

# The electrochemical techniques for the diagnosis and restoration treatments of technical and industrial heritage: three examples of metallic artefacts

Emmanuel Rocca · François Mirambet

Received: 6 May 2009 / Revised: 18 June 2009 / Accepted: 18 June 2009 / Published online: 14 July 2009  
© Springer-Verlag 2009

**Abstract** From technical and industrial heritage, curators are in charge of numerous and important collections of metallic items which are representative of the industrial and technical development of our societies. The diagnosis of the conservation state and the choice of the restoration treatment are important questions that have to be solved by curators to avoid expensive restoration works. This paper proposes to show how simple electrochemical techniques can be used as an efficient tool to contribute to the diagnosis of the conservation state of metallic artefacts and to monitor the restoration treatment through three examples. In the case of the very-corroded aluminium alloys of aircraft belonging to the Air and Space Museum (Le Bourget, France), stationary electrochemical measurements are able to characterise the allowable electrochemical effect of thick corrosion layer on the corrosion rate of metal but are not sufficient to give a complete diagnosis. In contrary, for the bronze part of the miner's lamp collection of the Mining History Centre of Lewarde, France and the

nickel-plated steel of an ancient typewriter of the Musée des Arts et Métiers, Paris, France, an inhibition treatment based on sodium carboxylate within the framework of temporary conservation treatment was applied with success, on the basis of the electrochemical results obtained in the present study.

**Keywords** Cultural heritage · Bronze · Aluminium · Carboxylate · Corrosion inhibition

## Introduction

One of the main problems encountered by curators in charge of metallic collections is related to their long-term conservation since metallic artefacts undergo corrosion phenomena which are the result of the interaction between the metal and its environment.

Since the 1970s, the number of collection registered in museums or protected buildings related to the technical scientific and industrial field has rapidly increased because society wishes to preserve those materials which constitute traces of our industrial development.

Compared to the collection of archaeological artefacts exposed in classical museums, the industrial and technical heritage is composed of numerous objects as the collection of 700 miner's lamp in the Mining History Centre of Lewarde, France or voluminous artefacts as aircrafts in the Air and Space Museum, Le Bourget, France and is composed of multi-materials as the technical objects of the collection of the Musée des Arts et Métiers, CNAM, Paris, France. Because of their size and number, this kind of collections is often stored or exhibited in uncontrolled atmospheric conditions as halls or hangars and sometimes outdoor.

---

E. Rocca (✉)  
Institut Jean Lamour (UMR CNRS 7198), Département CP2S,  
Nancy-Université,  
BP 70239, 54506 Vandoeuvre-lès-Nancy, France  
e-mail: Emmanuel.rocca@lcsm.uhp-nancy.fr

F. Mirambet  
Centre de Recherche et de Restauration des Musées de France  
(C2RMF),  
Palais du Louvre—Porte des Lions 14 Quai François Mitterrand,  
75001 Paris, France  
e-mail: francois.mirambet@culture.gouv.fr

F. Mirambet  
Laboratoire de Recherche des Monuments Historiques (LRMH),  
29, Rue de Paris,  
77420 Champs-sur-Marne, France

So, nowadays, curators and conservators have two main questions: how to diagnose and to predict the corrosion rate of these collections and how to choose or to develop specific treatments for this kind of objects?

The objective of this paper is to show how electrochemical measurements can bring some scientific and technical answers to these questions. For almost 40 years, electrochemical techniques are mainly used in the field of electrolytic treatments with the objectives of removing chemical species like chlorine anions from thick corrosion layers of marine or buried artefacts [1–3]. They were also applied to reduce corrosion products to strengthen the corrosion layer and to find again a metallic surface aspect. This electrochemical reduction of the corrosion layer was successfully applied in the case of lead artefact covered by white lead oxide and carbonates [4, 5]. Since the 1980s, electrochemical methods were also used for choosing and developing new conservation strategies in order to characterise the kinetic of the corrosion processes and to evaluate the efficiency of new protection systems [6, 7].

Now, the interest for those methods has also increased in the context of the preservation of scientific and technical metallic elements of cultural heritage since they are usually conserved in uncontrolled environmental conditions. To illustrate the electrochemical methodology that can be used in the field of the conservation of scientific and technical metallic artefacts, we present three examples in this paper.

The first one concerns the use of stationary electrochemical techniques to characterise the reactivity of corrosion layer on aluminium artefact. The objective is to contribute to a reliable diagnosis of degradation of aluminium alloys in the collections of the Air and Space Museum of Le Bourget. In fact, since 30 years, new metallic materials as aluminium or magnesium alloys appear in some industrial and technical collections.

The second one is related to the development of new non-toxic inhibiting treatment for the protection of bronze artefacts and in particular of a collection of miner's lamps belonging to the Mining History Centre of Lewarde. These protection treatments should be easy to apply, cheap and non-toxic. The two main conservation ethic rules applied in the cultural heritage domain should also be respected: no modification of the surface aspect and easily removable. Considering these constraints, soft treatments as application of corrosion inhibitors are one of the solutions that could satisfy these conditions. Corrosion inhibitors, like benzotriazole or toluotriazole, have been already used in the case of antique copper alloys conservation [8]. But now, these inhibitors cause some problems of toxicity for the applicants.

