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B. Ramírez Barat, E. Cano, "In Situ Electrochemical impedance Spectroscopy Measurements and their Interpretation for the Diagnostic of Metallic Cultural Heritage: A Review" *ChemElectroChem* **2018**, 5, 2698

<https://doi.org/10.1002/celec.201800844>

Advances for in-situ EIS measurements and their interpretation for the diagnostic of metallic cultural heritage: a review

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Abstract: Protecting metallic cultural heritage from corrosion is a major challenge for metal conservators. Electrochemical techniques offer a great potential for monitoring the conservation condition of this type of heritage, providing a powerful tool for designing conservation strategies. For this reason, the application of techniques such as electrochemical impedance spectroscopy (EIS) has aroused an increasing interest in the last years, although some difficulties in application and interpretation of results still keep it from being a routine practice. This review aims to picture a state-of-art on the use of EIS for in situ monitoring of metallic cultural heritage, focusing on spectra interpretation and different approaches proposed to perform field measurements since the 90's. In the first part, different cell designs based in the use of liquid or solid electrolytes for in situ measurements are reviewed. In the second part, a few general equivalent circuits are proposed as a basis for interpreting results on different metal surfaces after discussing different models proposed in literature. This overview intends to summarize and clarify the key points in the use of EIS, and encourage the use of this and other electrochemical techniques in the field of conservation science, for a better preservation of our cultural heritage.

1. Introduction

Scientific analytical methods have become an essential tool in the study and conservation of cultural heritage^[1]. Most conservation interventions are based in a previous scientific examination of the object to gather information on its composition and structure, aimed at a better understanding of its conservation problems and helping to plan out conservation treatments and strategies.

In the field of metal conservation, techniques such as x-ray fluorescence and metallography are used to characterize the metal alloy composition and microstructure respectively, while patinas and corrosion products are generally studied by x-ray diffraction or spectroscopic techniques such as FTIR or Raman. Additionally, microscopy techniques allow studying the morphology and structure of corrosion layers, either in surface or in cross-section, being scanning electron microscopy the most used. Other techniques such as radiography and tomography are very valuable tools to determine their internal structure and conservation, being almost indispensable in the case of archaeological metals^[2].

The study of corrosion products helps to understand corrosion mechanisms; their composition, structure (cohesion) and proportion is related to corrosion behavior. For instance, the presence of chlorides in corrosion layers always suggests active corrosion processes in iron and bronze, and for weathering

correlated to the corrosion rate through the Protective Ability Ratio, calculated as the relationship between the mass fraction of goethite and lepidocrocite^[3]. Nevertheless, the study of corrosion products has some limitations for conservation purposes, as they are the result of past events or past situations, and although they give a clue on the stability of the object, they cannot provide an unequivocal diagnostic of the present situation. Also they require the analysis of a representative number of samples, from the surface to the metal core. On the other hand, analytical techniques give little information on the effectiveness and duration of treatments. Of course, spectroscopy can tell if an organic coating has experimented chemical changes, but not how these changes have affected the corrosion protection properties of the coating.

As an alternative or as a complement to those methods mainly based on compositional analyses, electrochemical methods such as electrochemical impedance spectroscopy (EIS) give information on corrosion behavior. Thus, these methods have largely been used in the study of corrosion mechanisms and in the evaluation of protective systems (coatings and inhibitors). In the field of cultural heritage they started to be applied as a diagnostic tool in the 90's^[4] and their interest has risen in the last decades. Other electrochemical techniques can be used for studying the corrosion behavior of metals. Polarization curves provide information on anodic and cathodic reactions and have been used to evaluate patinas stability on laboratory coupons^[5] but they cannot be directly applied on cultural heritage objects, as they are destructive techniques. Techniques such as polarization resistance (R_p) or corrosion potential monitoring have been also been applied to cultural heritage studies^[6]; these are nondestructive techniques, but the information provided is much limited. The application of EIS to the diagnostic of cultural heritage provides a very powerful technique that can help conservators to know which object requires an intervention, to evaluate the effect of a treatment^[7], to choose the most adequate coating^[4a, 8] or to know when a coating has to be renewed^[9], optimizing time, resources and results. Despite its potential utility, EIS is still far away from being standardly or routinely applied. Difficulties both in applying this technique on heritage objects –requiring in situ measurements– and in the interpretation of results are the main constraints.

Heritage assets are unique in nature, composition and history. While we can reproduce the composition of the ancient metals, the manufacturing processes and, above all, the changes in their surface resulting from centuries of exposure to very different conditions cannot be recreated. Different conservation treatments are nowadays applied onto these unique surfaces, such as cleaning, and protecting with different inhibitors (benzotriazole derivatives, carboxilates, etc.), waxes (microcrystalline or ethylene waxes) and/or organic coatings (acrylics, etc.). Thus, in most cases, different analyses need to be carried out in-situ on the real artifacts to select and evaluate the efficiency of the conservation treatments. Mounting an electrochemical cell on these rough, curved, irregular and non-horizontal surfaces is not a trivial task, being this one of the main reasons that have precluded the widespread adoption of electrochemical techniques for the study of cultural heritage.

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steels (WS), the composition of the rust layer has been

The second relevant limitation to the development of EIS as a routine procedure for metal cultural heritage assessment is related to difficulties in analyzing results, especially those obtained in field measurements on heritage objects. Although basics of EIS fundamentals are outlined in a few works^[10], a comprehensive discussion on different models for interpretation of results from metallic heritage objects has not been yet accomplished. This may help to clarify some issues and contribute to a better understanding of the application of EIS to metallic cultural heritage conservation.

Thus, the aim of this paper is to carry out a comprehensive and critical review the use of EIS as a diagnostic tool for cultural heritage, focusing on the different experimental approaches for in situ applications and on the understanding of the results from heritage metal objects, to bring this technique closer to metal conservators and conservation scientist. Fundamentals of the technique will not be discussed here, as they are described in several papers and reviews^[10a, 11], technical notes^[12], and advanced text books or dedicated monographies^[13].

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Although laboratory studies of artificial patina and coatings are of interest, the complex nature of real systems and the need of monitoring outdoor sculptures and monuments to assess their conservation condition make in situ measurements necessary. Though, since the introduction of EIS in the field of cultural heritage, researchers began to develop portable devices.

The complete setup for in situ electrochemical measurements comprises a potentiostat, an electrochemical cell and a support fix the cell on the object. Although some researchers have designed their own instrument, commercial portable potentiostats such as Gamry Reference 6000 or different Ivium technologies models, capable of measuring with floating ground, are of common use.

Experimental conditions are quite similar in most cases. Typically, a small potential signal is applied, between 5-10mV and up to 50mV or even higher for highly resistive coatings, and the spectra is registered between 100kHz and 10mHz, at 10 points per decade. EIS measurements are usually performed at open circuit potential (OCP) after a conditioning/stabilization time which variates from few minutes to one hour, to avoid any alteration of the system under study. Nonetheless, for the analysis of certain electrochemical processes, a bias potential can be applied^[7c].

