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# *Characterization of oxide layers on copper by linear potential sweep voltammetry*

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The characteristics of the electrochemical reduction of copper oxide have been studied using linear potential sweep voltammetry. Copper(II) and copper(I) oxides, formed on copper electrodes during triangular potential cycling, reduced at potentials close to the reversible values for the $CuO-Cu_2O$ and $Cu_2O-Cu$ couples, respectively. The reduction of bulk $Cu_2O$ and CuO deposited on carbon paste, glassy carbon and copper electrode surfaces required significant overpotentials. Both oxide species could be distinguished from the potentials of their cathodic reduction peaks. In each system studied, CuO was reduced before $Cu_2O$. We discuss the implications of these findings on the Pops and Hennessy galvanostic method for determining oxides formed on copper in the wire industry.

## 1. Introduction

The presence of oxide layers on copper surfaces adversely affects the behaviour of this metal during manufacturing processes such as wire production. Hence methods for characterizing these oxide films are important to the copper industry.

Several authors have recognized that techniques based on electrochemical reduction can provide reasonably straightforward means for identifying and determining copper oxides [1–8]. Pops and Hennessy [4] recommended a galvanostatic method, involving cathodic reduction of the oxide to the metal, for monitoring oxide films on copper in the wire industry. These authors noted that two arrests usually appeared in the charging curve and ascribed this phenomenon to the different characteristics of reduction of copper(I) and copper(II) oxides.

The formation and reduction of oxide layers on copper elecrodes during triangular potential cycles in alkaline solution have been studied by a number of workers (see [8–12] and references therein). Copper(I) oxide is produced first on the positive-going scan and the formation of the bulk species commences close to the reversible potential of the $Cu-Cu_2O$ couple. Copper(II) species are formed when the potential is taken above the reversible value for the $Cu_2O-CuO$ or $Cu_2O-Cu(OH)_2$ couples. On subsequent negative-going scans, corresponding cathodic peaks appear on the voltammogram due to the reduction of copper(II) and copper(I) oxides. X-ray photoelectron spectroscopy has been used [8] to confirm the identification of oxide species produced electrochemically.

In contrast to the above observations, Pops and Hennessy [4] assigned the first arrest to the reduction of $Cu_2O$ and the second to the reduction of CuO. They based this assignment on a mechanism in which the cathodic process was controlled by kinetic rather than thermodynamic factors. Reduction was considered to develop outward from the copper–copper oxide interface and, since $Cu_2O$ is the favoured oxide in contact with copper metal, this species would react first.

Reduction of both copper oxides involves two electrons per oxygen atom. Thus, determination by the galvanostatic method of the total quantity of oxygen present on a copper surface does not require a knowledge of the particular species present; however, conversion to oxide layer thickness does, because the molar density of the two oxides differ considerably. Furthermore, $Cu_2O$ and CuO have different mechanical properties and influence industrial processes to a different extent. Thus it is important to establish the identity of the oxide giving rise to each

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potential arrest on the galvanostatic charging curve.

In this communication we present linear potential sweep voltammetric studies of the reduction of copper oxides prepared by a number of methods carried out to test the validity of the hypothesis put forward by Pops and Hennessy [4].

## 2. Experimental details

### 2.1. *Chemicals*

Copper(I) oxide ($Cu_2O$) was prepared by reduction of Fehling's solution (an alkaline tartrate solution of copper sulphate) with dextrose [13]. All other chemicals were of Analar grade. Both 0.1 M $Na_2B_4O_7$ and 0.1 M $Na_2CO_3$ were used as electrolytes. Electrodes were cut from Analar copper foil (0.1 mm thick) or from commercial electrolytic copper sheet (1 mm thick); both were 99.95% pure.

### 2.2. *Electrochemical equipment*

The electrochemical cell ($\sim$15 ml capacity) was constructed of Pyrex glass and was fully enclosed to exclude oxygen. It was fitted with a copper foil counter electrode and a reference electrode equipped with a fine Luggin probe adjusted to within 0.5 mm of the working electrode. Before each run the electrolyte was rigorously purged with nitrogen to remove traces of oxygen, and a rapid stream of nitrogen was passed over the electrolyte surface during the potential scans. Reference electrodes were Hg–HgO in the same electrolyte as used in the cell and all potentials quoted are versus this electrode. A saturated calomel electode (SCE) had a potential of $-27$ mV versus Hg–HgO reference in 0.1 M $Na_2CO_3$ and $-145$ mV versus Hg–HgO in 0.1 M $Na_2B_4O_7$. Potential scans were applied with an Amel 551 potentiostat programmed with an Amel 567 sweep generator and currents were recorded as a function of potential with a Hewlett-Packard 7046B *X–Y* recorder.

