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AN EIS STUDY OF THE CONSERVATION TREATMENT OF THE BRONZE SPHINXES AT THE MUSEO ARQUEOLÓGICO NACIONAL (MADRID)

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Abstract (500 words)

In any conservation project, conservators have to address several questions to design the appropriate intervention strategy. Among them, the effectiveness and duration of protective treatments is an important issue, not easy to evaluate. In the field of metallic cultural heritage, electrochemical techniques such as electrochemical impedance spectroscopy (EIS) can be used to evaluate patinas and protective coatings performance. Widely used in industrial applications, the use of these techniques in conservation science is much more recent and limited.

During the restauration process of the bronze sphinxes at the main façade of the National Archaeological Museum in Madrid, collaboration with conservators has been established to test the performance of a recently developed gel-electrolyte cell for the electrochemical evaluation of metal cultural heritage. Electrochemical measurements (EIS and Rp) of the patinas have been carried out before, during and after the conservation treatments, on two different areas of the sculpture. This has provided information on how the protective coatings have improved corrosion resistance by 3 orders of magnitude, and how this protection is starting to decrease with time; periodic measurements will allow verifying the performance of the treatment over time and detecting the failure of the protection treatment before its effects are visible on the surface.

Keywords (5-10):

Conservation, outdoor sculpture, bronze, Electrochemical Impedance Spectroscopy, protective coatings, diagnostic tools

Research aims (200 words)

The objective of this work is to test and validate on a real situation a recently developed agar gel-polymer electrolyte (G-PE) cell specifically designed for in-situ electrochemical measurements on metallic cultural heritage. These measurements allow quantifying the corrosion resistance of the patina in different areas and to assess the increase in the corrosion resistance of the metal provided by the coatings and other conservation treatments. With this development we would like to provide metal conservators with a useful diagnostic tool that allows corrosion resistance evaluation of patinas and coatings, its evolution over time and to predict the failure of the protective coatings before active corrosion starts again.

1. Introduction

The main façade of the National Archaeological Museum in Madrid is decorated by two bronze sphinxes, half woman, and half lioness, placed at both sides of the main staircase over a stone base. The sphinxes were designed inspired by the classical cannons by the Spanish sculptor Felipe Moratilla y Parreto, and lost-wax casted in the Madrilenian foundry Arias, in 1894. Due to their large dimensions (1.91 m. high, 3.52 m. depth and 1.06 m. width, and around 3.000kg) they were done in several pieces and joined together.

The sphinxes have remained in the same place –with a small displacement in 1970 due to the extension of the staircase- since the inauguration of the museum on July the 5th, 1895. During 2014, following the complete refurbishment of the Museum, all sculptures in the main façade, including the sphinxes have been restored under the supervision of the Instituto del Patrimonio Cultural de España (IPCE) [1].

In any conservation project, conservators have to address several questions to design the appropriate intervention strategy. Among them, the effectiveness and duration of protective treatments is an important issue, not easy to assess. Fortunately, for metallic objects, electrochemical techniques can provide some answers to this problem. Among these techniques, Electrochemical Impedance Spectroscopy (EIS) is a very well-established method to assess the anti-corrosive efficiency of protective coatings and inhibitors. However, EIS is less widespread for the study of patinas and coatings in the field of cultural heritage [2-6]. EIS is based on the application of a low-amplitude (usually 10 mV) alternating current (AC) voltage signal to the metallic sample using a conventional three electrode (working, i.e. the metal under study, reference and counter electrode) electrochemical cell. Measuring the AC current response of the system, the impedance is calculated at different frequencies. The impedance spectra profile provides information on the corrosion and other electroactive processes taking place on a metal surface. EIS can be used to quantify the effectiveness of a conservation treatment in terms of corrosion resistance gain and repetitive measurements over time allow monitoring the decrease in protection ability of these treatments, detecting failure before it is too late. Unfortunately, application of this and other electrochemical techniques in the field of cultural heritage is not always easy, especially for in-situ measurements as they usually imply the use of a liquid electrolyte in contact with the surface under study –which is not easy to handle-. On the other hand, the interpretation of results is usually hard work, as the irregularity and complexity of the surfaces and interferences from the environment do not always allow obtaining good quality spectra.