So the main difficulty at this point is how to place a traditional cell with a liquid electrolyte in contact with the irregular, non-flat and lean surface of a sculpture. Two main approaches have been considered by researchers to overcome this challenge. On one side, different systems for holding the liquid electrolyte in contact with the sculpture's surface have been designed. The second approach is based on the use of solid electrodes.

Liquid electrolytes are supposed to reproduce the corroding conditions the analyzed object is exposed to, so their composition is normally close to rainwater with different pollutants. Different electrolytes have been used such as mineral water^[4c], artificial rainwater^[14], diluted Na_2SO_4 or $\text{Na}_2\text{SO}_4/\text{NaHCO}_3$ solutions^[15] dilute Harrison electrolyte^[11b, 16]. Other electrolytes such as neutral or acidic NaCl solutions are used to evaluate more aggressive conditions on laboratory coupons, but these should not be used on real objects. Solid electrolytes may have a composition related to the environment as it is the case of agar gelled electrolytes^[14b, 17] or a complete different one^[18].

2.1. Portable devices with liquid electrolytes

The contact probe

The first innovative solution was devised by Paola Letardi, who developed a "contact probe" in which liquid electrolyte is supported by a cloth. The idea is to place a thin layer of electrolyte between the working electrode and counter electrode, that allows the electrochemical measurement while emulating the liquid layer in natural outdoor wetting conditions. This is not only a solution for of holding the electrolyte, but also this configuration is closer to the real situation and reduces the ohmic drop due to the electrolyte's low conductivity^[4c].

2. Instrumentation developments for in-situ EIS measurement in cultural heritage

Figure 1. Contact probe designed by Paola Letardi. Cell construction (left), and complete measurement setup (right).

Different cells differing in size, construction materials and assemblage were assayed resulting in a final design as the one shown in figure 1 [10a, 19]. A pseudo-reference electrode (RE) and a counter electrode (CE) formed by two cylinders of AISI 316 stainless steel are embedded in a plastic cylinder (PTFE) in a compact design, with a measuring surface area of 1.77 cm². A soft cloth soaked with the electrolyte (mineral water) is placed between the working electrode and the cylinder, keeping a cloth tail immersed in a small water reservoir, to avoid drying out during measurement. Stainless steel was chosen as electrode material as it is an inexpensive material with good conductivity, stability and corrosion resistance, with comparable performance to other electrode materials. EIS spectra registered with this contact-probe show the same overall shape as those acquired with a standard cell [4c].

This cell has been successfully used in the evaluation of different coatings and treatments on bronze coupons [4c, 10a, 19–20] as well as on outdoor sculpture [20b, 20c] through comparison of the impedance modulus ($|Z|$) at the minimum frequency (10mHz). Measurements in naturally exposed coupons and outdoor monuments have shown some limitations, certain scattering of data or some noise in the spectra, since many factors –difficult to control in field conditions– may influence data [21].

Although coating's evaluation is the most common application, this cell has also proved its utility for assessing conservation treatments such as the effect of laser cleaning [7a, 7b]. Figure 2 illustrates an example of this EIS study on the effects laser cleaning with different conditions (a, b, c), on three types of surfaces (A, B, C) from a nineteenth century outdoor bronze statue of Napoleon located in Milan, Italy. The values of $|Z|_{10\text{mHz}}$ show the differences in the corrosion susceptibility of the different areas, and how treatment c) leads to a lower impedance value, even lower than the initial situation for areas A and B. This is an interesting example of how EIS can help to choose the most appropriate cleaning method, beyond the visual appearance.

Figure 2. Low frequency impedance modulus as a function of laser cleaning conditions on three tested areas of an outdoor bronze statue measured with the contact probe designed by Paola Letardi. Reproduced from [7a] with a Creative Commons Attribution License 3.0, using the original data provided by the author.

Traditional cell designs

In parallel to different innovative solutions, researchers keep working in the adaptation of the traditional liquid cell to the monument surface, and different traditional-like cells have been used for in situ electrochemical measures.

Researchers from the Politecnico di Torino have designed several liquid cells together with a low-cost EIS system for in situ measurements, always using mineral water as electrolyte, as proposed by Letardi [4c]. The first cell consisted of a plastic vessel containing the electrolyte and electrodes, closed by a piston at the top and with a porous membrane at the bottom. The contact of the cell with the metal surface is sealed by a rubber ring [22]. Further development of the first prototype incorporated the cell to a compact hand-held measuring device [23]. It consisted of gun-shaped potentiostat including the electrochemical cell assembled to its body. Nevertheless, the focus of this work has been in the design of a low-cost portable instrument rather than in a cell design for in-situ measurements, and only a couple of laboratory examples have been shown which do not allow evaluating the applicability of the system for in-situ measurements. In any case, a rigid flat cell is not the most appropriate design for monument surfaces.

To overcome the limitation of this system for measuring in flat surfaces these authors have also worked on solid electrodes –which will be described in next section– and flexible cells. Thus, the second cell design for liquid electrolytes comprises a nylon cylinder with a central hole and a soft foam disk on the bottom, which adapts to the surface being measured. The cell is held onto the surface through a double-side adhesive tape. A Pt wire acts as counter electrode and no separate reference electrode is used, measuring in a two-electrode configuration. This configuration has been used to study corrosion of medieval wrought iron bar chains in the Amiens Cathedral [24]. Nevertheless this system does not solve the main limitations of handling a liquid electrolyte, not being appropriate for vertical or curved surfaces. This has led to the latest design, a rigid plastic cell, made of ABS, with a polyurethane disk in the contact side

to provide adaptability to “non-perfectly flat and/or rough surfaces” (figure 3). The cell has an inner chamber with a platinum CE, and is filled with the electrolyte through an inlet tube [15c].

Figure 3. Scheme of the ABS plastic cell designed by Grassini et al., illustration adapted from [15c].

As in the previous design, the cell is fixed to the monument surface by a double-side adhesive disk. The use of an adhesive to fix the cell to the surface is an important issue, as it has to be strong enough to avoid the leaking of the electrolyte but not too strong to avoid leaving residues or damaging the surface when removed. Thus, this method may not be appropriate for delicate or loose surfaces.

Figure 4. EIS results from a weathering steel sculpture obtained with ECG electrodes (symbols) and the ABS plastic cell (lines) in different areas. NE and SWE stand for North-East and SouthWest, red-orange (1) and red-brown areas; TL refers to a thin oxide layer while RL is a rough oxide layer (measures 1 and 2).

This system has been tested in the weathering steel monument “Reditus ad origines” in Ferrara, that has also been measured with ECG electrodes (see next section). Results

obtained with the different setups show notable dissimilarities in the spectra profile. This can be appreciated in figure 4, where data from EIS spectra recorded with both setups have been extracted from figures and plotted together for comparison using WebPlotDigitizer[25].

Other cell designs

With a similar idea to Letardi’s contact probe, Elsener and col. have recently proposed a sensor to monitor corrosion in the inside of historical brass instruments [6e, 6f]. This sensor uses an Ag/AgCl solid-state reference electrode and a platinum grid counter electrode embedded in a thin sponge. The sensor can be built in different shapes, as a flat electrode for flat surfaces as was done in the first prototype, or in a cylindrical shape to fit the inside of brass instrument; in this case, a balloon is used to press the sponge to the metal surface (figure 5). This sensor has only been used for Rp studies, so its performance for EIS cannot be compared with other cells. Nevertheless, it is a very interesting design, which has proven to give good results, compared to a traditional setup.

