

# Desarrollo de una celda electroquímica en gel para la evaluación in situ del patrimonio cultural metálico

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A mi madre.

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## CONTENIDOS PUBLICADOS Y PRESENTADOS

Los siguientes trabajos publicados forman parte de la tesis doctoral y como tales se incluyen en la misma con los correspondientes permisos del propietario de los derechos. El papel de la doctoranda en todos estos trabajos incluye el diseño y realización de la parte experimental, interpretación de los resultados y redacción del manuscrito.

- B. Ramírez Barat, E. Cano, ‘Advances for in-situ EIS measurements and their interpretation for the diagnostic of metallic cultural heritage: a review’, *ChemElectroChem*, (2018), 5, pp 2698–2716. DOI: 10.1002/celec.201800844.
  - Papel: revisión de todos los artículos y redacción del manuscrito.
  - Incluido en el capítulo 1 apartado 1.2.2. La aplicación de la EIS en patrimonio cultural. Estado de la cuestión.
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- B. Ramírez Barat, E. Cano, ‘The use of agar gelled electrolyte for in situ electrochemical measurements on metallic cultural heritage’, *Electrochimica Acta*, 182(2015) 751-62. DOI: 10.1016/j.electacta.2015.09.116
  - Papel: realización de la parte experimental, co-interpretación de los resultados y co-redacción del manuscrito.
  - Incluido en el capítulo 4. apartado 4.1
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- B. Ramírez Barat, E. Cano, P. Letardi, ‘Advances in the design of a gel-cell electrochemical sensor for corrosion measurements on metallic cultural heritage’, *Sensors & Actuators: B Chemical* 261(2018) 572-80. DOI: 10.1016/j.snb.2018.01.180
  - Papel: co-diseño y realización de la parte experimental, interpretación de los resultados y redacción del manuscrito.
  - Incluido en el capítulo 4 apartado 4.2.1. Construcción de la celda y optimización de los parámetros de diseño.
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- P. Letardi, B. Ramírez Barat, E. Cano, ‘Analysis of the influence of the electrochemical cell setup for corrosion measurements on metallic cultural heritage’, *European Corrosion Congress - EUROCORR*, Prague, 2017.
  - Papel: co-diseño y realización de la parte experimental, co-interpretación de los resultados y revisión del manuscrito.
  - Parte de los resultados de este trabajo se han incluido en el capítulo 4 apartado 4.2.2. Comparación con otros sistemas.
  - El material de esta fuente incluido en la tesis no está señalado por medios tipográficos ni referencias.

- B. Ramírez Barat, E. Cano: “Agar vs agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage”, *ChemElectroChem*, (2019), 6 (9), pp. 2553-2559. DOI: 10.1002/celc.201900344
  - Papel: diseño y realización de la parte experimental, interpretación de los resultados y redacción del manuscrito.
  - Incluido en el capítulo 4 apartado 4.2.2. Modificación del electrólito.
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- P. Letardi, B. Ramírez Barat, M. Albini, P. Traverso, E. Cano, E. Joseph, ‘Copper Alloys and Weathering Steel Used in Outdoor Monuments: Weathering in an Urban-Marine Environment’, en: R. Menon, C. Chemello, A. Pandya (Eds.), *METAL2016, 9th interim meeting of the ICOM-CC Metals Working Group*, New Delhi, India, 2016, pp. 320-8.
  - Papel: realización de la parte experimental, interpretación de los resultados y co-redacción del manuscrito en los apartados de metalografía, microscopía electrónica e impedancia.
  - Incluido en el capítulo 4 apartado 4.3.1.1. Evaluación de pátinas
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- B. Ramírez Barat, T. Palomar, B. Garcia, D. De la Fuente, E. Cano, ‘Composition and Protective Properties of Weathering Steel Artificial Patinas for the Conservation of Contemporary Outdoor Sculpture’, en: R. Menon, C. Chemello, A. Pandya (Eds.), *METAL 2016 9th interim meeting of the ICOM-CC Metals Working Group* New Delhi, India, 2016, pp. 314-9
  - Papel: diseño y realización de la parte experimental, interpretación de los resultados y redacción del manuscrito.
  - Incluido en el capítulo 4 apartado 4.3.1.1. Evaluación de pátinas
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- B. Ramírez Barat, E. Cano, ‘Evaluación in situ de recubrimientos protectores para patrimonio cultural metálico mediante espectroscopía de impedancia electroquímica’, *Ge-conservación*, 8(2015) 6-13. <https://ge-iic.com/ojs/index.php/revista/article/view/278>
  - Papel: diseño y realización de la parte experimental, interpretación de los resultados y redacción del manuscrito.
  - Incluido en el capítulo 4 apartado 4.3.1.2. Evaluación de recubrimientos
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.

- B. Ramírez Barat, A. Crespo, E. García, S. Díaz, E. Cano, 'An EIS study of the conservation treatment of the bronze sphinxes at the Museo Arqueológico Nacional (Madrid)', *Journal of Cultural Heritage*, 24(2017) 93-9. DOI: 10.1016/j.culher.2016.10.010
  - Papel: realización de la parte experimental, co-interpretación de los resultados y co-redacción del manuscrito.
  - Incluido en el capítulo 4 apartado 4.3.2.1 Estudio de las esfinges del Museo Arqueológico Nacional
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.
  
- B. Ramírez Barat, A. Crespo, E. Cano, 'In situ evaluation of outdoor sculpture with a gel polymer electrolyte cell', en: M.J. Mosquera, A. Gil (Eds.), *TechnoHeritage 2017. 3rd International Congress Science and Technology for the Conservation of Cultural Heritage*, Cádiz, 2017. CRC Press, pp. 83-85.
  - Papel: realización de la parte experimental, interpretación de los resultados y redacción del manuscrito.
  - Preprint incluido en el capítulo 4 apartado 4.3.2.3 Obras en el Museo de Escultura de Leganés.
  - Todo material de esta fuente incluido en la tesis está señalado por medios tipográficos y una referencia explícita.

## OTROS MÉRITOS DE INVESTIGACIÓN

Además de los resultados incluidos en la tesis, existen otros resultados relacionados con contenido y desarrollo de la misma, que se relacionan a continuación, y que incluyen congresos, cursos, capítulos de libro y artículos de colaboración:

### *Publicaciones:*

- G. Monrrabal, B. Ramírez-Barat, A. Bautista, F. Velasco, E. Cano, 'Non-destructive electrochemical testing for stainless-steel components with complex geometry using innovative gel electrolytes', *Metals*, 8 (2018).
- J. Redondo-Marugán, J. Piquero-Cilla, M.T. Doménech-Carbó, B. Ramírez-Barat, W.A. Sekhaneh, S. Capelo, et al., 'Characterizing archaeological bronze corrosion products intersecting electrochemical impedance measurements with voltammetry of immobilized particles', *Electrochimica Acta*, 246(2017) 269-79.
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### *Otros trabajos presentados en workshops y congresos.*

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### *Actividades de formación y difusión*

- "Evaluación del estado de conservación del patrimonio cultural metálico mediante técnicas electroquímicas in-situ" (1h). *Nuevos retos en la caracterización y conservación de los bienes del Patrimonio*. UIMP. Santander, 2-5 julio de 2019.
- Cultural "Avances en protección y diagnóstico del patrimonio cultural metálico. Aplicación de técnicas electroquímicas" (1.5h). *Innovaciones en conservación-restauración del patrimonio metálico arqueológico*. Escuela de Patrimonio Histórico de Nájera. 23-25 de mayo de 2018.
- "La ciencia al servicio de la conservación y restauración del patrimonio metálico" (1.5h) *VII Encontro de Conservación e Restauración: Conservación e restauración de metais arqueológicos*. Museo Provincial de Pontevedra 15-17 de noviembre de 2017.
- Prácticas con equipos portátiles in situ (4h) en el *Encuentro Metodologías avanzadas no destructivas: análisis de patrimonio (MetAnD)*. Universidad Internacional Menéndez Pelayo. 2017.
- 'In situ electrochemical impedance spectroscopy (EIS) for conservation assessment', *1st IPERION-CH Training Camp "HERITAGE SCIENCE IN PRACTICE"*, Nájera 14th-18th November 2016 (6h).

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*"Bástame solo suplicaros acojáis con benevolencia este insignificante trabajo en el que, como dije al principio, se contendrán grandes defectos debido sin duda a mi natural insuficiencia."*

Final del discurso para la obtención del grado de doctor de Santiago Ramón y Cajal

# RESUMEN

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A lo largo de toda la historia, la humanidad ha tratado de preservar ciertos objetos que por diversos motivos han adquirido un valor y un significado para la sociedad que los ha poseído, constituyendo su patrimonio cultural. En ese esfuerzo por preservar el pasado para las generaciones presentes y futuras, la investigación científica ha ido adquiriendo una relevancia progresiva. La ciencia de la conservación trata de comprender los problemas y aportar soluciones para la conservación del patrimonio, tanto desde el punto de vista tecnológico como estratégico o de sostenibilidad. El adecuado diseño y planificación de las estrategias de conservación de los objetos y colecciones del patrimonio cultural son fundamentales, y deben tener en cuenta las limitaciones tecnológicas y de recursos.

El fin de esta tesis ha sido contribuir desde la Ciencia e Ingeniería de Materiales a este objetivo, concretamente en el ámbito del patrimonio cultural metálico, desarrollando una herramienta de diagnóstico del estado de conservación y de los sistemas de protección para este tipo de bienes culturales.

El principal problema para la conservación del patrimonio metálico es la corrosión, que tiene lugar por interacción entre el objeto metálico y el medio que lo rodea. Para enfrentarse a este problema, los conservadores de patrimonio metálico cuentan con dos estrategias: el control de las condiciones ambientales –lo que no siempre es posible- o el empleo de recubrimientos protectores, que lo aíslen del medio, que es el método más habitual en la práctica de la conservación. Sin embargo, cualquier método presenta limitaciones, por lo que resulta de gran relevancia el poder evaluar la eficacia y la duración de los sistemas empleados, antes de que aparezcan efectos negativos en el objeto. Así, los recubrimientos habituales en conservación –principalmente ceras y barnices acrílicos- tienen una capacidad protectora bastante limitada y deben ser renovados cada cierto tiempo. Esto conlleva la necesidad de conocer y evaluar el comportamiento de los sistemas aplicados, con especial hincapié en su durabilidad.

La espectroscopía de impedancia electroquímica (EIS) es una técnica electroquímica que permite estudiar los procesos de corrosión en los metales en diferentes medios y evaluar la capacidad protectora de los recubrimientos, por lo que a priori resulta una



técnica idónea para este propósito. Sin embargo, la aplicación de la EIS a la conservación del patrimonio cultural metálico no es una práctica generalizada, por las dificultades particulares que presenta su aplicación en este campo. Las características propias de los bienes culturales, hacen que en muchos casos los estudios de laboratorio no sean suficientes, y que el objeto no se pueda trasladar, por lo que resulta imprescindible la realización de medidas *in situ*, directamente sobre la superficie del objeto a conservar.

La aplicación de técnicas electroquímicas requiere montar una celda electroquímica, en la que poner en contacto la superficie del material que se va a estudiar con un electrólito líquido y los electrodos auxiliares (electrodo de referencia y contraelectrodo). Esta tarea resulta compleja en el caso de superficies irregulares y no horizontales como las de una escultura. Para dar una solución a este problema, el objetivo de esta tesis ha sido el desarrollo de una celda electroquímica con un electrólito en gel, específicamente diseñada para la realización de medidas *in situ* sobre patrimonio cultural.

Para el diseño se han tenido en cuenta diversos factores relacionados con este tipo de medidas, tales como la forma y tamaño de la celda para facilitar su colocación en la superficie de la obra, la naturaleza, geometría y posición de los electrodos para obtener una señal de calidad, o el tipo de soporte adecuado para lograr una buena estabilidad mecánica.

El trabajo se ha estructurado en varios apartados, si bien no recorrido su no ha sido lineal, ya que los avances y dificultades en cada uno de los aspectos o subapartados han contribuido al desarrollo de los demás.

El primer paso ha sido comprobar la posibilidad de realizar medidas de impedancia utilizando un electrólito gelificado con agar, abordando cuestiones como la validez, reproducibilidad o repetitividad de los resultados. Una vez verificada la obtención de medidas de calidad y comparables a las de un electrólito tradicional, se ha estudiado en mayor detalle la contribución del agar en las medidas, para establecer la concentración más adecuada tanto desde el punto de vista electroquímico como mecánico. En esta misma línea, se ha comparado el comportamiento del agar y de la agarosa, uno de los dos polisacáridos que componen este material, y que es el responsable de las propiedades gelificantes.

El siguiente paso ha sido analizar en detalle el comportamiento del sistema completo, incluyendo los electrodos (de referencia y contraelectrodo) para optimizar el diseño. Así, se han estudiado diferentes configuraciones de celda con electrodos de distinta naturaleza y geometría, un factor que ha demostrado su relevancia para minimizar la aparición de artefactos en las medidas al emplearse electrólitos de baja conductividad.

En paralelo al desarrollo y estudio de la celda, se han realizado medidas sobre diferentes sustratos para evaluar la aplicabilidad del sistema desarrollado a la resolución de problemas de conservación. Por un lado, se han realizado ensayos de laboratorio sobre probetas de bronce y acero patinable con diversas pátinas y recubrimientos, simulando cuestiones que se abordan habitualmente en la conservación del patrimonio metálico; por otro lado, se han realizado estudios *in situ*, sobre obra real (principalmente escultura moderna y contemporánea del Museo Arqueológico Nacional, Museo de Escultura de Leganés y colección de escultura del campus de la Universidad Politécnica de Valencia), para comprobar y validar el diseño de la celda en su modo de aplicación final, e ir introduciendo las modificaciones necesarias para solventar las dificultades prácticas que se iban encontrando en diferentes situaciones.

Todo ello ha permitido concluir con éxito con el diseño de una celda electroquímica con electrólito en gel, adecuada para la realización de medidas electroquímicas *in situ* sobre el patrimonio cultural metálico, aportando una nueva herramienta para avanzar en la conservación de este tipo de patrimonio.

# ABSTRACT

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Along history, mankind has sought to preserve certain objects which, for multiple reasons, have acquired a special value and a meaning for the society that owned them, constituting their cultural heritage. In this effort to preserve the past for the present and future generations, scientific research has gained an increasing relevance. Conservation science aims at understanding problems and provide solutions for the conservation of heritage, both from the technological and sustainable point of view. The proper design and planning of strategies for the conservation of cultural heritage objects and collections is essential, and should take into account both technological and resources limitations.

The purpose of this thesis is to contribute through Materials Science and Engineering to this objective, in particular in the field of metallic cultural heritage, developing a tool of diagnosis of the state of conservation and evaluation of protection systems for this type of heritage.

The main challenge for the conservation of the heritage metal is corrosion, which takes place because of the interaction between the metal object and its environment. To deal with this problem, metal conservators have two strategies: control of environmental conditions - which is not always possible - or the use of protective coatings to isolate the metal object from the environment, which is the most frequent solution in conservation practice. Nonetheless, any method has certain limitations. For this reason, it is of great importance being able to evaluate the effectiveness and lifespan of protective systems before damage occurs.

Common coatings in heritage conservation –mainly waxes and acrylic varnishes- have a quite limited protective ability, and have to be renewed periodically. This entails the need of knowing and evaluating the behavior of applied protective coatings, with particular focus on durability.

Electrochemical impedance spectroscopy (EIS) is an electrochemical technique that allows to investigate corrosion mechanisms of metals in different environments and to

evaluate the protective properties of coatings. This makes EIS the ideal technique for this purpose.

Unfortunately, the use of EIS in metal cultural heritage is not a widespread practice, due to the particular difficulties in applying this technique in heritage objects. The special characteristics of cultural heritage assets make it necessary to carry out on site measurements, directly on the surface of the object to preserve.

The use of electrochemical techniques requires mounting an electrochemical cell, in which the surface of the material under study is placed in contact with a liquid electrolyte and the auxiliary electrodes (reference and counter electrode). This is not an easy task for irregular and non-horizontal surfaces as in a sculpture. To overcome this challenge, the objective of this thesis is to develop an electrochemical cell with a gelled electrolyte, specifically designed for conducting in situ electrochemical measurements on cultural heritage.

The design has taken into account various factors related to this type of measures, such as the shape and size of the cell to be placed on the surface of the object, the nature, geometry and position of the electrodes to obtain a quality signal, or the fixing system to ensure a good mechanical stability.

This work has been structured into several sections, although its progress has not been linear in time, since the advances and difficulties in each of the aspects or subsections have contributed to improve and develop the others.

The first step has been checking the possibility of performing impedance measures using an agar gelled electrolyte, addressing issues such as validity, reproducibility, or repeatability of the results. Once verified the quality of measurements, comparable to a traditional electrolyte, detail the contribution of the agar been studied in greater detail, to establish the most appropriate concentration both from the electrochemical and mechanical point of view. With the same purpose the behavior of agar and agarose has been compared.

The next step was to analyze in detail the behavior of the entire system, including electrodes (reference and counter electrode) to optimize the design. Thus, we have studied different configurations of cell with electrodes of different nature and

geometry, a factor that has shown its relevance to minimize the appearance of artifacts in the measurements when using low-conductivity electrolytes.

In parallel to the development and study of the cell, measurements on different substrates have been performed to assess the applicability of the developed system to solve conservation problems. On the one hand, laboratory tests on bronze and weathering steel coupons, with different patinas and coatings were performed, simulating issues usually addressed in metallic heritage conservation; on the other hand, studies have been conducted in situ on real work (mainly modern and contemporary sculpture of the National Archaeological Museum, Museum of Sculpture in Leganes and the sculpture collection at the Polytechnic University of Valencia campus), to check and validate the design of the cell in its final application mode, and to introduce the modifications necessary to solve the practical difficulties that were found in different situations.

This has allowed concluding successfully with the design of an electrochemical cell with a gel electrolyte, suitable for carrying out on-site electrochemical measures on metallic cultural heritage, providing a new tool for a better conservation of this kind of heritage.

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# 1. INTRODUCCIÓN

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## 1.1. La conservación del patrimonio cultural metálico.

### 1.1.1. Los metales como patrimonio.

Desde tiempos remotos, los metales han desempeñado un papel fundamental en la historia de la humanidad, estando su empleo estrechamente ligado al desarrollo de las sociedades, tanto a nivel tecnológico, como económico, social y cultural. La versatilidad de los metales gracias a sus propiedades mecánicas, durabilidad, conformabilidad y aspecto, ha permitido al hombre disponer de armas y herramientas, pero también de monedas, joyas, esculturas, etc. Por ello, el patrimonio metálico forma una parte importante del legado histórico y cultural que el hombre ha tratado siempre de conservar para sí y transmitir a generaciones futuras.

Como ocurre con todos los materiales, los objetos metálicos tienden a degradarse con el tiempo, y para luchar contra la pérdida de nuestro patrimonio la *ciencia de la conservación* trata de desarrollar herramientas adecuadas para su diagnóstico y conservación.

### 1.1.2. Degradación del patrimonio metálico.

Aunque los objetos metálicos también pueden sufrir daños mecánicos, el principal problema de conservación en el patrimonio cultural en metal es la corrosión. De hecho, la corrosión es la principal causa de deterioro de todos los materiales metálicos, formen o no parte de nuestro patrimonio, constituyendo un problema de dimensión global.

La degradación de los materiales metálicos por corrosión supone considerables pérdidas económicas; un conocido estudio de la NACE<sup>1</sup> realizado entre 1999 -2001 situaba las pérdidas anuales por corrosión en EE.UU. en 276 mil millones de dólares, aproximadamente el 3.1% del PIB [1]. En el caso del patrimonio cultural metálico, las

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<sup>1</sup> National Association of Corrosion Engineers.



pérdidas van mucho más allá de la dimensión económica ya que generalmente se trata de piezas únicas e irremplazables. Dada la magnitud del problema, la lucha contra la corrosión es un campo de estudio muy amplio y en constante desarrollo, que se aborda desde diferentes estrategias.

Tal y como se define en la norma ISO 8044:2015 [2] , la corrosión es una consecuencia de la interacción entre el objeto y el medio en el que se encuentra. En base a esto, podemos afirmar que existen tres estrategias de lucha contra la corrosión: modificar el medio, modificar el objeto, o evitar la interacción.

*ISO 8044:2015, ' Corrosión de metales y aleaciones. Términos principales y definiciones*

*"La interacción fisicoquímica entre un metal y su entorno que da como resultado cambios en las propiedades del metal, y que puede conducir a un deterioro significativo de la función del metal, el medio ambiente o el sistema técnico, del que forman parte".*

La modificación del objeto, mediante el diseño y selección de materiales, es una posible solución a nivel industrial, e incluso se podría aplicar en creación de nueva obra contemporánea, pero obviamente no es aplicable cuando hablamos de metales históricos o arqueológicos.

La modificación del medio ambiente supone actuar sobre los factores responsables de la corrosión, que en el caso del patrimonio cultural son básicamente la humedad y los contaminantes. Esta es –al menos teóricamente- una posibilidad en espacios interiores, pero constituye una opción muy limitada para actuar en obras concretas en el caso de espacios exteriores, más allá de los avances en la reducción de ciertos contaminantes en los últimos años.

Cuando no es posible actuar sobre el objeto ni sobre el medio, la única solución es tratar de evitar la interacción entre ambos. Por ello, el uso de recubrimientos protectores e inhibidores de la corrosión es probablemente uno de los campos más desarrollados a nivel industrial. Lamentablemente, la mayor parte de los avances en este sector no son trasladables al patrimonio cultural que, por sus características particulares, requiere abordar el problema de una forma diferente. Para entenderlo es

necesario introducir algunos conceptos sobre la conservación y restauración del patrimonio.

### 1.1.3. Conservación de metales. Criterios y metodología.

El concepto de conservación de los objetos del patrimonio cultural va más allá de la conservación material; lo que hace que un objeto forme parte de nuestro patrimonio incluye aspectos inmateriales como el significado, el valor para la sociedad que lo posee o su historia. Esta concepción es uno de los motivos por el que tanto los conceptos de conservación y restauración en sí como los métodos y los criterios nunca han sido uniformes, y han ido evolucionando a lo largo de la historia.

En el año 2008 el Comité de Conservación del Consejo Internacional de Museos (ICOM-CC) adoptó una resolución sobre la terminología de conservación para facilitar la comunicación ya que tradicionalmente los mismos términos se empleaban con diferentes significados en distintos lugares. De acuerdo con esta resolución [3], debemos hablar de:

**Conservación** – *Todas aquellas medidas o acciones que tengan como objetivo la salvaguarda del patrimonio cultural tangible, asegurando su accesibilidad a generaciones presentes y futuras. La conservación comprende la conservación preventiva, la conservación curativa y la restauración. Todas estas medidas y acciones deberán respetar el significado y las propiedades físicas del bien cultural en cuestión.*

**Conservación preventiva** – *Todas aquellas medidas y acciones que tengan como objetivo evitar o minimizar futuros deterioros o pérdidas. Se realizan sobre el contexto o el área circundante al bien, o más frecuentemente un grupo de bienes, sin tener en cuenta su edad o condición. Estas medidas y acciones son indirectas – no interfieren con los materiales y las estructuras de los bienes. No modifican su apariencia.*

**Conservación curativa** – *Todas aquellas acciones aplicadas de manera directa sobre un bien o un grupo de bienes culturales que tengan como objetivo detener los procesos dañinos presentes o reforzar su estructura. Estas acciones sólo se realizan cuando los bienes se encuentran en un estado de fragilidad notable o se están deteriorando a un ritmo elevado, por lo que podrían perderse en un tiempo relativamente breve. Estas acciones a veces modifican el aspecto de los bienes.*

***Restauración** – Todas aquellas acciones aplicadas de manera directa a un bien individual y estable, que tengan como objetivo facilitar su apreciación, comprensión y uso. Estas acciones sólo se realizan cuando el bien ha perdido una parte de su significado o función a través de una alteración o un deterioro pasados. Se basan en el respeto del material original. En la mayoría de los casos, estas acciones modifican el aspecto del bien.*

En base a estas definiciones, podemos entender que los criterios actuales de conservación se basan en la regla de mínima intervención: “*tan poco como sea posible, tanto como sea necesario*”. Es necesario actuar para frenar el deterioro del objeto, pero esa actuación se debe limitar para respetar sus valores materiales, estéticos, históricos y conceptuales. Esto implica que cualquier intervención debe ser mínima y no alterar el objeto original. Unida a esta idea de no alterar el original, se plantea la además la necesidad de que cualquier tratamiento debe ser reversible.

Para cumplir con estos criterios y considerando las dos posibles vías de lucha contra la corrosión, las estrategias en el campo de la conservación del patrimonio cultural metálico incluirán la actuación sobre el medio –conservación preventiva- y los recubrimientos protectores –conservación curativa-.

#### **1.1.3.1. Modificación del medio ambiente: Conservación preventiva.**

La conservación preventiva resulta siempre, desde el punto de vista teórico al menos, la opción más adecuada. Eliminando los factores de riesgo se elimina el daño sin intervenir sobre el objeto. Sin embargo, la conservación preventiva de los bienes metálicos presenta dos limitaciones. Por un lado, una gran parte del patrimonio metálico se encuentra expuesto en el exterior u otros ambientes sobre los que no se puede intervenir fácilmente. Por otro, el control de las condiciones ambientales en el interior de museos no resulta trivial: limitaciones en los recursos técnicos, económicos y humanos, o el equilibrio entre la conservación, la exposición y el discurso museístico, incompatibilidad de materiales en la misma vitrina o en el mismo objeto, etc. hacen que frecuentemente sea necesario recurrir a sistemas de protección adicionales, tales como recubrimientos e inhibidores.

### 1.1.3.2. Aislar del medio ambiente: Conservación curativa.

El empleo de recubrimientos para evitar el acceso o la actuación de los agentes de degradación –humedad y contaminantes- a la superficie metálica es el procedimiento más habitual como estrategia de conservación de patrimonio metálico. El procedimiento estándar de protección de una superficie metálica mediante un sistema de recubrimiento implica una limpieza exhaustiva de la superficie metálica – eliminando cualquier resto de contaminación o productos de corrosión- seguida de la aplicación de varias capas, imprimación, capa intermedia y acabado, constituidas por diferentes pigmentos y polímeros orgánicos. Este tipo de sistemas no son aplicables en patrimonio metálico, donde los recubrimientos deben cumplir una serie de exigencias basadas en los criterios generales de conservación:

#### *Requisitos que deben cumplir los recubrimientos*

- Deben respetar el original. Los tratamientos aplicados no deben alterar el material original. En muchos casos esto incluye también a la historia del objeto, de modo que en el caso de los metales deben conservarse las pátinas o capas de corrosión siempre que sea posible.
- No deben modificar el aspecto de la superficie. Por tanto, deben ser transparentes y con un brillo similar al del objeto.
- Deben ser estables. No deben modificar su aspecto ni descomponerse con el tiempo de modo que puedan comprometer el aspecto o la integridad del objeto sobre el que se han aplicado.
- Deben ser reversibles. Cualquier tratamiento aplicado a un objeto del patrimonio debe poder eliminarse para devolver a dicho objeto a su estado original. Esto, en algunos casos esto no es posible, pero entonces se exige que al menos permita la re-tratabilidad del mismo. Para el caso de recubrimientos, esto se traduce en que deben emplearse materiales que no creen películas insolubles o que impidan la adherencia de futuras aplicaciones.

De manera general, los recubrimientos habitualmente utilizados en la protección de metales son resinas acrílicas y ceras (ceras microcristalinas y ceras de polietileno),

aunque en los últimos años se está investigando en el desarrollo de nuevos recubrimientos alternativos, especialmente recubrimientos naturales y respetuosos con el medio ambiente como carboxilatos [4-7], sistemas sol-gel [8-10], biopátinas [11-14], etc.

Estos recubrimientos son transparentes, su color apenas se modifica por efecto de la radiación UV y son reversibles. Como contrapartida, tanto su capacidad protectora como su duración son bastante limitadas (entre 3 y 10 años, dependiendo de recubrimiento y las condiciones ambientales) y deben ser renovados cada cierto tiempo [15-17]. Las tareas de conservación y mantenimiento requieren del empleo de recursos humanos y materiales, que son limitados y deben ser empleados de la manera más eficiente posible. Por ello, resulta fundamental disponer de herramientas de evaluación y diagnóstico que nos permitan decidir sobre la necesidad y la prioridad de intervención sobre un objeto u otro, comparar distintos sistemas de aplicación y materiales a disposición del restaurador, y servir para evaluar la eficacia de nuevos recubrimientos.

Las técnicas analíticas habitualmente utilizadas para el estudio de recubrimientos orgánicos como las técnicas espectroscópicas (UV-Vis, FTIR) o cromatográficas (SEC) pueden proporcionar información sobre cambios físicos o modificaciones estructurales que tienen relación con la degradación de los materiales, pérdidas de solubilidad, amarilleamiento, etc. [18-20]. Sin embargo, ninguna de estas técnicas nos informa directamente de la relación entre estos cambios y la capacidad de seguir o no protegiendo el metal.

Ante la necesidad de disponer de técnicas de diagnóstico adecuadas, en los años 90 comienzan a introducirse las técnicas electroquímicas para el estudio de los problemas de corrosión y los sistemas de protección en el patrimonio cultural metálico. Dentro de las técnicas electroquímicas la espectroscopía de impedancia electroquímica (EIS) constituye una herramienta de gran utilidad en los estudios de corrosión y la evaluación de recubrimientos e inhibidores, cuya aplicación en el campo industrial está ampliamente consolidada. Su aplicación y adaptación a la problemática particular del patrimonio cultural metálico es el objeto de este trabajo.

## 1.2. La EIS como herramienta de diagnóstico del estado de conservación del patrimonio cultural metálico. Fundamentos y Estado de la cuestión.

### 1.2.1. Fundamentos de la técnica.

#### *i. Concepto de impedancia*

D.R.A.E.: impedancia

*Del fr. impédance.*

*1. f. Electr. Relación entre la tensión alterna aplicada a un circuito y la intensidad de la corriente producida, y que se mide en ohmios.*

*2. f. Fís. Relación entre la magnitud de una acción periódica y la de la respuesta producida en un sistema físico.*

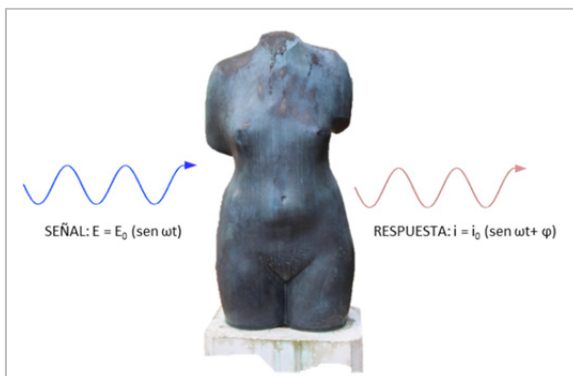
Como en el caso de otras *técnicas espectroscópicas*, la EIS se basa en aplicar una señal sobre un sistema y analizar su respuesta a lo largo de un cierto intervalo de frecuencias, pero a diferencia de otras técnicas, basadas en la radiación, la señal es una señal eléctrica. De manera habitual, se aplica una señal sinusoidal de potencial y la respuesta de sistema se produce en forma de corriente alterna. Matemáticamente, la impedancia viene definida por:

$$Z(\omega) = \frac{E(\omega)}{I(\omega)}$$

De acuerdo con la expresión anterior, podemos ver que la impedancia es una magnitud análoga a la resistencia eléctrica, según la define la ley de Ohm:  $R = E/I$ . Esta relación sin embargo sólo es aplicable en corriente continua; para el caso más general, la relación entre el potencial y la intensidad viene dada por la impedancia. La impedancia ( $Z$ ) se puede definir como la oposición que presenta un circuito al flujo de corriente alterna, expresada en ohmios.

## ii. Medidas de impedancia

La impedancia de un sistema se mide aplicando una pequeña señal de potencial sinusoidal (típicamente de unos 10mV) en un cierto intervalo de frecuencia. Esta señal desplaza al sistema de su equilibrio, que seguidamente experimenta un proceso de relajación produciendo una corriente sinusoidal de la misma frecuencia, pero diferente amplitud y ángulo de fase.



IMPEDANCIA: SEÑAL/RESPUESTA

$$Z(\omega) = \frac{E(\omega)}{I(\omega)} = \frac{E_0 \text{sen}(\omega t)}{I_0 \text{sen}(\omega t + \varphi)} = Z_0 \frac{\text{sen}(\omega t)}{\text{sen}(\omega t + \varphi)}$$

**Figura 1** Esquema y representación matemática de la impedancia.

Realizando un barrido de frecuencias, habitualmente entre 100 kHz- 10 mHz se obtiene la impedancia del sistema como una función de la frecuencia, caracterizada por el módulo,  $|Z|$  o  $Z_0$ , y el desplazamiento del ángulo de fase  $\phi$ . Aplicando la relación de Euler ( $e^{ix} = \cos x + i \text{sen} x$ ), la impedancia también se puede expresar como una magnitud compleja:

$$Z = \frac{E}{I} = \frac{E_0 \exp(j\omega t)}{I_0 \exp(j(\omega t - \varphi))} = Z_0 \exp(j\varphi) = Z_0 (\cos\varphi + j \text{sen}\varphi) = Z' + jZ''$$

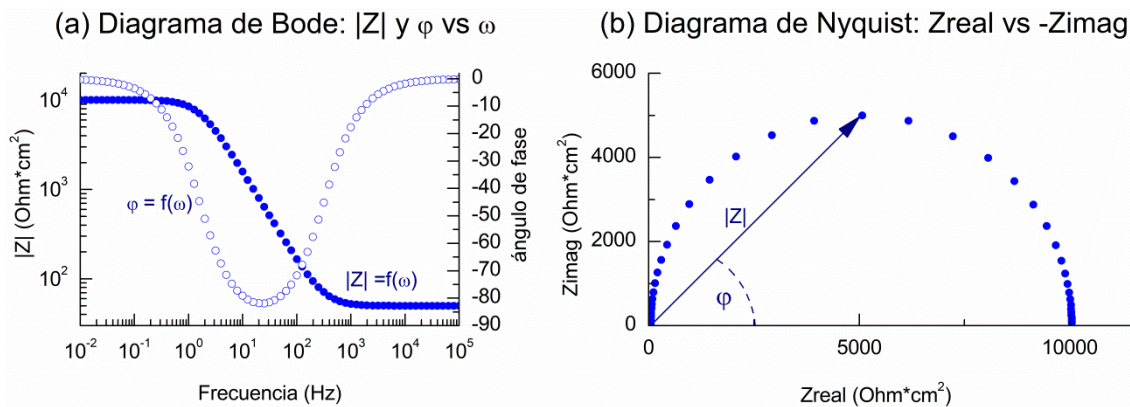
Donde  $j$  representa  $\sqrt{-1}$  (en electroquímica se usa la letra  $j$  en lugar de  $i$  para evitar su confusión con la intensidad de corriente)

## ii. Representación gráfica del espectro de impedancia:

A partir de las dos expresiones matemáticas de la impedancia se obtienen dos formas típicas de representar gráficamente el espectro de impedancia, el diagrama de Bode y el diagrama de Nyquist (figura 2). En el **diagrama de Bode** se representan el módulo de la impedancia ( $|Z|$  o  $Z_0$ ) y el desplazamiento del ángulo de fase ( $\phi$ ) frente a la

frecuencia en escala logarítmica. Si tomamos la expresión vectorial y representamos la parte real ( $Z_{re}$  o  $Z'$ ) en el eje de abscisas frente a la parte imaginaria ( $-Z_{imag}$  o  $-Z''$ ) en el eje de ordenadas, tendremos lo que se conoce como **diagrama de Nyquist**. El diagrama de Nyquist representa la curva formada por los extremos del vector impedancia a cada frecuencia, en coordenadas polares.

Ambas representaciones son equivalentes y la elección de una u otra es arbitraria, si bien en general el diagrama de Bode suele ser más adecuado para representar grandes variaciones en el valor de la impedancia, mientras que el diagrama de Nyquist facilita la visualización de ciertos elementos como la difusión.



**Figura 2.** (a) Diagrama de Bode. Representación de la variación del módulo de la impedancia y el ángulo de fase frente a la frecuencia. (b) Diagrama de Nyquist. Representación de la componente imaginaria frente a la componente real del vector impedancia[21].

#### iv. Interpretación del espectro de impedancia. Circuitos equivalentes.

Los espectros de impedancia proporcionan una gran cantidad de información sobre el sistema y permiten distinguir las contribuciones de distintos elementos que intervienen en el proceso de corrosión. Con ello es posible obtener información sobre los mecanismos involucrados en el proceso, las diferencias entre unos sistemas y otros o evolución con el tiempo, de forma cualitativa y cuantitativa. Sin embargo, estos espectros son complejos de interpretar en profundidad, por lo que a menudo se recurre a ciertas herramientas o simplificaciones.

Una herramienta habitualmente utilizada para calcular e interpretar los valores de los distintos elementos del sistema es el uso de *circuitos equivalentes* que reproducen las



propiedades eléctricas del sistema y proporcionan la misma respuesta de impedancia que sistema bajo estudio. Los diferentes elementos (resistencias, condensadores, inductores) que conforman el circuito, en serie o en paralelo, se relacionan con diferentes elementos o fenómenos físicos del sistema estudiado. Además, existen otros elementos que modelan situaciones específicas que se dan en sistemas electroquímicos, como la impedancia de Warburg, que modela la impedancia asociada a procesos de difusión; o los elementos de fase constante, CPE, que modelan comportamientos no ideales debidos a irregularidades del sistema (falta de uniformidad del recubrimiento, rugosidad, distribuciones no homogéneas de la corriente, etc.). En la tabla 1 se recogen los elementos más habituales, sus expresiones matemáticas correspondientes y los fenómenos físicos con los que se relaciona.

**Tabla 1.** Elementos que pueden aparecer en un circuito.

Elemento	Expresión matemática general	Fenómenos con los que se relaciona
Resistencia (R)	$Z_R = R$	Resistencia del electrólito ( $R_e$ ), resistencia de los recubrimientos, resistencia a la transferencia de carga ( $R_{tc}$ )
Condensador (C)	$Z_C = \frac{-1}{j \omega C}$	Capacidad de la doble capa ( $C_{dc}$ ), capacidad de un recubrimiento.
Inductancia (L)	$Z_L = j \omega L$	Procesos de adsorción-desorción de especies. Artefactos del sistema de medida.
Elemento de fase constante (CPE)	$Z_{CPE} = \frac{1}{Y_0 (j\omega)^\alpha}$	Condensadores imperfectos. Situaciones producidas por distribuciones no homogéneas de la corriente.
Impedancia de Warburg generalizada (W)	$Z_W = \frac{R}{(Tj\omega)^\alpha}$ $Z_W = \frac{R}{(Tj\omega)^\alpha} \tanh(Tj\omega)^\alpha$	Fenómenos de difusión (semi-infinita o en un espesor finito).
R = resistencia (ohm); C = capacidad (faradio); L = inducción (henrio); $Y_0$ = constante del CPE; $\alpha$ es parámetro empírico comprendido entre 0 y 1. En un CPE cuando $\alpha=1$ éste describe el comportamiento de un condensador ideal y para $\alpha=0$ , equivale a una resistencia. El exponente toma un valor de $\alpha=0.5$ , en la impedancia de Warburg.		

Matemáticamente existen múltiples circuitos equivalentes que proporcionan la misma respuesta en impedancia. Por ello es fundamental tener en cuenta las características de nuestro sistema a la hora de seleccionar los elementos y componer un circuito equivalente, de modo que todos los elementos tengan un significado físico. Para los sistemas habituales, como un metal limpio o un metal con un recubrimiento ideal en contacto con un electrólito, existen algunos circuitos más o menos establecidos que generalmente son aplicables a sistemas sencillos. En otros casos habrá que recurrir a modelos más complejos, adaptados a las particularidades del sistema estudiado. En la figura 3 se muestran algunos ejemplos de circuitos elementales junto con los perfiles característicos de los espectros que representan. Por ejemplo, para un sistema metal-recubrimiento ideal (figura 3a),  $R_e$  representa la resistencia del electrolito, mientras que un condensador ( $C_{rec}$ ) en paralelo con una resistencia ( $R_{rec}$ ) modelan la capacitancia y resistencia de la capa protectora. Si el recubrimiento está dañado o no es totalmente protector (figura 3b) entonces el circuito cambia; cuando el electrolito alcanza la superficie del metal a través de los poros y a la corrosión tiene lugar, aparece un nuevo par R-C. El proceso de corrosión puede ser representado entonces por un condensador para la capacitancia de doble capa ( $C_{dc}$ ) en paralelo con la resistencia de transferencia de carga ( $R_{tc}$ ). En este caso,  $C_{rec}$  representa la capacidad del recubrimiento y  $R_{po}$  la resistencia a la conducción iónica a través de los poros o defectos de éste. Cada par R-C suele manifestarse en el espectro de impedancia por un tramo inclinado en el diagrama de Bode o un semicírculo (completo o no) en el diagrama de Nyquist. En sistemas no ideales estos perfiles se presentan achatados, y es necesario recurrir a CPE en lugar de condensadores (figura 3c). Finalmente, en los sistemas en los que el proceso de corrosión está controlado por la difusión, suele emplearse un circuito como el representado en la figura 3d; la presencia de este fenómeno se manifiesta en el espectro como una recta a  $45^\circ$  en el diagrama de Nyquist.

En la práctica, los diagramas de impedancia obtenidos en pátinas y recubrimientos sobre metales históricos son muy complejos debido a la heterogeneidad de los sistemas estudiados: recubrimientos aplicados a mano sobre superficies irregulares, con productos de corrosión, etc., de modo que para su representación recurriremos siempre a CPE.

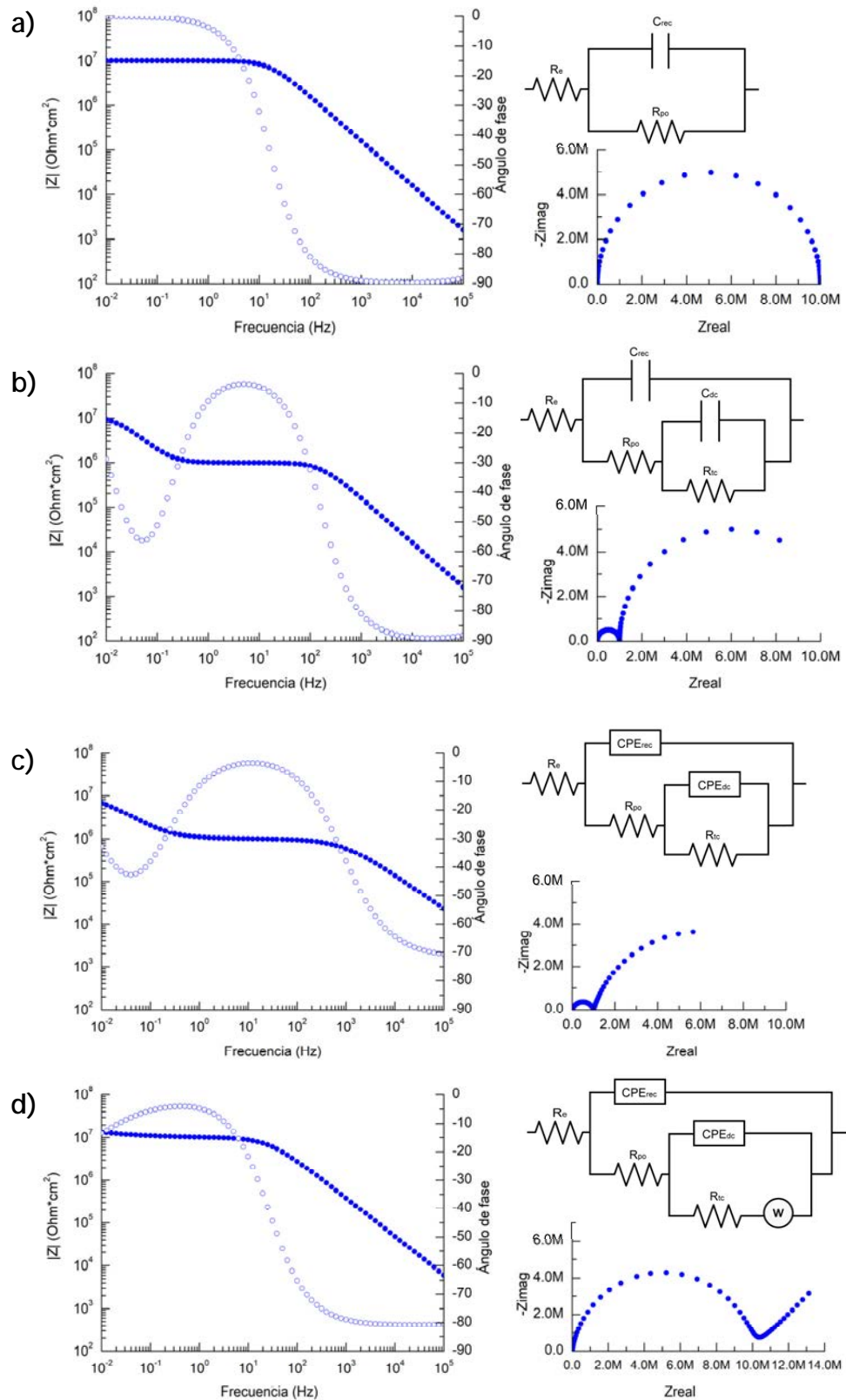


Figura 3. Diagrama de Bode y diagrama de Nyquist para algunos circuitos equivalentes habituales [21].

### **1.2.2. La aplicación de la EIS en patrimonio cultural. Estado de la cuestión.**

Como ocurre con muchas otras técnicas o metodologías, la ciencia del patrimonio recurre frecuentemente a la adaptación de herramientas y métodos de otras disciplinas. Sin embargo, en la mayor parte de los casos no es posible una transposición directa de la técnica, sino que es necesario un desarrollo posterior adaptado a las particularidades de los objetos y estudios en patrimonio cultural.

Las técnicas electroquímicas y en particular la EIS empiezan a aplicarse en la conservación<sup>2</sup> del patrimonio cultural metálico en los años 90 del siglo pasado. La primera publicación aparece en el año 93 y hace referencia a la aplicación de la resistencia de polarización lineal ( $R_p$ ) y la EIS para la evaluación de tratamientos de estabilización en hierros arqueológicos [22]. Poco después comienzan a aparecer estudios sobre recubrimientos protectores para el patrimonio metálico. En el 95, Price et al. evalúan el comportamiento de diversos recubrimientos a base de ceras para la protección del bronce mediante ensayos de inmersión, determinando el tiempo de fallo del recubrimiento cuando la impedancia en el diagrama de Bode se aproxima a la del metal desnudo [23, 24]. En las mismas fechas Letardi, otra de las pioneras en la aplicación de la EIS al patrimonio cultural, comienza el estudio sistemático de probetas de bronce desnudas y con distintos recubrimientos expuestas en atmósfera marina y propone el primer diseño de una celda portátil específicamente adaptada para la realización de medidas in situ en patrimonio cultural [25, 26].

En la siguiente década los trabajos en este campo aumentan notablemente. Bierwagen et al. ensayan diversos recubrimientos sobre probetas metálicas, que son sometidos a sucesivos ciclos de envejecimiento artificial según norma ASTM D5894, tratando de establecer un modelo para predecir su durabilidad a partir de la variación del módulo de la impedancia a bajas frecuencias con el tiempo [27, 28]. Letardi evalúa además la influencia de las pátinas en diversos tipos de recubrimientos (ceras microcristalinas, acrílicos y organosilanos) aplicados sobre probetas de bronce desnudo y patinado,

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<sup>2</sup> Debe quedar claro aquí que se habla expresamente de conservación, y no de tratamientos de restauración como las reducciones electroquímicas que se utilizan desde finales del siglo XIX.

sometidas a envejecimiento natural y artificial, observando que el comportamiento de dichos recubrimientos varía significativamente en función del sustrato [29].

En los últimos 10 años varios grupos han trabajado en esta técnica, centrándose principalmente en la evaluación de recubrimientos para diferentes metales, incluyendo la aplicación de nuevos sistemas de protección [30-33]. Otros autores, como C. Chiavari han trabajado en el examen de las pátinas y la corrosión bronce en ambientes contaminados y en especial en cómo la acidificación del pH del agua de lluvia afecta a estabilidad de las pátinas históricas [34].

Como ya hemos mencionado, la obtención e interpretación de los espectros de impedancia en objetos del patrimonio cultural no es sencilla. Muy frecuentemente los objetos de estudio se hayan cubiertos de pátinas o productos de corrosión de diversa naturaleza. En muchos casos estas pátinas forman parte de la historia y valor estético de estos objetos; en otros casos el estado de conservación del metal base no permite la eliminación de los productos de corrosión, por lo que los sistemas de protección se aplican directamente sobre ellos. Además, la aplicación se realiza a mano, por lo que el grosor nunca resulta uniforme. La irregularidad en estos sistemas hace que las medidas de impedancia den lugar a diagramas complicados, con pendientes variables en los diagramas de Bode y semicírculos solapados y achatados en los diagramas de Nyquist, que no se ajustan bien a los modelos teóricos. Por ello, la mayor parte de los estudios se basan simplemente en la evaluación del módulo de la impedancia  $|Z|$  a bajas frecuencias (10–50 mHz) y en su evolución con el tiempo de inmersión en diversos electrolitos o de exposición en tests de envejecimiento acelerado.[35]

En resumen, la aplicación de la EIS al estudio del patrimonio metálico presenta dos problemas fundamentales, uno de aplicación y otro de interpretación. Para tratar de analizar cada uno de ellos se ha realizado una revisión sobre los sistemas propuestos por otros autores y sobre los posibles modelos de aplicación para la interpretación de los resultados. Todo ello constituye el artículo de revisión sobre la aplicación de la espectroscopía de impedancia a la evaluación del patrimonio cultural que se presenta a continuación:

- B. Ramírez Barat, E. Cano, "Advances for in-situ EIS measurements and their interpretation for the diagnostic of metallic cultural heritage: a review", *ChemElectroChem*, (2018), 5, pp 2698-2716<sup>3</sup>.

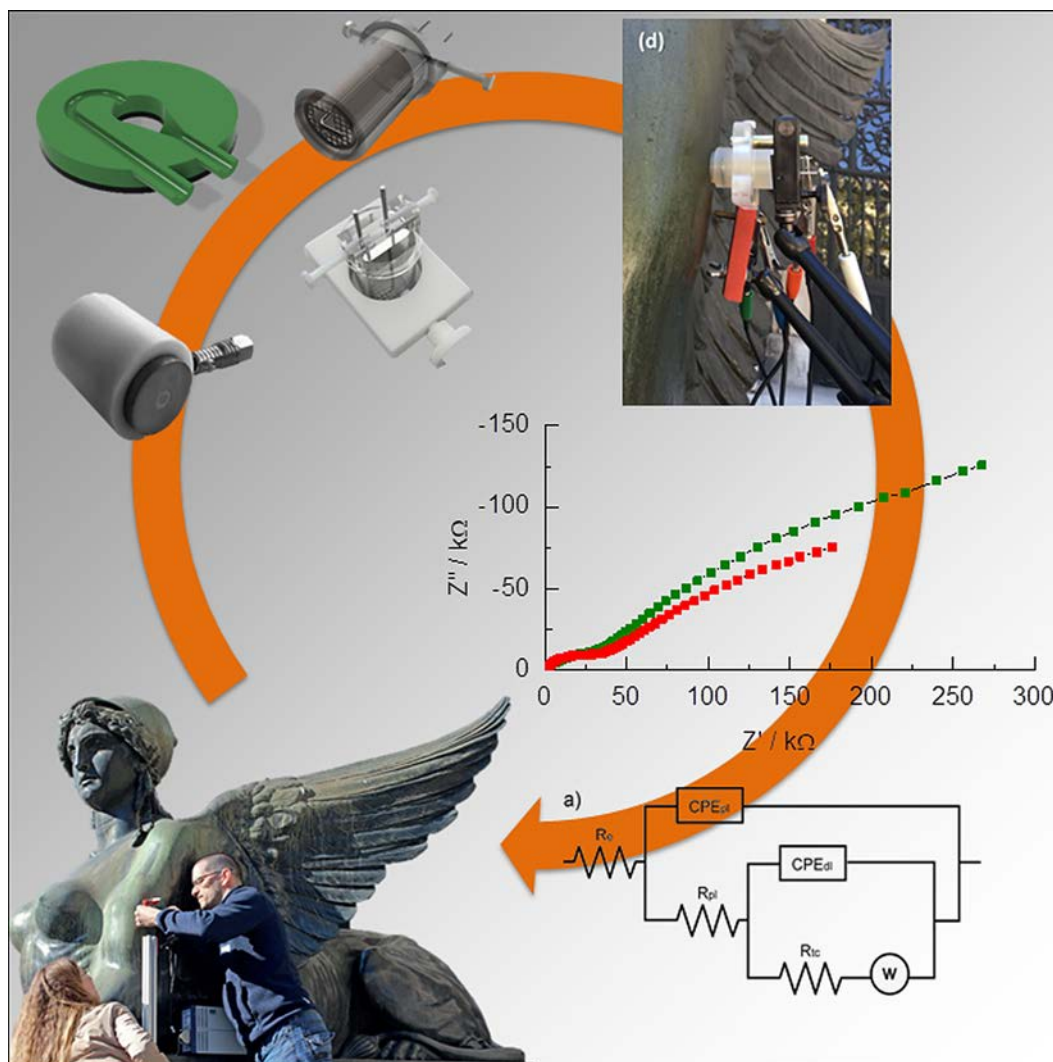
En este trabajo se realiza un repaso de los diferentes sistemas basados en el uso de electrolitos líquidos o sólidos para mediciones in situ, desde la primera celda propuesta por Letardi hasta la celda en gel objeto de esta tesis. En una segunda parte, se proponen algunos circuitos equivalentes generales como base para interpretar los resultados en diferentes superficies metálicas después de discutir diferentes modelos propuestos en la literatura. Con ello se pretende resumir y aclarar los puntos clave la aplicación de la EIS en la conservación del patrimonio cultural metálico, sirviendo de base y de resumen del estado del arte para el trabajo que se presenta en esta tesis.

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<sup>3</sup> Las referencias bibliográficas de esta publicación se corresponden con las referencias [23, 26, 27, 29, 32, 34-156] de la bibliografía general.

# *In Situ* Electrochemical Impedance Spectroscopy Measurements and their Interpretation for the Diagnostic of Metallic Cultural Heritage: A Review

Blanca Ramírez Barat<sup>\*,[a]</sup> and Emilio Cano<sup>[a]</sup>



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 increasing interest in recent years, although some difficulties in application and interpretation of the results still keep it from being routine practice. This Review aims to picture the state-of-the-art of using electrochemical impedance spectroscopy (EIS) for the in situ monitoring of metallic cultural heritage, focusing on spectra interpretation

and different approaches that have been proposed to perform field measurements since the 1990's. In the first part of the Review, different cell designs based on 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.<sup>[1]</sup> 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.<sup>[2]</sup>

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 steels (WS), the composition of the rust layer has been correlated to the corrosion rate through the Protective Ability Ratio, calculated as the relationship between the mass fraction of goethite and lepidocrocite.<sup>[3]</sup> 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 experienced 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<sup>[4]</sup> 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<sup>[5]</sup> 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;<sup>[6]</sup> 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,<sup>[7]</sup> to choose the most adequate coating<sup>[4a,8]</sup> or to know when a coating has to be renewed,<sup>[9]</sup> 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

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(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.

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,<sup>[10]</sup> 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,<sup>[10a,11]</sup> technical notes,<sup>[12]</sup> and advanced text books or dedicated monographies.<sup>[13]</sup>

## 2. Instrumentation Developments for In Situ EIS Measurement in Cultural Heritage

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 5–10 mV and up to 50 mV or even higher for highly resistive coatings, and the spectra is registered between 100 kHz and 10 mHz, 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.<sup>[7c]</sup>

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,<sup>[4c]</sup> artificial rainwater,<sup>[14]</sup> diluted Na<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub>/NaHCO<sub>3</sub> solutions<sup>[15]</sup> dilute Harrison electrolyte.<sup>[11b,16]</sup> 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<sup>[14b,17]</sup> or a complete different one.<sup>[18]</sup>



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## 2.1. Portable Devices with Liquid Electrolytes

### 2.1.1. 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.<sup>[4c]</sup>

Different cells differing in size, construction materials and assemblage were assayed resulting in a final design as the one shown in Figure 1.<sup>[10a,19]</sup> A pseudo-reference electrode (RE) and a

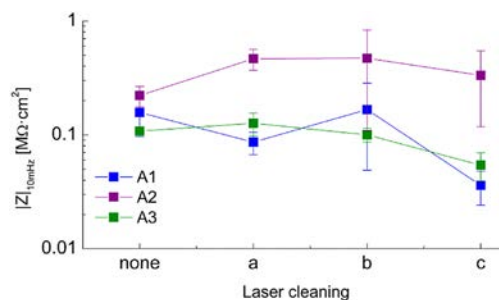


**Figure 1.** Contact probe designed by Paola Letardi. Cell construction (left) and complete measurement setup (right).

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 cm<sup>2</sup>. 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.<sup>[4c]</sup>

This cell has been successfully used in the evaluation of different coatings and treatments on bronze coupons<sup>[4c,10a,19–20]</sup> as well as on outdoor sculpture<sup>[20b,c]</sup> through comparison of the impedance modulus ( $|Z|$ ) at the minimum frequency (10 mHz). 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.<sup>[21]</sup>

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.<sup>[7a,b]</sup> 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



**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 Ref. [7a], using the original data provided by the author. Copyright (2015) The Authors.

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.

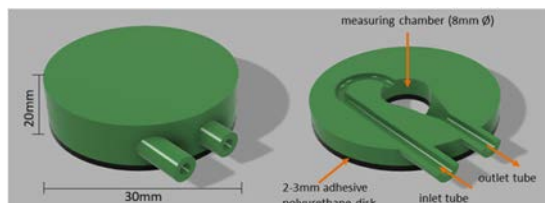
### 2.1.2. Traditional Cell Designs

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.<sup>[4c]</sup> 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.<sup>[22]</sup> Further development of the first prototype incorporated the cell to a compact hand-held measuring device.<sup>[23]</sup> 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.<sup>[24]</sup> 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



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

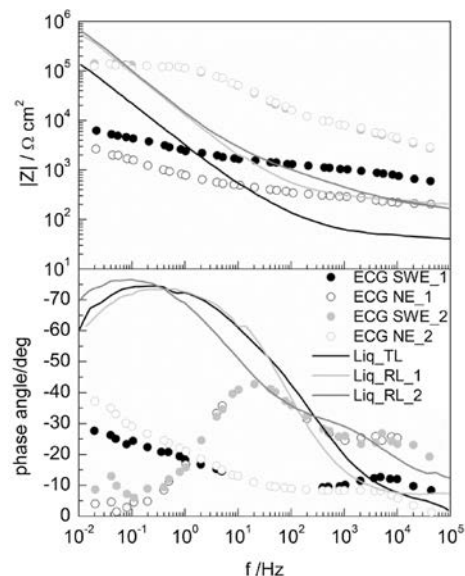
with a platinum CE, and is filled with the electrolyte through an inlet tube.<sup>[15c]</sup>

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.

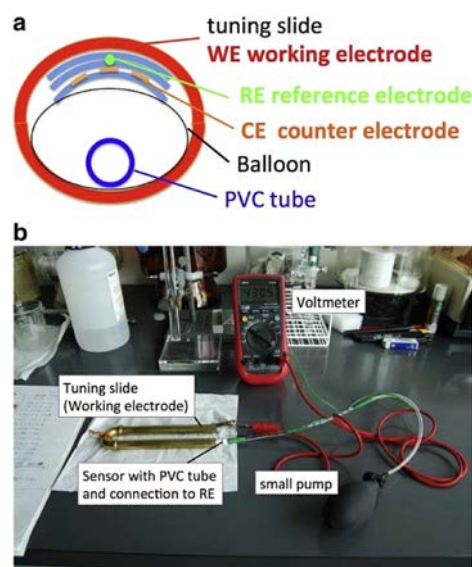
This system has been tested in the weathering steel monument “Reditus ad origines” in Ferrara, that has also been measured with ECG electrodes (see next section). Results obtained with the different setups show notable dissimilarities in the spectra profile. This can be appreciated in Figure 4, where data from EIS spectra recorded with both setups have been extracted from figures and plotted together for comparison using WebPlotDigitizer.<sup>[25]</sup>

### 2.1.3. Other Cell Designs

With a similar idea to Letardi’s contact probe, Elsener and co-workers have recently proposed a sensor to monitor corrosion in the inside of historical brass instruments.<sup>[6e,f]</sup> 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  $R_p$  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.

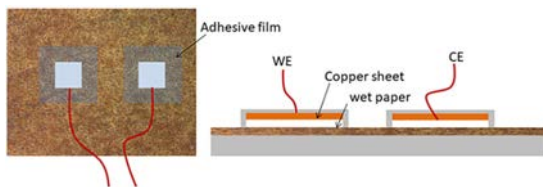


**Figure 4.** EIS results from a weathering steel sculpture obtained with ECG electrodes (symbols) and the ABS plastic cell (lines) in different areas. NE and SWE stand for North-East and South-West, red-orange (1) and red-brown oxide areas; TL refers to a thin oxide layer while RL is a rough oxide layer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



**Figure 5.** Scheme of the cell design showing the 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 (b) by Elsener et al. Reprinted with permission from Ref. [6e]. Copyright (2016) 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



**Figure 6.** Scheme of the cell configuration proposed by Jamali et al.<sup>[26]</sup>

copper sheet coated with platinum and the set is fixed to the surface by an adhesive tape (Figure 6).<sup>[26]</sup> 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.<sup>[27]</sup>

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<sup>[18]</sup> 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

#### 2.2.1.1. 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.<sup>[28]</sup> 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.<sup>[28b]</sup> This also reduces

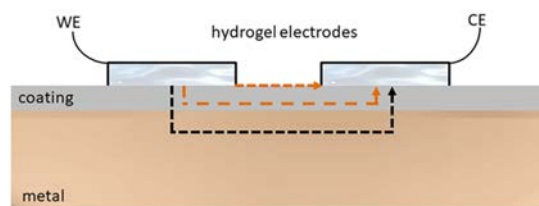
the adhesiveness of the electrode preventing the detachment of corrosion products when removing the electrode, which is other of the drawbacks of the ECG electrodes, but enlarges the time needed for field measurements. On the other hand, the thickness of the gel is not homogenous as the RE occupies part 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.<sup>[28b,c]</sup> The fact is that, as can be seen in Figure 10 of reference,<sup>[28c]</sup> 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.

#### 2.2.1.2. 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 sulfonic acid), poly (AA-AMPS), and equilibrated with different aqueous solutions to a better control of the properties.<sup>[18,29]</sup> The gels are cut into 1 cm<sup>2</sup> 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 (K<sub>2</sub>PIPES). 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.<sup>[30]</sup> As it has already been presented, this layout was later used by Jamali



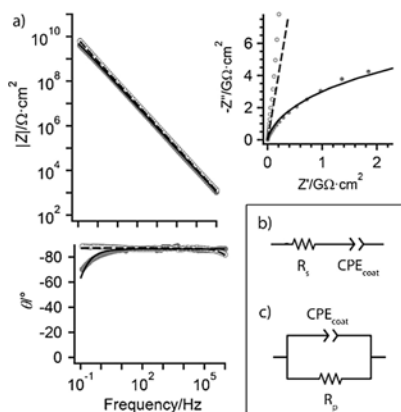
**Figure 7.** Scheme of the hydrogel two-cell EIS design, showing the theoretical current path proposed by authors in Refs. [18,29b] (black discontinuous arrow) and the other possible current paths (red discontinuous arrows).



et al.<sup>[27]</sup> 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 through the black path depicted in Figure 7, which equals two parallel cells. Thus, an area normalization factor is used to obtain the impedance,  $K_{\text{cell}}$ ,  $\text{area} = 1/A_1 + 1/A_2$ . 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.

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 with permission from Ref. [29b]. Copyright (2014) John Wiley & Sons.

This setup was tested in-situ on coated bronze sculptures<sup>[31]</sup> 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,<sup>[32]</sup> 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.

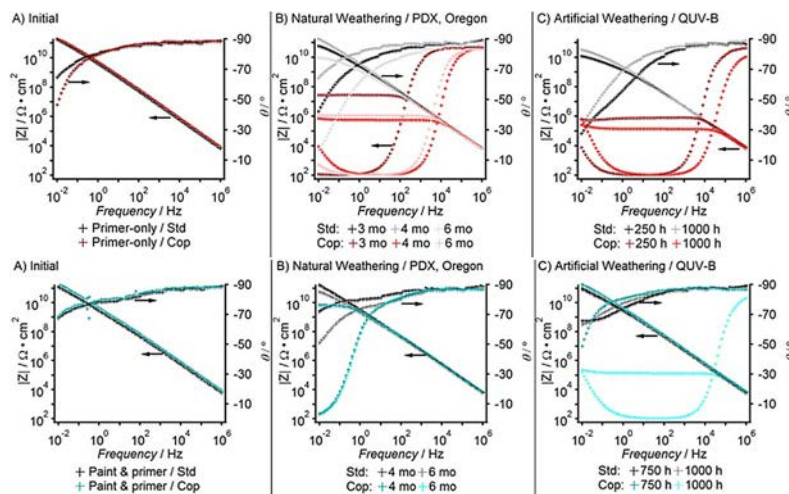
### 2.2.1.3. Agar G-PE Cell

As an alternative to these previous systems, Cano and col. have proposed a cell based on a liquid electrolyte gelled with agar.<sup>[33]</sup> 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,<sup>[14b]</sup> 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.

