ORIGINAL PAPER

Electrochemical criteria for evaluating conservative treatments applied to contemporary metallic sculpture. A case study

**Isabel Martínez-Lázaro · Antonio Doménech-Carbó ·
María Teresa Doménech-Carbó ·
María Teresa Pastor-Valls · Vicente Amigó-Borrás**

Abstract A combination of different electrochemical techniques, namely, voltammetry of microparticles, open circuit potential, potentiodynamic polarization, electrochemical impedance spectroscopy, and electrochemical noise was used for studying a contemporary kinetic sculpture: "I Hábitat en órbita baja de la Tierra" (1 Habitat in low-orbit around the Earth, Elvira Alfageme, 1981). It introduced the concept of 'electrochemical equivalence' in order to evaluate alternative conservative treatments consisting of *doré* and golden patination. Electrochemical information is relevant with regard to aesthetic and ethic problems associated to the conservation/restoration of works of art.

I. Martínez-Lázaro (✉) · M. T. Pastor-Valls
Instituto Valenciano de Conservación y Restauración de Bienes
Culturales de la Generalitat Valenciana,
Penyeta Roja s/n,
Castellón, Spain
e-mail: imartinez.lazaro@hotmail.com

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

M. T. Doménech-Carbó
Institut de Restauració del Patrimoni/Departament de Conservació
i Restauració de Bens Culturals,
Universitat Politècnica de Valencia,
Camí de Vera 14,
46022 València, Spain

V. Amigó-Borrás
Departament de Mecànica i Ciència dels Materials,
Universitat Politècnica de Valencia,
Camí de Vera 14,
46022 València, Spain

Introduction

Conservation of contemporary works of art involves enormous difficulties due to the variety of materials and techniques used by the artists. The difficulties for conservative intervention are enhanced by the creative concept itself, because, in most cases, the artistic idea and its originality prevail over technical aspects concerning the materials and their manufacture.

These problems are particularly significant for metallic sculpture, where corrosion can seriously deteriorate the surface of the piece, thus distorting not only its physic-chemical integrity, but also modifying the conceptual and aesthetic reading planned by the artist. Additionally, contemporary sculptors frequently use industrial methods rather than traditional procedures for treating metals. Accordingly, conservators/restorers working on contemporary metal sculpture must face a series of problems which can differ considerably from those encountered in the conservation of 'ancient' pieces [1].

In this context, electrochemical methods can be used: (1) as analytical procedures for characterizing materials, monitoring preparation methods, and/or deterioration processes and evaluating the state of conservation of the pieces [2–5] and (2) as valuable tools for cleaning, protecting, and eventually reconstructing the piece. This second aspect involves, by the one hand, removal of corrosion layers, and, by the second one, among others, coloring, bronzing, and patination strategies [6–8].

In this work a case study illustrating the availability of electrochemistry for evaluation alternative conservative

Fig. 1 Current state of the sculpture "*I Hábitat en órbita baja de la Tierra*" (1 Habitat in low-orbit around the Earth, Elvira Alfageme, 1981)

case implies aesthetical and ethical conflicts, namely, the acceptance of successive re-interpretations of the oeuvre by the artist, the possibility of modifying materials originally used in the pieces and the balance between conceptual–visual–material elements constituting a work of art.

In a recent work, several authors have emphasized the significance of electrochemistry for characterizing the conservation state of metallic pieces [2–5]. The current work is devoted to present a case study where electrochemical methods can be used for monitoring the 'aesthetic shift' suffered by the piece upon aging and/or conservative treatments. In order to characterize the composition and state of the piece, scanning electron microscopy with energy-dispersive X-ray detection (SEM/EDX) and electrochemical techniques were used. Alteration products were studied from Tafel analysis of square wave voltammograms in potassium phosphate buffer, using the methodology already reported [16–19], based on the voltammetry of microparticles approach [20–22]. For monitoring metallic
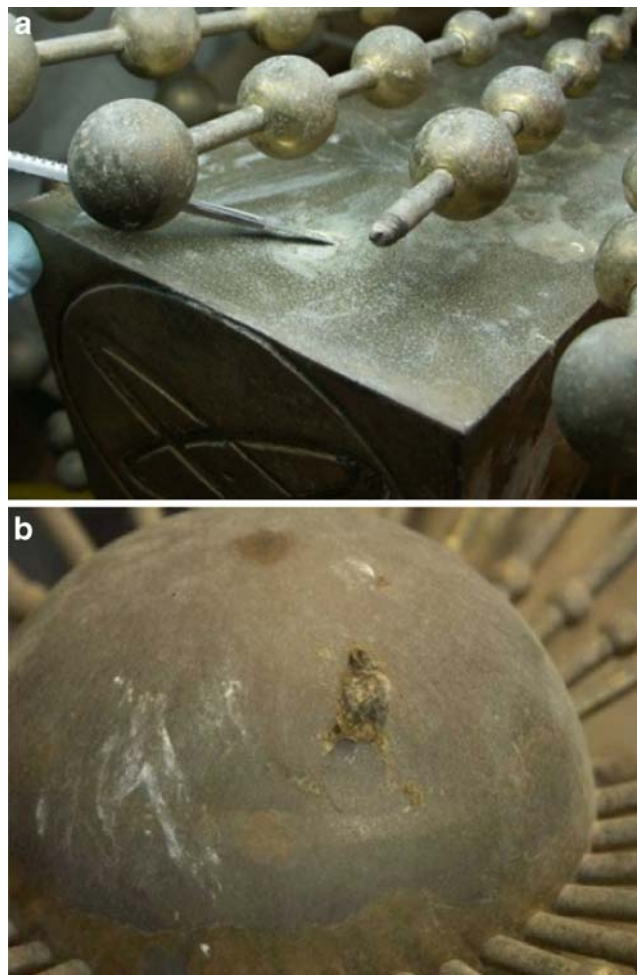
treatments is presented. It is focused on the study of possible restoration strategies to be applied to a contemporary sculpture: "*I Hábitat en órbita baja de la Tierra*" (1 Habitat in low-orbit around the Earth; see Fig. 1), made by Elvira Alfageme, a poet-informalist, geometric and optickinetic artist, in 1981. The sculpture was performed in brass and is exposed in the *"Vicente Aguilera Cerni"* Contemporary Art Mueseum of Villafamés (Spain). For the restoration of the piece at the Valencian Institute for Conservation and Restoration of Cultural Goods of the Valencian Regional Government, the sculptor was consulted. The author indicated that gold was electrodeposited over the brass skeleton in a plating workshop in 1981. However, analytical data denoted that brass (*doré*), a widely used treatment [8], rather than gold was deposited. As a result, a conflict was presented in order to restore the polished texture conceived originally by the author, synthesized in two alternatives: (1) perform an electrolytic polishing with a flash finishing, eventually complemented with brass *doré* plating, or, (2) use a gold plating. Subsequent use of protective/inhibitor coatings, also widely studied [9–15], will not be treated here. The first procedure maintains the 'real' material composition of the piece, one of the essential criteria for conservation science, whereas the second procedure follows the idea of the author whose intention was, explicitly, to cover the sculpture with a gold patina. From the point of view of conservation science, the studied

