 4000, Princeton Applied Research, Princeton, NJ, USA). The instrument was controlled by a personal computer and specific software (VersaStudio, PAR, USA).

Upon immersion in the simulated acid rainwater, the bronze samples were left disconnected for 1 hour to attain a stable open circuit potential value (OCP). Subsequently, anodic polarization curves were measured at a scan rate of 1 mV s^{-1} starting from their open circuit potential up to $+0.10 \text{ V}_{\text{SCE}}$.

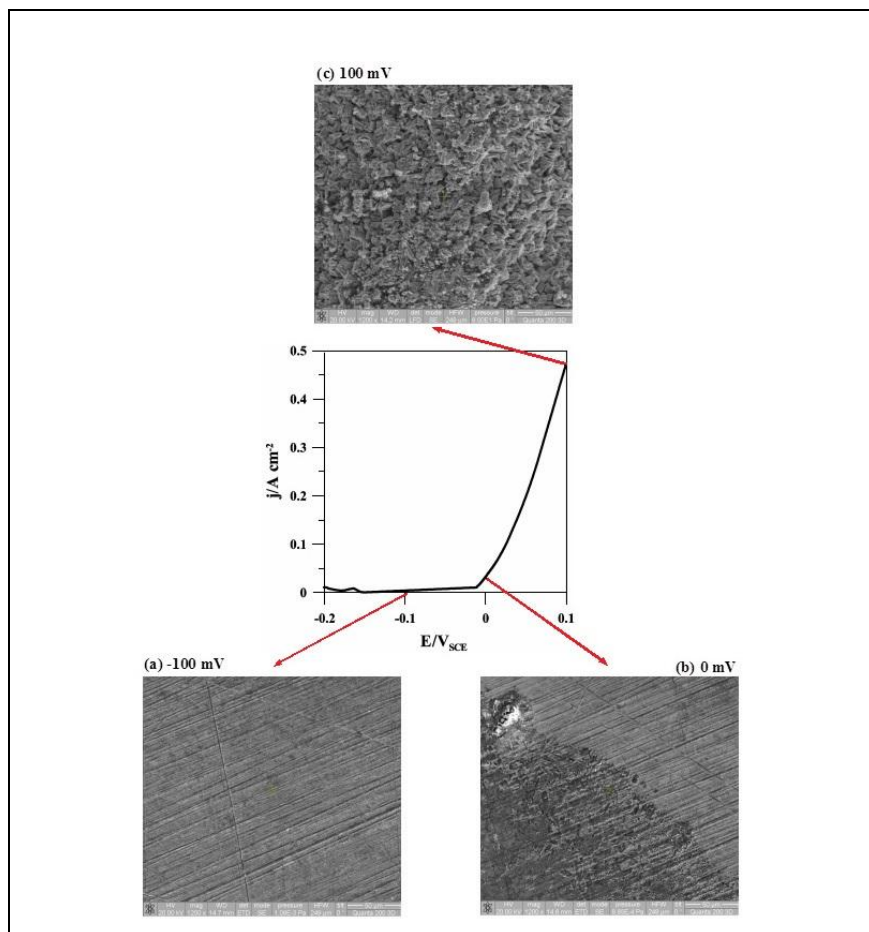


Figure 2. Typical anodic potentiodynamic polarization curve measured for bronze immersed in artificial rainwater at 25 °C and SEM micrographs of samples retrieved at different anodic potentials during potentiodynamic polarization: (a) -100, (b) 0 and (c) +100 mV_{SCE}.

Dynamic electrochemical impedance spectra (DEIS) were acquired at various potential values extending from the open circuit potential to the anodic dissolution range of the material, using 20 mV intervals. The AC potential signal was a sinusoidal wave of amplitude 10 mV, and the frequency range extended from 100 kHz to 1 mHz. The impedance spectra were fitted to a model electrical equivalent circuit for data analysis using a non-linear least-squares method fitting procedure (ZSimpWin, PAR, USA). The typical guidelines for the selection of the best-fit EC were followed: a minimum number of circuit elements were employed, the χ^2 error was maintained suitably low (namely, $\chi^2 < 10^{-4}$), and the error associated to each circuit element was not allowed to be greater than 5%. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between simulated and experimental data [6].

