REVIEW

Use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage: a review

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Abstract The best way to reduce the degradation of metallic cultural heritage is through preventive conservation measures but, in many cases, it is not possible to obtain adequate environmental conditions, and it is necessary to apply coatings to the artefacts in order to protect them against corrosion. There is a continuous search in the metal conservation community for new and improved coatings that provide a better protection to the objects whilst respecting the special requirements of the conservation–restoration ethics. Whilst electrochemical techniques have a long tradition in conservation–restoration treatments for metallic cultural heritage, the evaluation of protective coatings using electrochemical impedance spectroscopy (EIS) has only been used very recently. EIS is a very well-established method to investigate metal coatings for general purposes and has many advantages that make it especially suitable for testing coatings for metallic works of art. This paper makes a review of the use of EIS for testing coatings for metallic cultural heritage from the first publications in the mid-1990s to the last papers. The experimental setup used, the types of coatings and metals investigated and the interpretation of the results are reviewed and compared with the use of EIS for testing general purpose anti-corrosive coatings.

Keywords Metals · Corrosion · Protection · Coating · Electrochemistry · EIS · Impedance · Conservation · Restoration

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Introduction

The main degradation phenomena that affect the metallic cultural heritage are the corrosion reactions with its environment: the burial soil, the outdoor atmosphere or the indoor environment of the museum, display cases or storage. The best way to avoid, or at least delay, such degradation is through *preventive conservation*. According to the Conservation Committee of the International Council of Museums (ICOM-CC), *preventive conservation* is defined as: "all measures and actions aimed at avoiding and minimising future deterioration or loss. They are carried out within the context or on the surroundings of an item, but more often a group of items, whatever their age and condition. These measures and actions are indirect—they do not interfere with the materials and structures of the items. They do not modify their appearance" [1]. Thus, preventive conservation to prevent metal corrosion would include measures such as the reduction of the environmental relative humidity, the reduction of the pollutants, the use of vapour-phase corrosion inhibitors, etc.

However, it is usually difficult, due to technical or economical reasons, to assure long-term good conservation conditions for most of the objects, so it is a common practise to protect metallic artefacts against corrosion using protective coatings. Compared with industrial applications where the protective properties of the coating are the main parameter for their selection, when choosing coatings for conservation treatments for cultural heritage, other properties should be considered:

- Visual appearance: coatings should be transparent, with a similar gloss to the original substrate and should produce no or little change in the surface appearance.

- Reversibility: any treatment applied to a cultural heritage artefact should be as reversible as possible, that is, it should be possible to remove it and return the object to its original state. That is not always possible, but it is an issue that should always be considered.
- Respect to the original object: treatments should not modify the material of the original artefact. This includes, in most cases, the modifications suffered by the history of the object, such as patinas or corrosion layers, as far as they do not threaten the conservation of the object and its legibility.
- Long-term efficiency and easy maintenance: since heritage artefacts are intended to be preserved for a long time (as long as possible), any treatment should have long-term efficiency and since any coating will eventually be renewed, an easy maintenance is an advantage.

These considerations impose some important limitations in the selection and application of corrosion protection coatings: coatings should be not pigmented (what hinders their protective properties), should be usually applied over pre-existing corrosion products (making difficult a good adhesion and providing weak points for corrosion restart) and should be easily removable after many years without damage to the original.

A recent survey in the Mediterranean region has shown that, for the protection of historic metals in museums, conservators–restorers use mostly Paraloid B72™ (an acrylic resin, dissolved in xylene, toluene or acetone) as protective coating, to a lesser extent, microcrystalline waxes and, in some cases, combinations of both [2]. For outdoor bronzes, Incralac™ (an acrylic resin solution containing benzotriazole) is the most common protective coating [3–5]. However, failure of those coatings with severe damage to the underlying metal has been reported in many cases [6, 7].

The testing of coatings for metallic cultural heritage also raises some additional difficulties when compared with coatings for industrial applications. The main one is the extreme variability in the substrates to which those coatings are to be applied, both because the different composition of the metallic substrate and because the different surface of the objects, ranging from the clean metal of industrial or scientific heritage to the more or less uniform patina of outdoor bronze sculptures or to the thick crust of corrosion products of archaeological objects. For this reason, in many cases, there is a need of studying the performance of the coating applied on the object itself. On the other side, when there is a need for studying coatings in the laboratory, it is difficult to prepare metal coupons reproducing a historic or an archaeological metal covered with a layer of corrosion products developed over many years. Finally, those objects are exposed to very different environments ranging from

the very low corrosiveness of a controlled museum display case to the extreme corrosiveness of the outdoor exposure in very polluted areas. Considering all these special requirements for the coatings and the unique value of most of the objects composing the metallic cultural heritage, it is clear that there is a need in the metal conservation community for improved protection systems that can provide a better protection whilst fulfilling the conservation criteria [8, 9].

