short communications

In situ synchrotron far-infrared spectromicroscopy of a copper electrode at grazing incidence angle

F. Hahn,[a] Y.-L. Mathis,[b] A. Bonnefont,[c] F. Maillard[d] and C. A. Melendres[e]*

[a]UMR 6503, CNRS, Université de Poitiers, 40 avenue du Recteur Pineau, F-86022 Poitiers, France, [b]Synchrotron Light Source ANKA/Institute for Synchrotron Radiation (ISS), Forschungszentrum Karlsruhe, PO Box 3640, D-76021 Karlsruhe, Germany, [c]Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, UMR 7177, CNRS/ULP, 4 rue Blaise Pascal, BP 1032, F-67070 Strasbourg, France, [d]Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, UMR 5631 CNRS/INPG/UJF, 1130 rue de la Piscine, BP 75, F-38402 Saint Martin d'Hères, France, and [e]The SHD Institute, 216 F Street, PMB 114, Davis, CA 95616, USA.
E-mail: camelendres@shdinstitute.org

Synchrotron far-infrared spectroscopy *in situ* was successfully carried out on a copper microelectrode using a grazing-angle objective attached to a Bruker IRscope II microscope. The thin-layer spectroelectrochemical cell was constructed out of Teflon and fitted with a 20 µm-thick Mylar window; the copper electrode was 500 µm in diameter. Measurements were carried out in 0.1 M NaOH solution as a function of applied potential between -1.4 and 0 V *versus* a Hg/Hg_2SO_4 reference electrode. Results demonstrate that with the present technique it is possible to obtain *in situ* spectra with excellent signal-to-noise ratio for surface oxide films formed electrochemically with less than 1 nL of active solution volume. The surface film on copper at 0 V consisted mainly of CuO with possibly some $Cu(OH)_2$ also present. This interpretation is consistent with previous works and thermodynamic calculations.

Keywords: far-infrared spectromicroscopy; electrochemistry; oxide film on copper.

1. Introduction

Synchrotrons provide a novel source of well collimated infrared (IR) radiation which is about a thousand times brighter than conventional laboratory globar sources (Melendres & Tadjeddine, 1994). This increase in intensity has opened up new opportunities for investigating classic problems in various areas of science and technology. In interfacial electrochemistry, for example, the *in situ* measurements of low-frequency vibrations in the far IR for surface oxide films on copper (Melendres *et al.*, 1998) and halide (Melendres & Hahn, 1999) as well as oxyanions (Melendres *et al.*, 2000) adsorbed on gold electrode surfaces have been demonstrated and are now possible, despite the strong attenuation of the IR beam by interfacial water. The first experiments (Melendres *et al.*, 1998) made use of a conventional copper rod electrode using a silicon window; the second set (Melendres & Hahn, 1999; Melendres *et al.*, 2000) involved a gold film vacuum evaporated on a silicon hemicylinder as electrode using the attenuated total reflection technique.

The finely focused synchrotron beam is particularly well suited for the study of small particles and areas. Advantage of this has been made use of in IR microscopy (Dumas & Tobin, 2003). We have explored the use of the technique of IR spectromicroscopy for the investigations of microelectrodes. We report here our results on the identification of the oxide film on copper *in situ* in an aqueous solution environment using an IR microscope fitted with a grazing-angle objective (Bruker Hyperion 2000 IR microscope). We believe that this is the first time the experiment has been successfully carried out and will open new applications in other fields of interface science and technology.

Microelectrodes have found extensive use in electrochemistry (Montenegro *et al.*, 1991) owing to a number of advantages, *e.g.* they allow the use of very small amounts of solution (thin layers, small volume), the measurement of fast electrode processes, and electrochemical studies in very dilute electrolyte and highly resistive solutions (including organic solvents). We envisage the use of IR spectromicroscopy with solutions so thin and approaching monolayer amounts of material to study adsorbed molecules under the influence of an applied electrical potential. This form of 'electrochemical surface science' could bridge the gap between UHV surface science and conventional electrochemistry. We have already carried out far-IR synchrotron spectromicroscopy of a Pt microelectrode in perchloric acid solution and initial results have been presented (Hahn & Melendres, 2005).

The IR detection of very thin layers of materials (*e.g.* oxide film, adsorbed molecules, ions) can be carried out with highest sensitivity at glancing angles of incidence (approaching 90° with respect to the surface normal) and using *p*-polarized radiation (the plane of polarization of the incident radiation being perpendicular to the electrode surface). With the micrometer-size synchrotron IR beam, the use of a grazing-angle objective (GAO), attached to a microscope, allows high angles of incidence (75–85°) to be achieved. *In situ* spectromicroscopic measurements in an electrochemical cell are rather difficult because of the very short working distance between the objective and the electrode surface (less than 1 mm), the presence of solution, and the need to use an IR window of suitable material for the cell. We have constructed a suitable thin-layer spectromicroelectrochemical cell made of Teflon and have successfully carried out measurements to identify the

composition of the oxide film on copper in an aqueous solution environment.

