EIS Measurements for the Assessment of the Conservation State of Metallic Works of Art

E. Angelini, D. Assante, S. Grassini, M. Parvis

Abstract**—**The in-situ conservation of metallic artefacts of artistic and historic interest is a scientific challenge. The characterization of surface conditions of the artefacts is mandatory to estimate the effect of the atmospheric corrosion on the metal. Electrochemical impedance spectroscopy (EIS) is a technique that can be employed in order to investigate the phenomena involved at the electrochemical interfaces and to predict the corrosion process. In this paper, a portable instrument specifically realized for EIS measurements on metallic works of art is presented, and the measurement results on two case studies are discussed: the iron bar chains in the Notre Dame Cathedral in Amiens (France) and a large weathering steel monument exposed outdoor in Ferrara.

***Keywords* -** Electrochemical Impedance Spectroscopy, Metallic works of art, Cultural Heritage, Corrosion products, Protection.

I. INTRODUCTION

The increasing attention to the conservation of metallic works of art induces conservators and restorers to take more and more into account the concepts of preventive conservation [1]. According to ICOM-CC (Conservation Committee of the International Council of Museums) preventive conservation my be defined as "*all measures and actions aimed at avoiding and minimizing future damages*". Thus preventive conservation is based on the principle that deterioration may be avoided or slowed down to negligible values and that aging is the result of the interaction with well-defined environmental chemical-physical parameters such as light, temperature, humidity, atmospheric aggressive agents that can be properly controlled.

Two tailored strategies are currently in use: i) the maintenance of the works of art in a controlled environment, for example a showcase with controlled atmosphere and humidity [2], ii) employment of inhibitors and/or protective coatings with high barrier effect in order to slow down the corrosion rate of the metallic alloys [3-5]. The corrosion of metals is an electrochemical reaction, consequently the electrochemical techniques have been employed from a long time both in the industrial field for the study of the corrosion behaviour of different materials and in the niche sector of Cultural heritage in the monitoring of the conservation state of metallic artefacts [6-9]. These techniques allow a direct access to the corrosion rate and do not need indirect measurement of the time dependence of the formation of a specific corrosion product. Furthermore, because of their high sensitivity, the electrochemical techniques cover a wide range of corrosion rates from highly stable to highly unstable materials. Among them, Electrochemical Impedance Spectroscopy (EIS) is a well-established technique extensively employed to investigate metal coatings for general purposes and, due to the possibility of performing the measurements in situ, is particularly suitable for testing the protective effectiveness of barrier layers spontaneously grown or deposited with different techniques on metallic works of art [10-11].

Electrochemical impedance spectroscopy (EIS) consists in the measurement, at different frequencies, of amplitude and phase of the surface impedance of coated metallic objects in order to highlight either the protective effectiveness of the coating or the stability of a corrosion product layer grown onto the metallic surface [12-13].

The impedance measurement is usually carried out by applying an AC potential to an electrochemical cell and then measuring the current, which flows through the cell. The cell contains an electrolytic solution that allows the measurement system to establish electrical connection with the coating and has three electrodes: the counter electrode C, the reference electrode R, and the working electrode W, that is the metallic artefact to be tested. The impedance of interest is defined as the ratio of the voltage between W and R and the current flowing from C to W, as a consequence of the small alternating voltage, 10-20 mV, applied between the two electrodes. The electrochemical potential established between R and W has to be compensated by superimposing a proper DC bias voltage between C and W. The bias voltage has to be continuously adjusted to follow the potential drifts in time.

The excitation signal is generally expressed as a function of time:

$$E(t) = E_0 \sin(\omega t) \qquad (1)$$

where E(t) is the potential at time t, E_0 is the amplitude of the signal, and ω is the radial frequency.

In a linear, or pseudo-linear, system the response signal is shifted in phase (ϕ) and has an amplitude I_0:

$$I(t) = I_0 \sin(\omega t + \phi) \qquad (2)$$

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The following expression allows to calculate the impedance of the system as:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \tag{3}$$

The impedance is expressed in terms of a magnitude, Z_0, and a phase shift, ϕ.