Electrochemical impedance spectroscopy (EIS) has been extensively used in the last three decades for the study of coatings for metals corrosion protection. EIS is especially suitable for the study of surfaces having a high electrical or electrochemical impedance and is, therefore, particularly suitable for the degradation evaluation of highly resistive protective organic coatings on metals. Additionally, it can provide not only a quantification of the protection capabilities of the coating but also information on the mechanisms involved in this protection and their degradation. However, the application of this technique for the evaluation of coatings for metallic heritage protection has been more recent, and its use, in contrast to its application in industry, is not yet widely known and accepted.

The aim of this paper is to make a review of the use of electrochemical impedance spectroscopy for the study of protective coatings for metallic cultural heritage. A brief history of the use of different electrochemical techniques in metal conservation will be presented, followed by a short review of the use of EIS in general-purpose metal coatings studies and, finally, a review of the applications of EIS in metal conservation studies will be detailed.

History of the use of electrochemical techniques in metal conservation

Electrochemical techniques are mainly known in conservation and restoration of metallic heritage as a tool for treatment of the objects involving the reduction of the corrosion products or the electrochemically aided removal of chlorides. In this field, it is usually distinguished between "electrolytic reduction", when the source of energy is an external source (a battery or generator) and "electrochemical reduction", when the source of energy is the formation of a galvanic cell between the object acting as cathode and a less noble metal, usually zinc or aluminium, acting as anode [10].

The history of the use of electrochemistry for the treatment of metallic cultural heritage dates back to the end of the nineteenth century when Friedrich Rathgen began to apply electrolytic reduction for treatment of active corrosion problems in archaeological bronzes and irons using a potassium cyanide electrolyte and three Daniell

cells in series. He was also a pioneer in the use of zinc granules for electrochemical reduction of bronze and copper coins [11]. Similar procedures were used during the first two thirds of the twentieth century and were recommended for many restoration treatments for different metals in the famous Plenderleith's book, *The Conservation of Antiquities and Works of Art* [10]. All those treatments were very radical and removed all the corrosion products leaving only the clean metal surface.

Since the conservation–restoration criteria evolved and the importance of the corrosion products was recognised as part of the history of the object and, in many cases, the only remaining of the original surface or decorations, those radical treatments were abandoned in the 1970s–1980s. Today, many conservators–restorers detest electrochemical techniques for the use that was made of them in those times. But it must be recognised that many other treatments (chemical, mechanical, thermal, etc.) have produced the same devastating effect, and the problem (from today's criteria point of view) was not the techniques used but the final result that was sought.

The inflexion point in the progressive abandonment of electrochemical techniques in metal conservation was the publication of a paper by Carradice and Campbell on the treatment of lead objects [12]. The main innovation was the use of a three-electrode cell allowing for potentiostatically controlled treatments. Since then, many authors have used this potentiostatic reduction for the treatment of lead [13, 14], silver [15] and gilded silver [16]. For iron- and copper-based objects, electrochemical treatments have been shown to be effective in the stabilisation of archaeological objects though chloride removal, accelerating and improving the chloride removal when compared with traditional washing treatments [17–20].

Another application of electrochemistry for conservation of metallic cultural heritage that has gained popularity in recent times is its use for analytical purposes. Different authors have demonstrated the applicability of E_{corr} monitoring, galvanostatic and potentiodynamic techniques for the identification of metals in alloys or components of a patina or corrosion products layer [21–29]. Some other applications of electrochemical techniques in metal conservation include the monitoring of the corrosion of objects in situ or during their storage or treatment or the cathodic protection of submerged or buried objects.

Polarisation resistance measurements (R_P) or polarisation curves have also been used for the evaluation of the protective character of different naturally or artificially grown patinas on bronze monuments [30–32] and protection systems such as inhibitors or conversion coatings for lead exposed to acetic acid environments [33, 34] or iron [35–37]. R_P has also been used as an alternative method to the "Oddy Test" for the evaluation of the potentially

corrosive materials for their use in storage or display cases of metallic artefacts [38]. For all these applications, R_P has been recognised as a very valuable tool for the conservators–restorers since it is a non-destructive technique that can provide quantitative values of corrosion rates in a shorter time than natural exposure tests, giving them invaluable information for their selection of materials for the restoration or conservation of the objects.

