Advances in the design of a gel-cell electrochemical sensor for corrosion measurements on metallic cultural heritage

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) is widely used in corrosion studies and coatings evaluation for metals. However, its applicability to conservation problems in the field cultural heritage is limited by the practical difficulties of performing in-situ measurements on sculptures and monuments. Authors have proposed use of a gel polymer electrolyte (GP-E) cell as an electrochemical sensor to overcome the difficulties of handling liquid electrolytes on irregular surfaces. The aim of this paper is to optimize the design of the G-PE cell for in-situ EIS measurements on metallic cultural heritage, and to characterize in detail the possible effects of the configuration of the cell on the EIS spectra. Parasitic impedances from the reference electrodes have been analyzed to discriminate the response of the working electrode from that arising from artifacts from the cell setup, in order to be able to make an accurate interpretation of the results. This has allowed optimizing the different parameters and designing an effective tool for conservation assessment in metallic cultural heritage.

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1. Introduction

The use of electrochemical impedance spectroscopy (EIS) for the evaluation of patinas and coatings in the field of cultural heritage has raised some interest in the latest decades. Traditional coatings usually applied by conservators such as acrylic resins and waxes have been evaluated using this technique, which has also been used for testing in the development of new coatings and inhibitors [1–8]. Besides these studies, researchers have also worked in the development of portable systems to carry out EIS measurements directly on sculptures and monuments [9–12]. As in other applications, to measure in-situ corrosion, specific sensors need to be developed which are specially adapted to the characteristics of the system under study [13–15]. These field studies are of great importance for cultural heritage conservation, as they provide a proof of coatings performance in real conditions and allow evaluating the conservation condition of the object under study and, in consequence, helping to assess conservation treatments and decisions [16].

The difficulties in applying this technique in the field of metallic cultural heritage can be summarized in two aspects. From a practical point of view, mounting an electrochemical cell on the irregular and non-flat surface of a monument is not an easy task. The second challenge is in interpreting results obtained from complex surfaces with low conductivity electrolytes. Practical difficulties and the different approaches that have been proposed to tackle them have already been discussed in previous papers [17–19]. Among the possible solutions to use EIS for in situ measurements, authors have proposed an agar gelled electrolyte (G-PE) cell which has given promising results [18,20]. The gelled electrolyte has shown to provide good quality and reproducible results without damaging the surface of the sculpture or monument [18]. Another advantage of the G-PE cell over other alternatives is the fact that it is not limited to a pseudo-reference electrode, and a real reference electrode can be incorporated in the cell. For convenience, the initial setup of the G-PE cell used a pseudo-reference electrode, but the use of a real reference electrode would allow measuring the real electrochemical potential of working electrode.

A rough comparative approach based on the low frequency impedance modulus may sometimes be used. Nonetheless a full exploitation of the information content in the EIS spectra, besides the complexity of the surface, requires taking into consideration the possible contribution of the measuring setup also. Authors have already drawn attention on the fact that the use of low conductiv-

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ity electrolytes needed to avoid alteration of the metallic cultural heritage surface can make the cell impedance not negligible [21]. It has been demonstrated too that, on a 3-electrode measurement configuration, artifacts can appear on EIS measurements due to the coupling of the working, reference and counter electrodes [22,23]. Depending on the geometry of the cell and the conductivity of the electrolyte, these artifacts can distort the EIS in the frequencies of interest for corrosion studies (typically 100 kHz to 1 mHz) [24–26], and therefore an accurate interpretation of the working electrode impedance requires special attention to these issues. Another source of distortion of the EIS spectra is the impedance of the reference electrode, which is usually neglected. However, it has been demonstrated that a high-impedance reference electrode can be responsible for parasitic elements in the fitting equivalent circuit [27].

The aim of this paper is to optimize the design of the G-PE cell for in-situ EIS measurements on metallic cultural heritage, and to characterize in detail the effects on the results of the configuration of the cell, including composition of the electrolyte, type of reference and counter electrodes used, and geometric arrangement of the different elements. A deep understanding of these effects is necessary to be able to make an accurate interpretation of the result obtained on real heritage objects using this cell.

2. Experimental

2.1. Cell construction

From the initial prototype [20] several changes have been introduced in the cell design to improve its performance and handling. The cell design is based on a traditional three electrode cell, in which the electrolyte is introduced into a cylinder container with the reference (RE) and counter-electrode (CE) and then placed over the object under study, i.e., the working electrode (WE). The container is made of two hard plastic pieces which act as a mold for the gel. One cylindrical piece supports the electrolyte and electrodes; a second piece acts as a cap and it is removed after the electrolyte solidifies, leaving the first millimeters of the gel cylinder exposed to allow good contact with the WE (Fig. 1).