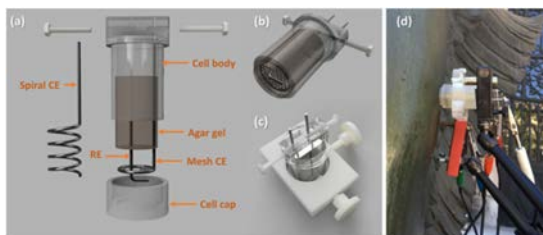
Figure 10 shows the construction of the cell, in which a counter electrode and a (pseudo) reference electrode (made of AgCl coated Ag or AISI 316 stainless steel) are placed in a plastic container. The aqueous electrolyte (artificial rain) is jellified by addition of 3% agar, poured in the container 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.<sup>[34]</sup> 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.

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.<sup>[9,35]</sup> 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.

Other researchers have followed this work developing other applications of the agar G-PE cell. Di Turo and col.<sup>[17]</sup> have recently applied a similar design, using an agar cell with screen printed electrodes, for the characterization of patinas in archaeological bronzes. Also, Monrabal and col.<sup>[36]</sup> 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



**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). Spectra of the fresh (A), naturally aged (B) and artificially aged (C) are presented. 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 with permission from Ref. [32]. Copyright (2017) John Wiley & Sons.



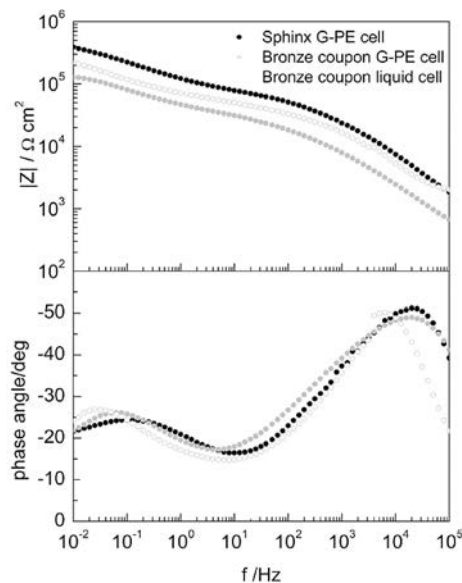
**Figure 10.** G-PE cell design: exploded view (a), mounted cell (b), and support (c). The complete measuring setup on the surface of an outdoor sculpture (d). Reprinted with permission from Ref. [34]. Copyright (2018) Elsevier.

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

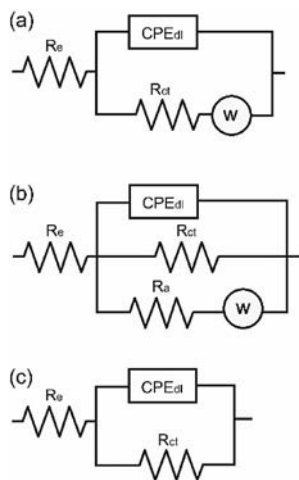
Besides practical difficulties in measuring discussed in last section, specific challenges have to be faced in the interpretation of results when applying EIS to study historic metals. The frequently complex and irregular nature of the metal substrate, together with external interferences, and limitations 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



**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.

conservation science literature.<sup>[4b,11b,16,20a,c,21,37]</sup> 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



**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 0.1 M  $\text{Na}_2\text{SO}_4$  (c)

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<sup>[35c]</sup>. In the same way, charge transfer resistance ( $R_{ct}$ ) can sometimes be obtained from the low frequency semicircle.<sup>[38]</sup> The main drawback of this approach is that it is not always easy 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  $-1$ .<sup>[39]</sup>

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 constants.<sup>1</sup> This has been related to low conductivity electrolytes, such as rain water, and uneven and porous nature of patinas.<sup>[40]</sup> However it

<sup>1</sup> 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,<sup>[11d]</sup> pp. 24–25.

has been demonstrated that it is related rather to the electrochemical/potential inhomogeneity than to the geometric irregularities of the patina surface.<sup>[41]</sup> 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  $s^{-\alpha} / \Omega$ , thus  $Y_0$  cannot be used as a direct equivalent to capacitance, especially to quantitatively determine other system parameters.<sup>[42]</sup> Different mathematical formulas have been proposed to obtain capacitance value from  $Y_0$ ,<sup>[42–43]</sup> which may be used for different time-constant distributions.<sup>[44]</sup> 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.<sup>[45]</sup> 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.<sup>[34,46]</sup> 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 that 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:

- "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.
- 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.
- 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.

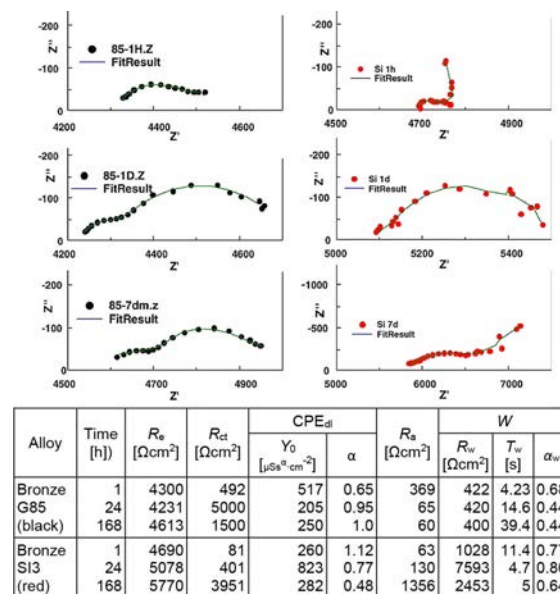
### 3.1. Clean Metals

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 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.<sup>[5a,47]</sup> 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.<sup>[48]</sup> 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.<sup>[48a]</sup> 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<sup>[14b,49]</sup> (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



**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 with permission from Ref. [49]. Copyright (2006) Elsevier.



diffusion impedance, both in copper and brass.<sup>[50]</sup> More recently, Vera et al. have studied copper corrosion in 0.1 M Na<sub>2</sub>SO<sub>4</sub>; unexposed copper coupons spectra fitted the classical Randles circuit, without the diffusion element,<sup>[51]</sup> 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.

Occasionally, EIS spectra from copper shows three time constants; this seems to be the case when the Cu<sub>2</sub>O 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.<sup>[50a]</sup> 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.<sup>[52]</sup> Rios et al.<sup>[53]</sup> 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,<sup>[54]</sup> 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.<sup>[8]</sup>

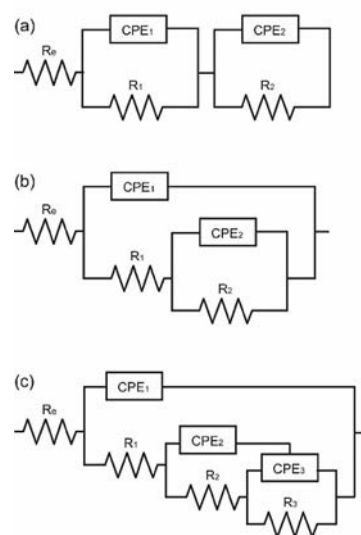
### 3.2. Metals with Patina

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.

#### 3.2.1. 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<sup>[55]</sup> 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

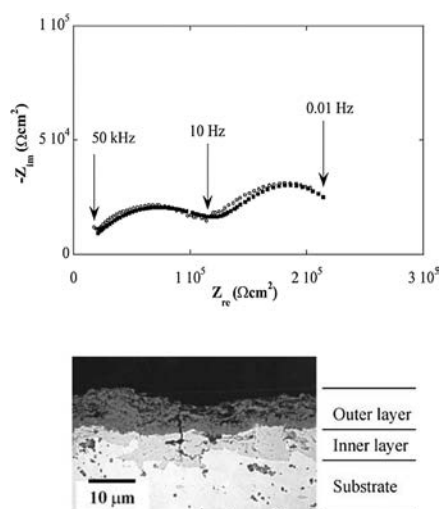


**Figure 14.** EC for a thin barrier layer covered by a porous outer layer (a), two nested R-CPE model for a double layer patina structure or a patina-metal surface response (b), and three-time-constant EC (c).

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 ~ 30  $\mu$ S/cm),<sup>[40,56]</sup> 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.<sup>[57]</sup> These examples, perfectly match the case of a typical bronze outdoor sculpture.

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.<sup>[58]</sup> However, this model, which implies no signal coming from the faradaic process at the metal surface (the pair  $CPE_{dl}-R_{ct}$  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,<sup>[40]</sup> the electrolyte surely reaches the metal surface through the pores and cracks (Figure 15). In a subsequent study



**Figure 15.** EIS spectrum (○) and fitting curve (■) in rainwater and cross-sectional image from a natural copper patina. Reprinted with permission from Ref. [40]. Copyright (2002) Elsevier.

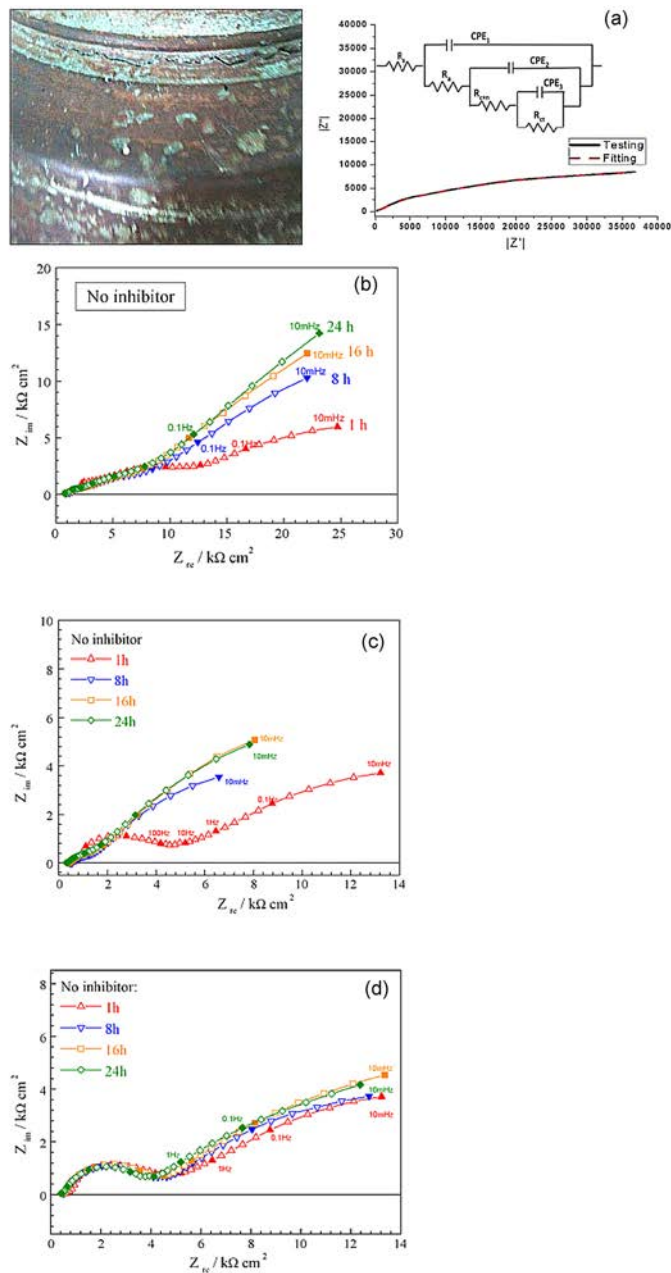
by same authors, this interpretation is replaced by the EC in Figure 12(b), with two nested (R-CPE), representing the impedance of the inner and outer patina layer.<sup>[56]</sup> Considering the values from fitting the EIS spectrum, the exponent value close to 0.5 from the CPE in the inner layer, suggests 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  $CPE_1$  related to the patina response and  $CPE_2$  with copper oxidation was used to study the response of bronze roman coins<sup>[17]</sup> and natural copper patinas formed during 1–3 years in Chile in different environments, with different thickness and porosity depending on the location.<sup>[51]</sup> This second interpretation of circuit elements is in a better accordance to the copper corrosion mechanism previously described.

Patinas showing a three-time-constant EIS spectra, have been explained by the EC in Figure 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,<sup>[59]</sup> and has also been used in the study of different archaeological bronzes.<sup>[15a,60]</sup> 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  $Cu(0) \rightleftharpoons Cu(I)$  or  $Cu(I) \rightleftharpoons Cu(II)$  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).

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 0.1 M NaCl. Though the spectrum showed, apparently, only two time constants, it fitted the EC in Figure 17(a).<sup>[61]</sup> This EC was also used by Souissi et al. to study patina formation under different conditions on archaeological bronze.<sup>[55]</sup> Although using a genuine archaeological fragment, patinas were artificially produced by immersion in different electrolytes of the polished metal surface, this 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 0.3 M–5% agar electrolyte<sup>[17]</sup> and in mineral water.<sup>[62]</sup> 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.

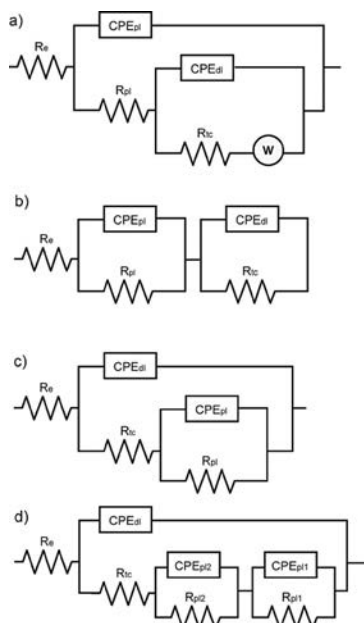


**Figure 16.** Nyquist plot and three-time-constant equivalent circuit for “in situ” impedance obtained from a brown patina on a Historic Bell (a). Reprinted with permission from Ref. [57]. Copyright (2016) The Authors. Nyquist plots of different artificial patinas immersed in artificial acid rain ( $0.2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.2 \text{ g L}^{-1} \text{ NaHCO}_3$  at pH 5) for different times: sulfate patina (b), chloride patina (c) and electrochemical patina (d). Reprinted with permission from Ref. [59b]. Copyright (2007) Elsevier.

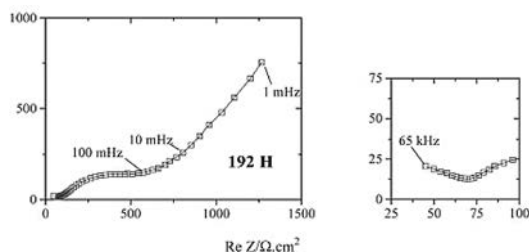
### 3.2.2. Iron and Steel

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,



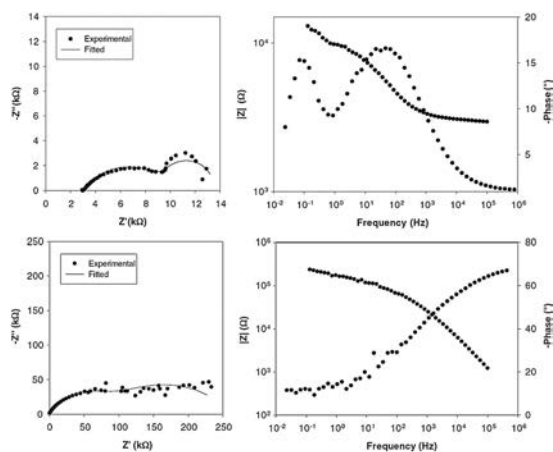
**Figure 17.** Different EC proposed for archaeological copper alloys.



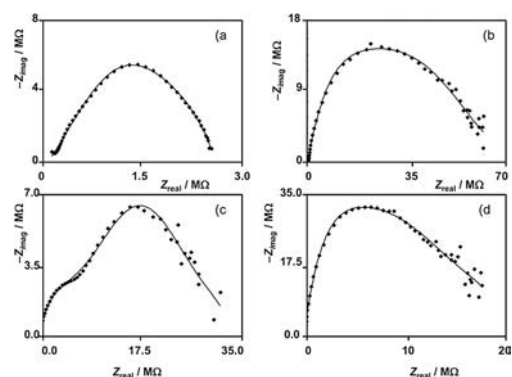
**Figure 18.** Nyquist plots ( $Z_{im}$  vs  $Z_{re}$  in  $\Omega \text{ cm}^2$ ) from patinas grown by immersion of archaeological bronze in 0.1 M NaCl solution, fitting EC in Figure 17a. Reprinted with permission from Ref. [55b]. Copyright (2006) John Wiley & Sons.

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.<sup>[63]</sup> 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



**Figure 19.** Nyquist and Bode plots from different archaeological coins with an agar cell fitting EC in Figure 17b). Reprinted with permission from Ref. [17]. Copyright (2017) Elsevier.

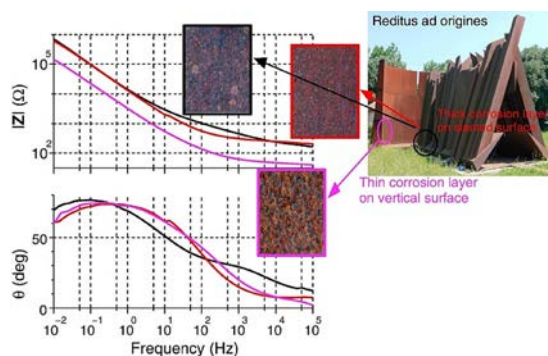


**Figure 20.** Nyquist plots from different archaeological coins with mineral water showing apparently two more or less overlapping capacitive loops, fitting EC in Figures 17c and 17d. The representation of the Nyquist plot, nevertheless, does not use isometric axes, so the shape of the spectra is distorted. Reprinted with permission from Ref. [62]. Copyright (2017) Elsevier.

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.<sup>[64]</sup> 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,  $R_{p1}$  and  $CPE_{p1}$  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  $CPE_{dlr}$  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.<sup>[65]</sup> Thus, EIS spectra on WS can be explained with the same EC than bronze, only differing in the origin of the Warburg impedance.

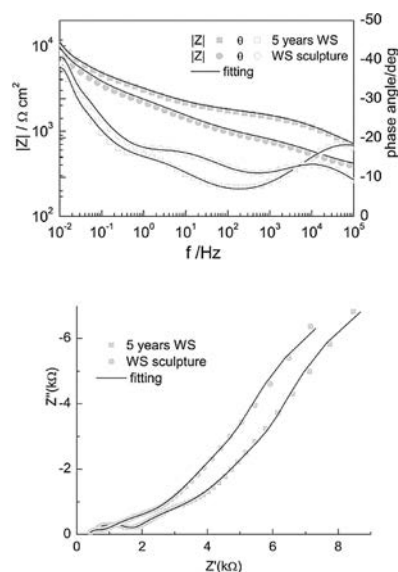
Regarding electrochemical studies on weathering steel sculptures, although several papers have been published<sup>[15c,28b,35b,c,66]</sup> and some of them comment on EC, there has been only one attempt to fit the spectra to a EC.<sup>[15c]</sup> In this paper, the spectra have been fitted using a two-cell 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 Figure 6 of reference<sup>[15c]</sup> (Figure 21), which is neglected by authors and would



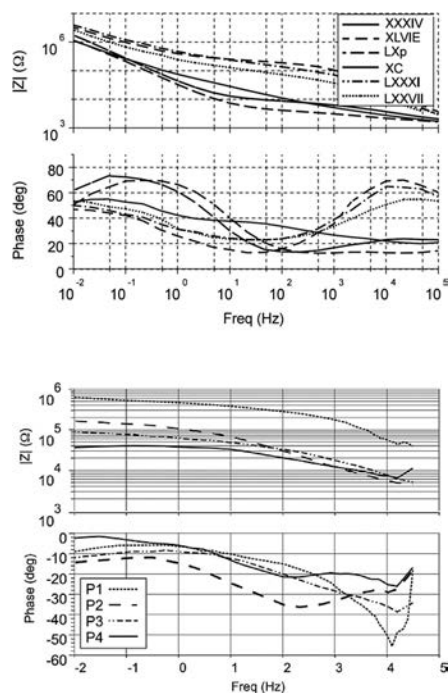
**Figure 21.** EIS spectra for the sculpture Reditus ad origines, with the setup described in Figure 3. At the lower frequencies the phase angle changes from 0 to lower values (as the value represented in the Figure is  $-\theta$ ), suggesting an additional process. Reprinted with permission from Ref. [15c]. Copyright (2018) Elsevier.

require additional elements in the EC. This 3-time constants spectra have also been reported in other works,<sup>[35b,c]</sup> 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<sup>[35d]</sup> and on a weathering steel coupon after five years of natural outdoor exposure<sup>[35a]</sup> 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.

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<sup>[24,66–67]</sup> (Figure 23). Several EC have been discussed for this type of objects in different papers, while the latest model proposed<sup>[66b]</sup> is the same as the general EC in Figure 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



**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.



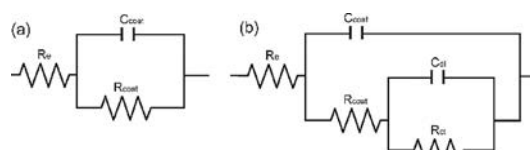
**Figure 23.** EIS spectra from different areas of the wrought iron bars chains of the Amiens Cathedral, measured with the nylon cylinder liquid cell previously described in different campaigns. Reprinted with permission from Ref. [24] (top). Copyright (2013) Springer. Reprinted with permission from Ref. [66b] (bottom). Copyright (2014) NAUN.



enough to explain the general behavior and evaluate the conservation state of an iron object.

### 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

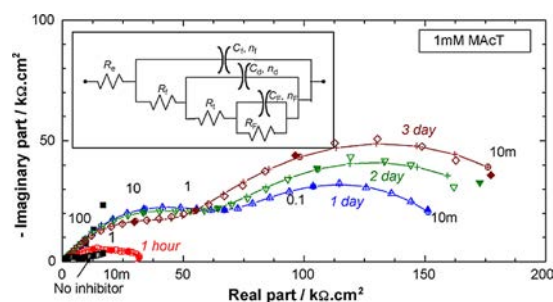


**Figure 24.** EC describing an ideal metal-coating system (a) and a non-ideal or damaged coating (b).

can be represented as capacitor and a resistance in parallel for the capacitance ( $C_{\text{coat}}$ ) and resistance ( $R_{\text{coat}}$ ) of the coating in series with the resistance of the electrolyte,  $R_e$ . In highly protective coatings  $R_{\text{coat}}$  is very high, which reduces the system to a  $C_{\text{coat}}$  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  $C_{\text{dl}}$  is the double layer capacitance and  $R_{\text{ct}}$  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.<sup>[8,14a,35e,68]</sup> 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.

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.<sup>[69]</sup>

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  $C_{\text{dl}}$ . 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.<sup>[15a,47c,59a,b,70]</sup> An example is presented in Figure 25 from a study



**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 with permission from Ref. [15a]. Copyright (2007) Elsevier.

on the inhibitor effect of imidazole and thiazol derivatives on patinated bronze, by Muresan et al.<sup>[15a]</sup> 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.

## 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,<sup>[10b,71]</sup> while others are focused in certain uses of impedance, such as coatings evaluation.<sup>[11a]</sup> 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.<sup>[17,36a]</sup> 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.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** electrochemical impedance spectroscopy · cultural heritage · in situ analysis · diagnostics · conservation

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## 2. OBJETIVOS

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Tal y como se acaba de presentar, la principal motivación de esta tesis es dar respuesta a una necesidad en el sector de la conservación del patrimonio cultural metálico: dotar a los conservadores, restauradores y científicos del patrimonio de una herramienta de evaluación y diagnóstico que permita el estudio del estado de conservación de un objeto metálico y los sistemas de protección presentes, y la toma de decisiones respecto al mismo. Para ello, y como indica su título, el objetivo general de este trabajo es:

**Diseño, desarrollo y validación de una celda electroquímica con electrólito en gel para la realización de medidas electroquímicas in situ sobre el patrimonio cultural metálico.**

Para alcanzar este objetivo general es necesario abordar de forma progresiva una serie de objetivos parciales que darán respuesta a diferentes cuestiones:

- **Evaluación de la viabilidad del empleo de un electrólito gelificado para la realización de medidas de espectroscopía de impedancia electroquímica.**

El abordaje de este primer objetivo pretende dar respuesta a algunas cuestiones elementales pero imprescindibles ¿Es posible hacer medidas electroquímicas con un electrólito gelificado? ¿El resultado obtenido es comparable al del electrólito líquido? ¿Cuánto y cómo influye el empleo de un gel?

- **Conocimiento del sistema y optimización de la geometría y diseño de la celda**

Una vez validado el empleo de un electrólito gelificado es necesario conocer y analizar los diferentes aspectos que condicionan la obtención de los resultados para una correcta interpretación. Al mismo tiempo hay que tener en cuenta el diseño del sistema completo de cara a su utilización en medidas de campo, con las dificultades de carácter técnico o práctico que ello conlleva.

- **Validación de la celda para la evaluación de pátinas y recubrimientos.**

El siguiente objetivo es validar el uso de la celda en condiciones de laboratorio sobre diferentes pátinas y recubrimientos, similares a los que nos encontraríamos en casos reales, para comprobar que el diseño es adecuado para medir este tipo de sistemas y se obtienen medidas de buena calidad.

- **Aplicación a casos reales**

Finalmente se tratará de aplicar la celda al estudio de diversos problemas o situaciones reales, en esculturas expuestas en el exterior y en distintos estados de conservación, para confirmar la aplicabilidad de este diseño a la problemática del patrimonio cultural.

Los diferentes objetivos y su desarrollo constituyen los tres principales apartados del capítulo 4, aunque en la práctica el abordaje no de estos objetivos no es lineal, sino que en muchos casos transcurre en paralelo: de forma simultánea se ha ido aplicando el prototipo desarrollado a diversos problemas o casos prácticos. Con ello se ha podido evaluar su comportamiento en diferentes situaciones y al mismo tiempo ver qué dificultades o particularidades presentaban las diferentes aplicaciones en la práctica, para así mejorar el diseño.

Por ello, aunque la presentación de los resultados se realiza siguiendo la estructura de los objetivos propuestos, las publicaciones que recogen estos resultados no siguen una secuencia temporal.

Con la consecución de estos objetivos se pretende contribuir al desarrollo de una metodología para la aplicación de las técnicas electroquímicas y en especial de la EIS al diagnóstico y evaluación de los tratamientos de conservación y con ello contribuir a una mejor conservación de nuestro patrimonio.

## 3. MATERIALES Y MÉTODOS

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Prácticamente la totalidad del desarrollo experimental se ha basado en la realización de medidas de espectroscopía de impedancia electroquímica con diferentes modelos de celda y sobre diferentes materiales metálicos. De forma ocasional se han realizado otro tipo de medidas electroquímicas como resistencia de polarización, para comparar con los resultados de EIS, o curvas de polarización, para estudiar por separado los procesos anódico y catódico, o se han empleado otro tipo de técnicas para obtener algunos datos complementarios, como el espesor de las capas estudiadas o variaciones de color. Los métodos, detalles experimentales y condiciones de trabajo empleados en cada caso se recogen específicamente en los artículos publicados. En este apartado describen las condiciones generales de trabajo y la relación de materiales utilizados.

### 3.1. Selección y preparación de materiales metálicos.

#### 3.1.1. Probetas metálicas.

##### 3.1.1.1. Selección de materiales.

Para selección de materiales para la preparación de probetas se aplicaron dos criterios según el tipo de ensayos a realizar. Para los ensayos de caracterización y optimización del funcionamiento de la celda y el electrolito era necesario disponer de muestras simples y estables, para poder distinguir entre las variaciones o efectos debidos a las diferentes configuraciones de la celda y los debidos a las características o comportamiento del material de la probeta. Para ello se eligieron acero inoxidable y bronce binario. Por otra parte, para evaluar el funcionamiento de la celda en la práctica era necesario disponer de materiales lo más parecidos posible a los objetos sobre los que luego se iba a aplicar; así, se utilizaron probetas de bronce de fundición con pátinas tradicionales y acero patinable con pátinas naturales y artificiales, como los materiales más representativos de la escultura metálica. Así mismo, se prepararon algunas probetas con recubrimientos utilizados habitualmente en conservación y restauración.

### 3.1.1.2. Composición y preparación de las probetas.

- *Acero inoxidable*

Se utilizaron probetas de acero inoxidable AISI 316 (composición expresada como porcentaje en peso Fe 69, Cr 18, Ni 10, Mo 3), de dimensiones 5 x 5 cm y 1.2 mm de espesor, sin lijar, para preservar la capa pasiva original y disponer de una superficie estable.

- *Bronce binario*

Se utilizó bronce laminado EN 1652 de 5x5 cm y 1.5 mm de espesor y composición expresada como porcentaje en peso: 94.07 Cu, 5.85 Sn, 0.055 P, 0.002 Ni, 0.008 Zn, 0.005 Pb y 0.005 Fe.

Inicialmente se emplearon probetas lijadas manualmente con lija de grano 360, 600 y 1200 sucesivamente, realizando 3 pasadas en cada sentido, de manera alterna y lavando con agua destilada. Una vez lijadas se desengrasaron con acetona. Los primeros ensayos demostraron que la superficie recién lijada era muy activa e iba cambiando durante los ensayos, produciendo una distorsión de los resultados. Por este motivo y después de realizar pruebas con diferentes acabados superficiales, se optó por emplear dos tipos de superficies:

- Probetas en estado de recepción. Se comprobó que la superficie no lijada, cubierta de una fina capa de óxido formado de manera natural, resultaba bastante estable. El inconveniente de emplear este tipo de acabado es la limitación en la cantidad de muestras disponibles con un estado superficial adecuado, es decir, libre de manchas, arañazos, etc.
- Probetas lijadas y expuestas al aire durante 6-8 semanas antes de su utilización. Con este sistema se consigue la formación de una fina capa de óxido natural que reduce la reactividad de la superficie, aumentando la estabilidad de las medidas. Se comprobó que de este modo se obtenían resultados equivalentes.

- *Bronce de fundición*

Para trabajar con un material lo más parecido al que posteriormente se iba a encontrar en la realidad se contactó con una fundición tradicional, la fundición Codina, y se encargaron probetas de bronce realizadas con las técnicas y materiales de la escultura tradicional. Se prepararon dos series de probetas de bronce fundido EN 1982 CC491K, de composición nominal como porcentaje en peso: 85 Cu, 5 Sn, 5 Pb, 5 Zn, de 7 x3.5 cm y 7 mm de grosor. El material se fundió y coló en moldes por técnicos de la Fundición Codina simulando el proceso utilizado para la fundición de esculturas.



**Figura 4.** Proceso de patinado de las muestras en la fundición (izda) y pátinas resultantes: pátina tostada a base de sulfuro potásico (inferior) y pátina verde de cloruro amónico sobre base de sulfuro (superior).

Las probetas fueron granalladas y posteriormente patinadas, siguiendo los procedimientos habituales utilizados en la fundición: la primera serie con sulfuro potásico al 10% (potasio sulfuro QP, Manuel Riesgo) en agua aplicado en caliente con brocha (pátina tostada) y la segunda serie aplicando sobre la misma pátina de sulfuro potásico un segundo tratamiento con una disolución de cloruro amónico (cloruro amónico técnico RWN, Manuel Riesgo), también al 10% en agua, aplicado en frío con spray (pátina verde). En la figura 4 se muestra una imagen del proceso de patinado y el aspecto final de las muestras. Estas probetas se han utilizado como referencia para comprobar el comportamiento de la celda con materiales próximos a los de la escultura tradicional y también para comparar medidas de laboratorio con medidas de campo en materiales semejantes.

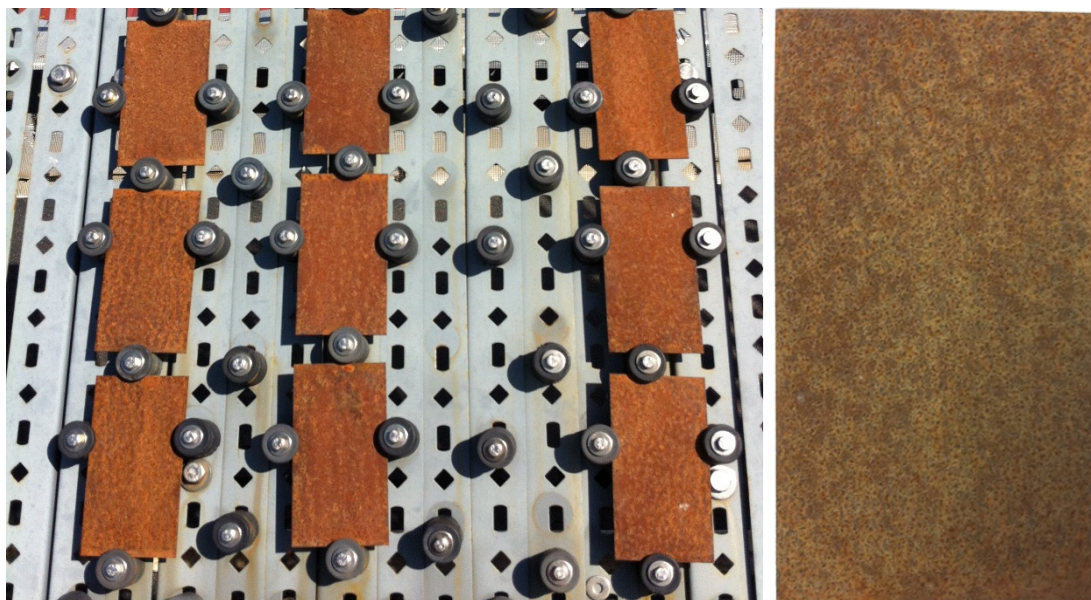


- *Acero patinable*

Se utilizaron probetas de acero patinable Arcelor S355J2W, EN 10025-5-2004, de composición expresada como porcentaje en peso: 0.057 C, < 0.05 Si, 0.35 Mn, 0.017 P, < 0.010 S, 0.57 Cr, 0.30 Ni, 0.35 Cu, 0.025 Al, < 0.010 Nb, resto Fe. Las dimensiones de las probetas eran 10 x 5 cm y 2 mm de espesor, Las probetas fueron tratadas por granallado con corindón para eliminar los óxidos de la superficie.

Una primera serie de probetas había sido expuesta a la intemperie en una estación de corrosión atmosférica en el CENIM según norma ISO 8565:1992 [157] durante 1, 3 y 5 años para la obtención de una pátina natural. Estas probetas formaban parte de otro estudio del grupo CAPA y fueron cedidas para estos ensayos.

Una segunda serie de probetas fue patinada de forma artificial mediante tratamiento con diferentes oxidantes (HCl, H<sub>2</sub>O<sub>2</sub>, NaHSO<sub>3</sub> y un producto comercial, "Rust Activator", fabricado por Modern Masters) para simular los tratamientos de patinado artificial realizados por los artistas contemporáneos. Posteriormente estas probetas también fueron expuestas para permitir su evolución natural con el tiempo. Los tratamientos se detallan en el trabajo correspondiente [144].



**Figura 5.** Probetas de acero patinable oxidadas artificialmente y expuestas a la intemperie (izquierda). Probeta con capa de óxido formada por exposición natural durante 5 años (derecha).

### 3.1.3. Recubrimientos orgánicos.

Para evaluar la respuesta de la celda sobre recubrimientos protectores se prepararon algunas series de probetas con recubrimientos orgánicos, eligiéndose una muestra representativa de los principales productos utilizados por los profesionales de la conservación-restauración del patrimonio metálico: barnices acrílicos y ceras. Siguiendo el mismo criterio que en el caso anterior, los recubrimientos se aplicaron sobre bronce binario lijado para tener un modelo sencillo que facilitase la interpretación, y sobre bronce patinado para disponer de ejemplos comparables a las esculturas en este material.

También se estudió la adecuación de la celda en la evaluación de la capacidad protectora de los diferentes recubrimientos frente al envejecimiento. Para ello se realizaron algunos test de envejecimiento natural y artificial en dos grupos de probetas de bronce recubiertas (ver apartado 4.3.1.2).

#### 3.1.3.1. Recubrimientos aplicados.

Los recubrimientos orgánicos se prepararon a base de resinas acrílicas y cera microcristalina, todos ellos suministrados por Kremer Pigmente GmbH & Co (Alemania). Los productos seleccionados fueron los siguientes:

- Paraloid B-72: copolímero de etil metacrilato y metil metacrilato.
- Paraloid B-67: metacrilato de isobutilo.
- Paraloid B-44: copolímero de metil metacrilato y etil acrilato.
- Paraloid B-48N: copolímero de metil metacrilato y butil acrilato.
- Incralac®: producto comercial preparado a partir de Paraloid B-44 disuelto en tolueno, con benzotriazol y otros aditivos.
- Cosmolloid 80 H: cera microcristalina.

Los barnices se prepararon disolviendo la resina al 15% en xileno, excepto el B-67 que se disolvió en White Spirit y el Incralac que viene ya preparado y se usó sin diluir. De cada uno se aplicaron dos capas, y se dejaron secar 24 h entre capa y capa.

La aplicación de los recubrimientos se ha realizado de dos formas diferentes, según en el enfoque del estudio a realizar:



- Aplicación por inmersión, para lograr una superficie lo más lisa y homogénea posible.
- Aplicación con brocha, para reproducir con mayor fidelidad las condiciones reales, ya que es el método utilizado habitualmente en restauración. En este caso es habitual la aplicación de dos capas sucesivas, en dirección perpendicular.

Los recubrimientos se dejaron secar durante un tiempo mínimo de 4 semanas antes de su medida, para asegurar un buen curado y una completa evaporación del disolvente [158].

Además de estos recubrimientos se realizaron medidas sobre otras probetas de bronce con diferentes combinaciones de Paraloid B44 y/o dos tipos de ceras microcristalinas, Cosmolloid H80 y Soter (un preparado comercial a base de cera y benzotriazol) que fueron suministradas ya preparadas por restauradores del Opificio delle Pietre Dure (OPD) de Florencia, en el marco de un proyecto europeo (IPERION-CH<sup>4</sup>).

### **3.1.3.2. Tratamientos de envejecimiento.**

Tanto para el envejecimiento de los recubrimientos aplicados como para permitir el desarrollo o evolución de pátinas naturales y artificiales se emplearon sistemas de envejecimiento natural y artificial, disponibles en el CENIM.

- *Envejecimiento natural*

El envejecimiento natural de las probetas se realizó por exposición a la intemperie en una estación de corrosión atmosférica, según norma ISO 8565:1992[157], en la azotea del Centro Nacional de Investigaciones Metalúrgicas en Madrid (figura 6 y figura 7). Según la norma, las probetas se expusieron sujetas en soportes inertes, con una inclinación de 45° y orientadas al sur. Las muestras no están cubiertas ni protegidas de ningún modo, quedando expuestas a la radiación solar y

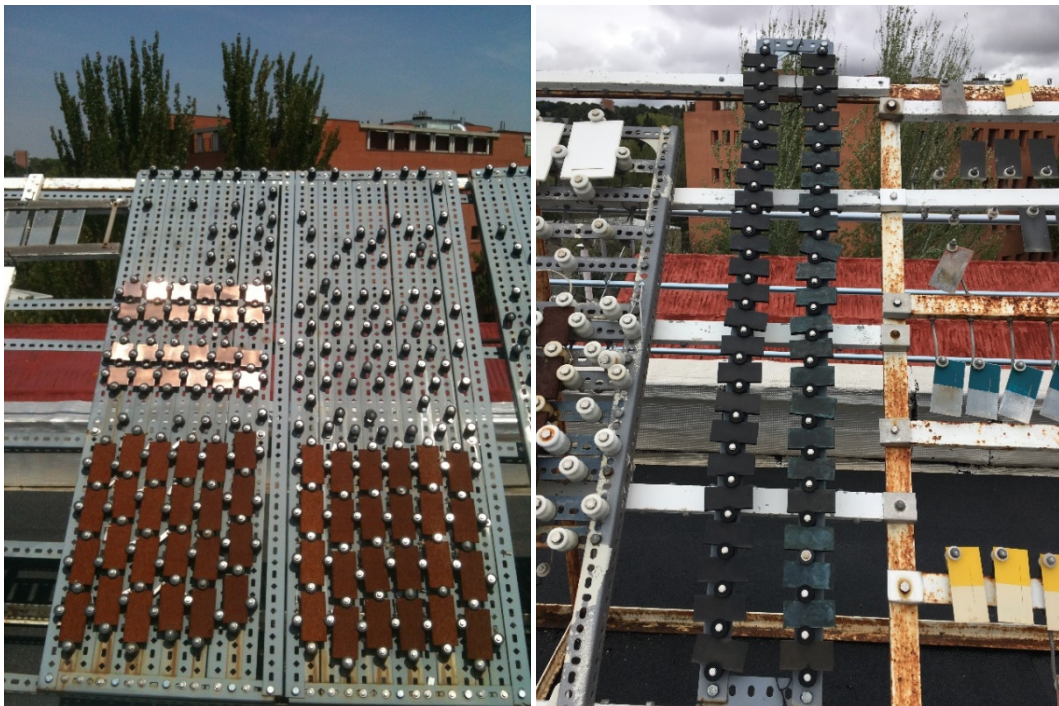
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<sup>4</sup> Proyecto "Integrated Platform for the European Research Infrastructure ON Cultural Heritage" (IPERION-CH) Comisión Europea. H2020-INFRAIA-2014-2015 Grant agreement nº 654028. Mayo 2015-octubre 2019.

precipitaciones naturales. La corrosividad de esta atmósfera corresponde a una categoría C2, de tipo urbano, según la norma ISO 9223:2012 [121].



**Figura 6.** Estación de corrosión atmosférica en la azotea del CENIM.



**Figura 7.** En la imagen izquierda se pueden ver las probetas de bronce lijado con diferentes recubrimientos junto con aceros patinables. En la imagen derecha se sitúan las probetas de bronce con pátinas preparadas en la fundición Codina.

- *Envejecimiento artificial*

Para obtener recubrimientos envejecidos en un periodo de tiempo corto, también se realizó un envejecimiento artificial, de acuerdo a la norma UNE-EN ISO 11507:2007 [159]. El tratamiento se llevó a cabo en una cámara QUV del fabricante Q-Lab, alternando ciclos de radiación ultravioleta (lámpara UVB-313) y humedad (condensación) de 4 h de duración (figura 8). Las probetas se sujetaron a los correspondientes soportes con una cinta adhesiva de doble cara.

El tratamiento realizado se resume en la siguiente tabla:

**Tabla 2.** Condiciones de envejecimiento artificial para las probetas de bronce con recubrimientos.

Ciclo	Radiación	Temperatura
4h UV	0.63 W/(m <sup>2</sup> ·nm)	60 ± 2.5 °C
4h Condensación	Oscuridad	50 ± 2.5 °C



**Figura 8.** Cámara de envejecimiento acelerado de ultravioleta-condensación.

## 3.2. Técnicas electroquímicas.

Todas las medidas electroquímicas se realizaron con la celda desarrollada en este trabajo, cuya construcción forma parte de los resultados y por tanto se describe en el apartado 4.1. En este apartado se detallan los diferentes tipos de electrodos y electrólitos utilizados, así como las condiciones experimentales generales.

### 3.2.1. Electrodos.

Como parte de la optimización de la celda se ensayaron tres tipos de electrodos de referencia y dos contraelectrodos diferentes. En el caso de los electrodos de referencia se compararon electrodos de pseudo-referencia con un electrodo de referencia real, mientras que para el caso de los contraelectrodos se probaron dos geometrías diferentes, del mismo material (figura 9). Los electrodos ensayados fueron los siguientes:

#### *Electrodos de referencia (RE)*

- Pseudo-referencia de alambre de plata 99.9% (Goodfellow). 5.5mm de diámetro, recubierto de cloruro de plata depositado electroquímicamente a partir de una disolución de KCl 0.05M, aplicando una diferencia de potencial de 3V [160].
- Pseudo-referencia de alambre de acero inoxidable AISI316, diámetro 1.4 mm-.
- Electrodo de referencia Ag/AgCl (KCl 1M), CH Instruments (ref CHI111P).

#### *Contraelectrodo (CE)*

- Contraelectrodo de alambre de acero inoxidable AISI316, diámetro 1.4 mm, enrollado en espiral.
- Contraelectrodo de malla de acero inoxidable AISI316, dispuesta de manera paralela a la superficie a medir y sujeta a un anillo del mismo material fabricado con alambre de 1.4 mm de diámetro.

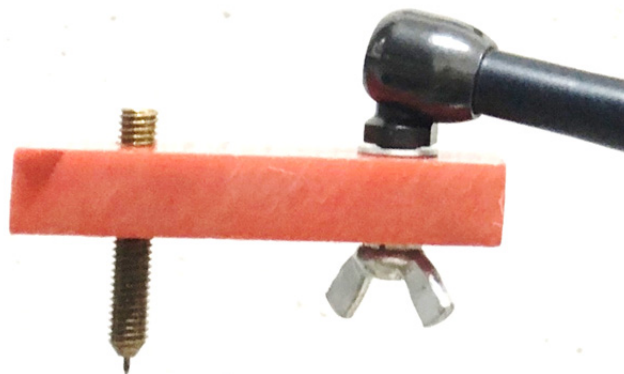




**Figura 9.** Electrodo de referencia (plata y acero) y contra electrodos (malla y espiral).

### *Electrodo de trabajo (WE)*

El electrodo de trabajo lo constituye la probeta o el bien cultural a estudiar, con el que se hace contacto eléctrico de diversos modos dependiendo del objeto a medir. En los estudios sobre probetas metálicas (ver apartado 3.1.2) el contacto se ha hecho directamente con el cocodrilo del cable del potencióstato. Para los estudios sobre obra real, el contacto se ha hecho a través de un tornillo de latón con una punta de acero, presionada sobre la superficie metálica, y conectando el cocodrilo al tornillo. El giro del tornillo, insertado en una pieza de metacrilato, permite ejercer la presión necesaria para ello.



**Figura 10.** Detalle del sistema de contacto con el electrodo de trabajo.

### 3.2.2. Electrólitos.

Uno de los requisitos fundamentales de aplicación de la técnica es no alterar la superficie de medida. Aunque la EIS es en sí una técnica no destructiva, el empleo de un electrólito agresivo puede provocar por sí mismo daños sobre las pátinas. De hecho autores como P. Letardi emplean agua mineral para evitar introducir elementos extraños en la obra [25]. El inconveniente de utilizar agua mineral es la disponibilidad geográfica de una marca concreta y el riesgo de que deje de producirse y se carezca del electrólito de referencia.

#### *Electrólito líquido:*

En la primera fase del desarrollo de la celda de agar se empleó como electrólito una disolución de NaCl al 0.3% en peso, como electrólito sencillo y bien conocido en estudios de corrosión. Sin embargo, se comprobó que podía dejar marca en algunas pátinas, por lo que ha sido necesario buscar una alternativa. Tras considerar las distintas posibilidades se ha optado por utilizar agua de lluvia artificial, [161] concentrada 10 veces para obtener una disolución suficientemente conductora. La disolución, cuya composición se recoge en la tabla 3, se ha ajustado a pH 6.5 con HNO<sub>3</sub>.

**Tabla 3.** Composición del electrólito

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

#### *Gelificante:*

Para gelificar el electrólito se han empleado dos tipos de gelificantes añadidos al electrólito líquido.

- Agar técnico Cultimed (Panreac 401792.1210).
- Agarosa Basic (Panreac A8963)

El agar o agarosa se dispersan en frío en el electrólito previamente preparado, y se calientan a ebullición durante el tiempo necesario para la completa disolución. A continuación, se vierten en el molde y se deja enfriar a temperatura ambiente hasta solidificación.

Para realizar una comparación precisa entre el electrólito líquido y el electrólito gelificado se ha empleado la misma celda y geometrías. Cuando ésta se emplea con el electrólito líquido, la superficie a medir se delimita con un aro de silicona y la celda se coloca en un soporte de tal modo que queda presionada contra la silicona y se evita la salida del líquido (figura 11).

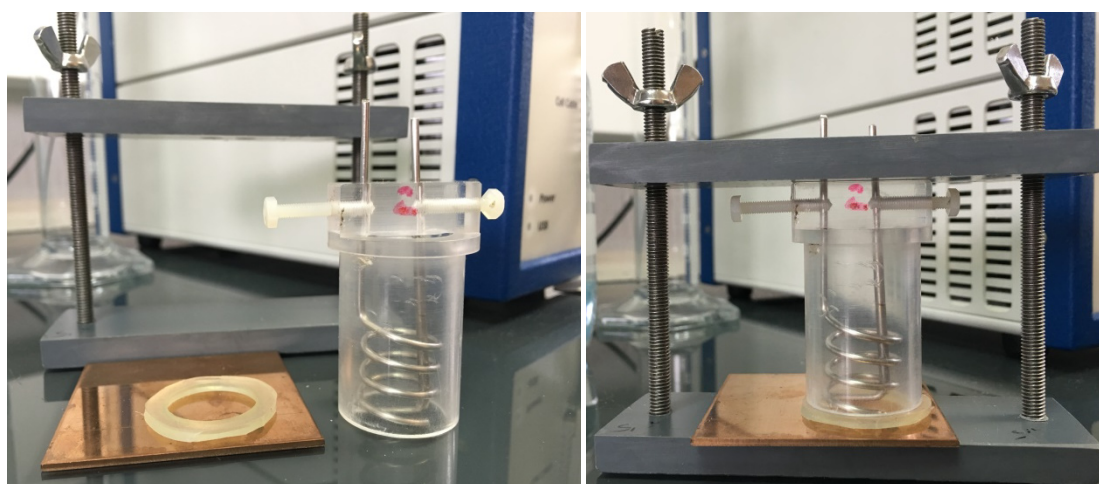


Figura 11. Detalle del montaje con la celda líquida.

### 3.2.1. Técnicas electroquímicas.

Las medidas electroquímicas se realizaron utilizando un potenciostato Gamry Reference 600, con tierra flotante y un cable de 60 cm de longitud. En algunas medidas de campo se utilizó un cable de 1.5 m.

Se realizaron tres tipos de medidas: EIS, resistencia de polarización ( $R_p$ ) y curvas de polarización. En cada uno de los artículos publicados se detallan las medidas realizadas y el objetivo de cada una de ellas.

El tiempo de estabilización de las muestras a circuito abierto ha sido de 1800 s, aunque se han realizado algunos ensayos con tiempos mayores para comprobar la estabilización de las muestras. Tras 1800 s la estabilización no es completa pero si

permite obtener medidas reproducibles, por lo que teniendo en cuenta que se trata de establecer un método para medidas de campo, se considera suficiente.

### 3.2.1.1. Espectroscopía de impedancia electroquímica (EIS).

Descrita en la introducción, la EIS es la técnica principal para la que se ha desarrollado este trabajo y la más adecuada para estudiar recubrimientos orgánicos sobre metales y/o capas gruesas de productos de corrosión.

Los espectros de impedancia se han obtenido con un barrido logarítmico de frecuencia de 100 kHz a 10 mHz, con una amplitud de 10 mV RMS y 10 puntos/decada, excepto en las medidas de recubrimientos que la amplitud ha sido de 20 mV para tratar de mejorar la relación señal/ruido. Todas las medidas se normalizan a un área expuesta de 3.14 cm<sup>2</sup>.

Para la interpretación de los resultados, en algunos casos se ha recurrido al valor del módulo de la impedancia en el límite de bajas frecuencias. En otros casos se ha ajustado el espectro obtenido al circuito equivalente correspondiente mediante el software Zview® (Scribner Associates) o mediante el programa Echem Analyst® (Gamry). Ambos programas son equivalentes y utilizan la misma fórmula para definir la impedancia de los elementos del circuito a excepción de la difusión de Warburg: mientras que el Zview® utiliza las expresiones de la tabla 1, el Echem Analyst® utiliza las siguientes fórmulas:

Difusión semi-infinita: 
$$Z_W = \frac{\sigma_W}{\omega^{1/2}} (1 - j)$$

Difusión finita: 
$$Z_W = \frac{\sigma_W}{\omega^{1/2}} (1 - j) \tanh\left(\delta \left(\frac{j\omega}{D}\right)^{1/2}\right)$$

Donde  $\sigma_W$  = coeficiente de difusión de Warburg;  $\delta$ = espesor de la capa de difusión;  $D$ = coeficiente de difusión. En cualquier caso las expresiones son matemáticamente equivalentes en ambos programas.



El circuito equivalente empleado principalmente en este trabajo para la interpretación de los resultados, salvo ejemplos en los que se detalla otro circuito, es el que se muestra en la figura 12. Este circuito equivalente, al que nos referiremos como "circuito general" permite explicar en la mayoría de los casos los espectros obtenidos tanto en bronce como en aceros patinados, aunque con diferente interpretación. En este circuito  $R_s$  representa la no compensada (principalmente la resistencia del electrolito), el primer par ( $CPE_1 R_1$ ) la capacidad de la pátina y/o recubrimiento y resistencia del electrolito en los poros y defectos de los mismos; y el subcircuito ( $CPE_2[R_2W]$ ) los procesos que ocurren en la superficie del metal: la reacción de transferencia de carga, caracterizada por  $R_{tc}$  y la capacidad de la doble capa electroquímica, representada por  $CPE_2$  o  $CPE_{dl}$ , y los fenómenos de difusión,  $W$ . En el caso de pátinas en aleaciones de cobre estos fenómenos de difusión están relacionados con el transporte de iones cobre en la capa de óxido superficial [45], mientras que para el acero se relacionan con la difusión del oxígeno a través de la capa de óxido [108, 109]. En algunos casos, y en especial en medidas de campo, es necesario introducir una pseudoinductancia,  $L$ , que modela interferencias producidas por acoplamiento entre los electrodos y posiblemente otras interferencias para mejorar el ajuste en la zona de altas frecuencias. Estos artefactos, que se discutirán más adelante, no interfieren en la región de interés y no se comentarán en la interpretación de los resultados de medidas de campo, aunque su valor se reflejará en las tablas para denotar su presencia.

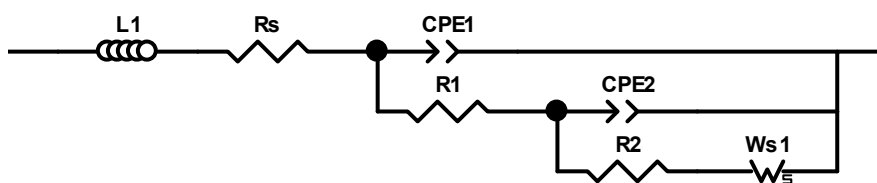


Figura 12. Circuito equivalente general empleado en los ajustes.

### 3.2.1.2. Resistencia de polarización ( $R_p$ ).

La resistencia de polarización lineal se ha utilizado en algunos casos para tener una segunda medida electroquímica del sistema y comprobar la obtención de los mismos resultados con dos técnicas complementarias.

La polarización lineal se basa en aplicar una pequeña polarización en el entorno del potencial de corrosión y medir la intensidad de corriente producida; en esta región, las curvas de polarización presentan un tramo recto, cuya pendiente es la resistencia de polarización.

Los ensayos de resistencia de polarización se han registrado realizando un barrido lineal en un intervalo de -10 a +10 mV frente al OCP a una velocidad de barrido 0.1667 mV/s.

### 3.2.1.3. Curvas de polarización.

Para la caracterización del comportamiento del gel sobre probetas metálicas se han utilizado curvas de polarización de forma puntual, si bien esta no es una técnica aplicable para los estudios de patrimonio por ser una técnica destructiva. Las curvas de polarización se obtienen realizando un barrido de potencial amplio (del orden de los centenares de milivoltios) en dos tramos. En primer tramo se recorre un intervalo de potencial catódico desde un valor arbitrario hasta el potencial de corrosión, en el que únicamente está teniendo lugar la reacción catódica (generalmente la reducción del oxígeno); seguidamente se invierte el signo del potencial y se comienza un barrido anódico en el que se produce la oxidación del metal. Las características de los dos tramos de las curvas, nos dan información separada sobre los procesos anódico y catódico.

En este caso las curvas de polarización se han registrado para un intervalo de  $\pm 150$  mV frente al potencial de circuito abierto (OCP) a una velocidad de barrido de 0.1667 mV/s.

### 3.3. Otras técnicas.

De manera complementaria se han utilizado otras técnicas para caracterizar la morfología, composición o cualidades cromáticas de las superficies estudiadas. En el caso de empleo de técnicas de caracterización habituales en el estudio de materiales, los detalles experimentales se han incluido en las publicaciones correspondientes; únicamente se hará mención aquí a dos técnicas con una aplicación más específica para el estudio de las pátinas y recubrimientos sobre los metales.

#### 3.2.1. Colorimetría.

El análisis colorimétrico permite relacionar la evolución en la composición o el comportamiento de pátinas o recubrimientos con el tiempo con sus valores cromáticos y de luminosidad. Estos parámetros son importantes en el caso de los objetos de patrimonio, en los que las características visuales y/o estéticas son de suma importancia.

Las medidas de color se han realizado mediante un espectrofotómetro Kónica Minolta CM 700D utilizando un iluminante estándar D65 y un ángulo de observador de 10°. La presentación de los datos se realiza conforme al sistema CIE  $L^*a^*b^*$ , que permite representar los parámetros de color (tono, saturación y luminosidad) en un espacio tridimensional. El color se representa en este modelo en función de tres variables: la luminosidad  $L^*$  (0-100, desde negro hasta blanco puros), y las coordenadas cromáticas  $a^*$  y  $b^*$ . La variable  $a^*$  representa un eje que va desde el rojo (+60) al verde (-60), y la variable  $b^*$  corresponde al eje que va desde el amarillo (+60) a azul (-60).

#### 3.2.2. Medidas de espesor.

La determinación del espesor de las pátinas y/o capas de recubrimiento nos permite relacionar este parámetro con el comportamiento más o menos protector de las mismas. La capacidad protectora de una capa depende, entre otros factores, de su grosor, por efecto barrera, y de su compacidad, de modo que el conocimiento del espesor en relación con los valores de los parámetros electroquímicos nos proporciona información sobre las características de dicha capa.

Las medidas de espesor se han realizado con un Elcometer 456, con sonda para metales férricos y para metales no férricos, de acuerdo a la norma UNE-EN 13523-1:2017 [162]. La sonda para metales férricos se basa en el principio de inducción magnética, midiendo la variación del campo magnético generado por la sonda causada por el sustrato magnético. La sonda para metales no férricos se basa en la generación de corrientes inducidas sobre el sustrato metálico, y midiendo el cambio de la impedancia de la sonda causado por las mismas.

## 4. RESULTADOS Y DISCUSIÓN

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### 4.1. Prueba de concepto: diseño de un prototipo y validación de la idea.

El desarrollo de una celda electroquímica específicamente diseñada para la realización de medidas de impedancia in situ se enmarca dentro de los proyectos CREMEL<sup>5</sup> y CREMEL II<sup>6</sup>. En el momento de inicio del primero de estos proyectos, los únicos intentos de utilizar electrólitos gelificados para medidas en patrimonio cultural habían sido los trabajos de Angelini y col. con electrodos de electrocardiograma [68], aunque pronto aparecieron los primeros trabajos de Clare y col.[163]. Sí existían antecedentes de la utilización de electrólitos sólidos en otras aplicaciones (como baterías, dispositivos electrocrómicos, etc. [164-167]) pero excesivamente alejadas de nuestro campo y aunque otros autores habían sugerido el empleo de geles de agar o agarosa para la realización de ensayos electroquímicos [168-170] o estudios de corrosión [171], el número de estudios era muy limitado y no se había realizado un trabajo sistemático para la validación de esta aplicación en concreto. Por ello, el primer paso antes de abordar otras cuestiones era comprobar la posibilidad de realizar medidas de impedancia utilizando un electrólito gelificado con agar y diseñar una celda adecuada para la realización de dichas medidas. La posibilidad de utilizar un electrólito gelificado suponía responder a una serie de cuestiones:

- ¿Es posible obtener un espectro coherente utilizando un electrólito gelificado?
- ¿Son reproducibles los resultados?
- ¿El resultado es comparable al de un electrólito tradicional?
- ¿En qué medida afecta el gel a los resultados?
- ¿Qué consistencia debe tener el gel para que sea adecuado para medir?

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<sup>5</sup> “Conservación-restauración del Patrimonio Cultural metálico por técnicas electroquímicas: desarrollo de una metodología específica adaptada al diagnóstico y tratamiento” (CREMEL) MICINN- Proyectos Investigación Fundamental no Orientada-Convocatoria 2011. HAR2011-22402. Enero 2012 – septiembre 2015.

<sup>6</sup> “Conservación-restauración del patrimonio cultural metálico por técnicas electroquímicas: investigación y aplicación” (CREMEL II) MINECO, Programa Estatal de I+D+i Orientada a los Retos de la Sociedad 2014. HAR2014-54893-R. Enero 2015 – junio 2018.

Para dar respuesta a estas cuestiones, incluidas el objetivo 1, se diseñaron una serie de ensayos, primero para comprobar la posibilidad de medir –tanto en laboratorio como en campo- y luego para abordar el resto de las cuestiones en mayor detalle: determinar en qué grado el agar influye en el comportamiento del electrólito y cuál es la concentración más adecuada, tanto desde el punto de vista de los resultados electroquímicos como de la realización práctica de los ensayos.

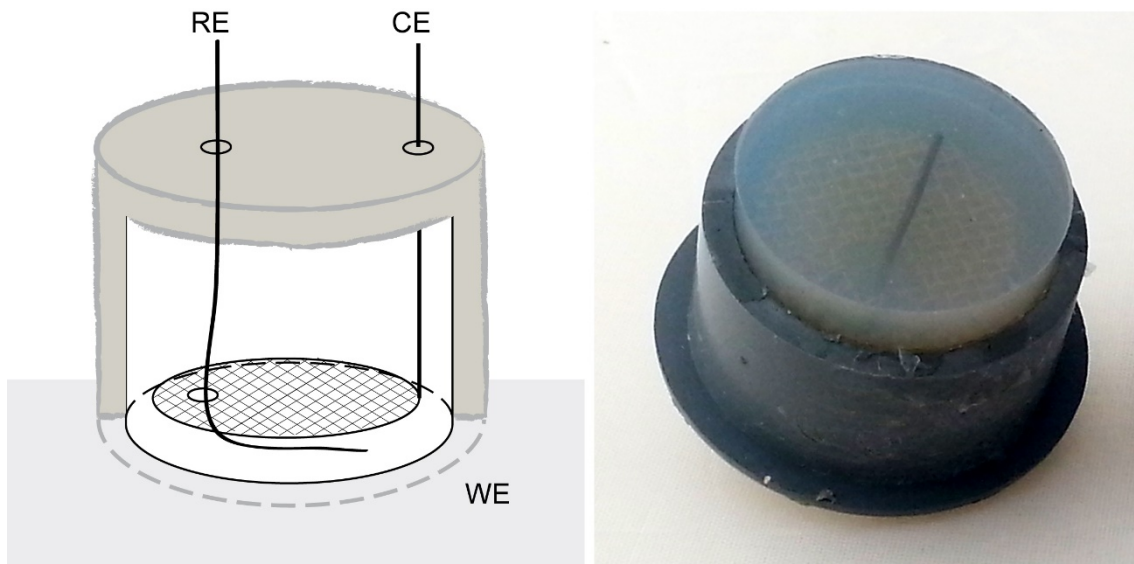
Respecto a las características de la celda en sí, se partió de una serie de premisas para la construcción del primer prototipo (figura 13), para adecuarlo a las particularidades de las medidas en campo:

### *Forma y tamaño*

Para utilizar la celda en campo era necesario que fuera fácil de transportar y de adaptar a geometrías complejas y huecos difíciles. Por otra parte, el tamaño debía poder medir una superficie representativa, dentro de la natural heterogeneidad de las superficies de bienes metálicos expuestos al exterior, y ser suficiente para proporcionar una adecuada relación señal-ruido. Aunque un tamaño pequeño facilitaría su colocación, podría no responder a las premisas de proporcionar una respuesta adecuada. La solución adoptada fue fabricar una celda cilíndrica, de 3.2 cm de diámetro externo y 2.2 cm de altura, con un área de medida de 5.72 cm<sup>2</sup>.

### *Elección de los electrodos*

Para la elección de los electrodos se consideró la necesidad de tener un sistema robusto y resistente. Así, se decidió como primera opción utilizar un electrodo de pseudo-referencia formado por un hilo de plata recubierto de cloruro de plata, que evitaría manejar electrodos de referencia de vidrio más frágiles y delicados, y un contraelectrodo fabricado con una malla de acero inoxidable, con un orificio circular a través del cual se podía colocar el electrodo de referencia para aproximarle lo más posible a la superficie a medir. Así, los electrodos quedarían paralelos a la superficie para evitar distribuciones no homogéneas de la corriente, que en trabajos previos con electrodos sólidos se habían demostrado que podían causar distorsiones de los resultados e incertidumbres sobre el área efectiva que estaba siendo medida [106].