A good indicator of the current importance of electrochemical techniques in metal conservation is the fact that this topic was one of the five themes selected for the working programme of the Metal Working Group (WG) of the ICOM-CC in the triennial period 2005–2008. In the triennial meeting of the group, the Metal 07 conference held in Amsterdam in 2007, the communications were organised in the same themes. Table 1 shows the number of communications presented in each theme. It can be seen that ten out of 60 communications (17%) were in the "Use of electrochemical techniques in conservation" theme, which is a significant number. But a deeper analysis of the other themes shows that electrochemical techniques have also been used in many papers presented in the other themes. Considering it, almost one third (19 out of 60, 31%) of the communications have used electrochemical techniques for the study or the treatment of metal objects.

Use of EIS as a tool for studying the protective properties of metal coatings

EIS is probably the most important electrochemical technique used for the investigation of coatings for metals corrosion protection in industrial or decorative applications. A simple search in online databases such as ISI Web of Knowledge [39] or Scopus [40] with the terms "(EIS

Table 1 Number of communications in the different themes in the Metal 07 conferences that use electrochemical techniques (ET)
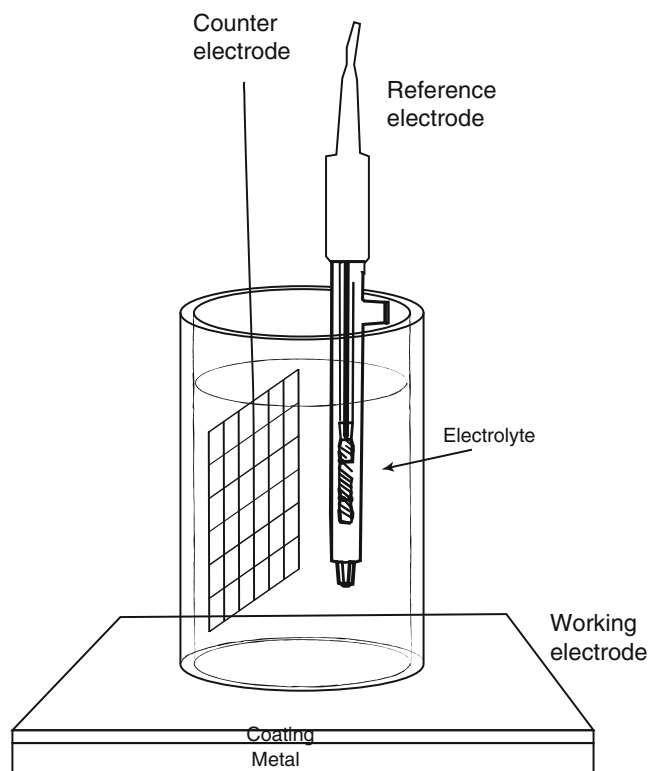
Metal 07

Theme	Communications	Communications using ET
Where archaeometry and conservation meet	15	0
Innovative investigation of metal artefacts	11	2
Study and conservation of composite artefacts	6	0
Protection of metal artefacts	18	7
Use of electrochemical techniques in metal conservation	10	10
Total (%)	10 (17%)	19 (31%)

OR impedance) and coating" yields more than 4,000 results. Several extensive reviews on the application of EIS to coatings evaluation have been published covering the different applications, the experimental details and the interpretation of results [41–46]. In this paper, only the main details that will be useful for the later comparison with the use of EIS for metallic heritage coatings will be detailed.

EIS is based on the application of a low-amplitude alternating current (AC) voltage signal (usually 10–20 mV) to the coated metallic sample using a conventional three-electrode (working, i.e. the coated metal under study, reference and counter electrode) electrochemical cell [42, 44]. Measuring the AC current response of the system, the impedance is calculated at different frequencies. A typical experiment is carried out making a logarithmic frequency swept from about 100 kHz to a few milihertz, acquiring five or ten points per decade [42, 44].

The typical electrochemical cell for coated metals consists in a vertical cylinder containing the electrolyte and the reference and counter electrodes attached to the horizontal coated flat metal sample (Fig. 1). However, variations on this configuration have been employed for testing different geometries [45] or in combined experiments [47, 48].