Since the mid 90´s conservation scientists have started to use this technique in the evaluation of protective coatings for metallic cultural heritage [7-11], and in the last three decades several researchers have been working in the development of specific methodologies and portable devices to its application in the in-situ evaluation of patina and coatings on outdoor sculpture and monuments [12-18]. Concurrently with the restoration process of the sphinxes and within the framework of CREMEL project (Conservation-REstoration of Metal cultural heritage with ELectrochemical techniques) authors have been working in an agar gel-polymer electrolyte (G-PE) cell specifically designed for in-situ measurements on cultural heritage overcoming some of the limitations of previous designs [19, 20]. This cell had already been successfully tested in the evaluation of protective coatings on bronze coupons [21], but it has not yet been applied in a systematic way on a real conservation problem. Now it was a good opportunity both to test the performance of the cell on a real situation and to evaluate the effectiveness of the applied treatments on the sphinxes. The complete treatment has been published in the museum´s technical bulletin [1]: The internal structure has been reinforced, and after a cleaning process, 2% benzotriazole in a water-alcohol mixture was applied, followed by three layers of Incralac. In the first layer the product was used in a 15% solution in xylene, in the second layer concentration was increased to 20% in same solvent. Then, a third layer of 30% Incralac in acetone was applied followed by 10% microcrystalline wax (Cosmolloid 80 H) in white spirit.

Electrochemical measurements were performed using the G-PE cell on the left sphinx before, during and after the restauration process. Figure 1 shows the left sphinx during measurements before and after restoration. Measurements before restauration allowed evaluating the corrosion resistance of different areas of the sphinx. During the restoration process they gave information of the additional resistance provided by protective coatings and supported the decision on the number of layers to apply. Finally, after the restoration, periodical measurements are being done to follow the evolution of coatings over time. The objective is to detect the coating failure, i.e. the drop of resistance to initial levels, before the sculpture can be affected.

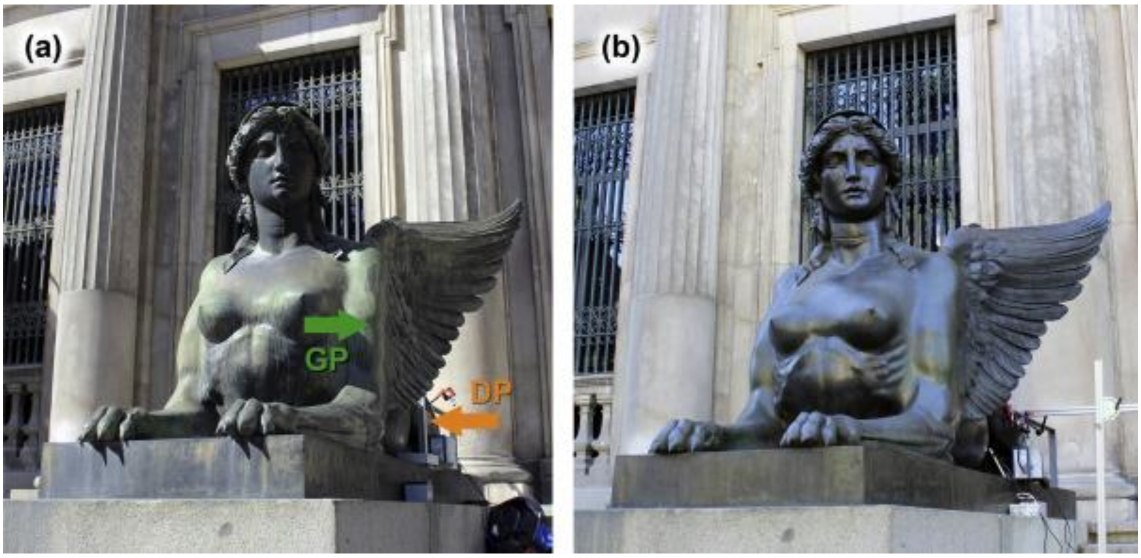

Fig. 1. Left sphinx during measurements before restoration (a) and after restoration (b). Arrows indicate the green patina (GP) and dark patina (DP) test areas.

