Synchrotron infrared reflectance microspectroscopy study of film formation and breakdown on copper

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This work demonstrates the utility of synchrotron infrared reflectance microspectroscopy in the far- and mid-IR for the determination of the composition of electrogenerated surface films formed during the general and localized corrosion of copper in alkaline and bicarbonate solutions. Back-reflection geometry has been employed to identify the anodic film formed on copper in 0.1 M NaOH solution at 0.3 V (*versus* a Ag/AgCl reference) to be mainly CuO. In 0.01 M NaHCO$_3$ solution general corrosion occurs with passive film formation below 0.2 V. The surface film at 0.2 V consisted mainly of bicarbonate, copper carbonate dihydroxide or malachite [CuCO$_3$·Cu(OH)$_2$], Cu(OH)$_2$ and possibly some CuO. At higher potentials the passive film breaks down and localized corrosion occurs leading to the formation of pits. The composition of the surface films inside the pits formed at 0.6 V was found to be essentially the same as that outside but the relative amount of Cu(OH)$_2$ appears to be higher.

Keywords: infrared microspectroscopy; copper corrosion in bicarbonate; film formation and breakdown; pitting.

1. Introduction

The advent of synchrotron storage rings as sources of high-brightness infrared radiation has opened up new opportunities for investigating classical problems in various areas of science and technology. Applications of synchrotron-based techniques toward the understanding of the structure of the solid–solution interface in electrochemistry have evolved and appear very promising (Melendres & Tadjeddine, 1994; Dumas & Tobin, 2003). Knowledge of interfacial structures is important not only from a scientific and theoretical standpoint but also for advancing various technological applications, *e.g.* energy storage and conversion devices (batteries, fuel cells), development of protective coatings (corrosion protection), heterogeneous catalysis, electrochromic devices. Our own interests lie in the development and application of infrared techniques for the determination of the structure of surface films and adsorbed layers on metal surfaces formed under the influence of an applied electrical potential. We developed the technique of synchrotron far-infrared reflectance spectroscopy (SFIRS) and demonstrated its utility for the study of halide and oxyanion adsorption on a gold electrode at the monolayer level (Melendres & Hahn, 1999; Melendres *et al.*, 2000). We used the technique of synchrotron infrared microspectroscopy with a grazing-angle objective (SIRM-GAO) to determine the

composition of the anodic films on copper formed in alkaline solution (Hahn *et al.*, 2007). Here we show the utility of synchrotron infrared reflectance microspectroscopy (SIRM), in the far- and mid-IR, to study film formation during general and localized (pitting) corrosion of copper in NaHCO$_3$ solution. We demonstrate the ability of the technique to determine the composition of the film inside the pits for the first time.

2. Experimental

A schematic diagram of the thin-layer spectroelectrochemical cell used has been shown previously (Hahn *et al.*, 2007). The cell body was made of Teflon and the electrolyte solution was conducted in and out of the cell through small Teflon tubings. We, likewise, employed a 500 µm-diameter copper wire as the working electrode. The use of a microelectrode was based on the premise that it would allow the use of a very thin (near monolayer) layer of solution without compromising the electrochemistry of the system (Montenegro *et al.*, 1991). The counter electrode was a copper ring concentric with the working electrode, but we have also used a gold counter electrode on some occasions. The reference electrode consisted of Ag/AgCl (in 3 M KCl). The electrolyte solutions used were 0.1 M NaOH and 0.01 M NaHCO$_3$. Control of the potential was made using a Princeton Applied Research

(PAR) model 173 potentiostat. A 20 µm-thick Mylar film or a PTFE film was usually employed as the window for the spectroelectrochemical cell. The far-IR measurements were carried out on beamline 1.4.3 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (Berkeley, CA, USA). A Nicolet Magna 760 coupled with a Spectra Tech Nic Plan IR microscope were used. The detector was a liquid-He-cooled bolometer (Infrared Laboratories, Arizona, USA). A standard back-reflection geometry was used, with no other attachment to the microscope. The objectives used were 10× and 32× for viewing the sample and for IR measurements, respectively. The beam diameter on the sample was about 15 µm. The mid-IR measurements were carried out at beamline U2B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (Upton, NY, USA). The spectrometer was a Thermo Nicolet Magna 860 with a Continuum IR microscope having 4× and 20× objectives for visual observation and a 32× objective for IR measurements. The detector was an MCT, cooled with liquid nitrogen, and had an extended sensitivity range from 4000 down to 400 cm^{-1}. The cell window consisted of polyethylene during the electrochemistry but was removed for IR studies. Thus the measurements were made *ex situ*; however, no significant change of the spectra with time could be observed (the sample chamber was continuously purged with nitrogen). Moreover, all results reported here represent the average of several reflectivity scans, at different areas of the surface, on several pits, and the experiments were repeated at different times (and days) to ensure their reproducibility and consistency.