Figure 5. Scheme of the cell design showing reference electrode (RE) and counter electrode (CE) embedded in a thin sponge pressed with a small balloon against the inside of the tuning slide (a) and photograph of the complete measuring system (a) by Elsener et al. [6e] reprinted with permission from Elsevier.

A contemporary study by Jamali et al. has proposed the use of a cell setup in which the electrolyte is absorbed in a piece of filter paper. In this design, electrodes are made by a piece of copper sheet coated with platinum and the set is fixed to the surface by an adhesive tape (figure 6) [26]. The main difference is in the cell configuration, placing two parallel electrodes on the surface of the object without direct electrical contact with the

metal, as proposed by Mills to evaluate industrial coatings by electrochemical noise technique [27].

Figure 6. Scheme of the cell configuration proposed by Jamali et al. [26].

This setup has been tested in a painted steel sculpture, but only the impedance modulus of the measures is presented, making difficult to evaluate the quality of results. On the other side, this system suffers from several of the drawbacks already discussed for other systems: it is only suitable for flat surfaces and uses an adhesive tape. This cell layout was firstly applied to cultural heritage by Clare and coworkers [18] and will be further discussed on section 2.2.1.

2.2. Portable devices with solid electrolytes

The most obvious way to avoid the inconveniences of a liquid electrolyte is not using a liquid electrolyte. For this reason the use of solid electrolytes for in-situ electrochemical studies on metallic heritage has been explored by several groups.

2.2.1. Gel electrodes

ECG gel electrodes

The first attempt to find an alternative solution to liquid electrolytes was the use of commercial electrodes such as those employed in medicine for electrocardiograms, explored by Angelini and col. [28]. These electrodes are made of an Ag/AgCl RE, a conductive gel and an adhesive. This solution avoids the difficulties in handling a liquid electrolyte, and the flexibility of the electrodes favors the adaptability to the surface.

From aforementioned studies, ECG electrodes apparently adapt well to flat surfaces, including weathering steel, but they did not gave good results on thick corrosion layers found on materials such as heavily corroded wrought iron. ECG electrodes have shown a series of limitations, both from the practical application and from the electrochemical results. Despite the flexibility of the gel, it cannot penetrate the pores of the corrosion layer, thus it gives much higher impedance than a traditional cell. To overcome this problem, it is necessary a pre-conditioning of the surface by wetting the corrosion layer about one hour prior to the measurement [28b]. This also reduces the adhesiveness of the electrode preventing the detachment of corrosion products when removing the electrode, which is other of the drawbacks of the EGC electrodes, but enlarges the time needed for field measurements. On the other hand, the thickness of the gel is not homogenous as the RE occupies part

of the thickness in the central area. This introduces distortions in the measurement because of inhomogeneous distribution of current as a function of the coating resistivity [28b, 28c]. The fact is that, as can be seen in figure 10 of reference [28c], results from ECG and dry electrodes (see section 2.2.2) are quite different from traditional cells, and the use of these electrodes has been discarded in subsequent studies by the same authors.

Hydrogel cells

To overcome some of the limitations of commercial ECG, Clare and col. have worked on the design of hydrogels based on formulations found in gel electrodes for medical applications, to optimize their use in cultural heritage. These are anionic gels are made of poly(acrylic acid-co-2-acrylamido-2-methyl-1-propane sulphonic acid), poly(AA-AMPS), and equilibrated with different aqueous solutions to a better control of the properties [18, 29]. The gels are cut into 1cm² squares and a piece of silver foil is placed on the top of the gel to provide electric contact to the potentiostat.

Two key points are considered in this approach. First, the gel properties for being used as an electrolyte in corrosion measurements; and secondly, the cell setup. For a certain hydrogel, equilibrating solution is responsible for the degree of swelling –which is also related to the gel strength- and the conductivity. The better compromise between conductivity and swelling without involving aggressive ions (such as chlorides) was found for dipotassium 1,4-piperazinediethanesulfonic acid (K₂PIPES). This is the first limitation of this system, as the selection of the electrolytes is constrained by the equilibrium of the gel, so its use for the evaluation of a coating in an *environment-like* electrolyte is limited, and cannot be selected by its convenience for the corrosion study.

In combination with the use of hydrogels, Clare et al. have proposed the use of a two-cell EIS (TCEIS) configuration (figure 7), based on the design suggested by Qi and col. [30]. As it has already been presented, this layout was later used by Jamali et al. [27]. This is indeed a very interesting methodological approach for non-invasive measurements in cultural heritage, in which the use of two gel electrodes as CE and WE circumvents the need to make direct electrical contact with the metal substrate.

In order to measure the whole coating/metal system, the current is supposed to flow though the black path depicted in figure 7, which equals two parallel cells. Thus, an area normalization factor is used to obtain the impedance, $K_{cell,area} = 1/A_1 + 1/A_2$. Nevertheless, there is more than one possible path for the current flow, depending on the properties of the coating, thus there is a degree of uncertainty of what is really being measured in the system, which explains the differences when compared to a traditional setup.

Figure 7. Scheme of the hydrogel two-cell EIS design, showing the theoretical current path proposed by authors in [18, 29b] (black discontinuous arrow) and the other possible current paths (red discontinuous arrows).

The comparison between the hydrogel and a traditional liquid cell was done by measuring EIS spectra on a brass coupon coated with Paraloid B44. Although the $|Z|$ is quite similar in both spectra, differences appear in the phase angle, and also different EC were required to fit the experimental results. While the spectrum from the liquid cell shows the electrolyte resistance in series to the coating capacitance, the spectra from the hydrogel cell is represented by the coating capacitance in parallel with the pore resistance. This indicates that different processes or effects are measured with each cell (figure 8).

Figure 8 Differences in the EC proposed for measurements with the hydrogel cell and a traditional setup. Bode ($|Z|$ and phase angle) and Nyquist plots for the liquid cell (gray/empty) and from hydrogel electrodes (gray/ filled). Reprinted from [29b] with permission from John Wiley and Sons.

This setup was tested in-situ on coated bronze sculptures [31] but results exhibited a significant amount of noise below 10 kHz. As signals derived from coatings response and faradaic processes usually appear at lower frequencies, the applicability of this configuration for in-situ measurements seems quite limited.

The fact that different processes are being measured with the traditional and TCEIS setups is considered in a more recent work [32], in which authors compare the traditional cell and the TCEIS (figure 9) on painted coupons and in situ on a painted

steel sculpture. In this work, the changes in EIS spectra over time are attributed to the changes in the “sheet resistance”, i.e., changes in the impedance of the current paths through the coating (red lines in figure 7). While this might be useful for assessing the superficial degradation of the coating, it disregards, the metal/coating interface, including faradaic process. This implies that the actual protective properties of the coating cannot be directly measured using this setup.

Figure 9. Bode plot for a primer (upper graphs) and a primer and coating system (lower graphs) with the TCEIS hydrogel cell (red and green traces) and a traditional setup (black and grey traces). As coating ages, EIS spectra from the TCEIS setup show differences with the traditional setup due different paths followed by current in the system. Reprinted from [32] with permission from Wiley and Sons.