**Figura 13.** Esquema e imagen del primer prototipo de la celda[132] .

Otra de las cuestiones relevantes del diseño es el contacto con el electrodo de trabajo. Mientras que en el caso de los ensayos de laboratorio sobre probetas planas es posible realizar el contacto por medio de un cocodrilo, utilizando una esquina de la probeta, para el caso de las medidas en campo es muy difícil establecer el contacto eléctrico de este modo. Al ser un bien cultural no es aceptable tampoco, limpiar una zona o realizar taladros, soldaduras o similares sobre el metal a estudiar. Teniendo en cuenta estas limitaciones, se utilizó un tornillo con una punta de acero fina, que se presiona sobre la superficie hasta hacer contacto con el metal, aprovechando algún poro o zona desgastada para no dejar marcas visibles sobre la superficie.

Los primeros ensayos con este prototipo se realizaron utilizando un electrólito estándar a base de NaCl 0.3M, gelificado con agar al 5%. Con este diseño inicial se obtuvieron resultados comparables al empleo de un electrólito líquido sobre probetas de laboratorio y se verificó la posibilidad de obtener espectros de calidad sobre obra real [119].

Seguidamente se evaluaron diferentes concentraciones de agar, entre el 1 y el 5%, comprobando la consistencia, adaptabilidad a la superficie y calidad de las medidas. Las distintas concentraciones de agar influyen en la consistencia mecánica del sistema de medida: una mayor dureza del gel puede resultar ventajosa para su manipulación, pero a costa de disminuir la capacidad de adaptarse a superficies irregulares. Estos

ensayos, en los que el NaCl 0.3M se sustituyó por agua de lluvia artificial, más acorde al medio en que se encuentran habitualmente las esculturas y menos agresiva, pusieron de manifiesto una cierta influencia del agar en la medida, especialmente a altas concentraciones. A partir de estos resultados se consideró que la concentración más adecuada para este tipo de medidas se encontraba en torno al 3%. Todo esto se presenta en detalle y se discute en la siguiente publicación:

- B. Ramírez Barat, E. Cano, "The use of agar gelled electrolyte for in situ electrochemical measurements on metallic cultural heritage", *Electrochimica Acta*, 182(2015) 751-62<sup>7</sup>.

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<sup>7</sup> Referencias bibliográficas [25, 26, 34, 35, 45, 53, 68, 104, 106, 112, 119, 122, 127, 128, 160, 161, 167, 172-186] de la bibliografía general.





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# 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.

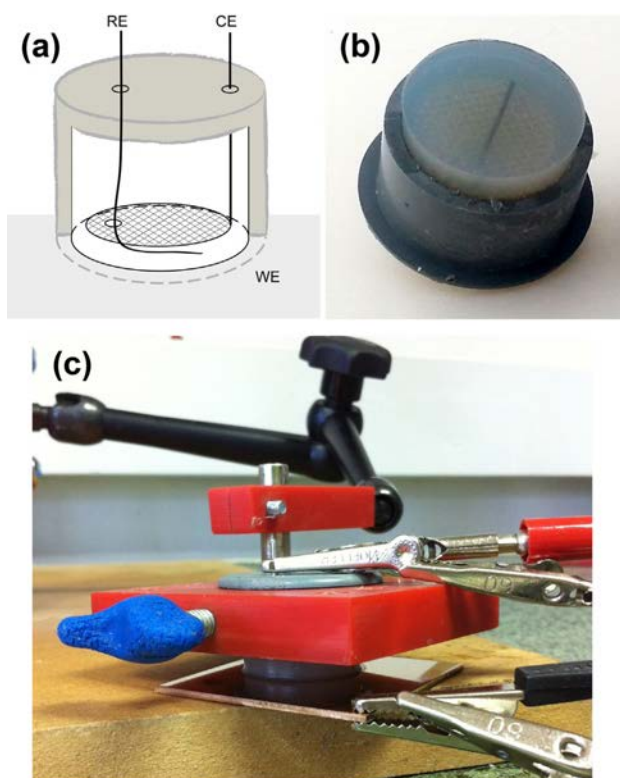
However, the application of this technique for corrosion studies in the field of cultural heritage poses some particular difficulties

[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 agarpectin, both made up of repeating units of agarobiose. While agarose is a neutral linear polymer, agarpectin is partially modified by different hydrophobic (methoxyl) 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 <sub>4</sub> ·2H <sub>2</sub> O	14.43
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	15.04
(NH <sub>4</sub> )Cl	19.15
NaNO <sub>3</sub>	15.13
CH <sub>3</sub> COONa	3.19

pH adjusted to 6.5 with HNO<sub>3</sub>.

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).

measurements, our interest is focused on its use with classical aqueous electrolytes usually employed to evaluate the behavior of one metal in different weathering conditions. In the case of evaluation of cultural heritage objects, several electrolytes have been proposed to simulate marine, urban or rural atmospheres. Nevertheless, the use of these electrolytes may damage the original surface of the object so authors working in this field have proposed mild electrolytes, included slightly mineralized water to avoid introducing aggressive ions on the patinas [7].

Taking this into account, and as an alternative to previously mentioned approaches, authors have recently developed a portable cell based on the use of agar as a gelling agent to support the liquid electrolyte [19]. While initial results have been promising, yielding results that are comparable to a conventional liquid cell, a deeper study of the effect of agar on the results is needed: changes in the electrolyte conductivity were observed with the addition of agar, but have not been studied; and the possible effect of agar in the corrosion process needs to be well understood before the extensive application of this cell for in-situ corrosion measurements.

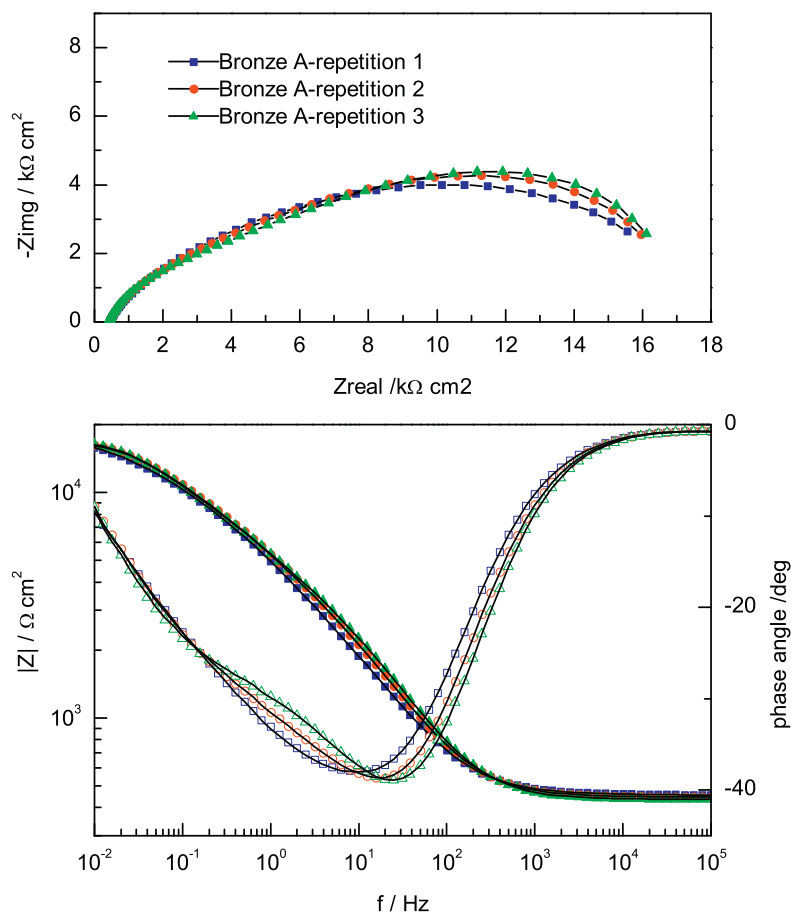
Therefore, the aim of this work is to evaluate the behavior of an agar-gelled electrolyte for its use in a portable cell for in situ electrochemical corrosion measurements on cultural heritage, in order to assess the stability and reproducibility of the measurements and the possible effect of agar in the results.

## 2. Experimental

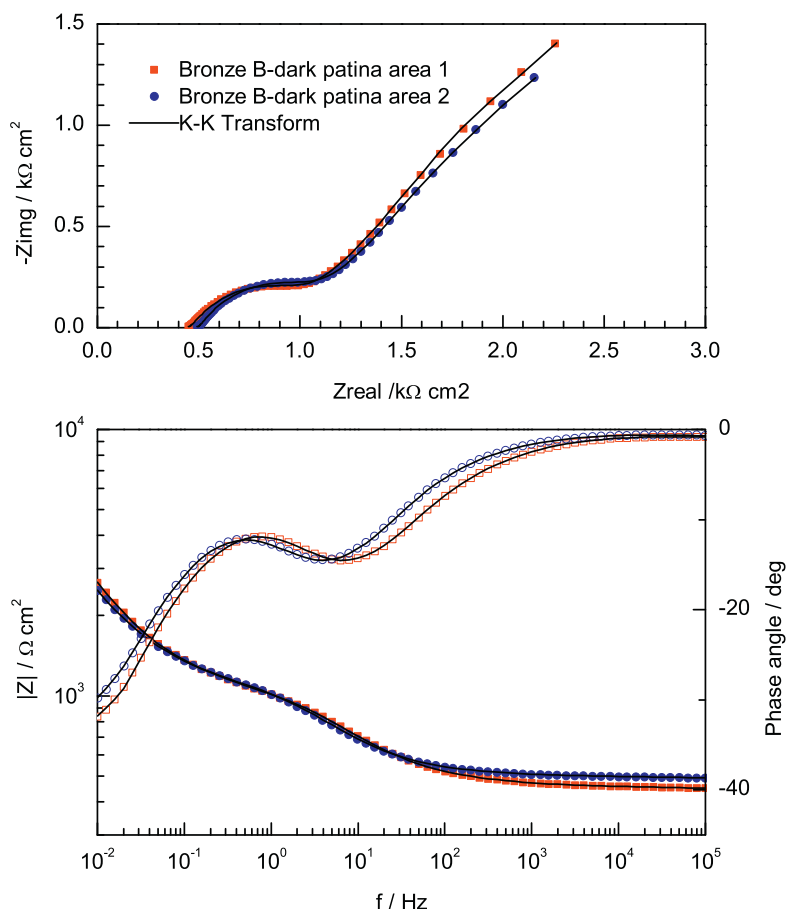
The design of the gel polymer electrolyte (GP-E) cell is described in a previous paper in detail [19], based on a traditional three electrode cell as shown in Fig. 1, where WE is the working electrode or the object under study, CE is the counter made with a AISI 316L stainless steel mesh and RE is a 99.9% silver wire (Goodfellow) electrochemically coated with AgCl, used as (pseudo) reference electrode [20].

The electrolyte has been prepared by gelling artificial rain with agar (technical grade). To minimize the introduction of aggressive ions and to mimic the conditions outdoor sculptures are exposed to, the selected liquid electrolyte has been artificial rain adapted from [21]. Since the conductivity of this solution is too low, it has been used ten times concentrated. The composition of the electrolyte is presented in Table 1. The chloride concentration in this solution is  $3.58 \cdot 10^{-4}$  M. This gives a potential of 0,462 V vs. SHE for the Ag/AgCl coated silver wire used as reference electrode, calculated from Nernst equation.

After the preparation of the liquid electrolyte, 1 to 5% w/v of agar powder has been dispersed in the solution, heated until dissolution, allowed to cool down for a few minutes and casted on the electrochemical cell containing the RE and CE. For comparison, the same electrochemical cell and electrode arrangement has also been used with the liquid electrolyte without agar (agar 0%). The addition of agar slightly increased the pH of the electrolyte, from a



**Fig. 3.** Nyquist (top) and Bode (bottom) plots showing three consecutive measurements on a bronze A coupon. GP-E cell with 3% agar electrolyte. Black lines represent the Kramers-Kronig fitting of data.



**Fig. 4.** Nyquist (top) and Bode (bottom) plots of two different areas from a bronze B coupon with dark patina. GP-E cell with 3% agar electrolyte. Black line represents the Kramers-Kronig fitting of data.

value of 6.6 measured in the liquid solution to a 7.0 value in the 5% agar electrolyte.

Electrochemical measurements have been carried out on two types of samples:  $50 \times 50 \times 1.5$  mm laminated EN 1652CuSn5 bronze coupons (95 Cu, 5 Sn %w), hereafter bronze A; and  $70 \times 35 \times 7$  mm EN 1982CC491K (DIN 1705-RG5) cast bronze coupons (85 Cu, 5 Sn, 5 Pb, 5 Zn %w), hereafter bronze B. Bronze A was selected as a simple model to minimize other variables in the study of the agar behavior, while bronze B was selected to have a system as close as possible to real cast bronze sculptures.

Bronze A was used as received to have a long-term natural oxide layer. Bronze B was prepared to mimic bronze sculptures by Codina Escultura, a traditional Spanish artistic foundry according to traditional materials and techniques: Bronze was casted in ingots, cut into coupons of the desired size and sandblasted. Then, two different artificial patinas have been applied to bronze B, a dark potassium sulfide patina and a green ammonium chloride patina, following traditional patination procedures for artistic sculpture. For the dark patina, a 10% w/v aqueous solution of potassium sulfide was applied by brush and then heated with a blowtorch. Green patina was obtained with a 10% w/v ammonium chloride aqueous solution applied with brush over the dark one. Fig. 2 shows the aspect of the coupons.

EIS spectra have been acquired using a Gamry 600 Potentiostat, using a frequency swept from 100 kHz to 10 mHz, 10 mV RMS amplitude (at the open circuit potential, OCP) and 10 points/decade. The area exposed to the electrolyte was  $3 \text{ cm}^2$ . Analysis of

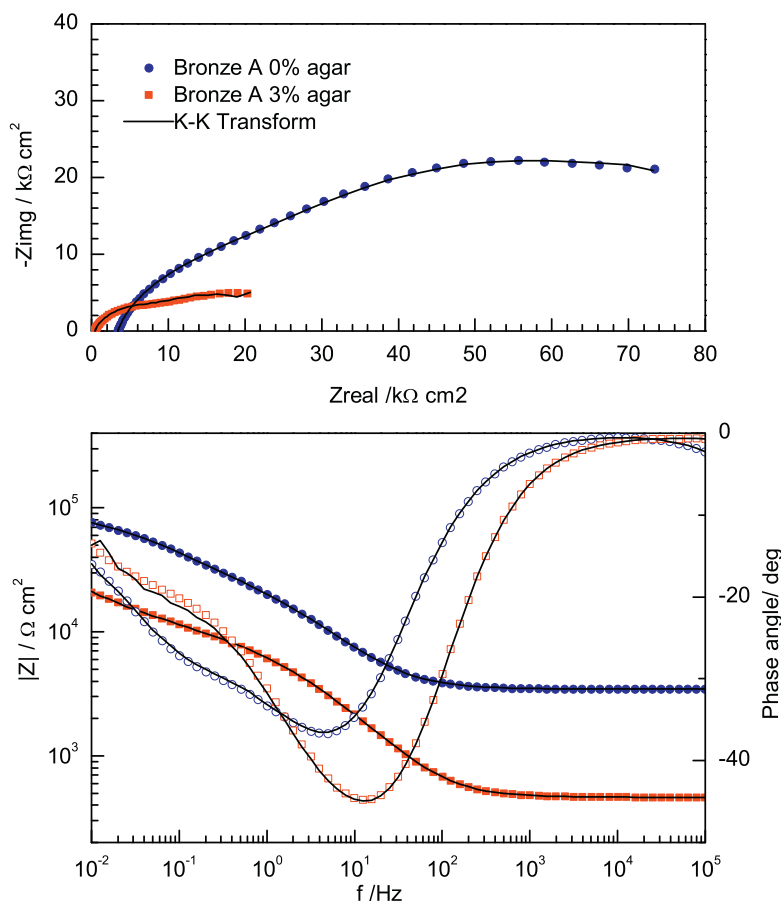
the data has been carried out using ZView software. Polarization curves have been obtained starting from  $-150 \text{ mV}$  vs. OCP and polarizing at  $0.16 \text{ mV/s}$  in the anodic direction.

The system was left to stabilize at OCP for 30 minutes before measurements. As it has been observed and confirmed by other authors [22], the most remarkable variations show in the first 30 minutes and stay small after that time. Between different measurements 5–10 minutes delay has shown to be enough for the stabilization of the OCP.

Conductivity and pH of the electrolytes has been measured with a Crison MM40 conductimeter/pHmeter.

### 3. Results and discussion

In order to validate the system and verify its stability three consecutive EIS measurements were performed on the same sample. Although the system takes some time to stabilize undergoing small changes with time, the general repeatability of the measurements is quite good. Fig. 3 shows an example of three consecutive measurements on a bronze A coupon. Only small differences in the mid frequency appear, being related to slight modifications of surface oxide layers in contact with the electrolyte. Kramers-Kronig analysis was applied to all curves demonstrating the linearity, stability, causality and finite value of all measurements. Results for the patina-covered bronze B samples were even more stable. The small changes in the spectra also demonstrate that the measurements do not alter the surface of the



**Fig. 5.** Nyquist (top) and Bode (bottom) plots of a bronze A coupon. GP-E cell with 3% agar electrolyte (squares) and same cell with liquid electrolyte (circles). Black line represents the Kramers-Kronig fitting of data.

bronze, i.e., the tests are non-destructive and can be safely applied to cultural heritage objects.

Repeatability was also checked in different areas of the same sample. In Fig. 4 two independent measurements on a bronze B coupon covered with dark patina show that measurements on similar surfaces give almost identical responses.

The possible effects of agar were evaluated comparing spectra registered with the same cell filled with liquid electrolyte and gelled electrolyte (3% agar) on different samples. Results are shown in Figs. 5 (bronze A), 6 (bronze B, dark patina) and 7 (bronze B, green patina). The outline from both curves is comparable, the same features being present, although the addition of agar results in a decrease of Z module and a shift of time constants to higher frequencies. As |Z| at high frequencies is related with electrolyte resistance, this indicates that agar addition increases the electrolyte conductivity. The decrease of |Z| at low frequencies and the frequency shift of time constants suggest a direct effect of agar in the corrosion process.

In order to obtain a better understanding of agar influence in our system, different agar concentrations, from 0 to 5% were assayed, using bronze A as a simple model to eliminate the effect of possible inhomogeneities of the different patinas. Agar addition might influence two processes: the resistance of the electrolyte and the corrosion reaction on the metal/electrolyte interface. For our system to be valid to carry out in situ measurements on metallic heritage, corrosion mechanisms should not be

significantly altered by the addition of agar. The electrolyte conductivity, on the other hand, is a parameter that can be subtracted from experimental EIS data, so it does not interfere on the interpretation of the results.

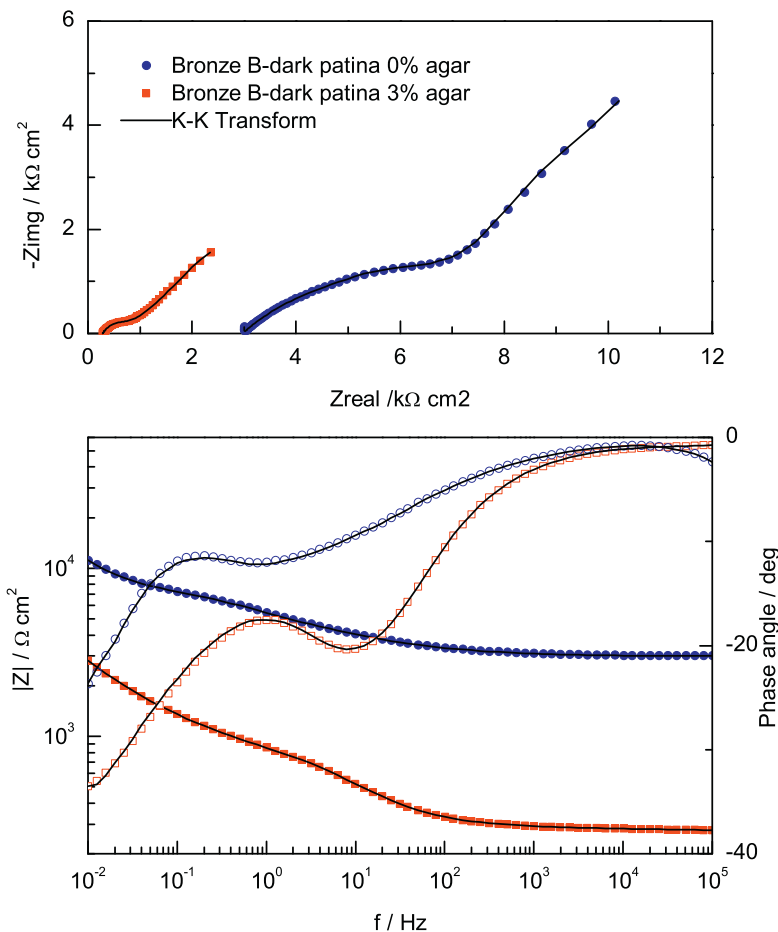
To see how resistance of the electrolyte changes with agar, conductivity of electrolyte with different agar concentrations (0-5%) was measured (Fig. 8). It can be observed that electrolyte conductivity increases proportionally to agar concentration, being a linear function of the concentration of agar plus the conductivity of the electrolyte, according to:

$$K = 76 + 221 [\% \text{agar}] \quad R^2 = 0.99 \quad (1)$$

An additional measurement was done with 3% agar in deionized water to separate the contribution of the liquid electrolyte (artificial rain), giving a value of  $720 \pm 10 \mu\text{S}$ . So, gelled electrolyte's conductivity is the sum of two contributions: agar's conductivity and artificial rain's conductivity, being agar the main responsible of the electrolyte's conductivity. This may represent an advantage for its application in cultural heritage, as it gives higher conductivity to the electrolyte without introducing other ions that may leave dangerous residues on the surface of the object.

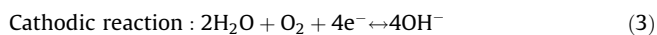
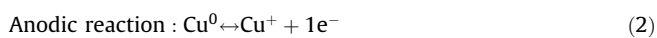
Aiming to understand the corrosion processes, several electrochemical measurements including EIS and polarization curves have been done for 0 to 5% agar. Polarization curves have been registered to elucidate the effect of the agar on the anodic and cathodic reactions. Fig. 9 show the polarization curves obtained in





**Fig. 6.** Nyquist (top) and Bode (bottom) plots of a bronze B coupon with dark patina. GP-E cell with 3% agar electrolyte (squares) and same cell with liquid electrolyte (circles). Black line represents the Kramers-Kronig fitting of data.

bronze A. Under our experimental conditions (aerated neutral pH electrolyte), the expected main anodic and cathodic reactions are:



The cathodic branch seems to follow a Tafel behavior with no significant changes in the slopes with the increasing concentration of agar. This indicates that the cathodic process (eq. (3)) is under charge transfer control and that the addition of agar up to 5% does not substantially change the kinetics of this reaction. On the other hand, agar clearly affects the anodic branch, increasing the anodic slopes as the concentration of agar increases, and suggests a direct interaction between agar and copper ions which shifts the anodic reaction towards the oxidation of copper (eq. (2)).

Experimental EIS data for 0-5% agar electrolytes are presented in Fig. 10. The general shape of the spectra shows two time constants. The increase of electrolyte conductivity with agar concentration is clearly appreciated in the impedance at high frequencies. Also, a decrease in the size of the capacitive loops in Nyquist plots is observed with increase in agar concentration.

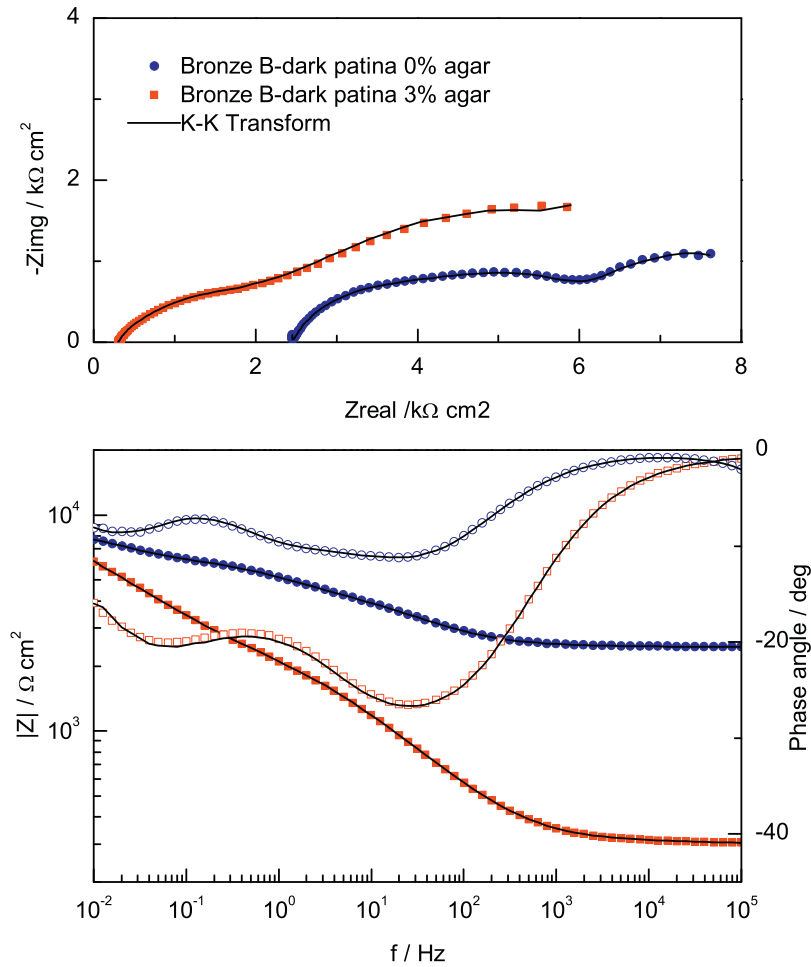
The large changes in the electrolyte resistance ( $R_0$ ) obscure the analysis of the effect of agar in the corrosion reactions on the metal-electrolyte interface. To avoid this effect, electrolyte resistance (obtained from intersection of the extrapolation of

high frequency loop with the real axis in Nyquist plots) has been subtracted from the EIS data. This representation eliminates the distortion induced by this resistance and allows better comparison of spectra [23]. Additionally, data above  $10^4$  Hz showed artifacts attributable to instrumental effects, and therefore have been eliminated for analysis. Corrected ( $Z-R_0$ ) impedance modulus and phase angle versus frequency data are presented in Fig. 11. The features of the curves for all concentrations of agar are similar, indicating that the addition of agar does not alter significantly the electrode reactions, thus supporting the use of this gelled electrolyte for EIS measurements.

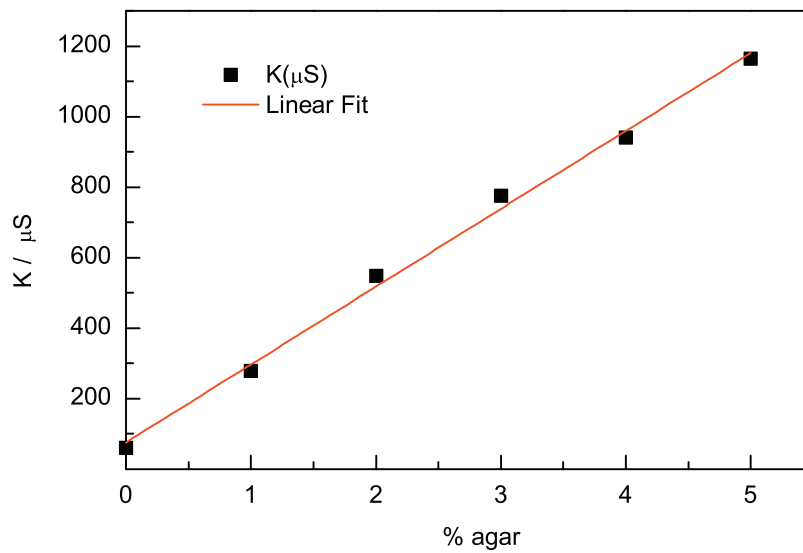
Two different slopes can be clearly observed in Fig. 11. The slope of the high frequency part of the data (above 10 Hz) gives a value of  $\sim -0.8$  for all measurements, and the low frequency part (below 1 Hz) has a slope between 0.3 and 0.35. These slopes depart from the ideal capacitive behavior (slope of -1), indicating a distribution of the time constants. This distribution of the time constants is commonly modeled by a constant phase element (CPE):

$$Z_{CPE} = \frac{1}{Y(j\omega)^\alpha} \tag{4}$$

whose actual physical meaning could be very different depending on the system: this response has been attributed to surface roughness and heterogeneities, to electrode porosity, to variation of coating composition, to slow adsorption reactions, and to non-uniform potential or current distributions [24]. As a first approach



**Fig. 7.** Nyquist (top) and Bode (bottom) plots of a bronze B coupon with green patina. GP-E cell with 3% agar electrolyte (squares) and same cell with liquid electrolyte (circles). Black line represents the Kramers-Kronig fitting of data.



**Fig. 8.** Conductivity increase of the electrolyte with agar concentration.

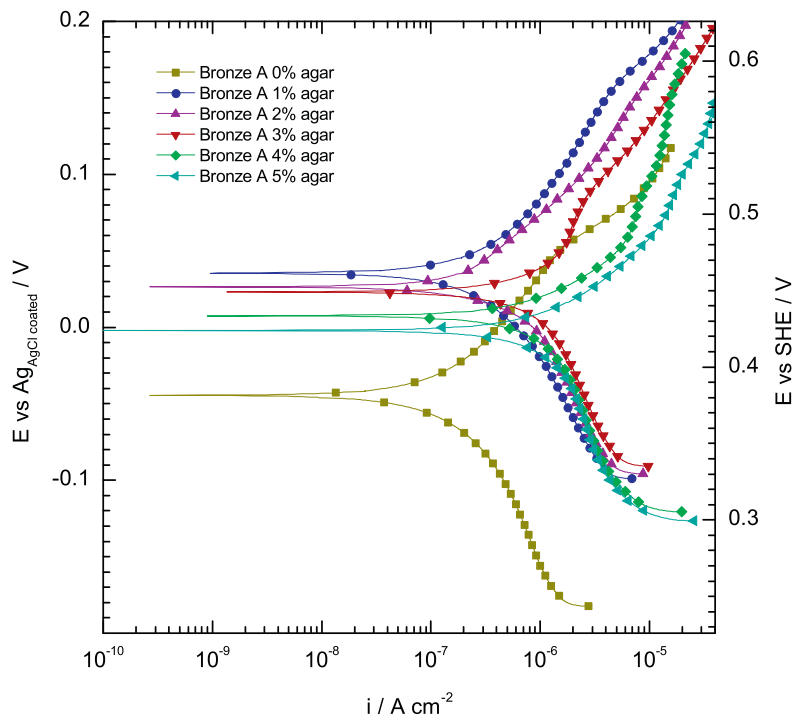


Fig. 9. Polarization curves obtained in bronze A with different agar concentration.

experimental data were fitted to an equivalent circuit with 2 nested CPE-R pairs, as shown in Fig. 12a. To give a physical meaning to the mathematical analysis several possibilities may be evaluated.

One approach is to interpret the results according to the classical equivalent circuit for modeling an imperfect metal-coating system, in which elements of circuit 12a are interpreted as:  $R_0$  represents the electrolyte resistance,  $CPE_1$  represents the pseudo-capacitance of the patina or oxide layer on the metal surface and  $R_1$  the resistance of the electrolyte through the pores; and  $CPE_2$  in parallel with  $R_2$  represent the pseudo-capacitance of the double layer at the metal-electrolyte interface and the charge transfer resistance of the corrosion reaction respectively. In this hypothesis the distribution of time constants of  $CPE_2$  would be related to inhomogeneous current distributions due to both irregularities in the metal surface [20] and to the presence of agar molecules at the interface. As agar molecules interact with the metal surface and favor the corrosion process, an increase of agar would explain the decrease of impedance contribution associated to  $CPE_2$ .

Nevertheless, the values of  $\alpha_2$  with this model are about 0.5 for all conditions. This value is too low to be attributed to inhomogeneities or roughness of the surface, especially considering the smooth and apparently regular surface of bronze A (see Fig. 2), that is was not altered by the measurements. Recent works have also demonstrated that pure geometric aspects (surface roughness) can not explain a CPE behavior [25,26].

A second tentative interpretation of the distribution of the time constant at low frequencies is to assign it to the impedance of a porous electrode. Under de Levie's assumptions (equal cylindrical pores uniformly distributed in the electrode surface), the impedance of a porous electrode is given by:

$$Z_{deLevie} = (R_c Z_0)^{0.5} \coth\left(\frac{l_c}{\lambda}\right) \quad (5)$$

being  $R_c$  the electrolyte resistance within the pore,  $Z_0$  the impedance of the flat electrode developed in the cylindrical pore,  $l_c$  the pore depth and  $\lambda = (Z_0/R_c)^{0.5}$  the penetration depth of the AC

signal in the pore [3,27]. Hernández et al. [3] found this kind of response on rough copper electrodes when exposed to NaCl. In our case, the short exposure times and the low aggressiveness of the electrolyte (the chloride concentration of our electrolyte is much lower) did not change the original smooth surfaces of the sample. Since according to eq. (5), when the pores are shallow the response of the electrode is similar to that of a flat electrode, it is not likely that the dispersion of the time constant can be attributed to porosity.

For copper corrosion in milder electrolytes, with composition and pH much similar to the one used in our study, the aforementioned article by Hernández et al. (using synthetic rain of Sao Paulo, pH5) [3] and a previous one by Feng et al. [28] (using synthetic tap water, pH 7.6) found that the dispersion of the time constants was attributable to diffusion of copper ions within the oxide layer and the electrolyte. The equivalent circuit modeling this behavior is presented in Fig. 12b in which the second CPE has been replaced by a generalized finite length Warburg impedance:

$$Z_{GLW} = \frac{R}{(Tj\omega)^\alpha} \tanh(Tj\omega)^\alpha \quad (6)$$

This expression is the solution to the one-dimensional anomalous diffusion equation subject to the absorbing boundary. When  $\alpha=0.5$ , this equation corresponds to the finite length Warburg impedance. The numerical data for the different parameters obtained by fitting to this equivalent circuit are presented in Table 2. It should be mentioned that for 4 and 5% agar, a third time constant seems to appear at the lowest frequencies. While it is not clearly defined as to propose an additional element in the circuit, it distorts the fitting at the last points, causing inaccuracies in the estimation of the parameters of the diffusional impedance for these conditions (values marked with asterisk in the table).

The values of  $\alpha_{GLW}$  are about 0.35 (corresponding to the slope of the low frequencies part of data in Fig. 11), therefore the diffusional impedance in our system does not follow the pure finite Warburg diffusion. The reason for this behavior is not clear, and



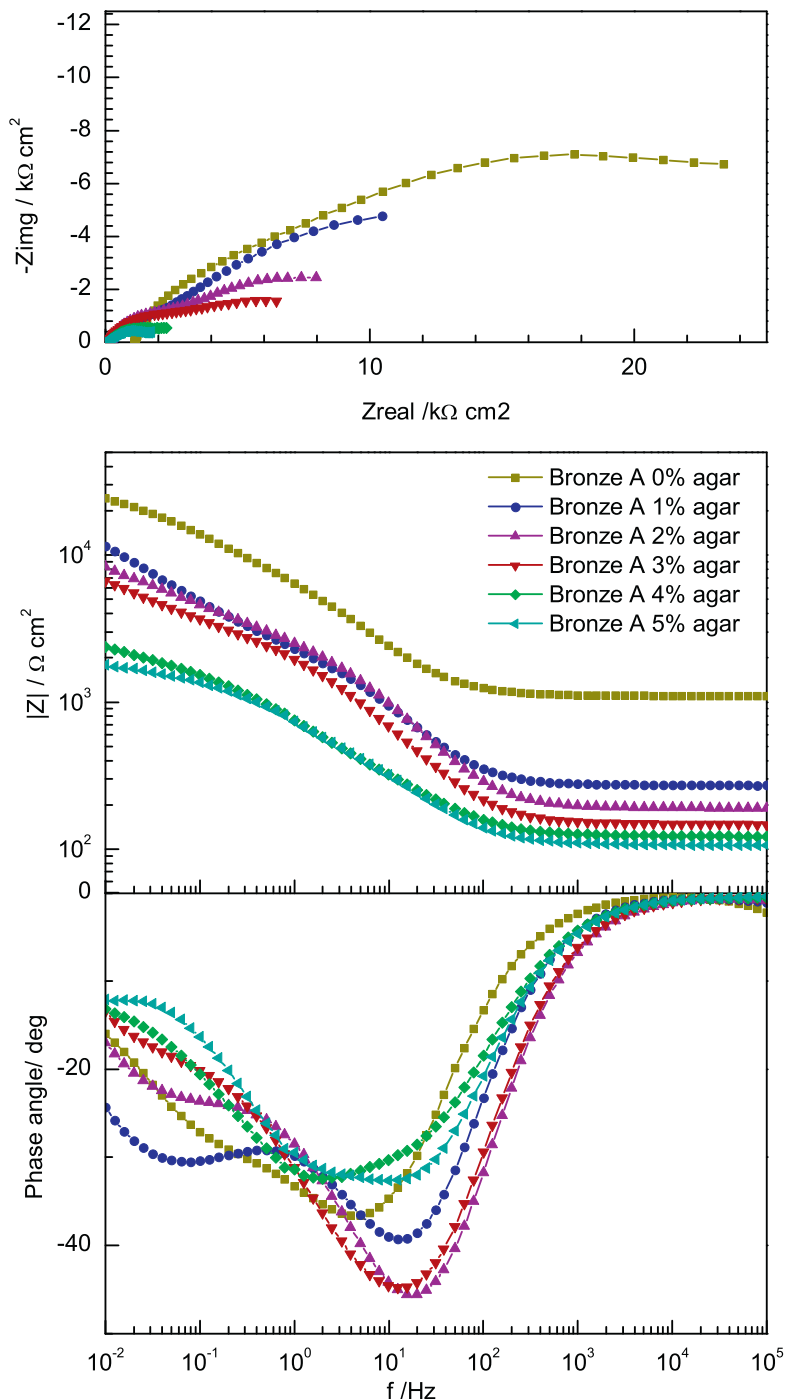
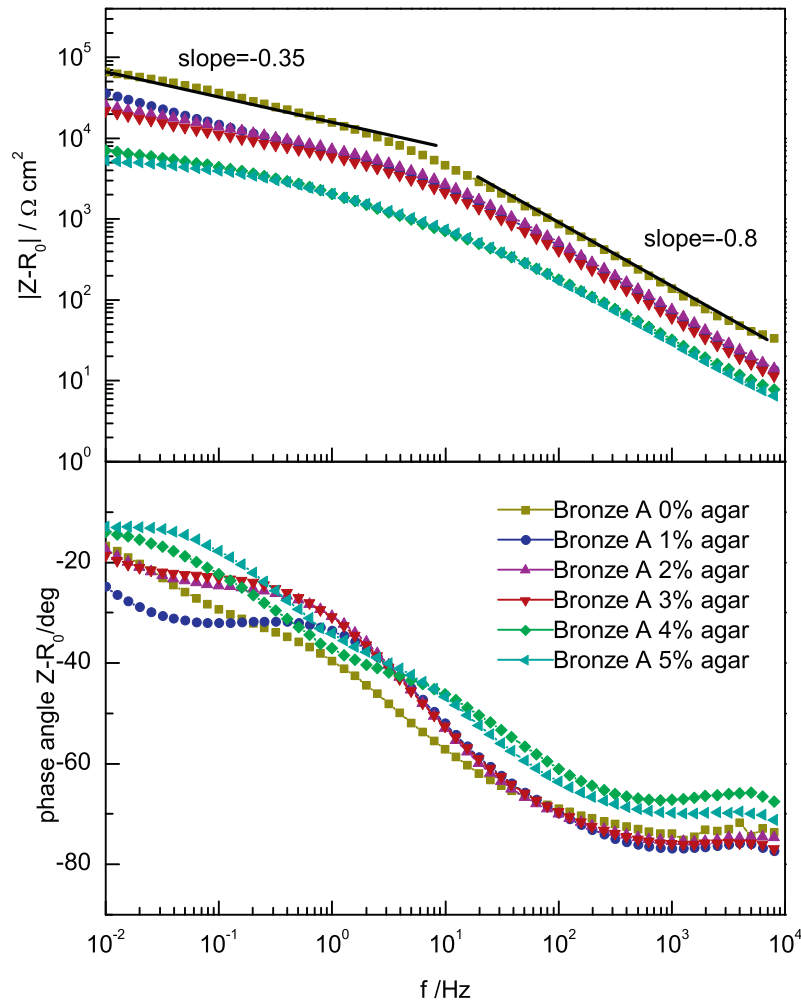


Fig. 10. Nyquist (top) and Bode (bottom) plots of EIS data for bronze A with different concentrations of agar 0-5%.

might be related with complex diffusion phenomena or to the overlapping of other processes, such as the impedance of the thin oxide layer on the metal surface. In any case, this behavior appears both in the liquid electrolyte and the gelified electrolyte, so it is not a consequence of the addition of agar.

From the analysis of these results, it can be inferred that the addition of agar slightly decreases  $R_{ct}$ , thus increasing the anodic dissolution of copper. An increase in  $C_{dl}$  is also observed, attributable to the interaction of charged moieties of agar molecules with the electrode surface. However, this increase is negligible until 3% agar. The affinity of agar and other biomolecules

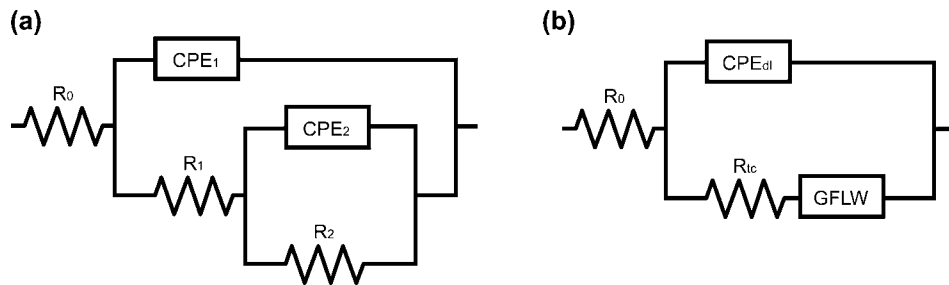
for metallic ions is not unknown. There are many studies on metal uptake by different biomaterials for environmental applications [29] and agar and algae *Gelidium* (which is the raw material for agar extraction) have been studied as biosorbents for copper removal in wastewater [30,31]. These biomaterials contain functional groups which may act as binding sites for metal ions, therefore acting as anodic depolarizers when used in corrosion studies. A more detailed study on binding equilibrium between agar and copper would be of interest although it is out of the scope of this work.



**Fig. 11.** Modulus (top) and phase angle (bottom) of corrected impedance ( $Z-R_0$ ) as function of frequency for bronze A with different concentrations of agar 0-5%.

Our results show that the addition of agar to the artificial rain electrolyte in concentrations up to 3% does not alter the corrosion mechanisms, although it increases the corrosion rate by decreasing faradaic impedance. The most evident effect of the addition of agar, the decrease in the resistance of the electrolyte, can be easily subtracted from experimental data, and can be even favorable for field measurements as it increases the range of measurable impedances. When using the gelled electrolyte for the assessment of protective properties of patinas or coatings on metallic cultural heritage these effects can be disregarded provided the results are reproducible and allow obtaining data comparing the protective

properties of different coatings or following their evolution with time. Although corrosion rate in a determinate electrolyte will be overestimated with the addition of agar, quantitative absolute values of corrosion rates are not usually of interest when evaluating patinas or coatings for atmospheric exposure, as in these atmospheric conditions the metal is not continuously immersed in the electrolyte. These comparative results permit choosing between different coatings or monitoring changes in corrosion resistance of a surface, thus being a powerful tool for establishing conservation strategies for metallic cultural heritage. This application of gelled electrolyte cell for the comparison of



**Fig. 12.** Equivalent electrical circuits used to analyze EIS data.

**Table 2**

Electrochemical parameters obtained from fitting to equivalent circuit in Fig. 12b of EIS measurements on bronze A with liquid electrolyte and gelled electrolyte with agar 1 to 5%.

Agar %	CPE <sub>dl</sub>		R <sub>ct</sub> (kΩ cm <sup>2</sup> )	Z <sub>GFLW</sub>		
	Y <sub>dl</sub> (μS s <sup>α<sub>dl</sub></sup> cm <sup>-2</sup> )	α <sub>dl</sub>		R (kΩ cm <sup>2</sup> )	T (s)	α <sub>GFLW</sub>
0%	6.4 ± 2	0.799 ± 0.004	8 ± 2	78 ± 5	26 ± 6	0.32 ± 0.02
1%	8.8 ± 0.2	0.846 ± 0.002	3.4 ± 0.1	45 ± 1	40 ± 3	0.397 ± 0.005
2%	8.6 ± 0.1	0.837 ± 0.001	4.0 ± 0.1	33.0 ± 0.8	57 ± 5	0.311 ± 0.004
3%	10.3 ± 0.2	0.845 ± 0.002	2.5 ± 0.2	31 ± 2	90 ± 20	0.294 ± 0.007
4%	39 ± 1	0.756 ± 0.04	0.8 ± 0.1	4.9* ± 0.3	1.9* ± 0.3	0.38* ± 0.02
5%	33.08 ± 0.8	0.785 ± 0.02	0.9 ± 0.1	3.9* ± 0.2	1.5* ± 0.3	0.37* ± 0.01

different patinas and coating systems is currently being tested in real conservation applications. Preliminary results have shown the applicability of the agar G-PE cell as a non-destructive diagnostic tool [32,33].

**4. Conclusions**

The agar gelled electrolyte allows to obtain repetitive and good quality EIS spectra. Some differences between the spectra of the liquid and gelled electrolyte have been observed, due to an increase in conductivity and a slight depolarization effect of the agar. For application on cultural heritage studies, these effects can usually be disregarded since the results are reproducible and allow obtaining comparative data of different substrates, patinas and coatings, and follow their evolution with time. In consequence, agar gel polymer electrolyte (GP-E) cell has proved to be an interesting alternative to carry out in-situ EIS tests on metallic cultural heritage, solving some of the difficulties of the experimental setups used by other authors. The information obtained by this technique can provide conservators-restorers quantitative data about the corrosion protection properties of patinas and coatings.

**Acknowledgements**

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## 4.2. Optimización del diseño.

Una vez validada la posibilidad de utilizar el agar como electrólito se planteó la mejora del diseño a partir de los resultados obtenidos. En este caso se abordaron dos cuestiones, en primer lugar, la evaluación y optimización de los parámetros de diseño, y en segundo lugar, posibles modificaciones del electrólito.

En cuanto al diseño de la celda, se ha trabajado en el estudio y mejora de dos aspectos: la construcción de la celda en sí y su soporte para adecuarla a la aplicación para la que ha sido diseñada, la realización de medidas de campo sobre objetos del patrimonio cultural; y la selección del tipo y posición de los electrodos para la obtención de las medidas electroquímicas.

Estas adaptaciones del diseño pretenden dar respuesta a las dos principales dificultades identificadas a la hora de realizar las medidas en los primeros ensayos, el reto de posicionar una celda electroquímica sobre la superficie irregular –y generalmente inclinada y con cierta rugosidad- de una escultura o monumento, y la dificultad en la interpretación de los resultados. En este sentido, además de la propia irregularidad de la superficie a estudiar, el empleo de electrólitos de baja conductividad aumenta la importancia de posibles efectos o contribuciones del sistema de medida al espectro de impedancia obtenido. Algunos estudios han demostrado que, dependiendo de la geometría de la celda y la conductividad del electrodo pueden aparecer artefactos en las medidas, motivados por acoplamientos entre los electrodos, y que en ciertos casos pueden interferir en la región del espectro de interés para los estudios de corrosión (típicamente 100 kHz - 1 mHz) [187-189]. Por este motivo se ha realizado un trabajo para estudiar la posible influencia del tipo y posición de los electrodos en la celda en la señal obtenida. Parte de estos estudios se realizaron en colaboración con la investigadora italiana Paola Letardi, del Istituto di Scienze Marine (ISMAR)- Consiglio Nazionale delle Ricerche, con la idea de comparar resultados entre diferentes sistemas de medida.

### 4.2.1. Construcción de la celda y optimización de los parámetros de diseño.

La construcción de la celda y especialmente el diseño de un sistema de sujeción adecuado para posicionarla durante las medidas no resulta una cuestión trivial, como se fue comprobando desde las primeras medidas de campo realizadas con el prototipo inicial. A lo largo de todo el desarrollo de este trabajo se fueron introduciendo modificaciones en la celda para ir solventando las dificultades que se iban encontrando en cada paso. Los principales aspectos considerados fueron:

- El diseño del molde que contiene el agar de tal modo que facilite la colocación de la celda y la obtención de una buena superficie de contacto entre el gel y la escultura.
- La construcción de un soporte adecuado que asegure la correcta sujeción de la celda, un buen contacto con la superficie de la obra y evite la tensión de los cables de conexión con el potencióstato.

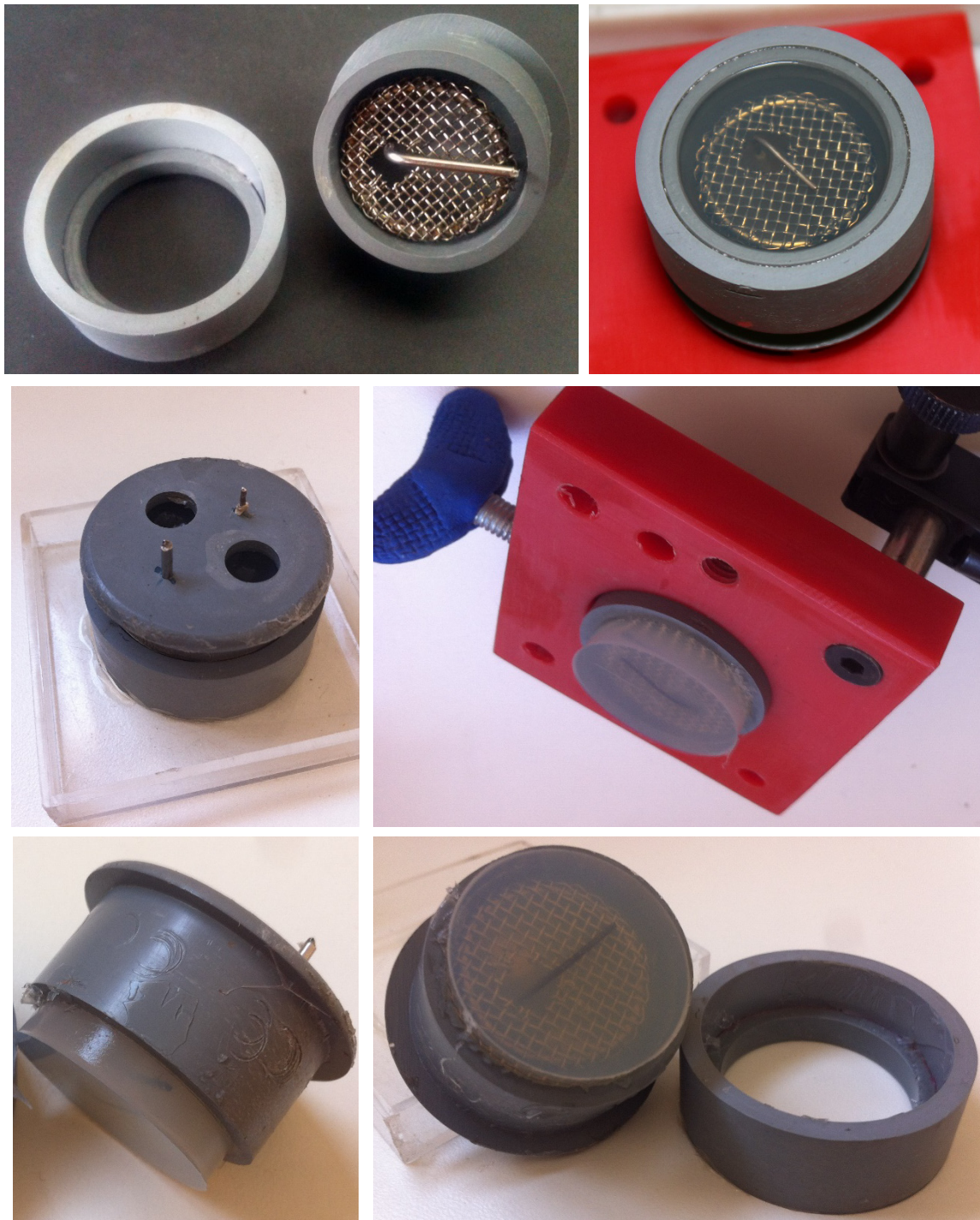
Teniendo en cuenta estas cuestiones, el diseño de la celda fue evolucionando desde el primer prototipo, en la figura 14, hasta el diseño utilizado en la actualidad, que se puede comparar en la figura 15 .

#### *Diseño del molde:*

El molde que contiene el gel se modificó en material, construcción y dimensiones. El PVC inicial se sustituyó por metacrilato transparente, para poder visualizar el interior de la celda y verificar tanto la correcta disposición de los electrodos (electrodo de referencia y contraelectrodo), como la ausencia de defectos en el gel. Para fijar la posición de los electrodos, que inicialmente se sujetaban por presión, se han colocado con unos tornillos de nylon. La construcción del molde se realiza en dos piezas, un cuerpo cilíndrico y un contra-molde ciego en la parte inferior; el agar se vierte por la zona superior, obteniéndose así una superficie de contacto perfectamente plana. Las nuevas dimensiones utilizadas para la celda han sido 2.5 cm de diámetro y 5 cm de altura, con un diámetro interno de 2cm, que proporciona un área de medida de  $3.14 \text{ cm}^2$ . La mayor longitud y menor diámetro de la celda facilitan su colocación en la superficie a medir y la visualización de la zona de contacto entre la



superficie de la celda y la superficie de estudio. Así, es posible conseguir una buena adaptación del gel a la forma y a la textura de la superficie estudiada (figura 16).



**Figura 14.** Diseño inicial del molde, con dos piezas de PVC gris y el soporte de metacrilato para sujetar la celda. En los primeros ensayos el vertido del agar se realizaba por la base, con la celda invertida. Posteriormente realizaron unos orificios en la parte superior para verter el electrolito a través de ellos con la celda apoyada sobre una placa de plástico. De este modo se obtenía una superficie más plana.



**Figura 15.** En las dos imágenes superiores se muestra el diseño final del molde de metracrilato, de dos piezas; en la parte superior se han realizado dos taladros para la colocación de los electrodos, que se sujetan a la altura deseada con dos tornillos de nylon. En las imágenes inferiores se puede ver la celda rellena con agar y el detalle de la colocación de la celda en contacto con una probeta metálica en una superficie plana (centro) y curva (derecha).





**Figura 16.** Capacidad de adaptación del gel a la textura y forma de la superficie medida.

***Diseño del soporte:***

Además de la celda con los electrodos y el electrolito ha sido necesario idear un sistema para situar y fijar la celda en contacto con la superficie a medir. Los aspectos clave a tener en cuenta en este caso son de tipo geométrico y de estabilidad: el soporte debe facilitar el acceso y el posicionamiento de la celda en la superficie a medir y tener la firmeza suficiente para mantener el contacto adecuado.

Las principales dificultades encontradas están relacionadas con mantener un buen contacto entre la superficie del gel y la superficie metálica. Por un lado, el potencióstato debe situarse a una distancia que está limitada por la longitud de los cables, cuya tensión puede tirar de la celda y separarla de la superficie. Por otra parte, el soporte debe ser firme para permitir la presión de la punta metálica en el electrodo de trabajo garantizando el contacto eléctrico. Como se ha comentado en el apartado anterior, el contacto eléctrico con el electrodo de trabajo, necesario para la realización de las medidas se realiza con una punta metálica. Para que este contacto sea efectivo la punta debe estar en contacto firme con la superficie metálica, lo que requiere una cierta presión, que se consigue enroscando el tornillo en la pieza que lo sostiene. En el primer diseño la punta metálica se insertaba en el mismo soporte de metacrilato que la celda (figura 17) sin embargo esto hacía que en ocasiones el gel se separase de la superficie de la escultura al presionar para hacer contacto, lo que se corrigió más adelante, separando el tornillo de contacto del resto de la celda (figura 18).

El soporte para la sujeción de la celda durante la realización de las medidas también se fue modificando, desde el primer sistema empleado en los ensayos iniciales, que se limitó a un pie de laboratorio (figura 19), hasta el sistema final. Como primer paso se introdujo un brazo extensible – (figura 20)- que posteriormente fue sustituido por un brazo articulado de fotografía, sujeto a una barra de aluminio. Este último sistema aportaba la gran ventaja de contar con una rosca que bloquea simultáneamente las diferentes articulaciones del brazo en la posición deseada.



Figura 17. Primer diseño de la celda posicionado sobre una escultura.

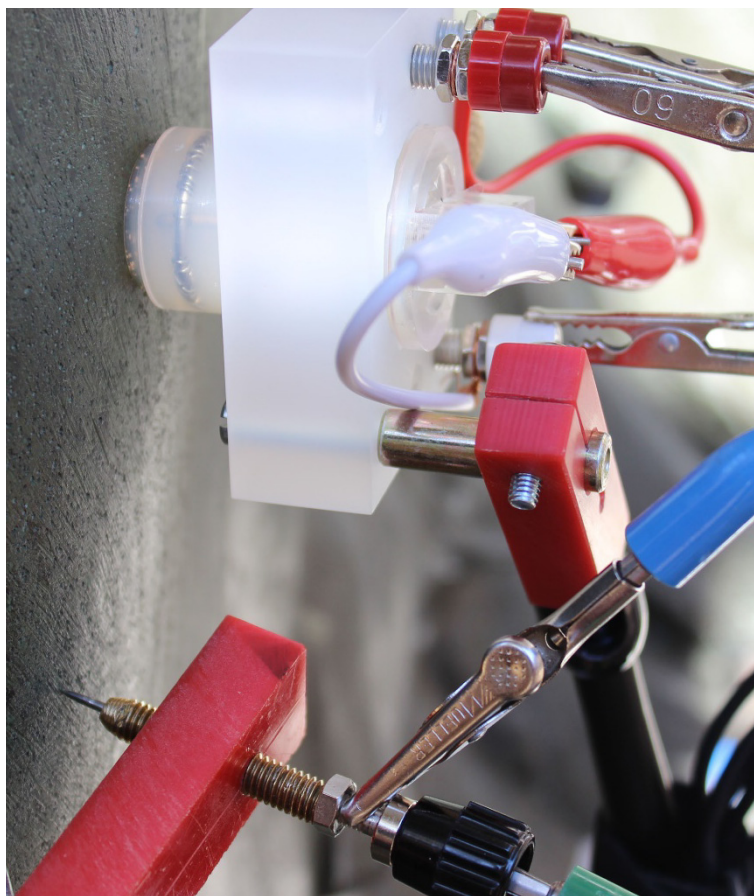
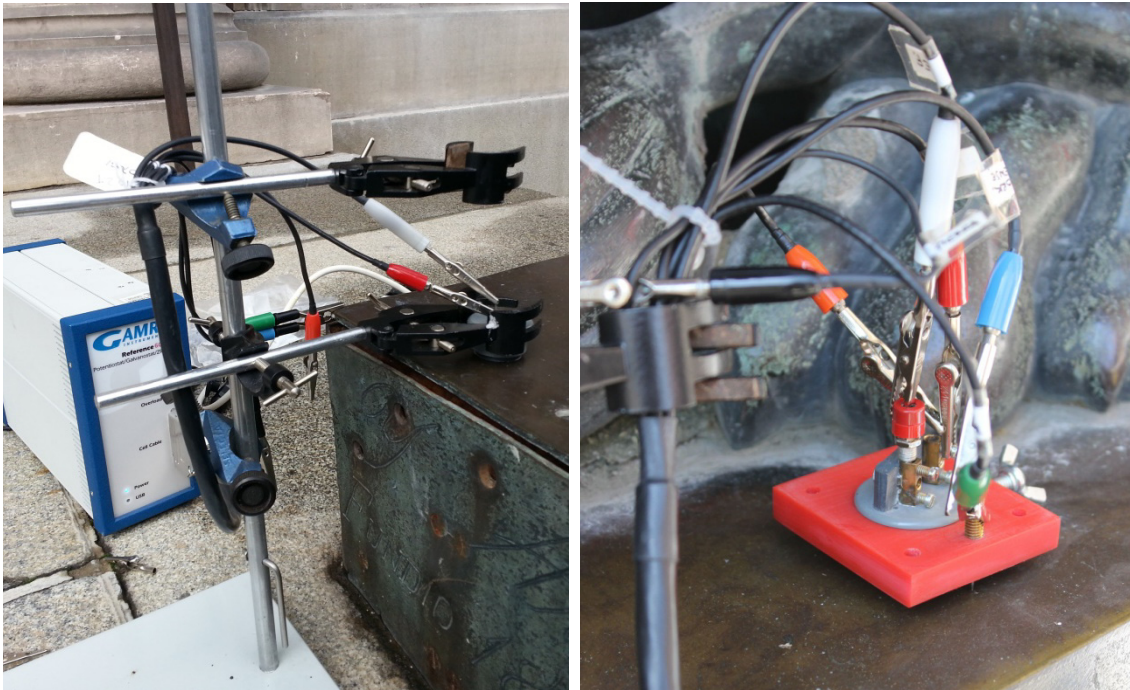


Figura 18. Separación del contacto del electrodo de trabajo y el resto de la celda.





**Figura 19.** Primer sistema de sujeción de la celda.

Para facilitar el acceso a las diferentes zonas y orientaciones de las obras a medir, se preparó un juego de barras de aluminio de cuatro ranuras con diferentes piezas de unión (figura 21). A este soporte se unían dos brazos articulados, uno para la celda y otro para el contacto; ambos brazos podían sujetarse en cualquiera de las cuatro caras de la barra de aluminio a la altura deseada. La separación de la celda y el contacto con el electrodo de trabajo supone una gran ventaja, tanto para facilitar la colocación del contacto en el punto más adecuado como para evitar la separación de la celda al presionarlo sobre la superficie.

Aunque este sistema era muy versátil, en ocasiones no ofrecía la estabilidad suficiente para evitar el desplazamiento de la celda, por lo que finalmente se optó por sustituirlo por un trípode de fotografía Manfrotto 475B Pro con un brazo 131DB (figura 22). En ambos sistemas se ha colocado un soporte para elevar el potencióstato y aproximar los cables al área de medida, evitando tensiones y la necesidad de emplear un cable largo.



Figura 20. Brazo extensible (izquierda) y brazo articulado con bloqueo (derecha) para la sujeción de la celda y el electrodo de trabajo.



Figura 21. Sistema de barras de aluminio para la colocación de la celda y el potenciostato





**Figura 22.** Montaje final de la celda sobre un trípode de fotografía. Para facilitar el transporte de los materiales y las baterías utilizadas para garantizar la autonomía del equipo se utiliza un caja de herramientas con ruedas.

### *Optimización de los parámetros de diseño*

Además de los trabajos mencionados al comienzo del apartado 4.2. sobre posibles efectos relacionados con los electrodos, la revisión de los diferentes sistemas de medida propuestos (ver apartado 1.2.2.) permitió comprobar diferencias en los resultados obtenidos por los diferentes diseños sobre sistemas metal-pátina o metal-recubrimiento similares, cuando no claros efectos del sistema de medida en sí, como distribuciones no homogéneas de corriente en el caso de los electrodos comerciales para electrocardiograma o el sistema de dos celdas paralelas que supone la existencia de diferentes caminos posibles para la conducción eléctrica [106, 190].

Por ello, se consideró relevante estudiar la posible influencia de la naturaleza de los electrodos y la geometría de la celda diseñada en los resultados, mediante una serie de medidas sistemáticas variando el tipo y posición de los electrodos. Así, se han estudiado el efecto de la geometría del contraelectrodo (malla paralela a la superficie o espiral), el empleo de un electrodo de referencia de Ag/AgCl frente a un electrodo de pseudo-referencia, o la influencia de la distancia al electrodo de trabajo. Los resultados han demostrado que la posición de los electrodos es un factor importante cuando se trabaja con electrolitos de baja conductividad, ya que puede producir artefactos en la medida, y que estos efectos son menos acusados cuando se emplea un electrodo de pseudo-referencia que usando un electrodo de referencia real. Los posibles efectos o diferencias relativos a la naturaleza, geometría y distancia entre los electrodos en la celda en gel se analizan en el siguiente trabajo:

- B. Ramírez Barat, E. Cano, P. Letardi, "Advances in the design of a gel-cell electrochemical sensor for corrosion measurements on metallic cultural heritage", *Sensors & Actuators: B Chemical* 261(2018) 572-80<sup>8</sup>.

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# 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.