2.3. Scanning electron microscopy

Surface morphology of the tested bronze samples after anodic polarization tests was analyzed by scanning electron microscope (SEM) combined with energy dispersive spectrometry (EDS) using a Quanta 3D instrument (FEI, USA).

3. Results and discussion

The establishment of the electrochemical behaviour of the bronze material immersed in artificial rainwater over its oxidation potential range was the main objective of the electrochemical tests. Therefore, the anodic potentiodynamic polarization curve from the open circuit potential (OCP) value was recorded first. Prior to application of the linear potential scan, the sample was kept in the solution for 1 hour. A typical j - E plot is depicted in Figure 2.

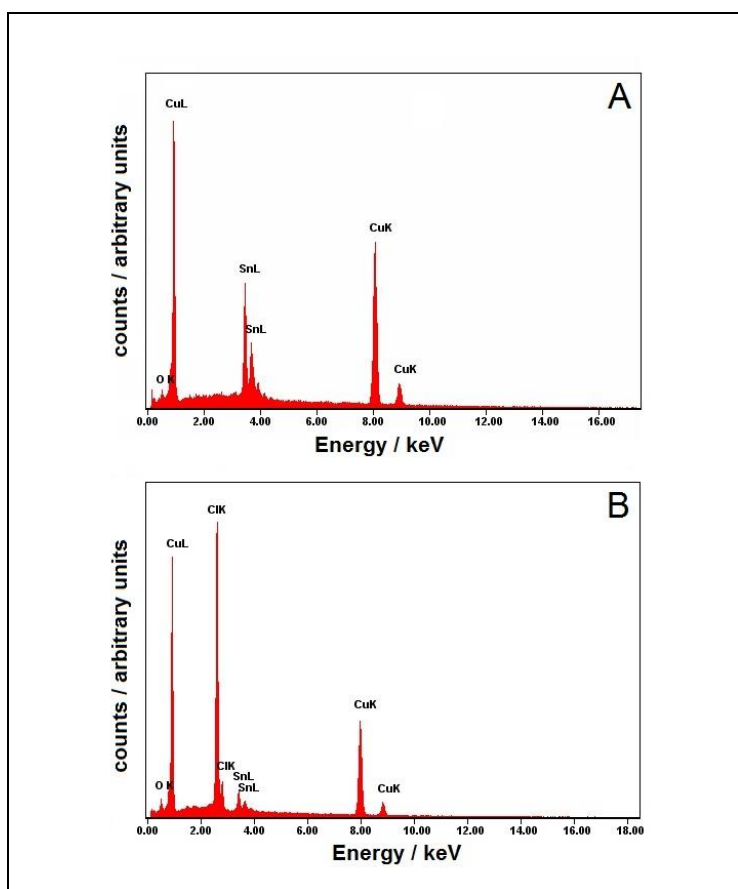


Figure 3. EDX spectra of bronze specimens retrieved after anodic potentiodynamic polarization up to: (a) -0.10 and (b) $+0.10$ V_{SCE} during immersion in artificial rainwater at $25^{\circ}C$.

During anodic polarization from the OCP, the establishment of a passive region characterized by an almost constant current density can be first observed, subsequently followed for a steep current increase associated with breakdown potential. Breakdown of the passive surface is evidenced by the sharp increase in the anodic current densities that occurred at ca. 0 V_{SCE}.