Fig. 2 Photographs of two fragments of the sculpture "*I Hábitat en órbita baja de la Tierra*" (Elvira Alfageme, 1981) show surface deterioration
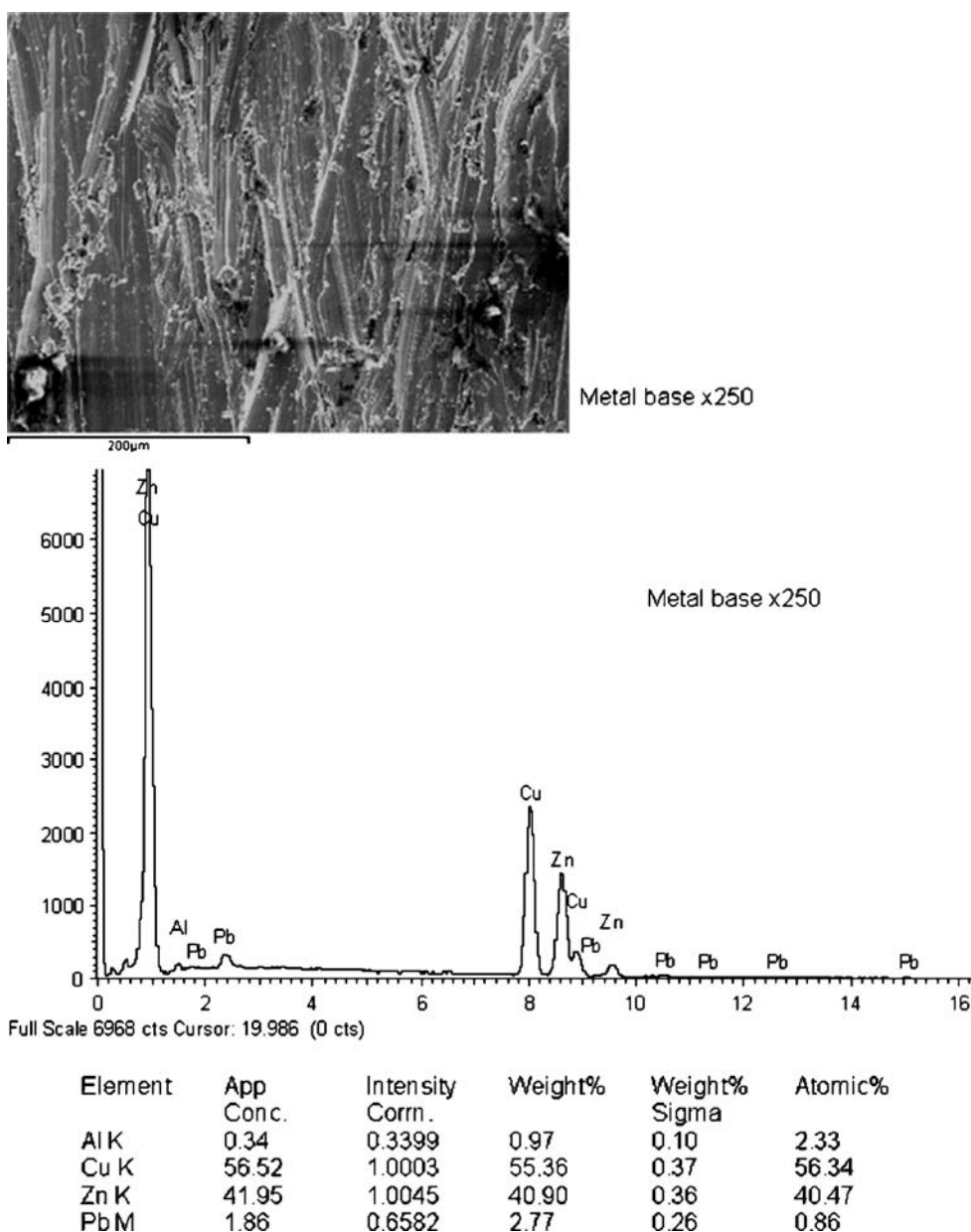
pieces, open circuit (or corrosion) potential (OCP) [23, 24], and electrochemical impedance spectroscopy (EIS) [25, 26], accompanied by electrochemical noise (EN) techniques were used in all cases involving (relatively) short-time experiments. Aqueous NaCl was used as supporting electrolyte because this electrolyte is typically used in corrosion tests and by the fact that gold electrodes become particularly active in the presence of chloride ions [28–31].

Experimental

Electrochemical experiments were performed using a CH I660C equipment. Measurements were performed in 0.10 M NaCl (Probus) in a thermostated three-electrode cell under argon atmosphere using a AgCl (3 M NaCl)/Ag reference electrode and a platinum-wire auxiliary electrode. Selected mobile parts of the sculpture, consisting of a 2.0- or 2.50-cm diameter sphere coupled to a 10 cm bar, were separated and used as a working electrode for electrochemical experiments so that only the lower part of the sphere (surface area exposed to the electrolyte 1 cm^2) remained in contact with the electrolyte solution. Electrochemical impedance spectroscopy measurements were performed in the 0.01 to 100,000 Hz frequency range with amplitude of 10 mV at the open circuit potential previously determined for each electrode. Electrochemical noise measurements were performed in both current–time and voltage–time responses. Potentiodynamic polarization curves were obtained after 24 h immersion of the electrodes in the electrolyte.

