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Simultaneous in situ time resolved SR-XRD and corrosion potential analyses to monitor the corrosion on copper

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Abstract

The focus of this study consists of examining how simultaneous SR-XRD and electrochemical measurements can provide information on the effectiveness of stabilization and storage treatments of copper artefacts in aqueous solution. The electrochemical cell used here was designed for in situ, time resolved SR-XRD studies of corrosion and inhibition studies on cultural heritage materials. Key objectives of the new cell were to monitor corrosion layers on alloys with realistic metallographic structures and to obtain co-incident, time resolved, electrochemical data such as reduction measurements, oxidation measurements and corrosion potential (E_{corr}) measurements. Here we present some early results from the cell. Firstly, a correlated SR-XRD and corrosion potential (E_{corr}) study of the reduction of nantokite during storage in sodium sesquicarbonate, which shows that the surface chemistry continues to change after E_{corr} has stabilized. Secondly, the use of X-ray data to identify specific changes occurring as a function of potential in the forced reduction of a more complex system.

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1. Introduction and objectives

Electrochemical methods are widely applied in corrosion science, including the conservation of cultural heritage metallic artefacts [1–13]. In the latter case, the use of treatments and analytical techniques is significantly constrained due to the fact that the objects under investigation are unique and precious. As a consequence, all conservation/preservation methods (e.g., cleaning, coating, passivation) need to be understood thoroughly (ideally before first use), and preferably are required to be non-invasive and reversible.

Until recently, electrochemical conservation/preservation methods have always been evaluated using ex situ techniques, including XRF, XRD, XAS, SEM, SIMS, etc. This dictates that the samples under investigation need to be transferred out of their solution and potential environment and sometimes into vacuum. This environmental change will almost certainly alter the surface. Therefore, it is likely that in situ techniques will bring a significant extra contribution to the understanding of surface reactions at electrodes, as they do not require an electrode transfer outside the cell, and in addition the electrode potential can be maintained during the complete surface characterization process. Most importantly, it becomes possible to characterize the surface using electrochemistry in parallel with SR-XRD, XAS or other analytical techniques. All of these aspects are crucial to the interpretation of time dependent surface reactions.

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In this study, we have evaluated an electrochemical cell for simultaneous monitoring of the surface and electrochemical behaviour of archaeological copper-based alloys during their storage and stabilisation.

The combination of SR-XRD, SR-XAS and electrochemistry has been described by a number of authors [14–23] many of whom have published suitable designs for electrochemical cells for use in situ in a synchrotron beam line. As a rule, this work has concentrated on surfaces which are ideal in some way, e.g., single crystals [14–20] or thin layers suspended on an X-ray-transparent membrane [21–23]. Here, we make use of a cell developed for rough, heterogeneous metal surfaces, either fragments of real artefacts, where these can be used, or close simulants. The surface roughness, which may be on a scale from 1 to 100's μm , arises from the normal state of the metal, or from the corrosion crust. The heterogeneity is that of a polycrystalline material which may (in the most complex case) be a multiphase alloy with inclusions coated with several corrosion products.

Archaeological copper-based artefacts recovered from wet and salty environments should not be exposed directly to the atmosphere as the metal usually corrodes at an accelerated rate in the oxygen-rich air [24]. Tap water and sodium sesquicarbonate are typical media for, respectively, the storage and the stabilisation of such artefacts [10,25,26]. Nevertheless, the metals often show certain instability, such as the transformation of the natural patina and the development of active corrosion [27,28], which means that process-monitoring is essential. In this study, we examine how corrosion potential measurements (E_{corr}) can provide information on the effectiveness of the stabilisation and storage treatments, as part of a research project which aims at giving a simple early warning system to conservators to monitor the treatment of copper artefacts in aqueous solution. The corrosion potential (=potential without sending a current through the cell) provides information about the solution, metal and interface (in this case the corrosion products) system. The hypothesis behind the method is that if the corrosion potential does not change as a function of time, the surface composition should be stable.