2. Materials and methods

Several electrochemical impedance spectroscopy (EIS) and polarization resistance (Rp) measurements were carried out on two different areas of the southern sphinx: a greenish patina (GP) on the left arm of the sphinx and a dark patina (DP) on the left thigh of the sphinx (fig. 1). These areas have been selected as representatives of two extreme conditions of the surface: GP is a thick, matt patina formed in areas exposed to atmospheric corrosion; and DP is a thin, semi-transparent patina remaining from the original artificial patination treatment.

Measurements have been performed with the gel polymer electrolyte (G-PE) cell previously developed by the authors [19, 20]. It consists of a plastic mold in which the counter electrode (CE) and a pseudo-reference electrode (RE) are attached. The CE is made with a stainless steel mesh to maximize its surface, and the RE is a 99,9% silver wire electrochemically coated with AgCl [22]. The mold is then filled with a traditional aqueous electrolyte that has been gelled by addition of 4% w/v of agar powder.

The liquid electrolyte in which agar is dissolved to obtain the gel electrolyte is synthetic rain adapted from Bernardi [23]. It contains 14.43 mg/L $CaSO_4 \cdot 2H_2O$, 15.04 mg/L $(NH_4)2SO_4$, 19.15 mg/L $(NH_4)Cl$, 15.13 $NaNO_3$ and 3.19mg/L CH_3COONa, prepared in distilled water. Synthetic rain has been chosen to mimic the corrosive environment which the sculptures are exposed to, so the interaction of the electrolyte with the metal, patina and coating is similar to actual degradation process, and the object is not exposed to other ions [24]. This solution has been used 10x concentrated with a final pH adjusted to 6.5 with HNO_3, to provide a mild electrolyte which prevents any damage to the patina, but with enough conductivity to measure. The agar powder has been dispersed in the electrolyte and heated until dissolution. After a few minutes, the liquid has been poured into the mold and left to cool until solidification. The cell is then mounted on a support with an articulated arm which allows positioning on the surface to be measured; the measurement area 5.72cm^2. A more detailed description of the cell has been provided in references [19, 20]. Figure 2 illustrates the realization of measurements on the sculptures. A closer view of the cell placed on the surface of the sculpture during measurements can be seen in figure 2 (a), while figure 2 (b) shows the RE and CE inside the cell, and the imprint of the surface texture on the gel. Measured areas were photographed in detail to ensure that no marks were left on the surface and that subsequent measurements were done on the same point (fig. 3).