In this way, the efficiency of non-toxic linear sodium monocarboxylates of the general formula  $\text{CH}_3(\text{CH}_2)_{n-2}\text{COONa}$  as corrosion inhibitors of Cu, Zn, Pb and Mg in aerated aqueous solutions was investigated in previous

studies for industrial applications, and now, developed in this paper for the protection of metallic cultural heritage [9–11]. These compounds are derived from fatty acids extracted from vegetable oil (colza, sunflower and palm). As proved by X-ray diffraction, infrared and X-ray photoelectron spectroscopy characterisations, carboxylates have the ability to form a thin film of metallic soap after an initial oxidation of the metal surface by the dissolved oxygen in the treatment solution [12]. In general, the material responsible of the corrosion protection on the metal has a general formulae:  $\text{M}(\text{CH}_3(\text{CH}_2)_{n-2}\text{COO})_2$  where the cation is  $\text{M}^{2+}$  and  $n$  is the carbon number of the carboxylate anion. A simple inhibition treatment is proposed and tested in real conditions.

The last one presents the work realised for the restoration of a typewriter TYPO model no. 1 of Manufacture which belongs to the collection of the Musée des Arts et Métiers, Paris. This object is mainly composed of nickel-plated steel. The restoration work performed by Juliette Zelinsky concerns the two aspects of the use of electrochemical techniques: the diagnosis of the metallic materials and the evaluation of the efficiency of the restoration treatment

## Experimental methods

The metallographic observations of archaeological samples were carried out after embedding in epoxy resins under vacuum. Then, the samples were polished with successively finer grades of SiC emery papers then with colloidal silica dispersed in water or with diamond suspension (particle size = 0.1  $\mu\text{m}$ ). Some elemental analyses were performed on metallographic cross-section by electron probe microanalysis (EPMA), and a scanning electron microscope (SEM Hitachi S-2500) was used to carry out the surface observations.

For the electrochemical measurements, the corrosive medium used is the American Society for Testing and Materials (ASTM) D1384-87 standard (noted ASTM corrosive solution) [13–15], which has the following composition: 148 mg/l  $\text{Na}_2\text{SO}_4$ , 138 mg/l  $\text{NaHCO}_3$ , 165 mg/l  $\text{NaCl}$ . Linear sodium heptanoate ( $\text{CH}_3(\text{CH}_2)_5\text{COONa}$ ) and sodium decanoate ( $\text{CH}_3(\text{CH}_2)_8\text{COONa}$ ) were prepared through neutralisation of heptanoic and decanoic acid by sodium hydroxide solution until pH 8 (98 wt.%; Sigma-Aldrich reagents). Acids were firstly dispersed in deionised water at around 40°C. Then, NaOH solution was added until pH 8. At room temperature, the carboxylate concentration and pH were adjusted by dilution and addition of NaOH solution. The ASTM corrosive solutions containing different concentrations of  $\text{NaC}_n$  were prepared, and their pH was adjusted to 8 with NaOH solution. Electrochemical tests were performed in a three-electrode electrochemical cell connected to an

**Fig. 1** **a** Mirage IV in the Air and Space Museum, Le Bourget, France, **b** macroscopic aspect of the inspection hatch under the wing of the plane (exterior face)



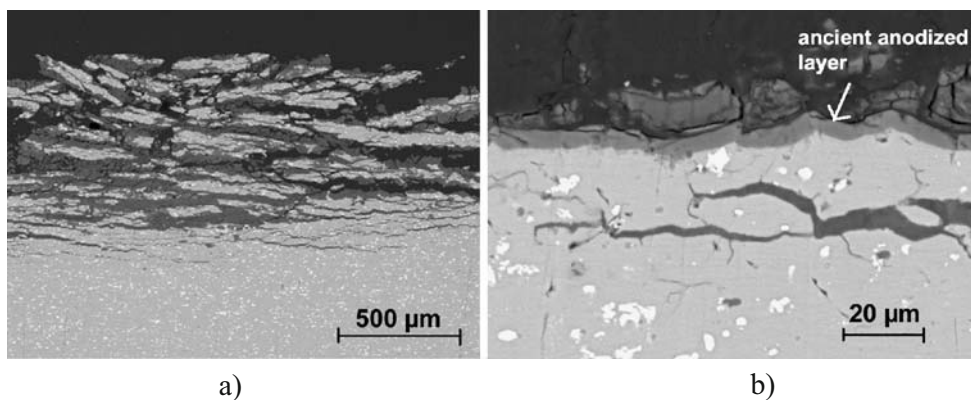
EGG PAR 273A potentiostat and driven by a computer. A circular and horizontal working electrode ( $2.8 \text{ cm}^2$ ) was placed at the bottom of the cell under a Pt-disc electrode. The reference electrode was a KCl-saturated calomel electrode ( $\text{Hg}/\text{Hg}_2\text{Cl}_2$ ,  $E=+0.242 \text{ V}/\text{SHE}$ ), and all working electrode potentials are given versus this reference electrode.

The measurement of galvanic coupling was carried out in a specific electrochemical cell constituted by the two metals, nickel and iron, and a reference electrode, driven by the same potentiostat. The two metallic electrodes have the same surface of  $3 \text{ cm}^2$ .

