APPLICATION OF ELECTROCHEMICAL TECHNIQUES TO THE CONSERVATION OF METAL ARTEFACTS: A REVIEW

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ABSTRACT

Electrochemical techniques are extensively used by scientists working in corrosion science to study corrosion mechanisms and corrosion resistance of materials in specific environments and protection systems. Such techniques have also been utilized in the conservation field, particularly to understand corrosion mechanisms affecting historic and archaeological metal artefacts where the composition of the alloy plays a major role. The study of active corrosion on bronze artefacts and pitting corrosion of aluminium alloys are well known examples.

Conservators use electrochemical techniques to monitor the storage of metal artefacts and to clean, stabilise and protect them. Often however, techniques designed originally to solve a specific conservation issue are treated as recipes and applied to any kind of material without consideration of side effects. An electrochemical technique that works well with one material is not necessarily suitable for another. Conservation electrochemists have recently designed some protocols to limit these side effects and achieve better treatments. Although these studies have been published, conservators still hesitate to use these techniques due to a lack of practical training.

This paper will present case studies and research projects related to the conservation of metallic alloys involving electrochemical techniques. Emphasis will be on the build-up of methodologies specifically adapted to conservation issues, the thorough training of conservators in the use of electrochemical techniques (e.g. monitoring of electrochemical parameters) and the necessity of a close collaboration between electrochemists and conservators during a conservation project.

KEYWORDS

Electrochemical and electrolytic systems, parameters, corrosion, value, cleaning, stabilization.

INTRODUCTION

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This paper presents case studies and research projects related to the conservation of metal artefacts involving electrochemical techniques. Emphasis will be on the build-up of methodologies specifically adapted to conservation issues, the thorough training of conservators in the use of electrochemical techniques (e.g. monitoring of electrochemical parameters) and the necessity of a close collaboration between electrochemists and conservators during a conservation project.

A BIT OF HISTORY

If electrolytic techniques\(^1\) have been used since the beginning of the 20th century to stabilise and clean archaeological artefacts \([1–5]\), it is only since the 1990s that these treatments were correctly monitored. One of the first scientist to employ them was certainly Rathgen (Berlin, Germany) who at the turn of the century applied cathodic polarisation to stabilise bronze artefacts \([3]\). He was followed in USA by Fink and Eldridge who worked extensively on Egyptian artefacts \([4]\). They designed the so-called “Fink method” that was later on criticised because of the formation with time of a blue-green excrecence that disfigured the artefacts.

New developments were performed in the middle of the century by Plenderleith (London, UK) \([6]\) not only on bronze but iron based artefacts. He preferred though electrochemical\(^2\) to electrolytic processes and was convinced that these treatments should be used in combination to mechanical ones. He suggested specific current values to clean and stabilise active artefacts. Cleaning of iron could be performed at 10A/dm\(^2\) and lower current densities (2A/dm\(^2\)) were given for iron. Once again this knowledge moved to the USA where Hamilton developed it for the conservation of marine artefacts \([7]\). North (Australia) \([8]\) further developed this approach and suggested to work at constant voltages to stabilise marine wrought (5V) and grey cast iron (3V).

Some major improvements were brought by the Valecka division of Electricity of France which reviewed the treatment of marine artefacts using electrolytic techniques from 1985 to 1995 \([9]\). Unlike previous approaches, cathodic potentials were

1 Techniques which use an external generator as a source of current.
2 The source of current is provided by the oxidation of a "sacrificial anode" such as zinc or aluminium or any other oxidation process.
chosen to monitor the cleaning and stabilisation processes. In 1988 this laboratory was in charge of the conservation of the first 2000 objects recovered from the Titanic wreck and new electrolytic techniques (electrolytic pencil, electrophoresis for organic materials) were developed at that occasion [9].