Fig. 3 SEM image of metal base and its composition from SEM/EDX analysis

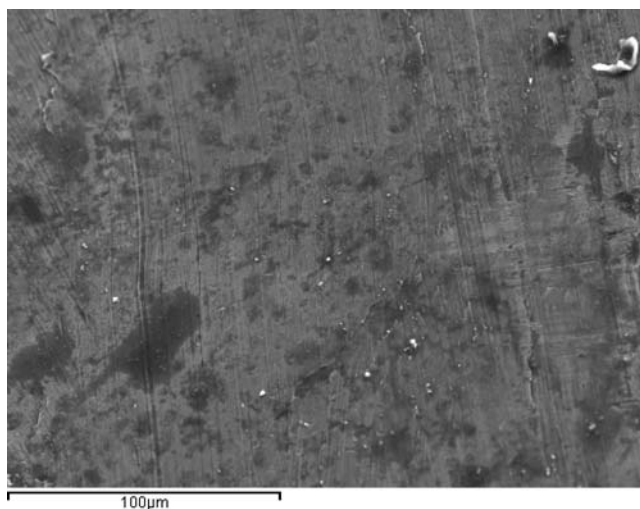| Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
Al K	0.34	0.3399	0.97	0.10	2.33
Cu K	56.52	1.0003	55.36	0.37	56.34
Zn K	41.95	1.0045	40.90	0.36	40.47
Pb M	1.86	0.6582	2.77	0.26	0.86

Fig. 4 SEM image of two regions of unaltered sculpture surface

Voltammetry of microparticles experiments were performed by taking ca. 0.1 μg of alteration products from the patina of sculpture pieces with the help of a microscalpel. These were powdered and extended on an agate mortar and abrasively transferred to a paraffin-impregnated graphite electrode (PIGE) by rubbing the electrode over that spot of sample. Square wave voltammograms (SQWVs) were then performed upon immersion into 0.50 M potassium phosphate buffer (Probus) at pH 7.0.

The original pieces were submitted to electrochemical *doré* plating in 1981, but no details of the materials and conditions were available. Six electrodes were tested: two pieces from the original sculpture submitted to cleaning treatment (BU1 and BU2), two moderately altered (BM1 and BM2), two severely deteriorated (BS1 and BS2) pieces, and two golden pieces (BG1 and BG2), which, after cleaning, was submitted to plating with gold (gold–cobalt) using cyanide bath provided by COVENTYA Technologis S.L. (Valencia, Spain). BU pieces were first submitted to cleaning with anionic surfactants in ultrasons bath at 60 °C during 3 min, further proceeding with an electrolytic cleaning in nitrilotriacetic acid (NTA, 70 g/L) bath at 25 °C during 60 s (current density 3–6 A/cm^2). After this, the piece was immersed during 30 s in 1% (*V/V*) H_2SO_4 and rinsed in water (conductivity <5 S). The golden piece was submitted to identical treatment and was subsequently plated in a solution of KAu(CN)$_2$ (68.2% *w/w*) with cobalt sulfate and potassium citrate using a platinized titanium anode under soft agitation. Plating conditions were: Au concentration 4 g/L, cobalt concentration 1 g/L, pH 3.6–4.0, temperature 35 °C, current density 0.4–1.0 A/dm^2, and deposition rate 0.2 μm/min. Color characteristics fit to ISO 86542N/ISO 8654 3N tests and minimal thickness of 2.2 μm was obtained (NF CEE 94/27 test).

SEM/EDX analysis was performed with a Jeol JSM 6300 scanning electron microscope operating with a Link-Oxford-Isis X-ray microanalysis system. The analytical conditions were accelerating voltage 20 kV, beam current 2×10^{-9} A, and working distance 15 mm. Samples were carbon-coated to eliminate charging effects. Quantitative microanalysis was carried out using the ZAF method for correcting interelemental effects. The counting time was 100 s for major and minor elements.

Results and discussion

Materials

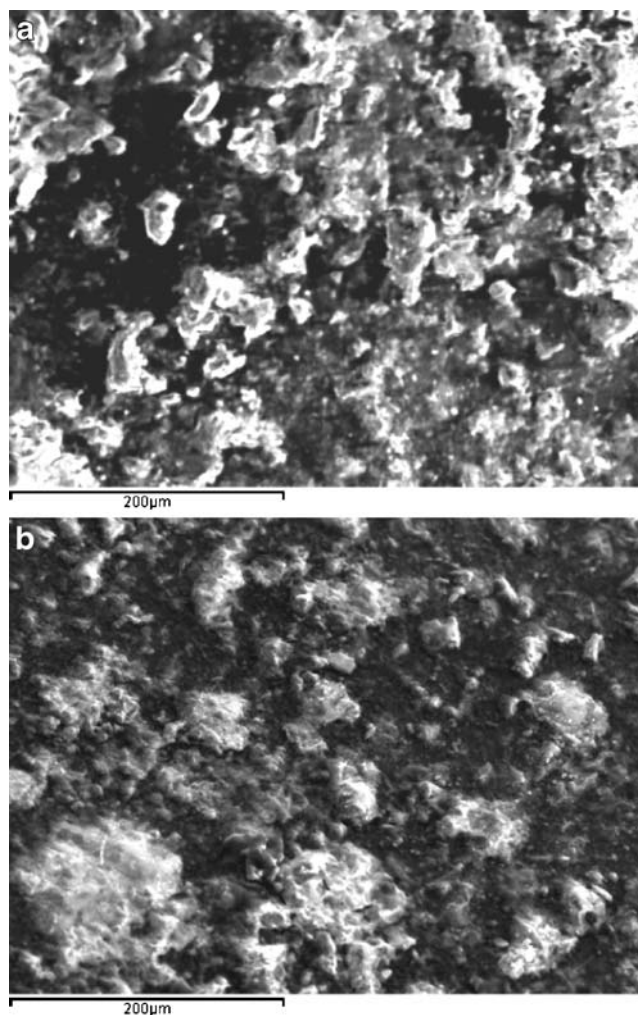Visual examination of the sculpture revealed the presence of a brown-greenish coverage in large surface areas of the

Fig. 5 SEM image of two altered regions with (**a**) moderate alteration and (**b**) severe alteration of the studied sculpture

Table 1 Typical composition from SEM/EDX of regions of the studied sculpture exhibiting moderate deterioration

Element/line	App. conc.	Intensity	Weight%	Weight %σ	Atomic %
O K	12.21	0.7724	43.75	0.76	70.93
Al K	0.09	0.5202	0.49	0.15	0.47
Si K	0.33	0.6438	1.43	0.15	1.32
S K	1.28	0.8280	4.26	0.19	3.45
Cl K	2.47	0.7218	9.46	0.26	6.92
K K	0.52	0.9802	1.47	0.13	0.97
Ca K	1.30	0.9570	3.77	0.17	2.44
Fe K	0.22	0.9274	0.66	0.16	0.31
Cu K	1.62	0.8551	5.23	0.36	2.14
Zn K	8.38	0.8558	27.11	0.64	10.76
Pb M	0.67	0.7804	2.37	0.64	0.30

piece, eventually accompanied by corrosion pitting (see Fig. 2). The composition of the metal base was determined from SEM/EDX analysis, revealing that it consisted of brass with percentages of 55.36% Cu and 40.90% Zn (w/w) accompanied by Pb (2.27%) and Al (0.97%; see Fig. 3). No traces of gold were detected in none of the examined parts of the sculpture. Analysis of unaltered regions of the surface (Fig. 4) revealed that brass with 58.87% Cu and 41.13% Zn was the unique coating forming the external surface of the sculpture being in turn responsible of its hue and brightness.

