

In-situ time-resolved monitoring of copper corrosion using an automated electrochemical cell

A novel electrochemical cell has been designed for *in-situ*, time-resolved X-ray studies of corrosion and its inhibition on cultural heritage materials. Major aims are to monitor corrosion layers on alloys with realistic metallographic structures and surface roughness and to obtain co-incident electrochemical data, such as corrosion potential measurements, both with a time resolution in the range of seconds. This article reports on how a novel cell, to be used for monitoring the corrosion of copper, was tested.

Copper has played an important role in human development. The earliest use was at least 10,000 years ago, and the first copper-based alloys were produced in the fourth millennium B.C. The intrinsic advantages of copper, such as easy extraction and handling, as well as excellent heat conduction, make it an ideal utilitarian metal.

As with many other metals, copper corrodes once it comes into contact with an aggressive environment, such as the sea or the atmosphere. In 'art', copper-based objects are often preferred in the corroded state, because of the aesthetically pleasing colours, and also because the presence of corrosion products provides evidence of time past and passing, thereby adding extra value to the object. However, corrosion could become a problem, especially when specific corrosion products, such as cuprous chlorides, come into contact with the metal core. Under certain conditions, the deterioration of the underlying metal will continue leading to the destruction of the object.

Corroded archaeological cuprous artefacts recovered from wet saline environments, are particularly susceptible to further corrosion. The objects are usually stored in tap water or a sodium sesquicarbonate solution to remove the chlorides. But, this treatment often results in instability of the artefacts, such as the chemical transformation of the natural patina and the development of active corrosion. The occurrence of these side effects means that monitoring of the treatments remains necessary.

This article reports on an ongoing study of the basic processes involved using copper samples artificially corroded with various corrosion products, soaked in sodium sesquicarbonate. The study was carried out using an automatic electrochemical cell (eCell) designed for time-resolved synchrotron spectroelectrochemistry.

The cell consists of three main modules: the hardware, a custom interface and potentiostat, and a data system written in Visual Basic™ 2005. The set-up was tested for the first time at Station MPW 6.2. The electrochemical cell was made from PCTFE for good chemical resistance and reasonable mechanical stability. It basically consists of a cylinder 60 millimetres in diameter and 100 millimetres high, containing a piston which is driven along the bore by

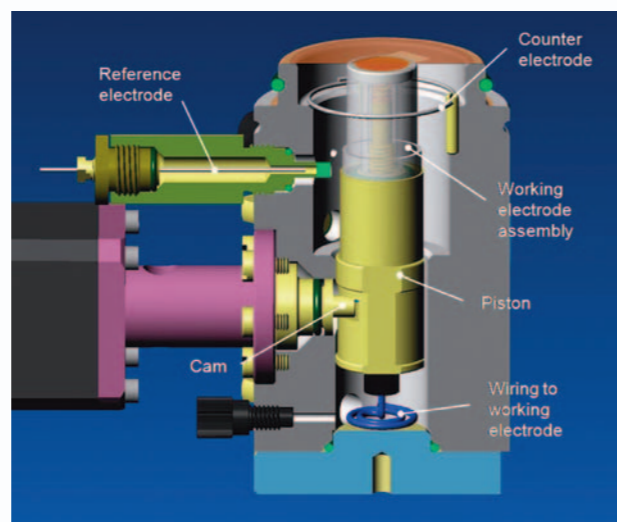


fig 1 Schematic of the eCell

a stepper motor through a dynamic seal. The working electrode, whose surface forms the sample for X-ray analysis, is mounted on the piston so that it can be moved from the analysis position, roughly flush with the top of the cell, to the electrochemical position where it is fully surrounded by electrolyte with a low impedance path to the counter and reference electrodes, shown in **figs 1** and **2**. The potentiostat and interface use a multifunction analogue card enabling the system to be controlled from a laptop PC. The analogue card controls a custom potentiostat, designed specifically for this application, capable of communicating with the interface down a 9 metre or greater length of cable. The system is complimented by a webcam, which allows video or stills of the eCell operation to be observed and captured. The data system offers the operator a simple and highly pictorial Graphical User Interface (GUI) for setting up experimental parameters and displaying the data. A great amount of effort has gone in to making it reliable, and easy to use without the need of a manual. The webcam image is used extensively for setting up and progress checking. In operation, the data system is programmed to raise and lower the working electrode