### 2.3. *Potential scanning procedure*

Potential scans were run at 1 or 0.5 mV $s^{-1}$. When reducing oxides the potential scan was started at the open circuit potential of the copper electrode.

### 2.4. *Electrochemical oxidation*

Electrodes used in electrochemical oxidation studies were embedded in Epoxy resin so that a flat surface of 0.5 $cm^2$ was exposed to the electrolyte. The electrodes were either oxidized during potential scans or at a set potential for a controlled period. Before each run the electrode was wet polished on P1200 silicon carbide paper. Surface oxides formed by exposure to air after polishing were normally removed by reduction at $-1400$ mV.

### 2.5. *Oxide phases*

The carbon paste electrode has been applied by a number of workers to the analysis of solid materials by mixing the solid with the carbon paste (see [14] and references therein). Another convenient and effective method of attaching the solid involves pressing the carbon paste electrode against a dispersion of the solid on a glass slide [15].

To obtain reproducible results the copper oxides had to be applied as very thin coatings. This was achieved by placing a drop of an ethanol suspension of the oxide on a glass slide and then removing the ethanol by evaporation. The oxide was then transferred to a Metrohm carbon paste electrode by pressing this against the coated glass slide.

Copper oxides were also fixed to a copper substrate. This was accomplished by placing a drop of a suspension of finely ground oxide in ethanol on copper foil electrode and removing the ethanol by evaporation in air.

### 2.6. *Oxidation of copper deposited on glassy carbon*

A thin film of copper was deposited on the tip of a cylindrical glassy carbon electrode (5 mm diameter) (Sigri Electrographit, West Germany) from acidic copper sulphate solution containing dextrin and thiourea as brighteners and grain refiners [16]. The copper was deposited on an area of about 1 cm$^2$ using a current of 30 mA for 1 s. The deposits were oxidized in an electric furnace as described in Section 2.7 for the copper sheet electrodes.

### 2.7. *Oxidation of copper sheet*

Copper tabs, 10 cm × 1 cm × 1 mm, were placed for short periods in a regulated electric furnace, then removed and allowed to cool in air. At 600° C the apparent oxidation rate was much faster for copper foil than for sheet, indicating that the sheet took a significant time to reach 600° C. The top end of the tab was cleaned with coarse silicon carbide paper to form a good contact for the potentiostat lead, and the tab was immersed to a depth of 1 cm in the deoxygenated electrolyte. Before each oxidation the electrode was polished with P1200 silicon carbide paper to provide a reproducible electrode surface.

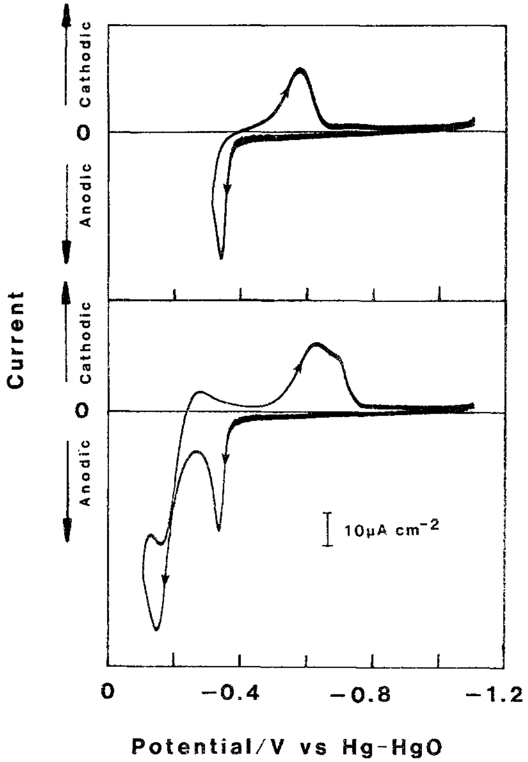

Fig. 1. Triangular potential scans at 1 mV s$^{-1}$ for 0.5 cm$^2$ copper electrodes in 0.1 M $Na_2B_4O_7$. Starting potential −1100 mV. (a) Positive scan limit −310 mV. (b) Positive scan limit −110 mV.