Figure 5a, b show SEM images of moderately and severely deteriorated regions of the sculpture, respectively. In the regions with moderate deterioration exists, the percentage (w/w) of Cu decreases to ca. 5%, whereas the Zn decreases to ca. 27%. Now, a 44% of oxygen appears, accompanied by significant amounts of Cl (9%), S (4%), and Ca (3%). In regions with severe deterioration, the percentage of Zn decreased to a 19% whereas that of Cu fits to a 5%. The proportion of oxygen (37%) is again high, while a significant percentage of C appears (31%), probably

associated to the deposit of organic matter. The elementary composition of moderately and severely corroded regions determined from SEM/EDX analysis is summarized in Tables 1 and 2.

Corrosion of copper and copper alloys (bronzes in particular) has been widely studied. The corrosion of such materials under outdoor exposures results in copper patination, the main products of the formed patinas being cuprite (Cu_2O), brochantite ($Cu_4SO_4(OH)_6$), antlerite ($Cu_3SO_4(OH)_4$), and posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$), accompanied, in marine environments, by atacamite-type minerals ($Cu(OH)_3Cl$) and CuCl (nantokite) [23, 24, 30–35]. In soils, malachite ($CuCO_3 \cdot Cu(OH)_2$) is commonly formed [33]. The main corrosion products of Zn in rural atmospheres are zincite (ZnO) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$), while in the presence of high chloride concentrations simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) is also formed [34]. Consistently with SEM/EDX data, square wave voltammetry of microsamples taken from the patina of *doré* spheres in contact with potassium phosphate buffer produced well-defined copper-centered reduction peaks, as

Table 2 Typical composition from SEM/EDX of regions of the studied sculpture exhibiting severe deterioration

Element/line	App. Conc.	Intensity	Weight%	Weight %σ	Atomic %
C K	22.51	0.4512	31.18	1.29	47.44
O K	37.12	0.6255	37.09	0.76	42.36
Mg K	0.17	0.4526	0.23	0.05	0.17
Si K	0.76	0.6921	0.69	0.04	0.45
S K	2.62	0.8489	1.93	0.07	1.10
Cl K	1.37	0.7502	1.14	0.05	0.59
K K	0.76	1.0252	0.46	0.04	0.22
Ca K	1.91	0.9847	1.21	0.05	0.55
Fe K	0.50	0.9079	0.35	0.05	0.11
Cu K	7.60	0.8087	5.87	0.18	1.69
Zn K	24.12	0.8065	18.69	0.42	5.22
Pb M	1.50	0.7993	1.17	0.18	0.10

shown in Fig. 6. For moderately altered samples (BM1, BM2), a prominent reduction peak at −0.15 V vs. AgCl/Ag was recorded (Fig. 6a). Tafel analysis of the rising portion of that peak, using reported procedures [17–19], permits to attribute it to any mineral of the atacamite group (possibly clinoatacamite) as the main component of the altered region. Minor component accompanying the above alteration product are cuprite and minerals of the group of copper sulfates. For severely altered pieces (BS1 and BS2), copper-centered peaks are accompanied by a cathodic peak at −0.70 V (Fig. 6b) which can be attributed to the reduction of Zn minerals whose identification is currently uncertain. These results are in principle consistent with the storage and conservation conditions of the sculpture in the Museum of Villafamés (Castellón, Spain), a village located near the Mediterranean Sea.

Electrochemical characterization

Figure 7 compares the potential/time responses obtained for OCP measurements for: (a) BS1, (b) BM1, (c) BG1, and (d) BU1 immersed into 0.10 M NaCl. In the case of altered pieces, BM1 (and BM2), and, in particular, BS1 (and BS2), irregular peak-shaped potential features are recorded. Such features can be attributed to patina rupture transients eventually associated to pitting initiation and propagation events. Such curves can in principle be considered as consistent with those reported by Leyssens et al. [23] for copper artifacts covered by usual corrosion products in contact with a different electrolyte. The response of BG1 (and BG2) was significantly uniform along time, whereas the unaltered piece (samples BU1 and BU2) presents the more negative OCP.

Consistently, potentiodynamic curves (see Fig. 8) provide corrosion potentials of −0.30 V for BU1 and −0.10 V for BG1, thus denoting that there is a relatively small difference between the noble character of doré and golden coatings. This feature can be correlated with the recognized stability of Au−chloride complexes resulting in the shift of oxidation potential of gold in contact with chloride-containing electrolytes [27–29, 36]. The relatively high-corrosion potentials of BM and BS (+0.20 and +0.70 V, respectively) suggest that the corrosion products covering the surface of doré pieces act, at least partially, as protective barriers. Passive currents were obtained in all cases, while inflections corresponding to pitting potentials were recorded in the positive region of potentials for BU samples.

Impedance spectra measured at OCP revealed significant differences between the tested electrodes. Bode plots of log (total impedance) vs. log(frequency) ($\log Z$ vs. $\log f$) for electrodes BS1, BM1, BG1, and BU1 are compared in Fig. 9. For BU, BM, and BS, a typical s-shaped Bode plot,
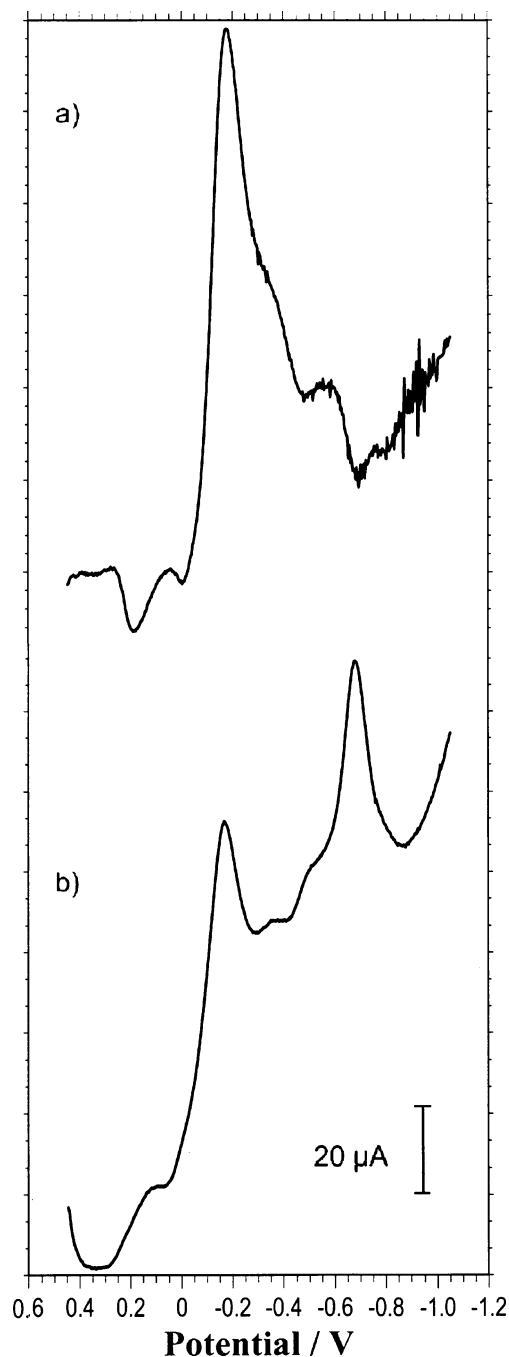