EIS data of coated metals are usually represented using Bode plots, which display the logarithm of the impedance

modulus, $|Z|$, and phase angle, ϕ, versus the logarithm of the frequency (Fig. 2). This plot has the advantage of being able to represent large variations in the Z values. Other authors have used Nyquist plots (Fig. 3), which represent more clearly features such as diffusion effects to represent EIS data of coated metals [43, 46, 48, 49].

For the interpretation of EIS results, equivalent electrical circuits are usually employed. Those circuits are analogues that reproduce the electrical properties of the system [50]. The different elements of the equivalent electrical circuit are assigned to different physical elements of the system under study, but there is no one-to-one correspondence between the EIS data and the equivalent circuit, and different circuits can be employed to model the same results [49–52]. Nevertheless, equivalent electrical circuits have proven to be useful to study the behaviour of the coatings and the evolution of different properties involved in the corrosion process [53–55]. Figure 2 shows typical Bode plots corresponding to a good, smooth and intact coating, two plots corresponding to a damaged coating where the electrolyte reaches the metal interface [one of them modelled using pure capacitors and the other using constant-phase elements (CPE)] and a plot corresponding to a coating where diffusive effects play a significant role.

Fig. 1 Electrochemical cell commonly used for testing metal coatings
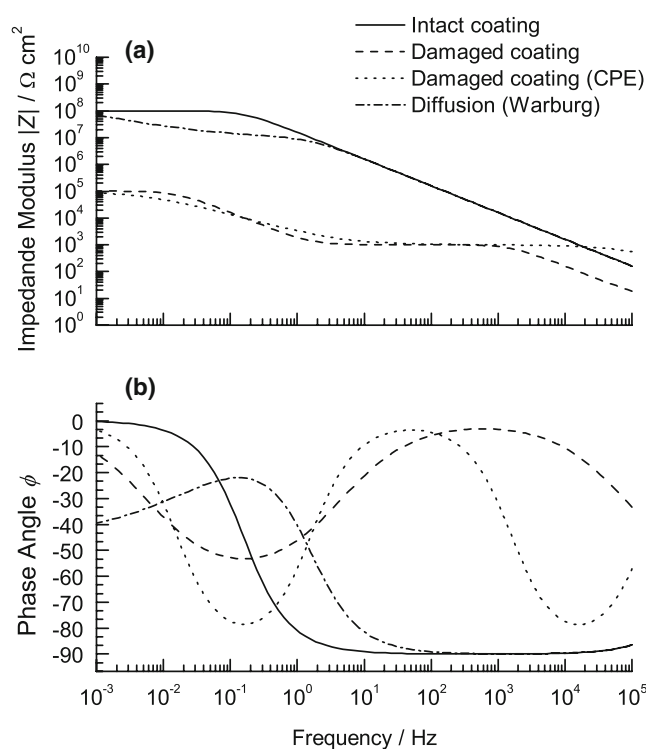
Fig. 2 a, b Typical Bode plots corresponding to a good, smooth and intact coating (*solid line*), two plots corresponding to a damaged coating (*dashed line*, *dotted line*) where the electrolyte reaches the metal interface (modelled using pure capacitors and CPE) and a plot corresponding to a coating where diffusive (*dashed-and-dotted line*) effects play a significant role
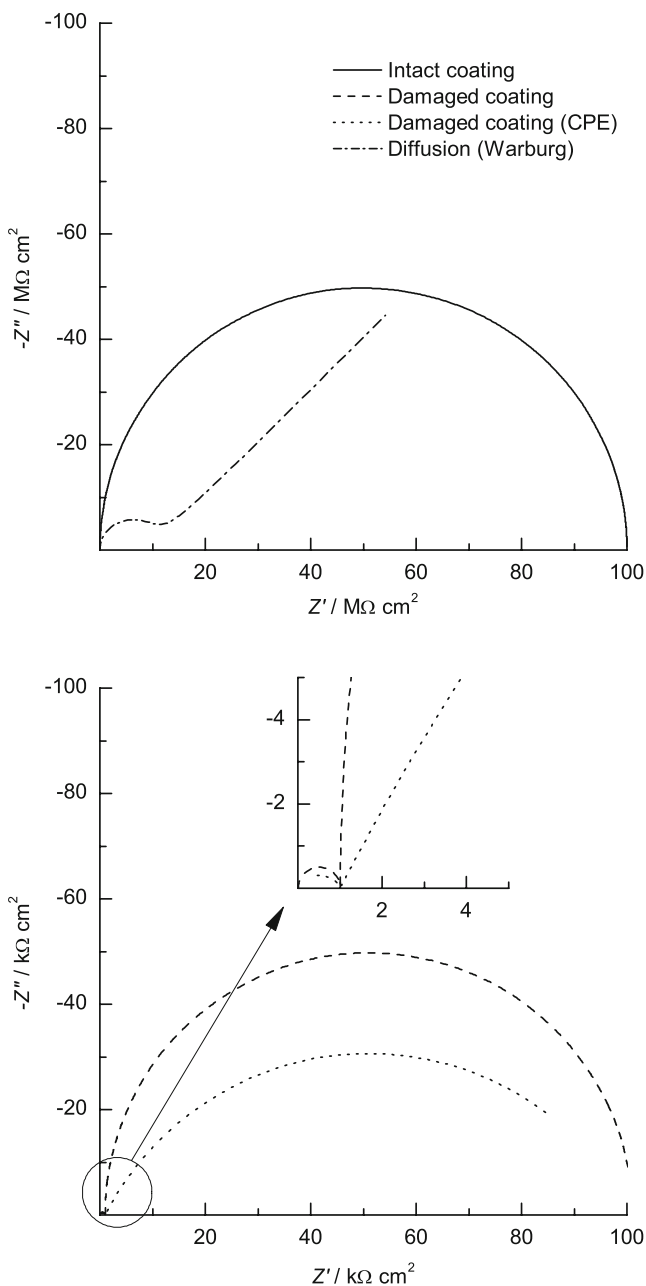
Fig. 3 Nyquist plots corresponding to the same data of Fig. 2