2. Experimental

2.1. Cell design

A specialized electrochemical cell compatible with synchrotron radiation XRD, and other X-ray based methods, e.g., EXAFS and ODXAS was used. This is described in more detail elsewhere [29]. Fig. 1 shows a schematic diagram of the cell. A precisely moveable working electrode is used to translate the reacting surface from a “normal” position, in proximity to a reference electrode, through an annular platinum counter electrode to a “diffraction” position close to a flexible 8 μm thick Kapton window. In the latter position, the path length for X-rays in the electro-

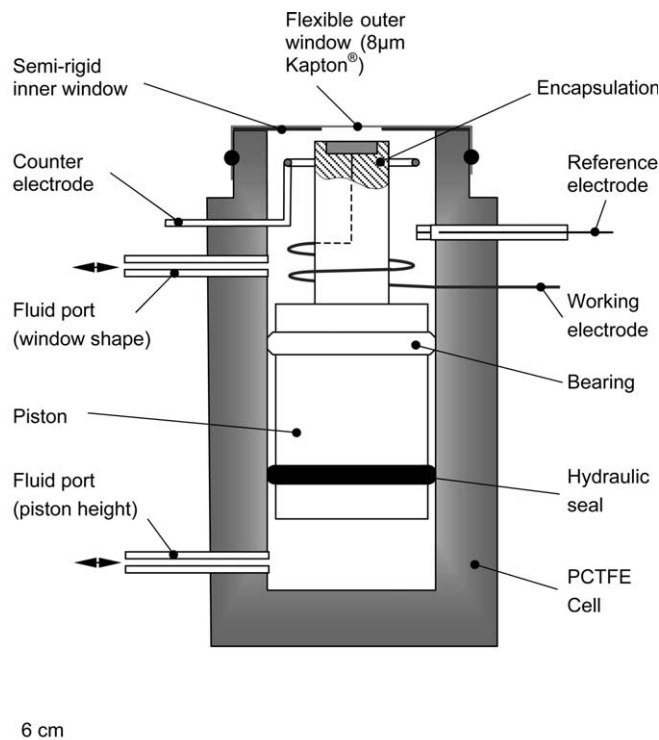


Fig. 1. Schematic drawing of the newly developed electrochemical cell.

lyte is a fraction of a millimetre to reduce scattering and X-ray absorption. In order to get permanent potential control on the electrode surface, a rigid polyethylene tetraphthalate inner window with a rectangular or elliptical hole in the middle is positioned just inside the Kapton, limiting the electrolyte thickness in a reproducible manner to 100–175 μm , depending on its thickness. In this way, the cell can be used down to X-ray energies below 8 keV. The two windows are tightly fastened onto the cell body by an O-ring. The cell is equipped with an inlet and outlet for electrolyte solution. The working electrode is mounted on a piston which is raised and lowered hydraulically using the electrolyte as the working fluid. Additional fine control over the thickness of the electrolyte layer is provided by drawing the outer window into the hole in the inner one by adjusting the hydrostatic pressure in the upper part of the cell. The cell is equipped with a silver/silver chloride reference electrode and a platinum counter electrode.

2.2. Sample preparation

Circular copper coupons, 12 mm in diameter (ADVENT, purity 99.9%) were ground on 1200 grit SiC paper to obtain a fresh surface. Further smoothing of the surface was carried out using a polishing cloth covered with alumina powder of 1 μm particle size. The adherent Al_2O_3 particles on the surface were removed by immersing the samples in an ultrasonic bath for 15 min and rinsing them thoroughly with deionised water. Afterwards, various corrosion protocols were used to obtain the different corrosion products. Copper covered with nantokite (CuCl) was ob-

tained by immersing pure copper coupons for 1 h in a saturated $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution. After rinsing with deionised water they were exposed to the air over night [30]. To obtain a mixture of atacamite and paratacamite (both isomers of $\text{Cu}_2(\text{OH})_3\text{Cl}$) a solution of 10.02 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 10.01 g NaCl in 100 mL deionised water was prepared. The copper samples were wetted twice a day with this solution for a period of five days. Between each application the samples were left to dry in air. They were then left in air for a further five days without any treatment [30].

2.3. Electrochemical measurements

All experiments were performed using a CHI1232 hand held electrochemical potentiostat (IJ Cambria Scientific Ltd.) connected to a laptop. A silver/silver chloride electrode (SSCE, $\text{Ag}/\text{AgCl}/\text{KCl}$ (3 M)) was used as reference electrode ($=0.440$ V vs. NHE). The prepared coupon disc electrodes were analyzed in 30 mL of electrolyte solution. No stirring was applied. The voltammograms were recorded with scan rates of 0.1 mV/s. Corrosion potential measurements as well as voltammetric curves were recorded in a 1 wt.% sodium sesquicarbonate solution (0.05 M $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3$).