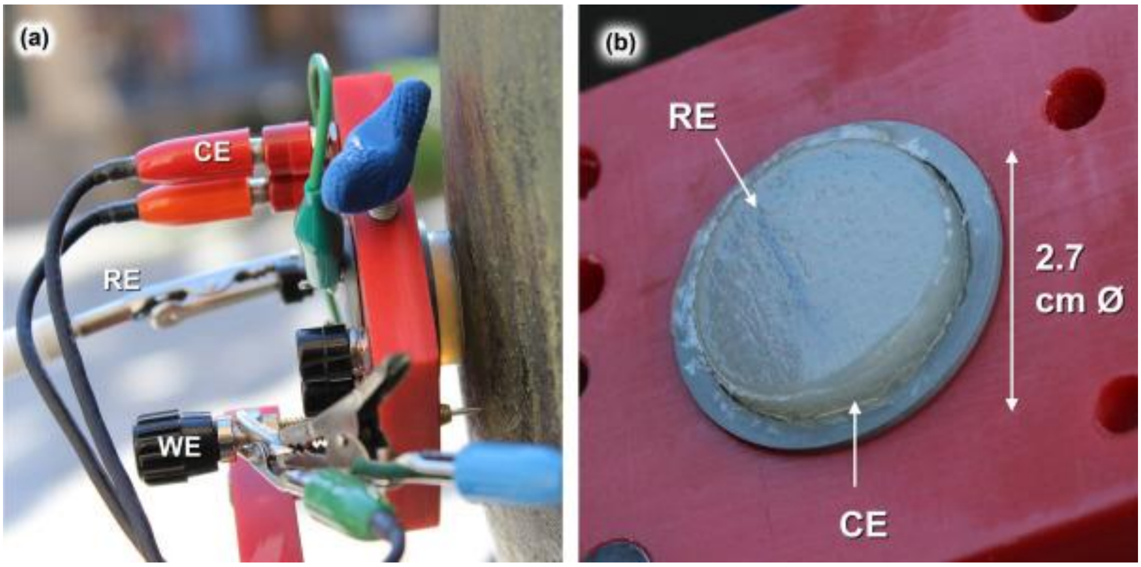

Fig. 2. Detail of the cell during measurements. It can be seen how the gel adapts to the surface of the sculpture (left) and the deformation of the cell surface after measurement (right).