Fig. 6 SQWV for microsamples of alteration products from samples (a) BM1 and (b) BS1, transferred to a PIGE immersed into 0.50 M potassium phosphate buffer (pH 7.0). Potential scan initiated at +0.45 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz

with $\log Z$ monotonically decreasing on increasing $\log f$ is obtained. Here, altered pieces provide large impedance modulus at all frequencies. Remarkably, the behavior of BG electrode is significantly different, with low impedance modulus but with an increase of impedance at high frequencies.
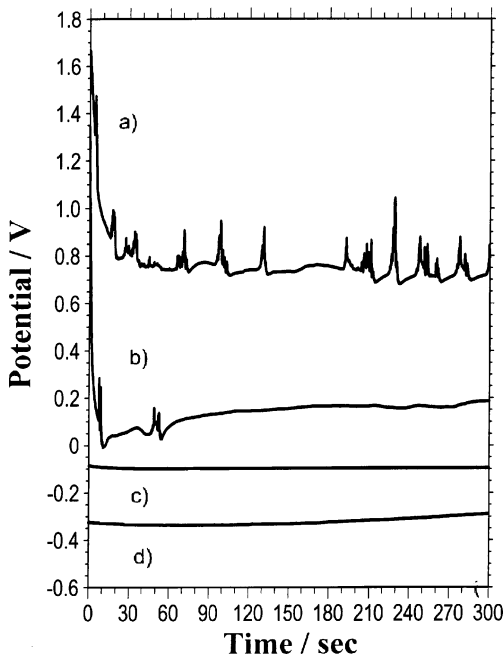
Fig. 7 Potential/time curves corresponding to OCP measurements for (*a*) BS1, (*b*) BM1, (*c*) BA1, and (*d*) BU1 immersed into 0.10 M NaCl

Fig. 9 Bode plots of log(total impedance) vs. log(frequency) for samples BS1, BM1, BU1, and BG1 immersed into 0.10 M NaCl

The different behavior of BU and BG electrodes was confirmed by Bode plots of phase angle vs. log(frequency) (φ vs. $\log f$), shown in Fig. 10. The Bode phase angle spectra of BG is close to that reported for polymer-coated Co-coated Si wafers by Bellucci et al. [37], the spectral profile revealing the existence of at least two time constants.

The Nyquist plot for BU1 (see Fig. 11a) exhibits a capacity depressed semicircle at low frequencies and a pseudo-inductive semicircle at low frequencies. This response, however, clearly differs from those recently reported for electrochemical corrosion of nanocrystalline

Fig. 8 Potentiodynamic polarization curves for (from *upper to lower*) BG1, BU1, and BM1 immersed into 0.10 M NaCl. Potential scan rate 2 mV/s
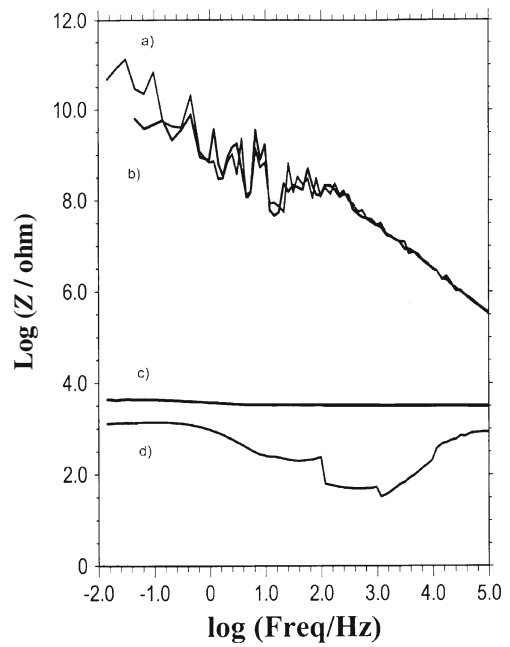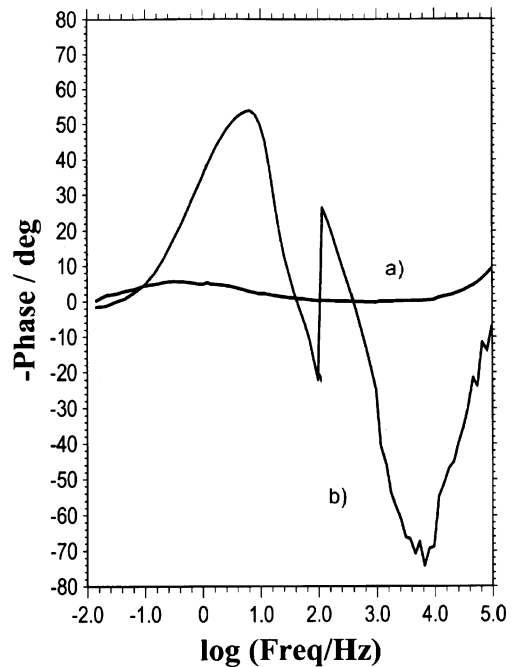