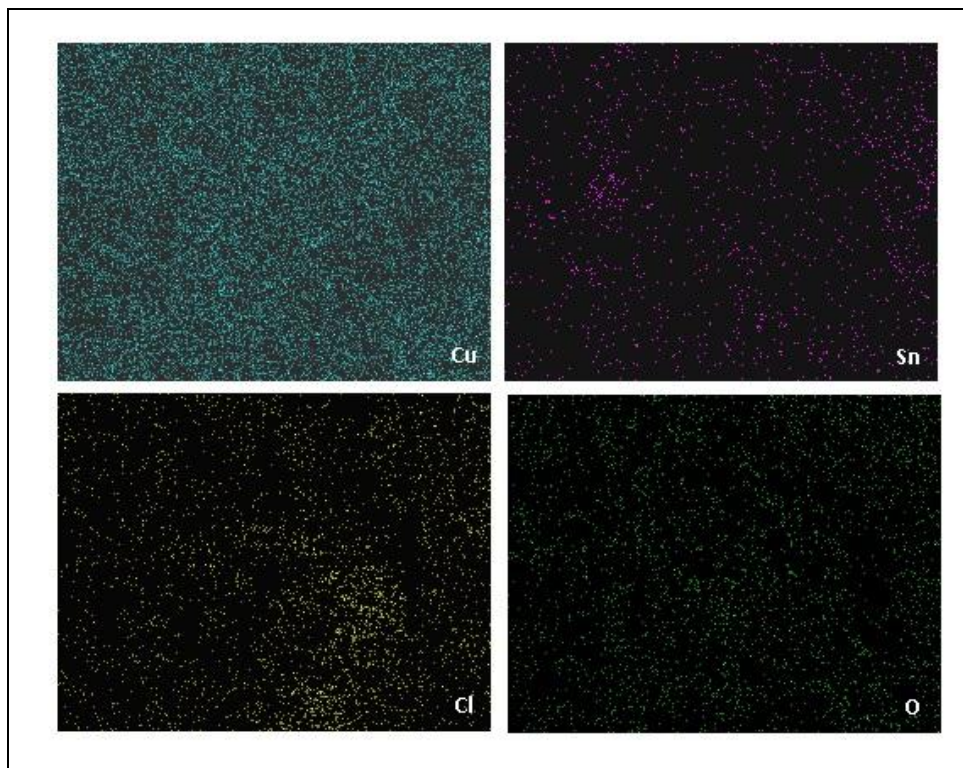


Figure 4. EDX images for copper, tin, chlorine and oxygen taken from the surface of a bronze specimen retrieved after polarization up to +0.10 V_{SCE} during immersion in artificial rainwater at 25°C.

The extent of surface attack related to the application of increasing anodic potential values to bronze samples exposed to artificial rainwater was revealed by SEM imaging. Apart from the observation of unavoidable scratches resulted from the prior polishing of the specimens, no other localized features such as pits and cracks were observed in bronze specimens retrieved after potentiodynamic polarization tests conducted up to -0.10 V_{SCE} (cf. micrograph in Figure 2a). Conversely, major surface changes were found for samples retrieved after anodic polarization extending to 0 V_{SCE} as shown in Figure 2b. At this potential value, corrosive attack of the bronze occurred in this environment with the development of a distribution of corrosion pits on the surface. Extensive surface degradation due to the corrosive attack on the metallic material was evidenced by SEM after polarization at +0.10 V_{SCE} in artificial rainwater (see Figure 2c). In this case, the morphology of the surface resulting from initial

polishing cannot be distinguished anymore, and a very rough surface is visualized instead.

The EDX spectrum measured on a bronze specimen retrieved at -0.10 V_{SCE} after anodic potentiodynamic polarization in artificial rainwater is shown in Figure 3a. The EDX spectrum only exhibits the signals corresponding to Cu, Sn, and O. In the case of samples retrieved at potential values beyond the breakdown of passivity of the material, EDX analysis shows the presence of Cl on the surface in addition to the signals of Cu, Sn and O (see Figures 3b and 4 obtained for a sample retrieved at $+0.10$ V_{SCE}). The breakdown of the protective oxide passive layer formed on the surface of the bronze has occurred as result of the transport of chloride ions into the surface film facilitated by the anodic polarization of the sample.

Electrochemical impedance spectroscopy analyses were also carried out on bronze samples polarized at different potential values separated 20 mV, extending from the OCP to the dissolution potential range for the bronze sample. Figure 5 depicts a three-dimensional representation of the resulting impedance spectra measured on a bronze sample when they are depicted in the form of Nyquist diagrams. From the inspection of Figure 5, it can be easily observed the sequence of change in the shape of the EIS plots related to the increase of the anodic potential applied to the bronze sample.