Figure 3 shows the same data represented in Nyquist diagrams. The intact coating is usually modelled using the equivalent circuit shown in Fig. 4a. It is composed by a capacitor C_{Coat} representing the capacitance of the coating, in parallel with R_{Coat} corresponding to the resistance of the coating, in series with R_s corresponding to the resistance of the electrolyte. When the coating is damaged and the electrolyte can reach the metal surface, the shape of the Bode and Nyquist plots change, and the electrical equivalent circuit commonly used to model its behaviour is the one shown in Fig. 4b: C_{Coat} and R_s have the same meaning; R_{Po} models the resistance or ionically conducting paths

across the coating ("pores"); C_{DL} models the double-layer capacitance, and R_P models the polarisation resistance of the corrosion process at the metal–electrolyte interface. It is common to find that ideal capacitors are not able to model experimental data in cases such as non-uniform coatings, surface roughness or inhomogeneous distributions of the current. In such cases, EIS data are commonly modelled using constant-phase elements instead of pure capacitors (Fig. 4c). The impedance of a CPE is defined by the empirical expression:

$$Z_{CPE} = \frac{1}{Y(j\omega)^{\alpha}} \tag{1}$$

where Y is a constant, $j=(-1)^{1/2}$, $\omega=2\pi f$, and the exponent α is $-1 \leq \alpha \leq +1$. When $\alpha=0$, the CPE is equivalent to a resistor; when $\alpha=1$, the CPE is equivalent to a capacitor, and, when $\alpha=-1$, the CPE is equivalent to an inductor. Finally, if $\alpha=0.5$, the CPE is equivalent to the Warburg impedance. Warburg impedance is an element that models the impedance associated to diffusion (i.e. mass transfer) processes and is commonly used when the diffusion of species through the pores of the coating or corrosion products controls the corrosion rate producing a distinctive 45º tail in the low-frequency region of the Nyquist plot (Fig. 3) [43, 44, 49, 56, 57]. A typical circuit modelling diffusive process is shown in Fig. 4d.

Circuits shown are simplified models that, in many cases, can help to explain the experimental results; but, in other cases, the EIS diagrams are more complex, and other more sophisticated equivalent electrical circuits have been proposed including additional R–C subcircuits [15, 58] or several R–C circuits in parallel modelling different areas or a multilayer coating [59].