3. Results and discussion

3.1. Passive film on copper in alkaline solution

It was of interest to explore initially the sensitivity of the back-reflection technique for the identification of electro-generated thin surface oxide films on metals. We wanted to compare the results with our previous work obtained using a grazing-angle objective (GAO) attached to the microscope (Hahn *et al.*, 2007). Fig. 1 shows the far-IR spectrum of the surface film form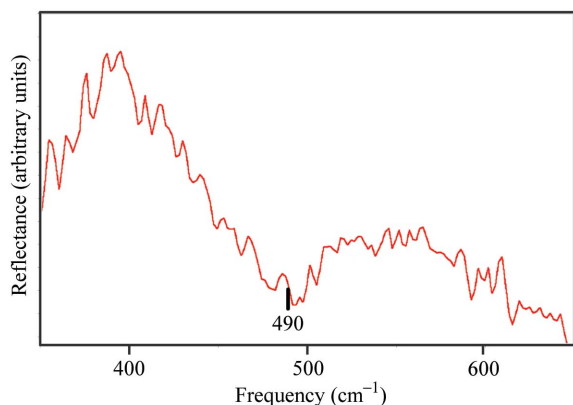ed on copper in 0.1 *M* NaOH solution by applying a potential of 0.3 V for 5 min. The spectrum is the average of five spectra (each taken with 512 interferometric scans) from different parts of the copper surface. The band owing to CuO at about 490 cm^{-1} (Hahn *et al.*, 2007; Melendres *et al.*, 1998) is clearly visible, albeit the signal to noise was understandably poorer compared with what we have obtained using the GAO. There appears to be absorption above 600 cm^{-1} which may be due to the presence of some $Cu(OH)_2$. However, being near the cut-off of the bolometer detector, the noise level is rather high and the exact band position cannot be ascertained. The results, however, are consistent with previous works (Hahn *et al.*, 2007; Melendres *et al.*, 1998; Poling, 1969; Narang *et al.*, 1992) and we decided to apply the technique to investigate thicker films formed on copper in NaHCO$_3$ solutions where the metal undergoes both general and localized (pitting) corrosion. This solution is of particular interest because it has been shown (Thomas & Tiller, 1972) that pitting occurs in the absence of the chloride, which is widely held to be responsible for film breakdown and pitting. The determination of the composition of the surface film inside the pit would be difficult to determine using the GAO, especially for deep pits with small openings, *i.e.* with high aspect ratio.

3.2. Corrosion and passivation behavior in bicarbonate solution

Fig. 2 shows a cyclic voltammogram (CV) of copper in 0.01 *M* NaHCO$_3$ solution, obtained from our previous work (Melendres *et al.*, 1995). The two anodic waves 1a and 2a are due to the electro-oxidation of copper to Cu (I) and Cu (II), respectively, while the cathodic waves 1c and 2c correspond to the electrochemical reduction of the surface films formed. A notable feature of the CV is the hysteresis observed between 0.2 and 0.6 V, which is attributed to the phenomenon of localized or pitting corrosion. The current increase is due to the breakdown of the protective (passive) film at 'active' spots resulting in an increase in the corrosion rates at those areas and hence to the formation of pits or holes. This phenomenon is of great interest in corrosion science and its practical importance can be easily appreciated by looking at the spotted
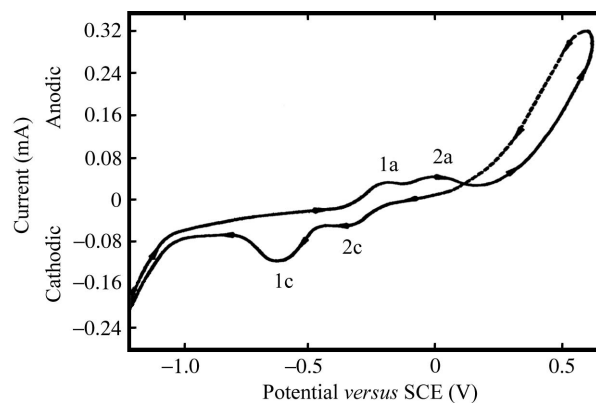

Figure 1
Far-IR spectrum of Cu oxidized for 5 min at 0.3 V (*versus* Ag/AgCl) in 0.1 *M* NaOH solution.