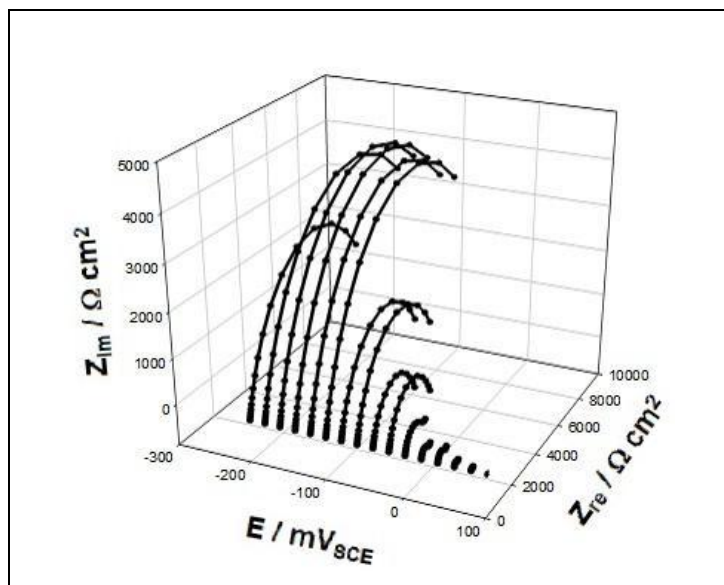


Figure 5. Electrochemical impedance versus potential diagrams measured for a bronze sample immersed in artificial rainwater at $25^{\circ}C$.

In order to describe the characteristic three behaviours that can be observed in the EIS spectra, the Nyquist diagrams corresponding to the specimen polarized at -0.10 , 0 , and $+0.10$ V_{SCE} are shown in Figure 6.

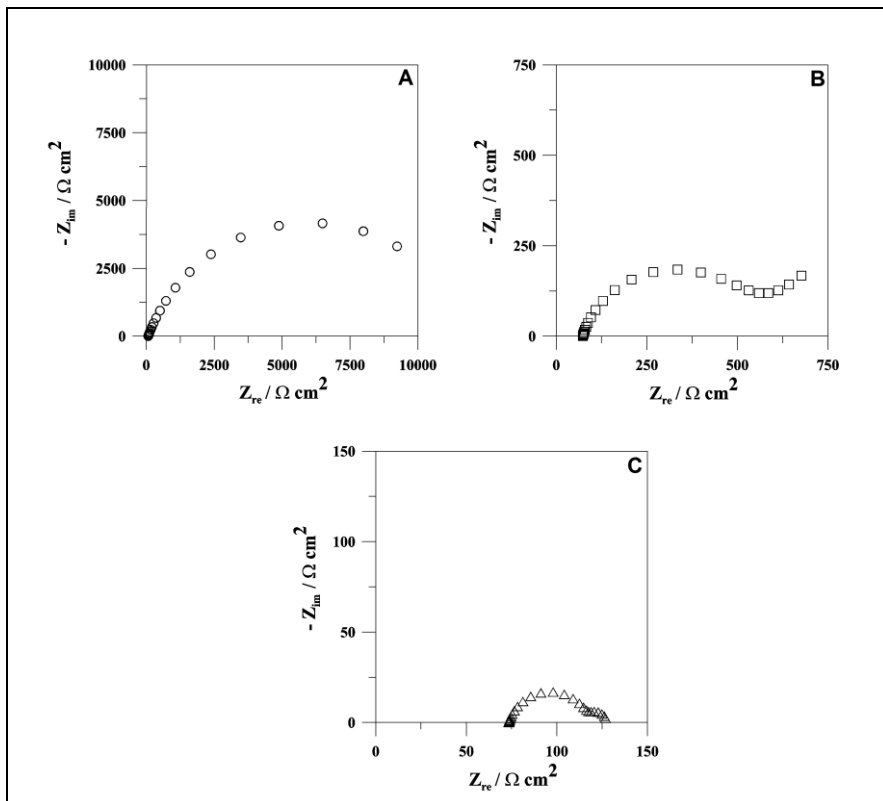


Figure 6. Nyquist representations of the EIS data measured for a bronze sample immersed in artificial rainwater at 25°C when polarized at: (a) -0.10 , (b) 0 and (c) $+0.10 \text{ V}_{SCE}$.