With the Eulers relationship:

$$\exp(j\phi) = \cos\phi + j\sin\phi \tag{4}$$

the impedance may be expressed as a complex function:

$$Z = Z_0 \exp(j\theta) = Z_0 (\cos\theta + j \sin\theta) \tag{5}$$

$$Z(\omega) = Z_{real} + j\, Z_{im} \tag{6}$$

The electrochemical impedance is typically measured in the frequency range 1 mHz - 100 kHz, acquiring 3 to 10 points per decade, while the expected impedance amplitude depends on the area of the surface layer exposed to the solution. For $1 cm^2$ electrode surface, the amplitude ranges from 1 kΩ, for non protective surface layers, to 10 GΩ, for high barrier coatings at low frequency [14].

In the Cultural Heritage field, in situ EIS measurements may be useful, because of the difficulty to move works of art due to their noteworthy dimensions and/ or for security reasons.

Several commercially available EIS instruments show excellent performances, however their design and dimensions prevent an easy moving. Battery operated portable instruments have been recently developed, which allow to perform in situ EIS measurements in a broad frequency range, 1 mHz - 1 MHz [15].

The development of a portable instrument for in situ EIS measurements is subjected to some constrains. The low value of the minimum frequency and the high changes in the impedance values, both with the frequency and the coating quality, may require stable expensive components in order to achieve an acceptable overall accuracy. Moreover, the instrument has to deal with rather critical noise conditions, mainly for measurements at frequencies close to the main frequency. The problems may be solved by employing a measurement system based on a digital approach, a digital signal processor (DSP) [16].

This paper reports the results of two monitoring campaigns carried out by means of in situ EIS measurements in order to acquire information on the conservation state of an indoor artefact, an iron bar chain in the Notre-Dame Cathedral of Amiens (France) and an outdoor artefact, a weathering steel monument in Ferrara (Italy).

II. EXPERIMENTAL

The impedance measurements, widely employed in electrochemical characterizations of materials [17-20], were carried out by means of a portable equipment specifically designed by the authors to work in the field [16]. The instrument is battery operated and may work either as a stand-alone device, storing the results into its memory, or in conjunction with a personal computer to observe the impedance traces as the measurement proceeds. It works in the frequency range 10 mHz - 40 kHz and can measure impedances in the range 1 kΩ–10 GΩ.

The measurement is performed by stimulating the sample with a small alternating voltage, in the range 10–100 mV, while compensating the open corrosion potential (E_{OCP}). Commercially available (Kendall/Tyco ARBO) Bio-Medical Instr. Inc., Warren, MI (US) electrodes, usually employed for electrocardiogram (ECG) measurements were employed in order to avoid any contact of the surface artifacts with possible aggressive electrolytes. These low-cost electrodes are composed of an Ag/AgCl electrode, 25 mm in diameter, surrounded by a conductive gel, 100 Ωm resistivity, with an adhesive material surrounding the gel. The EIS measurements were performed after a 30 min preconditioning of the electrodes surface with mineralized water, in order to avoid possible abnormal behavior due to the difficulty of the polymeric gel to follow the surface roughness and to penetrate inside porous corrosion products, thus losing information on diffusion and ionic charge transfer processes.

On each measuring area, three electrodes have been positioned in order to assess the corrosion layer stability and the measurement reproducibility.

As for many other properties of materials that benefit from modeling, also EIS benefits of the equivalent circuit modeling, as show below [21-24]. The behavior of each element of the cell is described in terms of "classical" electrical components (resistors, capacitors, inductors) plus a few specialized electrochemical elements, as Warbug diffusion elements.

A. Iron bar chain of the Notre-Dame Cathedral of Amiens (France)

The original design of the flying buttresses around the choir of the Cathedral, shown in Fig. 1, had them placed too high to counteract the force of the ceiling arch pushing outwards resulting in excessive lateral forces being placed on the vertical columns. The structure was secured when, centuries later, masons placed a second row of more robust flying buttresses that connected lower down on the outer wall.

This fix failed to counteract similar issues with the lower wall, which began to develop large cracks around the late Middle Ages. This was solved by another patch that consisted of a wrought iron bar chain being installed around the triforium level to resist the forces pushing the stone columns outward.

