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Electrochemical Polarization as a Sustainable Method for the Formation of Bronze Patina Layers on a Quaternary Copper Alloy: Insight into Patina Morphology and Corrosion Behaviour

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Abstract: The bronze patina is aesthetically pleasing and enhances the corrosion resistance of the metallic object. This corrosion product layer can develop naturally, through aging or artificially. However, artificial methods require substances that are hazardous to human health and the environment. In this study, a sustainable approach to patina development, based on the anodic polarization of a 85.5Cu-4.2Pb-4.5Sn-5.7Zn copper alloy immersed in 0.1 M NaCl + 0.01 M NaHCO₃ were characterized using polarization curves, chronoamperometry, electrochemical impedance spectroscopy, electrochemical noise measurements, X-ray diffraction, and scanning electron microscopy. The results indicate that the anodic potential modifies the current density as well as the diffusion coefficient of oxygen associated with a thicker corrosion product layer. Electrochemical Impedance spectroscopy and electrochemical noise show that the porous behaviour and corrosion resistance increases as the potential becomes more anodic due to the formation of a protective layer. This behaviour corresponded with the results acquired by chronoamperometry. The surface characterization shows that the potential applied changes the surface morphology and composition of the corrosion products, being identified the crystalline phases of nanokite and atacamite although Cu, Cl, O, Zn, and Pb elements were also detected.

Keywords: bronze; patina; EIS; porous electrode; corrosion resistance



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1. Introduction

Bronze is a copper alloy widely employed since at least 2000 years ago in different cultures; thus, its presence forms part of the cultural heritage of antique societies [1] as well as for archaeologists [2,3]. Several artefacts have been manufactured with bronze alloys whose composition is influenced by several factors such as (a) the mineral sources, (b) the technology used at that time [4] and (c) the object's applications [5]. These issues have influenced the range of compositions of the alloys such as binary (Cu-Sn), ternary (Cu-Pb-Sn) and quaternary (Cu-Pb-Sn-Zn) bronzes [4]. The quaternary copper alloy was developed by Greeks and Romans [5], so, the composition has been commonly related to Hellenic archaeological bronze [6]. In the past, quaternary bronze was employed for the casting of sculptures [7] and nowadays it is used in the manufacture of bearings [8]. In addition, bronze can develop a protective and colourful corrosion product film called a patina that naturally grows on the metallic surface due to its interaction with the corrosive environment. The patina layers grow in a stratified way with an inner film mainly composed of Cu₂O, CuO, SnO, Sn₂O₄ and an outer layer formed by the interactions of ions from the environment, leading to the formation of a layer composed of Cu₂Cl(OH)₃, Cu(OH)₂CO₃ and Cu₄SO₄(OH)₆ [9,10]. Also, the presence of chloride can lead to the formation of CuCl underneath the Cu₂O layer. However, the influence of the aggressive ions changes the composition and the structure of the patina leading to the classification of *patina type I* and *patina type II* proposed by Robbiola et al. [11]. Patina type I provides protection to the metallic substrate, and it is more stable than patina type II which contains

chloride compounds that provoke bronze disease or the loss of the surface appearance. For two centuries [12], copper alloys have been the focus of research of several works due to the interest in understanding patina formation [9,11,13,14] in order to establish adequate protection systems to decrease the corrosion rate of bronze materials [15–17]. Also, patina characterization provides information about long-term corrosion processes of copper alloys in different applications, such as the developing of canisters for nuclear waste deposits [18]. Patina formation can be induced by several methods such as the wet and dry method [19], dripping [20], torch [21,22], immersion [23,24], dabbing [25], exposition to acid vapours [26] and electrochemical polarization [5,27]. However, with exception of the electrochemical polarization, the vast majority of these methods require the use of acid substances (HCl, H₂SO₄, HNO₃) which need more caution to use due to the risk that represents to human health and environment. Also, the traditional torch method is based on the use of highly corrosive substances (FeCl₃, K₂S), as well as the application of heat through the combustion of fuel that promotes the formation of combustion gases and corrosive vapours. Then, the electrochemical method is a sustainable approach to develop patina layers showing the stratified growth and corrosion products similar to these typically formed in natural conditions. A literature review shows that the electrochemical method is used to produce artificial patinas in laboratory coupons resembling bronze alloys. Usually, these samples are characterized together with organic coatings, to enhance the corrosion protection of the alloy [28,29]. Nevertheless, the electrochemical response of the anodic patina has been scarcely studied. In this regard, Robbiola et al. [30] have reported the surface characterization of the anodic layers developed on Cu-10Sn. Their results show the influence of the applied potential on the morphology, composition, and thickness of the patina. Additionally, Ben Channouf et al. [31] have characterized the anodic patina formed on Cu-10Sn exposed to a chloride environment through X-ray photoelectron spectroscopy (XPS) showing that a destannification process can occur on the alloy. The electrochemical formation and evolution of a CuCl patina have been reported by Wang et al. [32] which indicates that the nantokite and water can react transforming into cuprite and hydrochloric acid. However, in acid rain conditions, nantokite can transform into cuprite, increasing the corrosion resistance. Also, Yang et al. [33] reported the electrochemical response of the different stages of evolution of this transformation, indicating a noticeable increase in the corrosion resistance after the thickening of the patina layer. On the other hand, quaternary bronzes are commonly used in artistic artworks, and then coupons of this alloy are used in laboratory scale investigations to study the patina formation, corrosion behaviour and the application of several protection systems. For example, Di Carlo et al. [26] have characterized the patinas developed on a quaternary alloy using accelerated acidic tests showing that the patina formation depends on the aggressiveness of the treatment employed for its formation. Additionally, Masi et al. [7] have characterized the patina layers formed under artificial shelter and unsheltered atmospheric corrosion conditions demonstrating that the patina exhibits a nano-porous structure associated with decuprification and the selective dissolution of Zn. Also, Bernardi et al. [34] have characterized the corrosion behaviour and the change of the composition of the patina layer of quaternary bronzes exposed to acid rain showing that the patina layer exhibits a porous structure formed mainly by cuprous oxide and (hydroxyl) oxide groups. Chiavari et al. [35] determined that the bronze quaternary alloy exhibits a high corrosion resistance in artificial rain conditions due to the formation of Pb and Sn corrosion products, which leads to low redox activity of the patina layer. Kosec et al. [36] reported the corrosion behaviour of a sulphide-patinated bronze covered with a fluoropolymer coating. Their results show that the application of these coatings improves corrosion resistance with remarkable protection efficiency. Mihelcic et al. [37] have studied the influence of polyurethane-based protective coatings on the electrochemical response of a quaternary bronze showing that doped organic coatings increase the corrosion resistance in comparison with commercial restorative products.