Since 1995, another French laboratory Arc’Antique specialised in the treatment of marine artefacts has been conducting research projects to assess the affect of electrolytic techniques on artefacts and to monitor properly the treatments considered [10]. As a result electrolytic parameters for the cleaning and the stabilisation of iron, copper, lead, silver are now well known and electrolytic techniques are considered as safe if used properly [11]. Further developments of these techniques are in progress [12]. Scientists try indeed to optimise the existing treatments [13] and to apply them to composites artefacts (metal/waterlogged wood or textile) [14, 15].

SOME WELL KNOWN APPLICATIONS

Major applications of these treatments concern both movable artefacts (metals and composite artefacts) and immovable structures [wall to desalinate (use of electrophoresis) and sculptures to protect (by cathodic protection)].

As regards movable artefacts the objective of the treatments is often to optimise results already achieved through the more traditional mechanical or chemical techniques, to work in much safer conditions (mechanical cleaning of soft metals might cause serious damage and the use of chemicals only might change drastically the appearance of some artefacts) and to have a more homogeneous action on the surface of the whole artefact. Some examples are presented below.

Cleaning and stabilisation of marine artefacts Apart from the removal of marine crust with hydrogen gas that evolves at the surface of the remaining material polarised cathodically, another important application is the stabilisation of active corrosion (due to chlorides salts) on copper or iron based alloys. Figure 1 shows a bell from the
wreck of the *Sundsborg* (1929, Finland) that presents areas of active corrosion (formation of green powdery atacamite and paratacamite). The cathodic polarisation of artefacts at required potentials permits the progressive removal of most of the chloride species at a faster rate than by immersion [Figure 2]. Sodium sesquicarbonate (pH=10) is used for copper based alloys [16] and potassium or sodium hydroxide for iron based alloys [17].

Innovative protocols have been designed for cleaning iron stains on non metallic artefacts such as the electrolytic pencil [Figure 3] or for removing iron salts from organic materials [Figure 4].

**Cleaning of silver tarnish** Silver tarnish is difficult to clean mechanically without damaging the surface of the precious metal. The application of a cathodic polarisation at a constant potential allows to get a less invasive and more homogeneous cleaning through the reduction of silver corrosion products (Ag₂S and AgCl) in silver. Figure 5 shows the different steps of the cleaning process on a silvered brass saxophone from the Music Museum of Paris [18].
Fig. 5  The different steps of the cleaning of silver tarnish on the surface of a Sax saxophone of the Music Museum of Paris. (a) before treatment. (b) during treatment. (c) after electrolytic cleaning and fine polishing with cotton (credit ART-Métal).

USE OF ELECTROCHEMICAL PROCESSES IN CONSERVATION: A REVIEW

Most conservation professionals have heard of the Nernst equations that refer to oxydo-reduction reactions and the E-pH diagrams (so-called Pourbaix diagrams [19]). Unfortunately most of them use electrochemical processes as recipes (cleaning provoked by the bubbling of hydrogen) without any consideration of the specificity of each material.

There is a need then of a better understanding of the role of some essential parameters such as $E_{corr}$ (corrosion potential) that requires the use of a reference electrode, the pH of the electrolyte and the cathodic and anodic potentials applied to the artefacts. These different parameters are reviewed in the following where the information gained from electrochemical systems without external current and electrolytic ones requiring an external current are clearly separated.
Without external current  When referring to electrochemical processes without any external current the most important parameter to use is $E_{\text{corr}}$. This potential represents all electrochemical reactions occurring on the metal surface while immersed in a solution. For a metal M immersed in water these reactions would be:

$$M \rightarrow M^{n+} + ne^- \quad \text{OXIDATION}$$

$$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad \text{REDUCTION}$$

As a result the precipitate $\text{M(OH)}_n$ is obtained. Each half electrochemical reaction gives a specific current ($I_a$: anodic current for the oxidation and $I_c$: cathodic current for the reduction) represented on the I-E diagram of Figure 6. $E_{\text{corr}}$ is the potential for which $I_a + I_c = 0$. Only one potential respects this condition.

$E_{\text{corr}}$ can be measured easily with a reference electrode (calomel, sulphate mercury, silver/silver chloride... ) and a multimeter. Both instruments have first to be checked to make sure that the potential measured is correct. The silver/silver chloride reference electrode is often used in conservation. Its potential versus the Standard Hydrogen Electrode (SHE) is 0.2V/SHE.