2.4. SR-XRD analyses

The synchrotron X-ray diffraction (SR-XRD) experiments were carried out using a 2-circle high-resolution powder diffractometer at station 2.3 [31–34] at the Synchrotron Radiation Source, Daresbury Laboratory. A parallel monochromatic beam with a wavelength of 1.597866 Å, calibrated against a high purity Si powder standard (NIST NBS SRM640c), was used to analyze the sample surface. The incident beam angle, θ , at the cell surface was fixed at 10° and post-monochromator beam-defining slits were positioned such that an area at the sample surface of 2 mm^2 was analyzed. The diffracted beam was passed through a parallel foil collimating assembly to an enhanced dynamic range scintillation counter, both of which were mounted on the 2θ circle. This arrangement gave a 2θ angular resolution of 0.065° . The detector was scanned between 2θ values of 24° and 50° (step size of 0.02° , counting time 1 s). In a fixed θ geometry it is usual to apply a geometric correction to the measured diffraction intensities to account for the variation of the detected scattering volume as a function of 2θ . However, since the present work is concerned only with relative changes in peak height at any given 2θ , such a correction was unnecessary.

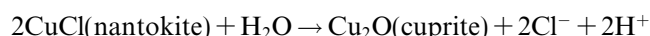
3. Results and discussion

3.1. Transformation of nantokite in sodium sesquicarbonate

In previous measurements we attempted to obtain the correlation between the surface behaviour of nantokite in a 1 wt.% sodium sesquicarbonate solution (0.05 M NaH -

$\text{CO}_3 \cdot \text{Na}_2\text{CO}_3$) and E_{corr} data using ex situ SR-XRD measurements as a function of time [35–37]. The measurements were done by removing the samples from their solution at regular intervals and performing SR-XRD measurements on a small sample of powder scratched from the surface. Results showed that nantokite (CuCl) transforms into cuprite (Cu_2O) over a period of a few hours. Ex situ measurements, however, imply the need for several duplicate samples. The surface composition is likely to change when exposed to air and the sample can as result not be re-used in the E_{corr} experiment after XRD analysis. In this study, we have avoided this problem by performing E_{corr} and SR-XRD analyses in parallel at the same time (in situ). This way of working not only avoids the sample being removed from the solution, but also allows us to acquire more XRD data per sample within a specific time frame.

Fig. 2 shows a typical SR-XRD profile of a copper sample covered with nantokite and some cuprite, while Fig. 3 shows the variation of the SR-XRD peak heights of nantokite and cuprite as a function of time. Each SR-XRD scan lasted 31 min under the conditions described in Section 2. The peak height of each individual measurement is plotted at the middle of each measuring period. The SR-XRD results clearly show the disappearance of nantokite as a function of time. In fact, after 120 min of immersion, the nantokite signal has disappeared into the background noise due to scattering in the fluid. The cuprite signal, on the other hand, grows by more than a factor of 3.5 over this time, from a small level due to the presence of some cuprite on the sample prior to immersion into the sodium sesquicarbonate solution. This is in agreement with the theory of Oddy and Hughes [25], which predicts that nantokite can react with water to form cuprite through the following reaction:



According to the same authors nantokite can also be transformed into paratacamite [25]. Previous ex situ experiments, in which the electrode was removed after one day of immersion and measured a few days later using SR-XRD, were able to confirm this [35,36]. Further investiga-

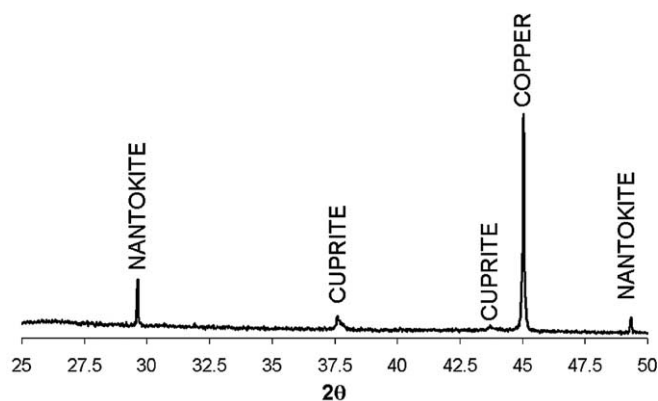


Fig. 2. SR-XRD spectrum of copper covered with nantokite.