Despite of the vast efforts to understand the patina formation and corrosion behaviour of quaternary copper alloys, there is a lack of information about the use of a green ap-

proach represented by the electrochemical formation of anodic layers growth on quaternary copper alloys.

The aim of this study consists of detailing the morphological, compositional, and electrochemical features of the anodic layers formed on a Cu-Pb-Sn-Zn alloy by applying several polarization potentials. The purpose of the research is to identify the influence of the applied potential on the passive behaviour of the patinas formed on a quaternary copper alloy in chloride and carbonate media as a method of patination bronze foundry before its exposure outdoors.

2. Material and Methods

2.1. Samples Preparation

The quaternary bronze alloy was commercially available with a nominal composition of 85.5Cu-4.2Pb-4.5Sn-5.7Zn wt% as measured by X-ray Fluorescence (XRF). This alloy is in accordance with the composition reported by Zohdy [8] and Di Carlo et al. [26] and represents the composition and microstructure employed in artworks [13].

The samples were cut into rods with a dimension of 1 cm in height and a diameter of 1.2 cm. Later, a copper wire was attached to the metallic surface to allow electric conduction and embedded on epoxy resin to control the exposed area. In addition, the samples were sanded with emery paper until 1000 grade, cleaned with distilled water, rinsed with ethanol, and dried using a hot air stream.

2.2. Electrochemical Characterization

2.2.1. Electrochemical Cell and Solution

The electrochemical cell consisted of a classical three-electrode arrangement with a saturated calomel electrode (SCE) as a reference electrode (RE), the bronze sample as the working electrode (WE) and graphite sheet as the counter electrode (CE). All potentials in this work were acquired with the SCE. The samples were immersed in a 0.1 M NaCl + 0.01 M NaHCO₃ solution with a pH 8 that was prepared with distilled-deionized water and reagents (JT Baker). The solution was naturally aerated, and the volume of electrolyte employed was approximately 100 mL. The tip of the reference electrode was carefully placed at a 2.5 cm from the sample. All the measurements were carried out at room temperature.

Additionally, the amount of dissolved oxygen was measured before and after the anodic polarization of the samples using a Milwaukee oxygen concentration probe with a stirred solution at room conditions. The concentration of dissolved oxygen was measured 3 min after the potentiostatic formation of the patina.

2.2.2. Electrochemical Techniques

The polarization curve, chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) were carried out in an Autolab PGSTAT 205. To identify the electrochemical response of the sample in the electrolyte employed, the polarization curve was performed with a scan rate of 10 mVs⁻¹ with a potential range from −400 mV to 1000 mV.

To develop the anodic layers, the samples were polarized with 200, 400 and 600 mV for 30 min in each case. The current behaviour was studied using CA, acquiring the data each 0.01 s for 30 min. The impedance measurements were initiated 30 min after the anodic polarization ended so as to allow for the system to stabilize. For the EIS testing, the frequency sweep was performed from 100 kHz to 0.01 Hz with 10 points per decade with a sinusoidal perturbation signal of 10 mV at OCP conditions. Additionally, to validate the stability of the EIS measurements, Kramers-Kronig tests were carried out using Nova software. The EIS experiments were repeated three times for reproducibility criteria.

The Electrochemical noise measurements (ENM) were conducted with an ACM Gill potentiostat with a three-electrode cell configuration similar to the EIS arrangement. In this case the graphite sheet was connected to the secondary working electrode (WE2) instead

of the CE as reported elsewhere [38]. All the electrochemical techniques were carried out inside a Faraday cage to avoid any electromagnetic perturbations.

2.3. Surface Characterization

The morphology of the patina layer was examined using a scanning electron microscope (SEM) FESEM JEOL JSM 5900 with an acceleration voltage of 20 kV coupled with an energy dispersive X-ray spectroscopy (EDS) device. The X-ray diffraction (XRD) analysis was carried out with a Rigaku Ultima IV equipped with Cu radiation ($\lambda_{\alpha} = 0.1540$ nm) from $2\theta = 25^{\circ}$ to $2\theta = 80^{\circ}$. According to the XRD configuration, the depth of analysis is of 100 μm .

3. Results and Discussion

3.1. Polarization Curve

Figure 1 shows the polarization curve for the bronze samples immersed in a solution containing chloride and carbonate ions. The plot exhibits a linear Tafel region [39] characterized by the linear relationship of the potential with the current, followed by a passive region in the anodic zone. The potentials selected for the formation of the anodic layers are labelled as I, II and III, corresponding to 200, 400 and 600 mV, respectively. The passivity of the alloy is related with the formation of a porous layer that spreads over the surface, blocking the access to aggressive ions to the metallic surface [40]. This layer is mainly composed of copper corrosion products formed by the interaction with the electrolyte. The composition, crystalline phases and morphology of the layers developed will be discussed later.