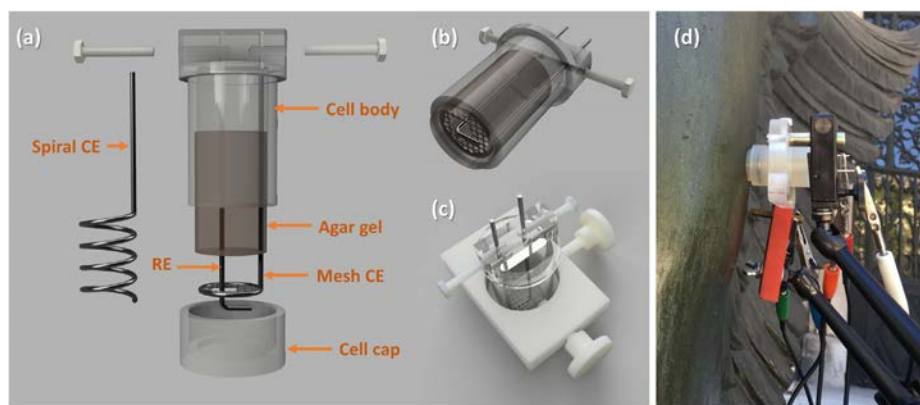


Fig. 1. Cell design: exploded view (a) mounted cell (b) and support (c). The picture in the right (d) shows the complete measuring setup on the surface of an outdoor sculpture.

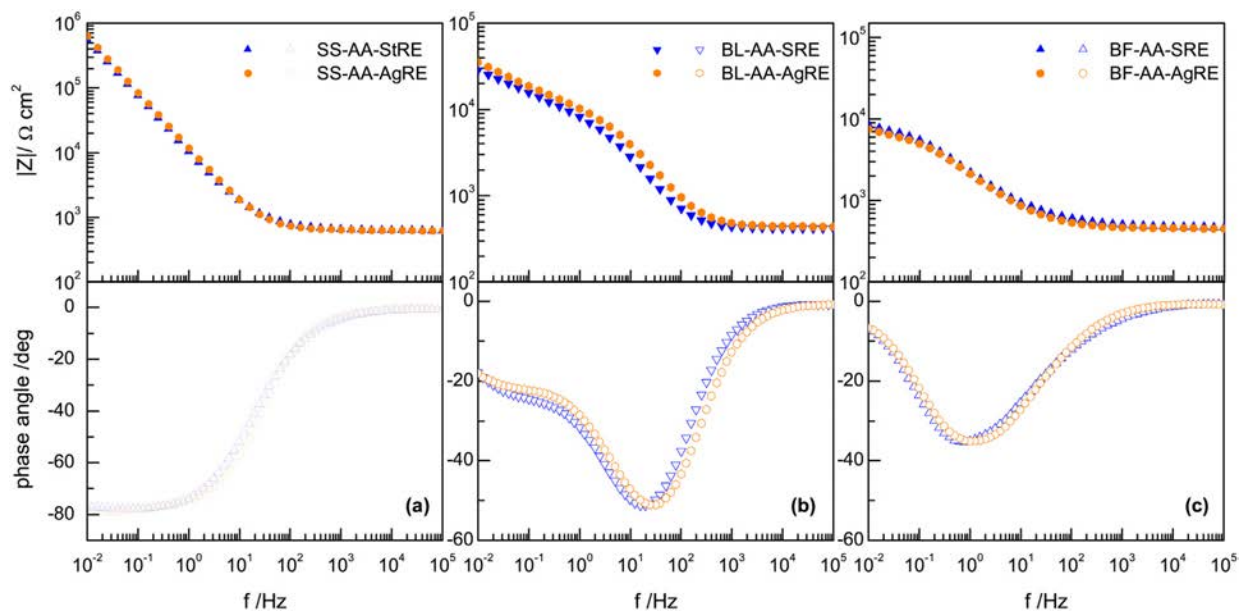


Fig. 2. EIS spectra with stainless steel and AgCl coated Ag pseudo-reference electrodes on stainless steel (a), laminated bronze (b) and cast bronze (c).

2.3. Electrolyte

The electrolyte has been prepared by gelling a liquid electrolyte with agar (technical grade). As liquid electrolyte, artificial rain (CaSO<sub>4</sub>·2H<sub>2</sub>O 14.43 mg/L, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 15.04 mg/L, (NH<sub>4</sub>)Cl 19.15 mg/L, NaNO<sub>3</sub> 15.13 mg/L and CH<sub>3</sub>COONa mg/L) has been used, adapted from [30]. The solution is prepared 1000 fold concentrated and pH adjusted to 5 with HNO<sub>3</sub> and stored at room temperature. This solution has then been diluted to a 10-fold concentration, with a final pH value of 6.5. This solution has been chosen because it has a similar composition to the natural electrolyte to which outdoor monuments are exposed and at the same time it is a mild electrolyte which prevents any damage to the surface. To prepare the electrolyte 3% w-v agar powder is added to the electrolyte in a beaker and gently heated in a microwave at low power until dissolution. The electrolyte is left to cool for a short time before pouring it on the mold, and then left to cool until solidification. After each use the gel electrolyte is removed from the cell and renewed. The measured conductivity was 72 μS/cm for the liquid electrolyte (LQ) and 716 μS/cm for the agar gelled electrolyte (AA).

2.4. Coupons

Electrochemical measurements have been carried out on different metal coupons. Laminated AISI 316 stainless steel (SS), has been used as received as bare reference testing material for different cell configurations. Stainless steel provides a passive, very reproducible, uniform and smooth surface, to reduce possible variations in the measurements attributable to changes in the working electrode and allowing a better discrimination of cell contribution from WE behavior. In addition, some measurements have been done in bronze coupons. As bronze is one of the most representative materials in metallic cultural heritage, this has been done to compare and validate with results obtained in the stainless steel reference system. Two different bronze coupons have been used. Laminated EN 1652 CuSn5 bronze (95 Cu, 5 Sn%w) was selected as a simple bronze model (BL). Bronze coupons were grit with 1200 emery paper to obtain a clean homogeneous surface, and left to the air for several weeks to allow a thin oxide layer to grow reducing the high reactiv-

ity of a freshly polished surface. EN 1982 CC491K (DIN 1705-RG5) cast bronze (85 Cu, 5 Sn, 5 Pb, 5 Zn%w) was selected as a simile to real cast bronze sculptures (BF). Casted bronze was prepared by Codina Escultura, a traditional Spanish artistic foundry according to traditional materials and techniques. These coupons were used as received, i.e. with a rough surface (sandblasted) covered by a native oxide layer.

Finally, to test the cell's performance for in situ measurements on real cultural heritage assets in comparison to laboratory tests, measurements have been done on two sculptures: The sculpture 'Mediterranea III', by the Spanish sculptor Martin Chirino, made out of stainless steel in 1971, and exposed in the Museo de Escultura de Leganés; and the right sphinx of the façade of the National Archaeological Museum in Madrid, made in 1894, by Felipe Moratilla y Parreto.

2.5. Electrochemical measurements

EIS spectra have been acquired using a Gamry 600 Potentiostat, using a frequency swept from 100 kHz to 10 mHz, 10 mV RMS amplitude (at the open circuit potential, OCP) and 10 points/decade. The system was left to stabilize at OCP for 30 min before measurements.

The area exposed to the electrolyte was 3.14 cm<sup>2</sup> for the G-PE cell and 2.84 cm<sup>2</sup> for the liquid cell. Analysis of the normalized spectra has been carried out using ZView software.

3. Results and discussion

Different series of measurements with different setups were performed to identify which design factors had a significant influence in the results and which ones where of minor relevance.

3.1. The nature of the pseudo-reference electrode

The AgCl coated silver wire from the first prototype [20] was compared to a stainless steel wire pseudo-reference electrode. The use of a pseudo-reference stainless steel electrode has been tested instead of the AgCl coated silver since it is cheaper, convenient and simplifies the experimental procedure, as does not require prepar-

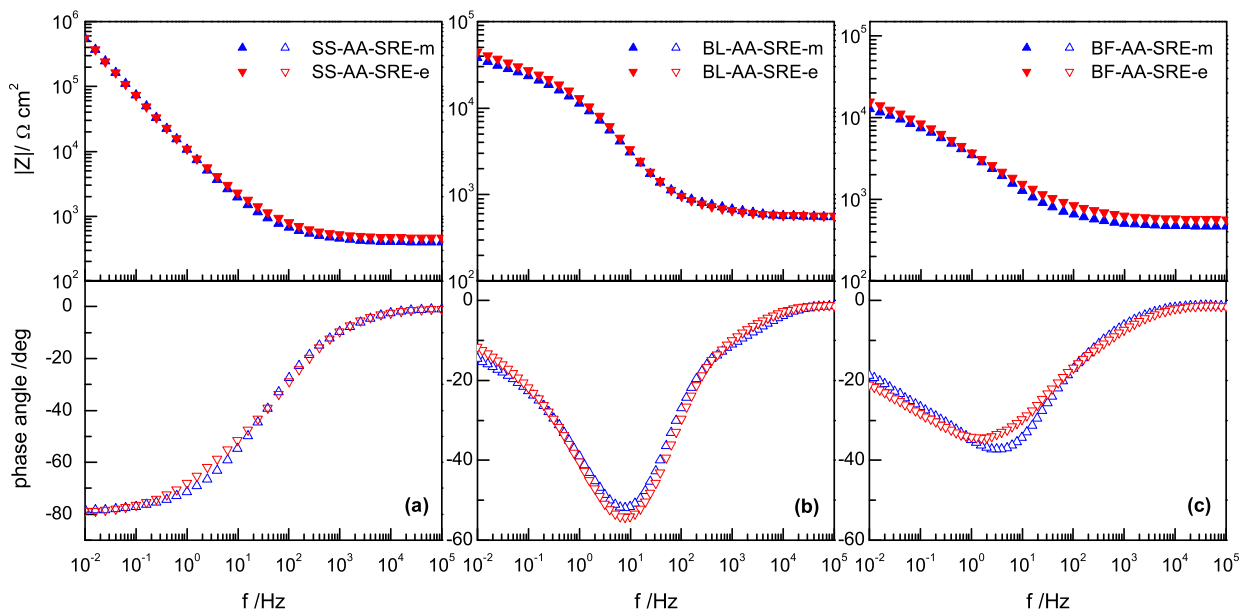


Fig. 3. EIS spectra using mesh and spiral counter electrodes on stainless steel (a), laminated bronze (b) and cast bronze (c).

ing the AgCl coat. Besides, this coat has to be eventually renewed as sometimes it becomes worn or detaches from the electrode. Results of impedance spectra of the gel cell with both electrode arrangements can be seen in Fig. 2, both in stainless steel (2a) and bronze coupons (2b and 2c). No meaningful differences can be enlightened between the AgCl coated silver and the stainless steel pseudo-RE, which supports the use of the latter.

A pseudo-RE does not have, in principle, an identifiable reversible electrochemical reaction nor a thermodynamically predictable behavior, therefore, these results are only valid in the reported conditions. For a stainless steel pseudo-RE, its potential and stability depends on the composition of the base alloy (mainly Fe, Cr, Ni and Mo), the nature of the passive layer (mostly a mixture of Cr and Fe oxides and hydroxides) and the species in the medium. Wilburn et al., have proposed a metal–metal oxide type pH-sensor behavior for stainless steel in a copolymer matrix of a fixed and constant pH value, in which the mixed oxide layer reacts reversibly with  $\text{H}^+$  ions ( $\text{M}/\text{M}_x\text{O}_y(\text{s}) + 2_y\text{H}^+ + 2_y\text{e}^- \leftrightarrow \text{M}(\text{s}) + y\text{H}_2\text{O}$ ); thus in a constant pH media, it will provide a constant potential value that can be calculated according to Nernst equation [31]. In our cell, reactions with other species in the electrolyte (including dissolved oxygen) might play a significant role, so the pH dependence might not be accurate. Whether it may be of interest in applications where the absolute value of potential is relevant, further investigation of this issue is out of the scope of this paper. The alternative in our cell, will be the use of a real RE, which is discussed in Section 3.3.

### 3.2. The shape of the counter-electrode

The simplification of the counter electrode has also been considered, substituting the stainless steel mesh by a stainless steel spiral, as it is easier to construct and facilitates the renewal of the gelled electrolyte after use. These two possible setups have been checked on different working electrodes (see Fig. 3), showing that, there are minimal differences between the mesh CE and the spiral CE, thus the differences are rather attributable to differences in the metal. Therefore, although the use of a mesh CE would be more appropriate from a theoretical point of view to ensure a uniform and parallel distribution of the current lines, from the practical point of view,

a spiral CE can be used if preferred. This can be an option when large and/or periodic series of measurements for field-monitoring campaigns.

### 3.3. Real reference electrode vs pseudo-reference electrode

To explore the possibility of using a real RE in the G-PE cell, measurements were done with an Ag/AgCl reference electrode and compared with a steel pseudo-reference electrode. These measurements were performed both in liquid and agar gelled electrolyte, to compare also the behavior of the G-PE cell with a traditional setup. Results of impedance spectra on stainless steel coupons can be seen in Fig. 4.

When substituting the pseudo-RE for the standard Ag/AgCl RE some relevant changes are observed. With the Std-RE uncompensated resistance, corresponding to the impedance at high frequencies appears to be lower. In the case of standard RE with the liquid electrolyte it can also be observed a distortion of the phase angle spectra at the high frequencies, between  $10^4$  and  $10^5$  Hz (Fig. 4b), which denotes the presence of an artifact.

The spectra distortion at high frequencies caused by the RE and other elements of the measurement setup is a long time known problem, which started to be discussed in the 80's [31,32]. In particular, the contribution of the RE can be significant in low conductivity media causing parasitic impedances [32,33], in which interactions between the three electrodes are involved [22,23]. These parasitic impedances, commonly referred as stray capacitances, frequently produce pseudo-inductive behaviors. While pseudo-inductive artifacts are easy to recognize as they appear as a loop in the fourth quadrant in Nyquist plot, capacitive artifacts might be more difficult to distinguish from real data [22].

The key question now is to which extent this kind of artifact is present in our system and if it is possible to discriminate it from the WE response. Although this effect is not visible in the G-PE cell, we cannot automatically discard it, as it may be linked to the lower value of uncompensated resistance  $R_e$  (the resistance of the electrolyte plus other contributions from the rest of the setup). The theoretical  $R_e$  value can be easily calculated from the electrolyte layer conductivity and geometry using Eq. (1), where  $\rho$  is the resis-

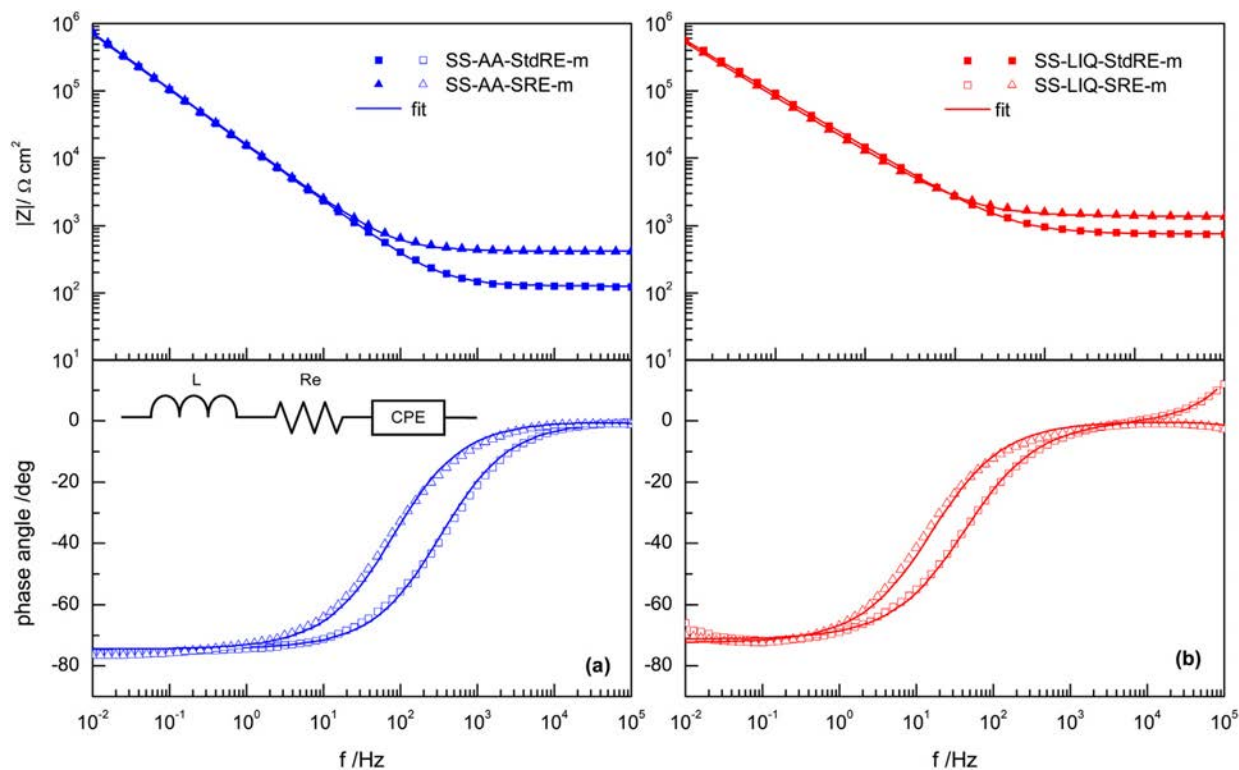


Fig. 4. EIS spectra comparing a real reference and a pseudo reference electrode on stainless steel coupons with gelled (a) and liquid electrolyte (b).

**Table 1**  
Fitting results for the real and pseudo reference electrodes with agar gelled and liquid electrolyte.

	L ( $\mu\text{H cm}^2$ )	Re ( $\Omega \text{ cm}^2$ )	CPE		Chi-Sqr
			Y ( $\mu\text{S s}^\alpha \text{ cm}^{-2}$ )	$\alpha$	
AA-SRE	$-8.8 \pm 0.9$	$418 \pm 2$	$13.65 \pm 0.08$	$0.828 \pm 0.001$	$4.00\text{E} - 03$
AA-StdRE	$-3.8 \pm 0.3$	$126 \pm 1$	$14.05 \pm 0.08$	$0.827 \pm 0.001$	$2.81\text{E} - 03$
LIQ-SRE	$-49 \pm 6$	$1384 \pm 6$	$17.84 \pm 0.09$	$0.805 \pm 0.002$	$6.85\text{E} - 03$
LIQ-StdRE	$280 \pm 10$	$750 \pm 2$	$15.90 \pm 0.05$	$0.792 \pm 0.001$	$1.53\text{E} - 03$

tivity in  $\Omega\text{-cm}$  (the inverse of the conductivity),  $d$  is the distance between the RE and WE in cm and  $A$  the contact area in  $\text{cm}^2$ .

$$R_e = \rho \frac{d}{A} \tag{1}$$

For a 3.2 mm distance between the RE and WE used in these experiments,  $R_e$  should be around 1556  $\Omega$  for the liquid cell and 142  $\Omega$  for the G-PE one. Thus, we can compare these calculated values with the experimental ones obtained by fitting the EIS spectra.

EIS spectra of agar and liquid cells with both real and pseudo RE have been fitted to the equivalent circuit in Fig. 4, where  $R_e$  is the uncompensated resistance, the passive layer of stainless steel is represented by a constant phase element (CPE), and an inductor,  $L$ , has been used to model the artifacts from the measuring system. As it has been demonstrated by other authors, this inductive element arises from the reduction to a 2-pole electrical equivalent circuit of the 3-pole (WE, RE and CE) circuit that constitutes the electrochemical cell; and the choice of an inductive or capacitive element is a matter of convenience and in no way does it suggest the inductive or capacitive behavior of the electrode [22,23], and it can even have negative values [29].

Fit results are presented in Table 1. Comparing experimental and calculated  $R_e$  values, it can be observed that, for the pseudo RE, the experimental value with agar is much higher and about 10% lower for the liquid electrolyte. With the real RE, the experimental value is about 10% lower for the agar, and half the value for the

liquid. A higher experimental value can be attributed to the contribution of other elements (such as interfacial impedances between the electrolyte and the RE), but a lower experimental value has no physical explanation, thus it is clearly caused by an artifact in this high frequency region [23]. Considering that in corrosion measurements a 10% deviation from the theoretical value can be considered reasonable, we can derive two practical consequences. In very low conductivity electrolyte as the artificial rain, the use of the real RE causes the presence of an artifact that, at least, affects the region of the electrolyte response, while the pseudo RE gives a more reliable result. With the agar gelled electrolyte (with low but higher conductivity than the liquid), it may be possible to use a real RE with no overlapping of parasitic responses, while the use of a pseudo-RE adds additional resistance to the high-frequency part of the EIS spectrum. In any case, this contribution can be separated from the contributions of the other elements of the corrosion system, and the results obtained for the region of interest –corresponding to faradaic processes and passive layers or coatings– are the same with both pseudo and real reference electrodes.

### 3.4. The influence of the WE-RE distance

The distance and relative position between electrodes is another relevant parameter affecting the cell response [29,33], since it will influence the values of the capacitances and resistances between



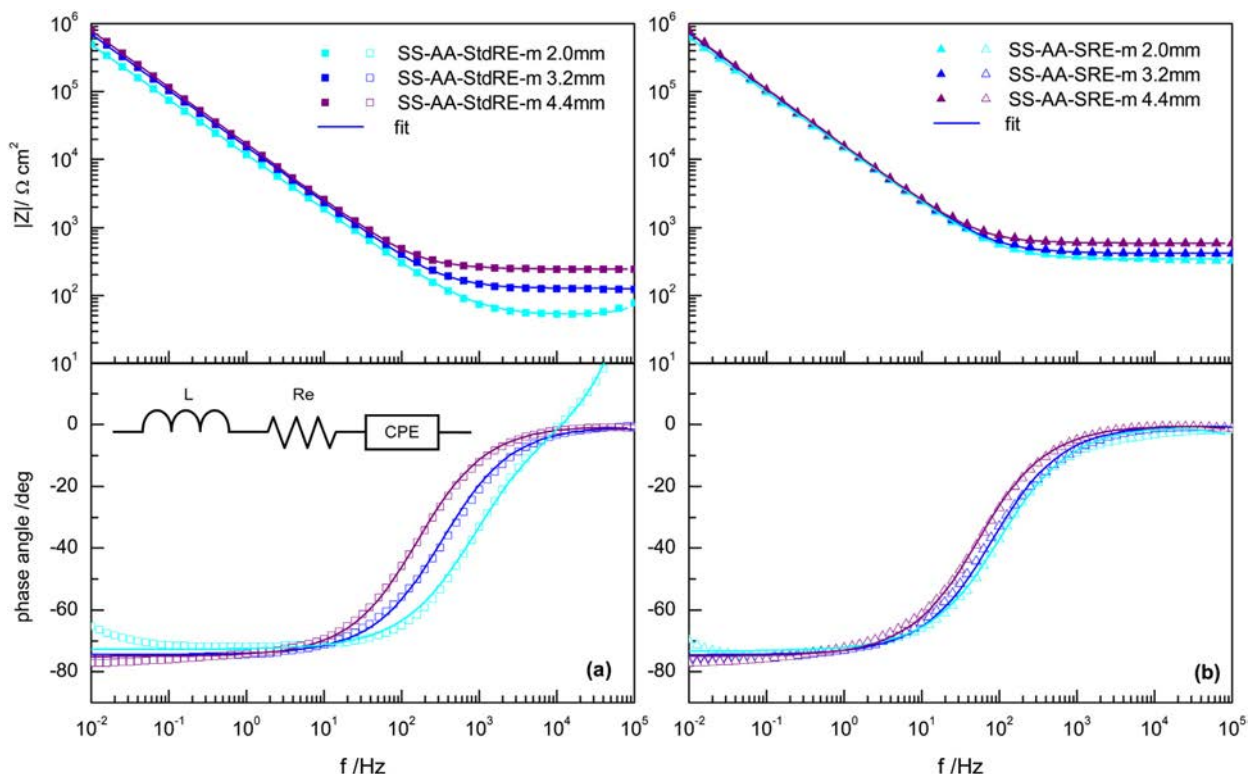


Fig. 5. Effect of the distance between the reference and the working electrode for a real reference electrode (a) and a pseudo reference electrode (b).

Table 2

Fitting results at different distances for the real and pseudo reference electrodes.  $R_{cal}$  is the value estimated for Re from Eq. (1).

	L( $\mu\text{H cm}^2$ )	Re ( $\Omega \text{ cm}^2$ )	CPE		$R_{cal}$ ( $\Omega \text{ cm}^2$ )	Chi-Sqr
			Y ( $\mu\text{S s}^\alpha \text{ cm}^{-2}$ )	$\alpha$		
AA-StdRE 2.0 mm	82 ± 2	52 ± 1	19.1 ± 0.1	0.808 ± 0.001	98	3.10E – 03
AA-StdRE 3.2 mm	–3.8 ± 0.3	124 ± 1	14.05 ± 0.04	0.827 ± 0.001	142	1.20E – 03
AA-StdRE 4.4 mm	–6 ± 4	243 ± 1	12.78 ± 0.03	0.834 ± 0.001	196	9.89E – 04
AA-SRE 2.0 mm	–33 ± 9	342 ± 1	14.99 ± 0.06	0.814 ± 0.001	98	2.60E – 03
AA-SRE 3.2 mm	–1.8 ± 0.9	421 ± 2	13.65 ± 0.08	0.828 ± 0.001	142	3.35E – 03
AA-SRE 4.4 mm	21 ± 2	587 ± 1	13.50 ± 0.1	0.808 ± 0.001	196	2.50E – 03

Table 3

Fitting results at different distances for the real and pseudo reference electrodes on bronze coupons.

	L( $\mu\text{H cm}^2$ )	Re ( $\Omega \text{ cm}^2$ )	CPE1		R1 ( $\Omega \text{ cm}^2$ )	W			Chi-Sqr
			Y ( $\mu\text{S s}^\alpha \text{ cm}^{-2}$ )	$\alpha$		$R_w$ ( $\text{k}\Omega \text{ cm}^2$ )	$T_w$ (s)	$\alpha_w$	
BL-StdRE 3.2 mm	1.95 ± 0.06	124.6 ± 0.3	9.5 ± 0.2	0.915 ± 0.003	1430 ± 50	20.7 ± 0.2	22.0 ± 0.7	0.396 ± 0.003	4.42E – 04
BL-StdRE 4.4 mm	–4 ± 3	203.9 ± 0.5	10.7 ± 0.4	0.911 ± 0.005	1390 ± 60	19.2 ± 0.2	19.8 ± 0.7	0.409 ± 0.003	7.01E – 04
BL-SRE 3.2 mm	–15 ± 7	431 ± 1	13.2 ± 0.6	0.834 ± 0.007	2000 ± 100	20.3 ± 0.4	24 ± 1	0.394 ± 0.005	8.64E – 04
BL-SRE 4.4 mm	–18 ± 9	517 ± 2	12.9 ± 0.7	0.885 ± 0.009	1510 ± 90	18.1 ± 0.3	22 ± 1	0.406 ± 0.005	1.25E – 03

the electrodes in the 3-pole cell. To analyze the influence of this parameter in our cell and optimize the RE-WE distance, a series of measurements at different distances with both Std-RE and pseudo-RE electrodes were carried out. Fig. 5 shows the EIS spectra with both RE at three different RE-WE distances: 2.0 mm, 3.2 mm and 4.4 mm, which may give around 98, 142 and 196  $\Omega$  for the electrolyte resistance between them. Results from fitting the experimental data to the equivalent circuit are presented in Table 2.

Pseudo-inductive responses are clearly present when using the real RE in the closest position (2.0 mm) while their value decreases as RE-WE distance increases. For 3.2 mm distance the spectra does not appear to be distorted but there is still a slight inductive contribution in the equivalent circuit. For the pseudo-RE pseudo-

inductive effects are negligible (in fact, fitting the spectra without the pseudo-inductive element yield the same results for other elements in the circuit) although the electrode contributes to the uncompensated resistance.

The values of CPE are all very close and can be considered equal for all setup but the 2.0 mm with a standard RE suggesting that the RE parasitic contribution (either inductive or resistive) does not affect the results from the stainless steel WE. This means that as long as the uncompensated resistance ( $R_e$ ) can be separated from the WE response, both RE electrodes are valid. To minimize interferences of artifacts in the frequency ranges of interest for the corrosion studies, the lower distance is more convenient when a pseudo RE is used not to increase the  $R_e$  value. On the contrary,

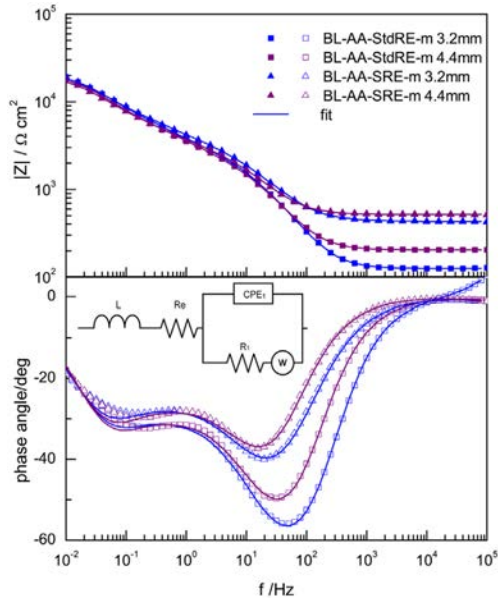


Fig. 6. EIS spectra comparing a real reference and a pseudo reference electrode at different distances on bronze coupons.

when using a standard RE a higher distance allows avoiding inductive artifact. The CPE values obtained with the pseudo RE are a little less sensitive to the different WE-RE distances tested. It has to be considered that, especially in field measurements on irregular surfaces, the real WE-RE may be slightly different (lower) from the design distance, due to the pressure applied to adapt the gel to the WE surface.

3.5. Bronze working electrode

As artifacts are the result of interactions between the three electrodes [22,23] the change in the nature of the WE may increase its

effects or overlap with the region of interest when measuring other surfaces. For this reason, once the contribution/behavior or the cell is clear enough it is necessary to verify this is also valid for bronze, which is probably the most relevant material for this application.

Thus, EIS spectra with the real and pseudo RE have been acquired on laminated bronze coupons at the two selected distances, 3.2 mm and 4.4 mm. Graphical and numerical results are presented in Fig. 6 and Table 3 respectively. EIS spectra have been fitted to the equivalent circuit in Fig. 6, where  $R_e$  is the uncompensated resistance, CPE1 and  $R_i$  represent the double layer and the charge transfer resistance while  $W$  is associated to diffusion of copper ions within the oxide layer and the electrolyte. This equivalent circuit has been previously used to explain the behavior of copper and bronze in mild neutral electrolytes [18,34]. Results from bronze coupons are coherent with those obtained for stainless steel,  $R_e$  values are almost identical for the same setup, while the rest of parameters are reasonably similar for the different setups. Pseudo-inductive artifacts are only appreciable for the lower RE-WE distance with the real reference, thus same considerations on RE and distances can be made for bronze.

3.6. In situ measurements

The final step is to test if the cell allows obtaining good quality data out of the ideal situation of model samples and laboratory conditions. So, along with the development of the cell design, it has been assayed in different materials and case studies [35,36]. These examples have allowed to validate the cell performance and to improve the design according to different difficulties being observed. In this section an example of EIS spectra recorded on a twentieth century stainless steel sculpture with the G-PE cell (stainless steel pseudo RE) is compared to laboratory measurements (Fig. 7). The sculpture is Mediterránea III, made by the Spanish sculptor Martín Chirino in 1971, which is owned by the Museo Nacional Centro de Arte Reina Sofía and exposed at the Museo de Escultura de Leganés. Although the spectra of the sculpture shows a couple of small discontinuities in the phase angle, it can be considered a good quality field measurement, showing

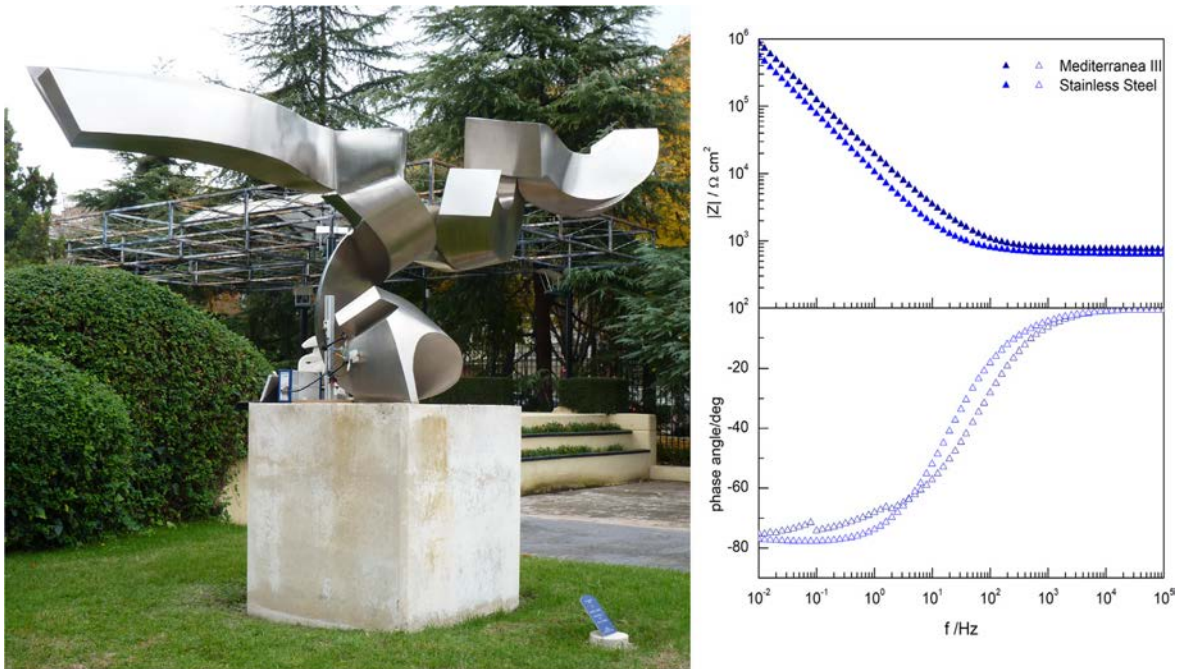
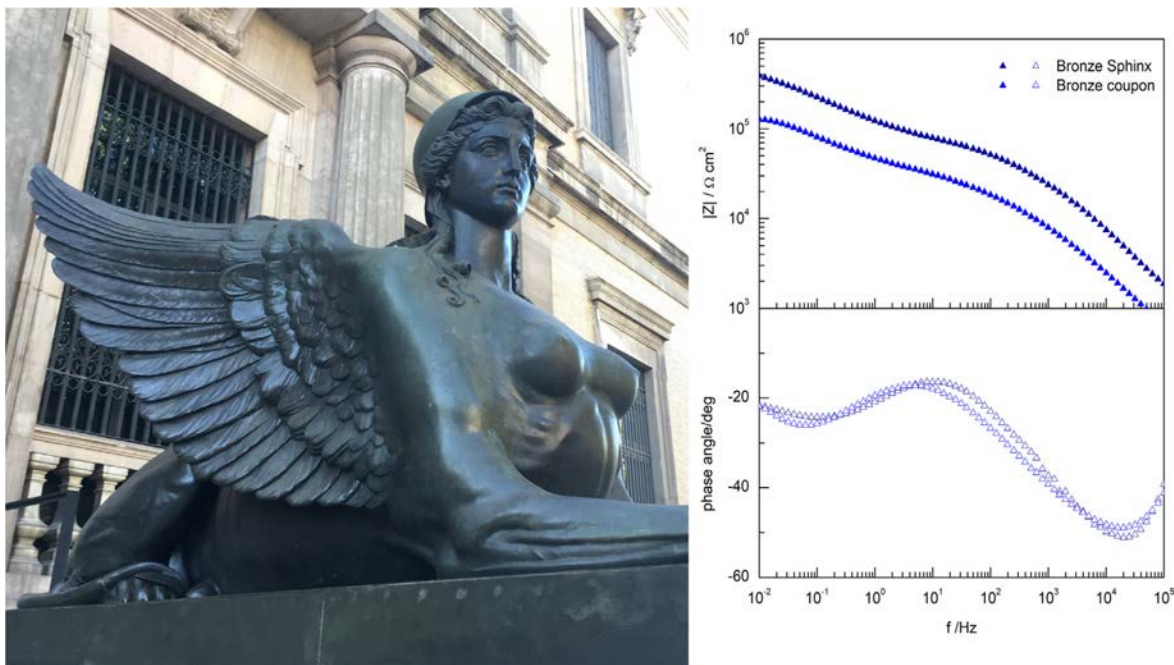


Fig. 7. Comparison between laboratory measures on stainless steel coupons and field measurements on the stainless steel sculpture, Mediterránea III, by Martín Chirino.



**Fig. 8.** Comparison between EIS spectra on an aged cast bronze coupon with a sulfide patina and Incralac coating with field measurements on right bronze sphinx from the Museo Arqueológico Nacional, restored and protected with Incralac.

an identical profile to those obtained on coupons under laboratory conditions. Slight differences at intermediate and high frequencies – higher impedance for the sculpture – can be attributed to the ageing of the passive layer of the metal exposed outdoors.

As an example of a bronze outdoor sculpture measurements on a bronze sphinx at the main façade of the Spanish National Archaeological Museum (MAN) in Madrid are compared with a cast bronze coupon (Fig. 8). The two bronze sphinxes from the MAN façade were restored a few years ago and protected with an acrylic coating (Incralac), commonly used for conservation treatments of copper-alloy sculptures [16]. The EIS spectra of the right sphinx two years after the treatment is compared to a bronze coupon with a dark sulfide patina prepared in the traditional way that has been also coated with Incralac and exposed to the atmosphere in Madrid for the same period. Again, results obtained in field measurements are comparable to laboratory results, considering the differences in the materials, validating the performance of the G-PE cell for in situ conservation assessment.

#### 4. Conclusions

Results support the suitability of the G-PE cell as an electrochemical sensor for corrosion measurements on metallic cultural heritage.

The analysis of different design parameters has allowed to improve the cell and to understand the influence of the nature and geometry of the electrodes in the EIS response. This has allowed also separating possible parasitic contributions from the response of the working electrode. As it has been demonstrated, the cell can be used either with a real reference electrode or with a pseudo-reference electrode, as a matter of convenience. When using a real reference electrode attention has to be paid not to place it too close to the working electrode surface to avoid pseudo-inductive effects. When using a pseudo-reference electrode it is more convenient using a closer distance to reduce the uncompensated resistance.

The G-PE cell has demonstrated to be a versatile and useful tool for conservation assessment, giving good results both in laboratory samples and field measurements.

#### Acknowledgements

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## Biographies

**Blanca Ramírez-Barat** has a degree in Chemistry and in Fine Arts, both from the Complutense University of Madrid, and a MSc in Materials Science and Engineering from Carlos III University. After several years in R&D management, she is currently working at the National Center for Metallurgical Research (CENIM-CSIC) in Madrid, Spain in the research group “Corrosion and protection of metals in cultural heritage and construction” at the CENIM-CSIC. Her research is focused in the application of electrochemical techniques for conservation assessment and diagnosis in cultural heritage.

**Emilio Cano** is Tenured Scientist at the Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC) in Madrid, Spain. He obtained his PhD in Fine Arts from the Complutense University of Madrid in 2001. His fields of expertise include corrosion and protection of metallic cultural heritage, indoor corrosion, electrochemical techniques applied to conservation science, XPS and corrosion inhibitors. He has published more than 100 research papers in international scientific journals and presented communications to about 60 scientific conferences, both in corrosion science and conservation science.

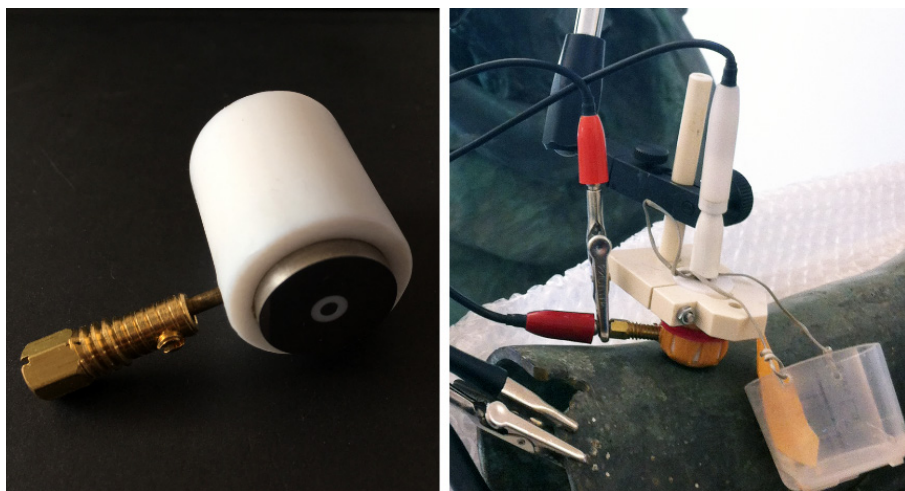
**Paola Letardi** has a degree in Physics and worked in the field of Material Science and Surface Spectroscopy, with particular interest in the development of methodologies and instrumentation. She has been active in national and international projects on diagnostics and monitoring for the Conservation of Cultural Heritage. Her research is focused on the study of corrosion of metals in the marine environment and on specific applications of electrochemical and spectroscopic techniques in the field of artifacts of historical interest.



#### 4.2.2. Comparación con otros sistemas.

Como continuación del análisis de la posible influencia del sistema de medida en los resultados obtenidos y para profundizar en el conocimiento del propio sistema, se está trabajando con P. Letardi en el estudio y comparación de la celda G-PE y la celda de contacto (CP) desarrollada por esta investigadora. Estos sistemas son, hasta la fecha, los que han demostrado un mayor desarrollo y trayectoria en su aplicación estudio del patrimonio cultural metálico. Al mismo tiempo, se trata de dos ejemplos de los dos tipos de soluciones propuestas para resolver el problema de la medida in situ.

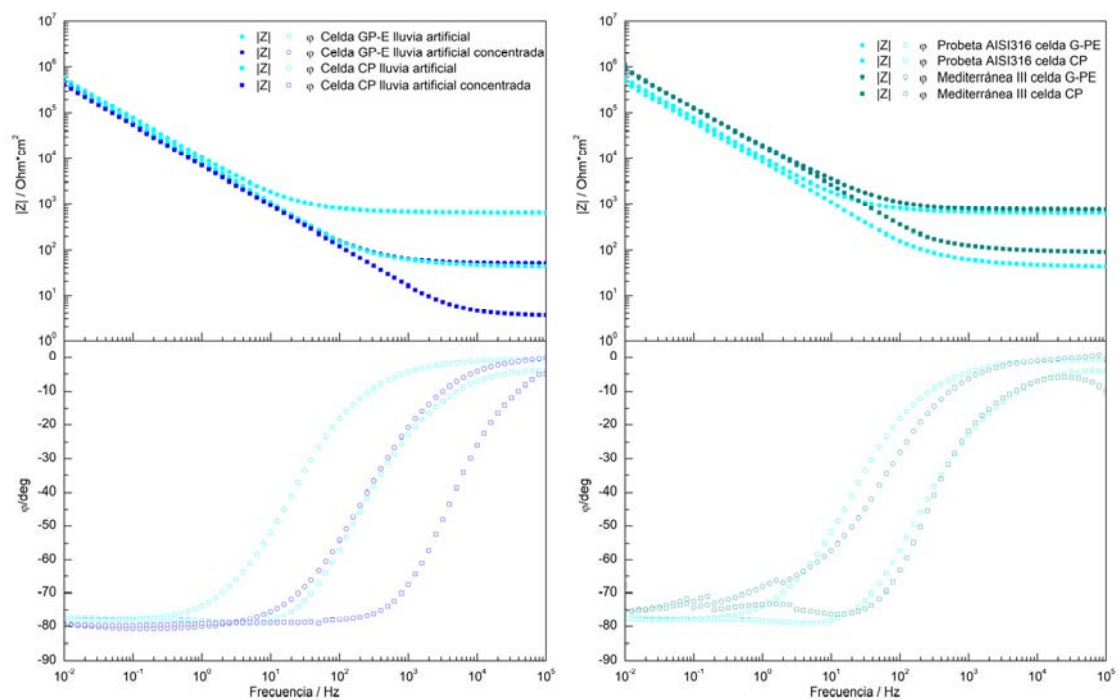
La CP desarrollada por Letardi[49, 204] consiste en un cilindro de teflón que contiene embebidos dos cilindros concéntricos de acero inoxidable AISI316, que actúan como electrodo de pseudo-referencia y contraelectrodo. Sobre este cilindro se sujeta un paño impregnado en el electrólito que se mantiene húmedo por capilaridad, mediante un extremo sumergido en un pequeño recipiente que contiene el electrólito (figura 23). El área nominal de contacto de la celda es de  $1.77\text{cm}^2$ .



**Figura 23.** Celda de contacto desarrollada por Letardi (izquierda) y montaje completo para la realización de las medida (derecha).

Además del análisis independiente de cada uno de estos sistemas, resulta interesante comparar medidas realizadas con las diferentes celdas en las mismas condiciones. De este modo, las diferencias obtenidas pueden atribuirse a la influencia del sistema empleado [205]. Por ello, caracterizar estas diferencias es de gran utilidad tanto para poder comparar medidas realizadas con diferentes sistemas como para comprender mejor los resultados de las medidas de impedancia e identificar las posibles fuentes de interferencias.

Los primeros estudios comparativos se han realizado sobre acero inoxidable AISI316 como sustrato estable, reproducible y de resultados fácilmente interpretables. Además, todas las medidas se han realizado conjuntamente en el mismo laboratorio y con el mismo electrólito para minimizar cualquier otro factor externo, durante una estancia en Madrid de P. Letardi y otra de la autora en Génova. Desde el punto de vista cualitativo, las principales diferencias se observan a frecuencias más altas, en especial en la resistencia no compensada y en la posición de las constantes de tiempo, a frecuencias más altas en la celda de contacto. En la región de frecuencias más bajas las diferencias son reducidas. Esto se puede apreciar en la figura 24, en la que se presenta un ejemplo de las medidas realizadas con los dos sistemas en una probeta de acero inoxidable con dos concentraciones diferentes del electrólito, y sobre una escultura de acero inoxidable, *Mediterránea III*, de Martín Chirino (Museo de Escultura de Leganés) en comparación con las medidas realizadas sobre la probeta (figura 25).



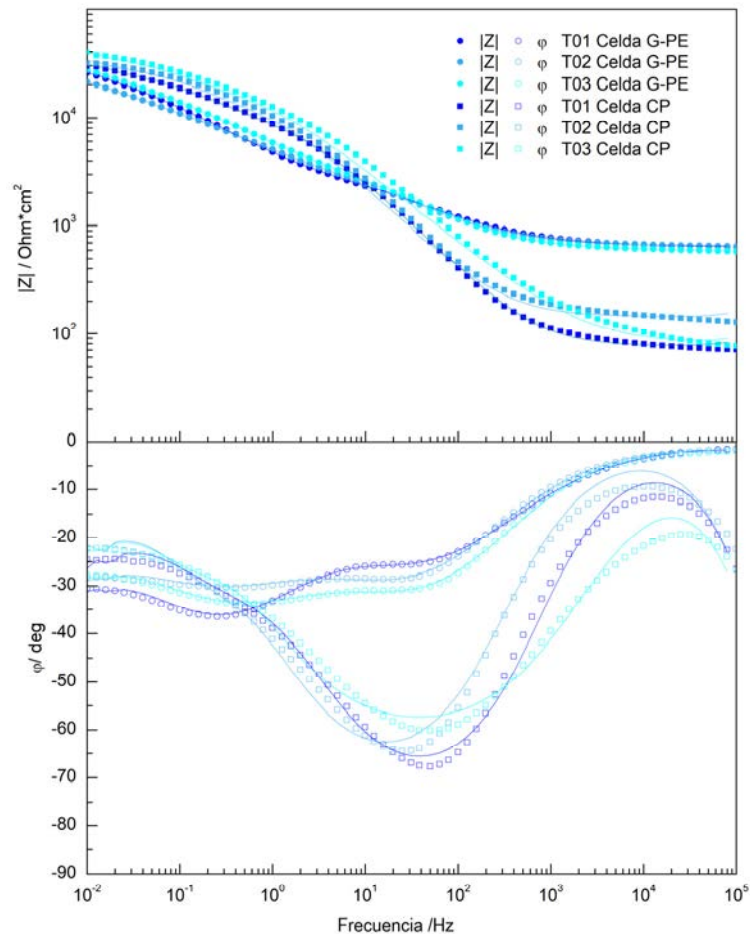
**Figura 24.** Ejemplo de medidas comparativas entre la celda G-PE y la CP sobre acero inoxidable con agua de lluvia artificial 10x y 1000x (izquierda). Comparación de los resultados obtenidos en probetas y en obra real *Mediterránea III* de Martín Chirino (dcha).

La menor resistencia del electrolito en la CP es coherente con el diseño de la misma ya que la distancia RE-WE es mucho menor que en el caso de la celda G-PE. De hecho, el espectro obtenido con la celda G-PE empleando un electrolito concentrado (agua de lluvia artificial 1000x) sobre una probeta de acero inoxidable resulta prácticamente idéntico al obtenido con la celda CP en la concentración habitual (agua de lluvia artificial 10x). En el caso de las medidas de campo sobre obra real, ambas celdas ofrecen resultados de la misma calidad, con las mismas diferencias en la región de altas frecuencias que en las medidas de laboratorio.



**Figura 25.** Realización de medidas de campo sobre la obra Mediterránea III con la CP y la celda G-PE.

Además de las medidas sobre acero inoxidable, se han realizado medidas en probetas de bronce, pertenecientes a la serie de probetas de bronce de fundición con pátina tostada a base de sulfuro potásico tras 16 meses de exposición atmosférica en el CENIM. En la figura 26 se presentan los resultados obtenidos para tres probetas distintas.



**Figura 26.** Comparación de los espectros obtenidos con la celda CP y G-PE sobre tres probetas de bronce patinado (T01-T03).

Los espectros obtenidos en este caso presentan mayores diferencias, aunque el valor máximo del módulo de la impedancia es muy similar en ambos casos. Los resultados de los ajustes de los espectros al circuito general (figura 12) pueden compararse en las tablas 4 y 5. Se puede comprobar que las diferencias en los parámetros calculados no son excesivamente grandes, aproximándose los valores en los elementos que aparecen a frecuencias más bajas (R2-CPE2, difusión). Por otra parte, el ajuste de los espectros realizados con la CP requiere la introducción de una inductancia antes de la resistencia del electrolito y el grado de ajuste es peor que en el

caso de la celda G-PE. Esto sugiere la presencia de algún artefacto en la medida con la celda CP, que pudiera estar relacionado con la reducida distancia entre el electrodo de trabajo y el electrodo de referencia, como se ha demostrado en el estudio realizado para la celda G-PE [206].

**Tabla 4.** Ajuste de los espectros obtenidos con la celda G-PE sobre tres probetas de bronce patinado.

Celda G-PE	T01	T02	T03
Re ( $\Omega \cdot \text{cm}^2$ )	642±1	651±1	592±2
CPE1 $Y_1$ ( $\text{S s}^{\alpha_1} \text{cm}^{-2}$ )	2.83±0.09E-05	2.6±0.1E-05	2.00±0.09E-05
$\alpha_1$	0.59±0.01	0.63±0.01	0.65±0.01
R1 ( $\text{k}\Omega \cdot \text{cm}^2$ )	3.2±0.1	3.5±0.2	3.5±0.2
CPE2 $Y_2$ ( $\text{S s}^{\alpha_2} \text{cm}^{-2}$ )	6.8±0.1E-05	9.3±0.1E-05	6.4±0.1E-05
$\alpha_2$	0.66±0.01	0.54±0.02	0.56±0.01
R2 ( $\text{k}\Omega \text{cm}^2$ )	26.9±0.7	25±2	30±2
R ( $\text{k}\Omega \cdot \text{cm}^2$ )	52±1	46±2	52±3
W T (s)	82±4	82±7	90±10
$\alpha_w$	0.73±0.02	0.73±0.03	0.70±0.04

**Tabla 5.** Ajuste de los espectros obtenidos con la celda CP sobre tres probetas de bronce patinado.

Celda CP	T01	T02	T03
L	-6.12E-05	-9.27E-05	-5.59E-05
Re ( $\Omega \cdot \text{cm}^2$ )	75±1	142±1	77±2
CPE1 $Y_1$ ( $\text{S s}^{\alpha_1} \text{cm}^{-2}$ )	1.18±0.09E-05	1.29±0.5E-05	1.37±0.04E-05
$\alpha_1$	0.83±0.01	0.81±0.01	0.70±0.01
R1 ( $\text{k}\Omega \cdot \text{cm}^2$ )	9.7±0.8	16±1	24±1
CPE2 $Y_2$ ( $\text{S s}^{\alpha_2} \text{cm}^{-2}$ )	6.6±0.6E-05	7±1E-05	9±2E-05
$\alpha_2$	0.67±0.08	0.8±0.1	1±0.2
R2 ( $\text{k}\Omega \text{cm}^2$ )	21±4	16±4	13±4
R ( $\text{k}\Omega \cdot \text{cm}^2$ )	52±6	48±5	58±8
W T (s)	70±10	60±7	70±15
$\alpha_w$	0.77±0.06	0.80±0.04	0.75±0.7

#### 4.2.2. Modificación del electrólito.

Los ensayos realizados con el gel de agar pusieron de manifiesto que el agar parece tener un cierto efecto de despolarización catódica en el bronce, aumentando levemente la velocidad de corrosión medida frente a un electrólito tradicional [132]. Este efecto puede ser minimizado utilizando bajas concentraciones de agar, y no supone un problema práctico para la aplicación pretendida en patrimonio cultural, puesto que para comparar la eficacia de distintos sistemas de protección o seguir su degradación con el tiempo siempre se recurrirá a medidas comparativas. A pesar de ello, se consideró de interés explorar la posibilidad de modificar el electrólito, con el fin de lograr una mayor aproximación a un electrólito líquido tradicional y profundizar en la comprensión del efecto del gelificante sobre las medidas

Al tratarse el agar de una mezcla de dos polisacáridos, agarosa y agarpectina, una mejor opción la ofrecería el empleo de agarosa pura, ya que teóricamente, por ser la fracción neutra del gel, presentaría las ventajas del agar sin sus inconvenientes. Partiendo de esta hipótesis se estudió el comportamiento de la agarosa tanto sobre probetas de laboratorio como en medidas de campo, en comparación con el agar y con el electrólito líquido. Los resultados de esta comparativa demostraron que efectivamente, la agarosa presenta un comportamiento más próximo al electrólito líquido, sin embargo, estas diferencias sólo se producen en superficies reactivas, como puede resultar una probeta de metal limpio y lijado. En el caso de probetas recubiertas, o de las medidas realizadas en campo sobre superficies expuestas largo tiempo a la acción de los agentes atmosféricos, no se aprecian diferencias significativas en el empleo de ambos gelificantes. Este estudio se recoge en la siguiente publicación:

- B. Ramírez Barat, E. Cano: "Agar vs agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage", *ChemElectroChem*, [2019] 6 (9), 2553–2559<sup>9</sup>.

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<sup>9</sup> Referencias bibliográficas [35, 45-47, 68, 91, 119, 122, 132, 143, 146, 147, 151, 155, 161, 168-170, 206-209] de la bibliografía general



# Agar versus Agarose Gelled Electrolyte for In Situ Corrosion Studies on Metallic Cultural Heritage

Blanca Ramírez Barat\* and Emilio Cano<sup>[a]</sup>

The use of gelled electrolytes has revealed an interesting solution for in situ electrochemical measures on cultural heritage, where liquid electrolytes cannot be easily handled. After developing an agar gelled electrolyte cell, other gelling agents such as agarose are being considered to improve it. In this work, the performance of agarose gels in different

concentrations has been studied and compared to agar and a liquid electrolyte. Measurements have been done on patinated quaternary bronze and weathering steel, as representative materials of outdoor monuments. Agarose gels have been validated for in situ corrosion studies on bronze and weathering steel sculptures.

## 1. Introduction

Development of new and improved diagnostic tools is a relevant subject in conservation science, and the application of electrochemical techniques has become an outstanding topic in recent years for the assessment of patinas and protective coatings for metallic heritage.<sup>[1]</sup> The unique nature of the objects, their irreplaceable value, the long-term evolution of patinas and corrosion products (which cannot be reproduced in the laboratory) and the requirement of conservators-restorers to have scientific evidence to support decisions on conservation treatments make necessary to carry out in-situ scientific analysis on the real heritage artefacts. The practical difficulties of doing in-situ electrochemical measurements has restrained the use of these techniques for conservation science.<sup>[2]</sup>

In this particular area, different authors have worked in the design of a solid electrolyte cell for in situ electrochemical measurements, where handling liquid electrolytes offers several difficulties. Commercial electrocardiogram electrodes,<sup>[3]</sup> synthesized anionic gels,<sup>[4]</sup> agar gelled electrolytes<sup>[5]</sup> or PVA<sup>[6]</sup> have been proposed for this purpose. The properties of the electrolyte together with the geometric design are the design key features, particularly for in situ studies.

The use of agar gelled electrolytes has recently been evaluated by different authors<sup>[7]</sup> showing that agar cells offer good performance and interesting properties for this purpose. Agar is a translucent, cheap, non-toxic, and quick and easy to prepare material, which admits a wide range of aqueous electrolytes and also contributes to conductivity. Its flexibility allows adaptation to irregular surfaces and can be improved by the addition of plasticizers,<sup>[7d,e]</sup> and its syneresis helps wetting the surface and allowing good contact. Other proposed materials, have shown other limitations: Commercial or synthesized anionic gels are very limited by the electrolyte choice, and

the use of PVA has to be more deeply studied, as preliminary results showed appreciable differences when compared to a traditional cell design. In previous studies agar showed a certain decrease in impedance values if compared to the liquid electrolyte, which was attributed to some anodic depolarizing effect in bronze, slightly increasing the measured corrosion rate if compared to a traditional liquid electrolyte. Though this effect can be minimized using low agar concentrations and it is not a problem for comparative studies,<sup>[7b,c]</sup> further improvements of the measuring system were considered.

Agar is a mixture of two polysaccharides: agarose, which is the neutral fraction, and agaropectin, modified by side groups. As this later seems to be the responsible for the interaction with copper ions, which accelerates the anodic reaction, the most intuitive approach to avoid this effect is the use of pure agarose instead of agar. Agarose may have same advantages as agar, while its neutral chemical nature will reduce the risk of undesired interactions with metal ions, effects that may be attributed to the agaropectin fraction. Another potential advantage of agarose is that being a purer and homogeneous substance, it is foreseeable to obtain consistent results between different commercial products, while agar may show differences according to its provenance.

A review of literature shows that other researchers have already suggested the use of agarose as a solid medium for conventional electrochemical measurements although very few articles have been published. Kaneko and co-workers studied the use of agarose gels as an electrolyte for electrochemical measurements, such as Electrochemical Impedance Spectroscopy or Voltammetry, providing similar results to liquid electrolytes.<sup>[8]</sup> These authors evaluated transport and electrochemical properties of agarose gels, finding out that were very close to aqueous systems. Despite the interest of this work, to our best knowledge, no application of agarose to corrosion studies has been done. For this reason, the aim of this work is to evaluate the behavior and applicability of agarose gelled electrolytes for corrosion studies in cultural heritage, in comparison with both a liquid electrolyte and with agar-based electrolyte, which has demonstrated its utility for in-situ measurements. Measurements have been done with the gel

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polymer electrolyte (G-PE) cell described in previous papers,<sup>[5,7c,9]</sup> under the experimental conditions presented in "Experimental Section". As base electrolyte, an artificial rain (AR) solution has been used, both as liquid and gelled with agar and agarose.

## 2. Results and Discussion

### 2.1. Agarose as a Gelling Agent

The behavior of the agarose gelled electrolyte has been studied over different substrates and compared with the liquid electrolyte and agar-gelled electrolyte. These include bare metal surfaces, artificially and naturally patinated metals and coated metals: AISI316 stainless steel has been chosen as reference material, and patinated cast bronze and weathering steel, as representative materials of outdoor sculptures.

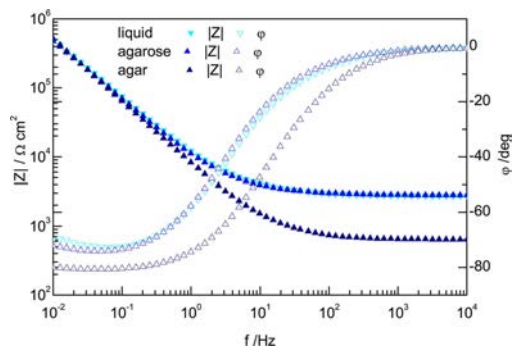
Figure 1 shows EIS spectra for the liquid, agarose-gelled and agar-gelled electrolyte obtained on stainless steel coupons. The high stability and uniformity of the passive layer formed on the stainless steel allows a precise comparison of the contribution of the different experimental setups<sup>[9]</sup> For this system, agarose and liquid results are almost identical, and differences appear only for agar and in the high frequency region. This difference

can be explained by the lower electrolyte resistance, due to the agar's increase of conductivity.<sup>[5]</sup>

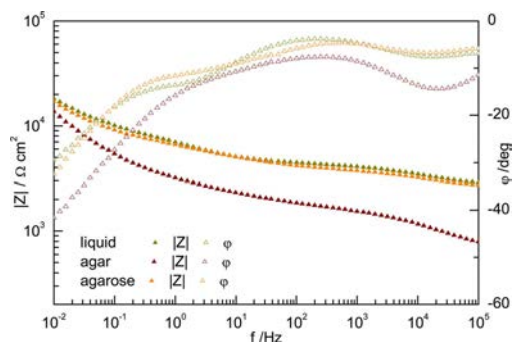
In the case of weathering steel (Figure 2) a decrease in the impedance of intermediate frequencies is also observable for agar, while results from liquid and agarose electrolyte can be considered almost equivalent. Due to the inhomogeneity of natural patinas in weathering steels, it is difficult to ascertain to which extent this effect is attributable to differences in the samples or to the effect of the composition of the electrolyte.

When measures are done on bronze (Figure 3), there is also a drop in impedance's value at low frequencies, together with a phase angle shift. This effect, which is slightly present in the agarose gel too, has been related to the interaction between copper ions and the gel matrix.<sup>[7c]</sup> When bronze is covered by a protective coating as Incolac® (Figures 4) this effect is minimized, and results obtained with the three electrolytes are comparable, taking into account that the measured surfaces are not identical (as have been individually prepared by hand, following the common practice of conservators-restorers in conservation treatments for real objects).

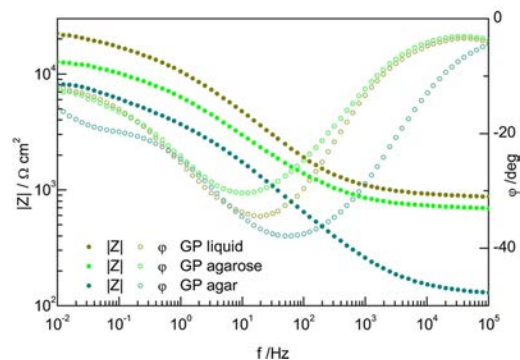
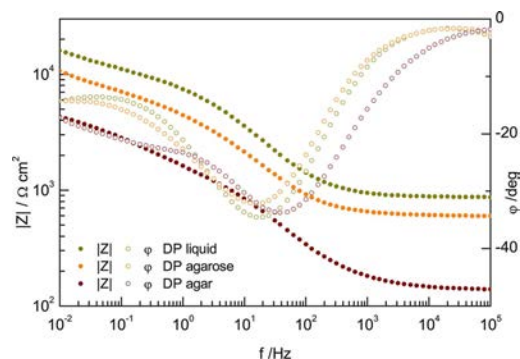
In general, it can be appreciated that EIS spectra obtained with agarose are quite similar to those acquired with the liquid electrolyte, while measurements with agar show lower impedances, especially at high frequencies. These differences are more or less pronounced depending on the working electrode material.



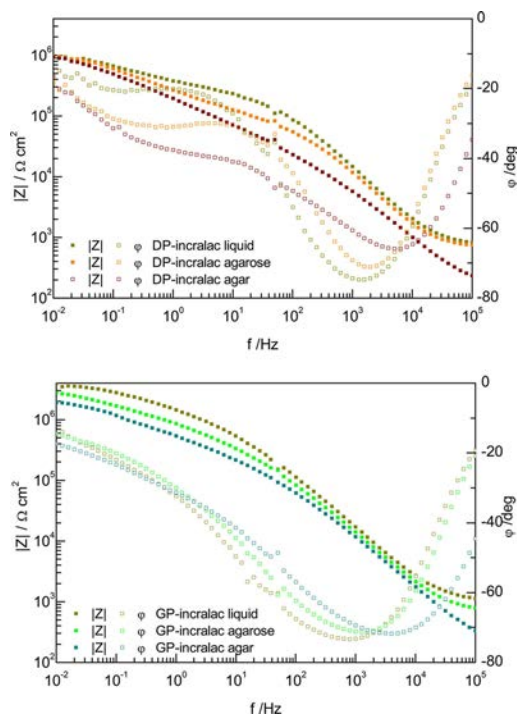
**Figure 1.** EIS spectra (Bode plot) obtained with liquid electrolyte, agarose and agar gels on AISI316 stainless steel.