The Nyquist impedance diagram for bronze sample in the artificial rainwater at -0.10 V_{SCE} (see Figure 6a) depicts only one semicircle, indicating that the corrosion process was under charge transfer control for the sample immersed in the electrolyte at this potential. In the case of bronze sample in the artificial rainwater polarized at 0 V_{SCE} (Figure 6b), a well-defined semicircle related to the charge transfer reaction at the metal-electrolyte interface is found in the high and medium frequency range. Next, in the low frequency limit, a Warburg impedance is developed, which is characterized by a straight line with an angle of approximately 45° with respect to both axes, which reveals the occurrence of a shielding effect on the mass transport of reactants and/or products involved in the corrosion reaction. Finally, the Nyquist diagram for the bronze sample recorded at even higher anodic polarizations given in Figure 6c, shows the presence of two semicircles in the Nyquist diagram. The semicircle appearing in the high frequency range is related to the double electrochemical layer developed for the dissolving metal [7], whereas that occurring at lower frequencies can be related to the presence of a precipitated layer of corrosion products layer that has been imaged in Figure 2c. These observations are in good

agreement with the different electrochemical behaviors deduced from the observation of the polarization curve in Figure 2.

Further analysis of the EIS data could be performed from the observation of the corresponding Bode diagrams given in Figure 7. The advantage of the Bode plot is that the data for all measured frequencies are shown, and that a wide range of impedance values can be displayed in one graph.

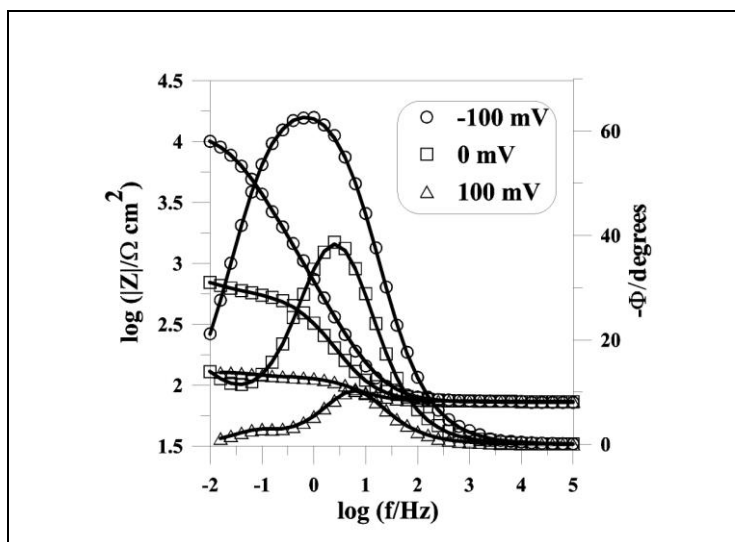


Figure 7. Bode representations of the EIS data measured for a bronze sample immersed in artificial rainwater at 25 °C when polarized at the potential values indicated in the graph.

The Bode-phase plot recorded for the bronze sample polarized at $-0.10 V_{SCE}$ exhibits one relaxation constant, i.e. only one peak is observed in the graph. In this case, the simple equivalent circuit (EC) model shown in Figure 8a adequately describes the observed EIS data. The characteristic parameters are the solution resistance, R_{sol} , and the elements R_I and Q_I that are attributed to a charge transfer process occurring at the alloy/oxide layer interface, which is related to the growth of the passive film. As the potential is shifted to 0 mV, the measured EIS data can be satisfactorily fitted (error smaller than 5%) to the transfer function of the EC presented in Figure 8b. In this EC, (R_I and Q_I continue describing the charge transfer processes at the bronze sample/oxide layer interface, whereas W is the Warburg impedance is associated to diffusion processes occurring in the electrolyte. On the other hand, the two peaks that are found in the Bode-phase plot evidence that at least two relaxation time constants operate on the material immersed in artificial rainwater when polarized at $+0.10 V_{SCE}$. The two relaxation time constants can be attributed to the existence of a porous surface film unable to effectively separate the underlying metal substrate from the electrolyte, which gets in contact with the unprotected metal inside the pores. The two relaxation processes are related to two charge transfer reactions, one corresponding to the portions of the metal still separated from the electrolyte