The evolution of the different elements in the model can help to study the evolution of the metal-coating system. Thus, C_{Coat}, given by the equation

$$C_{Coat} = \frac{\varepsilon \varepsilon^0 A}{t} \tag{2}$$

where ε is the dielectric constant of the coating; ε^0 (8.85×10^{-4} F cm^{-1}) is the dielectric constant of the vacuum; A is the exposed area, and t is the thickness of the coating; is commonly used to evaluate the changes in the dielectric constant caused by water absorption or changes in the pigment/polymer proportions of the protective/decorative coatings [60]. The volume percentage of absorbed water, V_{H_2O}, is usually calculated using

$$V_{H_2O} = 100 \frac{\log(C_t/C_{t=0})}{\log 80} \tag{3}$$

where C represent the capacitances at time, t, or initially ($t=0$).
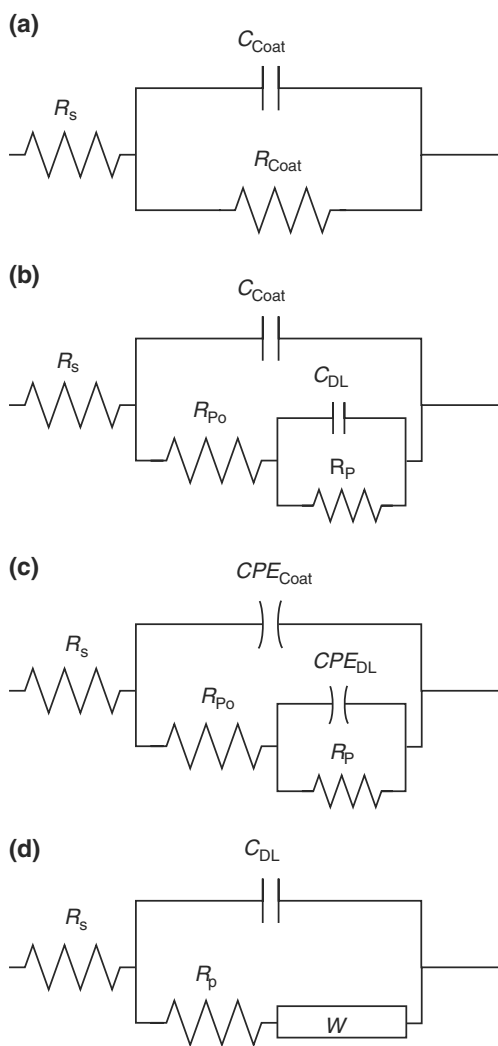
Fig. 4 a–d Equivalent electrical circuits used to model EIS data of Figs. 2 and 3

Typical EIS experiments for the evaluation of coatings usually measure the changes in EIS data with immersion time in the electrolyte but can also be used to evaluate the changes in the protective characteristics of the coating submitted to accelerated degradation, such as UV [52], mechanical stress [48] or salt-fog chamber [59]. Additional refinements of the technique have been used in combination with other techniques, such as quartz crystal microbalance or scanning Kelvin probe [61] or the application of the localised electrochemical impedance spectroscopy to the study of coatings [62, 63].

EIS in coatings for metallic heritage

We have seen that EIS has been extensively employed for the characterisation and evaluation of metal coatings and that electrochemical techniques have a long tradition in metallic heritage conservation, and their use has been growing in recent years. But, in spite of these facts, the application of EIS for evaluation of coatings for metallic heritage has been quite recent, and it is still far from being considered a standard.

The first significant publication (to the best knowledge of the authors) addressing this topic, taking into account the specific materials and special needs of metal conservation, is a paper presented by Price et al. in Metal 95, the International Conference On Metal Conservation of the ICOM-CC Metal WG. In this paper, several wax coatings for outdoor bronzes are characterised and their degradation upon immersion is studied using EIS [64]. These authors concluded in their study that EIS could be a useful technique for the evaluation of coatings for bronze conservation and that it can be used for evaluation of outdoor statues.

The evaluation of different wax coatings by EIS was continued by these researchers in the next years, evaluating also commercial mixtures of waxes and corrosion inhibitors [65] or the combination of artificial patination with wax coatings [66]. Bierwagen et al. have also tested different traditional (mainly Incralac™) and innovative coatings for outdoor bronzes using EIS after artificial ageing of coupons [3, 4, 67]. These authors measured the EIS response after QUV (UV light/water condensation cycles) and prohesion (fog/dry cycles) accelerated ageing tests according to ASTM D5894 [68] and proposed a quantitative lifetime prediction model based on the evolution of the low-frequency modulus of the impedance with time. McNamara et al. have studied the biodeterioration of Incralac™ and have characterised the evolution of the protective properties of this coating applied on bronze using EIS with an electrochemical cell inoculated with microorganisms collected from a real monument [5]. Clare and Lins have tested a water-borne polyvinylidene fluoride coating as an alternative to Incralac™ using artificially patinated bronze coatings [69]. Another alternative to traditional coatings for the protection of archaeological bronze artefacts that has been proposed and characterised using EIS is the deposition of SiO₂-like thin films using low-pressure plasma [70].