The iron bar chain is coated by corrosion products constituted by iron oxides and oxy-hydroxides organised in a very complex structure, determined by micro-Raman analysis [25]. The corrosion products are mainly composed by high percentages of ferridryte (46-57%) and goethite (28-35%), while the akaganeite (5-13%) and lepidocrocite (2-11%) fractions are quite small. Micro-characterisation results on transverse sections of the corrosion layers, published elsewhere [26], allow also to measure the thickness which is in the range of 90 - 210 µm.

Fig. 1 - Notre-Dame Cathedral of Amiens.

In situ EIS has been employed to investigate the phenomena involved at the electrochemical interfaces among the various corrosion products and to assess and predict their corrosion behaviour. The corrosion layers are characterized by the presence of cracks and by a variable porosity which can play a very important role in the corrosion mechanism, because they allow the penetration of the electrolyte until the metal surface where, due to the presence of active phases, the corrosion can proceed very fast.

Fig. 2 - In situ EIS measurements monitoring campaign on the iron bar chain of the Notre-Dame Cathedral with the portable instrumentation.

For all these reasons, and also because the expected measured impedance are quite high due to the high thickness of the corrosion products layers, the measurements have been carried out by means of specifically designed two electrodes cells. The cells are constituted by small teflon cylinders, which contain a small amount of mineralized water and a Pt wire as counter electrode. The measurements have been performed by applying a voltage, in the range 50-100 mV, while compensating the open corrosion potential (EOCP), in the frequency range 1 mHz -1 MHz. The portable instrument employed for the in situ measurements is shown in Fig.2 together with the electrodes.

Fig. 3 shows an example of the impedance measurements recorded on different areas of the artefact and presented as Bode diagrams (impedance modulus and phase). The value of the impedance modulus, |Z|, indicates the extent of the corrosion phenomenon at the metal/corrosion products layer interface. The higher the value of the impedance, the higher the electrochemical stability of the superficial layer and, consequently, its protective effectiveness against atmospheric aggressive agents. The Bode plot of a completely protective layer would be characterised by a pure capacitive behaviour with extremely high impedance at very low frequencies. In the case of a damaged film or of an electrochemically active layer, the impedance modulus, |Z|, decreases and a plateau develops at medium frequencies in the plot.

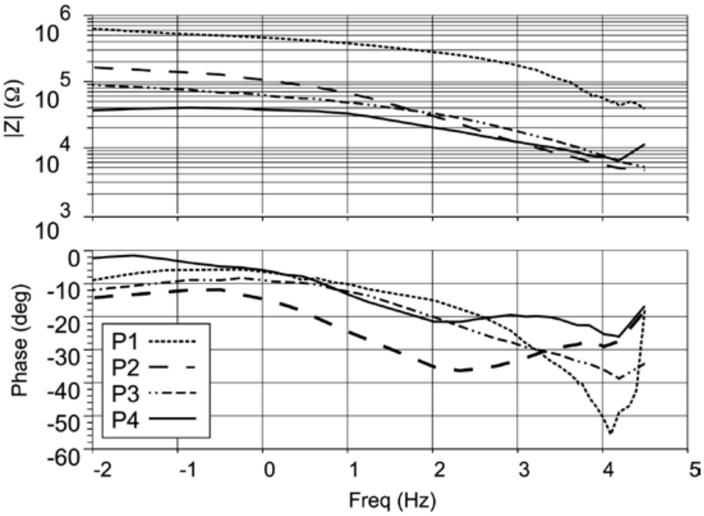

Fig. 3 - Bode plots (impedance modulus, |Z|, and phase) recorded onto different areas of the iron bar chain of the Notre-Dame Cathedral and the structural phase contents of the analysed areas.