The modern metallic coupons (steel XC38, nickel and bronze with 20 wt.% of tin) used as working electrodes was mechanically polished with successively finer grades of SiC emery papers. These samples were finally rinsed with distilled water and ethanol and dried. The archaeological samples used as working electrode were used as received. The following experimental sequence was used in aerated conditions:

1. measurements of the corrosion potential ( $E_{\text{cor}}$ ) and the polarisation resistance ( $R_p$ ) performed every 2 h for a duration of 20 h with a scan rate of  $0.166 \text{ mV}/\text{s}$  for a range of 40 mV ( $E_{\text{cor}} \pm 20 \text{ mV}$ ). The error in the  $R_p$  measurements was evaluated at  $<10\%$ .
2. recording of the potentiodynamic curve,  $i=f(E)$ , from  $-250$  to  $1,300 \text{ mV}$  versus  $E_{\text{cor}}$  with a sweep rate of  $1 \text{ mV}/\text{s}$ .

**Fig. 2** Metallographic cross-section of the inspection hatch of Mirage 4. **a** The external face, **b** the internal face



In the case of the miner's lamp study, the following test cycle in a climatic chamber (KBEA 300, LIEBISCH) was used: 8 h at 100% humidity and  $40^\circ\text{C}$ , then 16 h under the room conditions.

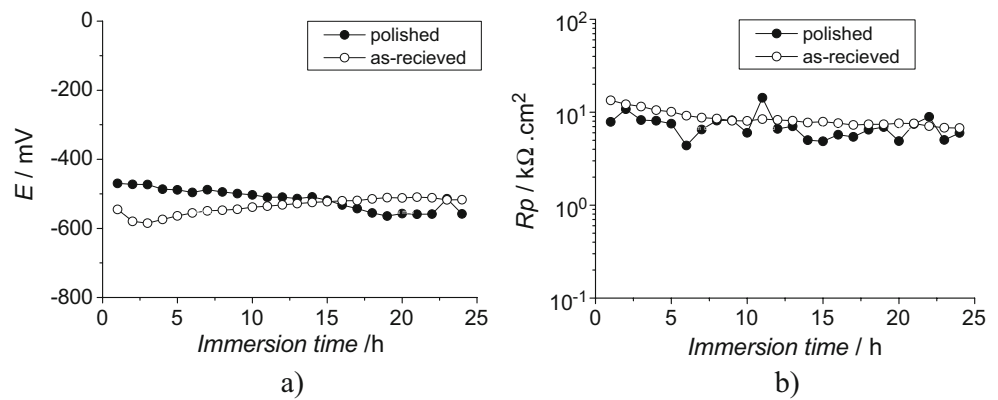
### Diagnosis of aluminium alloys in ancient aircrafts

Because aluminium alloys have been widely used for industrial purpose for almost 80 years, many aluminium elements are nowadays registered in museum collections. This fact is very significant in the case of air and space museums which preserve a large number of aircrafts mainly made of aluminium alloys.

Unfortunately, due to the large dimensions of these aircrafts, the conservation in controlled environmental conditions is often very difficult and forces the one responsible for the collection to store them outdoor. In these storage conditions, the aluminium surface undergoes important corrosion processes. Especially, the Al–Cu alloys used as structural materials in aircrafts which are very sensitive to atmospheric corrosion leading to the growth of thick corrosion product layers at the metal surface.

The aluminium long-term atmospheric corrosion and the effect of thick layers of corrosion products on the corrosion rate are still unknown and are important for the development of coherent conservation strategies. In the field of

**Fig. 3** Evolution of corrosion potential and polarisation resistance in ASTM corrosive water of polished Al alloy and as-received Al alloy, constituting the inspection hatch under the wing of Mirage 4 (Fig. 2a)



restoration, the question of the complete removal of the corrosion layer is recurrent. In fact, the thick corrosion layers can contain some historic information like identification marks and roundel that should be conserved for historical purposes, but they may often induce a negative effect on the corrosion rate of metal. On the other hand, the removal of these corrosion layers is generally difficult to perform and very expensive due to the large surface that must be treated. Thus, curators in charge of the conservation of these aircrafts need to have information to predict the reactivity of the metal covered with thick corrosion layer to propose a diagnostic of degradation and to avoid large and expensive restoration works.

In collaboration with the Air and Space Museum at Le Bourget, France, we have studied the corrosion behaviour of very-corroded aluminium alloys observed on these airplanes. At first, several samples were collected on aircrafts over a large period from 1930 to now. In this study, the electrochemical study realised on an inspection hatch of a French fighter aircraft Mirage IV was carried out (Fig. 1).

The metallographic analysis SEM image of the cross-section of the external face and internal face presented in Fig. 2 reveals the development of intergranular and lamellar corrosion processes which lead to the formation of thick laminated corrosion layers. The average thickness of the

corrosion layer is about  $500 \mu m$  on the external face. As aluminium oxide and hydroxide are more voluminous than aluminium metal, the internal growth of the corrosion products inside the metal induce important mechanical stresses in the intergranular region of metal as can be seen in the Fig. 2a [17]. Some authors have evaluated the local mechanical stress between grains of about 4 and  $5 MN m^2$ , which leads to the crumbling of the metal.