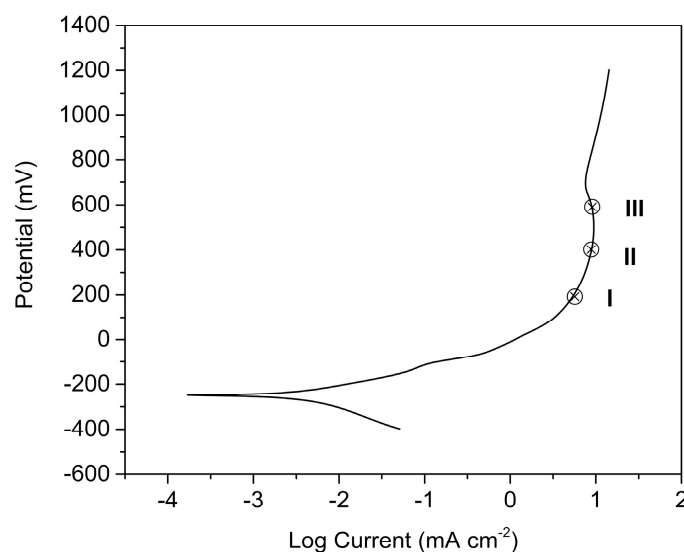


Figure 1. Typical polarization curve of the bronze samples immersed on a 0.1 M NaCl + 0.01 M NaHCO₃ solution with pH 8 obtained at 10 mVs^{−1}. The marked points I, II and III corresponds to the selected potentials used for the later formation of the anodic layers.

3.2. Formation of the Patina Layer

Figure 2a shows the typical potentiostatic transients acquired during the anodic formation of the patina layers. In general, the curves depict a rapid current increase to reach a maximum value, followed by a current decrease as polarization time proceeds. This behaviour is due to the metallic substrate rapidly dissolving, which is followed by the formation of a protective layer that spreads across the surface, reducing the current density. The current increase during the first seconds of polarization of the plot indicates the development of pitting corrosion phenomena [41]. A literature review [42] indicates

that this type of current transient is related with processes controlled by mass transfer which follow the equation below:

$$i = nF \frac{D^{\frac{1}{2}} \Delta c}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} \quad (1)$$

where n is the number of electrons transferred, F is the Faraday constant, D represents the diffusion coefficient, Δc is the concentration difference in the layer (corrosion products). Therefore, the behaviour of the current decay of Figure 2a indicates that the formation of the patina layer is diffusive controlled. Plots from Figure 2 were divided in two sections: (a) Region I and (b) Region II. The first region refers to the metallic oxidation that forms the corrosion products layer. Region II indicates the stable formation of the corrosion product layer with a linear current decrease.

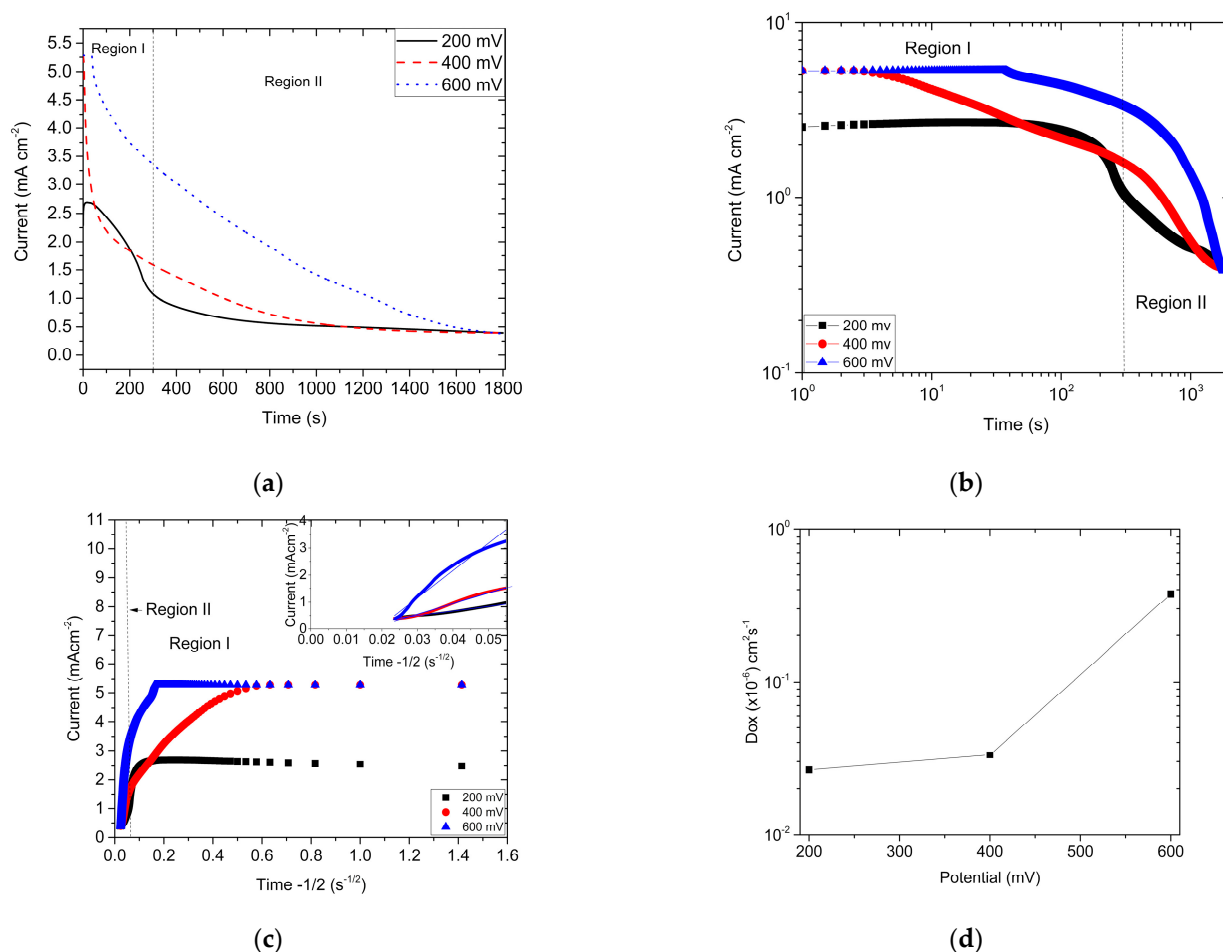


Figure 2. (a) Typical potentiostatic curves, (b) log current–log time plot of the transients obtained and (c) Current vs. reciprocal square root of time representation of the current transients acquired at several potentials in 0.1 M NaCl + 0.01 M NaHCO₃ at ambient conditions. (d) Variation of oxygen diffusion coefficient with potential applied.