Figure 2
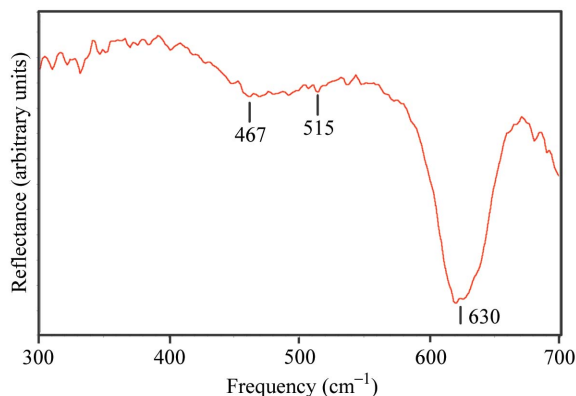Cyclic voltammogram of Cu in 0.01 *M* NaHCO$_3$ solution; scan rate = 10 mV s^{-1}.

Figure 3
Far-IR spectrum of Cu oxidized for 5 min at 0.2 V in 0.01 M NaHCO$_3$ solution.

appearance of car bodies riddled with pits. Its understanding and remediation is therefore of great interest. Fig. 3 shows the far-IR spectrum of a copper microelectrode which has been anodized in the passive region at 0.2 V (below the pitting region) for 5 min. At this potential, Cu has suffered only general corrosion and subsequent passivation. The surface is covered with a protective (passive) film but remains relatively smooth and free of pits. The bands at 467 and 515 cm^{-1} are probably due to CuO (Hahn *et al.*, 2007; Melendres *et al.*, 1998; Poling, 1969) superposed on a broad band owing to copper carbonate dihydroxide [Cu$_2$(OH)$_2$CO$_3$] (Bessiere-Morandat *et al.*, 1970). Previous work by others (Bessiere-Morandat *et al.*, 1970) indicate bands in this region, as well as around 300 cm^{-1} where we see some absorption, albeit weak and of low signal-to-noise ratio. We will discuss the justification for this assignment more extensively in the following paragraphs. The strong broad band at 630 cm^{-1} is most likely due to a mixture of a bicarbonate of copper with some Cu(OH)$_2$. Bicarbonates of metals have frequencies in the range 640 to 695 cm^{-1} (Bentley *et al.*, 1968) while Cu(OH)$_2$ has bands in the range 600 to 630 cm^{-1} (Hahn *et al.*, 2007; Melendres *et al.*, 1998). Their superposition could account for the broad band at 630 cm^{-1}. Further support for this assignment comes from the results of mid- and far-IR measurements to be discussed in the subsequent paragraphs.

3.3. Surface film composition after pitting

Fig. 4 shows a portion of a Cu microelectrode which has been oxidized in 0.01 M NaHCO$_3$ in the pitting region by applying a potential of 0.6 V for 15 min and then returning the potential back to the repassivation region at 0.2 V or to the open circuit potential of 0.09 V. The presence of pits of various sizes is evident; pit diameters ranging from about 2 μm to 100 μm are easily visible. The pits grow bigger with increasing time and potential; their development can be monitored nicely using a 15× microscope objective. A fundamental question of great scientific and technological interest is: what is the composition of the film inside the electrogenerated pit (bottom)? Similarly, how does it compare with the film composition outside the pit and the general external surface?
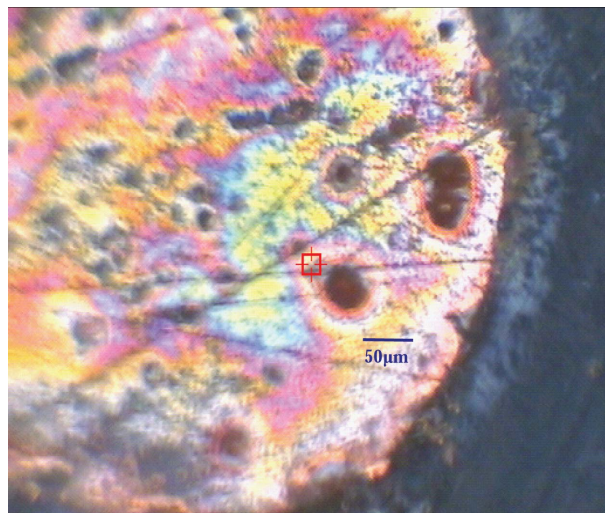