Using a specially designed "contact probe", Letardi et al. have performed in situ EIS measurements for the evaluation of the protective character of microcrystalline waxes, acrylic-based coatings (such as Incralac™) and organo-silanes applied to patinated or clean bronze samples (both naturally and artificially weathered) and real monuments [23, 71–73]. The patina has shown to have a significant effect on the protective efficiency of the coatings. Thus, EIS data for the same coatings show very different results when applied on clean artificially patinated or naturally patinated bronzes [65, 72]. Therefore, it is important to consider that a coating that behaves well on clean metal might have a poor performance on patinated metal and vice versa.

Due to the importance of bronze in metallic cultural heritage, coatings for this metal have received the most attention. However, coatings for other metals have also been investigated using EIS. Hallam et al. have tested different petrochemical coatings (film-forming coatings, waxes and oils) for their use for protection of historical steel [74]. They compared the performance of coatings using ASTM B117 salt spray test [75] and EIS and found a good agreement except in one of the coatings, which was explained by the different type of exposure, immersion versus airborne mist. In a subsequent work, the authors modified the experimental setup to study thin oil films, testing the oils applied on thin steel rods instead of flat coupons [76]. Corrosion inhibitors, applied as "dry films", have also been tested as protection systems for historic steel artefacts [77, 78]. Cano et al. have tested different traditional and innovative coatings for historical steel using EIS [79]. The main difference with previous works was that coatings were applied on pre-corroded steel coupons simulating historical objects. EIS results showed a good agreement with other accelerated exposure tests but had the advantages of a shorter test time and provided information about the mechanisms of protection and coating failure [9, 79, 80].

Protection coatings for silver and silver alloys have also been tested using EIS. Whilst corrosion layers and patinas on copper- and iron-based metallic artefacts are usually preserved and, therefore, the protection layers are to be applied over them, in the case of silver-based objects, the elimination of any corrosion layer or tarnishing is usually desirable, and the coatings are applied on the clean surfaces. This fact makes silver very appropriate for the application of thin electropolymerised or self-assembled layers. The protective properties of electropolymerised poly (3-amino-1,2,4-triazole) and self-assembled hexadecane–thiol coatings applied on silver have been studied using EIS and reflectance measurements: the results showed that the thiol film provided a good protection, was colourless and did not modify the visual aspect and, therefore, fulfil the already mentioned requirements of a coating for conservation of cultural heritage [15, 58]. SiO_x coatings applied by low-pressure plasma have also been proposed for protection of silver artefacts [81]. EIS results show that the layer can provide a moderate increase in the corrosion resistance of the silver and have the main advantage of being applicable immediately after an H_2 plasma reduction treatment for the elimination of the sulphide tarnishing [82]. With a different approach, looking for a coating easily applicable by conservators–restorers to objects of any size and shape, Vassiliou et al. have proposed the modification of the commonly used Paraloid B72™ by incorporating nanometric-size alumina particles. EIS results showed that the pigmented coating improved the protection of both

clean and sulphide-tarnished coupons but not when the surface was covered by AgCl [83].

Lead coatings had also received some attention. Whilst lead is quite resistant to corrosion by typical outdoor pollutants, it is easily corroded when exposed to acetic acid vapours that are quite abundant in some indoor environments especially in closed display cases of museums [84, 85]. Some protective coatings already developed for lead exposed to acetic acid have recently been characterised using EIS and spectroscopic techniques, allowing for a real-time characterisation of the growth of the coating thickness and its protective properties [86, 87].

In most of the aforementioned studies, the experimental setup for the EIS measurements was similar to the EIS tests for general-purpose coatings. The main differences are found in the type of coatings selected that are mainly chosen by their appearance and not their outstanding protectiveness; the application methods since usually coatings in conservation treatments are applied by hand and most to the research on this topic is done on coatings applied in this way, albeit it is known that the performance of the coatings can be reduced; and the preparation of the samples since, in many cases, coatings are applied on metals covered by patinas or corrosion layers. But in some cases modifications were introduced to adapt the experiments to the special requirements of the coatings or the samples. We will review now some of the most significant differences in the experimental details that have been made for the test of coatings for metallic cultural heritage.