due to the precipitation of corrosion products, and the second at the electrochemical interface developed on the metal directly exposed to the environment, respectively. The EC model employed to fit the EIS data is shown in Figure 8c. The corresponding EIS parameters obtained from the analysis of the spectra for the bronze sample in artificial rainwater under various polarization conditions are listed in Table 2.

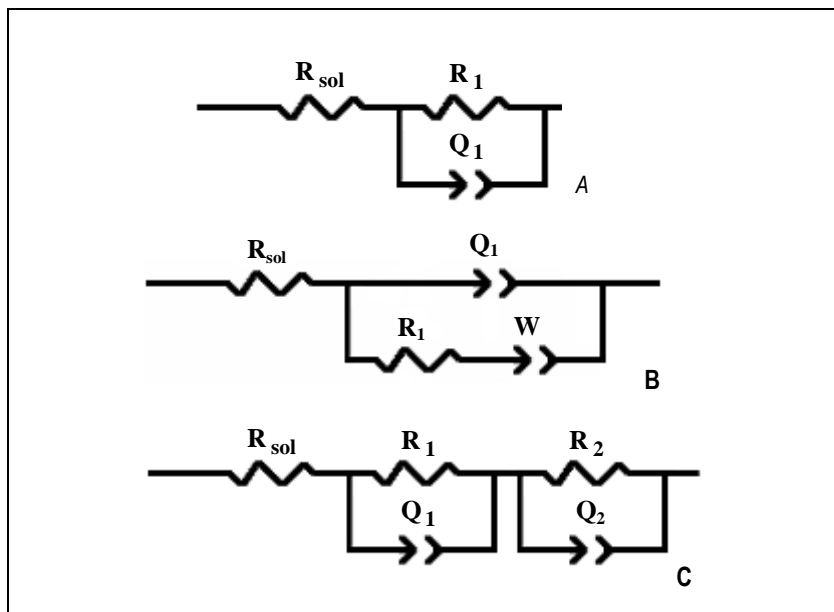


Figure 8. Electrical equivalent circuits employed to model the EIS spectra given in Figures 6 and 7. The kinetic control is: (a) compact surface film under charge transfer exclusively; (b) surface film under mixed charge transfer and diffusion controls; (c) unsealed surface film, whereas charge transfer reactions related to metal dissolution can occur on areas of the surface either directly exposed to the electrolyte or covered by a precipitated surface layer.

Table 2. Impedance parameters of bronze immersed in artificial acid rainwater derived from the EIS spectra in Figures 6 and 7.

Imposed potential (mV)	R_1 ($\Omega \cdot \text{cm}^2$)	Q_1 ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n_1	R_2 ($\Omega \cdot \text{cm}^2$)	Q_2 ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n_2	W ($\Omega \cdot \text{cm}^2$)
-100	41×10^3	5.7×10^{-4}	0.81	-	-	-	-
0	2.6×10^3	1.2×10^{-4}	0.61	-	-	-	115
+100	0.2×10^3	7.4×10^{-3}	0.58	0.1×10^3	5.9×10^{-3}	0.55	-

4. Conclusions

The dynamic electrochemical impedance spectroscopic (DEIS) technique was employed to evaluate the corrosion resistance of the bronze material artificial rainwater at ambient temperature.

The electrochemical impedance spectra measured under potentiodynamic conditions at -0.1, 0, and +0.1 V_{SCE} were represented in the form of Nyquist and Bode plots, and the physicochemical features operating at each polarization were described in terms of the electrochemical reactions operating in the system.

SEM images of corroded bronze surfaces retrieved from the electrochemical cell after different anodic potentiodynamic polarization treatments support the observations derived from the analysis of DEIS data.

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