Figure 4
Photographic image of a portion of Cu microelectrode after pitting corrosion for 15 min at 0.6 V and repassivation in 0.01 M NaHCO$_3$ solution.

These are open questions in corrosion science and engineering. We attempted to address these issues in this work.

Results of our measurements in the mid-IR are shown in Fig. 5 for areas inside the pit (*a*) and outside (*b*). The difference between the two appears rather subtle. For (*a*) the main band appears at 628 cm^{-1} and is visibly skewed to the right and broader, most probably due to a superposition of a number of bands. As had been discussed earlier, we believe this band to be due to bicarbonates and Cu(OH)$_2$. The bands
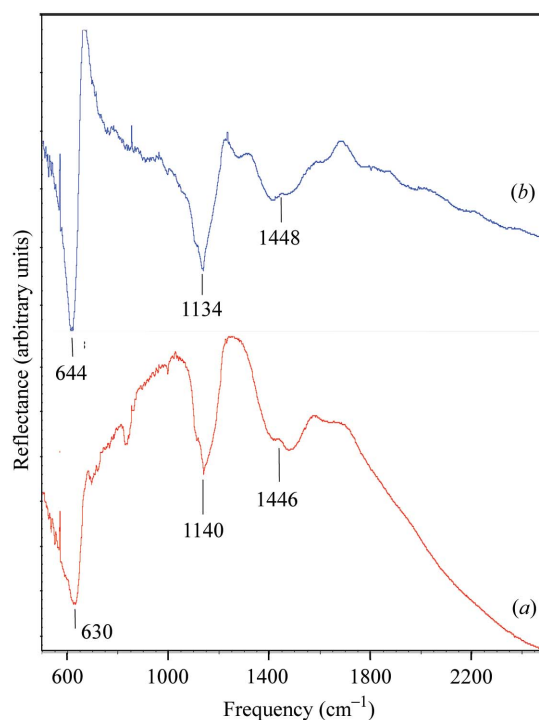

Figure 5
Mid-IR spectra of Cu microelectrode after pitting corrosion at 0.6 V and repassivation. (*a*) Area inside the pit, (*b*) areas outside the pit.

at about 1440 and 1135 cm^{-1} are attributed to copper carbonate dihydroxide [$Cu_2(OH)_2CO_3$]. This compound is also known as dibasic copper carbonate or malachite, the formula of which can also be written as $CuCO_3 \cdot Cu(OH)_2$ (Bessiere-Morandat *et al.*, 1970). At areas outside the pit, the spectrum is rather similar except for the main band at 644 cm^{-1} being narrower. From far-IR results, to be shown in the next paragraph, this is because the relative amount of $Cu(OH)_2$ in the external areas is lower. Otherwise, the film has essentially the same constituents.