As we have already mentioned, the unique characteristics of each object and even different areas of the same object make it very interesting to carry out the EIS measurements directly on the real artefact. With the focus of the in situ evaluation of outdoor bronze works of art, Letardi et al. developed a "contact probe" electrochemical cell that allowed for a direct evaluation of coatings applied to works of art [88, 89]. This probe consisted in a counter electrode and pseudo-reference electrode made of AISI 316 stainless steel inserted in a cylinder of PTFE. A cleaning cloth is soaked in mineral water, fixed to the cell and placed in contact with the object or coupon to be tested [71, 72]. An additional step in this direction has been the development of a handheld low-cost impedance spectroscopy system, incorporating in a single device the electronics for the measurement, the data acquisition system and the electrochemical cell [90, 91]. The authors have demonstrated the applicability of their system for the in situ study of metallic heritage evaluating, by EIS, the protective properties of the coatings applied to different areas of the railing of the Palazzo Reale in Torino [92]. Apart from these major modifications, other smaller changes that could be mentioned are the modifications in the typical flat cell that were made by Price et al. to avoid damage to wax coatings [64]

or the already mentioned thin steel rods used by Hallam et al. instead of the flat samples [76].

Concerning the electrolyte, most of the tests have been carried out using low-concentration (typically 0.1 M) NaCl aqueous solutions [64–66, 74, 82, 83]. The low concentrations are justified by the lower concentration of pollutants that are expected to be found in museums indoors. Dilute Harrison electrolyte [0.35 wt.% of $(NH_4)_2SO_4+$ 0.05 wt.% of NaCl in H_2O] has also been used to test the behaviour of coatings exposed to acid rain [3, 4]. For the tests over real objects, Letardi argues that no external contamination should be incorporated to the object by the electrolyte, so she defends and has used, in her work, mineral water [23, 71–73, 88, 89]. Finally, Hallam et al. used 0.25 M of K_2SO_4 for his tests of thin oil films [76], and Dowsett et al. used acetic acid containing electrolyte for the test of coatings for lead [87].

EIS data are presented using both Bode (as it is common for general-purpose metal coatings) and Nyquist plots. Nyquist plots can be preferable in some of these cases when there are no big differences in the impedance values of the different coatings, and other features (such as the depression of the semicircles or diffusion) can be better observed using this representation [15, 58, 78]. It should also be noted that, with few exceptions [76, 79, 89], there is an unfortunate tendency to publish only the |Z| data of the Bode plot, and the phase angle (ϕ) data are missed. This practise should be avoided since phase angle can provide very valuable information, and some parameters that can be directly obtained from this plot can be useful for the evaluation of the coating performance [42, 93].

Interpretation of the EIS data of coatings in the referred papers is usually based on a simple approach. Most of the works only evaluate the values of |Z| at low frequencies, which, in most cases, is about 10–50 mHz, and its evolution with immersion time or exposure to accelerated test [3, 66, 69, 71–73, 82, 92]. In some cases, the nested equivalent circuit (Fig. 4b) is used for fitting EIS data, but the values of the different components are not reported or a very limited discussion of the model and fitting values is made [5, 64, 65, 74]. Finally, few of the most recent papers make a fitting and discussion of the equivalent circuit used, discussing the evolution of different values of the elements or the application of different models according to the different properties of the coatings [15, 56–58, 76, 78, 79]. Nevertheless, it should be recognised that the EIS data obtained from coatings applied following conservation practises (by hand, without a good control on the coating thickness and, in many cases, over pre-existing corrosion layers or patinas) yield complex diagrams showing depressed semicircles in the Nyquist plots or non-constant slopes in the Bode plots that do not fit to the simple model of Fig. 4a. Some authors have used CPE or Cole–Cole

elements to model this dispersion of the time constants [56–58, 76, 79, 83]. Diffusive effects have also been found by some authors; the EIS results corresponding to these effects are commonly modelled using the Warburg element [56, 57]. Reproducibility is also a common issue in these measurements that has been tackled by some authors making a statistical treatment of multiple data [71–73].

Conclusions

Whilst EIS has been extensively used for testing anti-corrosive properties of metal coatings for almost 30 years, its application to the evaluation of coatings for conservation of metallic cultural heritage has been much more recent. In this field, EIS has begun to be used in recent years of the last century. Since then, its use has gained popularity, and it has been used for testing many different types of coatings for bronze, iron, silver or lead. The methodology has been adapted to the special requirements of the heritage artefacts and the requirements of the conservation professionals.

EIS has been demonstrated to be a very useful and valuable tool to help the conservators–restorers to choose the most appropriate coating for the conservation purposes. It can be used in specially prepared coupons or in situ on the heritage artefacts to evaluate the protective character of the coatings or the natural or artificial patinas. 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.

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