Fig. 10 Bode plots of log phase angle vs. log(frequency) (σ vs. $\log f$) for samples (*a*) BU1 and (*b*) BG1, immersed into 0.10 M NaCl
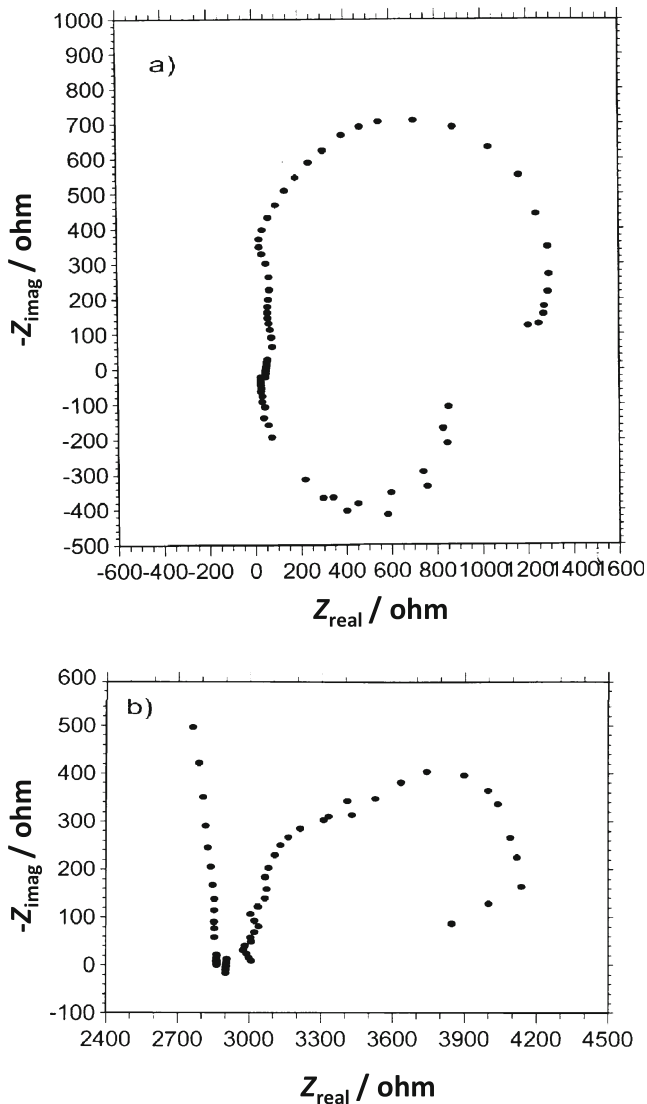
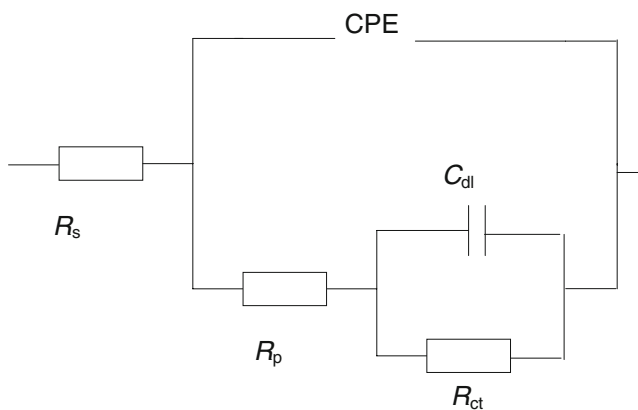Fig. 11 Nyquist diagram for samples BU1 and BG1 (**a** and **b**)

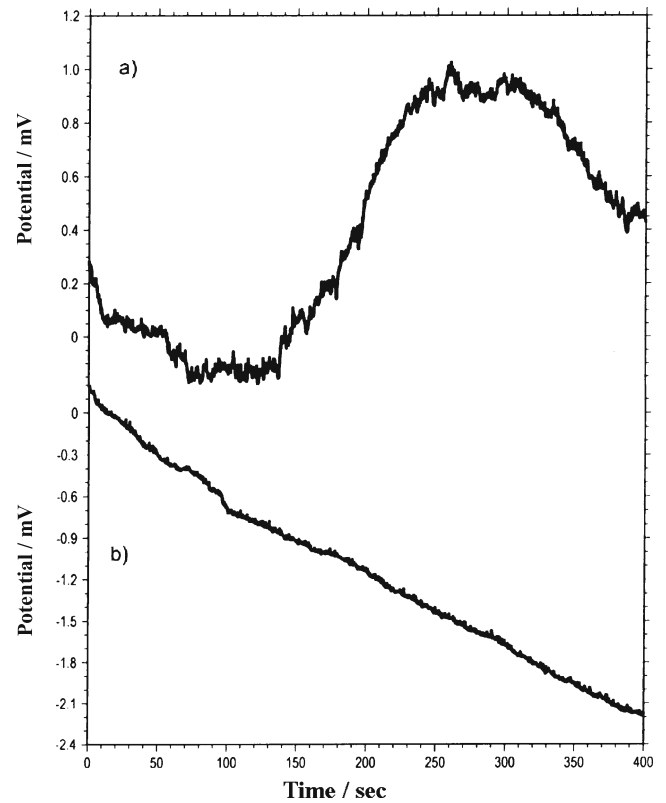Fig. 12 Equivalent circuit used for describing EIS of sample BU1

Fig. 13 EN potential/time records for (*a*) BU1 and (*b*) BG1 electrodes immersed into 0.10 M NaCl

Zn coatings in NaCl solutions [38–40]. The capacitive depressed semicircle can be modeled by an equivalent circuit constituted by a solution resistance, R_s, in series to a parallel combination of a constant phase element (CPE) close to a Warburg impedance [25, 26] and a resistance associated to the passive layer, R_p [41, 42]. The high frequency resistance and CPE can be attributed, following literature [43–45] to the effect of passive layer with ionically conducting paths, while the low frequency imped-
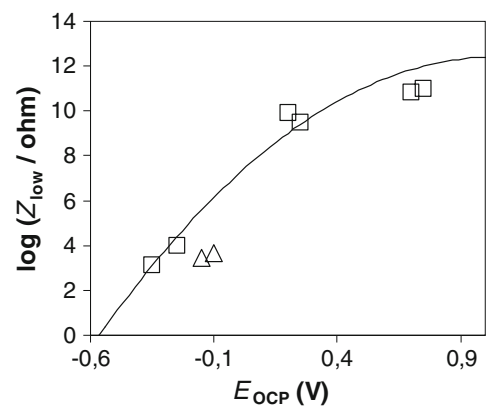

Fig. 14 Plot of the logarithm of total impedance at low frequencies, Z_{low}, as a function of the open circuit potential, E_{OCP}, for samples BU, BM, BS (*squares*), and BG (*triangles*)
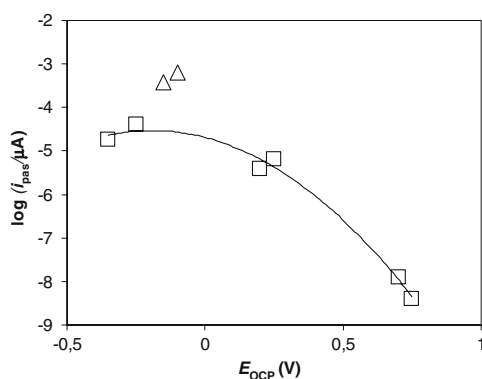
Fig. 15 Variation of the logarithm of passive currents obtained in potentiodynamic polarization curves as a function of the open circuit potential, E_{OCP} for the studied samples BU, BM, BS (*squares*), and BG (*triangles*)

ance can be modeled as a combination of double layer capacitance, C_{dl}, and the charge transfer (or polarization) resistance, R_{ct}, associated to the points where the solution reaches the metal surface and corrosion occurs. The semicircle depression (i.e., the rotation of the semicircle center by an angle below the real axis) being attributable to surface roughness, but also to cell geometry giving rise to time constant dispersion [46, 47]. This behavior is close to that reported for the pitting region of austenitic stainless steel in chloride-containing environments [48]. The overall equivalent circuit is depicted in Fig. 12.