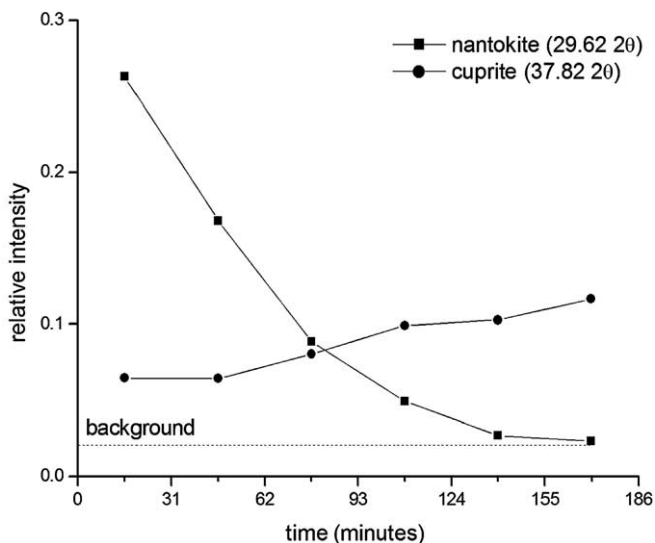


Fig. 3. Variation of the SR-XRD peak heights with time (2θ for $\lambda = 1.6 \text{ \AA}$). The signals are normalized versus the copper signal.

tion, however, is needed to detect whether the formation of paratacamite actually takes place after more than 3 h of immersion or whether it is formed due to contact with the atmosphere when the sample is taken out of its solution.

Fig. 4 shows the corrosion potential versus time plot corresponding to the data in Fig. 3. The x -axis shows the immersion time (the vertical grey lines indicate the start of each SR-XRD measurement). The y -axis gives the corrosion potential in Volts versus the Ag/AgCl/KCl (3 M) reference electrode. The variation of the corrosion potential with time recorded in the in situ cell looks very similar to results obtained using a standard electrochemical cell. The limited thickness of the fluid layer (175 μm) seems to have no significant effect on the transformation of nantokite in sodium sesquicarbonate. Nevertheless, when comparing the SR-XRD results with the E_{corr} data, the hypothesis that a stable E_{corr} means a stable surface is not supported. A significant decrease in the amount of nantokite might be expected during the first 30 min since the corrosion poten-

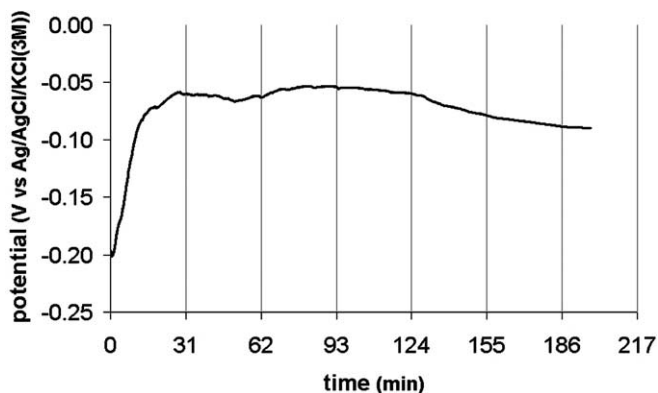


Fig. 4. Corrosion potential versus time plot of nantokite in 0.05 M $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3$.

tial shows a large alteration. In between 30 and 120 min of immersion the corrosion potential is more or less stable, implying, according to the hypothesis, no change in the surface composition. The SR-XRD data, however, tell a different story in that nantokite continues to decrease for at least 120 min. A possible explanation could be the inhomogeneity of the surface composition. Different areas on the surface can have more (or less) nantokite in their corrosion layer than the surrounding material. The time taken for the nantokite to disappear will then vary from place to place. Whereas the corrosion potentials measured give an average value over the whole surface, the SR-XRD measurements are only performed on small areas. Further experiments have to be performed to clarify this.

3.2. Reduction of nantokite, atacamite/paratacamite and cuprite

Applying a linearly varying potential from E_{corr} to -2 V/SSCE to a copper sample, covered with a mixture of corrosion products in a sodium sesquicarbonate solution, will result in a stepwise reduction of the corrosion products. Nantokite and paratacamite will be reduced at a potential of -0.1 V/SSCE . Atacamite is said to reduce at -0.26 V/SSCE . Finally cuprite will be reduced at -0.8 V/SSCE [30].