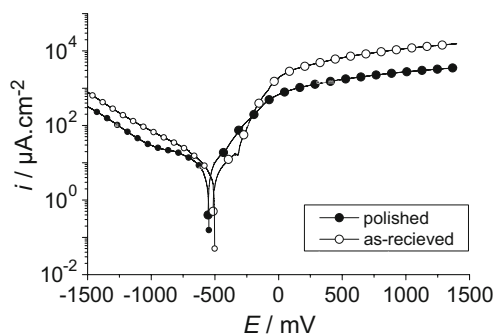
In contrary, the metallographic cross-section obtained for the inner face of the hatch show a much thinner corrosion layer as can be seen in Fig. 2b. In this case, better conservation conditions have allowed the preservation of the initial anodised layer. The homogeneous presence of several percents of sulphur and its regular thickness (about  $10 \mu m$ ) proves that this layer is the initial protective anodised layer.

Elemental analysis performed by EPMA shows that the aluminium matrix contains 3.8 wt.% of copper and 0.66 wt.% of manganese. A large amount of intermetallic precipitates can be seen in the metal with a chemical composition of  $Al(Cu, Fe, Mn)$  or  $Al_2Cu$ . This composition is very close to the AA2024 aluminium alloy composition [16].

Electrochemical measurements were performed versus the immersion time in ASTM corrosive medium on the sample covered with the thick corrosion layer, displayed on Fig. 2a, and the polished sample (clean metal). With or without the laminated corrosion layer, the aluminium alloy exhibits a very similar electrochemical behaviour as displayed in Fig. 3. During the immersion, the corrosion potential and the polarisation resistance values remain very stable at around respectively  $-500 mV$  and  $10 k\Omega cm^2$ .

However, the correct evaluation of the surface of the corroded sample, as displayed in Fig. 2a, is very difficult; so, the real surface and, consequently, the  $R_p$  values are slightly underestimated.

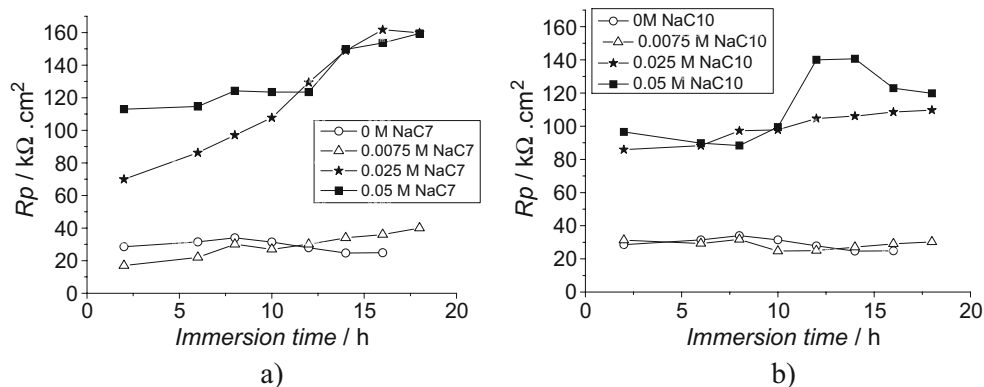
The resistance to pitting in the presence or not of the corrosion layer was evaluated by recording the potentiodynamic curves after 24 h of immersion (Fig. 4). As for the previous electrochemical measurements, the presence of a thick corrosion layer above the metal does not induce



**Fig. 4** Potentiodynamic curves of polished Al alloy and as-received Al alloy, constituting the inspection hatch under the wing of Mirage 4, after 24 h of immersion in ASTM corrosive water (Fig. 2a)



**Fig. 5** Polarisation resistance versus immersion time of bronze in ASTM corrosive water containing different amounts of **a** sodium heptanoate ( $\text{NaC}_7$ ) and **b** sodium decanoate ( $\text{NaC}_{10}$ )



change in the electrochemical behaviour. In fact, for the two samples, the current measured both on the anodic and cathodic regions are of the same order of magnitude. Consequently, electrochemical measurements performed in immersed conditions does not reveal significant differences between the corrosion behaviour of polished and as-received or corroded samples.

In others words, the presence of thick corrosion layer on aluminium alloys has a poor effect on the electrochemical kinetic of the corrosion phenomenon in immersed conditions. Moreover, if we consider that the apparent surface may be underestimated, the thick corrosion layer can be consider as slightly protective in the electrochemical point of view. This result is very different from what has been observed for iron artefact for which the composition of the corrosion layer can greatly influence the corrosion rate of iron underneath the oxide layer [18].

Nevertheless, aluminium hydroxides which are the main constituents of these corrosion layers can easily absorb some pollutants such as  $\text{SO}_x$ ,  $\text{NO}_x$ , and especially water. So, the variation of humidity and temperature in some conditions of conservation can affect the composition and the volume of the corrosion products and the cyclic change of corrosion products volume as a function of humidity and temperature can induce important mechanical stresses in these intergranular corrosion forms. The influence of sharp