For BG1 and BG2, however (see Fig. 11b), Nyquist plots exhibit three depressed capacitive-like semicircles with their centers in the real axis, one at high frequencies and two another at middle and lower frequencies. This response can in principle be described in terms of a corrosion process under mixed charge transfer and diffusion control, as described by Pérez-Herráez et al. [49], but sharp discontinuities in the record makes it difficult to correlate experimental data with possible equivalent circuits. The modification of that response with respect to that of BU can be attributed to the contribution of adsorption effects and/or chloride bonding to gold in the protective gold coating. This results in a significant modification of the charge transfer from the metal

to the electrolyte, reflected in the high-frequency EIS response.

The relevant point to emphasize is that the EIS response of BG electrodes clearly differs from that recorded for BU ones; i.e., that *doré* and golden coatings cannot be considered as equivalent from an electrochemical point of view (*vide infra*). Consistently, electrochemical noise (EN) measurements performed in both current/time and potential/time modes exhibited significant differences between BG and BU electrodes. In all tested samples, transients associated to the pitting initiation and propagation were recorded but, as can be seen in Fig. 13, potential/time responses for BU1 and BG1 electrodes are significantly different. At the expense of a more detailed interpretation of such data, it appears that BU and BG electrodes exhibited different electrochemical behaviors.

Implications for conservation science

Tentatively, we can introduce the concept of 'electrochemical equivalence' between two systems as the qualitative coincidence between the electrochemical responses of such systems under selected experimental conditions. More strictly, electrochemical equivalence should involve a reasonable uniformity in quantitative parameters (for instance, OCPs, etc.). In the studied case, a comparison of electrochemical properties of the studied probes reveals that gold-plated and *doré* pieces cannot be considered as electrochemically equivalent because OCP, NS, and EIS responses were found to be qualitatively different. This means that, apart from chemical composition, color, and possibly other physico-chemical properties, both types of treatment are not equivalent from an electrochemical point of view.

In order to evaluate the conservation treatment of the sculpture, another type of factors, however, can be considered: the change of the visual aspect of the piece and its resistance to degradation along time and possible future conservative/restorative treatments. To evaluate these factors, electrochemical data can be used. Thus, Fig. 14 shows a plot of the logarithm of total impedance at low

Table 3 Factors involved in alternative treatments of metallic pieces for conservation

Possible treatment	Advantages	Disadvantages
Plating with gold	Presumably long-time chemical, electrochemical, and chromatic stability	Material, mechanical, chromatic, and electrochemical properties differing from the original *doré*: the sculpture is necessarily 'new'
Cleaning	The original composition, color, and texture of the pieces are approximately maintained	Chemical, textural, and chromatic alterations with time; the sculpture varies with aging
Cleaning plus electrochemical *doré*	The composition, color, and texture of the pieces are close to the original	Strictly, the surface of the sculpture is entirely 'new' Chemical, textural, and chromatic alterations with time; the sculpture varies with aging

frequencies, $\log Z_{low}$, as a function of the open circuit potential, E_{OCP}. On first examination, both quantities can be considered as representative of the surface degradation of the piece, in turn representative, assuming stationary conservation conditions, of the duration of the corrosion process. However, E_{OCP} can be taken as a quantity associated with the composition change resulting from the corrosion process, Zn loss in particular [35, 50], while the impedance modulus at low frequencies can in principle be associated to charge transfer resistance plus uncompensated ohmic drop in the cell, roughly related with the nature and thickness of the corrosion layer covering the pieces. Accordingly, $\log Z_{low}$ can be regarded as a quantity which possibly is more sensitive than E_{OCP} to texture and color changes experienced by the piece. Accordingly, the variation of $\log Z_{low}$ on E_{OCP} depicted in Fig. 14 can be interpreted in terms of the modification of the visual aspect of the piece with time. A similar situation can be obtained on plotting the logarithm of passive currents from potentiodynamic polarization curves (see Fig. 8) vs. E_{OCP}, as can be seen in Fig. 15. Electrochemical data reveal that, under brass cleaning or *doré* plating, the sculpture undergoes a slow deterioration with time and a concomitant change in its visual characteristics.

Table 3 summarizes the essential considerations dealing with the possible alternative treatments for the conservation of the studied sculpture. Data presented here clearly suggest that, for the case studied here, there is no equivalence between the responses of *doré* pieces and the possible golden treatment. However, it is reasonable to conjecture that in other possible cases, the choice between different conservation/restoration alternatives (for instance, different types of *doré*, different modalities of cleaning/polishing, etc.) cannot be straightforward. In these circumstances, criteria for electrochemical equivalence should be of interest in order to select the most appropriate conservative treatment. Obviously, however, the concept of electrochemical equivalence has to be revised in the context of aesthetic and ethic demands in conservation science.

Final considerations

Electrochemical methods can provide a characterization of different electrochemical parameters (pitting potential, passive current density, etc.) able to be used for an electrochemical characterization of metal pieces from works of art. These parameters can be used for identifying pristine materials and alteration products as well as for monitoring the conservation state of the pieces. Application to the contemporary kinetic sculpture: "*I Hábitat en órbita baja de la Tierra*" (1 Habitat in low-orbit around the Earth) illustrate the use of electrochemical techniques for gaining

information on materials and conservative treatments to be applied to metallic works of art.

The concept of electrochemical equivalence can tentatively be proposed in order to establish the conditions for applying conservative treatments to works of art. This can in principle be used as a precondition to be accomplished by possible interventions on work of art pieces.

In most cases, the choice of a given conservative treatment involves aesthetic and ethic problems dealing with the materials, techniques and, lastly, in the conceptual and formal interpretation of the oeuvre. Electrochemical data can be used for obtaining information of interest for evaluating the above factors.