In this study, a sample covered with nantokite, atacamite/paratacamite and cuprite was submitted to a varying linear potential experiment as explained above. Fig. 5 shows the linear reduction plot obtained by scanning at 0.1 mV/s from OCP to -2 V/OCP . The top x -axis gives the potentials in V/SSCE, the bottom x -axis gives the corresponding immersion time. The y -axis presents the reduction current in A/cm^2 . Three reduction peaks can be seen: starting at -0.1 V/SSCE , at -1 V/SSCE and at -1.2 V/SSCE . Compared with an experiment in a standard electrochemical cell, the peaks are broadened due to restricted transport processes.

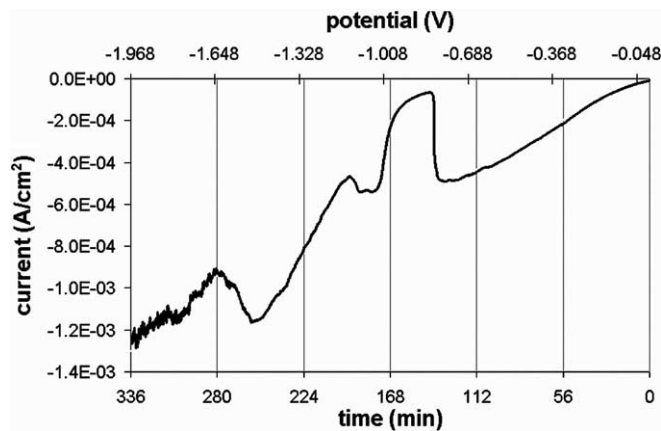


Fig. 5. Linear reduction curve of a corroded copper sample. The potential is varied from OCP to -2 V/OCP . The potential is measured with respect to an Ag/AgCl/KCl (3 M) reference electrode. The current density is presented in A/cm^2 . The measurement is performed in a 1 wt.% sodium sesquicarbonate.

A typical SR-XRD profile of a sample covered with nantokite, atacamite, paratacamite and cuprite is given in Fig. 6. The peak heights for these compounds as measured by SR-XRD are plotted in Fig. 7 as a function of time. Each SR-XRD experiment lasted 56 min. The peak height of each measurement is plotted in the middle of the measuring period. During the first 140 min the nantokite peak decreases significantly, while the amount of cuprite and atacamite/paratacamite (the resolution is insufficient to separate both signals) seems to stay more or less constant. After 140 min the nantokite peak is still decreasing slightly, but now a slight diminution of the atacamite/paratacamite peak becomes noticeable. It is only after 200 min that the cuprite peak starts to decrease.

By comparing the electrochemical and SR-XRD data, the first reduction peak (starting at -0.1 V/SSCE), which lasts from the start of the experiment to approximately 140 min later, can be assigned to the reduction of nantokite, while the second reduction peak, starting at -1 V/SSCE and

lasting from 160 to 200 min, can be assigned to the reduction of atacamite/paratacamite. Finally the last reduction peak, starting at -1.2 V/SSCE and lasting from 200 to 280 min, can be attributed to the reduction of cuprite.

4. Conclusions

Some of the first data from a new electrochemical cell for in situ analysis has been presented here. The cell is intended for use with rough, heterogeneous metal surfaces, either fragments of real artifacts, where these can be used, or close simulants. Based on the data from electrochemical and SR-XRD measurements, we confirmed that the in situ spectroelectrochemical cell works well for both electrochemical and SR-XRD measurements on artificially corroded copper electrodes. The relatively good control of the fluid pocket thickness allows us to use X-ray energies down to Cu K alpha and below.

By taking simultaneous SR-XRD and electrochemical data on Cu electrodes in sodium sesquicarbonate solution, we have observed the replacement of nantokite with the more benign cuprite in real time, but also shown that corrosion potential measurements (E_{corr}) do not necessarily provide useful information on the effectiveness of the stabilization and storage treatments. Further work is required before E_{corr} can be used as a simple early warning system for the treatment of copper artifacts in aqueous solution.

Similarly, we have shown the direct association between the potential at different stages in the reduction of a more complex system, and the removal of specific surface species in a realistic simulation of a cleaning treatment.