The choice of the appropriate electrolyte for a conservation treatment is based on E-pH diagrams. These diagrams give fields of stability of metallic species: either the metal is immune (M), corrodes (M$^{n+}$) or passivates (M(OH)$_n$). Figure 7a presents the E-pH diagram for Fe in standard conditions and Figure 7b a simplified version. Note that the potentials are given versus SHE. Furthermore the two diagonals (a and b) give the field of stability of the aqueous solvent. Above the upper diagonal water is decomposed in oxygen, below the lower diagonal it is decomposed in hydrogen.

The Fe Pourbaix diagram shows that to be safe the treatment should be performed in alkaline solutions (where passivation is observed). Often we use diluted NaOH or KOH solutions having a pH of 13 [17].
Fig. 7  E-pH diagram for Fe from Pourbaix [19].
(a) Standards conditions.
(b) [species] = 10^{-6} M.

Fig. 8  $E_{\text{corr}}$ vs. time for iron archaeological artefacts immersed in 0.5 M sodium hydroxide [20]. The preliminary decrease of $E_{\text{corr}}$ is due to the reaction/ transformation of the corrosion layer with the electrolyte. The thicker the layer is, the longer it takes to the potential to re-increase (normal trend of iron in sodium hydroxide).

$E_{\text{corr}}$ measurements can be used to monitor the behaviour of a metal surface with time in a specific solution. The plot obtained shows whether the metal passivates (increase of $E_{\text{corr}}$ with time) or corrodes (decrease of $E_{\text{corr}}$ with time). These trends are slightly modified when real archaeological artefacts are considered. Indeed thick corrosion layers covering the remaining metal surface are reacting with the electrolyte and change then the electrochemical behaviour of the artefact [Figure 8].
The understanding of electrochemical processes through the measurement of $E_{\text{COR}}$ is essential when studying the corrosion of an artefact conserved in-situ (in a burial or marine environment) and monitoring artefacts stored or stabilised in specific solutions [13].

**With external current** The potential of an artefact can be artificially modified with a power supply (or generator). The polarisation (or modification) is performed in the cathodic (decrease of potential from $E_{\text{COR}}$) or anodic (increase of potential from $E_{\text{COR}}$) fields. The objective here is to favour a specific electrochemical reaction for the more effective cleaning or stabilisation of an artefact. The use of a reference electrode is required to impose the correct potential as well as a counter electrode [anode (+) if the artefact is the cathode (-) or the other way round — see Figure 9]. An amperemeter can be added in the circuit to measure the current. The disadvantage of the technique is that the potentials applied are not easy to monitor when the power supply is of a poor quality (often the case). Furthermore the reactivity of the artefact might appear different than expected due to the presence of unknown corrosion products which electrochemical behaviour has still to be studied.

A simple application of this technique is the use of sacrificial anodes for the in-situ conservation of marine iron artefacts. In that case the power supply will be a zinc or aluminium anode and the potential applied will depend on the surface of the sacrificial anode.
A more advanced way of controlling electrochemical reactions on a metal surface is through the use of a potentiostat. This "sophisticated" power supply has three terminals instead of two [Figure 10]. The artefact is the Working Electrode (WE). The second terminal is for the counter electrode (CE) and the third one for the reference electrode (RE). Not only this instrument allows to work at constant potential (either cathodic or anodic) and to monitor the current with time but measurements can be made to define the conditions of a treatment. These measurements often start from $E_{corr}$ and the potential of the artefact is scanned (at a rate between 1 to 60mV/s) in the cathodic or anodic fields to reveal the different electrochemical reactions that can occur before the decomposition of water in hydrogen (cathodic side) or oxygen (anodic side).

Once the conditions of the treatment have been established a simple power supply can be used to apply the required potential. There are exceptions though where it is safer to use a potentiostat. For instance when the artefact is very small and requires very low current or when unknown corrosion products are present at the surface of the artefacts and need to be studied. The potentiostat can be controlled via a PC equipped with a corrosion software.