**Figure 2.** EIS spectra (Bode plot) obtained with liquid electrolyte, agarose and agar gels on weathering steel (three year natural patina).



**Figure 3.** EIS spectra (Bode plot) obtained with liquid electrolyte, agarose and agar gels on cast bronze with dark (top) and green (bottom) patina.



**Figure 4.** EIS spectra (Bode plot) obtained with liquid electrolyte, agarose and agar gels on Incralac coated bronze with dark (top) and green (bottom) patina.

## 2.2. Agar vs. Agarose in Field Measurements

Since the final aim of the G-PE cell is the in-situ electrochemical measurements on metallic heritage, the comparison of agar and agarose gelled electrolyte was done by field measurements on five different bronze and weathering steel sculptures, at different locations. The five sculptures were a bronze Sphinx at the National Archaeological Museum in Madrid, with an Incralac® coating; a bronze angel figure by Enrico Astorri from the Staglieno monumental cemetery in Genoa; a modern bronze sculpture, *Unidad Yunta* (Pablo Serrano, 1970) at the Polytechnic University of Valencia and two weathering steel sculptures located at the Museo de Escultura de Leganés (Madrid): *Templo* (2003) by Adriana Veyrat and *Zenon* (1980) by José Luis Sánchez (owned by Museo Reina Sofía).

In all cases, apart from the higher conductivity of agar, EIS spectra are very similar for agar and agarose in all examples, as can be appreciated in Figures 6–8. Measures on the *Angel figure*, with a thick highly washed patina, and *Zenon*, with a well-

developed and smooth patina, are almost identical for the two gelled electrolytes. Comparing the values of the low frequency limit of the impedance modulus (Table 1), it can be appreciated that values are very close for every couple of measurements (agar-agarose) on the same sculpture. The fact that in some cases agarose yield lower impedance and in other higher suggest that differences may be attributed to small patina inhomogeneity and/or differences in the wetted area, which in this in-situ measurements are higher than the differences due to the electrolyte that have been demonstrated in previous section. The largest differences seem to appear in one of the weathering steel sculptures, *Templo*, the one with the younger and presumably thinner patina, but numerical differences are in fact very little, though visual differences seem higher due to the scale of the graph. The higher difference when comparing values is in the coated bronze surface from the bronze *Sphinx*.

From these results, it can be considered that differences between both electrolytes in field measurements are not quite relevant. This difference with laboratory measurements can be explained by the fact that laboratory coupons are more homogeneous and uniform, and are more reactive than patinas of outdoor sculptures which have been exposed and washed through many years.

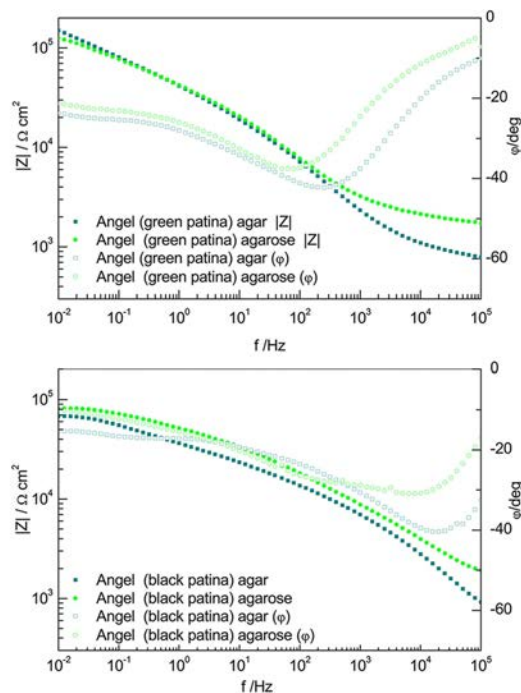
## 2.3. Agarose Concentration

As previously noted, the choice of 2% agarose was based on the fact that this would be the equivalent to 3% agar, so this concentration could be compared with previous results obtained with the agar cell. As shown in previous sections, 2% agarose gave spectra closer to liquid electrolyte than agar, though still showed a slightly lower impedance values in the more reactive bronze surfaces. Considering that results may be improved using a different agarose concentration, a series of EIS measurements at different agarose percentages were done on the two reference materials, patinated bronze (Figure 9) and weathering steel (Figure 10), and compared to the liquid electrolyte

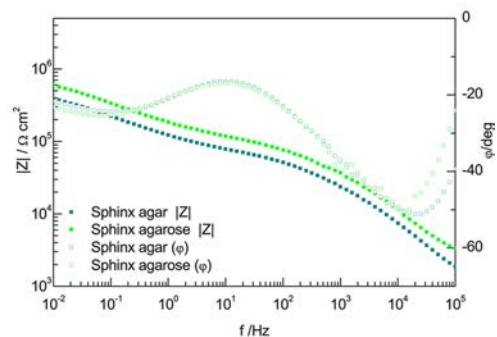
Though the lower is the agarose concentration more close is the EIS spectra to the liquid electrolyte, differences between agarose concentrations are relatively small. Table 2 shows the different electrolyte concentrations, pH and conductivity. The addition of agarose to the liquid electrolyte slightly increases the conductivity and does not modify the pH value, while agar produced more basic pH and significantly enhances conductivity, as previously described.<sup>[7c]</sup> As with agar, this increase in conductivity explains the lower  $|Z|$  values at high frequencies with the increasing concentration of agarose, but this effect is quite small, especially when compared with agar, so it can

**Table 1.** Comparison of the impedance modulus at the low frequency limit with agar and agarose gelled electrolyte for different sculptures.

$ Z _{\max}$ [Ohm cm <sup>2</sup> ]	Angel (green area)	Angel (black area)	Sphinx	Unidad Yunta	Templo	Zenon
	agar	1.50E+05	6.83E+04	3.89E+05	3.45E+05	9.44E+03
agarose	1.26E+05	8.12E+04	6.02E+05	2.78E+05	9.81E+03	1.93E+06



**Figure 5.** Bode plots from a bronze angel (pictured left), by Enrico Astorri (1859–1921) at the Staglieno cemetery in Genoa. Spectra from green (top right) and black (bottom right) areas on the left arm.



**Figure 6.** Bode plot (right) of the sphinx at the main façade of the National Archaeological Museum in Madrid (pictured left). The Sphinxes, casted in 1894, were restored and protected with Incralac® and wax a couple of years before.<sup>[7b,10]</sup>

Electrolyte	pH	Conductivity [mS]
AR	6.67	94.0
AR-agarose 1%	6.7 ± 0.2	120 ± 2
AR-agarose 1.5%	6.5 ± 0.2	126 ± 6
AR-agarose 2%	6.6 ± 0.2	132 ± 6
AR-agar 3%	7.42 ± 0.03	1524 ± 15

usually be disregarded. Considering these small variations, other effects, such as geometrical factors can be responsible for slight variations in high frequencies  $|Z|$  values in Figures 9 and 10: as  $R_s$  depends on the area and WE-RE distance, small variations due to the deformation of the gel when pressured to the working electrode surface, can explain this behavior. This is specially the case of the lower concentrations (1%), which produce a very soft gel, with low mechanical resistance.



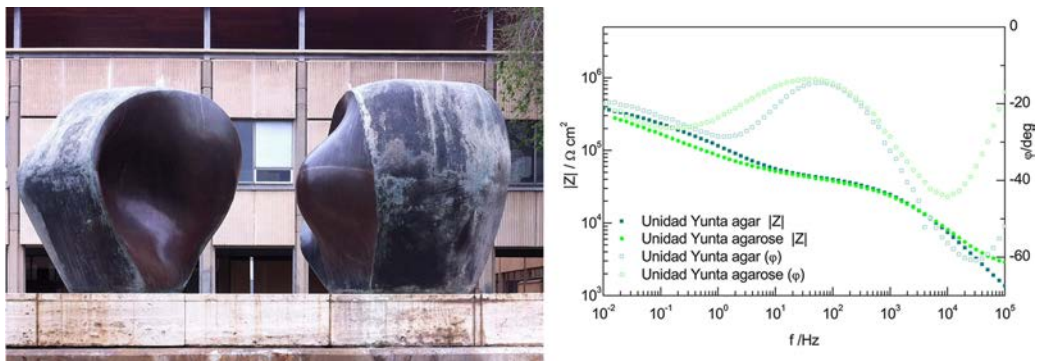


Figure 7. Bode plot (right) of a modern bronze sculpture (pictured left), *Unidad Yunta* (1970) by Pablo Serrano, on the brown polished area.

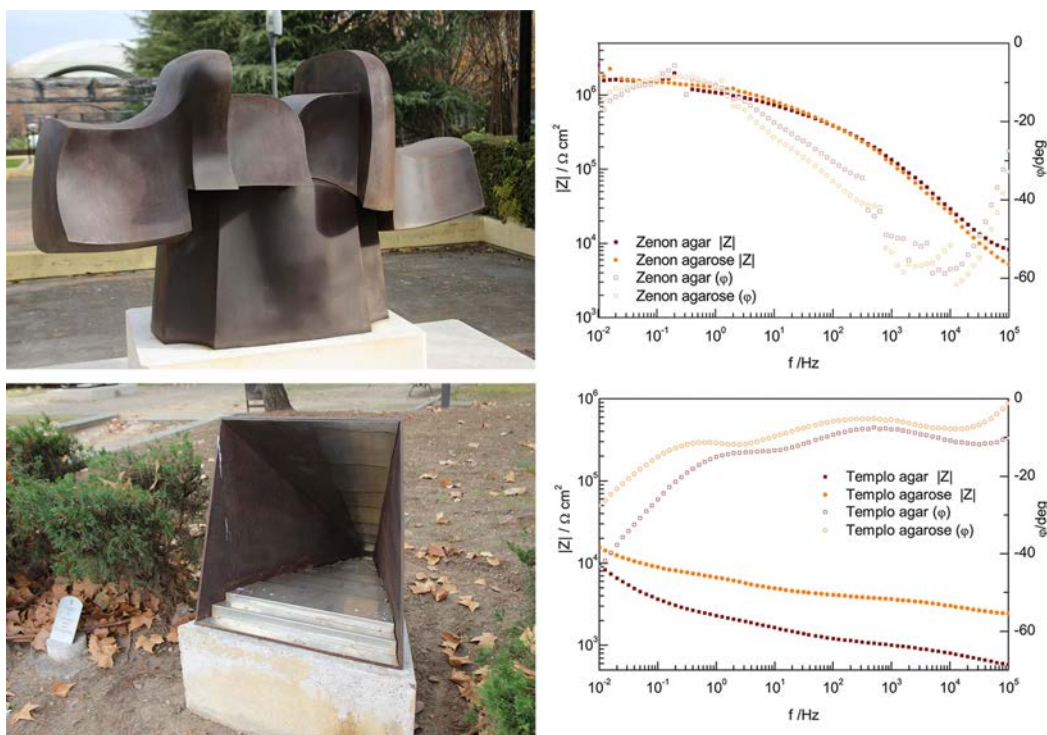
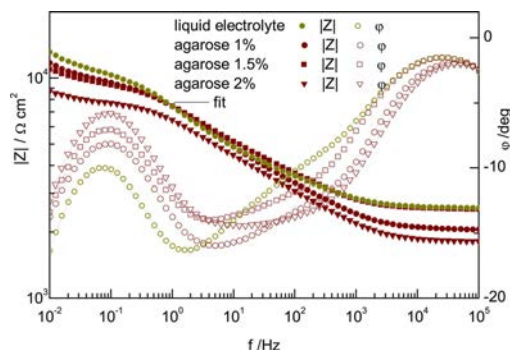


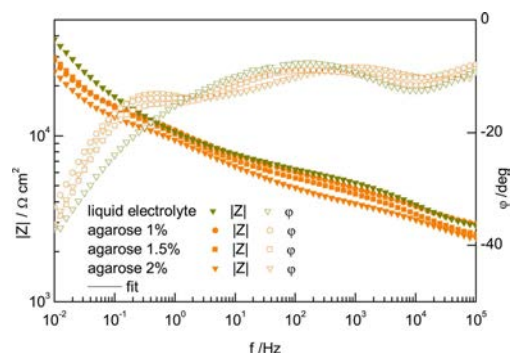
Figure 8. EIS spectra (Bode plots; right) on weathering steel sculptures at the Museo de Escultura de Leganés. *Zenon* (1980), by José Luis Sánchez (top left), and a weathering steel sculpture with a waxed and polished surface and *Templo* (2003), by Adriana Veyrat (bottom left), with a thin lepidocrocite patina.<sup>[11]</sup>

In order to elucidate the contribution of agarose to the EIS spectra at other frequencies, results were fitted to the general equivalent circuit presented in Figure 11. The use of this circuit has been discussed in a previous paper.<sup>[1]</sup>  $R_s$  is the resistance of the electrolyte, CPE1-R1 represent the resistance and capacitance of the patina or rust layer, CPE2-R2 the capacitance of the double layer at the metal-electrolyte interface and charge transfer resistance of the redox reactions and  $W$  represents diffusive effects related to copper ions diffusion in the patina

for bronze<sup>[12]</sup> and to oxygen diffusion through the pores in the rust layer, in the case of steel.<sup>[13]</sup> The values obtained for the different elements (Table 3) are also very close, moreover taking into account the irregularities of the patina surfaces and the unavoidable uncertainty in the measured area, in particular for the highly porous and absorbing rust layer in weathering steel. The values of  $R_2$  seem to decrease slightly with the increasing concentration of agarose, both for bronze and weathering steel. This indicates that agarose slightly increases the measured



**Figure 9.** EIS spectra of brown patinated bronze coupons with different agarose concentrations.



**Figure 10.** EIS spectra of 5-years-aged weathering steel with different agarose concentrations.

corrosion rate, although this effect is much less relevant than for agar.<sup>[7c]</sup> Diffusion does not seem to be affected by the use of the gel in the case of bronze, in agreement with a previous work,<sup>[7c]</sup> but for weathering steel the diffusive impedance is increased, what might be explained by the lower oxygen content of gelled electrolytes.<sup>[7d]</sup> In any case, as it has been shown in the results of previous section (Figures 5–8), the uncertainties of field measurements are higher than these

effects. For this reason, the use and concentration of agarose does not present a critical issue for in situ corrosion studies in cultural heritage. As a compromise between mechanical and electrochemical properties, 1.5–2% agarose would be a good option.

### 3. Conclusions

Agarose has shown to be a good option for electrochemical measurements on cultural heritage objects, where a conventional cell cannot be used and the use of gel electrolytes can offer many advantages.

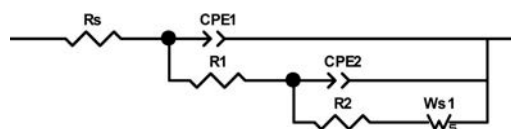
Results show that agarose gives a response quite close to the liquid electrolyte, thus it is a good option to carry out corrosion studies, where agar may have a higher effect on results. This would be the case of reactive surfaces as non-aged coupons or fresh patinas.

Field measurements on long-term weathered surfaces of monuments or in coated metals do not show significant differences between the two gelled electrolytes, so the use of agar is still valid if necessary. The natural conductivity of agar may offer an additional advantage in field measurements, especially for low impedance patinas such as those of weathering steels.

### Experimental Section

As mentioned in the introduction, measurements have been done with the gel polymer electrolyte (G-PE) cell designed by authors and described in detail in references.<sup>[5,7c,9]</sup>

The electrolyte has been prepared by gelling a liquid electrolyte with agar (technical grade) or agarose (basic, Panreac). As liquid



**Figure 11.** Equivalent circuit used for modelling EIS spectra of patinated metal coupons.

Table 3. Fit results of EIS spectra on bronze and weathering steel coupons for different agarose concentrations compared to the liquid electrolyte.										
	$R_s$ [kΩ·cm <sup>2</sup> ]	CPE 1 $Y_1$ [S s <sup>-1</sup> cm <sup>-2</sup> ]	$\alpha_1$	$R_1$ [kΩ·cm <sup>2</sup> ]	CPE 2 $Y_2$ [S s <sup>-1/2</sup> cm <sup>-2</sup> ]	$\alpha_2$	$R_2$ [kΩ cm <sup>2</sup> ]	$W$ $R$ [kΩ·cm <sup>2</sup> ]	$T$ [s]	$\alpha_w$
<b>Bronze</b>										
Liq	2.6	7.5E-06	0.64	1.8	5.1 E-05	0.58	7.4	17.1	123	0.72
1%	2.0	3.7E-06	0.69	1.7	4.2E-05	0.55	6.6	13.4	140	0.67
1.5%	2.5	4.7E-06	0.69	2.0	4.7E-05	0.58	5.4	11.6	117	0.72
2%	1.8	5.1E-06	0.66	1.9	4.7E-05	0.57	4.5	13.8	159	0.84
<b>W. Steel</b>										
Liq	2.3	1.35E-06	0.51	4.0	5.5E-05	0.48	10.4	138	80	0.54
1%	2.3	3.3E-06	0.44	3.7	6.0E-05	0.40	16.9	152	120	0.75
1.5%	1.9	2.8E-06	0.46	3.6	5.1E-05	0.47	13.1	154	150	0.70
2%	1.7	2.1E-06	0.46	2.5	4.2E-05	0.44	10.6	107	146	0.70

electrolyte concentrated artificial rain ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  14.43 mg/mL,  $(\text{NH}_4)_2\text{SO}_4$  15.04 mg/mL,  $(\text{NH}_4)\text{Cl}$  19.15 mg/mL,  $\text{NaNO}_3$  15.13 mg/mL and  $\text{CH}_3\text{COONa}$  3.19 mg/mL) has been used, adapted from.<sup>[14]</sup> The solution is prepared 1000 fold concentrated and pH adjusted to 5 with  $\text{HNO}_3$  and stored at room temperature. For the measurements, this solution is then diluted to a 10-fold concentration, with a final pH value of 6.5. This solution has been chosen because it has a similar composition to the natural electrolyte to which outdoor monuments are exposed and at the same time it is a mild electrolyte which prevents any damage to the surface. To prepare the electrolyte 3% w-v agar or 1–2% w-v agarose powder is added to the electrolyte in a beaker and gently heated in a microwave oven at low power until dissolution. The solution is poured into the mold and left to cool at room temperature. For comparison between agar and agarose gels, 2% agarose was used. As agarose represents two thirds of agar composition, 2% agarose would be the equivalent to the 3% agar gel used in previous work. A stainless-steel wire (AISI 316 L) has been used as pseudo-reference electrode and a spiral made of the same material has been employed for the counter electrode (CE). In all cases, the geometry of the cell and electrode positions have been kept constant.

The behavior of the different electrolyte compositions has been tested on AISI316 stainless steel coupons and on patinated cast bronze and weathering steel, as representative materials of outdoor sculptures. Different sets of reference coupons were used, prepared as:

- Quaternary (85 Cu, 5 Sn, 5 Pb, 5 Zn %w) EN 1982CC491K (DIN 1705-RG5) cast bronze coupons were prepared by a traditional Spanish foundry according to traditional methods for artistic sculpture. Samples were cast, sand blasted and artificially patinated with a dark patina (using a potassium sulfide solution) and a green patina (using an ammonium chloride solution). Patination solutions were applied by alternately brushing the solution on the metallic surface and heating with a torch. One layer of Inralac®, an acrylic coating used in conservation treatments of bronze sculptures, was applied by brush on some coupons.
- Weathering steel (Arcelor S355J2W, EN 10025-5-2004) with a natural patina developed by exposing the steel coupons to a mild urban atmosphere (Madrid, Spain) for 3 and 5 years in an atmospheric corrosion station (according to standard ISO 8565:1992).
- AISI 316 stainless steel has been used as a highly stable reference material, to minimize the effects of inhomogeneity in patina layers. Stainless steel coupons have been polished for homogenization of the surface and left to the air for several days to allow the formation of its natural passivation layer.

EIS spectra have been acquired using a Gamry 600 Potentiostat, using a frequency swept from 100 kHz to 10 mHz, 10 mV RMS amplitude (at the open circuit potential, OCP) and 10 points/decade. The area exposed to the electrolyte was 3.14 cm<sup>2</sup>. Analysis of the data has been carried out using ZView software. The system was left to stabilize at OCP for 30 minutes before measurements. Conductivity and pH of the electrolytes has been measured with a Crison MM40 conductimeter/pH meter.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** agarose · corrosion · cultural heritage · gel electrolyte · impedance

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### 4.3. Validación y aplicación (casos prácticos).

Además de los ensayos realizados con diferentes probetas para el diseño y evaluación de la celda, de manera paralela se han hecho estudios puntuales sobre diferentes sustratos para estudiar las posibilidades de aplicación a la resolución de problemas de conservación. Por un lado, se han realizado estudios de laboratorio sobre probetas con diversas pátinas y recubrimientos que simulaban las diversas circunstancias y cuestiones que se abordan habitualmente en la conservación del patrimonio metálico; por otro lado, se han realizado estudios *in situ*, sobre obra real, para comprobar y validar el diseño de la celda en su modo de aplicación final, e ir introduciendo las modificaciones necesarias para solventar las dificultades prácticas que se iban encontrando en diferentes situaciones.

#### 4.3.1. Ensayos de laboratorio: pátinas y recubrimientos.

El estudio de pátinas y recubrimientos tiene gran interés para la ciencia de la conservación. El estudio de la composición y características de las pátinas permite, entre otros objetivos, comprender mejor los mecanismos de corrosión y los factores que intervienen o determinar la estabilidad de un objeto en un determinado ambiente para anticipar problemas de conservación. Por ejemplo, poder predecir la evolución de las pátinas teniendo en cuenta el cambio climático, las variaciones en los niveles de contaminación, el traslado de lugar del objeto, etc. En patrimonio cultural, estos daños no tienen por qué ser necesariamente físicos o químicos, pueden ser también estéticos, tales como la alteración del color de la pátina. Por otra parte, estudio de la efectividad y la evolución de los recubrimientos protectores es sin duda una cuestión de gran relevancia para la conservación del patrimonio metálico. Los recubrimientos utilizados en conservación han de cumplir una serie de requisitos específicos impuestos por los criterios actuales de conservación, y se aplican en condiciones que no son las idóneas desde un punto de vista de optimizar su capacidad protectora. Por estas razones, resulta importante realizar estudios de estos productos para conocer sus prestaciones y evolución con el tiempo [35]

Las técnicas analíticas habitualmente utilizadas en este campo, como FTIR, DRX o Raman, permiten ver la evolución en la composición y estructura de una pátina o recubrimiento, pero no proporcionan una relación cuantitativa con la capacidad



protectora. Por ello, la posibilidad de aplicación de técnicas electroquímicas a estos estudios supone una valiosa contribución. En este capítulo, se presentan varios estudios realizados para demostrar las posibilidades reales de aplicación del sistema desarrollado a casos reales.

#### 4.3.1.1. Evaluación de pátinas.

Dentro de las posibilidades de utilización de la celda al estudio de pátinas se presentan dos ejemplos de aplicación. El primer caso es un trabajo sobre la caracterización de pátinas formadas sobre probetas metálicas para su utilización posterior como sustratos para la evaluación de tratamientos, en colaboración con el grupo del ISMAR-CNR y el grupo de la Dra. Joseph de la Universidad de Neuchâtel. Este trabajo se presentó en el noveno congreso del Grupo de Metales del Comité de Conservación del ICOM:

- P. Letardi, B. Ramírez Barat, M. Albini, P. Traverso, E. Cano, E. Joseph, "Copper Alloys and Weathering Steel Used in Outdoor Monuments: Weathering in an Urban-Marine Environment", en: R. Menon, C. Chemello, A. Pandya (Eds.), *METAL2016, 9th interim meeting of the ICOM-CC Metals Working Group*, New Delhi, India, 2016, pp. 320-8.

En este trabajo se estudiaron las patinas formadas sobre probetas de cuatro metales representativos del patrimonio, cobre, bronce terciario, bronce cuaternario y acero patinable, por exposición durante 18 meses a una atmósfera urbano-marina en Génova (Italia). Los resultados mostraron que las patinas desarrolladas sobre las probetas a lo largo de este periodo presentaban características similares a las pátinas formadas en los monumentos. Concretamente para las medidas de impedancia en las probetas de cobre y sus aleaciones los valores de  $|Z|_{10\text{mHz}}$  eran próximos a los medidos sobre obra real. Estos resultados avalan la posibilidad de obtener muestras adecuadas para la evaluación de tratamientos de conservación y restauración, mediante exposición de probetas a periodos de tiempo relativamente razonables.

El segundo ejemplo es el estudio de la evolución de pátinas artificiales sobre aceros patinables. Los aceros patinables, más conocidos en el campo del arte y la arquitectura por la denominación comercial de acero corten (o COR-TEN, que es la denominación original utilizada por el fabricante US Steel, que lo desarrolló), se caracterizan por desarrollar una pátina *protectora* bajo determinadas condiciones.

Además de ese cierto carácter protector, la pátina formada presenta un rango de tonalidades entre naranja y marrón que le confieren un valor estético, motivo por el cual son muy utilizados en las artes plásticas. En este caso, se ha aplicado la celda G-PE para la evaluación de la capacidad protectora de pátinas artificiales desarrolladas sobre aceros patinables. La utilización de la celda en este estudio permitiría evaluar el estado de conservación de esculturas tratadas de esta manera.

Los primeros resultados de la aplicación de la celda en el estudio de probetas de acero patinadas artificialmente muestran diferencias de comportamiento entre las pátinas aplicadas. El empleo de la celda ha permitido medir estas diferencias y compararlas con pátinas naturales y pátinas sobre obra real [146, 210-212], demostrando que es una herramienta adecuada para medir en este tipo de superficies que presentan una textura irregular y de elevada porosidad, adaptándose a la superficie y reteniendo adecuadamente el electrólito líquido. Los estudios iniciados en este tema, han sido el origen de otra tesis doctoral que se está realizando actualmente en el CENIM.

Los primeros resultados en la aplicación de la celda en el estudio de probetas de acero patinadas artificialmente también se presentaron en el congreso METAL 2016:

- B. Ramírez Barat, T. Palomar, B. Garcia, D. De la Fuente, E. Cano, "Composition and Protective Properties of Weathering Steel Artificial Patinas for the Conservation of Contemporary Outdoor Sculpture", en: R. Menon, C. Chemello, A. Pandya (Eds.), *METAL 2016 9th interim meeting of the ICOM-CC Metals Working Group* New Delhi, India, 2016, pp. 314-9.

Ambas publicaciones se presentan a continuación.

# Copper Alloys and Weathering Steel Used in Outdoor Monuments: Weathering in an Urban-marine Environment

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## Abstract

We exposed metal coupons to natural weathering for 18 months at the Experimental Marine Station (SMS) inside Genoa Harbour. Four different compositions related to metals used in outdoor monuments were selected: copper (CU), ternary bronze (TB), quaternary bronze (QB), and weathering steel (WS). For each alloy, subsets of samples were monitored *in situ* for colour variation at regular intervals. To fully characterise the natural urban-marine patina growth and its chemical-physical properties, several analytical techniques have been used. For a more effective comparison with patinas on metal monuments and ornamentations, both portable Non-destructive Techniques (NdT) and classical laboratory methods were adopted. First results showed a generally slower growth rate and evolution of the properties of patinas after 12-14 months. The patina on bronzes and pure copper showed the early formation of cuprite

followed by  $\text{Cu}_2\text{Cl}(\text{OH})_3$  polymorphs and copper sulfates, mainly brochantite on CU. On WS a thicker corrosion layer than on copper alloys had grown, mainly composed of iron oxyhydroxides lepidocrocite and akaganeite, with a higher corrosion rate in respect of copper alloys. The patina composition on 18 months weathered coupons corresponds to the main composition generally reported for outdoor artworks. These coupons would thus be useful to test the performance of treatments on complex patina layers.

## Keywords

corrosion, natural ageing, bronze, copper, weathering steel, X-Ray Diffraction (XRD), Electrochemical Impedance Spectroscopy (EIS), Fourier Transform Infrared Spectroscopy (FTIR)

## Introduction and research aims

We present the experimental design and first results of an inter-laboratory research activity aimed at a deeper understanding of the properties of natural patinas, further development of *in situ* characterisation of metal monuments and ornamentations and an improvement of metal conservation-restoration treatments based on clear scientific and ethical criteria. This initial characterization aims to establish the best understanding of the composition and corrosion behaviour of coupons to be used for testing corrosion protection treatments.

Extensive analytical studies on conservation strategies (e.g. cleaning and protective treatments) can be performed only on artificial coupons, due to the wide homogeneous

surface required to compare many different parameters (Pilz 1997, Joseph 2013). Nonetheless, to recreate specimens representing the surface structure that is the result of past technologies and of complex interactions with the changing environments for many years may be quite difficult. However, copper, bronze and steel coupons with patinas as similar as possible to the ones commonly found in outdoor monuments (Selwyn 2004) are necessary in order to evaluate the efficiency of novel treatments, which depend also on the interaction with the patina (Otieno-Alego 1998, Chiavari 2010). Despite extensive studies on atmospheric corrosion, knowledge of many relevant parts is still lacking (Odnevall 2014). To elucidate this topic, experiments on weathering of coupons in standard

conditions are widely used (Tidblad 2012). Their surface characterisation by *in-situ* Non destructive Techniques (NdT) is not a standard practice, even though it could provide a valuable tool in the field of cultural heritage. In fact, it would allow a straightforward comparison between the measurements performed on coupons and those on monuments in terms of patina characterization and performance of tested treatments (Letardi 2016).

Among others, electrochemical techniques have raised a growing interest in the field of metal conservation and EIS has proved to be an effective tool to non-destructively characterise the corrosion behaviour of patinas and the efficiency of conservation treatments (Cano 2010, Letardi 2013, Albini 2015, Sansonetti 2015). A full exploitation of EIS data in metal conservation is not yet well established, especially for patina characterisation (Letardi 2007), and a deeper multi-analytical investigation will help in reaching that goal.

We focused our attention to the patina development on coupons exposed outdoor in a marine-urban environment, also considering the role of composition on corrosion. We applied NdT characterisation techniques to coupons, preferentially using *in situ* methods usually applied on artworks. Moreover, we wanted to take advantage of laboratory techniques to gain a better insight on both the effectiveness of NdT measurements on metal artworks and the analysis of electrochemical properties of the patinas. Finally, we addressed the use of these weathered coupons for the testing of treatments on outdoor monuments.

This paper presents the natural weathering exposure program of metal coupons and the first results on their characterisation over 18 months.

## Materials and methods

### Coupons and weathering conditions

Four different metal/alloy compositions were chosen:

- Cast copper (CU).
- Cast ternary bronze (TB) with nominal composition Cu90/Sn8/Pb2.
- Cast quaternary bronze (QB) with nominal composition Cu85/Sn5/Zn5/Pb5.
- Weathering steel (WS) Arcelor S355J2W, EN 10025-5-2004 similar to CorTen steel.

The surface was polished with SiC grinding paper up to 1200 grit size, rinsed in deionised water and air-dried immediately before exposure. Two unexposed samples (3 × 3 cm) of each alloy were stored in the laboratory as reference. Two sets composed of 16 (6 × 6 cm-designed as large) and 12 (3 × 3 cm-designed as small) coupons for each alloy were exposed at the ISMAR-SMS site inside Genoa harbour, classified in corrosivity category C3 according to standard (ISO 9223:1992), with a chloride deposition rate of about 30 mg/(m<sup>2</sup>d) (ISO 9225:2012). The samples faced south and were positioned 45 degrees from the horizontal level (ISO 8565:1992) (Figure 1).



Figure 1. Exposure rack at the beginning (top) and after 14 months exposure (bottom)

The large samples were intended for future treatments testing and comparison; therefore, they were characterised only with NdT. The small samples were intended for monitoring patina growth and a wider use of analytical techniques. They were removed in pairs at regular intervals (1-3-6-12-18 months) in order to characterize the corrosion layer, both with portable NdT and laboratory measurements. The large coupons showed an almost even overall appearance after 18 months weathering, with a perceivable uneven texture at smaller scale (Figure 2a). The same appearance more or less characterised the small coupons at all weathering times (Figure 2b) with more relevant border effects, which is the reason why the larger coupons should be adopted for treatment testing.



Figure 2. Typical coupons appearance after weathering: a) large samples after 18 months; b) small samples at different exposure times

**Characterisation techniques**

For each alloy, subsets of 3 large samples and 3 small samples were monitored *in situ* for colour variation at regular intervals with a portable spectrophotometer Minolta d2600 [8 mm diameter measurement area, 360-750nm, illuminant D65, 10° observer, UV 100%]. Measurements were done using a positioning mask to repeat the measurement on the same points, in order to minimise scatter of data due to small-scale lack of homogeneity. The results are expressed according to the CIE 1976 L\*a\*b\* colour reference space: the variable L\* represents lightness, while a\* (red-green) and b\* (yellow-blue) are the chromatic coordinates.

A PHYNIX Surfex PRO FN Thickness Gauge was used to measure the patina’s thickness at the end of the exposure time. The instrument was zeroed and calibrated with 12 µm and 51 µm thickness standard, using a freshly polished unexposed sample as bare reference for each alloy. On each sample an average of 9 readings (5 mm diameter measurement area) evenly distributed over the whole area was acquired.

Patina composition was characterised on small samples by XRD and FTIR measurements on the coupons surface, without any sampling performed. FTIR spectra in Atten-

uated Total Reflectance (ATR) mode were recorded in the range 4000-550 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> on Perkin Elmer Spectrum Two™ IR spectrometers as the average of 32 scans with Spectrum software. Thermo Scientific Omnic software was used for post-run processing. XRD spectra were recorded on a Rigaku Geigerflex D/max-B series diffractometer with Cu Kα radiation in the range of 7°-75° 2θ.

Corrosion behaviour was characterised by Polarisation Resistance (R<sub>p</sub>) and EIS measurements with a Gamry Ref600 potentiostat with two different electrochemical cells designed for *in situ* measurements (Letardi 2004, Cano 2014, Ramírez Barat 2015). A ten-fold concentrated artificial rain solution (Bernardi 2008, Agnoletti 2011) was used as electrolyte; the composition is reported in Table 1. Polarization resistance measurements were obtained from -20 to +20 mV vs. open circuit potential (OCP) at a scan rate of 0.167 mV/s. EIS spectra were acquired in potentiostatic mode at OCP in the frequency range 100KHz-10mHz with 10mV applied potential.

Table 1. Composition of synthetic rain used.

A solution at 1000x concentration was prepared in deionised water and then diluted at 10x to be used as electrolyte in electrochemical measurements. Analytical grade salts were used

Salt	Concentration mg/L
CaSO <sub>4</sub> .2H <sub>2</sub> O	1.443
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.504
NH <sub>4</sub> Cl	1.915
NaNO <sub>3</sub>	1.513
CH <sub>3</sub> COONa	0.319
HNO <sub>3</sub> 65%	Some drops of 50% solution diluted in water to adjust pH to 5

The small samples were analysed also with metallographic techniques to fully characterise the natural urban-marine patina growth morphology on the different metal substrates. Metal samples were embedded in epoxy resin and ground with SiC grinding paper up to 2000 grit size followed by polishing with 3 and 1 µm diamond paste. For bare alloys characterisation, the weathering steel was etched with 2% nital solution and the copper alloys with ferric chloride in alcohol solution.

Weathered sample surface was examined by scanning electron microscopy (SEM). The SEM micrographs were obtained using the secondary electrons detector of a Hitachi S-4800 microscope, equipped with a cold-cathode field emission electron gun.



**Results and discussion**

Copper and bronze show the characteristic casting microstructure (Figure 3). Copper has small and regular polygonal phase- $\alpha$  grains about 25  $\mu\text{m}$  in size; no cast shrinkage porosity is observed. Both ternary and quaternary bronze show as-cast microstructure with large irregular grains of  $\alpha$ -phase and solidification defects such as pores and shrink cavities. Dark spots appear due to segregation of tin surrounded by  $\delta$ -phase. Small grey segregates can be observed in QB alloy, probably lead, due to its limited solubility in copper. WS is a hypoeutectoid steel with very fine and equiaxial grains. Microstructure consists of a ferrite matrix with small perlitic colonies.

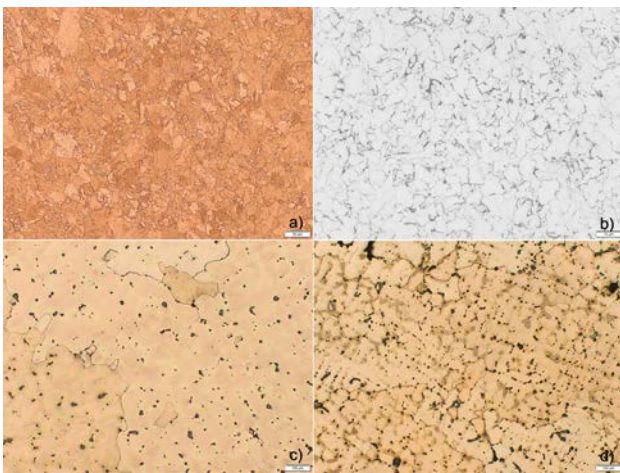


Figure 3. Metallographic examination of CU (a), WS (b), TB (c) and QB (d)

Bronze coupons TB and QB are characterised by fairly similar colour values (Figure 4); they show almost the same colour variation upon weathering, with slightly higher  $b^*$  (tendency to yellow) for TB. Copper samples are darker (lower  $L^*$ ) and more reddish (higher  $a^*$  values). A bigger colour variation than for the bronzes is measured for CU in the first months of exposure, while after one year the general trends of pure copper and its alloys are quite similar. WS samples undergo a larger chromatic variation, with the major colour changes in the first 3-6 months. For all alloys, the colour became more stable after about 14 months of exposure.

The patina thickness of WS samples increased rapidly in the first months (Figure 5), with a slower growth rate after 6 months which led to about 60  $\mu\text{m}$  after 18 months. On CU, TB and QB samples, the patina seemed to develop slower and patina thickness started increasing only after 6 months, with a slower growth rate after 1 year; on bronzes the patina thickness after 18 months reached about 5  $\mu\text{m}$  while on copper it was just about 3  $\mu\text{m}$ .

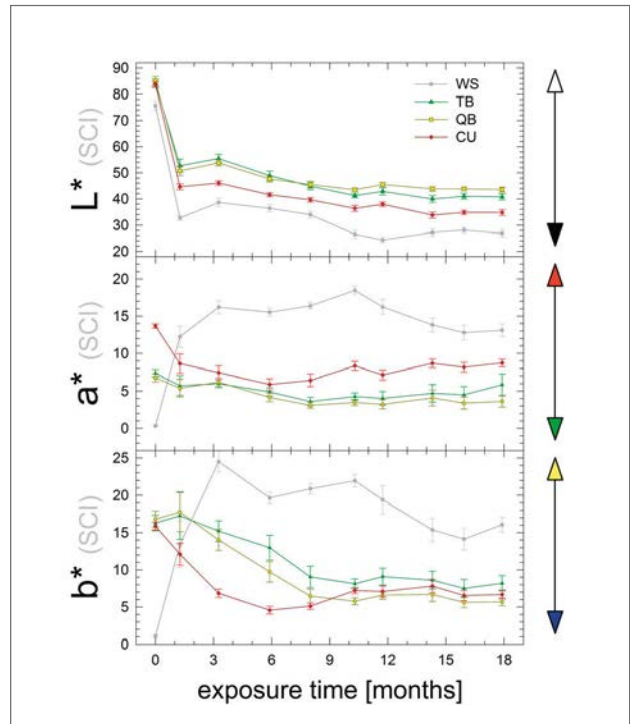


Figure 4. CIELab color values as function of exposure time

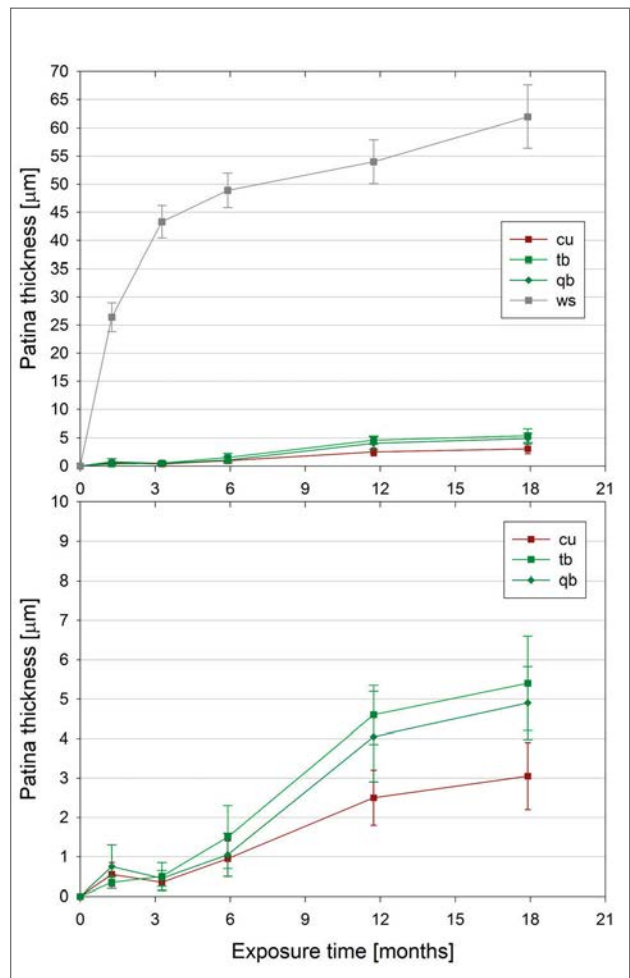


Figure 5. Patina thickness as function of exposure time; (top) all the four alloys considered; (bottom) detail for copper and copper alloys



ATR-FTIR measurements for CU samples (Figure 6a) reveal the gradual formation of copper hydroxychlorides  $\text{Cu}_2\text{Cl}(\text{OH})_3$  with characteristic vibrational bands in the  $3450\text{--}3320\text{ cm}^{-1}$  and  $990\text{--}820\text{ cm}^{-1}$  regions. Also, copper phosphates (cornetite, libethenite, and pseudomalachite) were observed at  $637, 613\text{ cm}^{-1}$  after 1 month of exposure but their presence decreased thereafter. On the contrary, the presence of some copper hydroxysulfates, in particular brochantite, was ascertained and slightly increased with time ( $3589, 3567, 1121, 1113, 1101, 872, 782, 739, 642, 625, 600\text{ cm}^{-1}$ ). Traces of Nantokite ( $804, 787$  and  $703\text{ cm}^{-1}$ ) could also be present along the exposure time. TB and QB samples were characterized by a similar patina composition with the formation of copper hydroxychlorides and copper phosphates (as for CU samples). Nantokite was slightly visible on QB samples but not on TB samples (maybe due to a concentration lower than the detection limit of the FTIR spectrometer). Moreover, we observed mixed basic lead carbonate/sulfate minerals leadhillite and hydrocerusite ( $1392, 1097, 1046, 840, 684\text{ cm}^{-1}$ ) that gradually disappeared in favour of the formation of copper hydroxysulfates, such as brochantite. (Figures 6-b and 6-c). On WS samples, the presence of iron oxyhydroxides, such as lepidocrocite (L) and possibly goethite (G) and akaganeite (A), was observed ( $1148$  (L),  $1092$  (A),  $1021$  (L),  $903$  (G),  $891$  (L),  $806$  (G),  $788$  (L/A),  $744$  (L) and  $690\text{--}670$  (G/A)  $\text{cm}^{-1}$ ), as mentioned in the literature (Raman et al 1991, Thickett 2004), (data not shown).

XRD spectra on CU, TB and QB are dominated by metal peaks for  $2\theta$  greater than  $41^\circ$ , while corrosion products peaks ranges mainly at lower  $2\theta$ ; all measurements show the early formation of cuprite and its continued growth during weathering. As already mentioned for FTIR results, several  $\text{Cu}_2\text{Cl}(\text{OH})_3$  polymorphs (atacamite, botallackite, clinoatacamite) can be identified; the monoclinic form(s) (Jambor 1996) can be recognised from the first months, while atacamite is clearly visible from 6-12 months onward on CU, TB - QB; a small peak from nantokite is generally present. Copper sulfates are much better identified on CU, where brochantite peaks are clearly visible at 18 months (Figure 7) along with posnjakite in the first months of exposure, while antlerite (A) may be recognised on TB and QB. Copper phosphates cannot be clearly identified on CU, while libethenite may be identified on alloys along with cornetite on TB and pseudomalachite on QB at longer exposure times. On QB lead carbonate hydrocerussite is clearly identified after 1 month exposure with intensity of peaks not very

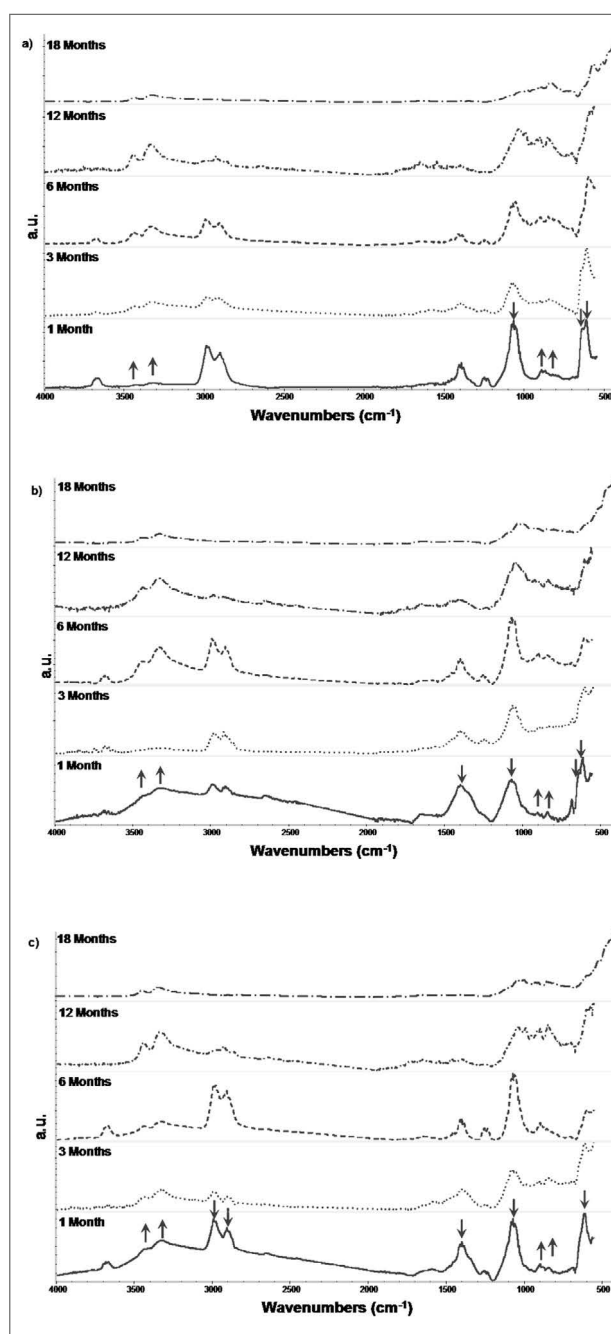


Figure 6. ATR-FTIR spectra recorded after 1, 3, 6, 12 and 18 months of exposure on a) copper, b) ternary bronze and c) quaternary bronze coupons. Upward arrows: peaks from copper hydroxychlorides; downward arrows: peaks from copper phosphates, and (b,c only) lead mixed carbonate-sulfate minerals

dependent on exposure time. On WS coupons, which are characterised by a thicker rust layer, peaks from the underlying metal disappeared after 1 month (Figure 8); the rust layer is known to be composed of a large amount of X-ray amorphous substances (Yamashita 1998) which, along with a wide distribution of particle sizes, give rise to non-intense and well-defined Bragg peaks; lepidocrocite is clearly identified in all XRD spectra on WS coupons, with traces of akaganeite; identification of goethite is not

obvious for any of the samples; however, magnetite and/or maghemite (Yamashita 1998) may be present.

Although the main compounds identified by ATR-FTIR and back-reflection XRD are the same, some differences may be seen, such as the identification of lead carbonate on QB samples for different exposure times. We suggest this can be linked to the different penetration depth of ATR-FTIR (0.3-3  $\mu\text{m}$ ) compared to XRD (2-120  $\mu\text{m}$ ) with respect to the patina growth. This issue is of relevance for *in situ* characterisation of monuments. Further investigations are in progress.

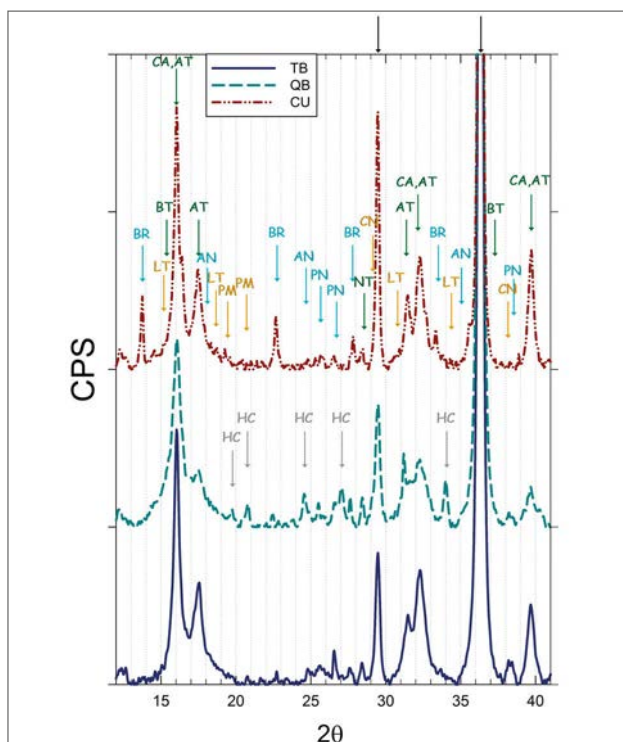


Figure 7. XRD spectra on CU, TB, QB after 18 months exposure Copper oxide cuprite: black arrows; copper chlorides: clinoatacamite (CA), atacamite (AT), nantokite (NT), botallakite (BT); copper sulfates: brochantite (BR), antlerite (AN), posnjakite (PN); copper phosphates: libethenite (LT), cornetite (CN), pseudomalachite (PM); lead carbonate: hydrocerussite (HC)

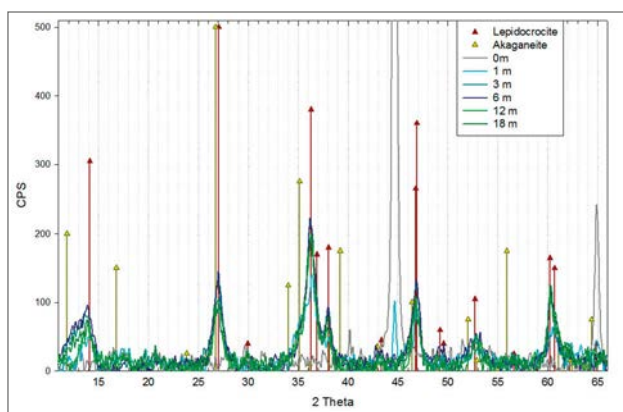


Figure 8. XRD spectra on WS at different weathering time

The mixed composition of cuprite with copper hydroxylchlorides (atacamite, clinoatacamite) and hydroxysulfates (brochantite, antlerite) on copper alloys coupons and the mixed iron oxyhydroxides, including akaganeite, on WS coupons after 18 months exposure corresponds to the main components of the patina generally reported for outdoor monuments (Selwyn 2004, Aramendia 2011), when chloride pollution is present. The large coupons weathered for 18 months would thus be useful to test treatment performance on complex patina layers.

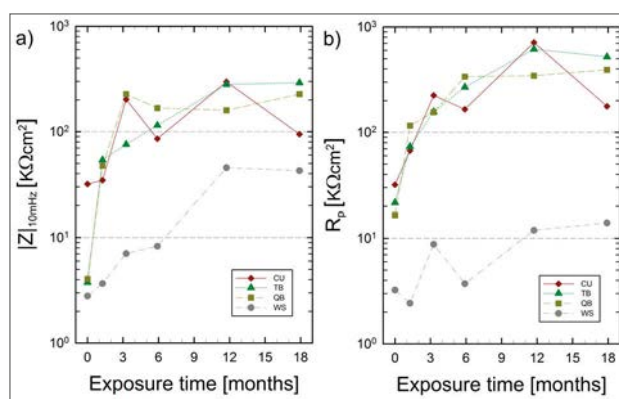


Figure 9. (a) Low frequency Impedance module and (b) Polarisation Resistance  $R_p$  as function of exposure time

Preliminary values of  $|Z|_{10\text{mHz}}$  and  $R_p$  obtained (Figure 9) show a similar behaviour, especially for copper alloys. Some discrepancies are clearly visible, mainly for WS. As is well known, especially in the case of bare metals, a lower frequency may be required for  $|Z|$  to approximately equal the Polarisation Resistance. A deeper analysis of electrochemical measurements is in progress for better exploitation of the results. Nonetheless, we can generally observe a higher corrosion rate for WS than copper alloys in the marine environment selected. As expected, data also show a lowering trend of corrosion rate with increased weathering time, which is more marked for copper alloys than for WS and in the first 9-12 months. For longer weathering time, copper alloys are characterised by  $|Z|_{10\text{mHz}}$  of the order of  $100\text{K}\Omega\text{cm}^2$  as the one measured on outdoor bronze monuments (Sansonet 2015, Letardi 2016).

SEM (Figure 10) on the surface of CU samples show a thin layer of fine grained corrosion products at 1 month which can be associated to the early formation of cuprite. After 6 months, this layer grows in an irregular pattern. At 18 months, the corrosion products layer seems thicker without clearly defined crystals. TB and QB show similar

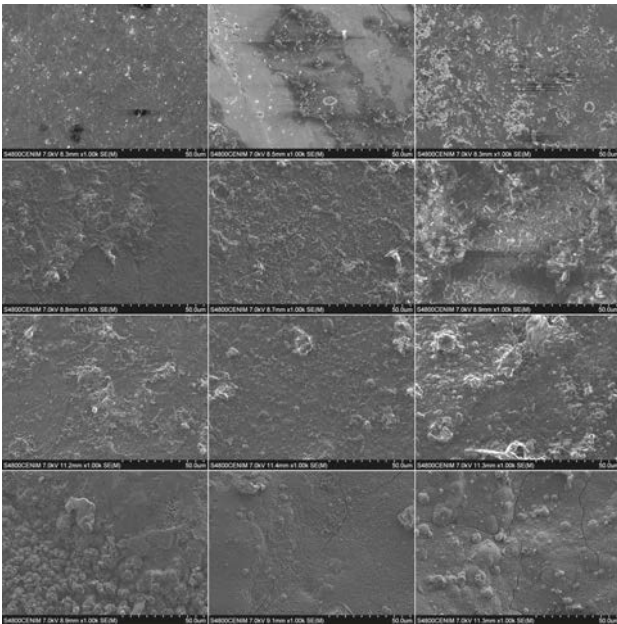


Figure 10. SEM microphotographs at 1000x magnification on the surface of 1, 6 and 18 months exposure (from left to right) of CU, TB, QB and WS (top to bottom) samples

features, with thin irregular crusts of corrosion products visible from the first month. These crusts thicken and form coarser aggregates with time. Thin cracks are visible in this crust on QB from month 6. Finally, WS corrosion products present two morphologies: after 3 months, globular shaped aggregates (bottom-left) and flake shaped crystals that seem to grow over them; at 6 and 18 months the entire surface is uniformly covered by these small-size flakes, but large cracks appear, breaking this surface. According to literature (Díaz 2012) the outer layer is mainly formed by lepidocrocite. Further analyses are in progress.

## Conclusions

Weathering of copper, ternary bronze, quaternary bronze and weathering steel coupons for 18 months by exposure in the mildly aggressive urban-marine SMS site in Genoa allowed comparison of the patina growth for different metals and alloys of interest for outdoor metallic cultural heritage. The wide characterisation program includes both the measurements with the same setup directly applicable for *in situ* measurements on artworks as well as Lab techniques.

Preliminary results enlightened the following features of interest for outdoor metal conservation:

- the patinas grown at SMS after 18 months show interesting similarities with those on outdoor monuments which would be suitable for treatment testing;

- the non-destructive characterisation of patina thickness and composition without scraping from surfaces along with laboratory measurements on metallographic sections can provide relevant information for *in-situ* diagnostic measurements.

Through the completion of planned measurements, the overall analysis of experimental data and an informed dialogue between conservators and scientists, we can glimpse an improvement in metal conservation-restoration methodologies based on clear scientific and ethical criteria.

## Acknowledgements

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# Composition and Protective Properties of Weathering Steel Artificial Patinas for the Conservation of Contemporary Outdoor Sculpture

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## Abstract

Weathering steels (such as Cor-Ten®) are known for their ability to produce beautiful and protective oxide layers when exposed to a mild urban atmosphere. For this reason, they have been extensively used in contemporary art and architecture. Nevertheless, the natural patina formation is a slow process, requiring many years and specific environmental conditions. For aesthetic purposes, artificial patinas are created by treatment with different oxidants. The composition, structure and properties of these patinas have not been yet investigated, so it is not known how future conservation will deal with this type of patination. The aim of this work is to evaluate the characteristics and properties of these artificial patinas compared to natural patina and follow their evolution over time, in order to make recommendations for contemporary art conservation. Four artificial patinas obtained by treatment with different

oxidants (hydrogen peroxide, sodium bisulfite, hydrochloric acid), as well as a commercial product (Metal Effects Rust Activator Solution) and a well-formed five year natural patina have been studied by colorimetry, optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Corrosion behavior has been evaluated by Electrochemical Impedance Spectroscopy (EIS) with a gel polymer electrolyte (G-PE) cell specifically developed for *in-situ* measurements of cultural heritage. Results show that artificial treatments produce thin irregular patinas, mainly composed of lepidocrocite, with non-protective properties, that show less corrosion resistance than the bare metal.

## Keywords

patina, corrosion, weathering steel, contemporary sculpture, Electrochemical Impedance Spectroscopy

## Introduction

Weathering steels (such as Cor-Ten®) are types of steel alloys capable of acquiring a natural protective oxide layer when exposed to a mild urban atmosphere with wetting and drying cycles for a certain amount of time. It is known that the formation of a good quality patina on these steels takes some years under specific conditions (Morcillo 2013). Besides its protective properties, this patina has an attractive range of orange to purple colors, making it widely used in art and architecture in the last century. When used for artistic purposes, the quick acquisition of a rusty appearance is demanded, so artificial patinas are created by treatment with different oxidants such as hydrogen peroxide, hydrochloric acid, or commercial products specifically developed for this purpose. This acceleration of the process may produce a different composition and/or microstructure of the patinas, rendering them less protective and posing a problem

for the conservation of these works. If these patinas lack the protective properties expected for this material, the corrosion rate will increase and may compromise their conservation. In that case, additional protection strategies might need to be considered, such as the employment of corrosion inhibitors or protective coatings. The purpose of this paper is to evaluate the protective properties and the composition of artificial patinas produced on weathering steels with different accelerated treatments, and to compare them with natural patina, in order to propose recommendations for contemporary art conservation.

## Materials and methods

Weathering steel (Arcelor S355J2W, EN 10025-5-2004) coupons were prepared by sandblasting, the usual procedure in modern sculpture. The composition of



the alloy is shown in Table 1. Natural patina (patina N) was produced by exposing the steel coupons to a mild urban atmosphere for five years, in an atmospheric corrosion station (Madrid, Spain). Artificial patinas were produced by brushing a 1M aqueous solution of different oxidants: hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, patina A1), sodium bisulfite (NaHSO<sub>3</sub>, patina A2) and hydrochloric acid (HCl, patina A3), and a commercial product called “Metal Effects Rust Activator Solution” (PA904) by Modern Masters (patina A4), which is an acidic aqueous solution of copper salts. Loose oxide was removed with a soft brush and wetting and drying cycles were applied for a week, spraying the coupons twice a day with demineralized water to avoid introducing additional ions.

Table 1. Weathering steel composition (% weight)

C	Si	Mn	P	S	Cr	Ni	Cu	Al	Nb
0.057	<0.05	0.35	0.017	<0.010	0.57	0.30	0.35	0.025	<0.010

After one week, all samples presented a non-uniform thin rust layer covering the whole surface of the sample (Figure 1).

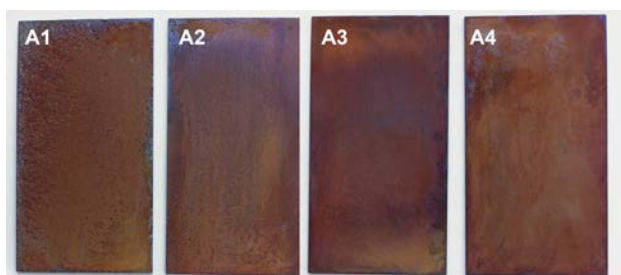


Figure 1. Visual aspect of artificial patinas formed after one week of treatment for artificial patina formation, with H<sub>2</sub>O<sub>2</sub> (A1), NaHSO<sub>3</sub> (A2), HCl (A3) and commercial product “Metal Effects Rust Activator Solution” (A4)

The color of the patinas was measured by a Konica Minolta CM700D spectrophotometer, using an 8 mm diameter mask, D65 standard illuminant and 10° observer. The colorimetric results were reported in CIE L\*a\*b\* color space. The surface morphology was characterized by SEM using a Hitachi S4800 scanning electron microscope equipped with a cold-cathode field emission electron gun, using the secondary electron detector. Metallographic cross sections were prepared by embedding in a cold-curing resin, dry-cutting and polishing with SiC grinding paper up to 2000 grit size, followed by polishing with 3 and 1 μm diamond paste, to measure the thickness and observe the structure of the rust layer. Samples were observed by optical microscopy using polarized light. Protective properties of the patinas

were measured by electrochemical impedance spectroscopy (EIS), with a Gamry Reference 600 potentiostat using a gel-polymer electrolyte (G-PE) cell specifically developed for *in-situ* measurements of cultural heritage. This G-PE cell uses a classical 3 electrode configuration, using as electrolyte a 10x concentrated artificial rain solution gelified with 3% agar (Cano 2014, Ramírez Barat 2015).

## Results and discussion

### Visual appearance

All the treatments produced a rusty surface with similarity in appearance. Colorimetric measurements (Figure 2) placed the patinas in positive values of both a\* and b\*, which correspond to red and yellow hues respectively, and a luminosity, L\* (10°/D65) around 40 in a scale from 0 to 100. Compared with the natural patina, this is darker and tends to have cooler hues, and the three color parameters are 15-25% lower than in the artificial patinas. However, the differences between the 4 different artificial patination procedures are smaller, all of them showing a similar color.

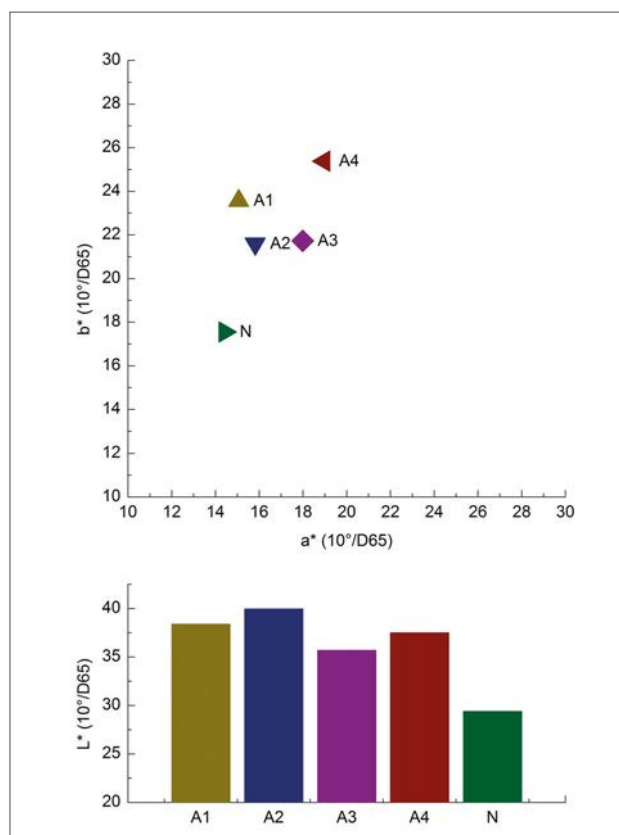


Figure 2. CIELAB color values of artificial and natural patina where L\* represents lightness (from 0 to 100), while a\* (red-green) and b\* (yellow-blue) are the chromatic coordinates (in a scale from +60 to -60)

Structure

Macro photographs of the surface taken under a stereomicroscope show the differences in texture (Figure 3). A1 is clearly non-homogenous in thickness, showing the underlying metal in some areas. A2 is also irregular but less transparent, although the metal surface is revealed in some spots. A3 and A4 seem thicker and more homogeneous, although A3 presents some dark spots and A4 a coarser texture.