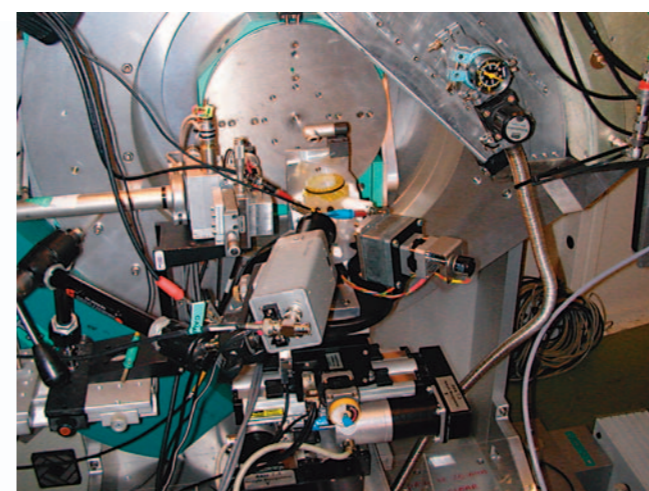


fig 2 Photograph of the eCell mounted on Station MPW6.2

periodically, typically every few minutes. The electrode remains in the X-ray position for around 10 seconds, and the data system issues a trigger pulse to the acquisition system as soon as the electrode is in position.

The cell concept has been proven previously using Station 2.3, where sequential X-ray Diffraction (XRD) measurements in solution were successfully collected in parallel with electrochemical data, over periods of several hours. The amount of data collected as a function of time at Station 2.3 however, was limited by the scan time of the detector, 30 minutes for 2θ values of 24° to 50° with a step size of 0.02° and counting time of one second. Acquisition times of the order of 10s of seconds to a few minutes however, are essential in many cases so that data for different products can be recorded contemporaneously, fast reactions can be studied and short-lived by-products can be observed.

Moreover, it is ultimately important to be able to collect the electrochemical data in a mode where the reaction takes place in the bulk of the electrolyte i.e. allowing the optimization of transport processes in the electrochemical cell and to raise the working electrode to the cell window for a short time for analysis. Otherwise, the reactions are distorted by the restricted fluid volume between the working electrode and the window. This was not possible on Station 2.3 due to the extended acquisition time. In addition, the electrochemical cell used in that experiment did not allow the automatic movement of the electrode from outside the hutch. This meant that the experiments were always carried out with the electrode surface close to the window, hampering the electrochemical reactions in a manner which could only be evaluated or eliminated with faster detection.

The new design alleviates the above-mentioned obstacles and was tested by means of a corrosion monitoring experiment. This involved the simultaneous acquisition of XRD data and corrosion potential (E_{corr}) values from a copper substrate covered with a layer of nantokite (cuprous chloride), immersed in a 1wt% sodium sesquicarbonate solution, as a function of time. **Fig 3** shows the behaviour of the XRD peak areas for nantokite and cuprite (cuprous oxide) and demonstrates that nantokite disappears as a function of time, while the cuprite signal increases.

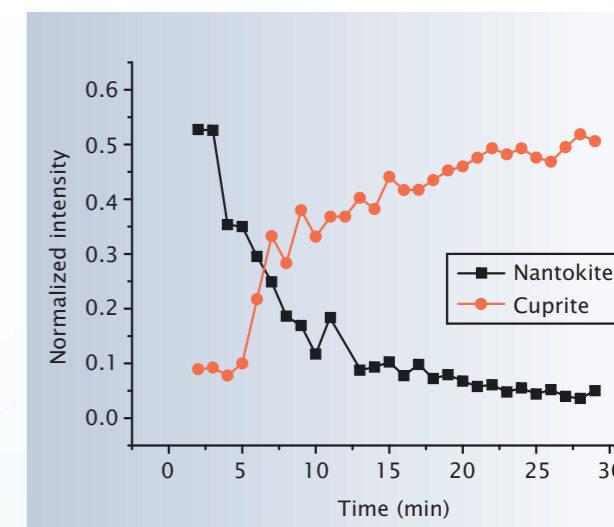


fig 3 Shows the behaviour of the XRD peak areas for nantokite and cuprite (cuprous oxide) and demonstrates that nantokite disappears as a function of time, while the cuprite signal increases.

When it comes to the E_{corr} data, a steady increase is seen for the first hour (*not shown*). E_{corr} values provide useful information on surface reactivity as they are based on the composition of the sample and its interface with the solution. The variation of these values as a function of time therefore confirms the change in surface chemistry.

In conclusion, interfacing the automated electrochemical cell to Station MPW6.2 went smoothly and the cell was mounted, aligned and ready to use within 30 minutes. In addition, the Station systems were highly-compatible with the cell operation and the experimental objectives. Data collected on the copper corrosion products were able to confirm earlier results concerning the immersion in sodium sesquicarbonate, allowing the *in-situ* E_{corr} data with a time resolution of minutes. Having established the methodology for using eCell on Station MPW6.2, the next step is to examine the high-speed early stages of reactions which produce simulated patinas and corrosion products as these are an essential precursor for the testing of conservation strategies.

General References:

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