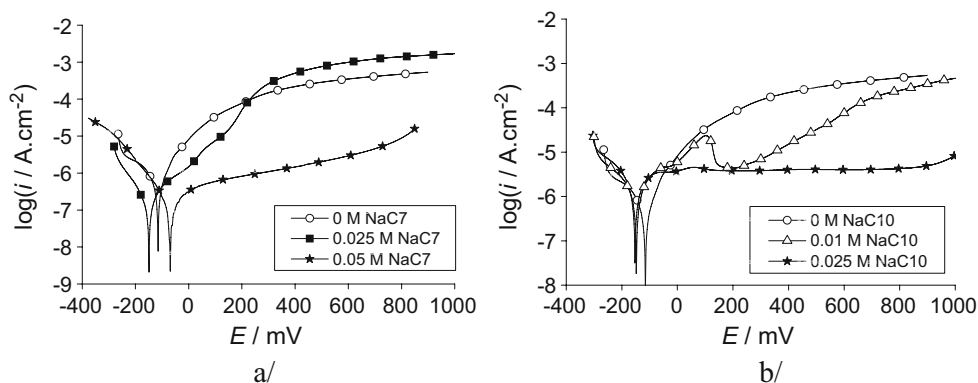
temperature and humidity fluctuations is not modelled and the influence of the mechanical properties of the corrosion layer is not considered in electrochemical measurements in immersed conditions.

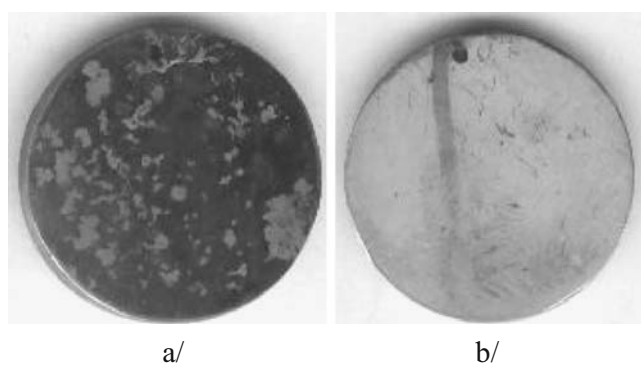
In this case, electrochemical measurements are not sufficient to conclude about complete recommendations on conservation or restoration treatments. Further work should be devoted to the study of cyclic hydration and swelling of corrosion products of aluminium, which can be the main threat for the conservation of aluminium artefacts in cyclic atmospheric conditions. Then, the objective of future protection systems could be a stabilisation of the aluminium hydroxide compounds versus the hydration processes.

### Protection of miner's lamp in bronze

The development of new soft processes which can contribute to a decrease of the corrosion rate of metallic artefacts is one of the objectives of research in conservation. This kind of research is mainly motivated by large requests of curators responsible of metallic collections who try to avoid systematic and expensive restoration works. This is the case of the collection of 700 miner's lamp of the Mining History Centre of Lewarde localised in an old colliery.

**Fig. 6** Polarisation curves of bronze after 24 h of immersion in ASTM D1384 water containing different amounts of **a** sodium heptanoate ( $\text{NaC}_7$ ) and **b** sodium decanoate ( $\text{NaC}_{10}$ )





**Fig. 7** Photographs of bronze coupons after 21 days in the climatic chamber **a** without inhibiting treatment and **b** treated in a 0.05-M sodium decanoate solution during 24 h

In this part, we report the results obtained with sodium carboxylate compounds for bronze protection. The efficiency of heptanoate and decanoate anions was evaluated by both stationary electrochemical measurements and accelerated tests in a humidity chamber. Then, an inhibition treatment was set up and applied on parts of miner's lamp in bronze.

#### Inhibition efficiency on bronze (20 wt.% Sn)

Firstly, the inhibition efficiency on bronze coupons was evaluated. Figure 5 shows the evolution of the polarisation resistances of bronze in both ASTM corrosive water and the same electrolyte containing different amounts of sodium carboxylates. For carboxylate concentrations higher than 0.0075 M, the  $R_p$  values reach a 100- to 150-k $\Omega$  cm<sup>2</sup> range, which corresponds to an inhibition coefficient (IC) of about 85% ( $IC = (R_{p_{with\ inhibitor}} - R_{p_{without\ inhibitor}}) / R_{p_{with\ inhibitor}}$ ). The  $R_p$  values recorded in the presence of NaC<sub>7</sub> seems slightly higher than the one with NaC<sub>10</sub>. Nevertheless, the two carboxylates exhibit comparable protection at corrosion potential.

The polarisation curves recorded on the bronze soaked in ASTM corrosive water containing sodium carboxylates confirm their inhibiting character (Fig. 6).

Without inhibitor, the current density in the anodic region rapidly increases until 0.1 mA/cm<sup>2</sup>, which indicates a fast dissolution of the metal in this corrosive medium. In the presence of carboxylates, the cathodic reduction of oxygen on bronze is poorly affected by the presence of the passive layer formed by the carboxylate anions, as shown by the shape of the cathodic region of the polarisation curves. In contrast, a threshold concentration is necessary to drastically affect the anodic region and to form a large passive plateau with a passive current around 10<sup>-6</sup> A/cm<sup>2</sup>. This threshold effect is also confirmed by the  $R_p$  measurements.

We can notice that the threshold concentration to obtain an efficient passive plateau is around 0.025 M with the

decanoate anion and around 0.05 M with the heptanoate anion.