As an application Figure 11 shows how would react a metal surface covered with a specific corrosion product immersed in a solution that is electrochemically inactive. When its potential is scanned in the cathodic field from $E_{corr}$ to the decomposition of the aqueous solution in hydrogen, the voltammetric curve shows first a plateau corresponding to the reduction of oxygen dissolved in the solution. A peak starting at $E_{cp}$ (cp refers to cathodic peak) appears afterwards and corresponds to the reduction of the metallic species $M^{n+}$. Finally the important wave corresponds to the evolution of hydrogen, starting at $E_{H2}$. We are here below the field of stability of the aqueous electrolyte.
Voltammetric curves are sometimes difficult to interpret, particularly in the case of real artefacts where complex corrosion layers are present. Several peaks might overlap and no clear conclusion can be drawn as regards the corrosion products present (no characteristic Ecp can be determined). Therefore to define the conditions of a treatment, voltammetric curves are plotted on artificial coupons that simulate real artefacts but are covered with thin corrosion layers made of specific corrosion products.

**A BETTER DEFINITION OF ELECTROLYTIC PARAMETERS AND MONITORING OF CONSERVATION TREATMENTS: SOME CASE STUDIES**

**Cleaning of silver tarnish** The reduction of Ag₂S (or AgCl) in Ag only occurs when the potential of the peak corresponding to the reduction of Ag⁺ in Ag is reached [18, 22]. Attention has to be paid not to apply a too negative potential otherwise the silver reduced as small particles might be disrupted with the evolution of hydrogen [Figure 12]. It is common practise in fact to perform the reduction at the maximum of the reduction peak. The reduction process can then be monitored by plotting the current versus time as represented on Figure 13.

Problems occur when the artefact is not made of pure silver but contains some copper or is made of a silvered copper alloy. In that case there is some chance that copper corrosion products form on the metal surface. Because the reduction of copper oxide and copper sulphide happen almost at the same potential as the reduction of silver sulphide, the formation of reduced copper is expected. If in large proportion, this reduced copper will change the appearance of the metal surface.
Silver tarnish (Ag₂S or AgCl) form too on gilt silver due to the diffusion of silver through the gold layer in atmospheres rich in sulphur species. If reduced in a same way as before, the surface of the gold will be covered with reduced Ag. For that reason another electrolytic step is required to dissolve the reduced Ag in Ag⁺. This time the artefact is polarised anodically at the potential corresponding to the maximal oxidation of Ag in Ag⁺ (Figure 14a – [23]). Such an approach (preliminary cathodic polarisation followed by an anodic polarisation) has been used to clean the gilt silver plates of the shrine of St Sigismund’s children (St Maurice Abbey – CH) at the Laboratory of the Museum of Art and History (Geneva, CH). Figure 14b shows the treatment of one of the plates monitored with a potentiostat.

After the cleaning process the artefact is often quite dull and to recover the initial shine a slight polishing with cotton is needed.
Conservation of marine metal artefacts  

Figure 7b shows that depending on the value of the potential of the metal above or below diagonal b, the aqueous solution will or will not decompose in hydrogen. Still the potential at which this electrochemical reaction occurs has to be determined kinetically with a potentiostat. Figure 15 is showing the voltammetric curve for iron in 1% (w/v) KOH solution (pH=13). When scanning the potential from $E_{corr}$ to the evolution of hydrogen two peaks are revealed. The first one corresponds to the reduction of Fe$^{3+}$ in Fe$^{2+}$ and the second of Fe$^{2+}$ in Fe before the wave of the decomposition of water in hydrogen.

If cleaning of the marine crust is required, the potential to apply will have to be below $-1.6\text{V/ESS}$ (sulphate mercury reference electrode: $0.658\text{V/shE}$). In this range of values Fe$^{2+}$ will be reduced in Fe too. Once the crust is removed the stabilisation of the iron artefact can proceed at a lower potential. Since iron oxyhydroxide ($\text{bFeOOH}$) containing chloride species are decomposed at around $-1.45\text{V/ESS}$, this potential is chosen for the stabilisation process.

