J Solid State Electrochem (2010) 14:349–351
DOI 10.1007/s10008-009-0934-y

EDITORIAL

Electrochemistry for conservation science

Antonio Doménech-Carbó

Received: 19 August 2009 / Accepted: 19 August 2009 / Published online: 16 September 2009

Conservation science can be viewed as an interdisciplinary scientific field devoted to the preservation of cultural goods for future generations. Within this field, a wide variety of objects and materials are involved, from archeological or historical sites, monuments to works of art and archeological pieces, including textiles to ceramic ware, from metallic artifacts to wooden pieces. Monuments and objects reflect the culture and history of the past and present whose "reading" stems from the transmitted historical, cultural or figurative message. Their conservation requires the work of conservators, curators, art historians, and scientists in order to safeguard the significance and the materials constituting the archeological piece or work of art. It should be emphasized that electrochemical methods must be viewed within the context of the scientific examination of works of art and archeological pieces and, therefore, as complementary to other techniques (from X-ray diffraction of scanning electron microscopy, from infrared spectroscopy to chromatography) for obtaining the required analytical information on materials and pieces.

Obviously, scientific examination of cultural goods is an essential task for conservation science. In particular, electrochemistry plays an important role in the context of conservation and restoration of cultural heritage. Electrochemical techniques can be used in conservation science for two general purposes: (a) as analytical methods in order to determine the composition of the materials forming the object and, eventually, their alteration products, adherences, materials incorporated in prior restorations, etc.; (b) as restorative/conservative methods in order to restore the original state of the piece and/or incorporate protective materials for ensuring the future conservation of the piece. Within the first item one can include the use of electroanalytical methods for determining the composition of the environment of the piece (atmosphere, waters, soils) in its archeological site and monitoring the composition of the environment in the current monument or object site in museums, stores, etc.

The intersection between electrochemistry and conservation science has a long tradition, initiated in the 18th century. The first specialized laboratory dedicated to this type of work was established in 1888: the *Chemisches Labor der Königlichen Museen zu Berlin* (Chemical Laboratory of the Royal Museums of Berlin, now the *Rathgen-Forschungslabor*) whose work was divulgated in the famous Rathgen treatise published in 1898 [1]. The corrosion of metals, the bronze disease in particular, focused promptly the interest of scientists like Mond and Cuboni [2] and Berthelot (1894) [3]. The latter scientist, in 1901, emphasized the importance of chloride-assisted corrosion for bronze disease [4]. Today, there is an increasing interest in the conjunction of electrochemistry and conservation science, with growing presence in both electrochemical and conservation journals. Recent (1st European Conference on Electrochemical Methods Applied to the Conservation of Artworks, Valencia, 2008) and proximal (Lorentz Conference on Electrochemistry in Historical and Archaeological Conservation, Leiden, scheduled January 2010) international meetings reflect the interest of the scientific community in the electrochemistry for conservation science.

This monographic issue of Journal of Solid State Electrochemistry presents a complete overview of the current status and future developments of electrochemistry

A. Doménech-Carbó (✉)
Departament de Química Analítica, Universitat de València,
Dr. Moliner, 50,
46100 Burjassot, València, Spain
e-mail: antonio.domenech@uv.es

"in" conservation science through four reviews. Christian Degrigny reviews the use of electrochemical techniques for the conservation of metal artifacts and Joaquín Barrio, Jorge Chamón et al. provide a detailed analysis of the development of electrochemical techniques for the conservation of archeological metals in Spain. This is a historical review where several stages for the implementation of electrochemical techniques for treating metal artifacts in Spain are discerned and accompanied by an accurate revision of potentiostatic methods. From these reviews, a detailed picture of the application of electrochemistry for metal conservation emerges. Electrolytic treatments for cleaning metal pieces rise rapidly at the beginning of the XXth century under the impulse of very influential text such as those of Rosemberg (1917) and, in particular, Plenderleith (1956). Further treatises (Stambolow (1965), France-Lanord (1965), and Organ (1968)) emphasized the need of preservation of the original patina of the object and contributed to a radical change of tendency. Since the 70s, aggressive electrolytic cleaning has decayed considerably. These two reviews provide a detailed description of the successive rise and fall of electrolytic cleaning and an interesting view of the current situation of electrochemical techniques in the context of metal conservative treatments where the "uniform" paradigm (electrolytic cleaning for all pieces and deterioration types) has been replaced by a "critical" paradigm (each conservation case has to be individualized for adopting the more adequate conservation treatment). Here, the purely electrochemical contribution (better knowledge of corrosion processes, control of electrolysis, alternative electrochemical treatments, corrosion inhibitors) meet with the orientations in conservation science contained in the famous *Carta del Restauro* (Roma, 1972) inspired by the work of Brandi (introducing very restrictive aesthetic and ethic criteria on the intervention on artistic objects).

Although historically, the use of electrochemistry in conservation science has been concentrated into metals, in the last two decades it has been extended to a variety of materials, namely, textiles, ceramics, glazes and glasses, and paintings in all their varieties (frescoes, polychromed sculptures, oil painting). This extension was prompted by the voltammetry of microparticles (VMP) methodology, developed by Scholz et al. in 1989, that allowed for obtaining qualitative, quantitative, and structural information on solid micro- or nanosamples. As far as conservation science demands a variety of information using nondestructive methods or using minimal amounts of sample, this methodology provides a rapid and sensitive method for analyzing works of art in order to characterize the artistic techniques and technologies of production, the dating and authentication of works of art and/or assessing their state of conservation, and/or detect failures, reintegrations or prior conservative treatments. The application of voltammetric methods for analyzing works of art is reviewed by Antonio Doménech-Carbó. The performance of the VMP approach for the identification, speciation, and relative quantification of components in microsamples from paints, sculptures, textiles, ceramics, etc. has been recently improved by the application of different strategies of bivariant analysis and multivariate chemometric methods, in particular allowing for an absolute quantification of selected species in samples from works of art.