For all of these studies, the benefits of in situ analysis are the avoidance of air and vacuum exposure with consequently unknown surface changes, and the minimization of the number of samples required. The latter point is especially important because it means that the method can be used on the restricted numbers of real artefact fragments which can be released for testing.

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References

- [1] R. Bertholon, B. Bell, J.-M. Blengino, N. Lacoudre, in: *Proceedings of the International Conference on Metal Conservation*, 1995, James & James (Science Publishers) Ltd., London, 1997.
- [2] W. Carlin, D. Keith, J. Rodriguez, *Studies in Conservation* 46 (2001) 68.
- [3] I.A. Carradice, S.A. Campbell, *Studies in Conservation* 39 (1994) 100.

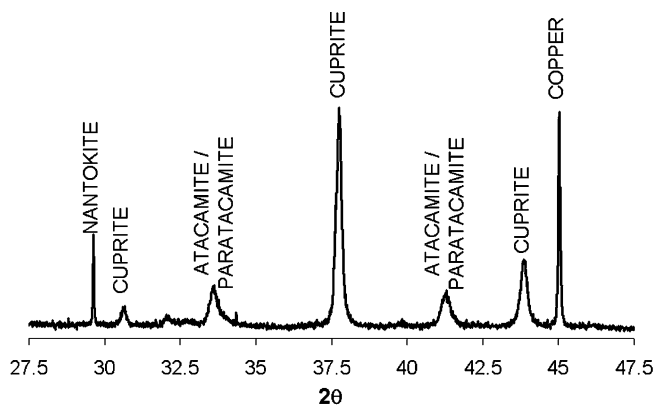


Fig. 6. SR-XRD spectrum of copper covered with a mixture of nantokite, paratacamite, atacamite and cuprite.

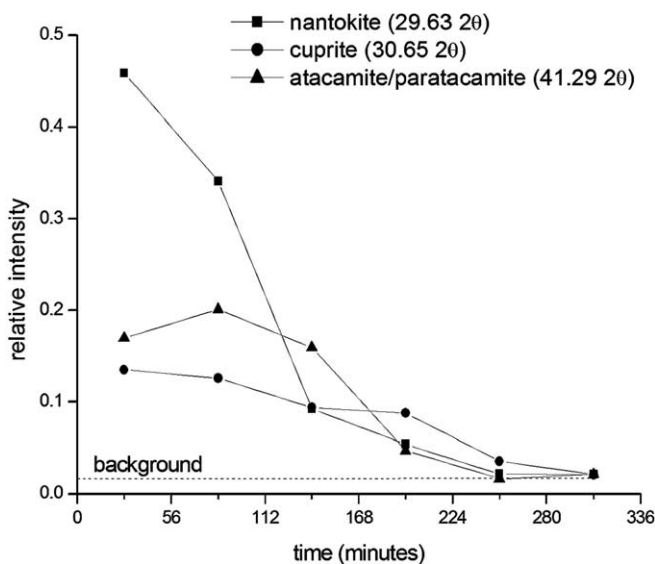


Fig. 7. Variation of the SR-XRD peak heights with time (2θ for $\lambda = 1.6$ Å). The signals are normalized versus the copper signal.