Figure 2b displays the full logarithmic scale representation of the current transients demonstrating a linear behaviour between log (current)–log (time). As displayed in Region II, the slope of the linear relationship changes with the potential applied, being higher as the anodic character of the potential increases. This behaviour is likely due to the formation of an oxide layer with a growth rate that enhances as the potential applied becomes more anodic. Li et al. [43] have studied the effect of copper content on the pitting resistance of super austenitic stainless steel, identifying a similar negative slope in the total logarithmic scale plots of potentiostatically-formed oxide layers. This behaviour indicates that the rate of formation is higher than the rate of dissolution, with a protective effect to the substrate.

Thus, considering the results of Figure 2, it can be seen that the corrosion products provide a protective effect which reduced the metal oxidation as seen in the total current decrease. These corrosion products are formed by several compounds as indicated by XRD results (Section 3.4).

Figure 2c displays the current i 's reciprocal square root of time, showing that the current decreases as the polarization time increases. Additionally, Figure 2c inset exhibits a linear relationship in Region II, showing that the slope increases depending on the anodic character of the potential applied. Souto et al. [44] have studied the pitting of copper in alkaline solutions containing chloride ions identifying similar behaviour and suggesting that this increase is due to the change of Δc with the potential employed. Therefore, in the current study, after the potentiostatic formation of the patina layers the dissolved oxygen content in the solution was measured to confirm these results.

Based on the slope of the linear fitting (Figure 2b) and equation 1, the diffusion coefficient was computed. The data employed is displayed in Table 1, with $n = 2$ and $F = 96,485 \text{ [}\frac{\text{C}}{\text{mol}}\text{]}$.

Table 1. Parameters employed to determine the Diffusion Coefficient of Oxygen.

Potential Applied mV	Dissolved Oxygen, Δc g/L	Slope Determined mA/cm ² s
200	0.6	3.33×10^{-4}
400	0.7	4.33×10^{-4}
600	0.8	1.67×10^{-3}

The diffusion coefficient computed is shown in Figure 2d demonstrating that the anodic character of the potential applied increases the rate of access of oxygen to the surface, allowing the rapid formation of a corrosion product layer. Thus, as the anodic character of the potential applied increases, both the Δc as well as the D_{ox} becomes higher, allowing an increase in the formation rate of the patina layer.

In summary, all the above results indicate that the patina developed is under diffusion control, protecting the metallic substrate despite the pitting corrosion phenomena seen during its formation. This protective behaviour shows consistency with other results reported in literature [30,32,33].

Additionally, the applied potential modifies the growth rate of the layer because it changes the kinetic of the species towards the metallic surface.

3.3. Corrosion Measurements

The protective properties of the anodic layers were assessed through EIS and ENM measurements. Figure 3 shows the (a) Nyquist and (b) Bode diagrams of the patina layer acquired at OCP conditions for the patina formed at 200, 400 and 600 mV. The Kramers-Kronig tests were also performed, and the residual error remained below $\chi^2 < 10^{-5}$ throughout the whole frequency range. The Nyquist plots (Figure 3a) show a flat semi-arc associated with the parallel resistive-capacitive response of the system. Also, as observed in the phase angle plot (Figure 3b), the system exhibits distinct features showing maximum phase angles at 10^5 Hz and the second constant in the frequency range between 10^1 – 10^{-1} Hz. However, another process can be considered in the low-frequency region between 10^{-1} – 10^{-2} Hz. Therefore, three time constants can be observed. The impedance modulus increases at a higher frequency range showing a strong correlation with the applied potential. These results indicate that the anodic potential applied promotes the formation of a porous layer that increases its porosity as the potential becomes more positive as seen by the increase of the phase angle in the high-frequency (HF) region. This porous behaviour coincides with the work reported by Hernandez et al. [25] which studied the patina formation on pure copper exposed to a marine environment, suggesting that the patina layer behaves like a porous electrode.