With 0.01 M of NaC<sub>10</sub>, we observe an oxidation peak at around +100 mV, which corresponds to the oxidation of metal, before the formation of a small passive plateau. In fact, the concentration of carboxylates seems to be not sufficient to naturally form a protective layer of metallic soap, according to the mechanism mentioned in previous studies [8-11]

Finally, the sodium carboxylates with seven and ten carbons have a similar efficiency to inhibit bronze corrosion with a maximum IC of about 90%. Nevertheless, a long carbon chain is required to assure a sufficient protection at high potential and relatively low concentration. For example, at 0.025 M, decanoate anion allows to form a more stable passive layer than heptanoate on bronze, as shown in the Fig. 6.

These electrochemical results are confirmed by the photographs of treated and non-treated bronze coupons after 3 weeks of climatic chamber test. The inhibition treatment with carboxylates is a simple dipping in a 0.05-M sodium decanoate solution (pH 8) during 24 h to form the passive layer that is certainly constituted by metallic soap, as previously determined on others metals [9-12]. As can be seen in the Fig. 7, the treated samples with sodium decanoate show a slightly tarnished surface after 3 weeks of climatic cycle, though the non-treated sample present a dark and thick corrosion layer with some pits.

#### Applications and efficiency on miner's lamp

The final goal is to evaluate the efficiency of this inhibitor for the treatment of real samples as the miner's lamp collections of the Mining History Centre conserved in



**Fig. 8** Collection of miner's lamp in the Mining History Centre of Lewarde, France

**Fig. 9** **a** Typewriter TYPO model no. 1 of Manufrance (1913–1923), **b** a key in nickel-plated steel of the typewriter used for the electrochemical measurements



uncontrolled conditions; the inhibition treatment with sodium decanoate was tested on the copper alloy part of a miner's lamp (Fig. 8). After several months of exposition in the atmosphere of the museum, no visible corrosion is observed.

#### Diagnosis and protection of a typewriter in nickel-plated steel

Another feature of the objects of the technical and industrial heritage is that their forms are complex and they are composed of several pieces and materials. Moreover, the question of the restoration in “working in order” of some technical object is important in the project of museums. This is the case of a mechanical artefact, a typewriter TYPO model no. 1 of Manufrance (1913–1923), belonging to the collection of the Musée des Arts et Métiers, Paris, France. The major part of the mechanical pieces of the typewriter was made in nickel-plated steel. The greenish colour and the presence of orange pits on these pieces indicate important corrosion, which are unattractive for museum exposition and prevent the working of the mechanism (Fig. 9).

So, the objectives are to evaluate the corrosion behaviour of the materials, which can be named “corroded nickel-

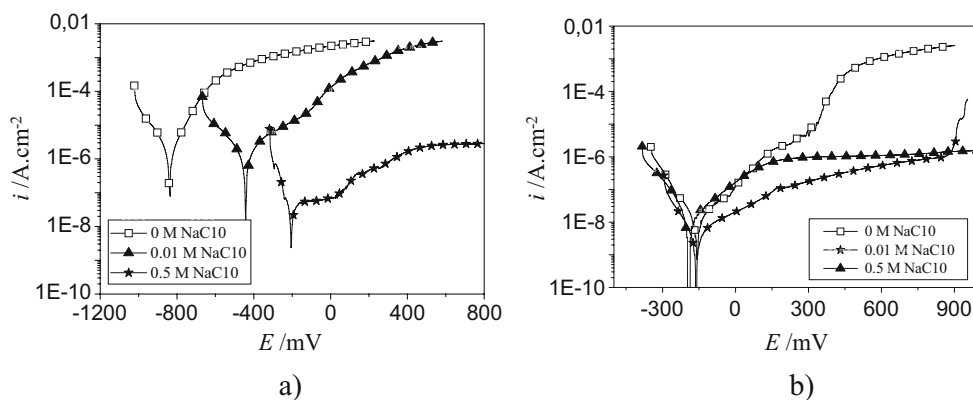
plated steel”, and to propose an inhibition treatment adapted to this kind of object (work performed by Juliette Zelinsky).

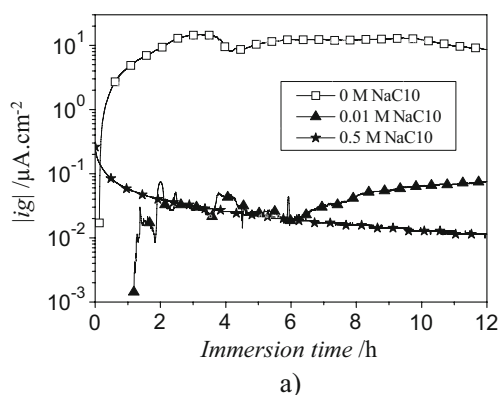
In the same way, the use of a soft protective treatment with a corrosion inhibitor is the chosen strategy for the conservation treatment.

In this case, the potentiodynamic curves of steel and nickel in these materials were recorded after 24 h of immersion in ASTM solutions containing different concentrations of sodium decanoate (Fig. 10). The steel sample shows a relatively low corrosion potential value without inhibitor in the ASTM corrosive water (around  $-800$  mV) and is rapidly corroded when the potential increases. We can note an anodic current density of  $1$  mA/cm<sup>2</sup> at about  $-200$  mV. With the addition of sodium decanoate, the large increase of the corrosion potential value until  $-200$  mV is associated by the measurement of a large passivation plateau with a passive current density of about  $10^{-6}$  to  $10^{-7}$  A/cm<sup>2</sup> as revealed on the Fig. 10a. The inhibiting effect on steel corrosion increases with the increase of sodium decanoate concentration. Overall, the corrosion rate of steel with decanoate is approximately decreased by two orders of magnitude.