References

1. Green LR, Thickett D (1991) Modern metals in museum collections, saving the 20th century: the conservation of modern materials. Conference Proceedings of Symposyum '91, Ottawa, Canadian Conservation Institute, pp 261–272
2. Campbell SA, Gillard SP, Beech IB, Davies W, Monger G, Lawton P (2005) Trans Inst Metal Finish 83:19
3. Guilminot E, Baron G, Memet JB, Huet N, Le Noc E, Roze JP (2007) In Degrigny C, Van Langh R, Joosten I, Ankersmith B (eds) Procs. of Metal 7 Interim Meeting of the ICOM-CC Metal WG. Amsterdam (vol. 3) p. 38
4. Delard F, Gourbeyre Y, Degrigny C (2002) Stud Conserv 47:117
5. Costa V, Dubus M (2007) Impact of the environmental conditions on the conservation of metal artifacts: an evaluation using electrochemical techniques, Museum Microclimates, T. Padfield, ed., The National Museum of Denmark pp 63–65
6. La Niece S, Craddock P (1993) Metal plating and patination: cultural, technical and historical developments. Butterworth-Heinemann
7. Hugues R, Rowe M (1997) The colouring, bronzing and patination of metals. Tames and Hudson Ltd., London
8. Degrigny C, Wery M, Vescoli M, Blengino JM (1996) Stud Conserv 41:170
9. Roca E, Steinmetz J (2001) Corros Sci 43:891
10. Roca E, Bertrand G, Rapin C, Lebrune JC (2001) J Electroanal Chem 503:133
11. Bobichon C, Degrigny C (2000) Stud Conserv 45:145
12. El-Letre AY, Abdallah M, El-Tantwy ZE (2005) Corros Sci 47:385
13. Abelev E, Starosvetsky V, Ein-Eli Y (2007) Electrochim Acta 52:1975
14. Raja PB, Sethuraman MG (2008) Mat Lett 62:113
15. Quachick O, Bouyanzer A, Bouklah M, Desjobert J-M, Costa J, Hammouti B, Majidi L (2009) Surf Rev Lett 16:49
16. Doménech A, Doménech-Carbó MT, Gimeno JV, Bosch F, Saurí MC, Casas MJ (2001) Fresenius J Anal Chem 369:576
17. Doménech A, Doménech-Carbó MT, Martínez-Lázaro I (2008) Microchim Acta 162:351
18. Doménech A, Doménech-Carbó MT, Edwards HGM (2008) Anal Chem 80:2704
19. Doménech A, Doménech MT, Costa V (2009) Electrochemical methods in archaeometry, conservation and restoration. Springer, Berlin

20. Scholz E, Meyer B (1998) In: Bard AJ, Rubinstein I (eds) Electroanalytical chemistry, A Series of Advances, vol. 20. Marcel Dekker, New York, pp 1–86
21. Grygar T, Marken F, Schröder U, Scholz F (2002) Coll Czech Chem Commun 67:163
22. Scholz F, Schröder U, Gulabowski R (2005) Electrochemistry of immobilized particles and droplets. Springer, Berlin
23. Leyssens K, Adriaens A, Pantos E, Degrin YC (2004) Study of corrosion potential measurements as a means to monitor the storage and stabilization processes of archaeological copper artefacts. In: Ashton J, Hallam D (eds) Procs. Metal 04, National Museum of Australia, pp 332–343
24. Leyssens K, Adriaens A, Dhooghe F, Depla D (2006) Anal Chem 78:2794–2801
25. Letardi P (2000) Electrochemical impedance measurements in the conservation of metals. In: Creagh DC, Bradley DA (eds) Radiation in art and archeometry. Elsevier, Ámsterdam, pp 15–39
26. Letardi P (2004) Laboratory and field tests on patinas and protective coating systems for outdoor bronze monuments. In: Ashton J, Hallam D (eds) Procs. Metal 04, National Museum of Australia, pp 379–387
27. Cadle SH, Bruckenstein S (1974) Anal Chem 46:16–20
28. Burke LD, O'Sullivan JF (1992) Electrochim Acta 37:2087–2094
29. Doménech A, Doménech-Carbó MT, Osete L (2004) Electrochemistry of archaeological metals: an approach from the voltammetry of microparticles. In: Brillas E, Cabot PL (eds) Trends in electrochemistry and corrosion at the beginning of the 21st century. Universitat de Barcelona, Barcelona, pp 857–871
30. Graedel TE (1987) Corros Sci 27:721–740
31. Feliu S, Morcillo M, Feliu S Jr (1993) Corros Sci 34:415
32. Veleva L, Quintana P, Ramanauskas R, Pomes R, Maldonado L (1996) Electrochim Acta 10:1641–1646
33. Robbiola L, Blengino J-M, Fiaud C (1998) Corros Sci 40:2083–2111
34. Fonseca ITE, Picciochi R, Mendonça MH, Ramos AC (2004) Corros Sci 46:547–561
35. Morcillo M (2004) Atmospheric corrosion in Ubero-America. In: Brillas E, Cabot PL (eds) Trends in electrochemistry and corrosion at the beginning of the 21st century. Universitat de Barcelona, Barcelona, pp 633–657
36. Oyama T, Okajima T, Ohsaka T (2007) J Electrochem Soc 154: D322–D327
37. Bellucci F, Mitton DB, Thompson GE, Latanision RM. The relationship between substrate mass loss assessed by vibrating sample magnetometer and corrosion rate measured by electrochemical impedance spectroscopy for a polymer-coated metal. In: Brillas E, Cabot PL (eds) Trends in electrochemistry and corrosion at the beginning of the 21st century. Universitat de Barcelona, Barcelona, pp 905–921
38. Manov S, Lamazouere AM, Aries L (2000) Corr Sci 42:1235
39. Li MC, Zeng CL, Luo SZ, Shen JN, Lin HC, Cao CN (2003) Electrochim Acta 48:1735
40. Li MC, Jiang LL, Zhang WQ, Qian YH, Luo SZ, Shen JN (2007) J Solid State Electrochem 11:1319–1325
41. Lee SJ, Pyun SI (2007) J Solid State Electrochem 11:829
42. Skale S, Dolecek V, Slemnik M (2007) Corros Sci 43:269
43. Pébère N, Riera C, Dabosi F (1990) Electrochim Acta 555:35
44. Titz J, Wagner GH, Spähn H, Ebert M, Jüttner K, Lorez WJ (1990) Corrosion 221:46
45. Baril G, Pébère N (2001) Corros Sci 471:43
46. Bastidas JM, Polo JL, Cano E, Torres CL, Mora N (2000) Mater Corros 51:712
47. Silverman DC (1989) Corrosion 45:824
48. Bastidas JM, Polo JL, Torres CL, Cano E (2001) Corros Sci 43:269
49. Pérez-Herráez V, Montanez MT, García-Antón J, Griñón JL (2001) Corrosion. Nace Internat 57:835–842
50. Capobianco G, Guildi F, Moretti G (2004) An EIS study of the corrosion behaviour of PECVD coated brass surface. In: Brillas E, Cabot PL (eds) Trends in electrochemistry and corrosion at the beginning of the 21st century. Universitat de Barcelona, Barcelona, pp 967–978