Agar G-PE cell

As an alternative to these previous systems, Cano and col. have proposed a cell based on a liquid electrolyte gelled with agar [33]. This cell follows the general design of a typical flat cell, but with a flexible solid electrolyte, that adapts to surface roughness. Different electrolytes can be chosen to fit the specific requirements of each research. A detailed study of the effect of the agar addition has shown that using a low concentration, results are similar to a traditional liquid electrolyte [14b], showing only a slight enhancing effect of the corrosion process, which is not a relevant issue for comparison studies, i.e., between different coatings or different exposure times.

Figure 10 shows the construction of the cell, in which a counter electrode and a (pseudo)reference electrode (made of AgCl coated Ag or AISI 316 stainless steel) are placed in a plastic container. The aqueous electrolyte (artificial rain) is jellified by addition of 3% agar, poured in the container and allowed to cool down. The cap of the container is then removed, exposing a protruding gel cylinder, which is placed on the surface of the object to be studied. A complete description of the system and different variants can be found in reference [34]. The main advantages of this design are the possibility of choosing the electrolyte, the ease of preparation –involving no chemical synthesis–, the low cost of materials, and the good contact with

the surface due to the combination of syneresis and flexibility of the gel.

Figure 10. G-PE cell design: exploded view (a) mounted cell (b) and support (c). The picture in the right (d) shows the complete measuring setup on the surface of an outdoor sculpture. Reprinted from reference^[34], with permission from Elsevier.

This design has been successfully applied in the evaluation of bronze and weathering steel, both in laboratory and field studies, allowing to carry out comparison of different coatings and patinas and their evolution over time^[9, 35] An example of results obtained with the G-PE cell on one of the bronze Sphinxes from the Museo Arqueológico Nacional (Madrid, Spain) and on a bronze coupon of similar composition, measured both with the G-PE cell and a traditional liquid cell are shown in figure 11.

Figure 11. Example of EIS spectra obtained with the G-PE cell for in situ measurements on a bronze Sphinx and laboratory measurements with the G-PE cell and a liquid electrolyte cell on a bronze coupon.

Other researchers have followed this work developing other applications of the agar G-PE cell. Di Turo and col.^[17] have recently applied a similar design, using an agar cell with screen printed electrodes, for the characterization of patinas in

archaeological bronzes. Also, Monrrabal and col.^[36] have further worked in this idea developing an agar-glycerol cell as an alternative to the saline aqueous solutions for evaluation of pitting corrosion behavior of metals. Although this research is focused in the inspection of irregular surfaces and hard-to-access areas of complex geometry, such as welded joints and angles, it is of potential interest in our field, and the addition of plasticizers to the G-PE has to be explored.

3. Understanding EIS in cultural heritage

Besides practical difficulties in measuring discussed in last section, specific challenges have to be faced in the interpretation of results when applying EIS to study historic metals. The frequently complex and irregular nature of the metal substrate, together with external interferences, and limitations in number and time of measurements, can turn data analysis and interpretation of results into a challenging task.

Different levels of information can be extracted from EIS data, according to the quality of data and aim of the measurements. The simplest analysis, commonly used in metallic heritage studies, is to take the value of $|Z|$ at the low frequency limit as a global measure of corrosion resistance. Many examples of the use of the $|Z|$ at the low frequency limit as comparative measure of corrosion can be found in the conservation science literature^[4b, 11b, 16, 20a, 20c, 21, 37]. This approach is substantiated in the fact that this value represents the contribution of all the impedances of the different processes occurring in the corrosion mechanism, thus, the larger the impedance value, the more hindered the corrosion is. This simplification is useful for comparative studies, when we only want to know whether a system is working better than another or how corrosion rate is evolving with time. It can also be an option when the spectra are too noisy or different phenomena overlap making quite difficult a reliable fitting. However, this approach does not fully exploit the potential of EIS to inform about different processes taking place in the surface, and is prone to misinterpretation of the data in complex scenarios.

In other cases, the interest is just focused on the protective properties of the patina or corrosion layer, which can be calculated from the diameter of the high/medium frequency semicircle in the Nyquist plot^[35c]. In the same way, charge transfer resistance (R_{ct}) can sometimes be obtained from the low frequency semicircle^[38]. The main drawback of this approach is that it is not always easy to give a precise definition of the semicircle, as semicircles obtained in these objects are usually quite flattened, and overlapped, which can lead to wrong estimations. Similarly, the slope of the $|Z|$ at mid frequencies (between 0.1 Hz and 1 MHz) has been proposed as a quick method to assess the quality of a coating, as defined by a pure capacitive behavior, thus showing a value closest to -1^[39].

More and better information on the system properties and corrosion mechanisms can be obtained from spectra analysis by equivalent circuits (EC), in which passive electric elements such as resistors (R), capacitors (C), etc. are used to reproduce the electric behavior of the system. Although each element or

combination of elements –in series or parallel– gives a characteristic response, the irregularity of cultural heritage surfaces deviates the experimental results from the ideal behavior, showing a dispersion of the time constants¹. This has been related to low conductivity electrolytes, such as rain water, and uneven and porous nature of patinas^[40]. However it has been demonstrated that it is related rather to the electrochemical/potential inhomogeneity than to the geometric irregularities of the patina surface^[41]. Fitting these results to an EC require the use of constant phase elements (CPE) instead of pure capacitors. While the impedance of a capacitor is $Z_C = 1/j\omega C$, the impedance of a CPE is given by $Z_{CPE} = 1/Y_0(j\omega)^\alpha$. When using CPE, it is important to notice that only when $\alpha = 1$, a CPE equals a capacitor and the value of Y_0 is equivalent to the capacitance. Nevertheless, is a common mistake to take Y_0 as an equivalent for the capacitance of the corroding system for $\alpha < 1$, and express Y_0 units as $F (s/\Omega)$. The correct Y_0 units are $S \cdot s^\alpha$ or $\cdot s^\alpha / \Omega$, thus Y_0 cannot be used as a direct equivalent to capacitance, especially to quantitatively determine other system parameters^[42]. Different mathematical formulas have been proposed to obtain capacitance value from Y_0 ^[42-43], which may be used for different time-constant distributions^[44]. EIS spectra of these non-ideal systems yield depressed semicircles in the Nyquist plot. Being this a relevant graphical feature, is it important to represent these plots using isometric axes, which is not always the case in the reviewed articles. Otherwise, the depression of the semicircles (and other features such as the angle of diffusion tails) will be distorted depending of the scale of the axes.

In addition to the complex response from the system, environmental interferences and measuring artifacts may appear when using a low conductivity electrolyte^[45]. As the use of a mild electrolyte is mandatory in order not to compromise the conservation of the measured surface, it is important to understand the behavior and limitations of measuring systems under this requirement^[34, 46]. Artifacts from the cell, cables or electronics of the measuring system can produce generally pseudo inductive effects or stray capacitances. Also, interferences from the environment, which is usually not controlled when making in-situ measurements on heritage objects, such as parasitic currents or electromagnetic noise, influence of light and temperature, especially the metal surface heating under sunlight, etc. may affect the quality of the measurement or the results.