The corrosion current densities of nickel are lower than the values of steel; however, we can notice that nickel is subject to pitting phenomenon in this low corrosive media with a pitting potential at about

**Fig. 10** Potentiodynamic curves of steel (**a**) and nickel (**b**) coupons in ASTM reference corrosive water without and with 0.01 or 0.05 M of NaC<sub>10</sub> after 24 h of immersion





**Fig. 11** Galvanic current density between iron and nickel versus immersion time in ASTM reference corrosive water without and with  $\text{NaC}_{10}$

300 mV. The addition of sodium deaconate has no detectable effect on the corrosion potential and corrosion current density of nickel because the corrosion rate of nickel is already very low in the ASTM corrosive water. Nevertheless, the presence of 0.5 mol/l of  $\text{NaC}_{10}$  is able to suppress the pitting phenomenon of nickel and stabilise an efficient passive plateau with a passive current about  $10^{-6}$  A/cm<sup>2</sup>.

An important characteristic of corroded nickel-plated steel materials is the galvanic coupling between nickel and iron, which is responsible for the appearance of the orange pits in cauliflower forms on the object surface. For that, the galvanic current between nickel and iron were recorded in the presence of inhibitor. As can be seen on Fig. 11, the presence of  $\text{NaC}_{10}$  allows to almost suppress the galvanic coupling by maintaining a very low galvanic current around  $10^{-7}$  to  $10^{-8}$  A/cm<sup>2</sup>. Indeed, in presence of sodium decanoate, the corrosion potential of steel increases until a value close to that of nickel, as observed in the Fig. 10,

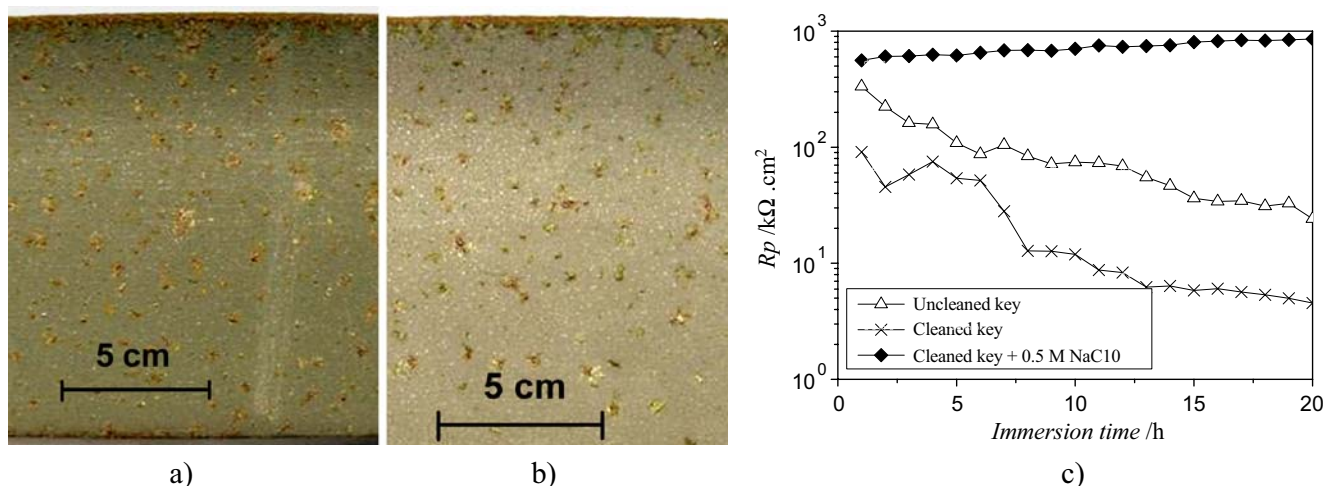
which explains the quasi-complete inhibition of the galvanic coupling between the two metals.

Preliminary measurements on modern coupons are necessary, but the archaeological materials are often more complex in composition because they are partially oxidised and inhomogeneous. So, in the case of this typewriter, it was possible to test the efficiency of the proposed procedure of restoration, especially the cleaning and the inhibition treatment on the surface of a key, represented in the Fig. 12. Only non-destructive electrochemical measurements as polarisation resistance are possible on real archaeological samples.

On Fig. 12a, b, we note that the careful washing procedure allows to clean the nickel surface, but not to remove the iron corrosion products inside the pits. Moreover, the polarisation resistance measurements show clearly that the washing procedure increases the metal reactivity and then the corrosion rate of the object, as revealed in Fig. 12c. In fact, the corrosion products and the layer of dirt on the surface act as a protective layer on this kind of object. In this case, the washing procedure increases by a factor of 10 the corrosion rate of the material.

So, a protection treatment is necessary before storing the object in the museum. For that, the addition of sodium decanoate allows to increase by two orders of magnitude the polarisation resistance of the corroded nickel-plated steel.