In the first prototype the cell was constructed with a 2.7 cm diameter grey PVC tube. In this second design the overall shape of the cell has been modified. The base cylinder is now longer and thinner, 2 cm diameter, and has been made with transparent methacrylate. This shape facilitates positioning of the cell in field studies. However, the exact size of the cell can be modified according to the needs of the precise surface to be measured: larger areas might improve the signal, resulting in cleaner spectra; and smaller

areas can be used to measure in narrow spaces or complex geometries. The transparency of the material allows seeing if any bubbles have been trapped in the gel and also the contact between the electrolyte and the metal surface. Electrodes are fastened with a couple of nylon screws to a fixed distance (Fig. 1a and b).

The cell is fixed on a square plastic support (Fig. 1c) which is attached to a double articulated arm, that can be locked in any position with a single central locking knob. This arm is fixed on a tripod with an extensible arm, which allows positioning the cell in the desired place (Fig. 1d). A light pressure is applied, making the flexible gel to adapt to the irregular surface and causing an expulsion of a small amount of electrolyte from the gel (syneresis) which ensures a proper wetting of the surface and assures the ionic conductivity.

The same base cylinder may be used as a standard cell setup if filled with liquid electrolyte; this design allow for a more straightforward comparison between the setup usually adopted for laboratory measurements and the G-PE cell setup to be used on field measurements.

2.2. Electrodes

Pseudo reference electrodes made of stainless steel wire (AISI 316L) and 99.9% silver electrochemically coated with AgCl have been compared to an Ag/AgCl (KCl 1M) reference electrode by CH Instruments. The electrochemically AgCl coated silver wire was prepared as follows: the silver wire was polished with 2000 grain emery paper and then introduced in a 0.05 M KCl solution and an anodic 3.0 V potential vs Ag/AgCl reference electrode was applied for 10–20 min until the surface was coated with a grayish-white layer of silver chloride [28]. A stainless steel mesh or a stainless steel spiral (AISI 316L) have been used as a counter electrode.

Shape and position of electrodes has been designed to minimize ohmic drops and current distribution inhomogeneity, taking into account that measurements will be done always in low conductivity electrolytes. Pseudo reference electrodes are L shaped, with the lower part close to the WE, to minimize the ohmic drop, and parallel to the surface the WE. The non-measuring part of the electrode is covered with a heat shrink sleeve. The CE was also placed parallel to the WE surface and above the RE, covering an area as equal as possible to the WE. This configuration was chosen to ensure a uniform and parallel distribution of the current lines, and having the sensing part of the RE in an equipotential line [25,29].

Results obtained with different electrodes are shown in the figures with the following labels: <StdRE>, <SRE> and <AgRE> for "standard", "stainless steel" and "AgCl coated Ag wire" reference electrodes respectively, while the suffix <−e> or <−m> stands for spiral or mesh CE.
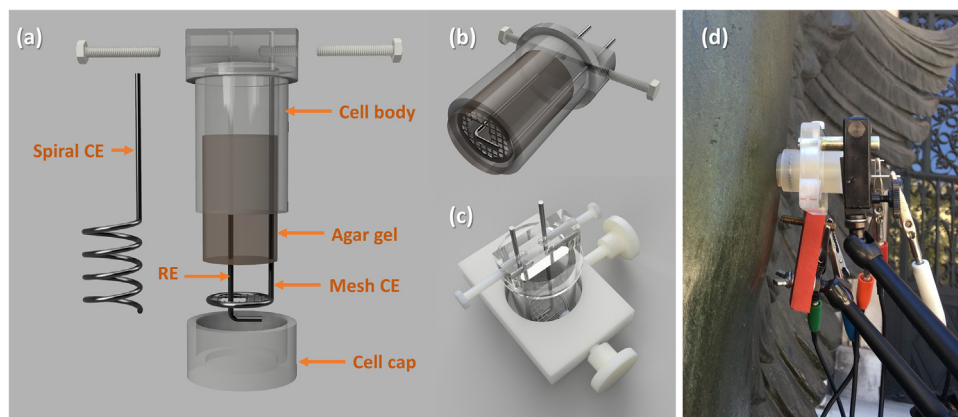

Fig. 1. Cell design: exploded view (a) mounted cell (b) and support (c). The picture in the right (d) shows the complete measuring setup on the surface of an outdoor sculpture.