All these possible constraints should be taken into account when interpreting experimental data. In most cases, these effects may not be present, may appear in a frequency range out of the measurement region, or may be modelled and isolated with some additional circuit element, but it is necessary to be aware of them. Regarding possible environmental contributions,

it is also important to contemplate them specially when comparing measurements.

To be able to distinguish data from interferences or artifacts it is critical to consider the nature and characteristics in our system. From a mathematical point of view, different equivalent circuits may fit an EIS spectrum, thus it is important being able to establish coherent correspondence between the proposed element circuits and possible physical and chemical phenomena in our system. Sometimes, extremely complicated circuits are proposed with no other basis than the quality of the fitting, which is, by itself, not an indication of a valid model.

After these previous considerations, the first step for a proper interpretation of EIS results in cultural heritage is to consider the variability of situations that will give a different electrochemical response, which can typically be grouped in:

a) “Clean” metal objects, i.e. well preserved polished or bare metal objects from historical, artistic or scientific collections (armors, weapons, silverware, instruments, scientific objects, etc.). Although non-visible for the eye, these objects are usually covered by a thin oxide layer. These objects are usually stored in museums under controlled conditions (low RH and no pollutants) to avoid their degradation.

b) Metals with natural or artificial patinas or corrosion crusts. Typical examples are outdoor sculptures, archaeological objects. Metallic surface is covered by different layers of corrosion products, presenting a huge variability in composition (oxides, sulfides, sulfates, nitrates, chlorides...), thickness, compactness, adhesion, porosity, conductivity and reactivity. Frequently, these patinas present a double layer structure, with a thinner and compact inner layer and a thicker, porous, heterogeneous outer layer.

c) Coated metal objects, i.e. metals protected from the environment by an isolating layer, either applied during their manufacture or applied by conservators-restorers to protect them and restrain their degradation. In this group we can find transparent organic coatings of different nature (oils, waxes, synthetic polymers) and paintings (polymer + pigments). These coatings can be applied over a clean metal or –the common situation when they are applied by conservators-restorers– over an existing patina or corrosion crust.

Despite particular situations, most systems should respond to a few representative circuits. A general overview of the equivalent circuits proposed to analyze EIS results in cultural heritage is reviewed in next sections for the three situations already exposed. CPE instead of capacitors will be used in all EC despite the element used in the original paper from which each model is discussed.

3.1. Clean metals

The simplest situation is also the less likely in cultural heritage objects, as it is not common to find uncoated and unprotected metals in museum collections. Moreover, there is a certain risk of damaging the surface of a metal that has been kept indoors in a low-humidity environment by placing an electrolyte in contact with it. For these reasons, no EIS studies

¹ Although in a strict sense it is not correct, the term “time constant” is commonly used in corrosion science as an equivalent for an electrochemical process involving the parallel association of a resistance and a capacitor, and will be used in this paper in that sense. For a precise definition of time constant see reference^[11d], pp. 24-25.

on clean-surface metallic heritage artifacts are found in literature. Notwithstanding this, the understanding of the electrochemical behavior of the bare metal is of interest for conservation of metallic heritage, as the equivalent circuit describing the corrosion processes on the metal surface will be part of larger circuits such as those for metal-patina or metal-coating systems and will appear when using clean metal coupons as a reference in laboratory tests. Many laboratory studies concerning the electrochemistry of copper and its alloys (and patinas) on acidic media or in chloride solution have been published, mostly related to inhibitors development [5a, 47]. However, those aggressive electrolytes cannot be used for studies on real artifacts, so its interest in this case is limited. Focusing in mild electrolytes, which are a requirement to avoid damaging heritage objects, studies on copper corrosion in tap water can be an interesting model for understanding EIS spectra from historical objects on copper and its alloys. A few publications can be found in this subject, proposing similar interpretation, with small variations that could be explained from differences in experimental conditions.

According to Feng et al. [48] the corrosion mechanism of copper in slightly mineralized neutral aqueous solutions (such as tap water) seems to be controlled by diffusion of copper ions in the surface oxide layer. This mechanism can be represented by the typical Randles circuit in figure 12(a), where R_e is the electrolyte resistance; CPE_{dl} is the double layer capacitance at the electrode interface in parallel with the charge transfer resistance, R_{ct} , and W is the Warburg impedance for copper ions diffusion through the oxide film. Warburg impedance is a specific element used to model semi-infinite linear diffusion processes, and is mathematically equivalent to a CPE with $\alpha=0.5$.

Feng et al. [48a] propose a variation of the Randles circuit in which charge transfer resistances of cathodic (reduction of dissolved oxygen) and anodic (copper dissolution) processes appear in parallel in different branches of the circuit as shown in figure 12(b). This model has been used by other researchers to explain the EIS spectra of artistic bronze coupons in artificial rain [14b, 49] (figure 13). Other authors have used a simple two nested (R-CPE) couple circuit, but fitting results showing the exponent of the second CPE close to 0.5, thus suggesting a diffusion impedance, both in copper and brass [50]. More recently, Vera et al. have studied copper corrosion in 0.1M Na_2SO_4 ; unexposed copper coupons spectra fitted the classical Randles circuit, without the diffusion element [51], as shown in figure 12(c), whether as only numerical data without error estimation is presented, it is difficult to ascertain the quality of the fitting.

Figure 12. Classical Randles circuit with diffusion proposed for bronze in artificial rain (a). EC proposed by Feng et al. to describe corrosion of copper in simulated tap water (b). EC circuit proposed by Vera et al. for copper 0.1M Na_2SO_4 (c)

Alloy	Time (h)	R_e (Ωcm^2)	R_{ic} (Ωcm^2)	CPE _{dl}		R_a (Ωcm^2)	W		
				Y_0 $\mu S s^{n-1} cm^{-2}$	α		R_w (Ωcm^2)	T_w (s)	α_w
Bronze G85 (black)	1	4300	492	517	0.65	369	422	4.23	0.68
	24	4231	5000	205	0.95	65	420	14.6	0.44
	168	4613	1500	250	1.0	60	400	39.4	0.44
Bronze SI3 (red)	1	4690	81	260	1.12	63	1028	11.4	0.77
	24	5078	401	823	0.77	130	7593	4.7	0.86
	168	5770	3951	282	0.48	1356	2453	5	0.64

Figure 13. Nyquist plots (in the 10^2 to 10^{-3} frequency interval) and fitting results (from EC in figure 12b) for bronze alloys in artificial rain at different immersion times. The parameters in the Warburg element fit the following expression: $Z_w = [R/(Tj\omega)^{\alpha}] \cdot \tanh(Tj\omega)^{\alpha}$. Reprinted from [49] with permission from Elsevier.