The impedance spectra recorded on the iron bar chain allow to evidence different electrochemical behaviours. The area P1 is characterised by the highest impedance value. The measured impedance at low frequency is above 500 kΩ with nearly resistive phase, related to low values of the double layer capacitance. These high impedance values suggest that the corrosion layer is quite compact, indicating a high stability and highlighting its good barrier properties, thus protecting iron from further corrosion. On the contrary, the areas P2 and P3 show impedance values around 100 kΩ. These low impedance values, coupled with the phase trends, suggest that the corrosion layer is porous and not capable of protecting the underneath substrate from corrosion. Finally, the area P4 is characterised by a very low impedance value, below 100 kΩ, which can be related to the poor protective properties of the corrosion layer. The impedance values may be considered as an indicator of the electrochemical stability of the corrosion products layer. The stability of the layer in the measured areas decreases in the following order: P1 > P2 > P3 > P4. The impedance values are also related to the thickness of the corrosion products layer, which increases from an average value of 90 µm for P4, to 150 µm for P2 and P3, to 200 µm for P1. However the recorded impedance differences are much higher than the expected thickness effect. In order to investigate the electrochemical behaviour of the different compounds present in the corrosion products layers, the impedance spectra were fitted with the equivalent circuit shown in Fig. 4.

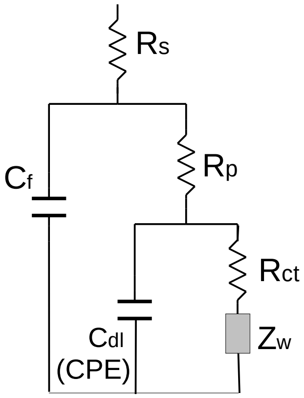

Fig. 4 - Equivalent circuit utilized for fitting the EIS spectra

For all the measurements, the film capacitance (C_f) is very low, hundreds of pF (picofarad) per cm^2; low values of the double layer capacitance (C_{dl}), µF (microfarad) per cm^2, were also obtained. The estimated values of the pore resistance are low, few kΩ. On the contrary, the EIS measurements highlighted differences in the charge transfer resistance, R_{ct}, whose values are shown in Table 1.

TABLE 1 – VALUES OF THE CHARGE TRANSFER RESISTANCE, RCT, OBTAINED BY FITTING THE EIS DATA WITH THE EQUIVALENT CIRCUIT MODEL OF FIG. 4.

Area	R_{ct} (Ω·cm^2)
P1	**$5.0 \cdot 10^5$**
P2	**$1.3 \cdot 10^5$**
P3	**$6.0 \cdot 10^4$**
P4	**$4.0 \cdot 10^4$**

Since R_{ct} is mainly connected to the capability of the ions to penetrate the layers inducing corrosion phenomena, high values are expected where the corrosion layer is mainly composed of stable phases, such as goethite, and in the presence of low amount of ferrihydrite. While low R_{ct} values are expected in presence of ferrihydrite-type reactive phases.

B. *Weathering steel outdoor sculpture*

The sculpture in weathering steel “Reditus ad origines” realized in 1983 by Agapito Miniucchi has been subjected to the EIS monitoring campaign [27]. The sculpture, which illustrates the initiatory path of man, is exposed to the outdoor atmosphere in the Scientific and Technological Pole of Ferrara University, an interesting example of architectural recovery of an industrial area, Fig.5.

Weathering steels or high-strength low alloy steels are a group of steels with the unique characteristic that as they corrode under proper conditions, they form a dense and tightly adherent oxide barrier that seals out the atmosphere and retards further corrosion [28-30]. The corrosion-retarding effect of the protective layer is due to the particular distribution and concentration of the alloying elements as Cu, Cr, Ni, Mn, etc., added in amounts of 0.2–0.3 wt%. The rust develops and regenerates continuously when subjected to the influence of the weather. The formation of the protective layer may be adversely affected by different environmental factors, as temperature and humidity and the presence of aggressive gaseous pollutants (SO_2, NO_x, etc) in the atmosphere.

Fig.5 – “Reditus ad origines” a sculpture in weathering steel by Agapito Miniucchi.

The sculpture under study, like most outdoor weathering steel artefacts, shows areas with different colours of the rust layer depending on the orientation of the metal plates and localized corrosion attacks on some weldments.

The characterization and monitoring campaign was carried out on several areas of the artefact surface, exposed to different orientations (South–West and North–East) and characterised by corrosion product layer of different colours and morphology. A noticeable part of the surface of the external walls is covered by a uniform well-adherent red–orange layer of corrosion products as the semicircular-shaped side of the sculpture, constantly exposed to sunlight.