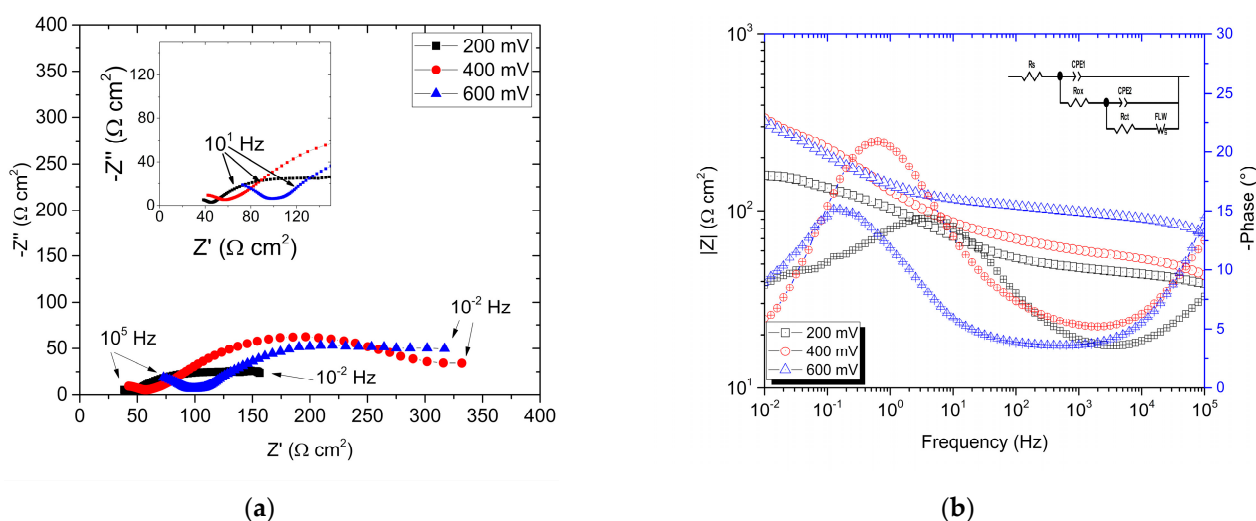


Figure 3. (a) Nyquist diagram and (b) Bode plots of the anodic layers formed on a quaternary bronze alloy exposed to a 0.1 M NaCl + 0.01 M NaHCO₃. Also the (b) inset show the electrical equivalent circuit (EEC) employed for the fitting of results.

The Nyquist and the Bode diagrams demonstrate that the resistance of the surface patina layer increases according to the impedance modulus at the HF region. It is also seen that the intersection of the first semi-circle with the real axis (Z') increases with the applied potential. This behaviour is consistent with the protective properties of the corrosion products identified during the potentiostatic measurements.

As displayed in Figure 3b, the total impedance of the system in the low frequency region increases with the anodic character of the applied potential. In a similar manner, the maximum angle phase of the second time constant displaces toward lower frequencies as the potential trends to anodic values. This indicates that the corrosion products provide higher protection to the metallic substrate due to the barrier effect provided by the patina that decreases the rate of access of aggressive ions to the metallic surface [17].

For quantitative analysis, the results were fitted to the equivalent electrical circuit shown as inset in Figure 2b using Nova software. Additionally, the parameter of adjustment to the electric equivalent circuit χ^2 remained in the order of 10^{-3} . The equivalent circuit employed shows the presence of three time constants represented by two $R \parallel CPE$ and a diffusive element FLW. A similar circuit was employed by Serghini-Idrissi et al. [45] in the study of an archaeological patina layer with a micro-cavity electrode, however the diffusive behaviour was modelled using a spherical diffusion element due to geometrical restrictions.

The equivalent circuit is composed of the following elements: R_s represents the solution resistance, the R_{ox} and CPE_1 elements are associated with the resistivity of the patina layer and the capacitive effect; these elements represent the time constant at higher frequencies. The second time constant corresponds to the electrochemical response of the areas that are not covered by the patina and exposed directly to the electrolyte and are represented by R_{ct} , that is the charge transfer resistance and the CPE_2 related with the capacitance of the electrochemical double layer [46,47]. As proposed by several authors [48,49], the CPE elements were employed to consider the roughening effect of the surface electrode using the Cole-Cole parameter n . The impedance of the CPE element is modelled by the equation [50]:

$$Z_{CPE} = \frac{1}{Y_{CPE}(j\omega)^n} \quad (2)$$

where Y_{CPE} represents the admittance of the CPE element, the angular frequency is ω and n the Cole—Cole exponent. The value of the exponent n modifies Z_{CPE} , changing the response from a pure capacitive ($n = 1$) to a Warburg diffusive behaviour ($n = 0.5$) or an inductive response ($n = -1$) [48].

Also, the *FLW* element represents the finite length Warburg diffusion behaviour. This diffusive element was considered as the mechanism of the mass transfer within the porous oxide, as indicated in the low frequency region of the EIS results, which concurs with literature [51,52]. This diffusive behaviour was modelled through the equation [52]:

$$Z_{\text{OFLD}} = \frac{1}{Y_o \sqrt{j\omega}} \tanh(B \sqrt{j\omega}) \quad (3)$$

The parameters from this equation are: $B = \frac{l}{\sqrt{D}}$ where l is the diffusion length, D the diffusion coefficient and B is the square root of the diffusion time constant. $Y_o = \frac{1}{\sqrt{2}\sigma}$ where Y_o is the magnitude of the admittance and σ is the Warburg coefficient. Additionally, the capacitance of the oxide layer (C_{ox}) can be obtained by means of [50]:

$$C_{\text{ox}} = \frac{(Y_{\text{CPE1}} R_{\text{ox}})^{\frac{1}{n}}}{R_{\text{ox}}} \quad (4)$$

where the parameters Y_{CPE1} and R_{ox} are related with the admittance of and the oxide resistance of the patina layer and n with the Cole-Cole exponent. Based on the C_{ox} , the thickness of the corrosion product layer can be obtained.

The average results of the fitting of the electric equivalent circuit (EEC) parameters are shown in Table 2.

Table 2. Parameters of fitting EIS results to the electrical equivalent circuit.

Parameters	Units	Potential mV		
		200	400	600
R_s	$\Omega \text{ cm}^2$	10	10	10
R_{ox}	$\Omega \text{ cm}^2$	38.4	58.36	65.28
CPE_1	$\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$	1.57×10^{-4}	1.16×10^{-4}	1.36×10^{-6}
n_1		0.41	0.37	0.65
C_{ox}	μFcm^{-2}	0.100	0.023	0.010
R_{ct}	$\Omega \text{ cm}^2$	106.8	225.8	205
CPE_2	$\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$	3.7×10^{-3}	2.3×10^{-3}	2.9×10^{-3}
n_2		0.48	0.52	0.43
Cdl	mFcm^{-2}	1.3×10^{-5}	1×10^{-6}	3.1×10^{-6}
Y_o	$\Omega^{-1} \text{ cm}^{-2} \text{ s}^{1/2}$	0.16	0.02	0.01
B	$\text{s}^{1/2}$	4.6	0.9	0.8

The fitting of the EEC shows that the applied potential modifies the resistance of the oxide layer and the charge transfer resistance, demonstrating their increase at higher anodic potentials. This is attributed to the increase of the corrosion resistance of the samples due to the formation of resistive patina layers. Additionally, this behaviour coincides with the impedance modulus already described. Hernandez et al. [25] have studied the patina formation on pure copper exposed to a marine environment, suggesting that the corrosion resistance increase is likely due to the decrease of the pore diameter and the pore number. This assumption can be also valid for the patina developed in this study, since the composition of the patina layer is similar.