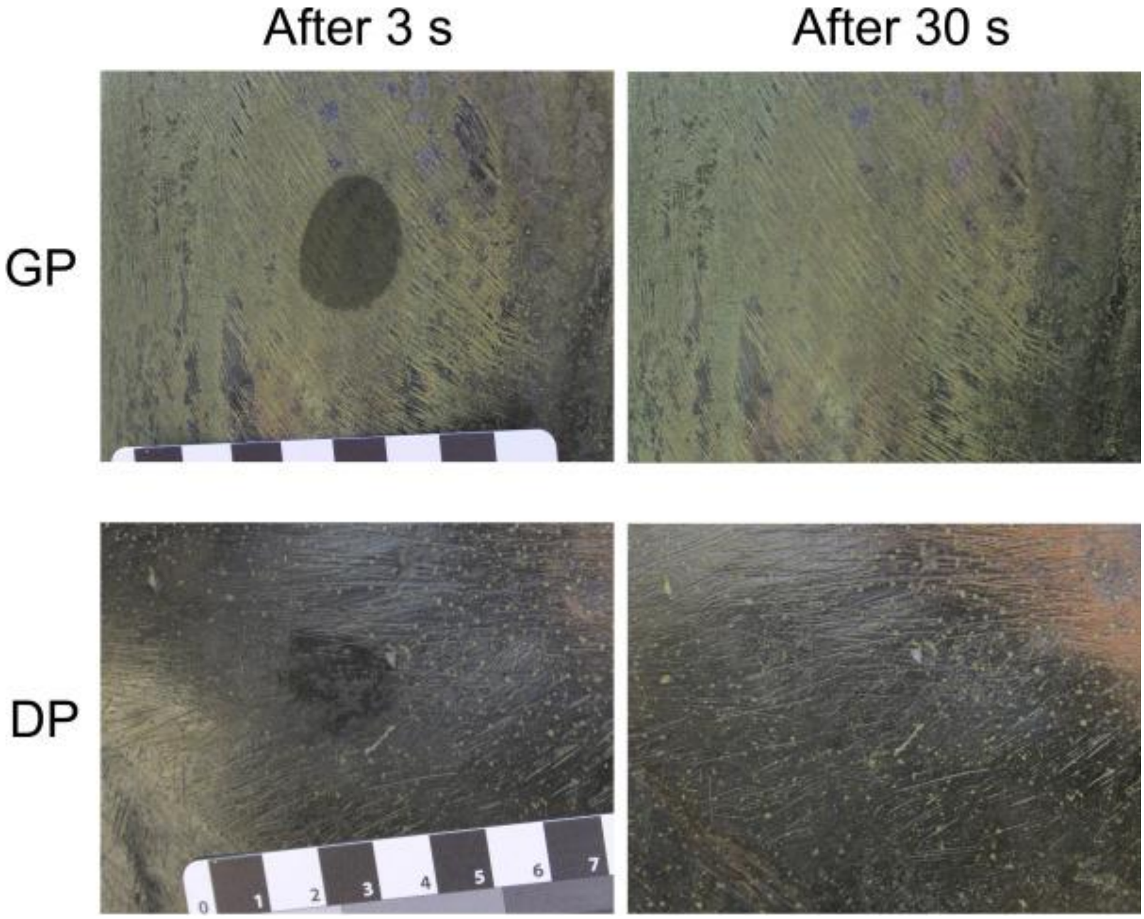

Fig. 3. Detail of the surface after measurement showing that no marks are left after it (before conservation treatment).

First data were taken in March 2014, before restoration; a second set of measurements was done in July during restoration treatment (after cleaning and first coating layer), then after restoration, in early January, May and November 2015 and in June 2016 (approximately 5, 10, 16 and 23 months later). EIS and Rp measurements were performed consecutively each patina. EIS spectra have been acquired with a Gamry 600 Potentiostat, using a frequency swept from 100 kHz to 10 mHz, 10 mV RMS amplitude and 10 points/decade. Polarization resistance (Rp) has been measured using the same setup, performing a 0.16 mV/s swept from -10 to +10 mV vs. open circuit potential. All results have been normalized to the measurement area. Due to the limited access to the sphinxes, single measurements were made at each time. However, the reproducibility and repeatability of measurements using this system has been validated in a previous work by the authors [20].

3. Results and discussion

G-PE cell has shown to fulfil the requirements for in situ measurements, on rough, leaning and slightly curved surfaces. In figure 2, the flexibility and adaptability of the cell to the surface under study, following the roughness of the patina, can be appreciated. The non-destructive character of the measurements has also been verified in the worst case scenario, i.e., before protection treatment. Figure 3 shows the visual appearance of the patinas just after removal of the gel-cell (left) and a few seconds later (right). It can be observed how the wetted area dries out immediately leaving no traces on the surface proving the non-destructive character of the technique [25]. On the long term, no visible effects have been observed after the series of measurements.

The evolution of the impedance's modulus for DP and GP is presented in figure 4. EIS spectra are rather noisy at the high frequency region. As the museum is located in the city center, surrounded by traffic, subway and train tunnels, the quality of EIS spectra may be affected by environmental interferences. Similar noisy spectra at high frequencies has also been observed by other authors in on-site EIS measurements in sculptures [17]. This effect is more important after the restoration process, as the application of a thick layer of Incralac highly reduces the intensity of the electric signal decreasing the signal to noise ratio. The noise of the EIS data does not allow an in-depth analysis of the corrosion and protection mechanisms from the electrochemical results. Despite this, the results clearly show some general features and trends that allow comparing the result in different areas and study the evolution of impedance over time.