Occasionally, EIS spectra from copper shows three time constants; this seems to be the case when the Cu_2O layer has a certain thickness (and also in patinas). E.g. Shim and Kim found

that for copper continuously immersed in drinking water the spectra changed from two time constants to three after about a month [50a]. While two time constant spectra are easy to understand and link to a generally accepted corrosion mechanism for copper, the process related to the third constant is not so clear. Shim and Kim propose that the third constant arises from an additional electrochemical response from the oxide layer. Although this could be a reasonable explanation, the oxide layer composition and structure presented is unusual and the experimental data presented are not enough to support their explanation. The oxide layer structure and composition cannot be derived from the XPS results presented, as it is not possible to distinguish between copper products using only the photoemission peak, being necessary to resort to the Auger peaks, which not included in their work [52]. Rios et al. [53] observed three time constants in much shorter immersion times and assigned the additional time constant, at higher frequencies, to the oxide layer on the surface, being the medium and low frequency time constants related to the copper corrosion mechanism already described.

Regarding historical steel, electrochemical studies on heritage artifacts made of this material are still harder to find, but again we can use some examples of steel in water [54], to support the proposed model. For historic steel objects, the EIS spectra can be explained by a simple Randles circuit if the surface is clean. When some corrosion products are present on the surface, even only on localized areas, a second RC pair will appear, and the circuit will change to the classical EC for metal covered by an oxide layer discussed in next section [8].

3.2. Metals with patina

Most outdoor metal sculptures and monuments are made of bronze or weathering steel, which are naturally or artificially covered by patinas. Metallic archaeological objects covered by a layer of corrosion products, can also be considered in this group. Although very different in nature and behavior, those patinas are generally constituted by two different layers, which can give an independent or overlapped response. Different circuits have been proposed to describe them, though in most cases, a general common model gives the best explanation.

Copper and alloys

Very few examples of EC analysis of EIS measurements on ancient naturally developed patinas can be found in literature, while there are a few more papers dealing with artificially produced –chemically or electrochemically– ones. This is also the case for archaeological bronzes, where part of the very few studies are focused on the corrosion process of the metal in different media [55] and not in the study of the patina.

Outdoor copper and bronze patinas generally show a double layer structure with an inner layer of cuprous oxide and an outer, more porous, layer of cupric compounds: basic copper sulfates, chlorides, carbonates or other compounds depending on the environment to which the object has been exposed. The EIS spectra from these kind of patinas usually present two

(sometimes three) time constants, frequently not clearly resolved. Different EC have been proposed to explain the EIS spectra of this patina structure. Figure 14 shows the different EC that have been used in the literature to model the behavior of outdoor copper or bronze patinas. Figures 14(a) and 14(b) have been proposed for different samples of copper from churches roofs in urban environments in Scandinavia using simulated rain water (conductivity $\sim 30 \mu\text{S}/\text{cm}$) [40, 56], while the EC in figure 14(c) was used to analyze the behavior of different patinas from Mexican Baroque bronze bells by Arceo-Gómez et al. [57]. These examples, perfectly match the case of a typical bronze outdoor sculpture.

Figure 14. EC for a thin barrier layer covered by a porous outer layer (a) two nested R-CPE model for a double layer patina structure or a patina-metal surface response (b) three time constant EC (c).

The first EC approach for explaining the double layer patina structure is based on the models proposed for the study of anodized layers in aluminum, which consist of a thin barrier layer covered by a porous outer layer [58]. However, this model, which implies no signal coming from the faradaic process at the metal surface (the pair $\text{CPE}_{\text{dl}}-\text{R}_{\text{ct}}$ is not present) is valid for a very compact and adherent layer as alumina, but does not seem suitable for an irregular and porous corrosion layer. In fact, from the SEM image of the patina in figure 4 of reference [40], the electrolyte surely reaches the metal surface through the pores and cracks (figure 15). In a subsequent study by same authors, this interpretation is replaced by the EC in figure 12(b), with two nested (R-CPE), representing the impedance of the inner and outer patina layer [56]. Considering the values from fitting the EIS spectrum, the exponent value close to 0.5 from the CPE in the inner layer, suggests that this CPE can be replaced with a Warburg impedance, related to the diffusion of copper ions within the inner oxide layer. The same EC although considering CPE1 related to the patina response and CPE2 with copper oxidation was used to study the response of bronze roman coins

[17] and natural copper patinas formed during 1-3 years in Chile in different environments, with different thickness and porosity depending on the location [51]. This second interpretation of circuit elements is in a better accordance to the copper corrosion mechanism previously described.

Figure 15. EIS spectrum (○) and fitting curve (•) in rainwater and cross-sectional image from a natural copper patina, reprinted from [40] with permission from Elsevier.

Patinas showing a three time constant EIS spectra, have been explained by the EC in fig. 14(c), showing three nested (R-CPE) pairs. This EC was proposed by Marušić et al. in several papers to explain the electrochemical response of different artificial patinas in Na_2SO_4 - NaHCO_3 electrolyte [59], and has also been used in the study of different archaeological bronzes [15a, 60]. According to Marušić et al., the first (R-CPE) pair represents the resistance and capacitance of the patina, the second (R-CPE), at intermediate frequencies, represents the corrosion process on the metal surface, while third (R-CPE) couple that corresponds to the low frequency loop is explained as a result of oxidation–reduction processes of the corrosion products taking place at the electrode surface. These processes involving different copper species $\text{Cu}(0) \rightleftharpoons \text{Cu}(I)$ or $\text{Cu}(I) \rightleftharpoons \text{Cu}(II)$ and dissolved oxygen, will result in a Faradaic resistance and Faradaic capacitance. The extent of these processes could explain the reason why sometimes only two time constants show in the EIS spectra.

Some examples of EIS spectra fitting an EC with three nested (R-CPE) pairs is shown in figure 16. The first example corresponds to an in situ EIS measurement on the aforementioned Mexican Baroque bronze bells by Arceo-Gómez et al., while the other three are from laboratory studies of different artificial patinas by Marušić et al. It can be appreciated that all Nyquist plots show more or less depressed semicircles,

which can be relatively well defined, as in figure 16(c), or completely overlapped, as in figure 16(a).

Figure 16. Nyquist plot and three time constant equivalent circuit for “in situ” impedance obtained from a brown patina on a Historic Bell (a), reprinted from [57] under a Creative Commons Attribution 4.0 International License. Nyquist plots of different artificial patinas immersed in artificial acid rain ($0.2\text{ g L}^{-1}\text{ Na}_2\text{SO}_4 + 0.2\text{ g L}^{-1}\text{ NaHCO}_3$ at pH 5) for different times: sulphate patina (a), chloride patina (b) and electrochemical patina (c). Reprinted from [59b] with permission from Elsevier.