As shown in Table 2, the fitted capacitance (C_{ox}) decreases with the applied potential, which is also related to the thickening of the patina layer [53]. To corroborate this assumption, the thickness of the dielectric layer that is mainly formed by Cu_2O [40] was computed. Thus, it is considered that the total capacitance obtained from the fitting of the EEC is distributed according to the following equation [46]:

$$\frac{1}{C_{\text{ox}}} = \frac{1}{C_H} + \frac{1}{C_{\text{diel}}} \quad (5)$$

where C_{ox} represents the total capacitance obtained in the fitting procedure, C_H is the Helmholtz layer capacitance with a nominal value of $50 \mu\text{Fcm}^{-2}$ and C_{diel} is the capacitance of the patina layer. Then, based in the C_{diel} determination, the thickness of the dielectric layer was computed as follows [54,55]:

$$C_{diel} = \frac{\epsilon\epsilon_0}{\delta} A \quad (6)$$

where ϵ represents the dielectric constant of the patina layer with a value of 80 for hydrated Cu_2O [25], ϵ_0 corresponds with the vacuum permittivity at $8.85 \times 10^{-14} \text{ Fcm}^{-1}$, δ is the thickness of the dielectric layer and A is the area exposed to the electrolyte.

To determine the influence of the thickness of the patina layer with the polarization resistance of the samples, both parameters were plotted in Figure 4. According to the plot, the thickness value of the patina layer enhances at higher polarization potentials. This result corresponds with the behaviour determined by Robbiola et al. [30] which suggests a linear dependence of the thickness of the patina with the applied potential in the formation of a patina layer on a Cu-10Sn alloy. The polarization resistance ($R_{pol} = R_{ox} + R_{ct}$) was also obtained [54], which demonstrates that the applied potential increases the polarization resistance, indicating the growth of the corrosion resistance of the samples due to the enhancement of the protective properties of the patina layer. Additionally, the capacitance C_{diel} has an average value of 10^{-6} Fcm^{-2} , which indicates that the capacitive measurement is attributed to the corrosion product layer as reported elsewhere [46].

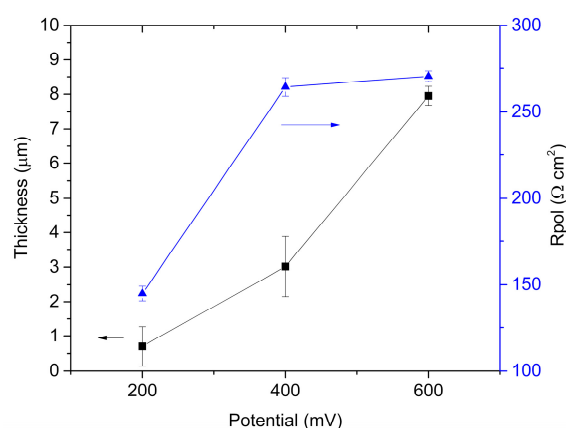


Figure 4. Polarization resistance (R_{pol}) and thickness of the anodic layer developed on a copper quaternary alloy.

The Cole-Cole exponent of the first Randles circuit n_1 shows values of approximately 0.5, commonly attributed to a diffusive process [56]. This correlates with the diffusive behaviour determined in the potentiostatic formation of the patina layer already discussed. On the other hand, the double-layer capacitance slightly decreases with the applied potential, indicating the diminishing of the active surface [32]. This parameter, in conjunction with the increase of the R_{ct} and the decrease of the C_{dl} indicates higher protective properties of the patina layer [57]. The parameter n_2 of the second RC circuit shows an almost constant behaviour at around 0.5; the interpretation of this parameter is attributed to the creation of diffusive paths during polarization associated with the increase of the oxide layers as reported elsewhere [49]. All these results confirm that the patina layer thickens with better protective properties at higher anodic potentials. These results are concurring with the results discussed in the potentiostatic analysis.

Additionally, based on the fitted parameters B and Y_0 of the FLW (Table 2), the diffusion length and the Warburg coefficient were computed. The results are shown in Table 3. The diffusion coefficient of oxygen was considered to have a value of $10^{-5} \text{ cm}^2\text{s}^{-1}$ because this value is commonly employed to model free corrosion processes [58,59]. The

behaviour of both parameters is inversely proportional amongst them, i.e., the diffusion length decreases with the applied potential while the Warburg coefficient increase. Collazo et al. [58,60] have evidenced that the decrease rate of the oxygen diffusion to the metallic surface is due to the oxide particles deposited into the electrode. These particles have a length of 130–54 μm . Therefore, the patina layer formed on a quaternary copper alloy represents a barrier layer where the diffusion length parameter modified depending on the amount of corrosion products. The increase of the Warburg coefficient associated with the decrease of the active surface area corresponds with the diffusion length parameter results.

Table 3. Thickness corresponding to the diffusion layer and Warburg coefficient.

Potential vs. SCE	200 mV	400 mV	600 mV
l [μm]	48.6	9	8.7
σ [$\Omega\text{cm}^2\text{s}^{-1/2}$]	4.2	25.9	21.4

In order to corroborate the corrosion behaviour determined by EIS, the samples were characterized using electrochemical noise (ENM). The time series acquired is shown in the Supplementary Materials. To determine the influence of the applied potential in the corrosion resistance of the patina layer, the time series was statistically analysed with the noise resistance (R_n), standard deviation and the localization index. These parameters are shown in Figure 5a,b. The noise resistance was acquired using the formula $R_n = \frac{\sigma_E}{\sigma_I}$ where σ_E represents the potential standard deviation and σ_I is the current standard deviation [59]. Also, the localization index (LI) is a parameter that can elucidate the corrosion mechanism carried out in the sample. For localized, mixed, and general corrosion, the values are $1 < \text{LI} < 0.1$, $0.1 < \text{LI} < 0.01$ and $0.01 < \text{LI} < 0.001$, respectively [61]. Figure 5a shows that the noise resistance increases with the applied potential while the standard deviation decreases, indicating that the corrosion layer is more stable and provides better protective properties at higher anodic potentials [58]. This behaviour correlates with the above results already discussed in this study and with literature [24]. On the other hand, Figure 5b shows that the applied potential slightly modifies the corrosion mechanism to a localized corrosion type.

