



The use of agar gelled electrolyte for in situ electrochemical measurements on metallic cultural heritage



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ABSTRACT

Electrochemical techniques, such as electrochemical impedance spectroscopy (EIS), are widely used for corrosion studies. However, their applicability to studies on metallic cultural heritage has been less spread due to the practical difficulties of performing measurements in-situ on sculptures or monuments. One interesting approach to this application is the use of gel polymer electrolytes (GP-E) to overcome the difficulties of handling liquid electrolytes on irregular leaning surfaces. In this paper, the behavior of an agar gelled electrolyte with a portable cell is evaluated for EIS measurements over three types of bronze coupons, and compared with a traditional liquid cell. The influence of the addition of agar in the reproducibility and repeatability of measurements is assessed, as well as the possible interaction of agar with the corrosion process. Results show that, although agar slightly accelerates the anodic process, it does not significantly affect the cathodic reaction and does not introduce new reactions in the corrosion mechanism. It is demonstrated that the GP-E allows obtaining reproducible and good quality EIS spectra, comparable to the liquid cell. Hence, it can be used for comparative in-situ measurements, being a very valuable tool for the evaluation of patina and coatings on metal cultural heritage.

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1. Introduction

Electrochemical Impedance Spectroscopy (EIS) is a widely used technique for corrosion studies, as it gives qualitative and quantitative information on corrosion processes and corrosion resistance. In the field of metallic cultural heritage it can be a very useful tool as it can be used to evaluate the actual situation of an object, i.e., if there is an active corrosion process or it has a stable patina, how much a protective coating has increased its corrosion resistance, which coating offers the better corrosion protection or when a protection treatment is beginning to fail [1]. The answer to these questions can help to take conservation decisions and establish priorities when time and resources are limited. For this reason, EIS constitutes a very valuable complement to classical analytical methods widely used in conservation science (XRF, Raman, XRD, FTIR, etc.), which give information on composition and structure, but cannot give quantitative information on their corrosion behavior.

However, the application of this technique for corrosion studies in the field of cultural heritage poses some particular difficulties

[1]. Some studies have been carried out using artificial coupons that try to mimic the original composition of metallic artifacts [2–5], or patinas scrapped from the monuments [6], using traditional laboratory techniques. Nevertheless, this kind of laboratory studies provide limited information, due to the impossibility to reproduce the composition and characteristics of patinas that have formed over several hundred years. On the other hand, it is always desirable to evaluate conservation conditions on the real objects to undertake conservation decisions. At this point, the main issue is how to perform electrochemical measurements using a conventional three electrode cell with a liquid electrolyte on a non-flat, irregular and leaning surface as is usually the one of metallic sculptures and monuments.

Since the beginning of application of electrochemical techniques to cultural heritage, mainly electrochemical impedance spectroscopy, researchers have worked on portable devices with different approaches. On one side, methods for retaining the liquid electrode in contact with the object have been developed, as the Letardi's contact probe [7,8]. This method has been successfully applied to the evaluation of cultural heritage, but still has the disadvantage of handling a liquid electrolyte. On the other side, commercial gel electrodes or prepared gel electrodes based on same type of gels have also been proposed [9,10]. This system avoids the liquid electrolyte, so it is convenient for field use. Nevertheless, the conductivity of these gels is poor, so irregular