A few additional studies on archaeological objects have been published, giving different interpretations on the EIS response. Equivalent circuits and some examples of EIS spectra are presented in figures 17 to 20. First example is the EIS spectrum of a fragment from a brass object excavated from the archaeological site of Tharros, in 0.1M NaCl. Though the spectrum showed, apparently, only two time constants, it fitted the EC in figure 17(a) [61]. This EC was also used by Souissi et al. to study patina formation under different conditions on archaeological bronze [55]. Although using a genuine archaeological fragment, patinas were artificially produced by immersion in different electrolytes of the polished metal surface, thus cannot represent archaeological patinas. The EIS spectra showed three time constants regardless the chosen electrolyte, which are related to the response of the corrosion products formed upon immersion, and the charge transfer process and mass transfer processes in a mixed activation-diffusion control of the reactions, respectively (figure 17(a)). More recently, two EIS studies on archaeological bronze coins have been published by Di Turo et al., using NaCl 0.3M-5% agar electrolyte [17] and in mineral water [62]. In the first study, the EIS spectrum from the

roman coins was explained by the EC in figure 17(b). In the original publication, this EC is depicted in a different order ($R_e[(R_{ct}-CPE_{dl})(R_{pl}-CPE_{pl})]$); although it is mathematically equivalent—as EC are only circuits that give the same EIS response as a system—we consider that the order presented here is more recommendable, as it is closer to the physical disposition of the represented process. The second set of archaeological coins showed two different behaviors. Coins presenting moderate corrosion, fitted the EC in figure 17(c), while in the case of severe corrosion, i.e. a gross outer corrosion layer, the EC included a second parallel combination of resistance and CPE attributed by the authors to the ohmic resistance and charge separation in the porous external patina (figure 17(d)). Nevertheless, these EC would imply that the redox process ($R_{ct}-CPE_{dl}$) is taking place at the surface of the patina instead of at the metal-electrolyte interface, which is in discordance with all previous models.

Figure 17. Different EC proposed for archaeological copper alloys.

Figure 18. Nyquist plots (Z_m vs Z_{Re} in $\Omega\cdot\text{cm}^2$) from patinas grown by immersion of archaeological bronze in 0.1M NaCl solution, fitting EC in figure 17(a). Reprinted from^[55b] with permission from John Wiley and Sons.

Figure 19. Nyquist and bode plots from different archaeological coins with an agar cell fitting EC in figure 17(b). Reprinted from^[17] with permission from Elsevier.

Figure 20. Nyquist plots from different archaeological coins with mineral water showing apparently two more or less overlapping capacitive loops, fitting EC in figure 17(c) and 17(d). The representation of the Nyquist plot, nevertheless, does not use isometric axes, so the shape of the spectra is distorted. Reprinted from^[62] with permission from Elsevier.

Iron and steel

Two kinds of iron materials can be found in outdoor sculpture and monuments: iron or carbon steels that are commonly present as part of built heritage as well as in archaeological objects; and weathering steel, which is widely used in contemporary art and architecture. The rust presents again a two-layer structure, with a thinner inner layer and an outer thick and heterogeneous corrosion crust. For iron and carbon steel this layer is not protective and tends to delaminate, causing material loss; weathering steels, on the other side, form a much more compact and stable rust layer that slows down the corrosion rate, and is considered as a protective patina. Despite some similarities in the structure, the behavior of iron corrosion layers is quite different from copper patinas. The corrosion

mechanism of iron –although still being discussed in detail– involves a cyclic process of reduction and oxidation of iron phases [63]. This means that depending on the step, different redox reactions can take place. While the atmospheric corrosion mechanism of iron is quite complex, fortunately, in most cases, EIS spectra can be explained by simple circuits, and in general, there is more consensus among different studies.

Fortunately in this case, in addition to the very few examples of EIS studies on historic iron and weathering steel sculptures, as weathering steel is also a common material in architecture and civil engineering, there is an extensive literature on this material, including some examples on naturally weathered steel. Several years ago Wang et al. carried out a series of studies on weathering and carbon steel in different natural and artificial conditions [64]. The main purpose of it was to find a reliable accelerated test to simulate natural exposure, thus they compared several year old natural patinas with corrosion layers grown through several accelerated test under cyclic wet/dry conditions. EIS spectra of natural patinas and artificial patinas after a certain number of cycles was characterized in the Nyquist plot by two depressed semicircles and a diffusion tail in the low-frequency region, which can be represented by the EC already presented in figure 14(a). In this circuit, R_{pl} and CPE_{pl} would represent the resistance and capacitance of the rust layer, R_{ct} the charge transfer resistance (associated with both the anodic and/or cathodic reactions), and CPE_{dl} , the double layer capacitance. The Warburg element is associated with diffusion of oxygen to the steel surface through the pores in the rust layer, which acts as a diffusion barrier. Subsequent studies with a similar experimental approach support the same model for carbon and weathering steel [65]. Thus, EIS spectra on WS can be explained with the same EC than bronze, only differing in the origin of the Warburg impedance.

Regarding electrochemical studies on weathering steel sculptures, although several papers have been published [15c, 28b, 35b, 35c, 66] and some of them comment on EC, there has been only one attempt to fit the spectra to a EC [15c]. In this paper, the spectra have been fitted using a two-cell EC like the one in figure 17(b), to describe the impedance of the two interfaces: metal/rust layer and rust layer/electrolyte, respectively. However, a third time constant seems to appear at low frequencies, visible in the phase angle in fig. 6 of reference [15c] (figure 21), which is neglected by authors and would require additional elements in the EC. This 3-time constants spectra have also been reported in other works [35b, 35c], for which the aforementioned $R(RC(C[RW]))$ model still seems the best match. To check this model, previous measurements carried out with the G-PE cell, on a weathering steel sculpture from Adriana Veyrat^[35d] and on a weathering steel coupon after five years of natural outdoor exposure^[35a] have now been fitted to the proposed $R(RC(C[RW]))$ equivalent circuit. EIS spectra of both measurements are presented on figure 22, together with the fitting results, supporting the proposed EC.

Figure 21. EIS spectra for the sculpture *Reditus ad origines*, with the setup described in figure 3. At the lower frequencies the phase angle changes from 0 to lower values (as the value represented in the figure is $-\theta$), suggesting an additional process. Reprinted from^[15c] with permission from Elsevier.

Figure 22. Bode and Nyquist plots for a weathering steel coupon after five years of natural outdoor exposure and in situ measurements of a sculpture "Templo" from Adriana Veyrat in Madrid

Besides weathering steel, researchers from the Politecnico di Torino have also carried out EIS measurements on historic iron bar chains from the Notre-Dame Cathedral of Amiens and the Metz Cathedral, in France^[24, 66-67] (figure 23). Several EC have been discussed for this type of objects in different papers, while the latest model proposed^[66b] is the same as the general EC in fig.17(a) for weathering steel. This suggests that although more complex models can be used to explain the full complexity of the iron rust layers structure and behavior, this model is enough to explain the general behavior and evaluate the conservation state of an iron object.

Figure 23. EIS spectra from different areas of the wrought iron bars chains of the Amiens Cathedral, measured with the nylon cylinder liquid cell previously described in different campaigns. Reprinted from^[24] with permission from Springer (top figure) and ^[66b] with permission from NAUN (bottom figure)

3.3. Evaluation of coatings and inhibitors

Protective coatings consist of a more or less isolating layer which yields mainly a capacitive response in the EIS spectra. An ideal intact coating acts as a dielectric and can be represented by a capacitor in the EC. When defects are present, a resistive component representing the ionic conductivity through the coating appears in the circuit. The *classical* equivalent circuits for describing the behavior of protective coatings on metal substrates are depicted in figure 24. A metal-coating system can be represented as capacitor and a resistance in parallel for the capacitance (C_{coat}) and resistance (R_{coat}) of the coating in series with the resistance of the electrolyte, R_e . In highly protective coatings R_{coat} is very high, which reduces the system to a C_{coat} in series with R_e (as no current goes through the resistance). When the coating deteriorates allowing the electrolyte to penetrate and reach the metal surface starting corrosion, the circuit changes to the one in figure 24(b), where C_{dl} is the double layer capacitance and R_{ct} the charge transfer resistance of the corrosion process at the metal-electrolyte interface. This circuit, generally substituting capacitances for CPE to adjust the non-ideal behavior, has been applied to the study of organic coatings – including varnishes and waxes- for bronze and historic steel artifacts ^[8, 14a, 35e, 68]. Although other more complex circuits can be used –which may be needed to explain complex multilayered coatings- the simple RC circuit and the porous layer model may be used for most situations. In all examples cited above, which included clean metal and pre-corroded metal surfaces, liquid

and gelled electrolytes, the standard equivalent circuits were able to explain EIS results. This indicates that the electrochemical response is dominated by the contribution of the coating, and response from the patina or corrosion layers is either concealed under the coating's response or appearing out of the frequency range of the measurement.