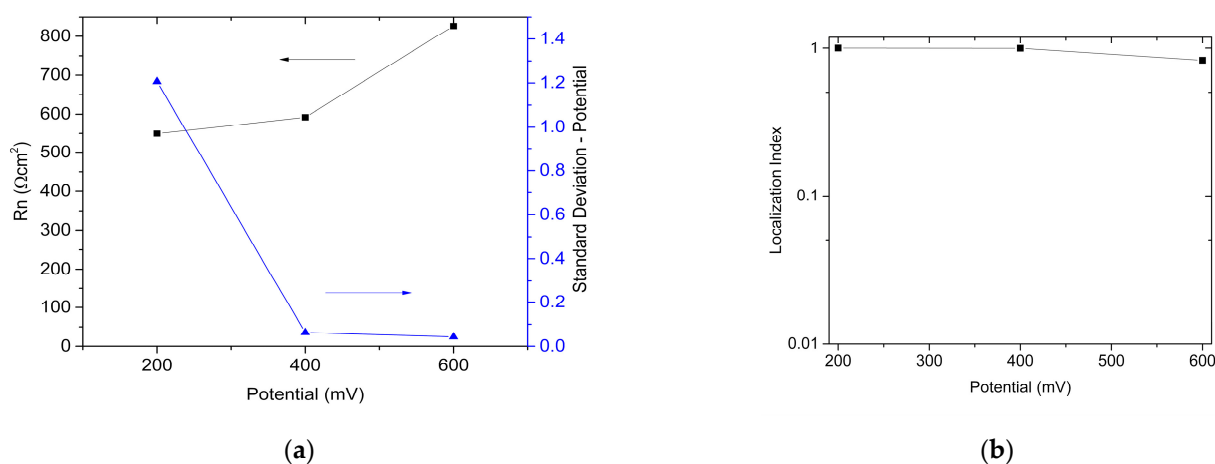


Figure 5. (a) Noise resistance and standard potential deviation, and (b) localization index obtained for the bronze samples patinated at distinct potentials.

Therefore, based on the corrosion measurements, it was demonstrated that at higher anodic potentials the features of the patina layers such as the porosity, the thickness, and the corrosion protection changed. The barrier effect of the porous layer becomes more evident at 600 mV given that the oxygen diffusion decreases. This behaviour is in agreement with Robbiola et al. [30] which indicate that a chloride formed patina can provide protection to the metal substrate. Also, Wang et al. [32] and Yang et al. [33] indicated that the CuCl

can react into Cu_2O increasing the corrosion protection of the patina layer in an artificial rain corrosion environment. However, it is necessary to consider the micro-environment to properly identify the rate of reaction and the consecutive increase in the protective behaviour of the patina.

3.4. Morphology and Composition of the Patina Layers

To identify the influence of the applied potential in the morphology and composition of the patina layers, the samples were characterized using SEM-EDS and XRD. Figure 6a–c show the micrographs of the patina layers formed at 200, 400 and 600 mV, respectively. The patina formed at 200 mV (Figure 6a) exhibits a compact surface with the presence of small polygonal plates; a similar morphology was observed by Souissi et al. [62] in archaeological bronze exposed to a chloride environment. Figure 6b displays the patina formed at 400 mV showing that the surface is covered with spongy and rougher corrosion products. On the other hand, the patina formed at 600 mV (Figure 6c) exhibits a similar appearance to the patina formed at 400 mV but it appears to be more compact with a greater volume and thickness. The change in the patina morphology is attributed to the applied potential given that the thickness and the porosity of the corrosion product layer changed, as demonstrated by EIS. Additionally, the composition of the patina layer was determined by EDS (Figure 6d–f), showing the presence of Cu, Cl, O, and Pb elements, suggesting the presence of oxide and chloride compounds as a part of the corrosion products. Constantinides et al. [63] reports a similar composition in the patina formed in a quaternary copper alloy, however Pb was not identified. In addition, Na that came from the testing electrolyte was also detected.