The other geometric shaped parts of the sculpture are mainly covered by a well-adherent red–brown corrosion product layer. The interstitial regions of the sculpture, the weldment areas, are subjected to some extent to localized attacks. Some large pits are observed with a consequent localized decrease of the thickness of the protective corrosion products layer.

In situ EIS measurements were carried out to correlate the different visual appearance and morphology with the protective effectiveness of the corrosion products layer. In Fig. 6 the impedance spectra representative of the two surface conditions, the red–orange and the red–brown layer, are shown. The data are presented as Bode diagrams, impedance modulus and phase.

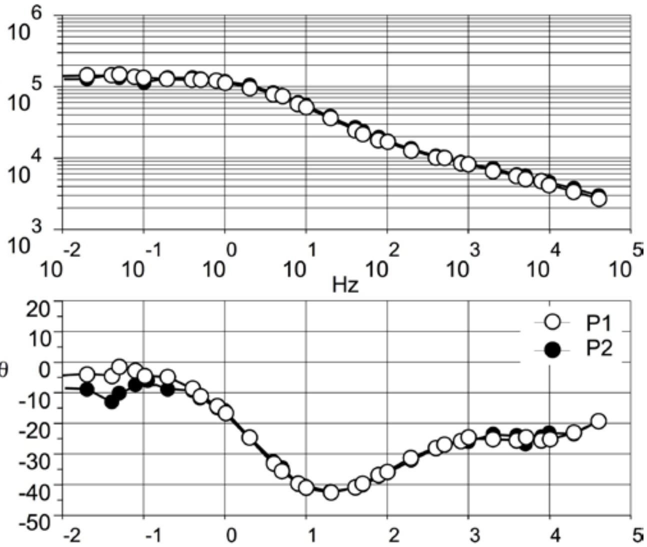

Fig. 6 - EIS spectra recorded on different areas of the sculpture: red–orange areas (top) and red–brown areas (bottom). P1 refers to areas in the South - West side pf the monument; P2 refers to areas of the North-East side of the monument.

The areas of the sculpture covered with the red–orange corrosion product layer show the lower impedance modulus, |Z|, values, from 3 to 8 kΩ. The phase changes vary from 40° to 0° thus indicating that the corrosion process is still in progress and involves mass transfer diffusion effects. The low |**Z**| values can be related to a lower thickness of the corrosion product layer, which is still growing onto the surface and has not yet reached a stable condition. Impedance values, one order of magnitude higher, are measured in the red–brown areas. |**Z**| values are higher than 100 kΩ, indicating that the surface is coated by a more homogeneous and well-adherent corrosion layer. The phase trends are characterized by only one-time constant and involve mass transfer diffusion effects.

Impedance values, one order of magnitude higher, are measured in the red–brown areas. |Z| values are higher than 100 kΩ, indicating that the surface is coated by a more homogeneous and well-adherent corrosion layer. The phase trends are characterized by only one-time constant and involve mass transfer diffusion effects.

A series of tests are planned on the sculpture on an annual basis in order to monitor the evolution of the protective effectiveness of the iron oxides layer in the different areas.

III. CONCLUSIONS

Understanding the degradation mechanisms which may affect a metallic artefact of artistic and historic interest, as a function of the constituent material, the corrosion products, the manufacturing technique, is the starting point for developing tailored approaches for stopping degradation and preventing further damages. Non-invasive techniques to assess the conservation state of the artefact by means of in situ measurements are consequently very interesting tools for restorers and art historians to obtain valuable information on the artefact conservation state.

The EIS approach to the evaluation of the protective effectiveness of the superficial layers of immovable metallic cultural heritage has been presented. The results of the measurements carried out on two case studies show how employing a simple test, which can be performed in situ without damaging the artefacts, it is possible to gain quickly a knowledge of the artifact conservation state highlighting potential danger conditions.

The EIS approach cannot replace morphological and structural analyses as SEM and XRD, performed to understand the chemical nature of the corrosion layers. However EIS measurements can give important information on the morphology and on the adhesion of the corrosion products layers to the metallic substrate evidencing also the presence of cracks.

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