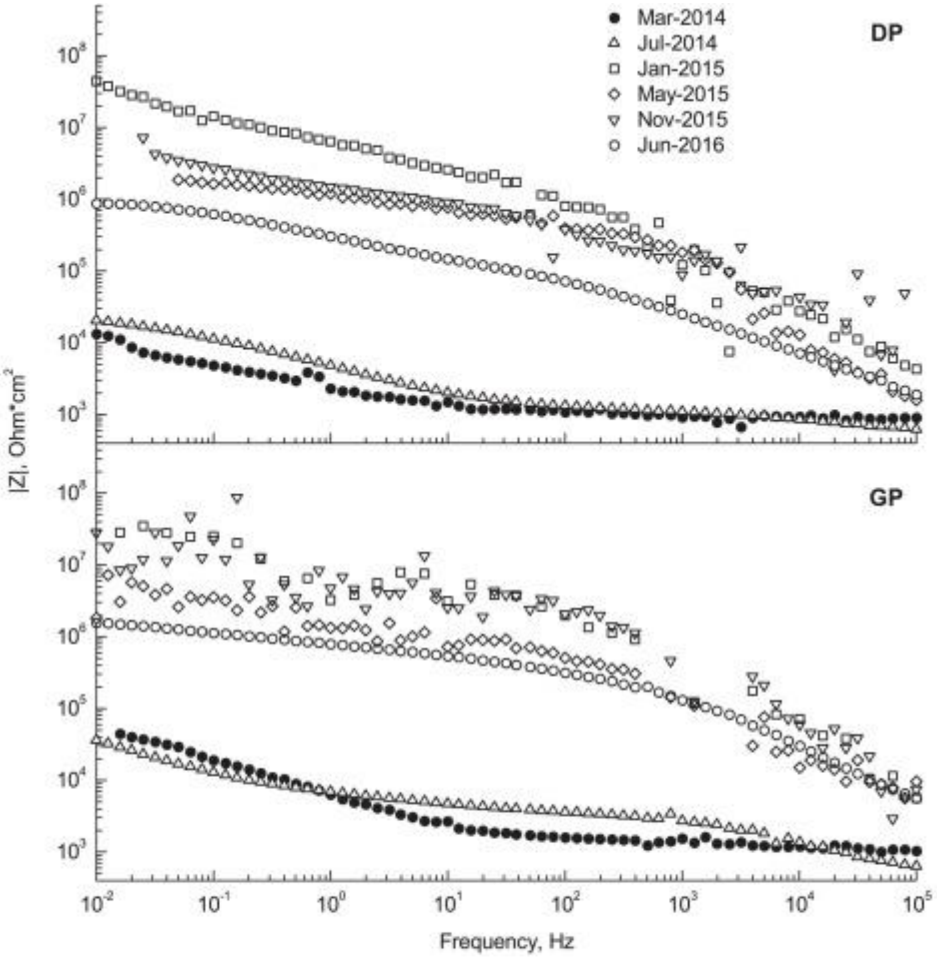

Fig. 4. Evolution of impedance modulus with time for dark patina (DP) and green patina (GP).

Impedance data are generally analyzed using equivalent circuits, in which passive electric elements such as resistors, capacitors, etc. are used to reproduce the electric characteristics of the system [3, 24]. Thus, to interpret the results we need to consider the nature of our system, a bronze sculpture covered with a patina, to which an organic coating has been applied. The corrosion of the sculpture takes place when the rain (electrolyte), containing dissolved oxygen and atmospheric pollutants, reaches the base metal and the corrosion reactions take place. The anodic process involves the dissolution of the metal (copper and alloying elements) while the cathodic reaction is the reduction of dissolved oxygen. For the corrosion reaction to take place several *resistances* (or impedances) have to be overcome. The charged species have to travel across the electrolyte, against the electrolyte resistance, and reach the coating. Conductivity through the coating has two contributions, the charge of the capacitor at both sides of the coating and the resistance through its pores, thus the impedance of a coating is usually represented by a capacitor and a resistance in parallel. The same behavior is to be expected for the patina. Finally, when the electrolyte reaches the metal surface, the corrosion process can be assimilated to another pair capacitor-resistance in parallel, representing the capacity of the electrochemical double layer and the charge transfer resistance. This is probably the simplest approach, in which the equivalent circuit could be represented by one resistance in series with two or three nested capacitor-resistance pairs [2, 11, 26, 27]. In practice, circuits can get much more complicated when other physicochemical phenomena get involved and several processes overlap [28]. In the first place, these systems do not follow the ideal capacitive behavior, and constant phase elements (CPE) have to be used instead of capacitors [3] adding new calculations to obtain capacity values from CPE parameters [29]. Also, diffusion effects may appear, requiring the introduction of other elements such as Warburg impedance and in some cases, reactivity of the patina itself require the employment of transmission lines [20, 30, 31]. There are several good reviews about EIS of coated metals which can be consulted for further information. [4, 32-34]