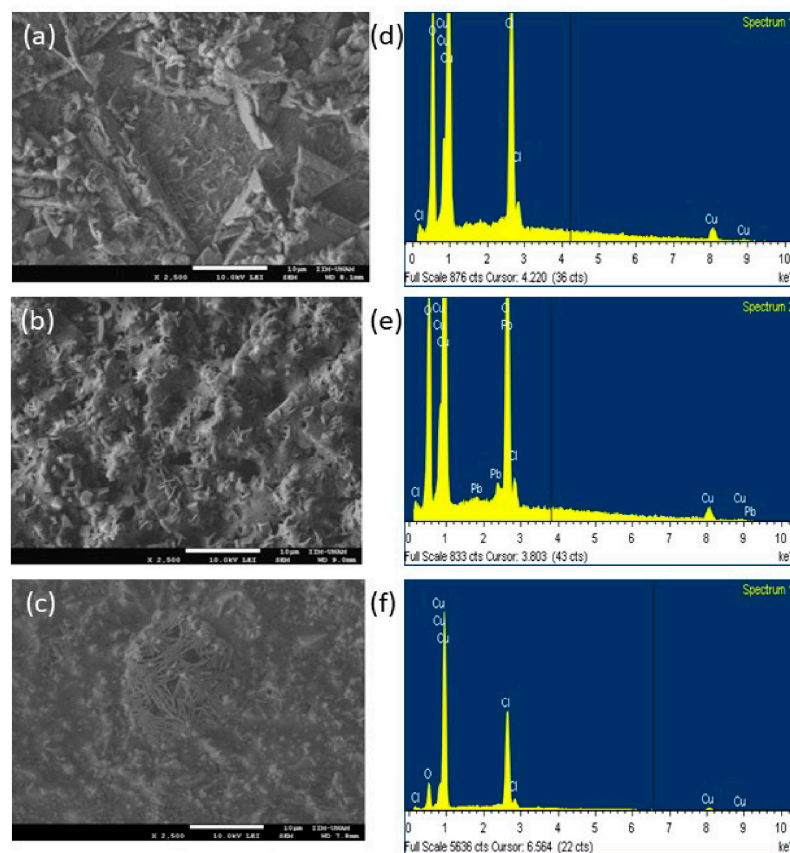


Figure 6. SEM Micrographs and EDS of the patina layers formed at (a,d) 200 mV, (b,e) 400 mV and (c,f) 600 mV during 30 min of constant polarization.

The corrosion products formed at different applied potentials were analysed using XRD; the diffraction patterns are shown in Figure 7. It can be seen that the peaks appearing

at 2θ angles 28.5° , 47.5° and 56.2° are related to the presence of CuCl according to the standard ICSD card no. 01-077-02383. Additionally, the peaks appearing at 2θ angles 36.3° , 43° , 49.9° , 52.3° , 53.6° , 56.2° and 62.2° correspond with $\text{Cu}_2\text{Cl}(\text{OH})_3$ following the standard ICSD card no. 01-087-0679. The copper-chloride compounds are in agreement with the corrosion products reported by Constantinides et al. [63]. In the other hand, the three peaks at 2θ angles 28.5° , 31.3° and 47.5° are associated with the presence of SnO, according to the standard ICSD card no. 01-072-2324. The other peaks appearing at 2θ angles 32.3° , 39.7° , 43° and 73.4° correspond with PbCl_2 according to the standard ICSD card no. 00-026-1150. Also, the 2θ angles 36.3° and 47.5° indicate the presence of ZnO under the standard ICSD card no. 01-075-0576. As displayed in the plot, at higher polarization potentials, the intensity of the peaks related to SnO and PbCl_2 increases, indicating that the formation of the patina layer becomes thicker. This behaviour correlates with the increase of roughness and porosity demonstrated by SEM and EIS, as already discussed. Therefore, the corrosion products identified through XRD and the EDS composition are all in agreement and are analogous to those reported in archaeological patinas [64].

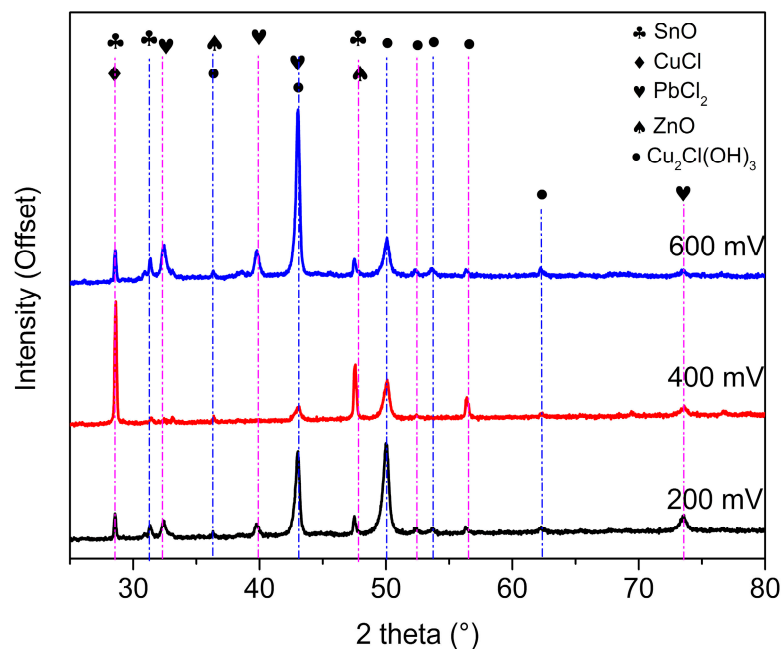


Figure 7. X-ray diffractograms obtained for the anodic layer grown on Cu-Pb-Sn-Zn alloy at 200, 400 and 600 mV during 30 min on 0.1 M NaCl + 0.01 M NaHCO_3 .

4. Conclusions

The effect of anodic potential on the electrochemical formation of patina layers on a quaternary bronze alloy of 0.1 M NaCl + 0.01 M NaHCO_3 was determined leading to the following conclusions.

Electrochemical techniques (CA, EIS, ENM) show that the increase of the anodic potential leads to a higher growth rate of the corrosion products. The patina layer is formed by the diffusion of species (O_2 , Cu^+ and chloride ions) throughout the corrosion products. These oxides show a porous semi-infinite behaviour together with a finite-length diffusive contribution. The applied potential increases the protective properties and thickness of the patina, which induces an increase of the oxygen diffusion coefficient. On the other hand, the surface characterization techniques demonstrate that the patina is formed of a compact layer covered with crystals, with a morphology and composition that depends on the applied potential. The patina is mainly composed of SnO, $\text{Cu}_2\text{Cl}(\text{OH})_3$. Therefore, the anodic potential employed in the formation of the patina layers modifies the growth rate, the protective properties of the corrosion layer, and the morphology of corrosion products while the composition remains almost constant for all the potentials. The results

in this study demonstrate that the patina formed through constant polarization becomes more protective when higher anodic potentials are employed. Based on these results, the authors suggest the use of a potential of 600 mV vs. SCE for patina formation in a chloride/carbonate solution with a slight alkaline environment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su15031899/s1>, Figure S1: Time series for the bronze samples patinated at (a) 200, (b) 400 and (c) 600 mV.

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