Electrolytic cleaning and stabilisation are applied systematically on encrusted marine grey cast iron artefacts. These artefacts are usually covered with a conductive graphitic corrosion layer that retains the original shape of the artefact. Wrought iron artefacts have often lost their original surface. Cleaning is performed mechanically then. Electrolytic stabilisation follows but it requires special care. Since no hydrogen bubbling is permitted, researchers have developed an innovative technique based on the use of pulsed currents [17] that favour fast electrochemical reactions (reduction of Fe$^{3+}$ in Fe$^{2+}$) instead of slow processes (such as the decomposition of the solution in hydrogen).
**Other applications** Aluminium alloys are very sensitive to pitting corrosion. This form of corrosion is characterized by a potential above which the corrosion develops very fast (the corresponding current increases drastically) as indicated on Figure 16a. This pitting potential is not an exact value but there is a range of potentials in which the probability of pitting increases [Figure 16b].

Aluminium alloys (Al-Cu, Al-Mg-Si, Al-Mn) from elements recovered from marine aircraft remains are impregnated with chlorides. Their stabilisation requires to immerse them in a neutral buffered solution (sodium citrate) [24]. The process can be monitored through the measurement of $E_{corr}$ versus time. It has been noticed that $E_{corr}$ increases faster for Al-Cu alloys than for Al-Mg-Si and Al-Mn [Figure 17]. Therefore the probability of pitting of the former alloys increases as well and requires more regular change of the stabilisation solution.

**CONCLUSION**
Electrochemical processes are quite complex ones. They require some basic theoretical knowledge before using them in the conservation field. Parameters such as $E_{corr}$ and the effect of pH, corrosion layers on its values are particularly important. Furthermore the information given by voltammetric curves are essential and conservators should be able to read them.
Still in parallel to this scientific knowledge a broad experience in the use of these techniques is needed if conservation professionals want to use them as efficiently as other more traditional techniques.

It is clear that the limited use of these techniques in the conservation of metal artefacts is due to the lack of practise. Training schools should absolutely insert the use of electrochemical and electrolytic treatments in conservation in the curriculum of the students. Furthermore more conservation laboratories specialised in these techniques should offer placements to students in order for them to gain the practical experience that they will never get otherwise.
REFERENCES


BIOGRAPHIC NOTE

Christian Degrigny obtained his engineering degree from the National School of Electrochemistry and Electrometallurgy in Grenoble in 1985, and later received a Ph.D. in analytical chemistry from the University of Paris VI (1990). He has conducted research in various conservation laboratories: Valestra group at Electricité de France, Conservation Annex of the Australian War Memorial, Laboratories Art Métal and Arc'Antique where he specialized in the development of electrolytic treatments in conservation. He then moved to Finland to coordinate training programmes at the Conservation Department at EVTEK – Institute of Art and Design. In 2003 he moved again to Malta to work as the head of the Diagnostic Science Laboratories at the Malta Centre for Restoration.

Since 2002 he is the coordinator of the ICOM-CC Metal WG and has been very active in promoting worldwide networking in metal conservation.

As a partner in different EU or international projects (COST Actions, INCO-MPCI PROMET, IAEA regional projects) he has been trying to use the funding possibilities of these projects to create bridges and meeting opportunities (training schools, workshops, seminars) to enlarge the skills and knowledge of conservation professionals. Currently he is a freelance expert, lecturing in different conservation schools (Oslo, La Chaux de Fond (CH), Amsterdam, Malta) and contributing to different EU projects (PROMET, COST D42). He is as well a member of the working group of Synchrotron SOLEIL/Cultural Heritage. Very recently he moved back to France to start with a colleague a cultural and scientific project at Château de Germolles, the only remaining palace of the Dukes of Burgundy (14th c.) in France. One of the objectives of the project is to setup summer schools, workshops dedicated to conservation professionals and (of course) related to a multidisciplinary approach of conservation.