Difficulties in the interpretation of EIS spectra from cultural heritage objects are not an unknown fact. Surface inhomogeneities together with environmental interferences in field measurements lead frequently to evaluate EIS data in terms of simplified approaches [3]. Thus the value of |Z| at the low frequency limit has been used as a measure of the protective effectiveness of the surface layers or the corrosion resistance and applied to comparative studies [5, 8, 10, 13, 35-37]. This value is the sum of the impedance of the coating plus all the other aforementioned elements (electrolyte resistance, charge transfer resistance, diffusion impedances, etc.). In the case of organic coatings, the contribution of these other elements is usually much smaller than the coating impedance, so the film resistance dominates the spectra at low frequencies. Although a deeper interpretation would be desirable, information given by this simplified approach has proven to be effective to assess the protective properties of coating systems for outdoor bronze monuments and its evolution over time [5, 37].

The variation of the impedance module, $|Z|$, at the lower frequencies for DP and GP on successive measurements, together with the Rp values are represented in figure 5. Although the EIS spectra were acquired from 100 kHz to 10 mHz, 15.8 mHz has been used as lowest frequency limit as some points are missing at the lowest frequency value. From this figure, several facts can be pointed out, supported both by $|Z|_{15.8mHz}$ and Rp results. Before restoration (March 2014) GP was about 5 times more protective than DP, while after treatments, both areas showed similar behavior. From data of July 2014 it is clearly appreciated that the first protective coating with 2% benzotriazole and 15% Incralac does not give an appreciable protection, as $|Z|$ has barely increased from its initial value, thus justifying the need of additional varnish layers. After the whole protection treatment has been applied, $|Z|$ has increased three orders of magnitude as can be observed in the measurement done in January 2016. Differences between DP and GP are now insignificant, indicating that the coating is the main responsible for protective properties of the system, thus being the patina contribution negligible. From this moment, the resistance of the coating begins a slow decay, although two years after application it is still offering a good protection when compared with the initial results before restoration. It also appears to be a seasonal effect that may increase resistance values in cooler months (comparing Jan. and Nov. 2015 vs. May 2015 and Jun. 2016); higher temperatures may induce higher conductivity of the aqueous solutions that penetrate into the coating and cause a progressive reduction of the impedance, as well as increase the anodic and/or cathodic corrosion reaction rates. This effect of temperature on measurements is currently under study.

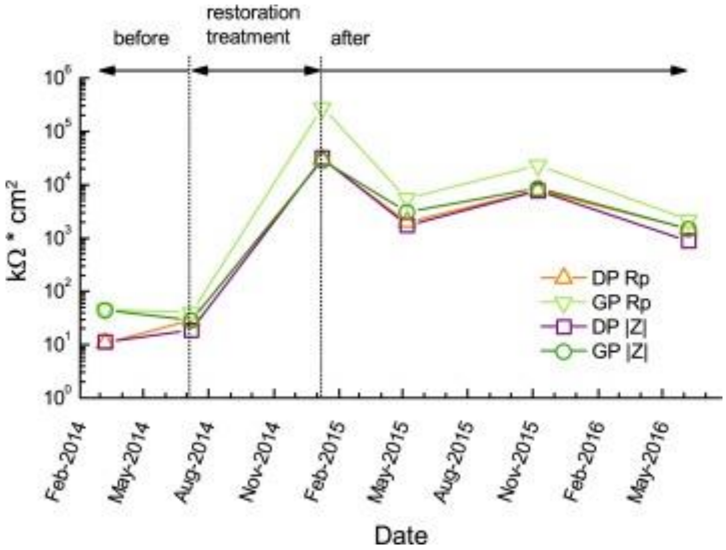

Fig. 5. |Z| limit and Rp before and after restoration treatments for dark patina (DP) and green patina (GP).