Figure 24. EC describing an ideal metal-coating system (a) and a non-ideal or damaged coating (b).

Fitting parameters of EC on coatings allow extracting a lot of information related to coating behavior and degradation such as water uptake, coating porosity, extent of delamination... For further reading there are several excellent reviews that give a clear insight of all the information that can be extracted from spectra analysis, as those by Mansfeld or Amirudin and Thierry ^[69].

Inhibitors reduce corrosion by adsorption of the molecules onto the metallic surface, hindering anodic, cathodic or both reactions. This reduction of the effective area of the metal exposed to the electrolyte is reflected in the EIS spectra in the increase of the R_p and/or reduction of the C_{dl} . Although adsorption/desorption of these molecules can also produce pseudo-inductive responses on the low frequency region of the EIS spectra, a literature review shows that for cultural heritage materials, EIS spectra of metals and patinas in the presence of an inhibitor show the same features as the spectra from the clean surface, only differing in the values of different parameters ^[15a, 47c, 59a, 59b, 70]. An example is presented in figure 25 from a study on the inhibitor effect of imidazole and thiadiazol derivatives on patinated bronze, by Muresan et al^[15a]. EIS spectra show the increase in the diameter of the semicircles in the Nyquist plot with the immersion time in the inhibitor solution, while the profile and EC remains the same.

Figure 25. Variation of EIS spectra of patinated bronze without inhibitor (black and red plots) and in presence of an inhibitor (blue, green and brown). Reprinted from^[15a] with permission from Elsevier.

4. Summary and outlook

As it has been shown in this review, the increasing interest in the use of EIS in cultural heritage has been noticeable in the present decade. In the first years of the decade a couple of papers and book chapters describing use of electrochemical techniques for the conservation of metals were published; some give a broad overview on electrochemical techniques^[10b, 71], while others are focused in certain uses of impedance, such as coatings evaluation^[11a]. This latter review on use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage by Cano et al. has had a relevant impact in the field, approaching to 100 citations in Scopus at this moment. One of the main issues highlighted in this paper was the need of performing studies on real objects, underlining the interest of in situ measurements, and concluding that *"Its application in this specific field will probably increase in the next years, and it is desirable that the new developments in the technique and the interpretation of the results made by corrosion and coatings scientists and electrochemists would be applied to this specific field through an interdisciplinary collaboration with the conservation– restoration professionals."*

As predicted in this paper, in recent years the number of research groups using EIS for cultural heritage studies has increased; since 2010 more than 60 new references related to this topic have been published, about half of them dealing with in situ measurements. Although it may seem not a high number, the fact is that more references have been published on the subject in the latest seven-eight years, than in the previous sixteen.

As it has been presented in section 2 of this review, several research groups have been working in the development of electrochemical cells specifically tailored for the needs of cultural heritage. Developments have followed two strands: devices to keep a liquid electrolyte in contact with the heritage assets; and cells based on different solid electrolytes. From the different systems proposed, some of them seem to have been soon abandoned, while others seem to have a longer trajectory of application. Amongst the liquid electrolyte cells, the contact cell developed by Letardi (or variations of it) is the one with a longest and more consolidated use. Solid electrolytes are more recent, but results with the agar G-PE cell are promising and the system has been adopted and further developed by other groups^[17, 36a]. The use of a two surface-mounted parallel cell configuration is an interesting approach to circumvent the problem of making electrical contact with the base metal, but the quality of the results published using this setup is still too poor to make this a real alternative.

Summarizing, none of the systems has been widely adopted, and further developments of these systems and/or newer proposals are to be expected in the near future. For these future developments, special attention needs to be paid to fully understand the limits and influences of the measuring systems

in the results. Comparative studies, both with traditional electrochemical cells and between different in-situ cells need to be carried out. Aspects such as the use of two or three electrode configurations, artefacts arising from the geometry of the cell and low-conductivity electrolytes need to be fully understood to be able to interpret correctly the results obtained in the complex surfaces of a sculpture or monument.

Regarding the interpretation of the results, many papers still adopt a simplistic approach of evaluating a single parameter of EIS (typically, $|Z|$ at low frequencies). While it might be a first approximation, a deeper interpretation of EIS results is necessary to fully exploit the potential of EIS for the diagnostic of metallic cultural heritage. Works that have been reviewed in section 3 demonstrate that the use of EC for the analysis of EIS spectra can provide very valuable information for the understanding of the different processes and elements of the complex metal-patina-coating system. For weathering steel and coated metals general EC are commonly accepted, but in the case of copper and bronze patinas there is less consensus on the interpretation of the EIS spectra. Sometimes, this lack of agreement is shown even in similar studies or by same authors. More studies and a comparative and critical approach are needed.

Considering the number of papers published in last years and research groups working in this topic, along with the rising interest in the development and application of in-situ non-destructive analytical techniques for the study and diagnostic of cultural heritage, relevant developments are to be expected in the near future in the application of in-situ electrochemical techniques, especially EIS. Advances in this field will allow developing more efficient conservation strategies and treatments for metallic heritage, resulting in a better preservation of this legacy for the future.

3. Acknowledgements

This work was supported by the Spanish Ministerio de Economía y Competitividad (projects HAR2011-22402 and HAR2014-54893-R, and grant BES-2012-052716), and GEOMATERIALES 2-CM Program Ref. S2013/MIT-2914 (Comunidad de Madrid).

Authors acknowledge Paola Letardi for the "contact probe" in figure 1 and the raw data to draw figure 2. Thanks are due also to Elsevier, ESG, IIC, North Atlantic University Union, Springer and Wiley and Sons for reprint permission of figures from reviewed articles.

COPAC group is a member of the Spanish Network on Science and Technology for the Conservation of Cultural Heritage (TechnoHeritage).

Keywords: Electrochemical impedance spectroscopy • cultural heritage • in situ • diagnostic • conservation

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REVIEW

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Page No. – Page No.

Advances for in-situ EIS measurements and their interpretation for the diagnostic of metallic cultural heritage: a review

Electrochemical impedance spectroscopy to save our metallic heritage: We present a comprehensive and critical review the use of EIS as a diagnostic tool for cultural heritage, focusing on the different experimental approaches for in situ applications and on the understanding of the results from heritage metal objects, to bring this technique closer to metal conservators and conservation scientist.