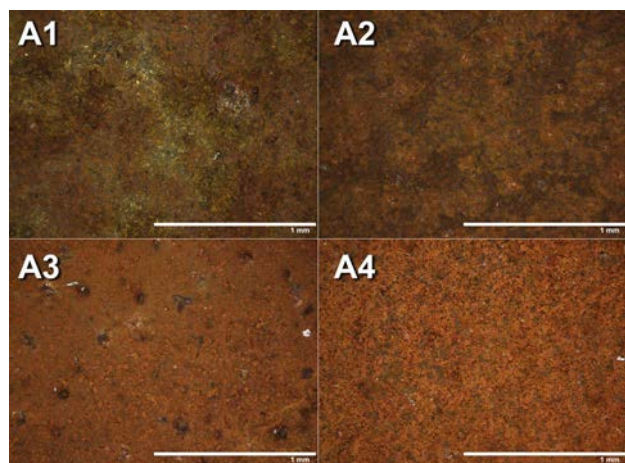


Figure 3. Macro photographs of the patina surface under a stereomicroscope

The surface of the patina has also been examined by SEM, showing large differences in patina texture depending on the patination procedure; 200x (Figure 4) and 5000x (Figure 5) magnifications compare the general texture and crystal morphologies. NaHSO<sub>3</sub> and HCl provide more regular patinas (A2 and A3), the A2 patina being the one with the smoothest surface. The patinas made with H<sub>2</sub>O<sub>2</sub> (A1) and the commercial product (A3) are more irregular, in particular A3 which has quite a rough surface. When surfaces are examined through higher magnifications, greater differences are observed. A1 consists of a cracked crust of corrosion products without a clear crystalline structure, under which poorly defined flake-like crystals seem to grow. A2 shows irregular aggregates of small flakes, while A3 creates a more regular network of larger and well defined crystals with some cracks. Finally, the commercial product (A4) forms a crust of small flakes with different compactness and crystal size. Comparing these patinas with the reference 5 years' natural patina (Figure 6), the A3 patina is the one that presents more similarities, although the natural crystals are much smaller and regular.

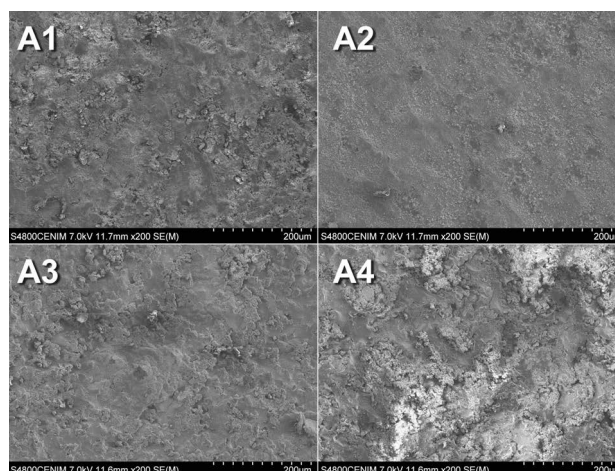


Figure 4. SEM photographs of artificial patina surfaces at 200x magnifications, patinated with H<sub>2</sub>O<sub>2</sub> (A1), NaHSO<sub>3</sub> (A2), HCl (A3) and commercial product "Metal Effects Rust Activator Solution" (A4)

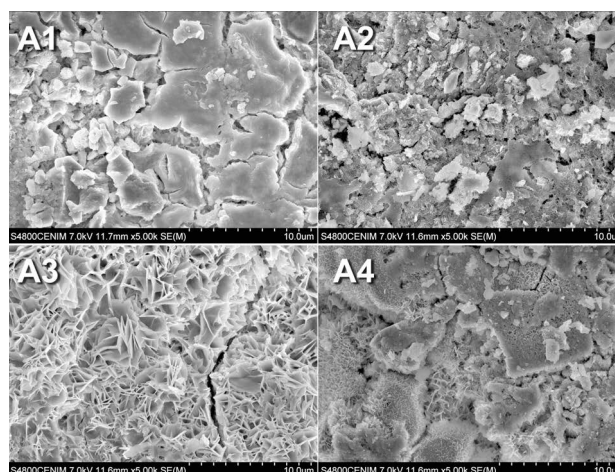


Figure 5. SEM photographs of artificial patina surfaces at 5000x magnifications, patinated with H<sub>2</sub>O<sub>2</sub> (A1), NaHSO<sub>3</sub> (A2), HCl (A3) and commercial product "Metal Effects Rust Activator Solution" (A4)

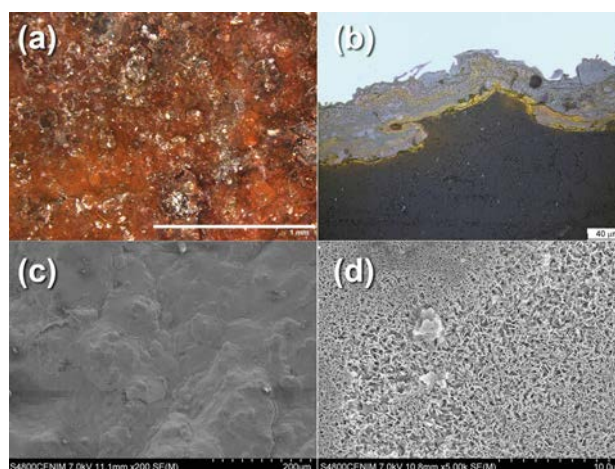


Figure 6. Five years natural patina: Macro photograph under stereomicroscope (a), cross-section under polarization microscope (b) and SEM images at 200x (c) and 5000x (d) magnifications



Cross-sections under a polarization microscope show a thin irregular layer of rust (Figure 7). A1 and A2 are thinner (less than 10 micrometers) than A3 and A4. In A1 and A2, the rust layer does not completely cover the surface of the metal, as was already observed in Figure 3. In A4, while the rust layer is thicker, it shows inclusions of particles (composed of different corrosion products or particles of the base metal), appearing in a dusty pink color under polarized light. The reddish color of the rust under polarized light is associated with lepidocrocite-rich rust layers. On the contrary, the rust layer formed upon natural patination is considerably thicker and shows a greyish aspect (Figure 6) associated with the goethite content (Díaz 2012).

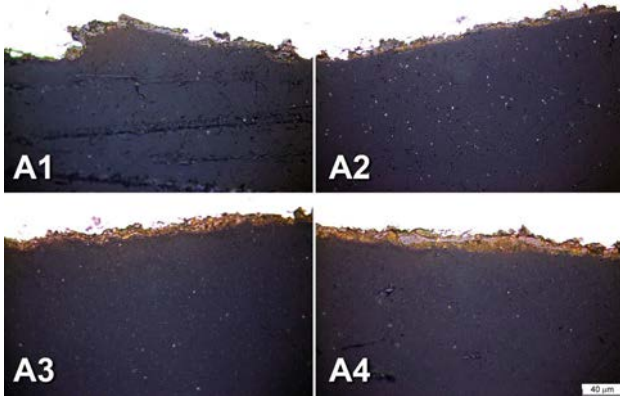


Figure 7. Cross-section of artificial patinas under polarization microscope, patinated with  $H_2O_2$  (A1),  $NaHSO_3$  (A2), HCl (A3) and commercial product "Metal Effects Rust Activator Solution" (A4)

### Composition

The patina composition was analyzed by XRD. The analysis mainly detected the underlying metal and lepidocrocite ( $\gamma$ -FeOOH) in all patinas. Two small peaks in the HCl patina suggest the presence of akaganeite ( $\beta$ -FeOOH). However, the patina thickness and the low crystallinity of corrosion products make the iron peaks predominant and make it difficult to distinguish the iron compounds. The 5-year patina clearly shows the presence of goethite ( $\alpha$ -FeOOH) in addition to lepidocrocite (Figure 8). Lepidocrocite is more abundant in the surface of the rust, which explains its prevalence in the XRD spectra obtained on the surface of the sample, while goethite is abundant in the deeper parts of the rust layer, as shown in optical microscopy (Figure 7).

### Corrosion behavior

Corrosion resistance of different patina has been studied by EIS with a gel polymer cell (G-PE). The G-PE cell

performed well in the electrochemical measurements of these rough surfaces, usually difficult to measure using a traditional liquid cell.

Figure 9 shows Nyquist plots of EIS results obtained on the artificial patinas and on the natural patina. Additionally, for comparison purposes, EIS was acquired from a bare weathering steel sample with the same material and surface preparation but without patina.

The Nyquist plot at the bottom is a detail of the spectra for good visualization of the response of patinated samples. The highest impedance is shown, as expected, by the natural patina. Two inductive loops followed by a diffusion tail can be observed, which can be attributed to the rust layer (loop at high frequencies), double layer capacitance in parallel with charge transfer resistance (loop at intermediate frequencies) and diffusion of ions in the rust layer (Bousselmi 1999). For the artificial patinas, no significant differences can be observed between them, all showing very similar EIS response. Two similar loops are observed in all cases, with similar attribution to the natural patina and the start of a third process at low impedances. The diameter of the high frequencies loop is similar to that of the bare steel, indicating that the patina does not have a significant protective character. It is remarkable, however, that the diameter of the low frequencies loop, associated with the faradaic processes on the surface, is higher in the bare metal than in the artificially patinated samples. This indicates that the corrosion process is faster in the artificially patinated samples than in the bare metal, and that the artificial patina accelerates the dissolution of the steel instead of protecting the base metal as in the case of the natural patina. The fact that no significant differences are observed between the different artificial patinas suggests that this acceleration could not be attributed to the presence of aggressive ions (chlorides or sulfates) remaining after the chemical treatment.

This paradoxical behavior should be attributed to the composition and structure of the artificial patinas. Lepidocrocite, which is the prevalent phase in these patinas, is not a protective phase. The *Protective Ability Ratio*, defined as a ratio between protective/non-reactive and non-protective/reactive phases in the rust layer, has been proposed as an index to assess the protective properties of rust layers (Díaz 2012). Different formulas have been proposed, but in all of them the goethite (considered the most stable and protective iron oxyhydroxide) is in the numerator and lepidocrocite (and akaganeite, if present)

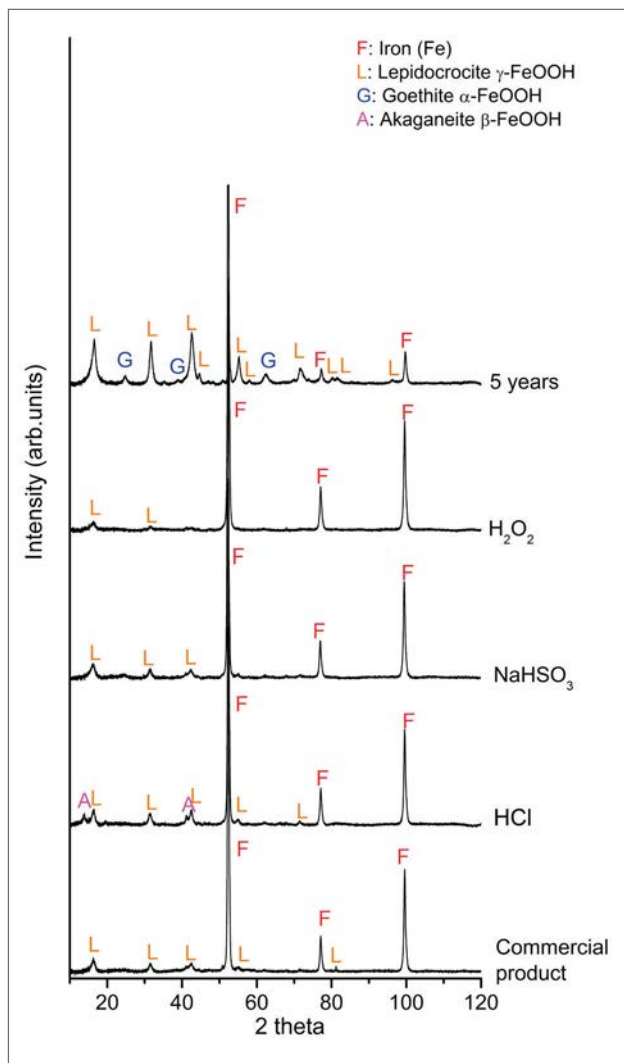


Figure 8. XRD spectra of natural and artificial patinas

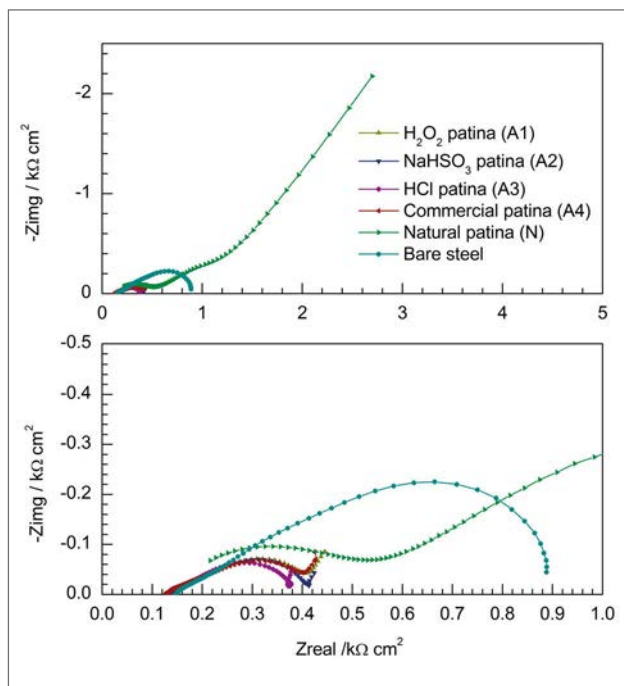


Figure 9. Nyquist plots for natural and artificial patinas, and bare metal

in the denominator (Yamashita 1994, Kamimura 2006). According to this relationship, expressed in equation [1], a higher mass fraction of  $\alpha$ -FeOOH and a low mass fraction of  $\gamma$  and  $\beta$ -FeOOH will result in a higher protective ability of the rust layer.

$$Protective\ Ability\ Ratio = \frac{\text{mass fraction } \alpha\text{-FeOOH}}{\text{mass fraction } \gamma, \beta\text{-FeOOH}} \quad [1]$$

It has been shown that reduction of lepidocrocite is the main cathodic reaction in some stages of the steel corrosion process, dominating over the reduction of oxygen (Evans 1972) and being the rate-controlling step of the whole corrosion process. Therefore, the large amount of lepidocrocite formed by the chemical treatment of the steel in artificial patination can explain the acceleration of the corrosion process when compared to the bare steel, and the eventual barrier properties of the rust layer (which in this case is very low, since the layers are thin and porous) are considerably exceeded by the increase of the cathodic reaction.

The evolution of these rust layers with time is currently being studied to determine the effects of the oxidation treatments in the long-term development of the rust layer and its protective properties. The final aim is to elucidate how these artificial patination procedures can endanger the conservation of contemporary outdoor sculpture.

**Conclusions**

The accelerated oxidation of weathering steels by direct treatment with an oxidant produces a rapid corrosion of the surface, yielding the desired rust layer. However, these layers are irregular and non-protective. The composition of these layers is mainly lepidocrocite, regardless of the chemical treatment employed, and probably other amorphous iron compounds.

These layers do not offer corrosion protection, their resistance being not only lower than a natural patina but even lower than the bare metal. These artificially prepared patinas are less stable and lack the excellent protective properties of natural patina. This means that at these initial stages a metal sculpture/artwork with an artificially applied patina is likely to corrode much faster. These patinas will evolve with time, and their protective properties can change, so our work will continue to assess whether this faster corrosion remains or not. This work has provided the foundation for the future development of this investigation that will be continued with the follow-up of

the evolution of artificial patinas, and with the evaluation of weathering steel sculptures exposed outdoors. This will help to determine if additional protection, such as corrosion inhibitors or protective coatings is needed for weathering steel artworks with artificial patina, and the degree of corrosion advance without protection.

### Acknowledgements

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#### 4.3.1.2. Evaluación de recubrimientos.

La evaluación de recubrimientos es una de las principales aplicaciones de la EIS en investigación de sistemas de protección de aplicación industrial. Dentro del campo de la conservación del patrimonio esta técnica resulta especialmente útil, dadas las características particulares de los sistemas de protección aplicados al patrimonio metálico. En primer lugar, los recubrimientos se aplican a superficies que en la mayor parte de los casos están recubiertas de productos de corrosión, resultan bastante heterogéneas y no siempre se conocen en detalle. La aplicación de la EIS, permite seleccionar el sistema de protección más adecuado en cada caso, ya que como se ha demostrado, la eficacia de un recubrimiento depende en parte del sustrato sobre el que se ha aplicado [29]. Por otra parte, la duración de los recubrimientos es limitada. La realización de series temporales de medidas, permite llevar a cabo un seguimiento de la evolución de la capacidad protectora del recubrimiento y detectar la pérdida de propiedades antes de que ello suponga un riesgo para la conservación del objeto.

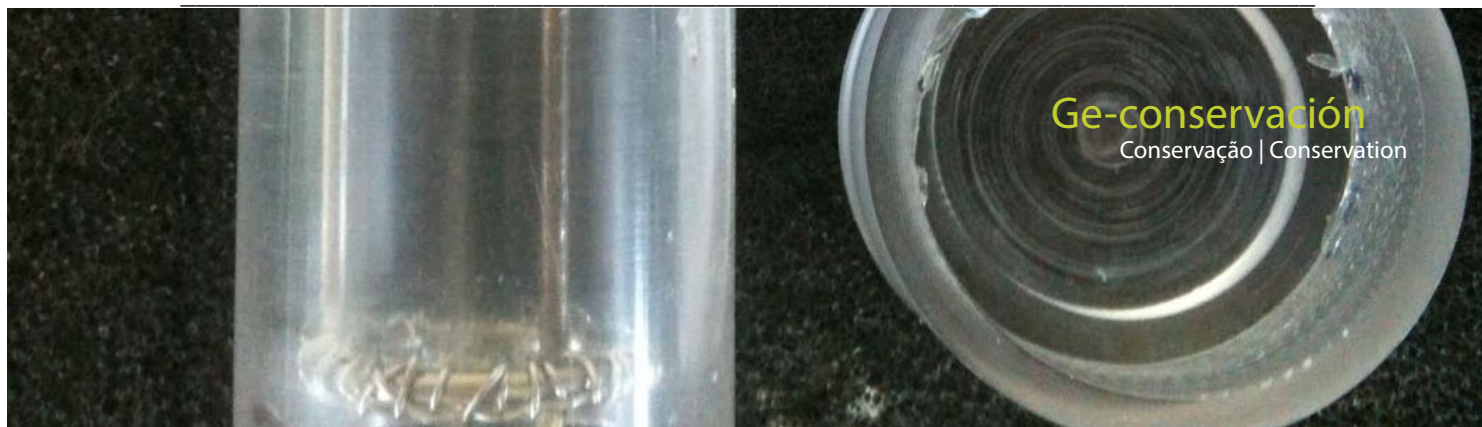
Con este fin, al tiempo que se fue desarrollando la celda se realizaron algunos ensayos con el fin de comprobar su aplicabilidad en la evaluación de recubrimientos para protección de patrimonio cultural metálico. Para los trabajos iniciales se eligieron unas probetas de bronce binario, con una selección de recubrimientos acrílicos y una cera, preparados como se ha descrito en la sección 3.1.3., para obtener una superficie simple que facilitara interpretar la respuesta del recubrimiento, y se expusieron en el exterior durante unas pocas semanas. Los resultados obtenidos reflejan claramente las diferencias de comportamiento inicial y frente a la exposición atmosférica de los diferentes sistemas y permiten ver la aparición de defectos en un recubrimiento mediante cambios en su espectro de impedancia. Esto demuestra la capacidad de la celda de medir este tipo de recubrimientos y de detectar los cambios producidos en poco tiempo. Estos primeros ensayos se recogen en el artículo:

- B. Ramírez Barat, E. Cano, Evaluación in situ de recubrimientos protectores para patrimonio cultural metálico mediante espectroscopía de impedancia electroquímica, *Ge-conservación*, 8, (2015) 6-13<sup>10</sup>.

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<sup>10</sup> Referencias bibliográficas [26, 29, 35, 49, 68, 104, 119, 160, 161] de la bibliografía general





## Evaluación in situ de recubrimientos protectores para patrimonio cultural metálico mediante espectroscopía de impedancia electroquímica

Blanca Ramírez Barat y Emilio Cano Díaz

**Resumen:** Los métodos electroquímicos como la espectroscopía de impedancia electroquímica (EIS) son herramientas ampliamente utilizadas para estudios de corrosión y evaluación de recubrimientos. En el campo de la conservación del patrimonio cultural metálico, sin embargo, su uso se encuentra menos extendido por la dificultad para la realización de medidas in situ sobre esculturas y monumentos. En este trabajo se presentan las posibilidades de aplicación de esta técnica al estudio de recubrimientos protectores para el bronce con una novedosa celda portátil con un electrolito gelificado con agar.

**Palabras clave:** agar, electrolitos sólidos, espectroscopía de impedancia electroquímica, patrimonio cultural metálico, recubrimientos

### In situ assessment of protective coatings for metallic cultural heritage using electrochemical impedance spectroscopy

**Abstract:** Electrochemical methods such as electrochemical impedance spectroscopy (EIS) are widely used for corrosion studies and coatings evaluation. Nevertheless, their use in the field of metallic cultural heritage conservation is less widespread because of the difficulty to perform in situ measurements on sculptures and monuments. In this paper the possibilities of applying this technique to the study of protective coatings for bronze with an innovative portable cell with an electrolyte gelled with agar are presented.

**Key words:** agar, coatings, electrochemical impedance spectroscopy, metal cultural heritage, solid electrolytes

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### Introducción

Todos los objetos metálicos en contacto con el medio ambiente sufren un proceso más o menos lento de deterioro por corrosión. La corrosión es un proceso inevitable; sin embargo, lo que determina en la práctica sus efectos, es la velocidad a la que se produce. Para reducir o retardar la corrosión es frecuente el empleo de recubrimientos e

inhibidores que ofrecen protecciones más o menos eficaces y duraderas según el producto, el sustrato y las condiciones ambientales. Conocer la eficacia de un recubrimiento aplicado sobre un objeto, así como su evolución o degradación con el tiempo, resulta fundamental a la hora de diseñar estrategias para la conservación del patrimonio cultural metálico y para ello es necesario disponer de técnicas de diagnóstico adecuadas.

La espectroscopía de impedancia electroquímica (EIS) es una técnica ampliamente utilizada en la evaluación de pinturas y recubrimientos industriales y que en los últimos años ha comenzado a utilizarse también en el campo del patrimonio cultural. Sin embargo, la aplicación de esta técnica en la conservación del patrimonio cultural metálico presenta una serie de particularidades que hace que su aplicación no se encuentre al mismo nivel de desarrollo que en otros campos. Por un lado la irregularidad de las superficies de medida se traduce en una distorsión en los espectros, que son difíciles de interpretar. Esto hace que la mayoría de los estudios se limiten a evaluar el módulo de la impedancia a altas frecuencias relacionándolo con la resistencia de la pátina o el recubrimiento (Cano et al., 2010). Por otra parte esta irregularidad junto con la falta de horizontalidad supone otra importante dificultad en las medidas, teniendo en cuenta que las celdas clásicas para la realización de ensayos electroquímicos están formadas por un recipiente rígido relleno de un electrolito líquido, que debe estar en contacto con la superficie a estudiar y abierto a la atmósfera. Para solventar estas dificultades diversos autores han propuesto sistemas portátiles basados en absorber el electrolito líquido en un soporte poroso como un paño o una esponja o en el empleo de electrodos comerciales como los utilizados para electrocardiogramas (Letardi, 2004, Letardi et al., 1998, Letardi y Spiniello, 2001, Angelini et al., 2006, Angelini et al., 2012). Algunos de estos sistemas proporcionan buenos resultados de medida pero tienen ciertas dificultades de manejo, mientras que en otros los resultados de las medidas son bastante irregulares.

Con la idea de buscar alternativas mejoradas a estos sistemas y explorar las posibilidades de aplicación de las técnicas electroquímicas a la conservación del patrimonio cultural metálico hemos desarrollado una celda electroquímica con electrolito polimérico en gel (G-PE por sus siglas en inglés) (Cano et al., 2014, Ramírez Barat y Cano, 2014). Esta celda permite la evaluación in situ y no destructiva de pátinas y recubrimientos, lo que supone una herramienta muy útil a la hora de abordar tratamientos de conservación/restauración. La gran sensibilidad de la técnica permite además detectar cambios en las propiedades del recubrimiento en cortos intervalos de tiempo, mucho antes de que sean apreciables visualmente y de que el deterioro del objeto sea irreversible. Así, tienen interés para decidir la necesidad de intervención sobre un objeto, para elegir el recubrimiento protector más adecuado evaluando su comportamiento directamente sobre el objeto en su entorno y para realizar un seguimiento en el tiempo de los tratamientos aplicados.

### Espectroscopía de Impedancia Electroquímica. Fundamentos de la técnica

La impedancia es una magnitud equivalente a la resistencia: la impedancia de un sistema representa su oposición al paso de corriente alterna. Del mismo modo que la ley de Ohm nos

da el valor de la resistencia de un sistema como la relación de proporcionalidad entre la intensidad de corriente (I) que circula por un conductor y la diferencia de potencial (E) entre sus extremos,  $R = E/I$ , la impedancia Z viene dada por la relación entre un potencial y una intensidad de corriente variables. Así, mientras que la resistencia es una magnitud escalar, es decir, un número, la impedancia es una magnitud vectorial, es decir, una función que depende de la frecuencia.

La impedancia de un sistema se mide aplicando una pequeña señal de potencial sinusoidal (10-20mV), suficientemente pequeña para no producir alteración de la superficie estudiada, y midiendo la respuesta de sistema en forma de una intensidad de corriente sinusoidal de la misma frecuencia, pero diferente amplitud y ángulo de fase.

$$\text{SEÑAL: } E = E_0 \text{ sen}\omega t \Leftrightarrow \text{RESPUESTA: } I = i_0 \text{ sen}(\omega t + \varphi) \quad (1)$$

Realizando un barrido de frecuencias, típicamente entre 100 kHz- 10 mHz, se obtiene la impedancia del sistema como una función de la frecuencia, caracterizada por el módulo  $Z_0$  o  $|Z|$  y el desplazamiento del ángulo de fase  $\varphi$

$$Z = \frac{E}{I} = \frac{E_0 \text{ sen}(\omega t)}{i_0 \text{ sen}(\omega t + \varphi)} = Z_0 \frac{\text{sen}(\omega t)}{\text{sen}(\omega t + \varphi)} \quad (2)$$

La representación gráfica de esta función proporciona el espectro de impedancia y su análisis permite separar las contribuciones de distintos elementos que intervienen en el proceso de corrosión de modo que se obtiene información tanto a nivel cuantitativo (capacidad de protección) como cualitativo (información sobre los mecanismos implicados). Existen diversas formas de representar los espectros o diagramas de impedancia; representando el valor del módulo y el ángulo de fase frente a la frecuencia se obtiene un diagrama de Bode, que es la representación que se va a utilizar en este trabajo.

Para la interpretación de los espectros de impedancia suele recurrirse al ajuste de los datos experimentales por medio de *circuitos equivalentes*, que reproducen las propiedades eléctricas del sistema estudiado y proporcionan la misma respuesta en impedancia. Estos circuitos se componen de una serie de elementos, principalmente resistencias y condensadores, en serie o en paralelo, que se relacionan con los diferentes elementos o fenómenos físicos del sistema estudiado. Además, existen otros elementos que modelan situaciones específicas que se dan en sistemas electroquímicos, como la impedancia de Warburg, que modela la impedancia asociada a procesos de difusión; o los elementos de fase constante, CPE, que modelan comportamientos no ideales debidos a irregularidades del sistema (falta de uniformidad del recubrimiento, rugosidad, distribuciones no homogéneas de la corriente, etc.).

Un sistema metal-recubrimiento puede representarse

mediante un circuito formado por un condensador ( $C_p$ ) y una resistencia ( $R_{po}$ ) en paralelo que representan la capacidad y la resistencia del recubrimiento respectivamente, en serie con una resistencia  $R_e$ , correspondiente al electrolito (figura 1a). En recubrimientos muy protectores la  $R_{po}$  suele ser muy elevada, con lo que en la práctica el circuito queda reducido a  $R_e$  en serie con  $C_p$ . Cuando el recubrimiento se deteriora y el electrolito penetra a través del recubrimiento y entra en contacto con el metal, iniciándose el proceso de corrosión, aparecen tres nuevos elementos en el sistema (figura 1b): una resistencia  $R_{po}$  que modela la resistencia al paso de corriente a través de los poros del recubrimiento, un condensador  $C_{dl}$  que representa la doble capa electroquímica en la interfase metal-electrolito y una resistencia  $R_{tc}$  que representa la resistencia de transferencia de carga en el proceso de corrosión en la interfase metal-electrolito (Cano et al., 2010).

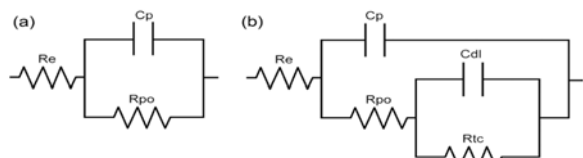


Figura 1: Circuito equivalente de un sistema metal-recubrimiento perfecto (a) y un sistema deteriorado o imperfecto (b).

**Materiales y métodos:**

Se utilizó bronce laminado EN 1652 de 5x5 cm y 1,5 mm de espesor (de composición expresada como porcentaje en peso: 94,07 Cu; 5,85 Sn; 0,055 P; 0,002 Ni; 0,008 Zn; 0,005 Pb y 0,005 Fe). Las probetas se lijaron con lija de grano 360, 600 y 1200 sucesivamente, realizando 3 pasadas en cada sentido, de manera alterna y lavando con agua destilada. Una vez lijadas se desengrasaron con acetona.

Sobre estas probetas aplicaron varios recubrimientos a base de resinas acrílicas y cera microcristalina, todos ellos suministrados por Kremer Pigmente GmbH & Co (Alemania). Se eligió una muestra representativa de los principales productos utilizados por los profesionales de la restauración-conservación del patrimonio metálico. Los productos seleccionados fueron los siguientes: Paraloid B-72 (copolímero de etil metacrilato y metil metacrilato), Paraloid B-67 (metacrilato de isobutilo), Paraloid B-44 (copolímero de metil metacrilato y etil acrilato), Paraloid B-48N (copolímero de metil metacrilato y butil acrilato), Incralac (producto comercial preparado a partir de Paraloid B-44 disuelta en tolueno, benzotriazol y otros aditivos), cera microcristalina Cosmolloid H80. Cada muestra se preparó por triplicado.

Los barnices se prepararon disolviendo la resina al 15% en xileno, excepto el B-67 y la cera Cosmolloid H80 que se disolvieron en White Spirit y el Incralac que viene ya disuelto y se usó en estado de recepción. De cada uno se aplicaron dos capas por inmersión dejando secar horizontalmente 24h entre capa y capa.

El grosor de las capas se midió con un medidor de espesor de recubrimientos Elcometer 300 utilizando la sonda para metales no férricos. Los espesores mostrados en la Tabla 1 son la media de 20 medidas realizadas sobre cada probeta. El espesor de la muestra R006 estaba por debajo del límite de medida del aparato (~5  $\mu\text{m}$ ) y no pudo determinarse.

Recubrimiento	Muestra	espesor ( $\mu\text{m}$ )
Paraloid B72	R001a	23 $\pm$ 6
	R001b	18 $\pm$ 5
	R001c	30 $\pm$ 4
Paraloid B67	R002a	20 $\pm$ 3
	R002b	22 $\pm$ 8
	R002c	28 $\pm$ 8
Paraloid B44	R003a	18 $\pm$ 6
	R003b	18 $\pm$ 6
	R003c	22 $\pm$ 6

Recubrimiento	Muestra	espesor ( $\mu\text{m}$ )
Paraloid B48N	R004a	15 $\pm$ 4
	R004b	26 $\pm$ 5
	R004c	19 $\pm$ 5
Incralac	R005a	18 $\pm$ 5
	R005b	18 $\pm$ 5
	R005c	24 $\pm$ 4
Cosmolloid H80	R006a	-
	R006b	-
	R006c	-

Tabla 1: Espesores medios de los recubrimientos aplicados en las probetas de Bronce

Los ensayos de EIS se realizaron sobre las probetas tras la aplicación y secado de los recubrimientos, y tras 6 semanas de exposición a la intemperie en una estación de corrosión atmosférica (según norma ISO 8565:1992) en la azotea del Centro Nacional de Investigaciones Metalúrgicas en Madrid. Según la norma, las probetas se expusieron sujetas en soportes inertes, con una inclinación de 45° y orientadas al sur. Las muestras no están cubiertas ni protegidas de ningún modo, quedando expuestas a la radiación solar y precipitaciones naturales. La corrosividad de esta atmósfera corresponde a una categoría C2, de tipo urbano, según la norma ISO 9223:2012.

Para la realización de las medidas se utilizó la celda G-PE (Figura. 2) previamente diseñada (Cano et al., 2014, Ramírez Barat y Cano, 2014). Esta celda consiste en un cilindro de metacrilato transparente en el cual se sitúan un alambre de plata pura (99,9%) recubierto electroquímicamente de cloruro de plata (Inamdar et al., 2009) que actúa como electrodo de referencia y un anillo con una malla de acero inoxidable AISI316 como contraelectrodo. El interior de la celda se rellena con el

electrólito que consiste en una disolución acuosa (electrólito líquido) gelificada con agar (agar técnico Cultimed /Panreac 401792.1210). Como electrólito líquido se ha empleado en este caso una disolución de composición similar al agua de lluvia (Bernardi et al., 2008) concentrada 10 veces para obtener una conductividad suficiente para las medidas. La disolución, cuya composición se recoge en la Tabla 2, se ha ajustado a pH 6,5 con HNO<sub>3</sub>.

Composición	Conc. mg/l
CaSO <sub>4</sub> ·2H <sub>2</sub> O	14,43
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	15,04
(NH <sub>4</sub> )Cl	19,15
NaNO <sub>3</sub>	15,13
CH <sub>3</sub> COONa	3,19

**Tabla 2:** Composición del electrólito

La conexión con el electrodo de trabajo se realiza directamente con cable del equipo a través del cocodrilo correspondiente en el caso de muestras delgadas o un tornillo de latón con una punta de acero para objetos de mayor volumen.

El equipo utilizado fue un potenciostato Gamry Reference 600, con un software de adquisición de datos Gamry Framework Software. Los espectros de impedancia se han obtenido con un barrido logarítmico de frecuencia de 100 kHz a 10 mHz, con una amplitud de 20 mV RMS y 10 puntos/década. El tratamiento de los datos experimentales se realizó mediante el ajuste a circuitos eléctricos equivalentes con el programa Gamry Echem Analyst.

**Resultados y discusión**

Las probetas se midieron antes y después de ser expuestas en el exterior durante un periodo de seis semanas con el objeto de verificar si era posible apreciar cambios en las propiedades de los recubrimientos desde esta fase temprana de exposición a la intemperie. En fases posteriores de esta investigación, estos recubrimientos serán evaluado tras exposiciones de meses o años para comprender el deterioro que se produce y poder establecer parámetros que nos permitan identificar de forma prematura fallos de los mismos. En las figuras 3 y 4 se representa el módulo de la impedancia para las diferentes frecuencias antes y después de su envejecimiento. Recordemos que el valor del módulo de la impedancia a bajas frecuencias se utiliza como una medida sencilla de la resistencia del recubrimiento y por tanto de su capacidad protectora.

Lo primero que se observa es que todos los recubrimientos acrílicos presentan unos valores del módulo de impedancia muy elevados a bajas frecuencias, siendo el Inctalac el más protector con diferencia, mientras que la cera Cosmolloid proporciona valores muy inferiores a los de los recubrimientos acrílicos. Tras 6 semanas de envejecimiento, a primera vista los recubrimientos no resultaban alterados frente a la muestra sin proteger que presentaba manchas irregulares de óxido, sin embargo las medidas de impedancia muestran que los recubrimientos experimentan diferentes comportamientos: algunos disminuyen su resistencia en mayor o menor proporción, mientras que otros la aumentan. En el primer caso encontramos en Inctalac, el Paraloid B72, Paraloid B48N y la cera Cosmolloid H80; en el segundo el Paraloid B44 y B67.

El Inctalac disminuye su resistencia, pero sigue presentando un elevado valor de Z y por tanto ofrece una buena protección, el Paraloid B72 sufre una leve



**Figura 2:** Diseño del molde (izquierda). Celda rellena con agar (centro) y detalle del contacto de la colocación de la celda en contacto con una probeta metálica.



pérdida de resistencia mientras que la cera se deteriora rápidamente aproximándose al metal sin proteger en tan solo 6 semanas, por lo que supone una protección muy pobre. El Paraloid B48N tampoco parece un buen recubrimiento ya que además de ser el que ofrece menor resistencia inicial de los recubrimientos acrílicos, también es el que experimenta, proporcionalmente, un descenso mayor en el módulo de Z.

En el otro lado tenemos que la impedancia del Paraloid B44 (resina base del Incralac) aumenta ligeramente aproximándose a la del Paraloid B72 y la del Paraloid B67 aumenta varios ordenes de magnitud, situándose en el límite de medida del equipo, motivo por el cual aparecen varios saltos en el espectro. El comportamiento de estas resinas contrario al esperado y sugiere la posibilidad de que experimenten reacciones de entrecruzamiento, perdiendo solubilidad. Este efecto no es deseable en los recubrimientos aplicados al patrimonio, ya que la reversibilidad de los tratamientos es uno de los criterios principales de aplicación.

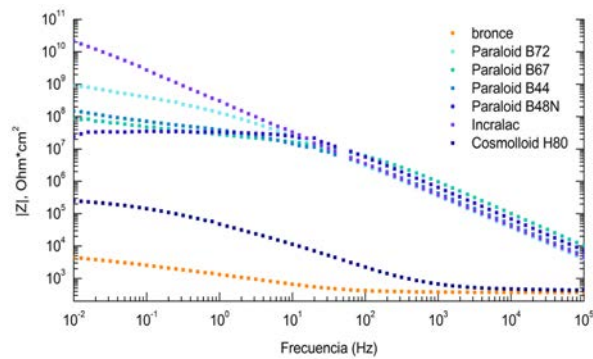


Figura 3: Variación del módulo de Z de los 6 recubrimientos aplicados frente al metal sin proteger

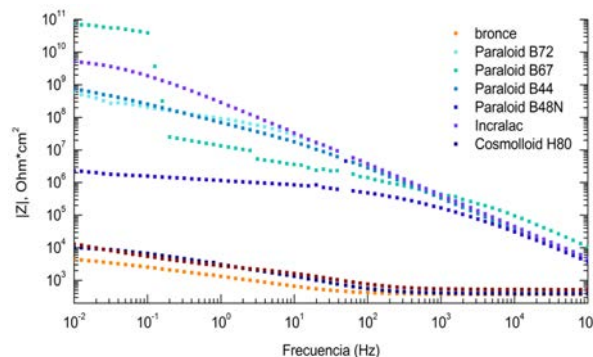


Figura 4: Variación del módulo de Z de los 6 recubrimientos aplicados tras 6 semanas de envejecimiento natural frente al bronce sin envejecer

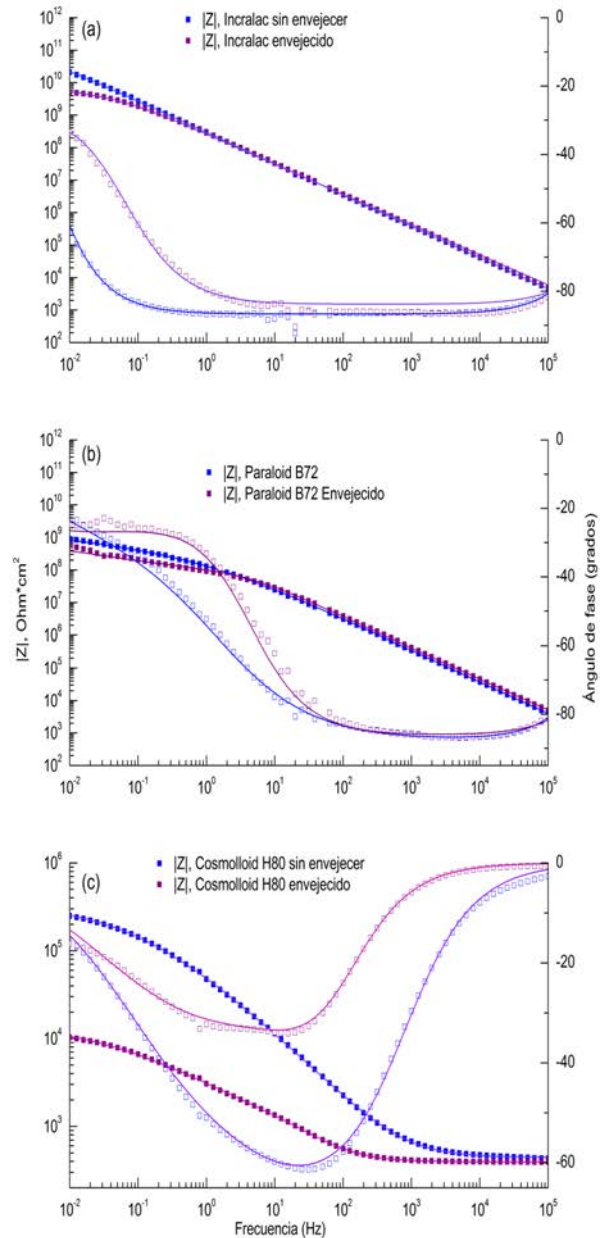


Figura 5: Diagrama de Bode de tres recubrimientos antes (azul) y después de 6 semanas de envejecimiento natural (violeta): ■ módulo de Z, □ ángulo de fase y – ajuste. Los recubrimientos comparados son (a) Incralac. (b) Paraloid B72 y (c) cera Cosmolloid H80

Finalmente hay que señalar que tal y como se muestra en los datos de la tabla 1, el espesor de los recubrimientos acrílicos es similar en todos los casos (entre aproximadamente 20-30 micrómetros) por lo que las diferencias en su capacidad protectora no puede achacarse al espesor de los mismos, sino a su naturaleza. Por el contrario, en el caso de la cera Cosmolloid, su espesor de pocas micras puede contribuir a la pobre respuesta obtenida.



Incralac	$R_e$ ( $\Omega \text{ cm}^2$ )	$CPE_p$		$R_{po}$ ( $G\Omega \text{ cm}^2$ )	$CPE_{dl}$		$R_{tc}$ ( $G\Omega \text{ cm}^2$ )
		$Y_p$ ( $nS \text{ s}^{\alpha_p} \text{ cm}^{-2}$ )	$\alpha_p$		$Y_p$ ( $nS \text{ s}^{\alpha_p} \text{ cm}^{-2}$ )	$\alpha_p$	
<i>Sin envejecer</i>	480 ± 80	0,557 ± 0,003	0,96 ± 0,00	50 ± 2	-	-	-
<i>Envejecido</i>	369,7 ± 0,1	0,677 ± 0,000	0,93 ± 0,00	3,44 ± 0,00	1,03 ± 0,00	0,44 ± 0,00	261700 ± 8
Paraloid B72	$R_e$ ( $\Omega \text{ cm}^2$ )	$CPE_p$		$R_{po}$ ( $G\Omega \text{ cm}^2$ )	$CPE_{dl}$		$R_{tc}$ ( $G\Omega \text{ cm}^2$ )
		$Y_p$ ( $nS \text{ s}^{\alpha_p} \text{ cm}^{-2}$ )	$\alpha_p$		$Y_p$ ( $nS \text{ s}^{\alpha_p} \text{ cm}^{-2}$ )	$\alpha_p$	
<i>Sin envejecer</i>	0 ± 90	0,66 ± 0,02	0,96 ± 0,00	40 ± 10	2,43 ± 0,08	0,40 ± 0,00	1800 ± 200
<i>Envejecido</i>	385,6 ± 0,1	0,56 ± 0,00	0,96 ± 0,00	66,0 ± 0,0	6,95 ± 0,00	0,46 ± 0,00	828,50 ± 0,00
Cosmolloid	$R_e$ ( $\Omega \text{ cm}^2$ )	$CPE_p$		$R_{po}$ ( $G\Omega \text{ cm}^2$ )	$CPE_{dl}$		$R_{tc}$ ( $G\Omega \text{ cm}^2$ )
		$Y_p$ ( $nS \text{ s}^{\alpha_p} \text{ cm}^{-2}$ )	$\alpha_p$		$Y_p$ ( $nS \text{ s}^{\alpha_p} \text{ cm}^{-2}$ )	$\alpha_p$	
<i>Sin envejecer</i>	440 ± 4	3,5 ± 0,3	0,76 ± 0,01	50 ± 30	4,8 ± 0,9	0,45 ± 0,06	290 ± 50
<i>Envejecido</i>	394 ± 3	17 ± 6	0,82 ± 0,04	0,9 ± 0,4	142 ± 6	0,47 ± 0,02	14 ± 1

**Tabla 3:** Parámetros electroquímicos del ajuste de los recubrimientos estudiados sin envejecer y tras 6 semanas de envejecimiento natural

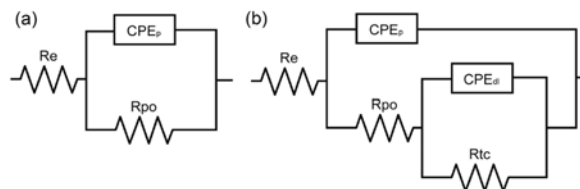
Es interesante comparar los espectros de cada una de las resinas antes y después del envejecimiento para analizar su comportamiento. En la figura 5 se muestran tres ejemplos representativos, el Incralac, el Paraloid B72 y la cera Cosmolloid H80, sobre los que se ha realizado un ajuste por medio de circuitos equivalentes para poder cuantificar la evolución de los elementos que intervienen en el proceso de corrosión. En la gráfica se pueden comparar los diagramas de Bode de los tres recubrimientos comparados antes (azul) y después de 6 semanas de envejecimiento natural (violeta). Los valores obtenidos de los ajustes a los circuitos equivalentes correspondientes a cada caso (figura 6) se recogen en la tabla 3.

El diagrama de Bode del Incralac (figura 5a) es un buen ejemplo de un comportamiento casi puramente capacitivo. Para todo el intervalo de frecuencias el módulo de Z aumenta con una pendiente constante y el ángulo de fase se mantiene próximo a 90°. Tras el envejecimiento se observa como en la zona de bajas frecuencias aparece un componente resistivo que se manifiesta por la aparición de un pequeño tramo horizontal al tiempo que el ángulo de fase cae rápidamente. Este comportamiento se relaciona con la resistencia a través de los defectos del recubrimiento.

El Incralac es un claro ejemplo del comportamiento descrito en la introducción. El recubrimiento sin envejecer se puede representar mediante un sistema de 1 CPE (figura 6a), análogo al circuito de la figura 1 en el que además de la resistencia del electrolito,  $R_e$ , estarían representadas la capacidad y resistencia –muy elevada– del recubrimiento. Al iniciarse el deterioro de la resina aparecería una segunda constante de tiempo, formada por un CPE y una resistencia en paralelo,

representando la reacción de corrosión que aparecería en los poros y defectos del recubrimiento, como se muestra en la figura 6b.

El diagrama de impedancia del Paraloid B72 (figura 5b) presenta un primer tramo dominado por la componente capacitiva con un módulo creciente y un ángulo de fase elevado pero para una frecuencia entre 1 y 10Hz hay un cambio de pendiente y una disminución de ángulo de fase que indican que su comportamiento se aleja del de un recubrimiento perfecto. El envejecimiento hace que el tramo capacitivo disminuya ligeramente, indicando una mayor contribución del resto de los procesos (paso del electrolito a través de los poros y procesos de transferencia de carga). Al no tratarse ya de un recubrimiento perfecto, es necesario recurrir a un circuito equivalente de 2 CPE (figura 6b) en ambos casos. Si nos fijamos en los datos del ajuste (tabla 3) podemos comprobar como la resistencia de transferencia de carga disminuye mientras que la capacidad de la doble



**Figura 6:** Circuitos equivalentes propuestos para el ajuste de los espectros de los recubrimientos estudiados. El modelo de la izquierda se corresponde al Incralac sin envejecer, mientras para que explicar el espectro del Incralac envejecido, el Paraloid B72 y la cera Cosmolloid H80 se recurre al circuito de la derecha

capa aumenta con el envejecimiento, lo que se explica por el aumento de la fracción de metal que se ve expuesta al contacto con el medio corrosivo.

En el último ejemplo, el de la cera Cosmoloid H80 (figura 5c), podemos ver que su comportamiento como recubrimiento es muy pobre. A altas frecuencias la impedancia del recubrimiento es tan baja que predomina claramente la resistencia del electrólito no empezando a ser apreciable la componente capacitiva hasta cerca de 1MHz en la cera recién aplicada y hasta unos 100Hz en la cera envejecida. Además, con el envejecimiento su resistencia decae rápidamente siendo de un orden de magnitud menor en sólo 6 semanas.

### Conclusiones:

La celda portátil con un electrólito gelificado con agar diseñada por el equipo de investigación permite obtener espectros de impedancia de calidad sobre objetos metálicos in situ sin los inconvenientes de las celdas líquidas convencionales. Los resultados obtenidos han permitido comparar las propiedades protectoras de varios recubrimientos acrílicos y una cera microcristalina y los cambios sufridos en un corto periodo de tiempo, confirmando el buen comportamiento del Inralac como recubrimiento protector y la limitada resistencia de la cera.

Estos resultados avalan la aplicabilidad de la celda en gel y su utilidad para el estudio del comportamiento y la evolución de pátinas y recubrimientos sobre el patrimonio cultural metálico. La capacidad de la espectroscopía de impedancia electroquímica de detectar cambios a corto plazo, mucho antes de que sean perceptibles a simple vista, junto con la posibilidad de aplicación in situ la convierten en una herramienta de gran interés para la selección del tratamiento protector más indicado en cada caso o para la evaluación de la necesidad de sustituir o renovar un recubrimiento.

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Tras estos primeros ensayos se han evaluado otros recubrimientos sobre probetas de bronce, plata y hierro en el marco del proyecto europeo IPERION-CH. En este caso, el objetivo era demostrar la capacidad del sistema desarrollado para evaluar diferentes recubrimientos orgánicos utilizados sobre distintos metales en patrimonio cultural, como parte de un trabajo más amplio de evaluación y comparación de técnicas de análisis para materiales del patrimonio.

A continuación se exponen como ejemplo los principales resultados obtenidos en el estudio de recubrimientos orgánicos sobre probetas de bronce y su envejecimiento artificial. Los resultados sobre plata y hierro no se incluyen, ya que no aportan información adicional sobre el empleo de la celda. Conjuntamente, estos trabajos han permitido validar el empleo de la celda para la evaluación de recubrimientos protectores en patrimonio metálico.

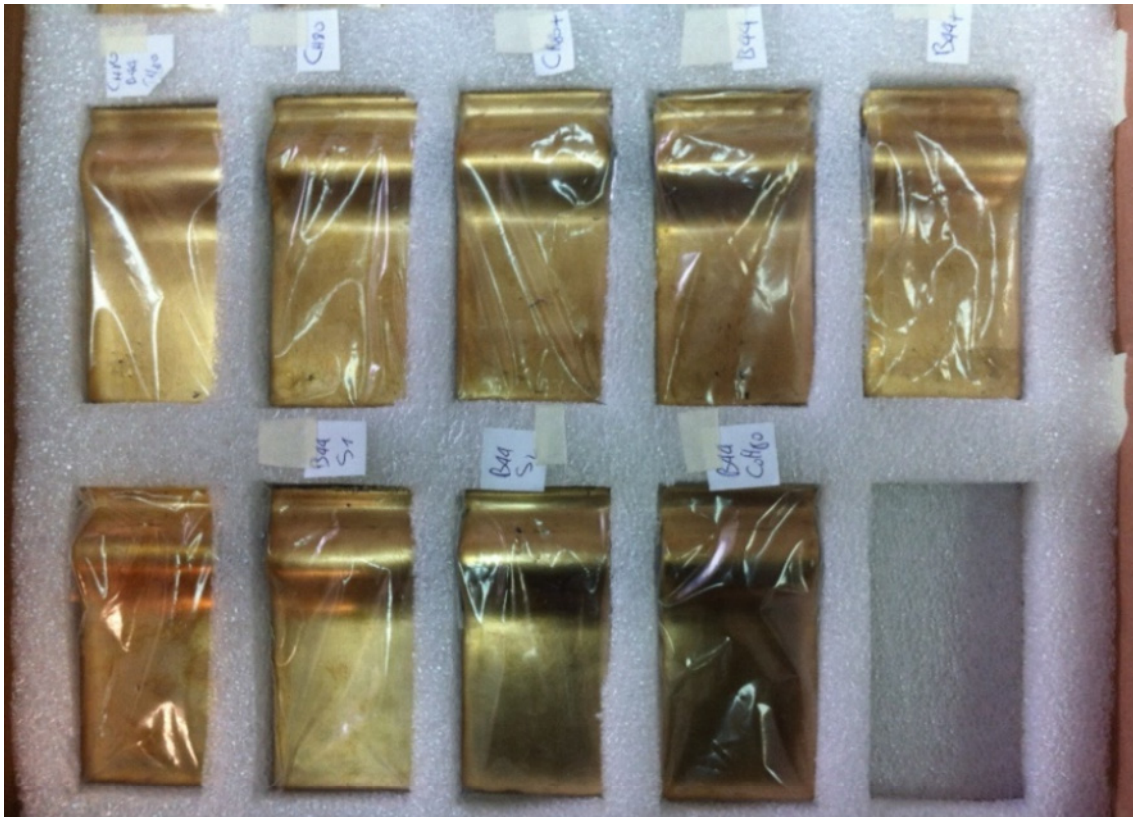
#### *Evaluación de recubrimientos sobre bronce sometidos a envejecimiento artificial*

Las muestras de bronce fueron preparadas por restauradores del Opificio delle Pietre Dure (Florencia) y enviadas al CENIM, para estudiar las diferencias en la capacidad protectora de los recubrimientos con la celda G-PE. Se trata de un conjunto de 14 probetas de bronce de fundición (ca. 95 mm x 50 mm), sobre las que se han aplicado diversas combinaciones de recubrimientos tradicionales, tal y como se recogen en la tabla 6. Junto a la descripción de las probetas también se incluyen los datos de espesor de los recubrimientos medidos con el medidor de espesores Elcometer 456. El dato reflejado corresponde al promedio de 20 medidas distribuidas por toda la zona plana recubierta de la probeta, con la correspondiente desviación estándar entre paréntesis. Los datos del espesor del recubriendo son un dato importante en especial a la hora de comparar entre diferentes formulaciones, ya que puede influir en la capacidad protectora, por efecto barrera.

**Tabla 6.** Probetas de bronce. Relación de recubrimientos medidos y espesor

NÚM.	DESCRIPCIÓN	Espesor, $\mu\text{m}$ ( $\sigma$ ) Elcometer 456 (N=20)
16	Sin tratar	-
17	Cera Soter concentración 1	2.3 (1.4)
18	Cera Soter concentración 2 (mayor)	1.8 (3.6)
19	Cera Soter concentración 1; dos capas cruzadas	1.6 (1.4)
20	Cera Soter concentración 2; dos capas cruzadas	3.0 (2.3)
21	Cera Cosmolloid	3.1 (1.2)
22	Cera Cosmolloid dos capas cruzadas	3.0 (2.8)
23	Paraloid B44	2.4 (3.3)
24	Paraloid B44 dos capas cruzadas	10.0 (3.3)
25	Dos capas: Paraloid B44 + Soter conc.1	4.6 (2.4)
27	Dos capas: Paraloid B44 + Soter conc.2	6.7 (2.4)
28	Dos capas: Paraloid B44 + Cosmolloid	7.7 (2.9)
29	Tres capas: Soter conc.1 + Paraloid B44 + Soter conc.1	3.6 (2.1)
30	Tres capas: Cosmolloid + Paraloid B44 + Cosmolloid	6.0 (2.1)





**Figura 27.** Colección de muestras de bronce estudiadas

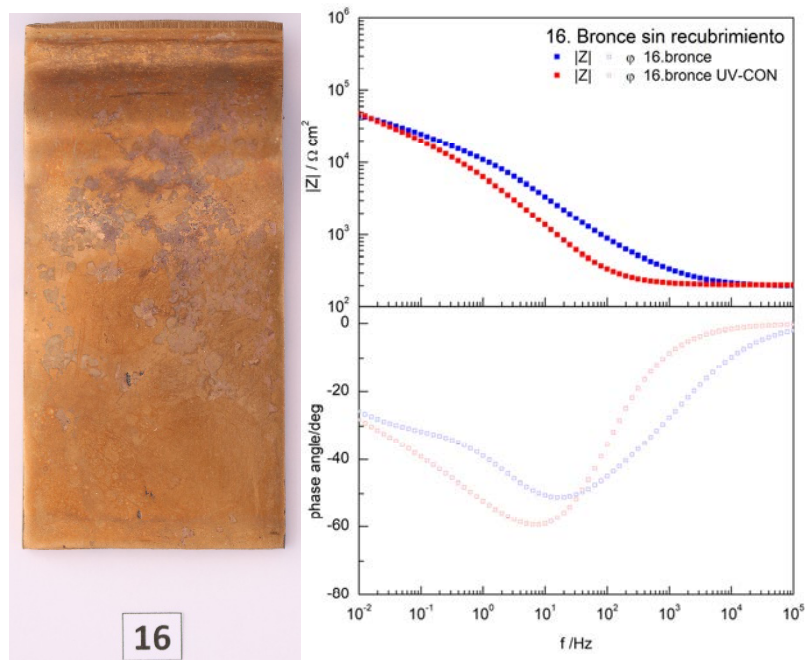
Las muestras se midieron inicialmente en las condiciones descritas en el apartado 3.2.1. A continuación, se sometieron a envejecimiento artificial en la cámara QUV, comprobándose que, al cabo de una semana de tratamiento, ya podían apreciarse cambios de color a simple vista (figura 28). A la vista de estas alteraciones se consideró que los recubrimientos ya habían sufrido modificaciones suficientes como para poder mostrar diferencias en los espectros de impedancia. Por otra parte, los cambios visuales en los recubrimientos aplicados permitieron apreciar la irregularidad en la aplicación del recubrimiento.



**Figura 28.** Probetas tras el envejecimiento artificial. [16: Sin recubrimiento; 17: Soter concentración 1; 18: Soter concentración 2; 19: Soter concentración 1, dos capas; 20: Soter concentración 2, dos capas; 21: Cosmolloid; 22: Cosmolloid, dos capas; 23: Paraloid B44; 24: Paraloid B44, dos capas; 25: Dos capas: Paraloid B44+Soter conc.1; 27: Dos capas: Paraloid B44+Soter conc.2; 28: Dos capas: Paraloid B44+Cosmolloid; 29: Tres capas: Soter conc.1+Paraloid B44+Soter conc.1; 30: Tres capas: Cosmolloid +Paraloid B44+Cosmolloid]

Los espectros de impedancia obtenidos para cada uno de los recubrimientos se han agrupado en función de sus composiciones para compararlos entre sí, antes y después del tratamiento de envejecimiento artificial:

- Bronce sin recubrimiento como material de referencia
  - Ceras
  - Barniz acrílico (Paraloid B44)
  - Sistemas de doble capa: barniz acrílico (Paraloid B44) y cera
  - Sistemas de triple capa: cera, barniz acrílico (Paraloid B44) y cera
- *Bronce sin recubrimiento*



**Figura 29.** Bronce sin recubrimiento. Espectro de impedancia antes (azul) y después (rojo) del envejecimiento artificial.

Aunque el valor de  $|Z|_{10\text{mHz}}$  prácticamente no varía con el envejecimiento, el módulo de impedancia de la probeta envejecida es ligeramente inferior en la región de medias frecuencias, asociada con las características de la pátina. Este resultado puede atribuirse al hecho de que la muestra no tratada está recubierta por una capa estable de óxido natural, que puede haberse desestabilizado ligeramente al exponerse a condiciones agresivas.



● *Recubrimientos de cera: Soter y Cosmolloid*

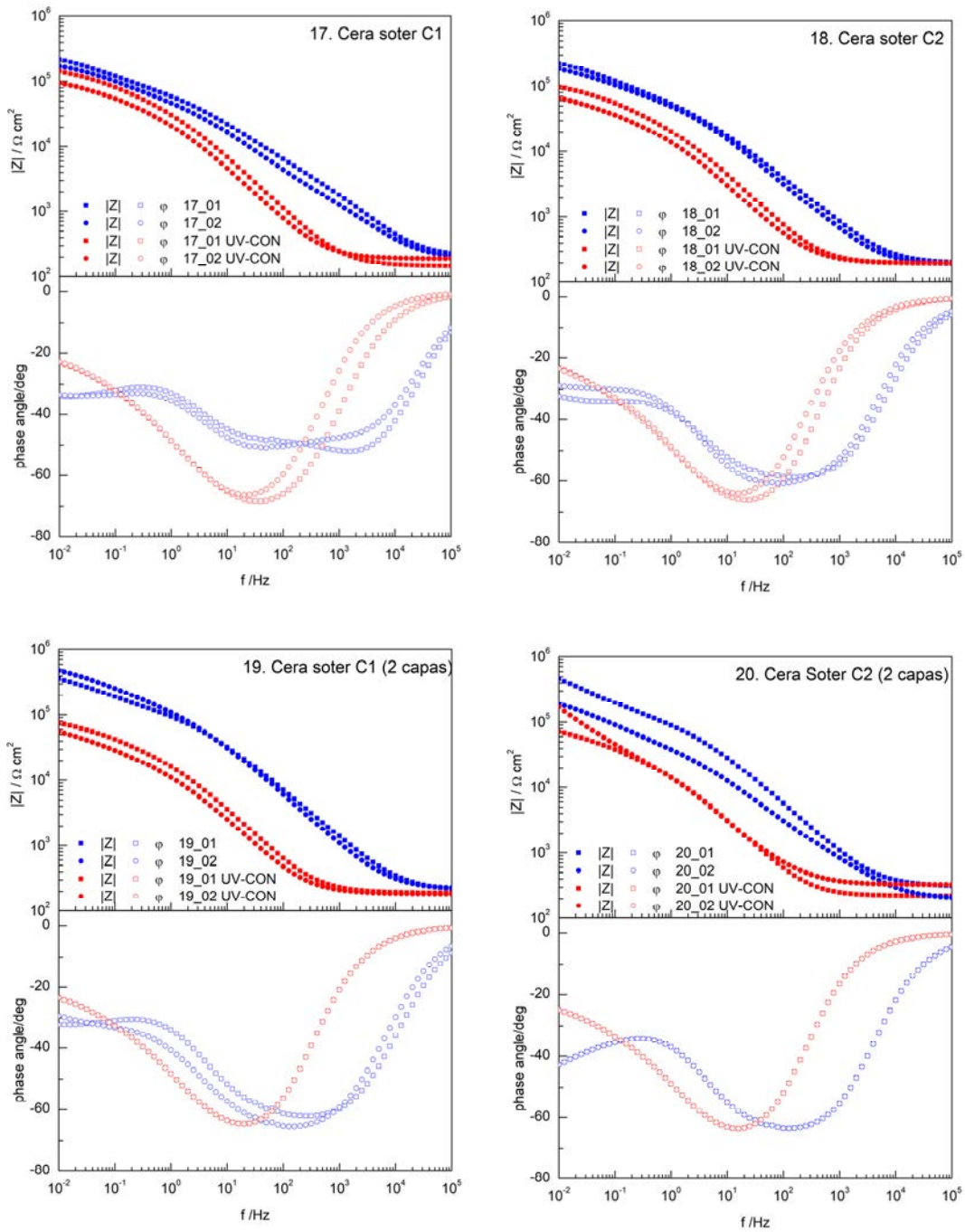


Figura 30. Recubrimientos a base de ceras . Espectro de impedancia antes (azul) y después (rojo) del envejecimiento artificial.

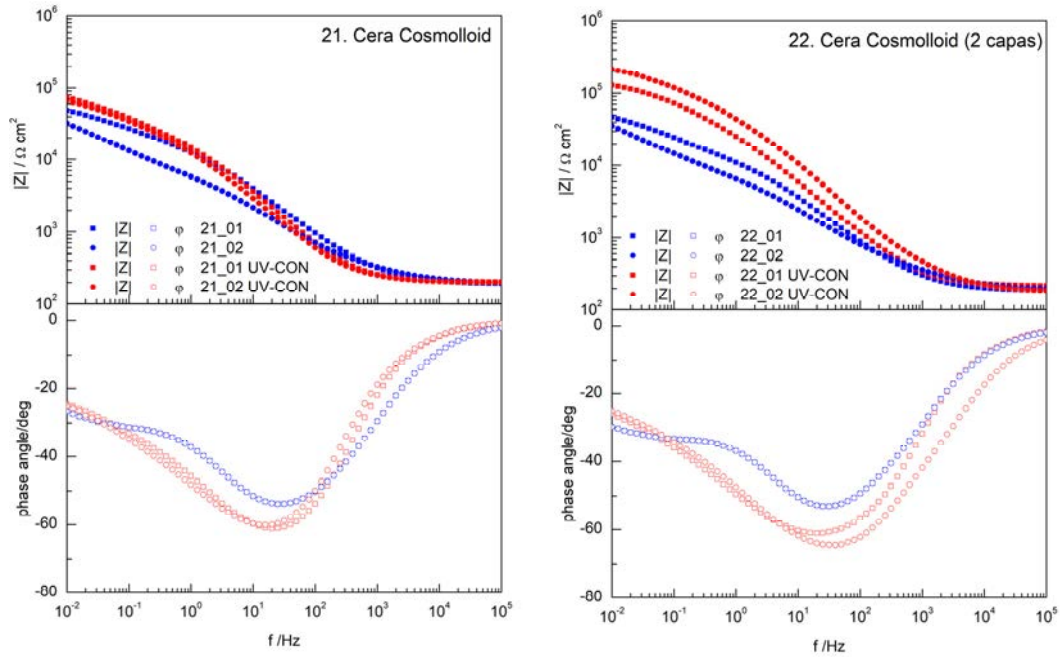


Figura 31. Recubrimientos a base de ceras . Espectro de impedancia antes (azul) y después (rojo) del envejecimiento artificial.