2. Experimental

A schematic diagram of the thin-layer spectromicroelectrochemical cell is shown in Fig. 1(a). It was constructed of Teflon and provided with small Teflon tubings (7, 8) for conducting the electrolyte solution in and out of the cell. A separate tubing (6) served as a salt bridge for the reference electrode. The working electrode consisted of a 500 µm-diameter copper wire (4), while the counter electrode was a 1 mm-diameter gold wire (5) embedded in the Teflon to form a ring around the Cu working electrode. The electrodes were polished with sandpaper and alumina powder down to 0.3 µm; they were washed thoroughly with high-purity water prior to each spectromicroscopy measurement. A mercury/mercurous sulfate reference electrode was used. The solution consisted of 0.1 M NaOH which was de-aerated by bubbling through high-purity nitrogen gas. Control of the electrode potential was made using a CH Instruments (Austin, TX, USA) model CH-1202 bipotentiostat. The potentiostat was computer driven and the current–potential curves were directly displayed on a laptop computer.

A 20 µm-thick Mylar film was used as the window (1) for admitting the IR beam. While the Mylar exhibits IR absorption of its own, this did not appear to cause problems with the spectral measurements in the far IR. A Bruker IR spectrometer (model IFS 66v/S) coupled

Figure 1
(a) Schematic diagram of the thin-layer spectromicroelectrochemical cell. 1: Mylar window. 2: Teflon cell top. 3: Teflon cell body. 4: Cu working electrode. 5: Au ring counter electrode. 6: reference electrode. 7: Solution inlet. 8: Solution outlet. (b) Cyclic voltammogram of a copper microelectrode in 0.1 M NaOH; scan rate = 10 mV s^{-1}.

with an IRscope II infrared microscope were used. The sample area of the microscope was enclosed in a Plexiglas box and purged continuously with dry nitrogen gas so as to minimize the interference of water vapor in the spectral measurements. An aperture of 0.9 mm and a 15× objective were used to define the synchrotron beam so that the footprint completely covered the active surface of the copper microelectrode. Spectroscopic measurements were carried out first in the mid-IR region using a liquid-nitrogen-cooled MCT detector. Subsequently, studies were made in the far-IR using a 4.2 K liquid-helium-cooled Si bolometer (Infrared Laboratories, Arizona, USA). A polarizer inserted into the beam path permitted the use of s- or p-polarized IR radiation; it was removed when it was desired to make use of the full intensity of the beam.

3. Results and discussion

Fig. 1(b) shows a cyclic voltammogram (CV) of the copper microelectrode in 0.1 M NaOH solution taken in the cell under actual operating conditions. The two anodic waves (A1 and A2), characteristic of the electrochemical oxidation of copper into Cu(I) and Cu(II), are evident, as well as the cathodic waves (C1 and C2) corresponding to the reduction of the surface oxides. The voltammetric waves appear 'drawn out' with a sloping baseline because of the high cell resistance inherent to the geometrical configuration of the electrodes and the thin layer of solution between them.

Spectroscopic measurements in situ were carried out initially in the mid-IR range. Interferograms (512) were accumulated starting at the open circuit potential of about −0.78 V. The potential was then scanned and held at various points in the CV corresponding to the formation of Cu(I) and Cu(II) species and their subsequent reduction. At each potential, 512 interferograms were taken and then ratioed to those taken at −1.2 V corresponding to a copper surface free of oxide film (or to those taken at the open circuit potential of −0.78 V). The results represent the reflectance spectra of the surface (the oxide film) at each potential. Unfortunately, the presence of interference patterns owing to the thin Mylar window made it difficult to make a clear interpretation of the results observed in the mid-IR region. Further work is needed to obtain a better signal-to-noise ratio and eliminate the interference fringes before we can make definitive conclusions on the nature of the oxide films on copper from the mid-IR spectroscopic data.

Measurements in the far-IR region yielded spectral results of better quality and the data were more easily interpretable. We employed the same potential-hold method as above, followed by IR spectral measurement. This yielded conclusive results as to the presence of an oxide film on copper at 0 V (referenced to the surface condition at −1.1 V or at the open circuit potential). However, the signal could be considerably improved by alternately switching the potential between 0 V and −1.1 V, and taking 128 interferograms at each potential. This process was repeated up to 15 times in order to improve the signal-to-noise ratio of the resulting spectra. Fig. 2(a) shows a set of five single-channel reflectances (power spectrum) at −1.1 V and 0 V, each derived from the 128 interferograms taken. The reflectance decreases with time at a given potential because of the decrease in the synchrotron beam current. The ratio of these single-channel reflectances at the two different potentials yield reflectance spectra which are then co-added to obtain an average spectrum with significantly improved signal-to-noise ratio (shown later).