- [4] V. Costa, *Reviews in Conservation* 2 (2001) 18.
- [5] V. Costa, in: J.H. Townsend, K. Eremin, A. Adriaens (Eds.), *Conservation Science 2002*, Archetype Publications Ltd., London, 2003, p. 88.
- [6] F. Dalard, Y. Gourbeyre, C. Degrigny, *Studies in Conservation* 47 (2002) 117.
- [7] C. Degrigny, R. Le Gall, *Studies in Conservation* 44 (1999) 157.
- [8] D.L. Hallam, C.D. Adams, G. Bailey, G.A. Heath, in: *Proceedings of the International Conference on Metal Conservation, 1995*, James & James (Science Publishers) Ltd., London, 1997.
- [9] P. Letardi, A. Beccaria, M. Marabelli, G. D'Ercoli, in: *Proceedings of the International Conference on Metal Conservation, 1998*, James & James (Science Publishers) Ltd., London, 1998.
- [10] I.D. MacLeod, *Studies in Conservation* 32 (1987) 25.
- [11] S. Païn, R. Bertholon, N. Lacoudre, *Studies in Conservation* 36 (1991) 33.
- [12] C. Price, D. Hallam, G. Heath, D. Creagh, J. Ashton, in: *Proceedings of the International Conference on Metal Conservation, 1995*, James & James (Science Publishers) Ltd., London, 1997.
- [13] B. Rosales, R. Vera, G. Moriena, *Corrosion Science* 41 (1999) 625.
- [14] B.M. Ocko, J. Wang, *Physical Review Letters* 65 (1990) 1466.
- [15] M.G. Samant, M.F. Toney, G.L. Borges, L. Blum, O.R. Melroy, *Journal of Physical Chemistry* 92 (1988) 220.
- [16] M.G. Samant, M.F. Toney, G.L. Borges, L. Blum, O.R. Melroy, *Surface Science* 193 (1988) L29.
- [17] T. Kondo, K. Tamura, M. Takahasi, J.-I. Mizuki, *Electrochimica Acta* 47 (2002) 3075.
- [18] Y. Soldo, E. Silbert, G. Tournillon, J.L. Hazemann, J.P. Lévy, D. Aberdam, R. Faure, R. Durand, *Electrochimica Acta* 47 (2002) 3081.
- [19] G. Tournillon, D. Guay, A. Tadjeddine, *Journal of Electroanalytical Chemistry* 289 (1990) 263.
- [20] Z. Nagy, H. You, *Electrochimica Acta* 47 (2002) 3037.
- [21] M. Fleischmann, A. Olivier, J. Robinson, *Electrochimica Acta* 31 (1986) 899.
- [22] M. Kerkar, J. Robinson, A. Forty, *Faraday Discussions of the Chemical Society* 89 (1990) 31.
- [23] A.J. Davenport, M. Sansone, *Journal of the Electrochemical Society* 142 (1995) 725.
- [24] D.A. Scott, *Copper and Bronze in Art: Corrosion, Colorants, Conservation*, The Getty Conservation Institute, Los Angeles, 2002.
- [25] W.A. Oddy, M.J. Hughes, *Studies in Conservation* 15 (1970) 183.
- [26] I.D. MacLeod, in: *Proceedings of the 8th Triennial ICOM-CC Meeting*, Getty Conservation Institute, Los Angeles, 1987, p. 1079.
- [27] C.V. Horie, J.A. Vint, *Studies in Conservation* 27 (1982) 185.
- [28] A.M. Pollard, R.G. Thomas, P.A. Williams, *Studies in Conservation* 35 (1990) 148.
- [29] M. Dowsett, A. Adriaens, unpublished.
- [30] C. Lamy, *Stabilisation d'objets archéologiques chlorurés en alliage cuivreux – Définition des conditions d'une polarisation cathodique à potentiel constant en solution de sesquicarbonate de sodium 1%*, unpublished Rapport du Stage, Université de Nantes ISITEM, 1997.
- [31] R.J. Cernik, P.K. Murray, P. Pattison, A.N. Fitch, *Journal of Applied Crystallography* 23 (1990) 292.
- [32] S.P. Collins, R.J. Cernik, P. Pattison, A.M.T. Bell, A.N. Fitch, *Review of Scientific Instruments* 63 (1992) 1013.
- [33] E.J. MacLean, H.F.F. Millington, A.A. Neild, C.C. Tang, *European powder diffraction*, pts 1 and 2, *Materials Science Forum* 321 (3) (2000) 212.
- [34] C.C. Tang, G. Salvini, J. Groves, *European powder diffraction*, pts 1 and 2, *Materials Science Forum* 378 (3) (2001) 248.
- [35] K. Leyssens, A. Adriaens, C. Degrigny, in: J. Ashton, D. Hallam (Eds.), *Proceedings of Metals 2004*, National Museum of Australia Press, Canberra, 2004, p. 332.
- [36] K. Leyssens, A. Adriaens, E. Pantos, C. Degrigny, in: *Proceedings of the 14th Triennial ICOM-CC Meeting*, James & James Publishers Ltd., London, 2005, p. 301.
- [37] K. Leyssens, A. Adriaens, E. Pantos, C. Degrigny, in: C. Parisi, G. Buzzanca, A. Paradisi (Eds.), *Proceedings of the 8th International Conference on Non-Destructive Investigations and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*, Italian Society of Non Destructive Testing Monitoring Diagnostics, Rome, 2005, p. 77.