● *Recubrimiento acrílico (Paraloid B44)*

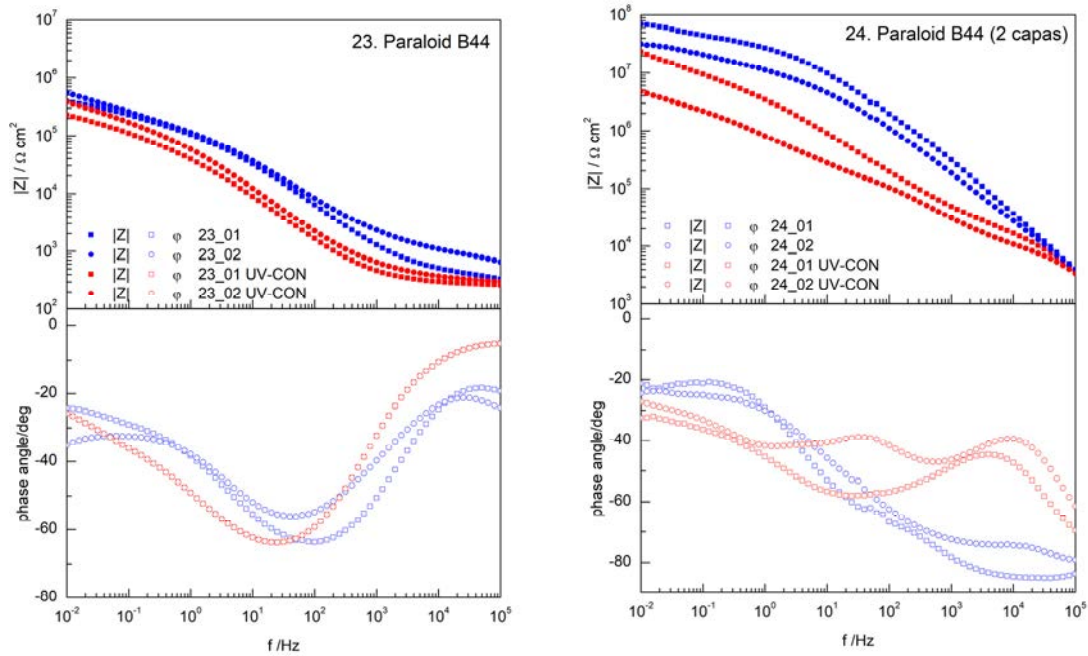
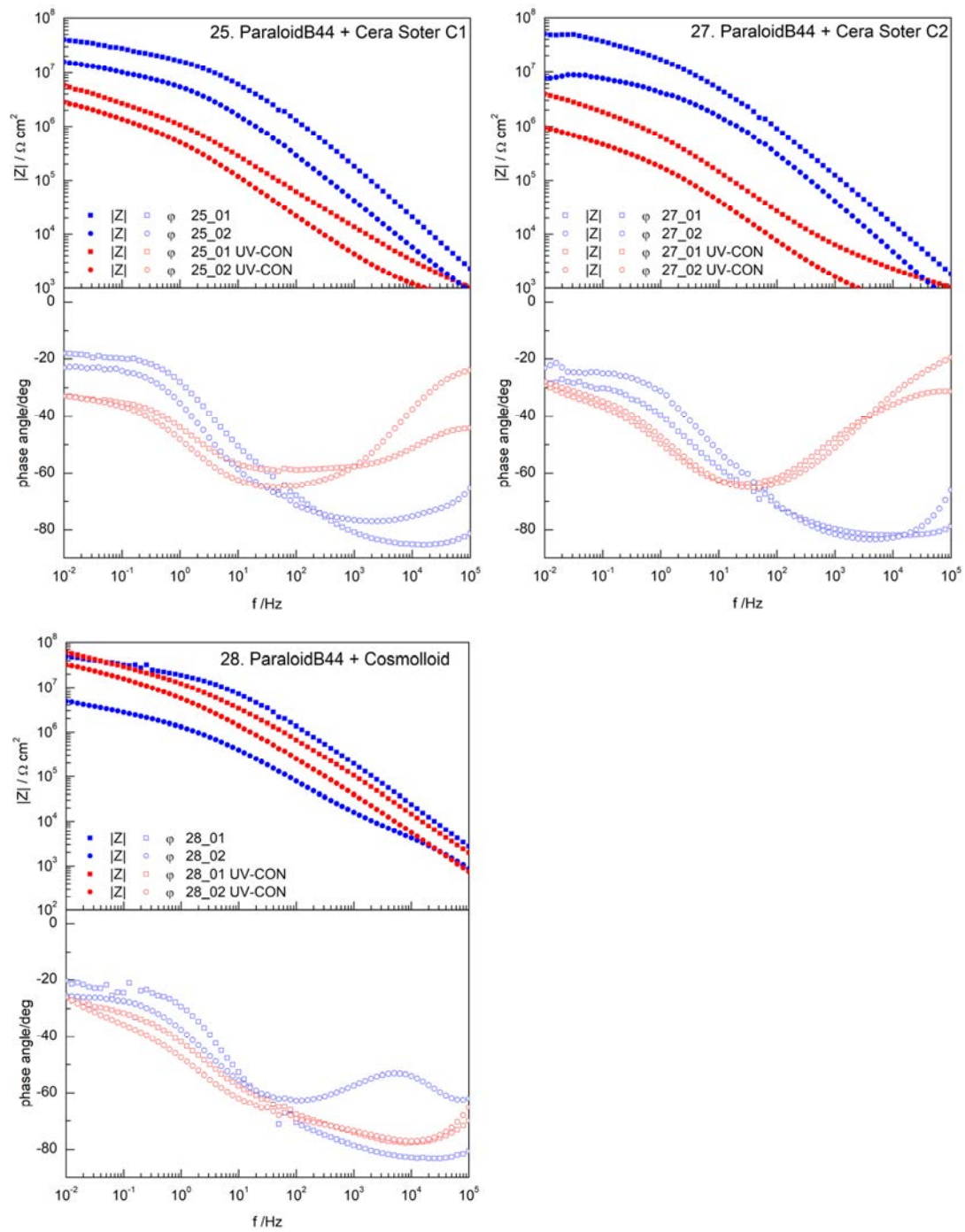


Figura 32. Recubrimientos de Paraloid B44 . Espectro de impedancia antes (azul) y después (rojo) del envejecimiento artificial.

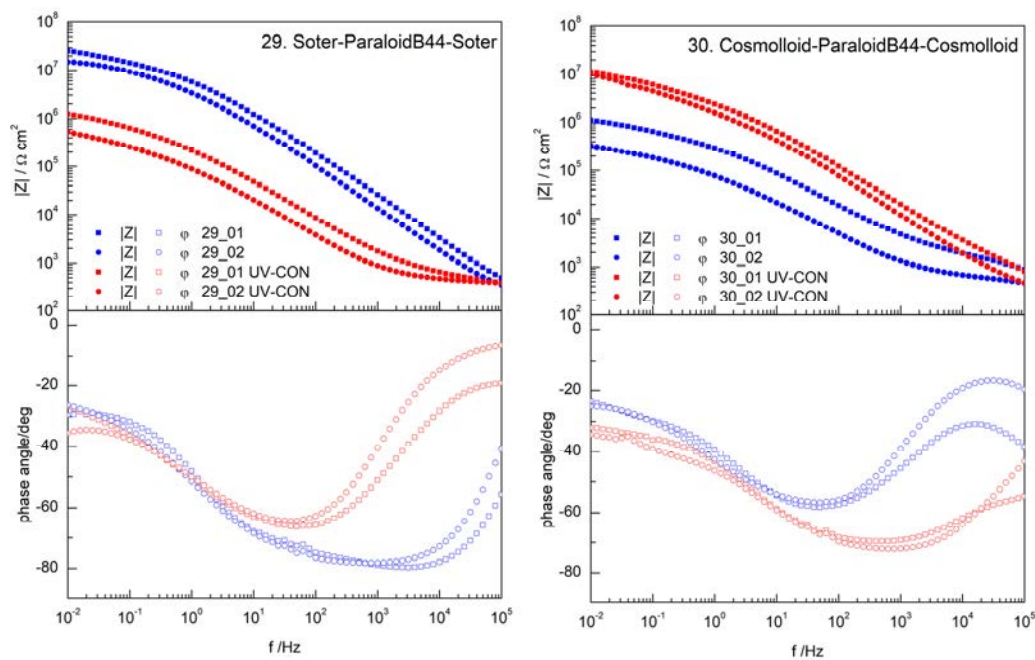


● *Recubrimientos de doble capa: Paraloid B44 + cera*



**Figura 33.** Recubrimientos de doble capa a base de acrílico y cera. Espectro de impedancia antes (azul) y después (rojo) del envejecimiento artificial.

● *Recubrimientos de triple capa cera +Paraloid B44 + cera*



**Figura 34.** Recubrimientos de triple capa a base de acrílico y cera. Espectro de impedancia antes (azul) y después (rojo) del envejecimiento artificial.

La comparación de los resultados de los diferentes recubrimientos se ha realizado a partir de los valores módulo de la impedancia en el límite de bajas frecuencias,  $|Z|_{10\text{mHz}}$ , que se representan gráficamente en la figura 35.

Los resultados indican que la aplicación de una cera más concentrada no aumenta la protección del bronce. La aplicación de dos capas puede aumentar ligeramente la impedancia por efecto barrera, pero no proporciona un mejor resultado con el envejecimiento. En el caso de la cera Cosmolloid, la aplicación de dos capas ha resultado incluso menos eficaz; esto podría deberse al arrastre de la primera capa con la brocha, al aplicar la segunda. Los resultados de espesores medidos (tabla 6) demuestran que el espesor total medio no aumenta, aunque si la desviación estándar del espesor en distintas zonas, indicando que la capa resultante es más irregular. Respecto a la comparación entre ambos productos, la cera Soter proporciona resultados ligeramente superiores a la Cosmolloid, posiblemente debido al contenido

en benzotriazol (BTA) de la primera, que es un conocido inhibidor de corrosión del cobre y sus aleaciones.

El comportamiento con el envejecimiento resulta opuesto en ambas ceras. La impedancia disminuye tras el envejecimiento en la cera Soter, pero aumenta en el caso de la Cosmolloid. Esto sugiere la posibilidad de reacciones de entrecruzamiento en el recubrimiento, que si bien pueden ser positivas desde el punto de vista de protección frente a la corrosión, podrían no ser deseables desde el punto de vista de la reversibilidad, al disminuir la solubilidad.

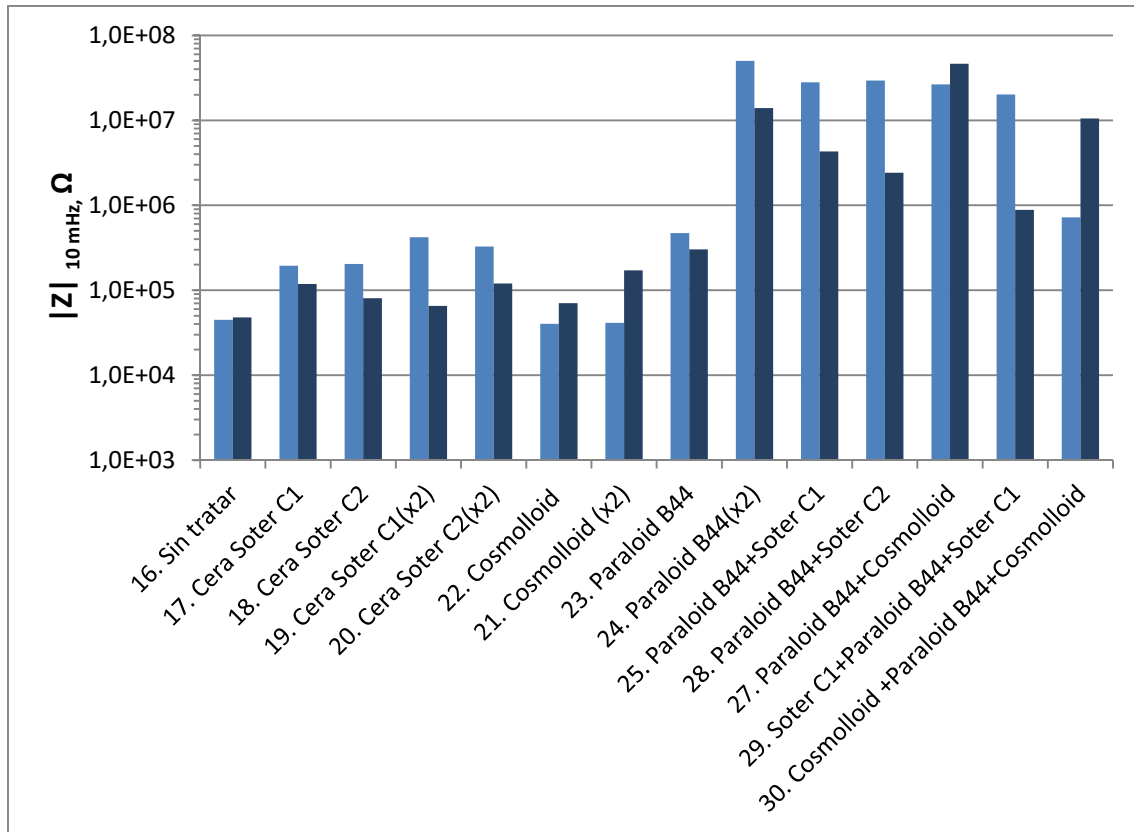
El Paraloid B44 ofrece una protección que podría considerarse relativamente buena. La aplicación de una segunda capa incrementa el máximo de  $|Z|$  en dos órdenes de magnitud, aunque los resultados son más desiguales por zonas. Sin embargo, este producto sufre un importante oscurecimiento tras el envejecimiento artificial, que además de poner de manifiesto la irregularidad en la aplicación, no cumpliría los criterios de los recubrimientos para conservación de patrimonio. Hay que tener en cuenta, no obstante, que los tratamientos de envejecimiento artificial resultan muy agresivos, y no implican necesariamente que este tipo de alteración se vayan a producir de la misma forma o magnitud en condiciones de envejecimiento natural. Sería necesario realizar un estudio detallado de este fenómeno que está fuera de los objetivos de este trabajo.

La aplicación de una capa de cera sobre el Paraloid B44 no produce una diferencia significativa inicialmente, aunque si mejora la respuesta al envejecimiento. Nuevamente, las probetas envejecidas han sufrido un notable oscurecimiento y muestran una aplicación muy irregular de los recubrimientos.

Las combinaciones cera + Paraloid B44 + cera no proporcionan una mayor protección en comparación con el sistema más simple Paraloid B44 + cera, sin embargo, parece tener un efecto positivo sobre el oscurecimiento, lo cual es de gran relevancia. En relación a las dos combinaciones ensayadas, con Soter o con Cosmolloid, esta última experimentó (como en el caso de las capas simples de cera) un aumento en el valor de la impedancia tras el envejecimiento.

Más allá de la valoración individual del rendimiento de cada recubrimiento y de su comportamiento con el envejecimiento, cuyo estudio detallado requeriría un estudio

sistemático con condiciones de aplicación más controladas, el estudio realizado bajo el proyecto IPERION CH demostró la aplicabilidad de la celda G-PE para la evaluación de recubrimientos en probetas que simulan bienes culturales. Los resultados de EIS obtenidos han servido como referencia para la interpretación de los resultados de otras técnicas empleadas en el proyecto.



**Figura 35.** Comparación del máximo del módulo de impedancia a bajas frecuencias para los diferentes recubrimientos antes (azul claro) y después del envejecimiento artificial (azul oscuro). Valor promedio de dos medidas.

### 4.3.2. Medidas de campo y casos reales.

Dada la finalidad práctica de este trabajo, el objetivo principal implica el traslado de los resultados obtenidos en laboratorio, que se han presentado en el apartado anterior, a casos reales, algo que se ha tratado de llevar a cabo desde el primer momento. En paralelo al diseño y a los ensayos en laboratorio se han realizado diversas medidas sobre esculturas en bronce y acero, que han servido para comprobar el funcionamiento de la celda in situ sobre obra real.

La mayor parte de estos resultados no han sido publicados como estudios independientes, sino que se han incluido para ilustrar los trabajos dedicados al diseño de la celda. Hay que tener en cuenta que la realización de medidas de campo no resulta sencilla, por motivos administrativos, meteorológicos, etc. y que, por otra parte, la realización de medidas aisladas sobre obras individuales tampoco proporciona resultados de especial relevancia para la conservación de las mismas, si bien nos han permitido conocer el comportamiento de la celda in situ, y por tanto resultan de gran importancia en su desarrollo. Algunos de ellos se han presentado en congresos de Patrimonio con el objetivo de dar difusión entre los potenciales usuarios finales; dado el enfoque práctico de este trabajo, el traslado de los resultados a los posibles usuarios se ha considerado un aspecto importante desde el principio.

Afortunadamente, los inicios del desarrollo de la celda coincidieron con la restauración de las esfinges que decoran la fachada principal del Museo Arqueológico Nacional, lo que sí ha permitido realizar un estudio de caso completo. En colaboración con las restauradoras responsables de la intervención, Soledad Díaz y Emma García, del Instituto del Patrimonio Cultural de España, se realizaron medidas antes y después de los tratamientos y se hizo un seguimiento de la evolución del sistema de protección aplicado durante dos años, demostrando el potencial de la celda como herramienta de diagnóstico para la conservación del patrimonio metálico. El estudio realizado sobre la restauración de las esfinges se publicó en la revista *Journal of Cultural Heritage* (ver apartado 4.3.2.1.).

Además de este estudio de caso, se incluyen a continuación otros ejemplos de medidas realizadas en diversas esculturas, que, aunque no forman parte de ningún estudio concreto o estudio en profundidad sirven para ilustrar las posibilidades del sistema y como referencia para futuros estudios, ya que actualmente existen pocos espectros de



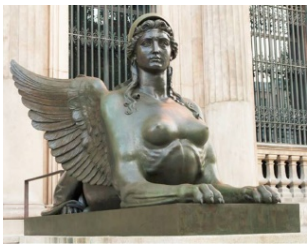


impedancia obtenidos en objetos reales. En estos ejemplos, la calidad de los espectros obtenidos es variable, ya que se han ido realizando en paralelo al desarrollo y perfeccionamiento de la celda, por lo que en algunos casos la interpretación o el ajuste que se puede hacer de ellos es limitada. Sin embargo, los resultados muestran en todo momento una coherencia con las características de la superficie medida.


Las obras sobre las que se han realizado medidas de impedancia con la celda G-PE, junto con las referencias de los artículos o congresos en los que han sido publicadas se resumen en la tabla 7. Seguidamente se recogen algunos ejemplos de los resultados obtenidos, organizados en tres apartados:

- Estudio de las esfinges del Museo Arqueológico Nacional, en Madrid.
- Esculturas de la Universidad de Valencia
- Esculturas del Museo de Escultura de Leganés

El primer apartado corresponde al único estudio completo realizado, enfocado específicamente a un caso de restauración, los dos siguientes apartados recogen colecciones de medidas realizadas en diferentes tipos de esculturas y acabados en Valencia y en Madrid para evaluar el funcionamiento de la celda en diferentes materiales y superficies. El resto de las medidas realizadas se encuentran en las publicaciones referidas en la tabla a modo de diferentes ejemplos, y no se incluyen aquí de nuevo.

Tabla 7. Resumen de las obras medidas in situ con la celda G-PE.

	<p>Obra: <i>Esfinges</i></p> <p>Localización: Fachada del Museo Arqueológico Nacional</p> <p>Técnica: Bronce</p> <p>Fecha: 1894</p> <p>Autor: Felipe de Moratilla y Parreto</p> <p>Referencias:</p> <ul style="list-style-type: none"> <li>• A.Crespo, B. Ramírez Barat, D. Lafuente, S. Díaz, E. García, E. Cano, "Non-destructive electrochemical evaluation of the patinas on the bronze sphinxes of the Museo Arqueológico Nacional in Madrid", en: <i>Art`14. 11 th Int. Conference on non-destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage</i>, Madrid, 2014.</li> <li>• B. Ramírez Barat, A. Crespo, E. García, S. Díaz, E. Cano, "An EIS study of the conservation treatment of the bronze sphinxes at the Museo Arqueológico Nacional (Madrid)", <i>Journal of Cultural Heritage</i>, 24(2017) 93-9.</li> <li>• B. Ramírez Barat, E. Cano, "Agar vs agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage", <i>ChemElectroChem</i> 2019, 6(9) 2553-2559.</li> </ul>
	<p>Obra: <i>Francesco</i></p> <p>Localización: Instituto del Patrimonio Cultural de España</p> <p>Técnica: bronce fundido con pátina de sulfuro</p> <p>Fecha:</p> <p>Autor: Francisco López Hernández</p> <p>Referencias:</p> <ul style="list-style-type: none"> <li>• B. Ramírez Barat, S. Díaz Martínez, E. García Alonso, E. Cano Díaz, "Aplicación de la EIS a la evaluación in situ de la resistencia a la corrosión de una escultura en bronce", en: E. Cano, J. Barrio (Eds.), <i>MetalEspaña 2015</i>, Segovia, 2015, pp. 102-9.</li> </ul>
	<p>Obra: <i>Unidad Yunta</i></p> <p>Localización: Campus de la Universidad Politécnica de Valencia</p> <p>Técnica: Bronce patinado</p> <p>Fecha: 1970</p> <p>Autor: Pablo Serrano</p> <p>Referencias:</p> <ul style="list-style-type: none"> <li>• Redondo-Marugán, J., et al. (2016), "Electrochemical study of a contemporary outdoor bronze sculpture (Poster)", en <i>5th INTERNATIONAL CONFERENCE YOUTH in CONSERVATION OF CULTURAL HERITAGE-YOCOCU 2016</i>, Madrid, 21-23 September, 2016, 204.</li> </ul>

	<p>Obra: <i>Crónica del viento</i>  Localización: Campus de la Universidad Politécnica de Valencia  Técnica: Bronce  Fecha: 1991  Autor: Martín Chirino  Referencias: no publicado</p>
	<p>Obra: <i>Angel</i>  Localización: Cementerio de Staglieno (Génova, Italia)  Técnica: Bronce  Fecha: s. XIX  Autor: Enrico Astorri (1859-1921)  Referencias:</p> <ul style="list-style-type: none"> <li>• B. Ramírez Barat, E. Cano, "Agar vs agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage", <i>ChemElectroChem</i> 2019, 6(9) 2553-2559.</li> </ul>
	<p>Obra: <i>Hachero</i>  Localización: Museo de Escultura de Leganés  Técnica: bronce patinado.  Fecha: 1926  Autor: Luis Marco Pérez  Referencias: no publicado</p>
	<p>Obra: <i>El Segador</i>  Localización: Museo de Escultura de Leganés  Técnica: bronce patinado.  Fecha: 1970  Autor: Venancio Blanco  Referencias: no publicado</p>

	<p>Obra: <i>Zenon</i></p> <p>Localización: Museo de Escultura de Leganés</p> <p>Técnica: acero corten, cera</p> <p>Fecha: 1980</p> <p>Autor: José Luis Sánchez</p> <p>Referencias:</p> <ul style="list-style-type: none"> <li>• B. Ramírez Barat, A. Crespo, E. Cano, "In situ evaluation of outdoor sculpture with a gel polymer electrolyte cell", <i>TechnoHeritage 2017. 3rd International Congress Science and Technology for the Conservation of Cultural Heritage</i>, Cádiz, 2017.</li> <li>• B. Ramírez Barat, E. Cano, "Agar vs agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage", <i>ChemElectroChem</i> 2019, 6(9) 2553-2559.</li> </ul>
	<p>Obra: <i>Templo</i></p> <p>Localización: Museo de Escultura de Leganés</p> <p>Técnica: acero corten</p> <p>Fecha: 2003</p> <p>Autor: Adriana Veyrat</p> <p>Referencias:</p> <ul style="list-style-type: none"> <li>• A. Crespo, B. Ramírez Barat, I. Diaz Ocaña, E. Cano Díaz, "Efecto del patinado artificial del acero Cor-Ten en la conservación de Templo, de Adriana Veyrat", en: <i>Conservación de Arte Contemporáneo 18ª Jornada</i>, MNCARS, Madrid, 2017, pp. 193-201.</li> <li>• A. Crespo, B. Ramírez Barat, I. Diaz, E. Cano Díaz, "Assessment of the protective properties of patinas on contemporary sculpture made out of weathering steel", en: <i>ICOM-CC 18th Triennial Conference</i>, Copenhagen, 2017.</li> <li>• B. Ramírez Barat, E. Cano, "Agar vs agarose gelled electrolyte for in situ corrosion studies on metallic cultural heritage", <i>ChemElectroChem</i> 2019, 6(9) 2553-2559.</li> </ul>
	<p>Obra: <i>Once Módulos</i></p> <p>Localización: Museo de Escultura de Leganés</p> <p>Técnica: acero corten, Paraloid B72</p> <p>Fecha: 1971</p> <p>Autor: Amador Rodríguez</p> <p>Referencias:</p> <ul style="list-style-type: none"> <li>• A. Crespo, B. Ramírez Barat, E. Cano, "Electrochemical evaluation of the patina of a weathering steel sculpture: Once Módulos", <i>TechnoHeritage 2019. 4th International Congress Science and Technology for the Conservation of Cultural Heritage</i>, Seville, March 26-30, 2019.</li> </ul>



#### 4.3.2.1 Estudio de las esfinges del Museo Arqueológico Nacional.

La fachada del Museo Arqueológico Nacional está decorada con dos Esfinges de bronce a ambos lados de la escalera que daba acceso a la puerta principal, cuya restauración coincidió con el inicio del desarrollo de la celda. Los primeros estudios de campo se hicieron sobre esta obra, y la realización de medidas sucesivas fue poniendo de manifiesto las diferentes dificultades para la realización de medidas de campo –fue a lo largo de este estudio cuando se desarrolló el soporte de medida- así como las posibilidades de aplicación de la celda.

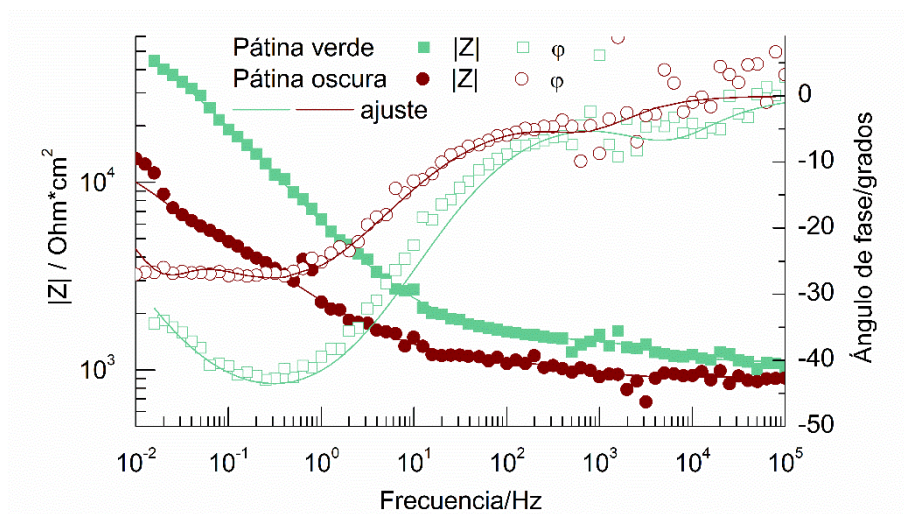
En la figura 32 se muestra la esfinge de la izquierda antes de la restauración, sobre la que se han llevado a cabo la mayor parte de las medidas. Como se puede apreciar, la superficie presentaba una pátina irregular, con zonas de escorrentía. En la cara frontal, más expuesta, la pátina era de color verde claro mientras que en el resto era de color negro, y mucho más fina. Las dos zonas seleccionadas para las medidas, representativas de cada una de estas pátinas, se indican mediante flechas en la figura.



**Figura 36.** Esfinge de la fachada del Museo Arqueológico Nacional. Las flechas indican las dos áreas de la pátina sobre las que se han realizado las diferentes medidas.



En este primer estudio de la pátina se empleó el primer prototipo de la celda y con agar al 4%, ya que aún no se había realizado la optimización del diseño ni la evaluación de la concentración del gel. A pesar de ello y de la limitada calidad de los espectros obtenidos, con bastante ruido en la zona de frecuencias más bajas, estas primeras medidas permitieron confirmar la aplicabilidad de la celda. La comparación de medidas de EIS mostró las diferencias de la capacidad protectora de la pátina en las dos zonas de la escultura, mucho mayor en la región frontal (pátina verde) comprobándose la coherencia de los resultados proporcionados por la celda [184]



**Figura 37.** Espectros de impedancia obtenidos sobre la pátina verde y la pátina oscura de la esfinge izquierda del Museo Arqueológico Nacional, con el primer prototipo de la celda G-PE.

Tras estas medidas iniciales las esfinges fueron restauradas y se realizó el seguimiento de la evolución del recubrimiento de protección aplicado, incluyendo una estimación de la posible duración del mismo que, aunque no ha podido comprobarse por motivos técnicos – se ha vuelto a colocar un andamio sobre la escultura resultando inaccesible- concuerda con los valores referidos en la literatura para el tipo de recubrimiento aplicado. Los resultados de este estudio se presentan seguidamente en la publicación:

- B. Ramírez Barat, A. Crespo, E. García, S. Díaz, E. Cano, *An EIS study of the conservation treatment of the bronze sphinxes at the Museo Arqueológico Nacional (Madrid)*, Journal of Cultural Heritage, 24(2017) 93-9.<sup>11</sup>

<sup>11</sup> Referencias bibliográficas [15-17, 23, 26, 27, 29, 30, 32, 35, 43, 49, 50, 67, 68, 78, 81, 95, 104, 117, 119, 121, 122, 132, 134, 160, 163, 183, 184, 194, 202, 207, 213-221] de la bibliografía general).



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Original article

## An EIS study of the conservation treatment of the bronze sphinxes at the Museo Arqueológico Nacional (Madrid)



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### ABSTRACT

In any conservation project, conservators have to address several questions to design the appropriate intervention strategy. Among them, the effectiveness and duration of protective treatments is an important issue, not easy to evaluate. In the field of metallic cultural heritage, electrochemical techniques such as electrochemical impedance spectroscopy (EIS) can be used to evaluate patinas and protective coatings performance. Widely used in industrial applications, the use of these techniques in conservation science is much more recent and limited.

During the restoration process of the bronze sphinxes at the main façade of the National Archaeological Museum in Madrid, collaboration with conservators has been established to test the performance of a recently developed gel-electrolyte cell for the electrochemical evaluation of metal cultural heritage. Electrochemical measurements (EIS and Rp) of the patinas have been carried out before, during and after the conservation treatments, on two different areas of the sculpture. This has provided information on how the protective coatings have improved corrosion resistance by 3 orders of magnitude, and how this protection is starting to decrease with time; periodic measurements will allow verifying the performance of the treatment over time and detecting the failure of the protection treatment before its effects are visible on the surface.

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### Research aims

The objective of this work is to test and validate on a real situation a recently developed agar gel-polymer electrolyte (G-PE) cell specifically designed for in situ electrochemical measurements on metallic cultural heritage. These measurements allow quantifying the corrosion resistance of the patina in different areas and to assess the increase in the corrosion resistance of the metal provided by the coatings and other conservation treatments. With this development we would like to provide metal conservators with a useful diagnostic tool that allows corrosion resistance evaluation of patinas and coatings, its evolution over time and to predict the failure of the protective coatings before active corrosion starts again.

### 1. Introduction

The main façade of the National Archaeological Museum in Madrid is decorated by two bronze sphinxes, half woman, and half lioness, placed at both sides of the main staircase over a stone base. The sphinxes were designed inspired by the classical cannons by the Spanish sculptor Felipe Moratilla y Parreto, and lost-wax casted in the Madrilenian foundry Arias, in 1894. Due to their large dimensions (1.91 m high, 3.52 m depth and 1.06 m width, and around 3000 kg) they were done in several pieces and joined together.

The sphinxes have remained in the same place – with a small displacement in 1970 due to the extension of the staircase – since the inauguration of the museum on July the 5th, 1895. During 2014, following the complete refurbishment of the Museum, all sculptures in the main façade, including the sphinxes have been restored under the supervision of the Instituto del Patrimonio Cultural de España (IPCE) [1].

In any conservation project, conservators have to address several questions to design the appropriate intervention strategy. Among them, the effectiveness and duration of protective

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treatments is an important issue, not easy to assess. Fortunately, for metallic objects, electrochemical techniques can provide some answers to this problem. Among these techniques, electrochemical impedance spectroscopy (EIS) is a very well-established method to assess the anti-corrosive efficiency of protective coatings and inhibitors. However, EIS is less widespread for the study of patinas and coatings in the field of cultural heritage [2–6]. EIS is based on the application of a low-amplitude (usually 10 mV) alternating current (AC) voltage signal to the metallic sample using a conventional three electrode (working, i.e. the metal under study, reference and counter electrode) electrochemical cell. Measuring the AC current response of the system, the impedance is calculated at different frequencies. The impedance spectra profile provides information on the corrosion and other electroactive processes taking place on a metal surface. EIS can be used to quantify the effectiveness of a conservation treatment in terms of corrosion resistance gain and repetitive measurements over time allow monitoring the decrease in protection ability of these treatments, detecting failure before it is too late. Unfortunately, application of this and other electrochemical techniques in the field of cultural heritage is not always easy, especially for in situ measurements as they usually imply the use of a liquid electrolyte in contact with the surface under study – which is not easy to handle. On the other hand, the interpretation of results is usually hard work, as the irregularity and complexity of the surfaces and interferences from the environment do not always allow obtaining good quality spectra.

Since the mid 90s conservation scientists have started to use this technique in the evaluation of protective coatings for metallic cultural heritage [7–11], and in the last three decades several researchers have been working in the development of specific methodologies and portable devices to its application in the in situ evaluation of patina and coatings on outdoor sculpture and monuments [12–18]. Concurrently with the restoration process of the sphinxes and within the framework of CREMEL project (Conservation-REstoration of Metal cultural heritage with Electrochemical techniques) authors have been working in an agar gel-polymer electrolyte (G-PE) cell specifically designed for in situ measurements on cultural heritage overcoming some of the limitations of previous designs [19,20]. This cell had already been successfully tested in the evaluation of protective coatings on bronze coupons [21], but it has not yet been applied in a systematic way on a real conservation problem. Now it was a good opportunity both to test the performance of the cell on a real situation and to evaluate the effectiveness of the applied treatments on the sphinxes. The complete treatment has been published in the museum's technical bulletin [1]: The internal structure has been reinforced, and after a cleaning process, 2% benzotriazole in a water-alcohol mixture was applied, followed by three layers of Inralac. In the first layer the product was used in a 15% solution in xylene, in the second layer concentration was increased to 20% in same solvent. Then, a third layer of 30% Inralac in acetone was applied followed by 10% microcrystalline wax (Cosmolloid 80 H) in white spirit.

Electrochemical measurements were performed using the G-PE cell on the left sphinx before, during and after the restoration process. Fig. 1 shows the left sphinx during measurements before and after restoration. Measurements before restoration allowed evaluating the corrosion resistance of different areas of the sphinx. During the restoration process they gave information of the additional resistance provided by protective coatings and supported the decision on the number of layers to apply. Finally, after the restoration, periodical measurements are being done to follow the evolution of coatings over time. The objective is to detect the coating failure, i.e. the drop of resistance to initial levels, before the sculpture can be affected.

## 2. Materials and methods

Several electrochemical impedance spectroscopy (EIS) and polarization resistance ( $R_p$ ) measurements were carried out on two different areas of the southern sphinx: a greenish patina (GP) on the left arm of the sphinx and a dark patina (DP) on the left thigh of the sphinx (Fig. 1). These areas have been selected as representatives of two extreme conditions of the surface: GP is a thick, matt patina formed in areas exposed to atmospheric corrosion; and DP is a thin, semi-transparent patina remaining from the original artificial patination treatment.

Measurements have been performed with the gel polymer electrolyte (G-PE) cell previously developed by the authors [19,20]. It consists of a plastic mold in which the counter electrode (CE) and a pseudo-reference electrode (RE) are attached. The CE is made with a stainless steel mesh to maximize its surface, and the RE is a 99.9% silver wire electrochemically coated with AgCl [22]. The mold is then filled with a traditional aqueous electrolyte that has been gelled by addition of 4% (w/v) of agar powder.

The liquid electrolyte in which agar is dissolved to obtain the gel electrolyte is synthetic rain adapted from Bernardi [23]. It contains 14.43 mg/L  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 15.04 mg/L  $(\text{NH}_4)_2\text{SO}_4$ , 19.15 mg/L  $(\text{NH}_4)\text{Cl}$ , 15.13 mg/L  $\text{NaNO}_3$  and 3.19 mg/L  $\text{CH}_3\text{COONa}$ , prepared in distilled water. Synthetic rain has been chosen to mimic the corrosive environment which the sculptures are exposed to, so the interaction of the electrolyte with the metal, patina and coating is similar to actual degradation process, and the object is not exposed to other ions [24]. This solution has been used 10× concentrated with a final pH adjusted to 6.5 with  $\text{HNO}_3$ , to provide a mild electrolyte which prevents any damage to the patina, but with enough conductivity to measure. The agar powder has been dispersed in the electrolyte and heated until dissolution. After a few minutes, the liquid has been poured into the mold and left to cool until solidification. The cell is then mounted on a support with an articulated arm which allows positioning on the surface to be measured; the measurement area 5.72 cm<sup>2</sup>. A more detailed description of the cell has been provided in references [19,20]. Fig. 2 illustrates the realization of measurements on the sculptures. A closer view of the cell placed on the surface of the sculpture during measurements can be seen in Fig. 2(a), while Fig. 2(b) shows the RE and CE inside the cell, and the imprint of the surface texture on the gel. Measured areas were photographed in detail to ensure that no marks were left on the surface and that subsequent measurements were done on the same point (Fig. 3).

First data were taken in March 2014, before restoration; a second set of measurements was done in July during restoration treatment (after cleaning and first coating layer), then after restoration, in early January, May and November 2015 and in June 2016 (approximately 5, 10, 16 and 23 months later). EIS and  $R_p$  measurements were performed consecutively each patina. EIS spectra have been acquired with a Gamry 600 Potentiostat, using a frequency swept from 100 kHz to 10 mHz, 10 mV RMS amplitude and 10 points/decade. Polarization resistance ( $R_p$ ) has been measured using the same setup, performing a 0.16 mV/s swept from –10 to +10 mV vs. open circuit potential. All results have been normalized to the measurement area. Due to the limited access to the sphinxes, single measurements were made at each time. However, the reproducibility and repeatability of measurements using this system has been validated in a previous work by the authors [20].

## 3. Results and discussion

G-PE cell has shown to fulfill the requirements for in situ measurements, on rough, leaning and slightly curved surfaces. In Fig. 2, the flexibility and adaptability of the cell to the surface under study,



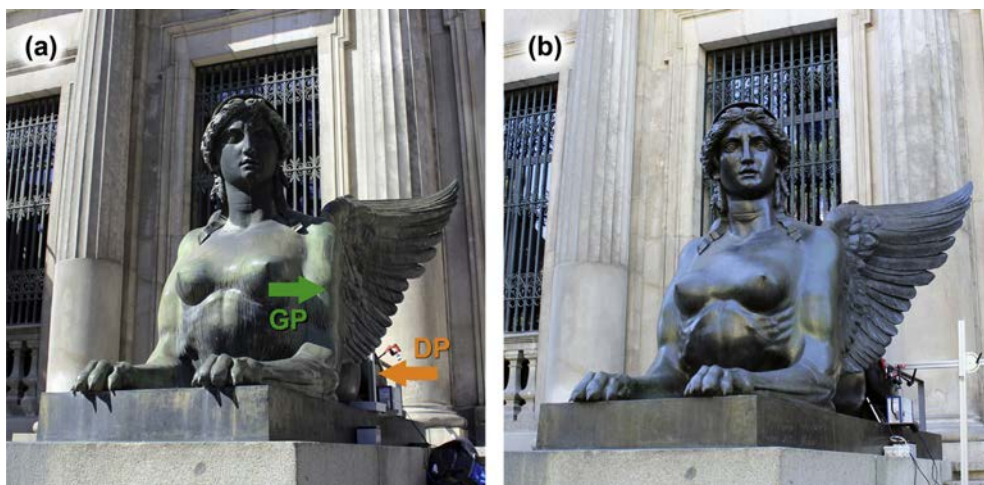


Fig. 1. Left sphinx during measurements before restoration (a) and after restoration (b). Arrows indicate the green patina (GP) and dark patina (DP) test areas.

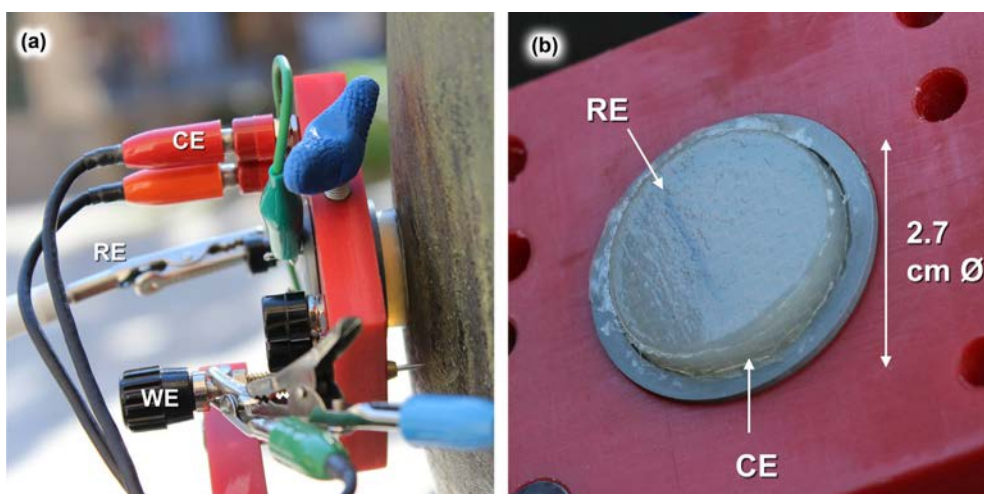


Fig. 2. Detail of the cell during measurements. It can be seen how the gel adapts to the surface of the sculpture (left) and the deformation of the cell surface after measurement (right).

following the roughness of the patina, can be appreciated. The non-destructive character of the measurements has also been verified in the worst case scenario, i.e., before protection treatment. Fig. 3 shows the visual appearance of the patinas just after removal of the gel-cell (left) and a few seconds later (right). It can be observed how the wetted area dries out immediately leaving no traces on the surface proving the non-destructive character of the technique [25]. On the long term, no visible effects have been observed after the series of measurements.

The evolution of the impedance's modulus for DP and GP is presented in Fig. 4. EIS spectra are rather noisy at the high frequency region. As the museum is located in the city center, surrounded by traffic, subway and train tunnels, the quality of EIS spectra may be affected by environmental interferences. Similar noisy spectra at high frequencies have also been observed by other authors in on-site EIS measurements in sculptures [17]. This effect is more important after the restoration process, as the application of a thick layer of Incralac highly reduces the intensity of the electric signal decreasing the signal to noise ratio. The noise of the EIS data does not allow an in-depth analysis of the corrosion and protection mechanisms from the electrochemical results. Despite this, the results clearly show some general features and trends that allow

comparing the result in different areas and study the evolution of impedance over time.

Impedance data are generally analyzed using equivalent circuits, in which passive electric elements such as resistors, capacitors, etc. are used to reproduce the electric characteristics of the system [3,24]. Thus, to interpret the results we need to consider the nature of our system, a bronze sculpture covered with a patina, to which an organic coating has been applied. The corrosion of the sculpture takes place when the rain (electrolyte), containing dissolved oxygen and atmospheric pollutants, reaches the base metal and the corrosion reactions take place. The anodic process involves the dissolution of the metal (copper and alloying elements) while the cathodic reaction is the reduction of dissolved oxygen. For the corrosion reaction to take place, several resistances (or impedances) have to be overcome. The charged species have to travel across the electrolyte, against the electrolyte resistance, and reach the coating. Conductivity through the coating has two contributions, the charge of the capacitor at both sides of the coating and the resistance through its pores, thus the impedance of a coating is usually represented by a capacitor and a resistance in parallel. The same behavior is to be expected for the patina. Finally, when the electrolyte reaches the metal surface, the corrosion process can be

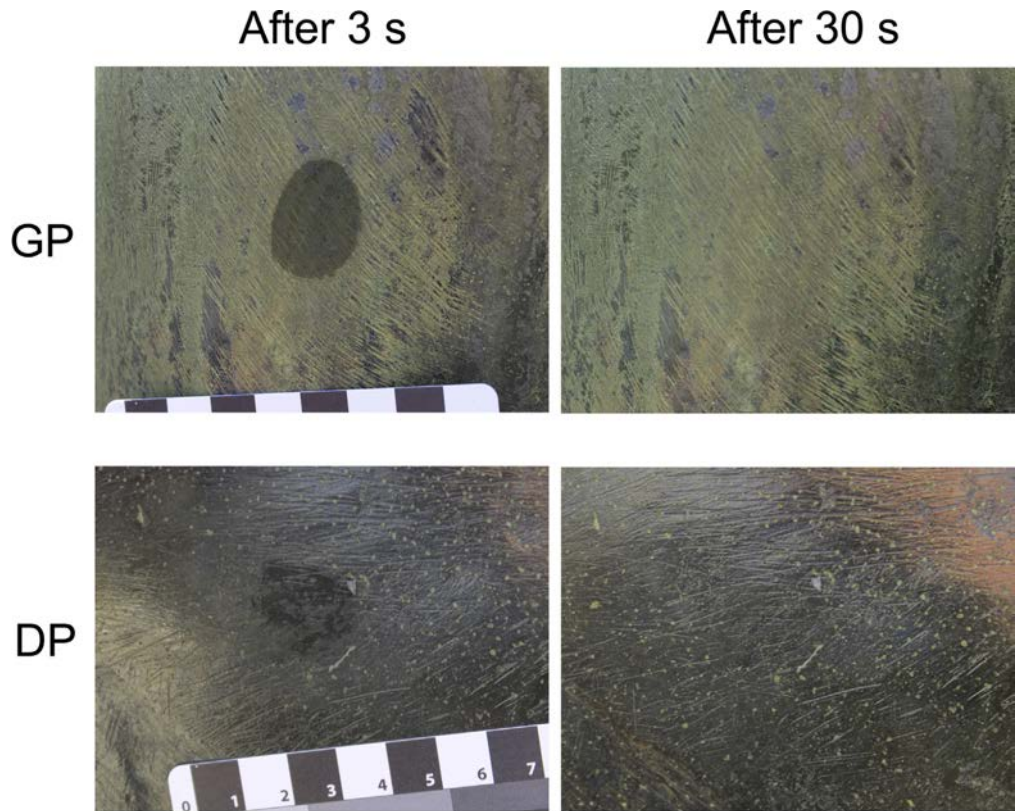


Fig. 3. Detail of the surface after measurement showing that no marks are left after it (before conservation treatment).

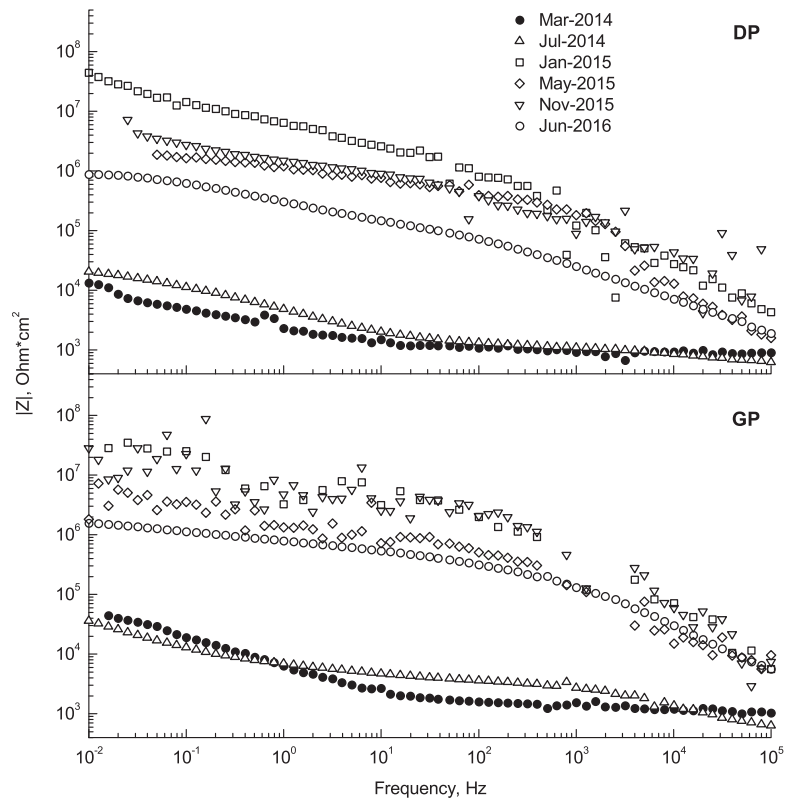


Fig. 4. Evolution of impedance modulus with time for dark patina (DP) and green patina (GP).



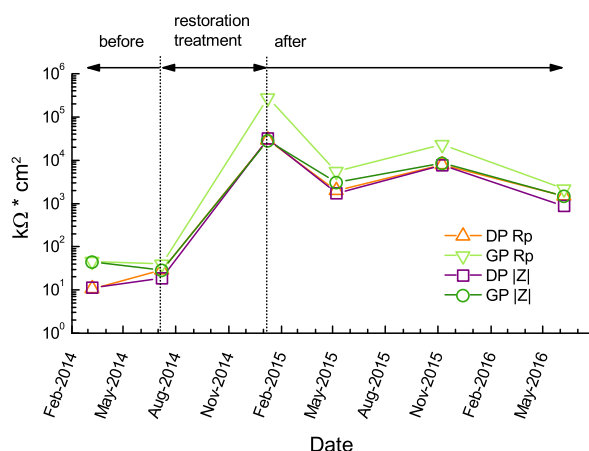


Fig. 5.  $|Z|$  limit and  $R_p$  before and after restoration treatments for dark patina (DP) and green patina (GP).

assimilated to another pair capacitor-resistance in parallel, representing the capacity of the electrochemical double layer and the charge transfer resistance. This is probably the simplest approach, in which the equivalent circuit could be represented by one resistance in series with two or three nested capacitor-resistance pairs [2,11,26,27]. In practice, circuits can get much more complicated when other physicochemical phenomena get involved and several processes overlap [28]. In the first place, these systems do not follow the ideal capacitive behavior, and constant phase elements (CPE) have to be used instead of capacitors [3] adding new calculations to obtain capacity values from CPE parameters [29]. Also, diffusion effects may appear, requiring the introduction of other elements such as Warburg impedance and in some cases, reactivity of the patina itself require the employment of transmission lines [20,30,31]. There are several good reviews about EIS of coated metals which can be consulted for further information [4,32–34].

Difficulties in the interpretation of EIS spectra from cultural heritage objects are not an unknown fact. Surface inhomogeneities together with environmental interferences in field measurements lead frequently to evaluate EIS data in terms of simplified approaches [3]. Thus the value of  $|Z|$  at the low frequency limit has been used as a measure of the protective effectiveness of the surface layers or the corrosion resistance and applied to comparative studies [5,8,10,13,35–37]. This value is the sum of the impedance of the coating plus all the other aforementioned elements (electrolyte resistance, charge transfer resistance, diffusion impedances, etc.). In the case of organic coatings, the contribution of these other elements is usually much smaller than the coating impedance, so the film resistance dominates the spectra at low frequencies. Although a deeper interpretation would be desirable, information given by this simplified approach has proven to be effective to assess the protective properties of coating systems for outdoor bronze monuments and its evolution over time [5,37].

The variation of the impedance module,  $|Z|$ , at the lower frequencies for DP and GP on successive measurements, together with the  $R_p$  values are represented in Fig. 5. Although the EIS spectra were acquired from 100 kHz to 10 mHz, 15.8 mHz has been used as lowest frequency limit as some points are missing at the lowest frequency value. From this figure, several facts can be pointed out, supported both by  $|Z|_{15.8mHz}$  and  $R_p$  results. Before restoration (March 2014) GP was about 5 times more protective than DP, while after treatments, both areas showed similar behavior. From data of July 2014 it is clearly appreciated that the first protective coating with 2% benzotriazole and 15% Incralac does not give an appreciable protection, as  $|Z|$  has barely increased from its initial value, thus

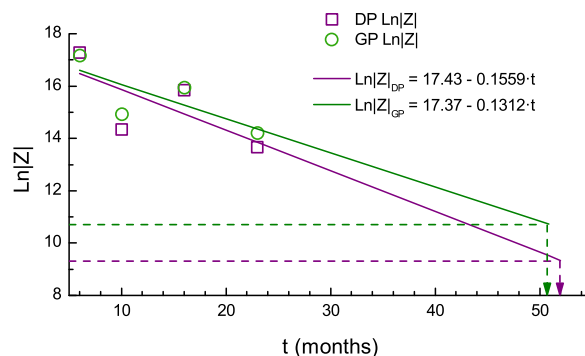


Fig. 6. Lifetime prediction of coatings from EIS data, based on a first order kinetic approach.

justifying the need of additional varnish layers. After the whole protection treatment has been applied,  $|Z|$  has increased three orders of magnitude as can be observed in the measurement done in January 2016. Differences between DP and GP are now insignificant, indicating that the coating is the main responsible for protective properties of the system, thus being the patina contribution negligible. From this moment, the resistance of the coating begins a slow decay, although two years after application it is still offering a good protection when compared with the initial results before restoration. It also appears to be a seasonal effect that may increase resistance values in cooler months (comparing Jan. and Nov. 2015 vs. May 2015 and Jun. 2016); higher temperatures may induce higher conductivity of the aqueous solutions that penetrate into the coating and cause a progressive reduction of the impedance, as well as increase the anodic and/or cathodic corrosion reaction rates. This effect of temperature on measurements is currently under study.

Overall, there is a good agreement between  $R_p$  and  $|Z|$  values, showing similar results and the same evolution with time, validating the approach of using  $|Z|$  at low frequencies as measure of the corrosion resistance of the system. In the case of GP after the whole protection treatment, some discrepancy between these parameters seems to appear. This might be related with diffusion or other phenomena that are disregarded by the simplification of taking the values of  $|Z|$  at low frequencies, or with inaccuracy of the estimation of this value in the noisy spectra. In any case, the evolution of both parameters shows the same pattern, leading to the same conclusions.

Although we have not enough experimental data for inferring a kinetic model for coating's resistance decay, we can try to obtain a rough estimate on the duration of our coating. Some attempts have been done to develop models or equations to predict service life for industrial coatings. Studies from Bierwagen et al. have found that the evolution of  $|Z|$  values in the low frequency portion of the spectrum that can be fit by a simple exponential decay function in time [38,39]. Fitting the values of  $|Z|$  to a simple first order equation:  $\ln|Z| = \ln|Z|_0 - kt$  (where  $|Z|$  is the variation of  $|Z|_{15.8mHz}$ ,  $|Z|_0$  the value before treatment in  $k\Omega$ ,  $k$  is the rate constant and  $t$  the time in months) and calculating the time for  $|Z|$  decay to its initial value, i.e. before restoration, the sphinx's coating will fail in about 4 years (Fig. 6).

This result is in agreement with previously reported duration of this kind of coatings, as long-term protection coatings for cultural heritage are estimated for 5–10 year service [40]. According to Brostoff, Incralac coatings are expected to last 3–5 years in outdoor environments [41] while some authors report up to 9 years with topcoats of wax and regular maintenance [42]. It is clear that the duration of the coating depends on too many factors such as substrate characteristics, thickness, regularity, defects and

environment, so a regular monitoring of the performance of the coating would be necessary for each individual artifact.

#### 4. Conclusions

This study has validated the utility and applicability of the agar gel polymer electrolyte (G-PE) cell for protective treatments evaluation on outdoor bronze sculpture. It has proven to be convenient for field measurements and has allowed carrying out electrochemical measurements on different positions and orientations of the surface of the monument.

On-site EIS and Rp results obtained using the G-PE cell have demonstrated to be a useful tool for conservation treatments assessment. Experimental data have shown the effectiveness of the protection layers and allowed to follow its evolution. Assuming an exponential decay of coating resistance, a rough estimation of the coating's duration can be extrapolated to about 4 years.

The systematic application of the G-PE cell in future work to a wider collection of outdoor sculpture will allow refining the model and obtaining more accurate predictions. This will help to establish a calendar for periodic inspections and design an efficient maintenance plan for these collections.

#### Acknowledgments

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#### 4.3.2.2 Las esculturas de la Universidad Politécnica de Valencia.

La Universidad Politécnica de Valencia cuenta con una importante colección de escultura contemporánea que se localiza en el campus de Vera. Dentro de esta colección se realizaron medidas de dos esculturas en bronce diferentes: *Unidad Yunta* (1970), de Pablo Serrano, y *Crónica del Viento* (1991), de Martín Chirino. Las dos esculturas se sitúan en los jardines del campus, que se encuentra a aproximadamente 1.9 km de la playa de la Malvarrosa.

Por su situación, las esculturas están expuestas tanto al agua de riego, como al aerosol marino. Estudios realizados por investigadores de la UPV y la UV [222, 223] han puesto de manifiesto que los productos principales de corrosión en estas obras son la cuprita, acompañada de carbonatos básicos de cobre y trihidroxicloruros de cobre. Los primeros aparecen en las muestras tomadas cerca del suelo y por tanto expuestas al agua de riego (con alto contenido en carbonatos en la región de Valencia), mientras que en zonas más elevadas predominan los cloruros, por influencia del aerosol marino. En algunas obras como es el caso también se han encontrado zonas en las que predominan trihidroxicloruros de cobre acompañados de abundantes agregados de anglesita ( $\text{PbSO}_4$ ) y otros compuestos de plomo. Esto se explica por la segregación del plomo, uno de los componentes característicos del bronce de la escultura tradicional, que es insoluble en el cobre a temperatura ambiente

##### *Unidad Yunta*



**Figura 38.** *Unidad Yunta* (1970), Pablo Serrano.

La escultura *Unidad Yunta* está formada por dos piezas redondeadas, enfrentadas entre sí, situadas sobre una gran losa rectangular. Cada una de ellas consta de dos partes diferenciadas, una cara interna, con una pátina lisa de color marrón, y una cara externa, con una pátina rugosa con zonas diferenciadas de tonalidades negruzcas y blanquecinas.

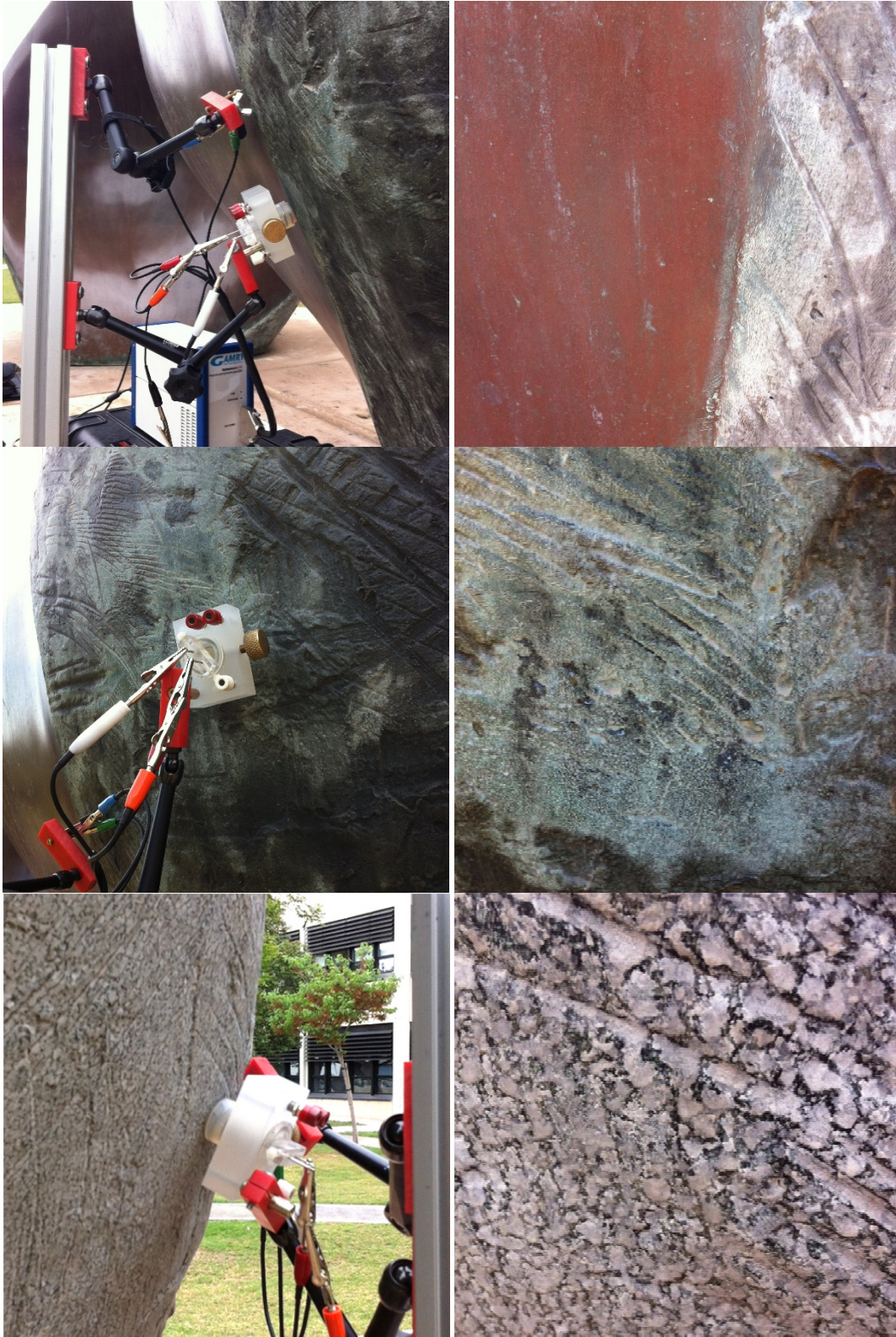
La pátina de la cara interna es fina, uniforme y de aspecto pulido, mientras que la pátina de la cara externa es muy irregular y presenta zonas de aspecto muy diferente. Debido a las grandes diferencias en el aspecto de las patinas se consideró interesante realizar una medida en cada una de las tres zonas con textura diferente y comparar los resultados. Además, se midió el espesor de cada una de las zonas utilizando el medidor de espesores Elcometer 456. Como se puede ver según los resultados recogidos en la tabla 8 (valores para 20 medidas), la pátina de la cara interna es fina y de espesor uniforme, mientras las patinas negra y blanquecina de la cara externa tienen mayores grosores y son más irregulares. Esto es apreciable a simple vista, especialmente en la pátina blanquecina.

**Tabla 8.** Medidas de espesor en las tres zonas de la pátina.

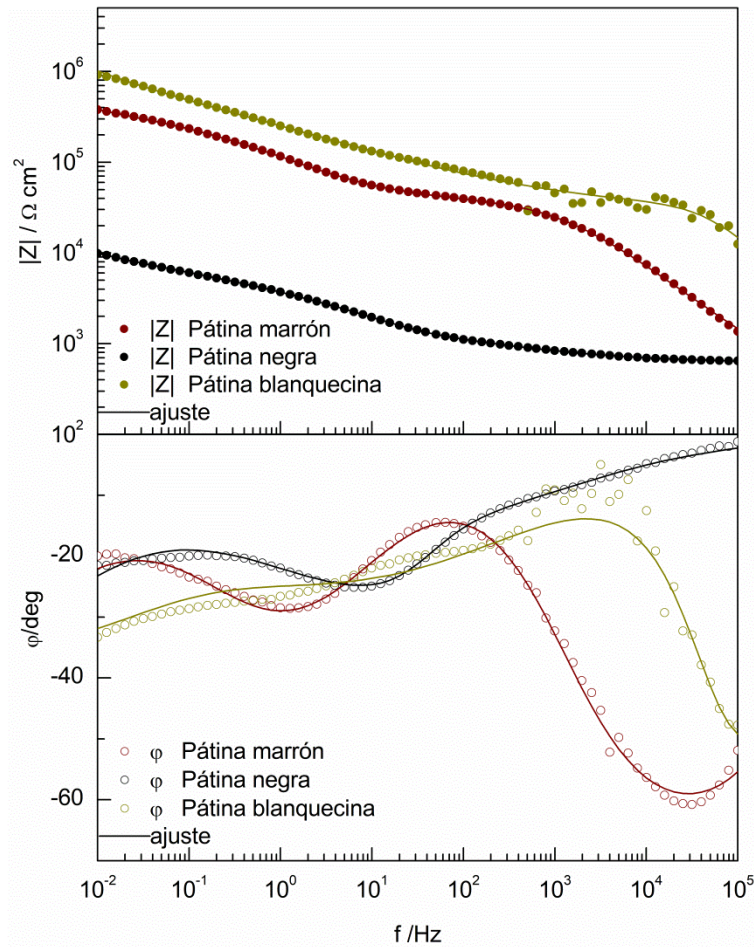
Grosor ( $\mu\text{m}$ )	Patina marrón	Patina negra	Patina blanquecina
Promedio	13.4	42.5	81.3
Desviación	2.9	11.5	24.0
Max.	19.1	69.9	122
Min.	8.6	23.1	44.7

En la figura 39 se pueden ver en detalle las diferentes texturas de la pátina y la realización de cada una de las medidas. Los espectros de impedancia se pueden comparar en la figura 40. Las medidas obtenidas sobre la pátina marrón y la pátina negra y la pátina blanquecina pueden ajustarse equivalente general (tabla 9), aunque la para medida sobre la pátina blanquecina el ajuste es aproximado.