Before presenting the final result, it is worthwhile pointing out here the surprising data, shown in Fig. 2(a), that the reflectances on the oxide-covered copper electrode at 0 V are higher than those from the
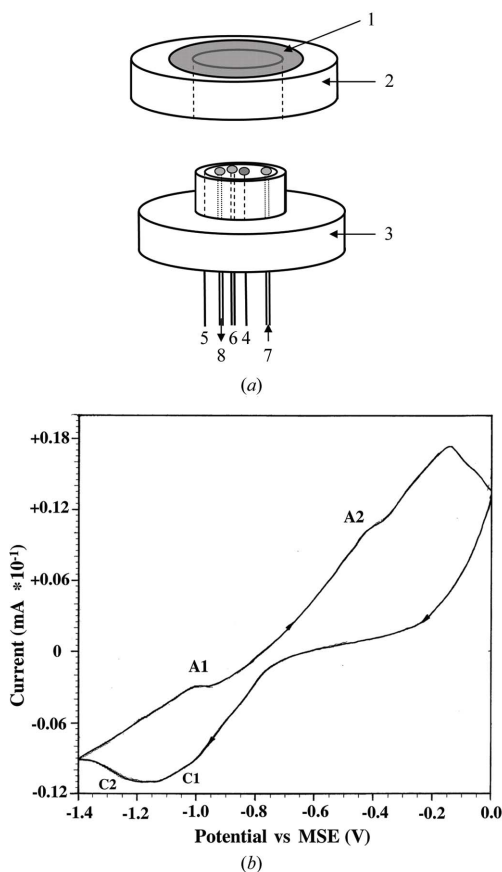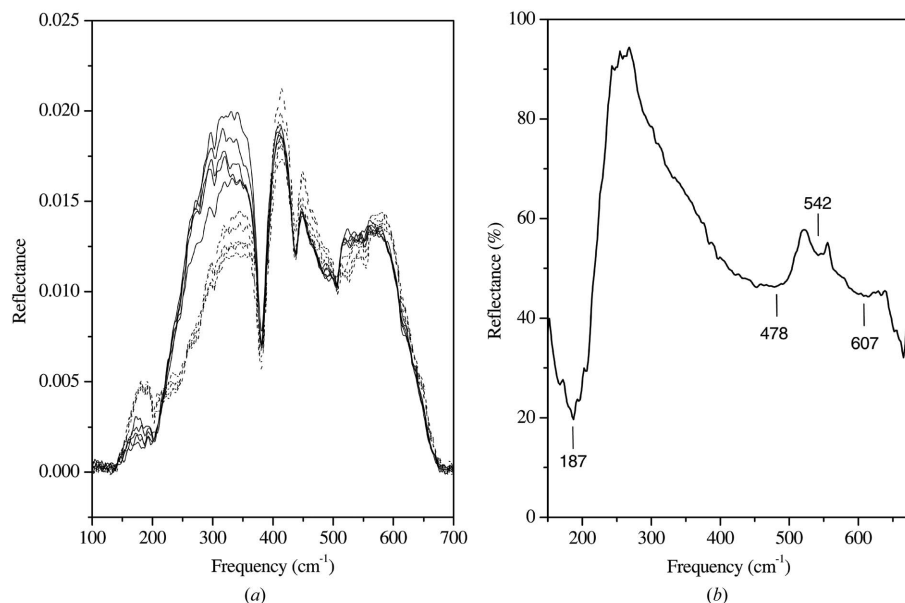
Figure 2
(a) Single-channel reflectances at −1.1 V (broken lines) and 0 V (solid lines). (b) *In situ* far-IR spectrum of a copper microelectrode at 0 V obtained with a grazing-angle objective (reference at −1.1 V).