Consequently, all the pieces in nickel-plated steel were treated by applying a sodium decanoate solution at 0.2 M (pH 8) with a paintbrush and then rinsed with water. Several applications were necessary to keep the metal into contact with the solution during approximately 1 h to form the protective layer of metal carboxylate. After cleaning, inhibition treatment and reassembling, the normal work of the mechanism of the typewriter is now possible because



**Fig. 12** **a** Surface morphology of corroded nickel-plated steel before cleaning, **b** surface morphology of corroded nickel-plated steel after cleaning, **c** polarisation resistance measurements of corroded nickel-plated steel versus immersion time in different states (case of a key)



the layer of metal carboxylate has some interesting tribological effects [19].

### Concluding remarks

Through these three examples, we tried to show that electrochemical measurements can be one of the important tools to study ancient metallic materials of the scientific, technical and industrial heritage. Because many curators have the responsibility for conserving large and numerous collections of metallic object, it is inconceivable to do a complete and detailed work of restoration on these collections due to its cost. Consequently, some curators begin to adopt the concept of “on-site maintenance” of the collections, which allow their conservation with an acceptable cost.

In the case of diagnosis, the measurement of the corrosion behaviour by stationary techniques in conditions of immersion can only give some information about the electrochemical corrosion of the ancient metallic materials. In fact, thick corrosion layers also undergo important mechanical stresses due to successive humidity and temperature variation in conditions of conservation. Moreover, some corrosion products are very efficient absorbent materials of pollutants in the museum. This kind of effect is very difficult to estimate by simple electrochemical measurements and constitutes the limit of these techniques.

On the other hand, in the way of “on-site maintenance” of the cultural heritage, the conservators should use low-cost, simple and non-toxic conservation treatments. The evaluation of the efficiency of the treatment can be rapidly performed by electrochemical measurements. To avoid the development of corrosion layers on the bronze surface, an inhibition treatment based on sodium carboxylate within the framework of temporary conservation treatment was applied with success, on the basis of the experimental results obtained in the present study. In fact, the ability of carboxylate to form insoluble metallic soaps on the metal surface is of great interest for the conservation of large collections of metallic elements of the cultural heritage. With these new protective systems based on the principle of regular maintenance, a low-cost conservation strategy can nowadays be proposed to curators in charge of bronze collections.

To conclude, the example of the corroded nickel-plated steel on the typewriter shows how simple electrochemical measurements can be used to monitor each step of the

restoration work. The necessary step of metal cleaning increases the reactivity and the corrosion rate of the metal. Then, an inhibition treatment is required before storing the object in the museum and was easily chosen with the help of electrochemical measurements.

In the field of the materials of metallic cultural heritage, simple electrochemical measurements can be easily used for the evaluation of protection treatment and the monitoring of the restoration.

**Acknowledgments** The authors thanks Agnès Paris, the curator of the Mining History Centre of Lewarde, France; Christian Tilatti, the curator of the Air and Space Museum at Le Bourget, France; Jacques Maigret, the curator of the Musée des Arts et Métiers, France and Juliette Zelinsky, who has done the restoration work of the typewriter TYPO in the context of the final report of the conservator degree at the Institut National du Patrimoine (INP Paris).

### References

- Bertholon R, Bell B, Blengino J-M, Lacoudre N (1995) METAL 95, Proceedings of the ICOM-CC Metal WG Interim Meeting, Semur en Auxois, France
- MacLeod I, Pennec S, Robbiola L (1995). Metal 95, Proceedings of the ICOM-CC Metal WG Interim meeting, Semur-en-Auxois France
- North NA (1987) Conservation of metals. In: Pearson C (ed) Conservation of marine archaeological objects. Butterworths, London, pp 207–252
- Degrigny C, Le Gall R (1999) Stud Conserv 44:157
- Rocca E, Mirambet F, Steinmetz J (2004) J Mater Sci 39:2767–2774
- Adriaens A, De Bisschop F, Dowsett M, Schotte B (2008) Appl Surf Sci 254:7351–7355
- Rocca E, Rapin C, Mirambet F (2003) Corros Sci 46:653–665
- Madsen HB (1967) Stud Conserv 12:163–167
- Rocca E, Bertrand G, Rapin C, Labrune JC (2001) J Electroanal Chem 503:133
- Georges C, Rocca E, Steinmetz P (2008) Electrochim Acta 53:4839–4845
- Rocca E, Steinmetz J (2001) Corros Sci 43:891
- Rocca E, Caillet C, Mesbah A, Francois M, Steinmetz J (2006) Chem Mater 18(26):6186–6193
- ASTM Standard D 1384 (1988) Standard test method for corrosion test engine coolants in glassware. ASTM, West Conshohocken
- Barchiche C-E, Rocca E, Juers C, Hazan J, Steinmetz J (2007) Electrochim Acta 53:417–425
- Rahim AA, Rocca E, Steinmetz J, Kassim MJ, Adnan R, Ibrahim MS (2007) Corros Sci 49:402–417
- Korb LJ (1987) Corrosion, volume 13 of the ASM metals handbook, 9th edn. ASM International, Materials Park
- Robinson MJ (1983) Corros Sci 23(8):887
- Dillmann P, Mazaudier F, Hoerlé S (2004) Corros Sci 46(6):1401–1429
- Peultier J, Rocca E, Steinmetz J (2003) Corros Sci 45:1703