Fig. 6 shows the far-IR microspectroscopy results of analysis for areas inside (*a*) and outside (*b*) the pits. The spectra represent the average for a number of pits and also at different positions external to the pits. The major band at about 643 cm^{-1} for (*b*) is due to bicarbonates (Bentley *et al.*, 1968); malachite has no bands in this region (Bessiere-Morandat *et al.*, 1970). The weak band at about 540 cm^{-1} is probably due to malachite and some to CuO (Hahn *et al.*, 2007; Melendres *et al.*, 1998; Poling, 1969). The broadness of these bands is also suggestive of a highly disordered structure of the surface film. Inside the pit (*a*) the spectrum is again rather similar with the major band at 644 cm^{-1} due to bicarbonates, but with a well resolved band at 600 cm^{-1} which is attributed to $Cu(OH)_2$. Again, we find a minor band at about 530 cm^{-1} which could be due to CuO, overlapping with carbonate bands. The results of the far-IR measurements are consistent with those using the mid-IR. The higher resolution obtainable in the far-IR is obviously a big advantage. The band at about 320–350 cm^{-1} is assigned to malachite (Bessiere-Morandat *et al.*, 1970).
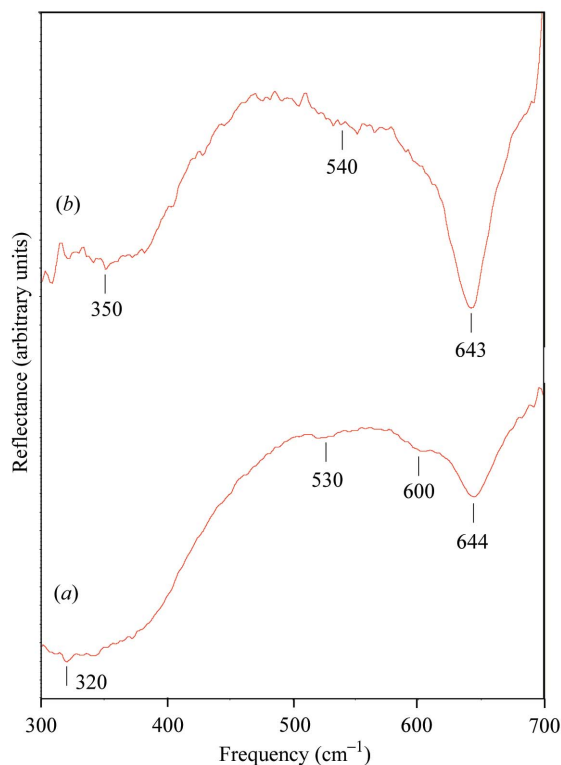
It is evident that the surface films formed on copper in bicarbonate solution differ in composition from that formed in alkaline solution. It appears reasonable, both from thermodynamic and electrochemical considerations, that copper bicarbonate, malachite and $Cu(OH)_2$ constitute the main components of the film in 0.01 *M* $NaHCO_3$ solution; a small amount of CuO is also probably present. The films are thicker, but not very protective. This is evidenced by the fact that they undergo breakdown at high potentials. In a basic solution of 0.1 *M* NaOH, the films are very thin (Hahn *et al.*, 2007), and their stability persists at high anodic potentials, being able to support the evolution of oxygen on the covered surface without breakdown. The cause of passive film breakdown continues to be a major subject of research in corrosion science and engineering. The process appears to be initiated at 'active' areas (presumably defects in the film) which are susceptible to attack by the electrolyte solution and further aggravated by the high anodic potential that is applied. The result is the formation of pits on the surface which continues as long as the high potential is maintained. Lowering the potential to below the pitting region causes repassivation of the surface. We have found here that upon returning the potential to 0.2 V in the repassivation region or allowing it to relax to open circuit potential at 0.09 V, following the pitting event (here at 0.6 V), essentially the same film exists on the surface both inside and outside the pit. The subtle difference is that the amount of $Cu(OH)_2$ relative to bicarbonate appears higher inside the pit than in the external areas.

4. Summary and conclusions

We have demonstrated the utility of synchrotron infrared reflectance microspectroscopy for the identification of surface films on copper formed during general and localized corrosion in aqueous solution environments. The film formed in 0.1 *M* NaOH at 0.3 V consisted mainly of CuO, in good agreement with previous works. We have shown for the first time that it is possible to determine the composition of the film inside pits formed by localized corrosion of copper in 0.01 *M* $NaHCO_3$. It consists mainly of copper bicarbonates, copper carbonate dihydroxide (malachite) and $Cu(OH)_2$, with possibly some CuO. The surface film in areas outside the pit differed only slightly in composition; the amount of $Cu(OH)_2$ relative to bicarbonate appears less than inside the pit. The films are also essentially the same as those formed in the initial passivation of the copper at 0.2 V following general corrosion. These findings can be important in theories of pit formation and repassivation in metals. There may be important roles played by $Cu(OH)_2$ in the process of passivation and of the carbonate anion in localized corrosion; these are not well understood.

Figure 6
Far-IR spectra of Cu microelectrode after pitting corrosion at 0.6 V and repassivation. (*a*) Area inside the pit, (*b*) areas outside the pit.

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