clean surface at −1.1 V. This can be understood by realising that the clean surface is covered by a layer of water (hence the reflectance is lower). This water was part of that utilized in the formation of the oxide *via* the reaction

$$Cu + H_2O \rightarrow CuO + H_2.$$

In order to obtain the spectrum of the oxide film, it is necessary to ratio the single-channel reflectance at 0 V to the water-free surface. We estimated the amount of water on the copper surface using the reflectance from the clean gold electrode in the empty cell. The water layer was about 100 Å thick and its absorbance was then subtracted from the absorbance curve at −1.1 V derived from Fig. 2(a). We have used the absorption coefficient of water from the results of Lane (1966) and we took the angle of incidence of the IR beam to be about 80°. Owing to lack of space here, details of these calculations will be presented elsewhere (Hahn *et al.*, 2007). The corrected reflectance curve at −1.1 V is then used as a reference in calculating the ratio with that at 0 V; the result is shown in Fig. 2(b). The curve is the average derived from the five pairs of single reflectances shown in Fig. 2(a) following correction for the water. From Fig. 2(b) it can be seen that the *in situ* spectrum of a copper microelectrode at 0 V shows broad absorption bands in the region around 187, 478, 542 and 607 cm^{-1}. There appears to be a band at about 660 cm^{-1} but data in this region cannot be relied upon because of the large noise level. The bands are broad presumably because of structural disorder and because they are a convolution of several bands (Melendres *et al.*, 1998). The band widths are, however, similar to those measured by Poling (1969) and Narang *et al.* (1992) on standard and more ordered samples of CuO. The bands we observed here are in good agreement with our previous work on reflectance measurements on large (conventional) electrodes (Melendres *et al.*, 1998). The resolution of the bands appears lower than what we have observed before. The first three bands are strongly indicative of the presence of CuO (Melendres *et al.*, 1998; Poling, 1969; Narang *et al.*, 1992); that at 607 cm^{-1} is probably due to some Cu(OH)$_2$. The band at 187 cm^{-1} has also a contribution in intensity due to water (Lane, 1966). Our spectral assignment is consistent with the results of Raman spectro-

scopic measurements (Hamilton *et al.*, 1986; Mayer & Mueller, 1992), as well as the results of thermodynamic calculations (Mayer & Mueller, 1992; Pourbaix, 1966). The thickness of the oxide film on Cu at 0 V can be calculated from the absorbance curve corresponding to Fig. 2(b); it amounts to about 1300 Å, assuming it to be all CuO. The thick film is probably due to growth by repeated cycling and surface roughening. The excellent signal-to-noise ratio suggests that even thinner films could be detected. Finally, it is also worthwhile pointing out that, in the present system, spectroscopy and electrochemistry were carried out with a solution layer thickness estimated to be less than 300 nm and no more than 1 nL of active solution volume involved in the electrolysis (Hahn *et al.*, 2007).

4. Conclusion

We have demonstrated for the first time the use of synchrotron far-IR spectromicroscopy at grazing-angle incidence, with a thin-layer spectromicroelectrochemical cell, to successfully identify *in situ* the composition of the oxide film on copper in 0.1 *M* NaOH solution. The results indicate the presence of CuO, and some Cu(OH)$_2$, in good agreement with previous works and consistent with thermodynamic calculations.

References

Dumas, P. & Tobin, M. J. (2003). *Spectrosc. Eur.* **15**, 17–21.
Hahn, F., Mathis, Y.-L. *et al.* (2007). *Fourth International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources (WIRMS 2007)*, Hyogo, Japan, 25–29 September 2007. To be presented.
Hahn, F. & Melendres, C. A. (2005). *Third International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources (WIRMS)*, Rathen, Germany, 26–30 June 2005. Abstract.
Hamilton, J. C., Farmer, J. C. & Anderson, R. J. (1986). *J. Electrochem. Soc.* **133**, 739–745.
Lane, J. A. (1966). *J. Opt. Soc. Am.* **56**, 1398.
Mayer, S. T. & Mueller, R. H. (1992). *J. Electrochem. Soc.* **139**, 426–434.
Melendres, C. A., Bowmaker, G. A., Leger, J. M. & Beden, B. (1998). *J. Electroanal. Chem.* **449**, 215–218.
Melendres, C. A. & Hahn, F. (1999). *J. Electroanal. Chem.* **463**, 258–261.
Melendres, C. A., Hahn, F. & Bowmaker, G. (2000). *Electrochim. Acta*, **46**, 9–13.
Melendres, C. A. & Tadjeddine, A. (1994). Editors. *Synchrotron Techniques in Interfacial Electrochemistry, NATO-ASI Series C*, Vol. 432. Dordrecht: Kluwer.
Montenegro, M. I., Queiros, M. A. & Daschbach, J. L. (1991). Editors. *Microelectrodes: Theory and Applications, NATO ASI Series E*, Vol. 197. Dordrecht: Kluwer.
Narang, S. H., Kartha, V. B. & Patel, N. D. (1992). *Physica C*, **204**, 8–14.
Poling, G. W. (1969). *J. Electrochem. Soc.* **116**, 958–963.
Pourbaix, M. (1966). *Atlas of Electrochemical Equilibria in Aqueous Solutions*, p. 388. London: Pergammon Press.