**Figura 39.** Detalle de las tres diferentes texturas de la pátina de la obra *Unidad Yunta* medidas por EIS. De abajo a arriba: pátina marrón, pátina negra y pátina blanquecina.



**Figura 40.** Diagrama de Bode obtenido de los espectros de impedancia de las tres pátinas de la obra *Unidad Yunta*.

**Tabla 9.** Valores del máximo del módulo de la impedancia y resultados del ajuste al circuito equivalente  $R_s(R_1CPE_1[CPE_2[R_2W]])$  de los espectros de las pátinas.

	Pátina marrón	Pátina negra	Pátina blanquecina
$ Z _{10\text{mHz}} \text{ ohm}\cdot\text{cm}^2$	3.80E+05	9.92E+03	9.21E+05
$\text{Re} (\Omega\cdot\text{cm}^2)$	$340 \pm 40$	$610 \pm 10$	$4000 \pm 1000$
$Y_1 (\text{S s}^{\alpha_1} \text{cm}^{-2})$	$2.5 \pm 0.1 \text{ E-}08$	$9 \pm 1 \text{ E-}05$	$1.1 \pm 0.6 \text{ E-}10$
$\alpha_1$	$0.77 \pm 0.01$	$0.41 \pm 0.02$	$1.00 \pm 0.04$
$R_1 (\text{k}\Omega\cdot\text{cm}^2)$	$36.5 \pm 0.8$	$1.8 \pm 0.6$	$26 \pm 2$
$Y_2 (\text{S s}^{\alpha_2} \text{cm}^{-2})$	$3.3 \pm 0.1 \text{ E-}06$	$3 \pm 3 \text{ E-}06$	$1.7 \pm 0.1 \text{ E-}06$
$\alpha_2$	$0.57 \pm 0.02$	$0.9 \pm 0.2$	$0.39 \pm 0.01$
$R_2 (\text{k}\Omega \text{cm}^2)$	$310 \pm 20$	$6.2 \pm 0.8$	$800 \pm 100$
$\sigma_w (\text{S}\cdot\text{s}^{1/2}/\text{cm}^2)$	$2.7 \pm 0.3 \text{ E-}05$	$6.3 \pm 0.4 \text{ E-}04$	$2.3 \pm 0.4 \text{ E-}06$

Las tres zonas medidas presentan diferentes valores de impedancia, lo que resulta coherente con las diferencias observadas entre las pátinas. La zona con menor impedancia, corresponde a la pátina negra irregular, mientras que las dos áreas con aspecto más regular y compacto, ofrecen una impedancia superior en un par de órdenes de magnitud. Es razonable que las pátinas compactas y homogéneas ofrezcan una protección superior a la zona de la pátina negra, de textura irregular y porosa.

Por otro lado, y aunque no se tiene un análisis de la zona de medida correspondiente a la pátina negra, esta es una de las esculturas en las que el estudio realizado por la UPV-UV detectó zonas con elevada concentración de plomo, lo que podría haber contribuido a este resultado.



### *Crónica del viento*

La segunda obra, *Crónica del Viento*, está formada por una espiral de bronce, situada a nivel de suelo y apoyada sobre un conjunto de losetas de piedra. Por los restos que se observan en algunas zonas, se piensa que la escultura pudo tener un recubrimiento en algún momento



**Figura 41.** Escultura *Crónica del Viento* (1991), Martín Chirino.

En esta obra también se han realizado tres medidas, una en la parte superior frontal de la espiral, otra en la cara posterior, y otra en la zona abierta de la espiral, donde aparecen restos del posible recubrimiento. Se trata de una capa porosa, compuesta por carbonato de calcio y arcillas [222]. En las otras dos zonas de medida el metal se encuentra recubierto únicamente por una pátina oscura, bastante fina y desgastada, especialmente en la parte frontal, aunque en algunas zonas menos expuestas también se observan restos de color blanquecino. Las medidas de espesor realizadas confirman la delgadez de la pátina oscura, a diferencia de la zona recubierta.

**Tabla 10.** Medidas de espesor en las tres zonas de la pátina.

Grosor ( $\mu\text{m}$ )	Zona superior	Zona posterior	Recubrimiento
Promedio	17.0	23.0	75.8
Desviación	4.9	6.1	27.5
Max.	26.3	34.4	154
Min.	7.9	8	43.1

En la figura 42 se muestra el detalle de las tres medidas realizadas y a continuación los espectros de impedancia obtenidos (figura 43). Las medidas realizadas en la parte cerrada de la espiral, en el anverso y reverso son bastante similares, siendo mayor la impedancia en el reverso, que se encuentra más resguardado. El ajuste de los espectros al circuito equivalente general (tabla 11) da algunos valores muy próximos, a pesar de las diferencias importantes en los espesores medidos. La falta de capacidad protectora de la zona con recubrimiento se puede explicar por la alta porosidad y deterioro de la misma, que hace que no tenga un efecto protector significativo.



**Figura 42.** Detalle de las medidas realizadas en la obra *Crónica del viento*: zona superior de la espiral, zona posterior y zona con restos de recubrimiento.



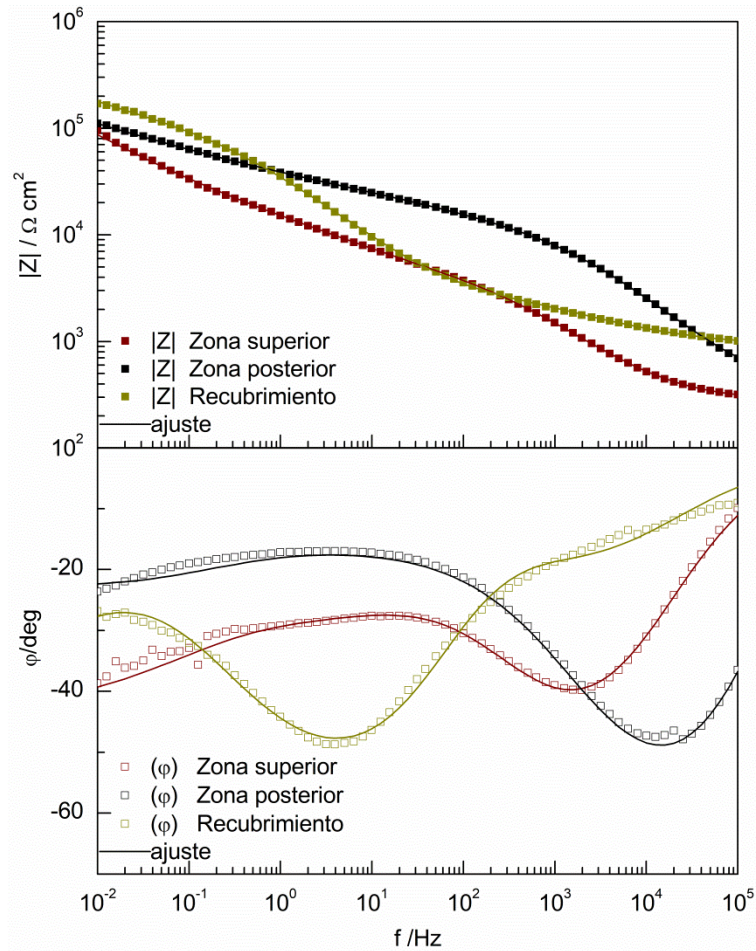


Figura 43. Espectros de impedancia obtenidos en tres zonas de la obra *Crónica del viento*.

Tabla 11. Valores del máximo del módulo de la impedancia y resultados del ajuste mediante el circuito equivalente general de los espectros de las pátinas de la obra *Crónica del Viento*.

	Zona superior	Zona posterior	Recubrimiento
$ Z _{10\text{mHz}} \text{ ohm}\cdot\text{cm}^2$	9.52E+04	1.10E+05	1.70E+05
Re ( $\Omega\cdot\text{cm}^2$ )	276 ± 7	370 ± 30	900 ± 30
CPE1			
$Y_1 (\text{S s}^{\alpha_1} \text{cm}^{-2})$	1.7 ± 0.3 E-06	8 ± 3 1E-08	5 ± 2 E-06
$\alpha_1$	0.67 ± 0.02	0.76 ± 0.03	0.54 ± 0.03
R1( $\text{k}\Omega\cdot\text{cm}^2$ )	4.0 ± 0.6	4 ± 3	2.5 ± 0.5
CPE2			
$Y_2 (\text{S s}^{\alpha_2} \text{cm}^{-2})$	2.5 ± 0.3 E-05	1.6 ± 0.2E-05	4 ± 1 E-06
$\alpha_2$	0.47 ± 0.04	0.23 ± 0.02	0.72 ± 0.04
R2 ( $\text{k}\Omega \text{cm}^2$ )	33 ± 9	160 ± 60	140 ± 20
$\sigma_w (\text{S}\cdot\text{s}^{1/2}/\text{cm}^2)$	2.26E-05	2.24E-05	6.02E-06

#### 4.3.2.3 Obras en el Museo de Escultura de Leganés.

El Museo de Escultura de Leganés es un museo de escultura al aire libre, que nace en el año 1984, y cuenta con una colección de escultura española desde finales del siglo XIX hasta nuestros días. Parte de las obras que alberga proceden del desaparecido Museo Español de Arte Contemporáneo, en Madrid, habiendo sido depositadas en el museo gracias a un convenio entre el Ayuntamiento y el Museo Nacional Centro de Arte Reina Sofía, titular de las mismas [224]. Dentro del museo se realizaron medidas sobre dos esculturas de bronce y tres esculturas en acero patinable.

##### *Esculturas en bronce: Hachero y El Segador*

Se trata de dos esculturas de bronce patinado en negro de diferentes autores y realizadas en momentos diferentes. *Hachero*, obra de Luis Marco Pérez (1926) y *El Segador*, realizada por Venancio Blanco (1970).



Figura 44. *Hachero* (izquierda) y *El Segador* (derecha) en el Museo de Escultura de Leganés.

El interés de realizar medidas en estas dos esculturas radicaba en poder comparar los resultados obtenidos en dos obras de bronce que, si bien habían sido realizadas en momentos muy distintos, sí que llevaban expuestas en un mismo entorno durante varias décadas. Por otra parte, a pesar de ser obras de autores diferentes es probable que ambas fueran realizadas en la misma fundición. La obra *Hachero* fue realizada en la Fundición Codina, en Madrid, apareciendo la firma de la fundición en la escultura; y aunque en la escultura *El Segador* no hay una firma visible, sabemos que Venancio Blanco trabajó con esta misma fundición. En cualquier caso, es razonable suponer que la técnica y materiales de ambas esculturas es la misma, un bronce cuaternario con una pátina realizada a base de sulfuro potásico.



**Figura 45** Firma de la fundición en la obra *Hachero*

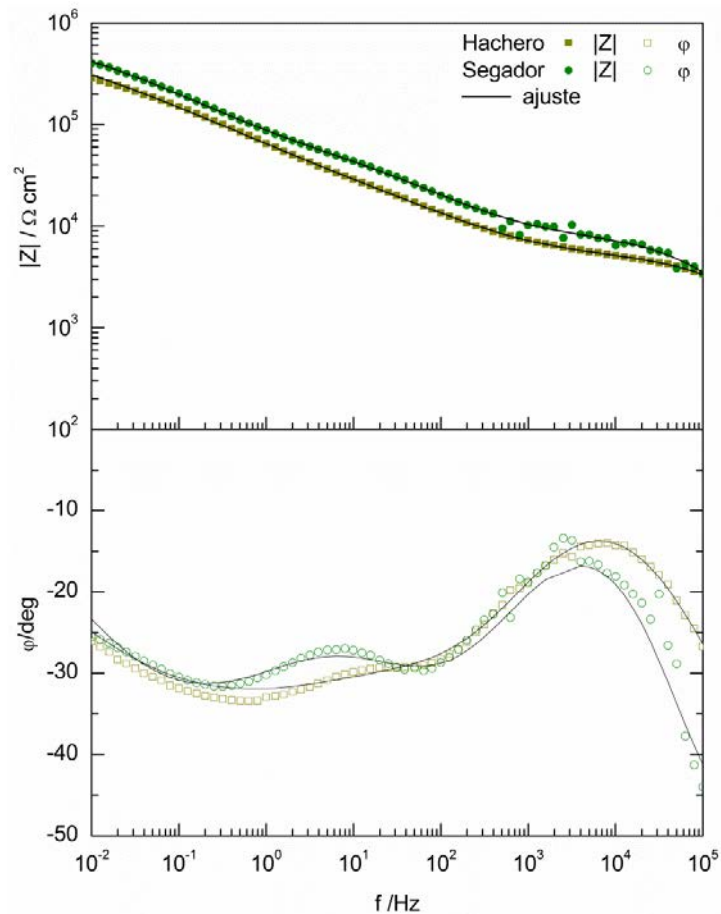


**Figura 46.** Iluminación irregular sobre la escultura *Hachero* (izquierda) y realización de la medida protegiendo la zona de la luz.

Estas esculturas no han sido aún estudiadas en profundidad, y únicamente ha sido posible obtener un par de espectros. Las medidas en estas obras, en especial en el caso de *El Segador*, no han resultado sencillas. Al estar situadas en un jardín, con mucha vegetación, la brisa modifica la posición de las hojas de los árboles que dan sombra sobre el bronce. Se ha podido observar que las variaciones de luz sobre las superficies de bronce provocan oscilaciones en el potencial, lo que a su vez puede relacionarse con la inestabilidad de las medidas; este efecto estaría relacionado con propiedades semiconductoras y fotoquímicas de la cuprita [225-227]. Para minimizar este efecto se ha empleado un parasol para mantener una sombra constante en la zona de medida (figura 46).

A pesar de estas limitaciones, podemos ver la coincidencia los dos espectros de impedancia tomados en cada una de las obras (figura 47). Este ejemplo permite ilustrar la capacidad de la celda diseñada para medir la respuesta característica de una escultura en bronce tradicional, y comprobar como a pesar de la diferencia de tiempo en su fabricación, la exposición a un medio similar durante varias décadas ha desarrollado sobre las obras una pátina con una capacidad protectora prácticamente idéntica.





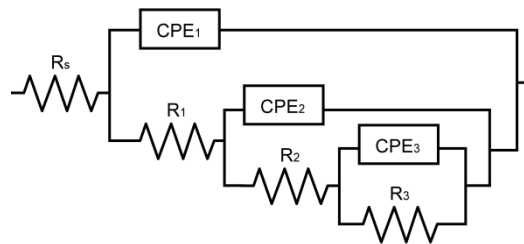
**Figura 47.** Espectros de impedancia obtenidos en las obras Hachero (Luis Marco Pérez, 1926) y *El Segador* (Venancio Blanco, 1970).

El ajuste de los espectros de impedancia en este caso al circuito equivalente general no es muy bueno, ajustándose mejor a un circuito equivalente formado por tres subcircuitos R-CPE anidados (figura 48), aunque para la figura *El Segador* no se puede calcular el valor de la resistencia del electrólito. Este modelo, propuesto por Marušić et al. [79, 81, 87, 112] es uno de los modelos aceptados para la descripción del comportamiento de bronce patinado [190]. En este caso el primer par R-CPE representa capacidad y resistencia la pátina, el segundo par R-CPE la doble capa eléctrica y la resistencia de transferencia de carga y el tercer par R-CPE está asociado a procesos redox en la superficie del electrodo.



**Tabla 12.** Resultados del ajuste de los espectros de impedancia de dos esculturas en bronce en el Museo del Leganés a un circuito equivalente con tres pares R-CPE anidados

	Hachero	El Segador
Re ( $\Omega \cdot \text{cm}^2$ )	700±300	0±700
CPE1 $Y_1$ ( $\text{S s}^{\alpha_1} \text{cm}^{-2}$ )	2±1E-09	4 ±4E-08
$\alpha_1$	0.87±0.05	0.62±0.08
R1( $\text{k}\Omega \cdot \text{cm}^2$ )	6400±500	5600±900
CPE2 $Y_2$ ( $\text{S s}^{\alpha_2} \text{cm}^{-2}$ )	1.4±0.3 E-06	1.2±0.6E-06
$\alpha_2$	0.57±0.03	0.64±0.06
R2 ( $\text{k}\Omega \text{cm}^2$ )	55.5±0.9	14.9±6
CPE3 $Y_2$ ( $\text{S s}^{\alpha_2} \text{cm}^{-2}$ )	5.3±0.2E-06	7.0±4E-06
$\alpha_2$	0.49±0.02	0.40±0.01
R3 ( $\text{k}\Omega \text{cm}^2$ )	770±60	870±70



**Figura 48.** Circuito equivalente formado por tres pares R-CPE anidados utilizado para representar el comportamiento de bronce patinado.

### *Esculturas en acero patinable:*

La mayor parte de las medidas realizadas en el Museo de Escultura de Leganés se han centrado en esculturas de acero patinable, con el objetivo de ensayar la celda en este tipo de material. El acero patinable es un metal muy apreciado en escultura contemporánea por las cualidades plásticas y por la capacidad protectora de la pátina que se forma sobre él, en comparación con el hierro o el acero al carbono. Sin embargo, como ya se ha comentado, la formación de una pátina protectora es un proceso lento, y que requiere unas condiciones determinadas; la ubicación, geometría u otros factores pueden afectar a la formación y propiedades de la pátina. Así, el objetivo de esta serie de medidas ha sido ensayar la celda en este tipo de material y comprobar su capacidad para determinar diferencias de comportamiento de las pátinas de una misma obra en función de su posición o geometría. Las obras sobre las que se han realizado las medidas han sido:

- *Zenon*, José Luis Sánchez (1980)
- *Templo*, Adriana Veyrat (2003)
- *Once Módulos*, Amador Rodríguez (1971)

La realización de las medidas sobre obras de acero patinable presenta ventajas y desventajas sobre las medidas realizadas en bronce. Por un lado, la adaptación del gel a la superficie es mucho más sencilla. Aunque la herrumbre sobre los aceros tiene una textura irregular, al tratarse de obras realizadas a base de uniones de planchas de metal, la superficie suele ser plana o suavemente curvada, sin el relieve de una obra fundida, lo que facilita mucho el posicionamiento y adaptación de la celda. La principal dificultad que se ha encontrado a la hora realizar medidas de campo sobre esculturas de acero patinable ha sido en establecer un buen contacto eléctrico con la superficie metálica. La menor conductividad del material junto con la continuidad de las capas – no existiendo zonas de desgaste pulidas como en el bronce- o el grosor en algunos casos de las capas de óxido, dificulta el contacto y la realización de las medidas. Esto fue especialmente complejo en el caso de la primera obra estudiada, *Zenon*, que además presenta la particularidad de ser una pátina tratada con cera. Aunque debido a la calidad de los espectros y a la particular composición y estructura de la pátina no ha sido posible realizar un ajuste y una interpretación en profundidad, estos resultados sí han servido para ilustrar las posibilidades de la celda para medir sobre este tipo de superficies.

## **In situ evaluation of outdoor sculpture with a gel polymer electrolyte cell**

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**ABSTRACT:** A gel polymer electrolyte cell is presented as a tool for diagnostic on outdoor metal sculptures. In this cell, a traditional liquid electrolyte has been gelled with agar, providing a solid but flexible electrolyte which adapts to lean and irregular surfaces. This design overcomes the difficulties of carrying out electrochemical measurements to evaluate corrosion resistance on non-flat surfaces of sculptures with a traditional liquid cell. An example of the different corrosion resistance assessed using this cell in different areas of a weathering steel sculpture (*Zenon*, by Jose Luis Sánchez) is shown.

### 1. INTRODUCTION

In the past few decades, development of new analytical techniques applied in the field of cultural heritage has been focused on the development of non-invasive techniques and portable instrumentation. The availability of handheld techniques that can be directly applied in situ and without sampling opens a lot of new possibilities in the area of heritage studies and conservation science.

Focusing in the field of metallic cultural heritage, besides general analytical techniques, electrochemical methods are of particular interest for conservation assessment. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) can give information on corrosion processes, corrosion rates and on the protective properties of coatings and inhibitors used in conservation treatments. In situ application of electrochemical techniques has to deal with some practical difficulties, being the one of the main challenges how to attach an electrochemical cell filled with a liquid electrolyte on the irregular surface of a sculpture. To overcome this problem we have developed an electrochemical cell, with a classical three-electrode design, in which the liquid electrolyte has been gelled with agar (Cano et al., 2014). The agar concentration has been selected after evaluating the performance of the electrolyte at different concentrations on electrochemical measurements on bronze coupons (Ramírez Barat and Cano, 2015b).

This cell has several advantages:

- As the electrolyte is solid, there is no risk of leaching,

- The gel flexibility allows it adapting to irregular surfaces.
- Different aqueous electrolytes can be employed for different purposes and besides, agar is a conducting material, which facilitates the measurements and even allows its use with distilled water in the case we don't want to introduce any external ion.

In this study the electrolyte is composed of an artificial rain solution, to imitate the environment which sculptures are exposed to.

The cell has been tested in different materials (copper, bronze, weathering and stainless steel, etc.) on laboratory coupons and in field measurements, and used for monitoring the evolution of patinas and coatings over time (Ramírez Barat and Cano, 2015a, Ramírez Barat et al., 2017, Crespo et al., 2017). An example of measurements on a weathering steel sculpture is presented to show the applicability of the gel polymer electrolyte (G-PE) cell for the conservation assessment of metallic outdoor sculpture.

### 2. MATERIALS AND METHODS

#### 2.1. The electrochemical cell

The cell follows the conventional three-electrode design, with a pseudo-reference electrode made of a AISI 316L stainless steel wire and a stainless steel spiral as the counter electrode, inside a cylindrical plastic mold. The artificial rain solution employed as electrolyte (Bernardi et al., 2008) has the following composition: 14.43 mg/l  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 15.04 mg/l  $(\text{NH}_4)_2\text{SO}_4$ , 19.15 mg/l  $(\text{NH}_4)\text{Cl}$ , 15.13 mg/l  $\text{NaNO}_3$ , 3.19 mg/l  $\text{CH}_3\text{COONa}$ ; due to its low conductivity, it has

been used 10-fold concentrated. A small amount of agar (3% w/v) is added to the liquid electrolyte and heated until complete dissolution, then poured inside the mold and left to cool. When the agar solidifies the outer part of the mold is removed leaving a gel cylinder which is placed in contact with the surface under study.

## 2.2. Electrochemical measurements

EIS measurements have been carried out with a Gamry Reference 600 potentiostat using a frequency swept from 100 kHz to 10 mHz, with a perturbation of 10 mV RMS amplitude at the open circuit potential and 10 points/decade. Measurements were done after 30 minutes of stabilization time. All results have been normalized to the measurement area, which is 3.14 cm<sup>2</sup>.

## 2.3. Zenon

Zenon (figure 1) is a weathering steel sculpture made by the Spanish sculptor José Luis Sánchez in 1980. The sculpture is owned by the Museo Nacional Centro de Arte Reina Sofía and since 2001 located outdoors in the Museo de Escultura de Leganés. According to the information from the museum, the author used to apply wax finishing to his works.



Figure 1. General view of the Zenon sculpture.

## 3. RESULTS

The sculpture has a nice smooth dark brown patina, which is apparently in good condition,

although some areas present a more irregular surface. In order to assess the differences in the protective properties of the patina in these areas, EIS measurements were carried out in three areas with different orientations: Zenon 1 was measured on a vertical smooth area (fig 2a), with south-west orientation. Zenon 2 (fig 2b) corresponds to on a sheltered area, in the south-east face. Zenon 3 on a vertical rough area (fig 1c) faced north-west. As shown in figure 1d, the flexibility of the gel cell allows it to adapt to the irregular texture of the patina.

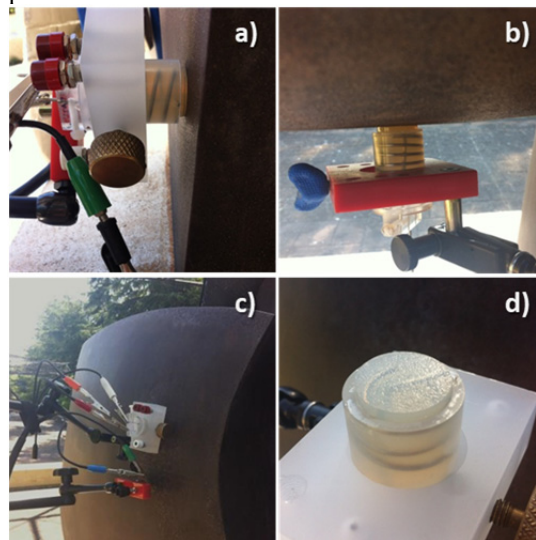


Figure 2. Different measuring areas on the weathering steel sculpture (a-c) and aspect of the gel surface after removal (d).

Results from the EIS measurements are presented in figure 3. Phase angle results are rather noisy at about 1 kHz, but notwithstanding this, the spectra show a good quality and allow comparing the different patinas.

The three patinas show an impedance modulus value at the lowest frequencies of above 2 KOhm·cm<sup>2</sup>. This is an empirical value generally accepted to classify a weathering steel patina as protective (Kihira et al., 1989), although strictly speaking, this criterion is only valid for natural patinas, without coatings and in relation to a given thickness. The most relevant feature of the spectra is that the results greatly differ from one area to the other. Differences are especially relevant in the mid-frequencies area of the spectra (1-100 Hz), which correspond to the protective properties of the patina and/or coating, with more than one order of magnitude of difference between the lowest resistance (Zenon 3) and the highest (Zenon 1). This different behavior can be related

with the appearance of the patina: Zenon 1 is smooth and homogeneous in color and texture, while Zenon 3 is rough and heterogeneous. Also, this seems to have a certain relation with the orientation. Zenon 1 is faced to the south-west, receiving direct sunlight most part of the time, while Zenon 3, in a shadier face, may remain humid for longer periods after raining or morning dew. Zenon 2, presenting an intermediate impedance value, was done in a face-down plane, thus, less exposed to the rain. It should be reminded that the development of a protective patina requires specific conditions, including dry and wet cycles. Therefore, the different behavior of the different surfaces can be explained by different local conditions, such as the different wetting-drying cycles dynamics.

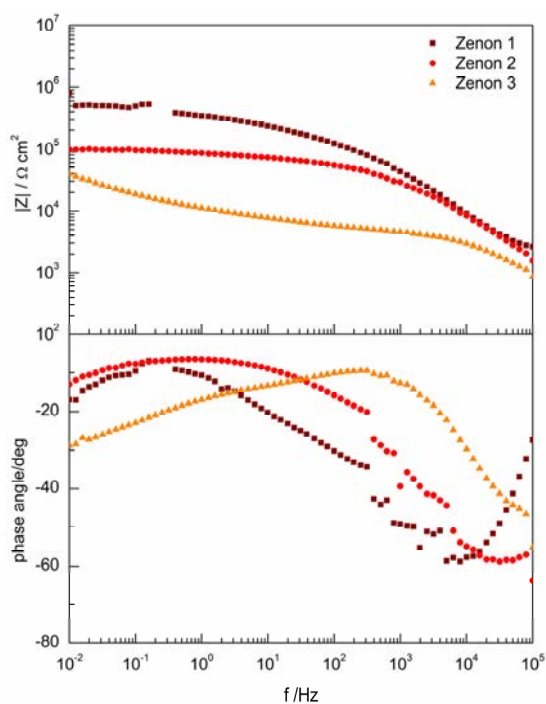


Figure 3. Bode plot of EIS measurements in three different areas of the sculpture.

#### 4. CONCLUSIONS

Agar cell has proved to be a suitable tool to carry out in-situ EIS tests on metallic cultural heritage, where the use of traditional cells is not possible. The use of a gelled electrolyte allows measuring in vertical or face down areas. It also adapts to surface texture.

In this example the G-PE cell has allowed to assess the protective properties of different areas of the Zenon sculpture. EIS results have shown

that different areas of the same sculpture present important differences in their corrosion resistance, which can be related to differences in surface and position.

#### 5. ACKNOWLEDGEMENTS

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#### 6. REFERENCES

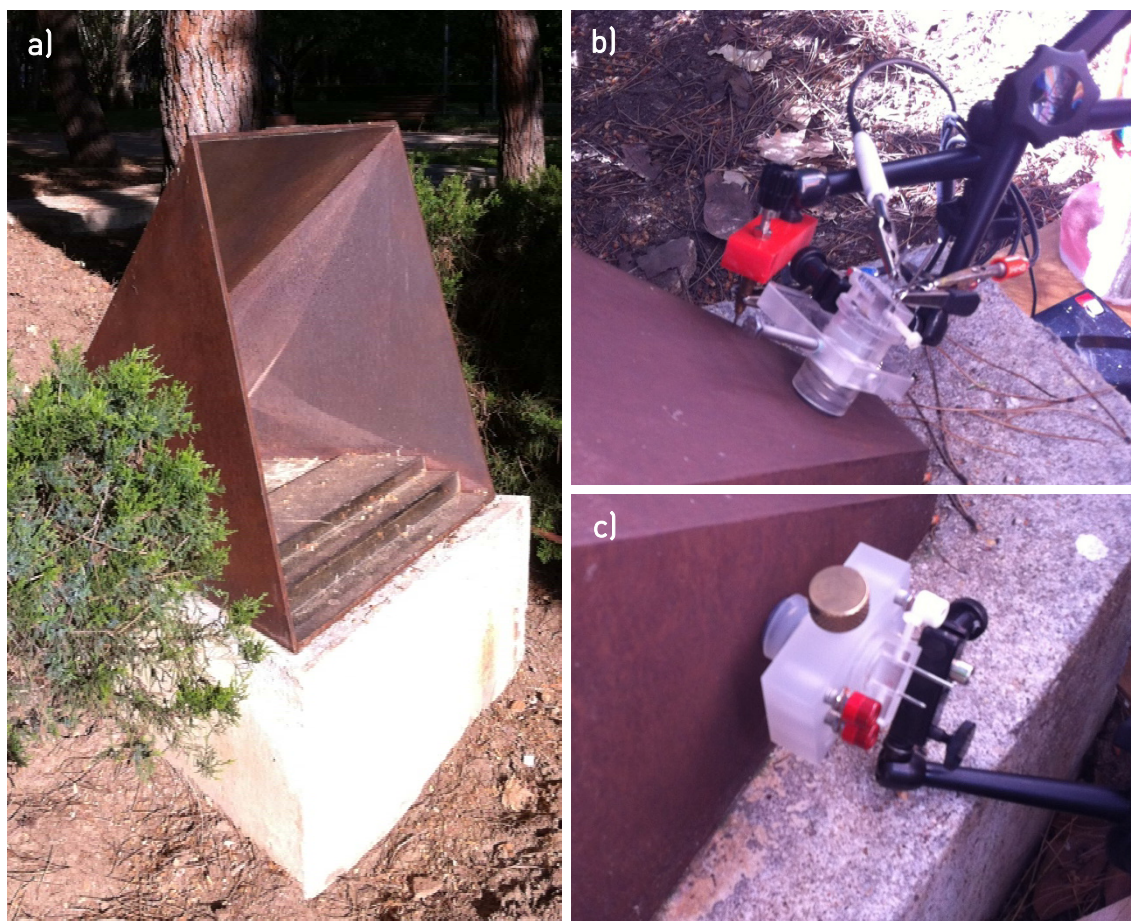
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Sobre las otras dos obras mencionadas se han realizado diferentes series de medidas. Algunos de estos estudios preliminares, en colaboración con Ana Crespo, han tenido un desarrollo posterior y se han presentado en diversos congresos nacionales e internacionales [146, 210-212], pero se encuentran ya fuera del objetivo de esta tesis y no se incluyen aquí. A continuación se presentan únicamente algunos ejemplos de las primeras series realizadas para poner a prueba el funcionamiento de la celda.

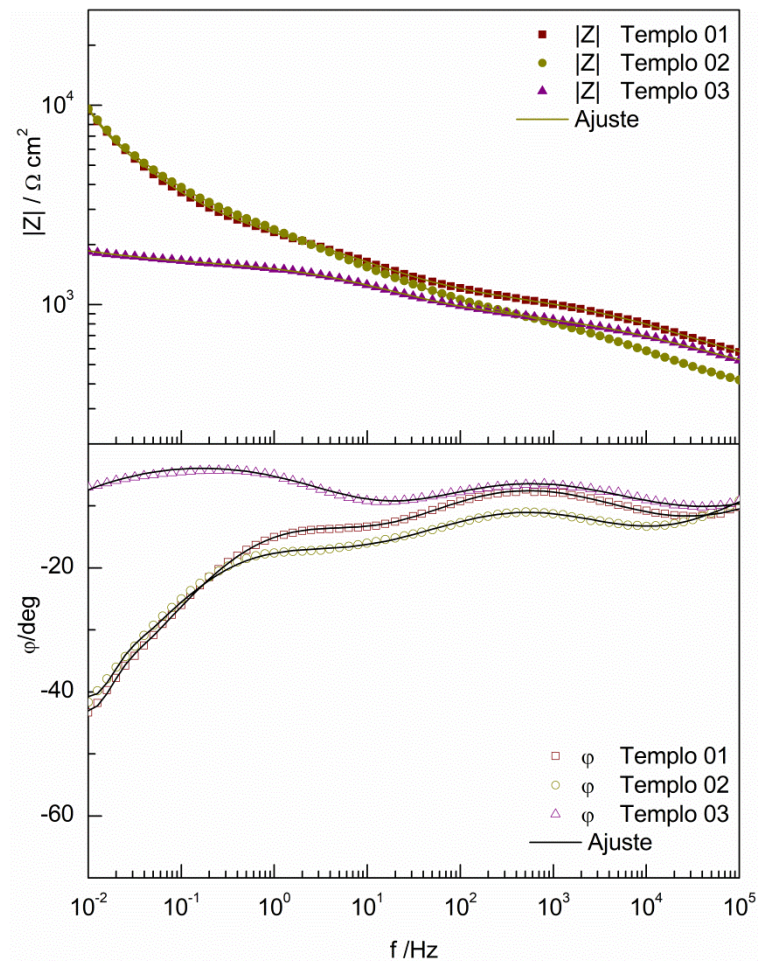
### *Templo*

Se trata de una obra geométrica, de pequeñas dimensiones y realizada con planchas de acero patinable. Las medidas tomadas en esta obra se realizaron para evaluar las diferencias en las características de la pátina en diferentes orientaciones. Se eligieron 3 zonas de medida, una en un plano lateral (*Templo 01*), una en el plano superior (*Templo 02*) y otra en la cara interior (*Templo 03*). En la figura 49 se puede ver la obra junto con dos de las medidas realizadas.



**Figura 49.** Escultura *Templo* (a) y detalle de dos de las zonas medidas en el plano superior (b, *Templo 02*) y lateral (c, *Templo 01*).

Los espectros obtenidos se recogen en la figura 50. Las dos caras exteriores muestran un comportamiento prácticamente idéntico, mientras que la cara interior presenta una impedancia menor. El ajuste de los espectros de impedancia al circuito equivalente general para el acero (tabla 13) muestra valores de la resistencia de la pátina muy similares en los tres casos, si bien existen diferencias en los valores de resistencia de transferencia de carga ( $R_2$ ) y de difusión entre las medidas de la zona externa (*Templo 01* y *Templo 02*) e interna (*Templo 03*). Las diferencias en los valores de  $R_{tc}$ , dado el proceso electroquímico es el mismo, estarían relacionados con diferencias en el área del metal base expuesta al contacto con el electrolito y, por tanto, con el carácter más o menos poroso y/adherente de la pátina.



**Figura 50.** Espectros de impedancia obtenidos en diferentes orientaciones de la escultura *Templo*.

**Tabla 13.** Resultados del ajuste de los espectros de impedancia y medidas de espesor [146] de la obra *Templo*.

		Templo 01	Templo 02	Templo 03
Espesor ( $\mu\text{m}$ )		27.3	21.2	27.8
Re ( $\Omega\cdot\text{cm}^2$ )		$418 \pm 8$	$340 \pm 4$	$369 \pm 9$
CPE1	$Y_1$ ( $\text{S s}^{\alpha_1} \text{cm}^{-2}$ )	$5.1 \pm 0.7 \text{ E-06}$	$5.3 \pm 0.8 \text{ E-06}$	$7.8 \pm 0.1 \text{ E-06}$
	$\alpha_1$	$0.50 \pm 0.01$	$0.55 \pm 0.01$	$0.47 \pm 0.01$
R1 ( $\text{k}\Omega\cdot\text{cm}^2$ )		$700 \pm 20$	$550 \pm 20$	$550 \pm 20$
CPE2	$Y_2$ ( $\text{S s}^{\alpha_2} \text{cm}^{-2}$ )	$8.0 \pm 0.4 \text{ E-05}$	$1.30 \pm 0.07 \text{ E-04}$	$1.16 \pm 0.04 \text{ E-04}$
	$\alpha_2$	$0.60 \pm 0.01$	$0.48 \pm 0.01$	$0.60 \pm 0.01$
R2 ( $\text{k}\Omega \text{cm}^2$ )		$1.3 \pm 0.4$	$2.5 \pm 0.1$	$0.69 \pm 0.2$
R ( $\text{k}\Omega\cdot\text{cm}^2$ )		$18.6 \pm 0.3$	$21.2 \pm 0.7$	$1.3 \pm 0.7$
W	T (s)	$65 \pm 1$	$58 \pm 2$	$300 \pm 300$
	$\alpha_w$	$0.56 \pm 0.01$	$0.58 \pm 0.01$	$0.46 \pm 0.02$



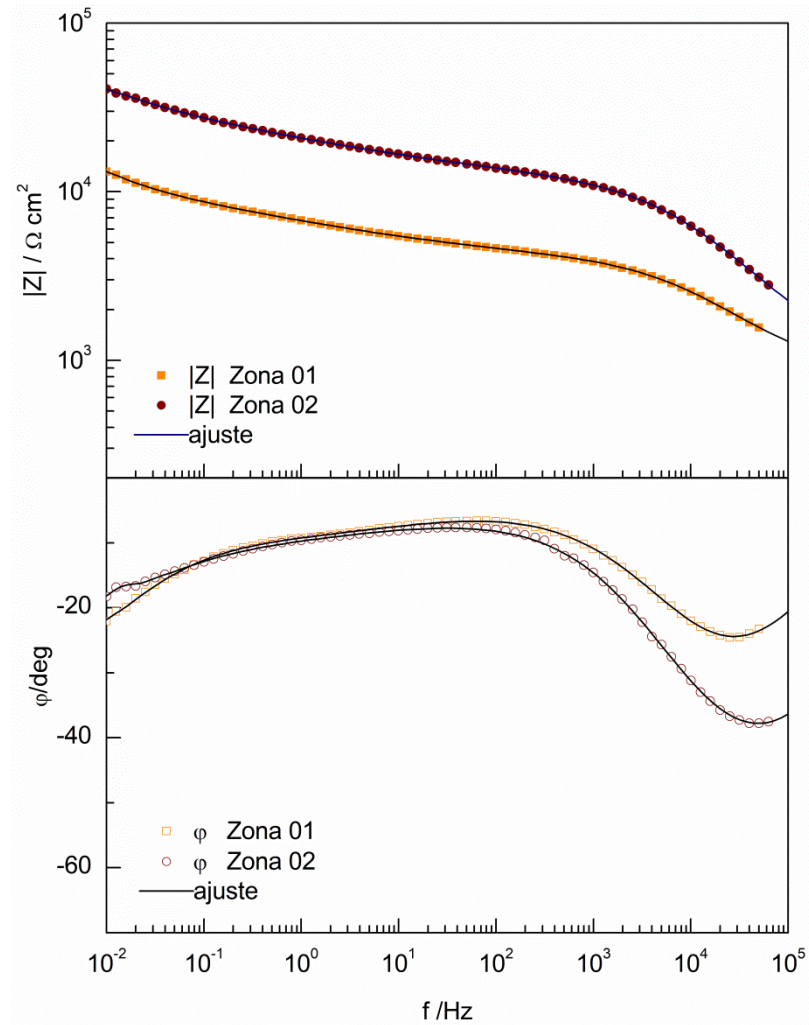
### *Once módulos*

*Once módulos* es una escultura realizada en 1971, obra de Amador Rodríguez. La escultura está formada por diversas piezas y tiene una geometría compleja.



**Figura 51.** Imagen de la obra *Once módulos* y de las dos zonas de medida. Detalle de la medida en la zona interior curva.

Como se puede apreciar en los espectros de impedancia (figura 52) y su ajuste al mismo circuito equivalente que en el caso anterior, en este caso es la zona interior la que muestra un mejor comportamiento a la corrosión (resultados del ajuste en la tabla 13). Este comportamiento, aunque en principio no sería el esperado, coincide con las características visuales de la pátina, mucho más uniforme en la zona 02.



**Figura 52.** Espectros de impedancia obtenidos en la zona frontal (Zona 01) y la zona curvada (Zona 02) de *Once Módulos*



**Tabla 14.** Resultados del ajuste de los espectros de impedancia y medidas de espesor [212] de la obra *Once Modulos*.

		Zona 01	Zona 02
Espesor ( $\mu\text{m}$ )		56.7	43.1
Re ( $\Omega\cdot\text{cm}^2$ )		830 $\pm$ 7	800 $\pm$ 15
CPE1	$Y_1$ ( $\text{S s}^{\alpha_1} \text{cm}^{-2}$ )	2.40 $\pm$ 0.8E-07	6.8 $\pm$ 0.2E-08
	$\alpha_1$	0.65 $\pm$ 0.01	0.67 $\pm$ 0.01
R1( $\text{k}\Omega\cdot\text{cm}^2$ )		3.15 $\pm$ 0.03	9.92 $\pm$ 0.08
CPE2	$Y_2$ ( $\text{S s}^{\alpha_2} \text{cm}^{-2}$ )	1.48 $\pm$ 0.04E-04	5.68 $\pm$ 0.05E-05
	$\alpha_2$	0.308 $\pm$ 0.007	0.232 $\pm$ 0.002
R2 ( $\text{k}\Omega \text{cm}^2$ )		10.4 $\pm$ 0.8	108 $\pm$ 7
R ( $\text{k}\Omega\cdot\text{cm}^2$ )		70 $\pm$ 6	830 $\pm$ 80
W	T (s)	150 $\pm$ 20	65 $\pm$ 4
	$\alpha_w$	0.63 $\pm$ 0.2	0.75 $\pm$ 0.2

#### 4.4. Discusión general.

El objeto de este trabajo ha estado centrado en el desarrollo de una celda electroquímica en gel para su empleo en la resolución de cuestiones de conservación del patrimonio cultural metálico. Como se ha planteado inicialmente, una técnica como la EIS, que ha demostrado ampliamente su utilidad en el estudio de la corrosión y de los sistemas de protección en otros campos, no ha tenido su reflejo en una aplicación al mismo nivel en el ámbito del patrimonio. Los obstáculos para la generalización de su empleo en esta área se encuentran, como se ha explicado en el apartado 1.2.2. de la introducción, en las dificultades prácticas para la realización de las medidas y en las dificultades para su interpretación. A lo largo del desarrollo de la celda con electrólito en gel con la que se pretendía dar solución a esta primera dificultad, se ha podido comprobar que algunos aspectos del diseño y de la realización de las medidas también están relacionados con la segunda cuestión, ya que de ellos depende la calidad de las medidas y la posible aparición de ruido, inestabilidad o artefactos en los espectros obtenidos, que afectan a la interpretación de los resultados.

La primera condición que impone el tipo de objeto de estudio es que la técnica sea no destructiva. Aunque la EIS en principio cumple este requisito, el electrólito elegido puede resultar agresivo para las superficies que se quiere medir. Por este motivo, tras la prueba de concepto (apartado 4.1) en la que se utilizó NaCl por ser un electrólito bien conocido, la solución ha sido emplear una disolución de agua de lluvia artificial con un pH próximo a la neutralidad. El empleo de agua de lluvia artificial resulta adecuado además porque es similar al electrólito al que se encuentra principalmente expuesto el patrimonio metálico en el exterior, aunque en algunos ambientes se trate de lluvia ácida o aerosoles marinos. Con esto se evita aportar a la superficie del bien cultural otros iones cuyos residuos pudieran dar lugar en el futuro a un deterioro acelerado de la zona estudiada. El principal inconveniente del agua de lluvia es su baja conductividad que acorta el intervalo entre el valor mínimo y máximo del módulo de la impedancia, disminuye la relación señal-ruido y favorece la aparición de artefactos de la medida dentro del rango de frecuencias de interés. Por eso es fundamental tener en cuenta todos los factores que pueden introducir ruido o distorsiones de otro tipo en las medidas, para evitarlos, minimizarlos o considerarlos adecuadamente al analizar los

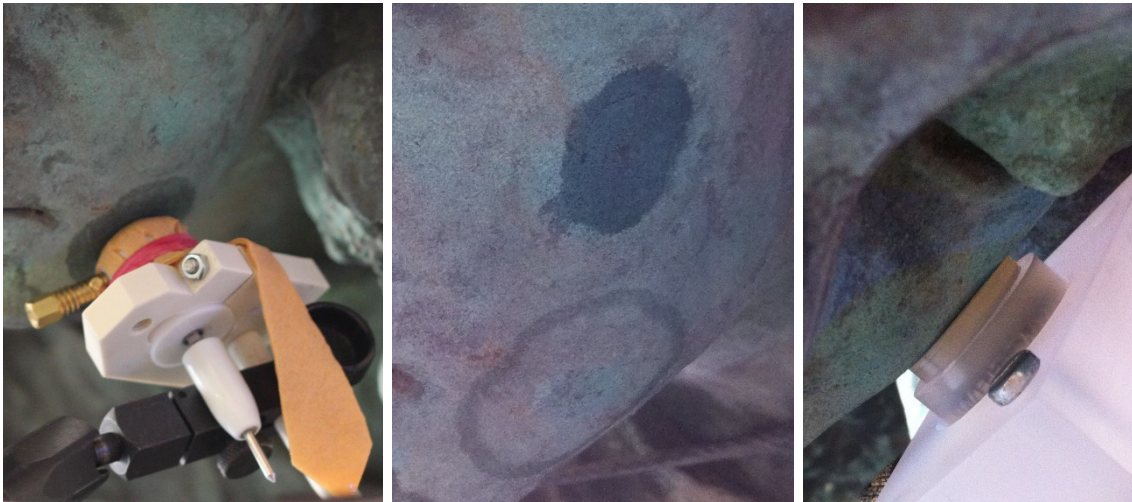
resultados. Este aspecto, que resulta fundamental para poder interpretar adecuadamente los resultados, no siempre recibe la atención suficiente.

Podemos considerar los factores que afectan a las medidas en dos grupos. Aquellos relacionados con el sistema de medida y aquellos propios de la realización de medidas de campo.

### *El sistema de medida*

Al emplear un electrólito de baja conductividad uno de los problemas posibles es la aparición de artefactos debidos a acoplamiento entre los electrodos de referencia, trabajo y contraelectrodo [193, 198]. Estos acoplamiento pueden dar lugar a efectos de tipo (pseudo)inductivo o (pseudo)capacitivo de diferente alcance, que es fundamental determinar ya que pueden interferir con la zona del espectro de interés [187-189]. Con las configuraciones de celdas y electrólitos habituales utilizados en estudios de corrosión, estos artefactos aparecen fuera del rango de frecuencias estudiadas (típicamente entre 100 kHz y 1-10 mHz). Para el caso de la celda G-PE el estudio sistemático del efecto de la naturaleza y posición de los electrodos, discutido en el apartado 4.2.1., ha permitido determinar en qué casos pueden darse estos efectos y cuál es la posición óptima de los electrodos para evitarlos. Este tipo de efectos pueden explicar las diferencias obtenidas con diferentes sistemas de medida sobre sustratos similares [190] y es uno de los aspectos que está en proceso de desarrollo futuro con la investigadora italiana P. Letardi [150].

El siguiente aspecto relativo al sistema de medida es la retención del electrólito. Ya se ha discutido ampliamente la existencia de dos enfoques para enfrentarse a esta cuestión: el diseño de sistemas para la retención del líquido frente al empleo de electrólitos gelificados. Aunque algunos de los sistemas con retención de líquido como el propuesto por Letardi [25] o más recientemente el sistema de Elsener [137, 138] han proporcionado buenos resultados, para las medidas sobre superficies muy porosas se ha comprobado que el gel retiene mejor el electrólito (figura 53), evitando la excesiva absorción del mismo por la pátina porosa. En este sentido, la celda G-PE desarrollada en este trabajo sería preferible para este tipo de sustratos, al facilitar la delimitación de la zona de medida, y evitar que la misma pueda ir cambiando a lo largo de la realización del ensayo de EIS, distorsionando los resultados.



**Figura 53.** Comparación de la realización de medidas con la celda de contacto (electrólito líquido), a la izquierda, y la celda G-PE, a la derecha, sobre una superficie muy porosa. En la imagen central se puede ver el tamaño de la huella del líquido en ambos casos.

Otra de las ventajas de la utilización del gel, como ya se ha visto, es su adaptación a la textura de la superficie, según se ha mostrado en las figuras 13 y 14. Es posible, además, modificar la concentración de agar para obtener geles con mayor o menor rigidez, permitiendo con ello modular la facilidad de manejo y la capacidad de adaptación a superficies complejas. La caracterización realizada del efecto de distintas concentraciones de agar (apartado 4.1) nos ha permitido conocer en detalle cómo afecta dicha concentración a las medidas.

Como ventaja añadida en el caso del agar, su conductividad natural contrarresta la baja conductividad del electrólito líquido. El principal inconveniente observado en el agar es el aparente efecto despolarizante anódico observado en las medidas en algunas superficies de bronce [132]; sin embargo, como ya se ha demostrado, este efecto puede minimizarse utilizando bajas concentraciones de agar, y únicamente es observable en el caso de superficies reactivas. Se ha podido comprobar que en obra real, cuya superficie se ha estabilizado por exposición a la intemperie durante largos periodos de tiempo, no hay diferencias significativas entre el agar y la agarosa, la fracción neutra de este producto natural, que en laboratorio sí presenta un comportamiento muy próximo al del electrólito líquido [228].

### *Las medidas de campo:*

La realización de medidas de campo conlleva una serie de dificultades añadidas a los estudios de laboratorio. La principal es la posible interferencia de factores externos que produce ruido en las medidas, a lo que se une la necesidad de medir con tierra flotante, lo que produce medidas de peor calidad. Algunas interferencias de tipo electromagnético son difíciles de detectar y más aún de evitar; en ocasiones los propios cables y alargadores pueden ser fuente de interferencias, habiéndose obtenido medidas de mejor calidad en ocasiones empleando baterías que cables alargadores para enchufar el equipo a una toma de corriente. Así, el uso de baterías sería ventajoso para evitar esta posible fuente de interferencias y para poder medir en localizaciones alejadas de una toma de corriente eléctrica. Como desventaja, la capacidad de las mismas puede limitar el tiempo disponible para realizar las medidas.

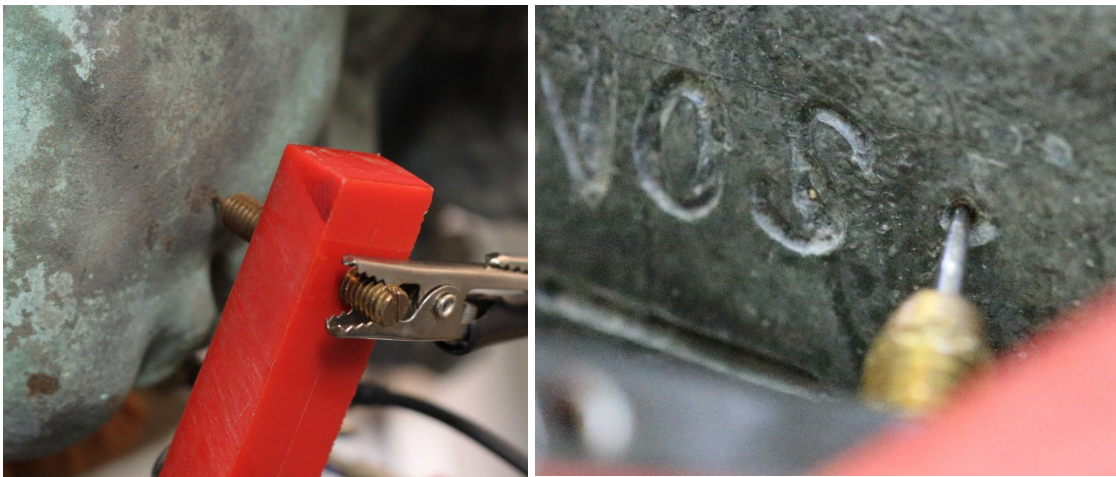
La longitud de los cables del propio potencióstato también añade una dificultad para el acceso a ciertas zonas de la obra a medir; y aunque existen cables de 1.5 y 3 m, éstos también pueden constituir una fuente de incertidumbre. Para evitar la necesidad de utilizar cables de gran longitud, se puede utilizar un soporte para el potencióstato que lo sitúe próximo a la superficie.

Otro aspecto importante en las medidas de campo son los posibles efectos de la luz y la temperatura. La temperatura influye en cualquier proceso químico, por lo que necesariamente medidas de la misma superficie con temperaturas ambiente diferentes, presentarán algunas diferencias, como ya se apuntó en el estudio de las esfinges del Museo Arqueológico [151]. La luz, como se ha comentado, produce cambios en el potencial medido de las superficies de cobre, que hacen las medidas inestables. Por ello, es recomendable, siempre que sea posible, medir en condiciones de sombra. De este modo se evita también el calentamiento excesivo de la superficie del metal por efecto del sol, que produce además la evaporación del electrólito y añade una nueva dificultad.

Finalmente, el último aspecto crítico en la realización de medidas de campo es la dificultad de realizar el contacto eléctrico con el metal. Aunque algunos autores han propuesto el empleo de un sistema de dos celdas paralelas para evitarlo, ya se ha discutido en el apartado 1.2.2 que esta no es una opción adecuada [190]. Otra posibilidad sería realizar un pequeño taladro en una zona no visible, sin embargo, esta



opción limita mucho las posibilidades, por lo que la alternativa de utilizar una punta metálica resulta adecuada y más respetuosa con la superficie. Esta solución funciona bastante bien para esculturas de bronce, en las que además es frecuente encontrar algún punto con desgastes o arañazos que exponen el metal facilitando el contacto (figura 54). En el caso de esculturas en acero patinable es más difícil y cuando se observen anomalías en los valores o el desarrollo del espectro de impedancia durante el proceso de medida, debe considerarse la posibilidad de que exista un mal contacto con la superficie metálica. También se ha comprobado que la calidad del contacto mejora cuando se dispone de un soporte suficientemente robusto para la sujeción del sistema de medida, por lo que es un detalle importante a tener en cuenta en el diseño.



**Figura 54.** Detalle del contacto eléctrico con una punta metálica sobre una zona desgastada (izquierda) y en un hueco de la superficie (derecha).

Aunque aún hay algunos aspectos que pueden mejorarse o desarrollarse en un futuro, esta investigación ha permitido diseñar un sistema que posibilita obtener medidas de calidad, al tiempo que ha proporcionado un conocimiento suficiente de los factores limitantes en las medidas de campo. Esto ha aportado una herramienta de utilidad para resolver problemas de conservación del patrimonio metálico, como se ha podido comprobar a través de los diferentes ejemplos y trabajos de colaboración a lo largo de este trabajo, que se han presentado en los apartados anteriores, tales como el seguimiento de procesos de restauración o la comparación entre diferentes sistemas de protección.

Además, abre la posibilidad de comenzar a realizar colecciones sistemáticas de medidas en campo, inexistentes en la actualidad, y en diferentes modelos de

laboratorio para entender mejor el comportamiento electroquímico de las pátinas y recubrimientos en escultura. Este debe ser el siguiente paso para seguir avanzando en la aplicación de esta técnica a la resolución de problemas de conservación del patrimonio cultural metálico.

## 5. CONCLUSIONES

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El trabajo desarrollado a lo largo de esta tesis ha permitido diseñar, desarrollar y validar una celda electroquímica con electrólito en gel para la realización de medidas electroquímicas in situ sobre el patrimonio cultural metálico.

Atendiendo a los objetivos parciales que se planteaban inicialmente, se pueden establecer las siguientes conclusiones:

- **El empleo de un electrólito gelificado con agar o agarosa permite obtener medidas electroquímicas reproducibles y de buena calidad sobre superficies metálicas.** Los resultados obtenidos son comparables a los de un electrólito líquido; la presencia del gel no introduce ningún artefacto o proceso adicional en el sistema, que responde al mismo circuito equivalente. En el caso de superficies reactivas, el uso de agar puede acelerar las velocidades de corrosión medidas, siendo posible en estos casos el empleo de agarosa, que tiene un comportamiento más neutro. En cualquier caso, este no resulta un efecto importante para la realización de medidas comparativas.
- **El análisis de los diferentes elementos del diseño,** como la naturaleza de los electrodos, geometría de la celda o sistemas de fijación **ha permitido la optimización del diseño de la celda,** garantizando la calidad y fiabilidad de los resultados obtenidos. Este diseño, junto con el sistema de soporte y colocación adoptado para su utilización en medidas de campo ha permitido solventar las dificultades prácticas de la realización de este tipo de medidas.
- **El uso de la celda es adecuado para la evaluación de pátinas y recubrimientos.** La evaluación del sistema sobre diferentes pátinas y recubrimientos en laboratorio ha demostrado la capacidad del sistema para poner de manifiesto las diferencias y la evolución de diferentes sistemas metal/pátina o metal recubrimiento. Esto permite utilizar la celda para realizar estudios sobre la idoneidad, el comportamiento o la evolución de tratamientos de conservación en laboratorio, que posteriormente puedan ser trasladados a obra real y monitorizados utilizando la misma metodología.

- **Se ha demostrado la aplicabilidad de la celda a situaciones reales relacionadas con la conservación del patrimonio metálico**, realizando el seguimiento de un trabajo de restauración. Asimismo, las medidas puntuales realizadas sobre diversos tipos de obras en diferentes ubicaciones han permitido apreciar diferencias relacionadas con la posición o geometría de las esculturas, que constituyen una información de interés para poder llevar a cabo tratamientos o estrategias de conservación.

La celda electroquímica en gel desarrollada en esta tesis proporciona a los conservadores e investigadores un sistema para la realización de medidas de campo sencillo y eficaz. Esto permitirá generalizar su empleo, recopilar medidas y estudios de caso, lo que a su vez contribuirá a un mayor conocimiento y comprensión del comportamiento y respuesta de las superficies metálicas en los objetos del patrimonio y con ello a su conservación.

## 6. OTROS DESARROLLOS Y FUTURAS LÍNEAS DE TRABAJO.

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En paralelo al desarrollo de la celda, las posibilidades de aplicación han dado lugar a otros trabajos y colaboraciones con otros investigadores. Además de los estudios sobre el comportamiento de las pátinas artificiales en escultura de aceros patinables que ya se ha comentado, otros autores han realizado nuevos avances o aplicaciones a partir de la celda inicialmente desarrollada en este trabajo. El más destacado, fuera del campo del patrimonio cultural, es la Tesis Doctoral de G. Monrrabal [229], que ha trabajado en la modificación del electrólito con plastificantes para poder aplicar la celda al estudio de la corrosión del acero inoxidable geometrías complejas [143, 155]. A su vez, los ensayos sobre el empleo de geles modificados con plastificantes para patrimonio cultural se han iniciado en nuestro grupo de investigación del CENIM en el marco de una beca JAE-Intro y es uno de los futuros estudios previstos para la celda. Esto podría tener aplicaciones especialmente en el campo de la arqueología, dadas las características morfológicas y superficiales de algunos objetos (objetos o superficies pequeñas o con capas de corrosión muy texturizadas). El interés de este campo de aplicación ya ha sido apuntado por F. di Turo, quien ha utilizado la celda para la evaluación de monedas de bronce de procedencia arqueológica[147], y ha sugerido el empleo de otros electrólitos poliméricos [208].

Para avanzar el estudio de esculturas al aire libre, la cuestión más importante a abordar a partir de ahora son los posibles efectos de la luz y la temperatura. El estudio de hasta qué punto influye la temperatura en los resultados es un tema pendiente; aunque se han diseñado algunos ensayos para su estudio éstos no han sido llevados a cabo todavía. Lo mismo ocurre con el problema de la luz, como se ha comentado en el apartado 4.3.2.3., se ha observado que las variaciones de luz provocan oscilaciones bruscas en el potencial, lo que produce la inestabilidad de las medidas. Estas cuestiones se abordarán mediante un conjunto de medidas sistemáticas a diferentes temperaturas dentro de un rango que abarque los valores a los que se puede encontrar la superficie de una escultura, y con diferentes intensidades de iluminación con una fuente regulable de luz día. El objetivo es establecer un modelo o unos



parámetros que permitan normalizar los resultados obtenidos en campo en función de estos valores, que son difícilmente controlables.

Además de las nuevas aplicaciones, la evaluación de la influencia del medio y de explorar posibles modificaciones del electrólito para aplicaciones concretas, otro objetivo relevante a partir de este momento, es realizar series sistemáticas de medidas sobre diferentes obras y materiales metálicos de patrimonio cultural para seguir avanzando en su comprensión. Una de las líneas de trabajo estaría orientada al estudio de recubrimientos, en patrimonio metálico; de hecho, la revisión y análisis de las aportaciones de la EIS al estudio de pátinas y recubrimientos es un tema que se ha abordado brevemente en el trabajo presentado al congreso METAL2019 [230]. La evaluación de nuevos recubrimientos se plantea en el marco de un proyecto vigente del grupo de investigación, COMPACT, aplicado a la conservación del patrimonio científico-técnico. En el proyecto COMPACT, "La Conservación de los Metales en el Patrimonio Científico-Técnico" (HAR2017-89911-R) se abordará, entre otras cuestiones, el empleo de recubrimientos e inhibidores innovadores y su adecuación al patrimonio científico-técnico, cuyo comportamiento in situ podrá ser estudiado con la celda G-PE. La aplicación de electrólitos gelificados con agar para el estudio de pátinas, y concretamente para el "análisis del proceso electroquímico de degradación de pátinas formadas artificialmente sobre bronce cuaternario y su relación directa con las condiciones atmosféricas" ha sido el objeto de un reciente TFM dirigido por el Dr. Ricardo Orozco, de la Universidad Veracruzana (México). Este TFM se enmarca en el proyecto "Escenarios de riesgo para el patrimonio en México: causas ambientales involucradas en su deterioro y estrategias de conservación", de la "Red de estudios interdisciplinarios sobre medio ambiente y conservación del patrimonio mexicano" con la que nuestro grupo está participando como colaborador externo.

Finalmente, como se ha mencionado en el apartado 4.3.1.2, parte de los resultados se han obtenido dentro del proyecto IPERION-CH. Este proyecto es último de una serie de proyectos –iniciados con la red LabsTech en el V Programa Marco– que han venido dando acceso a investigadores en patrimonio cultural a un conjunto de tecnologías de análisis y archivos de datos científicos en los últimos 15 años y que han constituido el

origen de la infraestructura E-RIHS<sup>12</sup>. E-RIHS (“European Research Infrastructure for Heritage Science”) es una infraestructura de investigación distribuida cuyo objetivo es dar soporte a la investigación en patrimonio cultural y natural, proporcionando acceso a herramientas tecnológicas de análisis más avanzadas y a archivos científicos a través de las cuatro plataformas: FIXLAB, para acceso a grandes instalaciones fijas; MOLAB, una flota de laboratorios e instrumentos portátiles que se trasladan para estudios in-situ; ARCHLAB, formado por colecciones de materiales y archivos de archivos de datos científicos, de carácter único y DIGILAB, que dará acceso online a datos y herramientas digitales.

El sistema portátil para la evaluación de pátinas y recubrimientos en metales basado en los desarrollos de esta tesis ha sido incluido como uno de los servicios del nodo español de esta infraestructura, dentro del MOLAB *“METAL.es. In-situ metal electrochemical studies for heritage science”*. Metal.es estará orientado al estudio in situ de las características y comportamiento de las superficies metálicas y evaluación de recubrimientos protectores mediante técnicas electroquímicas.

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<sup>12</sup> <http://www.e-rihs.eu>

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