Interestingly, the scope of available electrochemical techniques has been enhanced by virtue of the popularization of the electrochemical impedance spectroscopy (EIS), a technique of high value for the analysis of surfaces. The use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage is reviewed by Emilio Cano detailing the capabilities of the technique in the frame of conservation science and emphasizing that EIS provides interesting information with regard to the diagnostic of the state of metallic surfaces and the performance of protective coatings.

These two aspects, diagnosis and evaluation, are illustrated by the article of Rocca and Mirambet regarding restoration treatments of technical and industrial heritage, where three illustrative examples of application of chemical inhibitors to metallic artifacts are described. Remarkably, quite different materials (from aluminum alloys to nickel-plated steel) and sizes (from aircraft to pieces of an ancient typewriter) are involved. The use of electrochemical techniques for evaluation purposes can be seen in the article of Costa and Texier where the compatibility between metals and sealing products is studied in detail. Metal corrosion in stone statuary, metallic statuary, and stained glass windows, typical problems found in historical monuments, are presented here. A combination of techniques (EIS, corrosion curves) can be used for the evaluation of conservative treatments applied to contemporary metallic sculpture, studied by Martínez-Lázaro et al. Here, an ethic and esthetic problem, the maintenance of pristine materials during conservative treatments, is electrochemically faced. The diagnosis of the state of conservation and the characterization of metallic pieces submitted to stabilization can be seen in the article of Fonseca et al. where five coins from the archeological heritage of Portugal are studied.

Characterization of materials in samples from works of art or even in situ on the object or monument is an important task in conservation science as illustrated by the article of Virginia Costa, "Electrochemistry reveals archaeological materials" underlining the importance of unambiguously identifying materials for archeometric purposes using the VMP methodology. Identification of component can be facilitated by the use of different electrochemical strategies to the basic VMP methodology. The application of sequential potential steps to the identification of anthraquinonic and naphtaquinonic dyes is discussed by Doménech-Carbó et al.

Material identification and corrosion analysis can be conjugated by using polarization/corrosion curves for qualitative analysis of technical and scientific metallic objects as described in the article of Degrigny et al. The time variation of the corrosion potential is used for identifying metals and alloys through the SPAMT test project, an interesting electrochemical proposal for normalization and testing purposes.

Corrosion mechanisms and corrosion inhibition play an important role in metal conservation. These are important topics which can be faced not only from the point of view of conservation science, but also from the more general view of corrosion science. It should be noted that atmospheric corrosion, corrosion in aquatic media (marine, fluvial) and soils results in different corrosion patterns and that different types of soils can be involved. The first of the above aspects is treated in the article of Hassairi et al., where the processes of bronze degradation are studied in simulated archeological media. The scene is completed with the article of Soussi et al. in which the early stages of bronze corrosion in a Tunisian soil are studied in detail. These two articles develop two important issues: modeling corrosion processes under burial conditions by means of controlled experiments under laboratory conditions, and examination of real cases where variable conditions result in complex electrochemical responses.

The use of protective treatments on metal surfaces is an important issue in conservation science. Although, along the first half of the XXth century, electrolytic cleaning focused electrochemical treatments, the current conservation science limits considerably this practice. However, new developments permit to incorporate new materials and methods in order to use electrochemical cleaning. This is the case cathodic chloride extraction of a late Bronze Age artifact affected by bronze disease in an ionic liquid (1-Ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide) reported in the article of Bozzini et al.. The authors conclude that the presence of nantokite inside subsurface pits is crucial for the observed bronze disease and provide a detailed study on diffusion associated to chloride release. The peculiar properties of ionic liquids favor a "clean" electrolytic removal of corrosion products while minimizing undesired effects leading to repeated corrosion which appeared in traditional electrolytic procedures.

A variety of corrosion inhibitors have been considered for the protection of metal surfaces. The performance of different organic coatings for the protection of historical steel surfaces is studied by Cano et al. on the basis of corrosion curves and EIS. Unfortunately, most of the available materials (in particular those routinely used for conservators and restorers) are unsafe and environmentally dangerous. A variety of new materials (in particular plant extracts) are currently under study. An alternative approach is discussed in the article of Adriaens et al.; here, the effectiveness of the electrochemical deposition of dodecanoate on lead is compared with the traditional deposition by immersion. The possibility of control de uniformity and thickness of the protective coating and the shortening of the coating process are interesting factors offered by the reported electrodeposition process.

In summary, the reader will find in this special issue a comprehensive view of electrochemistry in conservation science where all available electrochemical techniques and the most important materials and problems in conservation science are considered. From Bronze Age artifacts to medieval coins, from aircrafts in Le Bourget museum to Roman epigraphic lead tablets, art and archaeology can be viewed in the following pages through an electrochemical "filter" where science and art are inextricably mixed.

Finally, I would like to express my appreciation and thanks to all authors and reviewers that have contributed to this monographic issue. I would like also to express my thanks to Prof. Fritz Scholz, Editor-in-Chief of Journal of Solid State Electrochemistry for inviting me to edit this issue and to Dr. Michael Hermes, Associate Editor, for his technical assistance.

References

1. Rathgen F (1898) Die Konservierung von Altertumsfunden (= Handbücher der Königlichen Museen zu Berlin [Band 7]), Konigliche Museen zu Berlin
2. Mond C, Cuboni G (1893) Atti Accad Naz Lincei 5(2):498–499
3. Berthelot MPE (1894) C R Hebd Seances Acad Sci 118:768–770
4. Berthelot MPE (1901) Ann Chim Phys 7(22):457–460