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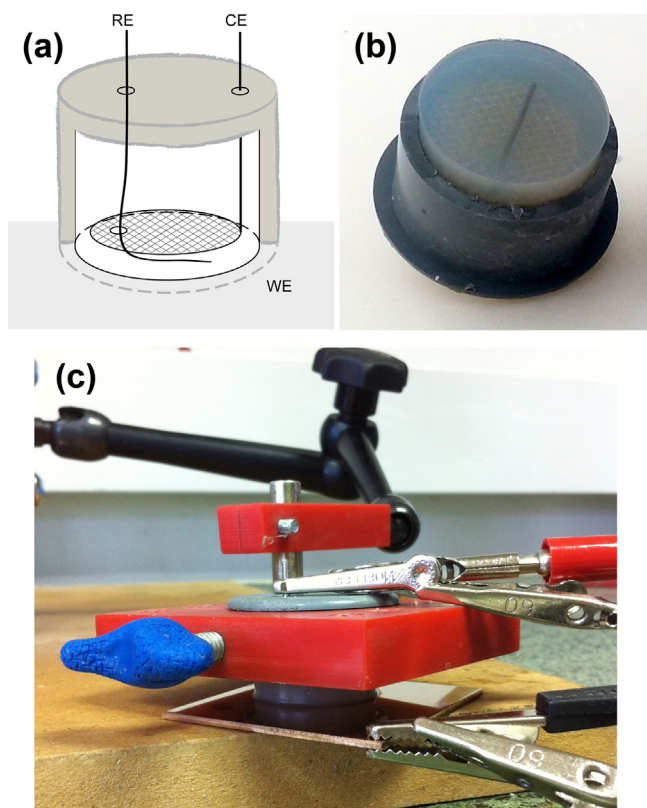


Fig. 1. Cell design scheme (a), picture of the cell with the gelled electrolyte from the side in contact with the WE (b) and picture of the cell/sample connection setup (c).

distribution of currents might mislead the results [11]. Additionally, the composition of the electrolyte cannot be selected to test the resistance of the metal to specific environments in commercial electrodes, or it is limited by the swelling equilibrium of synthesized (anionic) gels [12]. This is a major drawback of this approach, since for corrosion studies the composition and pH of the electrolyte play a key role in the process. So although the idea of gel electrolytes seems to be a good choice, solutions that allow the selection of the adequate electrolyte have to be further investigated.

The use of solid electrolytes has been explored in the last decades for applications where liquid electrolytes present inconveniences such as handling difficulties or risk of leaking or evaporation of the liquid [13]. The development of new and improved solid electrolytes has mainly focused in the fields of energy storage (lithium batteries, solar and fuel cells . . .) and electrochromic devices. Different kinds of polymers have been assayed as solid electrolytes, from polyethylene oxide (PEO) since the 70's of the last century to polymer mixtures, composites or hybrid inorganic–organic polymer electrolytes. In last years, natural polymers have been considered as a cheap and green alternative, including gelatin, chitosan, agar, etc. Among these, agar offers interesting properties making it a good candidate for these applications.

Agar is a natural polysaccharide extracted from certain species of red seaweeds. It is composed of two fractions, agarose and agaropectin, both made up of repeating units of agarobiose. While agarose is a neutral linear polymer, agaropectin is partially modified by different hydrophobic (methoxy) and polar (sulfate, pyruvate) side groups [14].

Since its discovery agar has been using as a gelling agent for many different uses. In this case it has been the choice as it is

Table 1

Composition of the 10x concentrated synthetic rain used as electrolyte.

Composition	Conc. mg/l
CaSO ₄ ·2H ₂ O	14.43
(NH ₄) ₂ SO ₄	15.04
(NH ₄)Cl	19.15
NaNO ₃	15.13
CH ₃ COONa	3.19

pH adjusted to 6.5 with HNO₃.

inexpensive, easy and quick to prepare and can support a wide range of aqueous electrolytes, forming translucent gels. Furthermore, agar has a very interesting property, syneresis, which is the ability of weeping or expelling liquid from a gel [15]. This helps wetting the surface and favors contact between the electrolyte and the working electrode (i.e., the metal under study) in field corrosion tests.

Previous studies have been carried out on agar based electrolytes, but these studies have focused on its preparation with different salts or acids in order to achieve the maximum conductivity, with good optical and mechanical properties [16–18]. For its use as electrolyte in electrochemical corrosion



Fig. 2. Bronze coupons used for the electrochemical tests: clean bronze A (top), and artificially patinated bronze B, with a dark potassium sulfide patina (bottom right) and a green ammonium chloride patina (bottom left).

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