Overall, there is a good agreement between Rp and |Z| values, showing similar results and the same evolution with time, validating the approach of using |Z| at low frequencies as measure of the corrosion resistance of the system. In the case of GP after the whole protection treatment, some discrepancy between these parameters seems to appear. This might be related with diffusion or other phenomena that are disregarded by the simplification of taking the values of |Z| at low frequencies, or with inaccuracy of the estimation of this value in the noisy spectra. In any case, the evolution of both parameters shows the same pattern, leading to the same conclusions.

Although we have not enough experimental data for inferring a kinetic model for coating´s resistance decay, we can try to obtain a rough estimate on the duration of our coating. Some attempts have been done to develop models or equations to predict service life for industrial coatings. Studies from Bierwagen et al. have found that the evolution of |Z|values in the low frequency portion of the spectrum that can be fit by a simple exponential decay function in time [38, 39]. Fitting the values of |Z| to a simple first order equation: $\text{Ln}|Z|=\text{Ln}|Z|_o-kt$ (where

|Z| is the variation of $|Z|_{15.8mHz}$, $|Z|_{0}$ the value before treatment in kOhm, k is the rate constant and t the time in months) and calculating the time for |Z| decay to its initial value, i.e. before restoration, the sphinx´s coating will fail in about 4 years (figure 6).

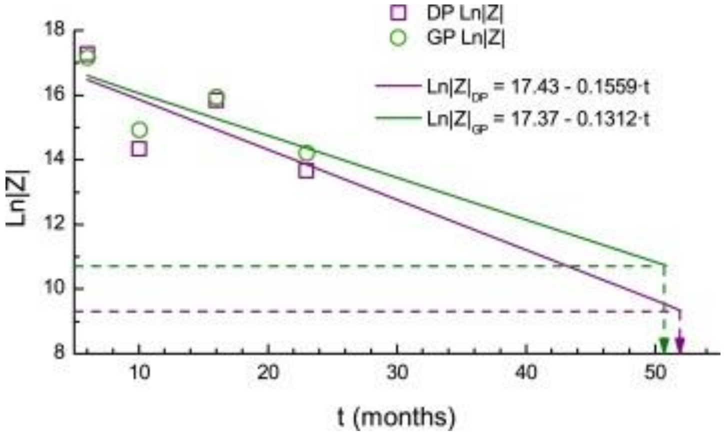

Fig. 6. Lifetime prediction of coatings from EIS data, based on a first order kinetic approach.

This result is in agreement with previously reported duration of this kind of coatings, as long-term protection coatings for cultural heritage are estimated for 5-10 year service [40]. According to Brostoff, Incralac coatings are expected to last 3-5 years in outdoor environments [41] while some authors report up to 9 years with topcoats of wax and regular maintenance [42]. It is clear that the duration of the coating depends on too many factors such as substrate characteristics, thickness, regularity, defects and environment, so a regular monitoring of the performance of the coating would be necessary for each individual artifact.

4. Conclusions

This study has validated the utility and applicability of the agar gel polymer electrolyte (G-PE) cell for protective treatments evaluation on outdoor bronze sculpture. It has proven to be convenient for field measurements and has allowed carrying out electrochemical measurements on different positions and orientations of the surface of the monument.

On-site EIS and Rp results obtained using the G-PE cell have demonstrated to be a useful tool for conservation treatments assessment. Experimental data have shown the effectiveness of the protection layers and allowed to follow its evolution. Assuming an exponential decay of coating resistance, a rough estimation of the coating´s duration can be extrapolated to about 4 years.

The systematic application of the G-PE cell in future work to a wider collection of outdoor sculpture will allow refining the model and obtaining more accurate predictions. This will help to stablish a calendar for periodic inspections and design an efficient maintenance plan for these collections.

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