## 3. Results and discussion

### 3.1. *Electrochemical oxidation*

Triangular potential scans for a copper electrode in 0.1 M $Na_2B_4O_7$ (pH 9.2) are shown in Fig. 1. An anodic peak is apparent at about −0.35 V, and when the upper potential limit of the scan is restricted to −0.31 V (curve a) a single cathodic peak is evident at about −0.58 V. The anodic and cathodic currents commence close to the reversible potential (−0.46 V) for the process

$$2Cu + H_2O \longrightarrow Cu_2O + 2H^+ + 2e \quad (1)$$

The anodic and cathodic peaks have been identified with the forward and reverse of Reaction 1, respectively, in a number of studies of the behaviour of copper electrodes in alkaline solution (see [8–12] and references therein). The anodic current falls after the peak due to passivation by the $Cu_2O$ product; a limiting $Cu_2O$ thickness of 1.0–1.5 nm has been reported for borate solution [8].

When the positive-going scan is taken to more positive potentials than in curve a, copper(II) oxide species can also form

$$Cu_2O + H_2O \longrightarrow 2CuO + 2H^+ + 2e \quad (2)$$

and/or

$$Cu_2O + H_2O + 2H^+ \longrightarrow 2Cu(OH)_2 + 2e \quad (3)$$

The reversible potentials of Reactions 2 and 3 are −0.26 V and −0.20 V, respectively. Thus we assign the anodic peak at about −0.15 V in Fig. 1b to Reaction 2 or 3 and the cathodic peak at about −0.25 V to the reverse process. Reduction of $Cu_2O$ now appears as a doublet centred around −0.65 V. The electrochemical formation of a duplex oxide film of a copper(II) oxide overlaying a copper(I) oxide has been reported by previous workers and X-ray photoelectron spectroscopic (XPS) studies [8] have indicated that the former species is highly hydrated.

The ratio of the anodic and cathodic charges was almost exactly equal when only the copper(I) oxide potential region was traversed. However, the total cathodic charge was much

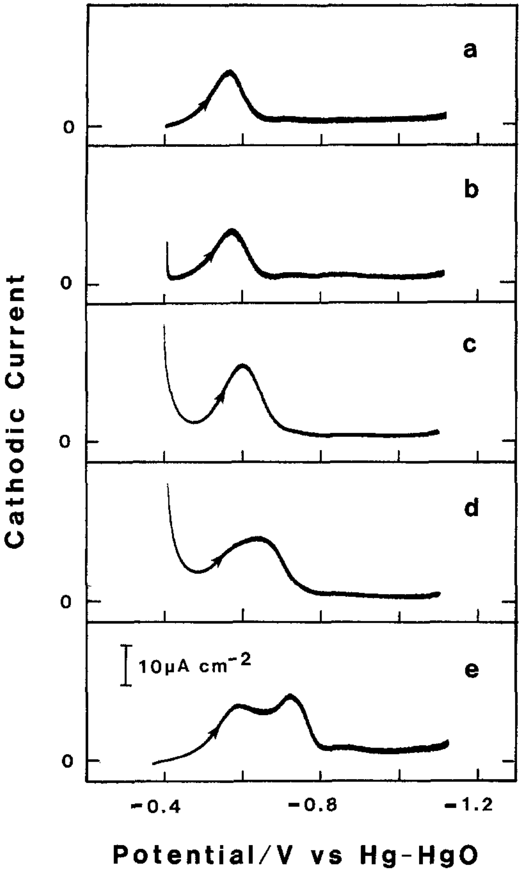

Fig. 2. Potential scans at 1 mV s$^{-1}$ from −0.4 V for the reduction of copper oxides formed on a copper electrode in 0.1 M $Na_2B_4O_7$ after (a) electrode exposed to air; (b) potential held at −350 mV for 100 s; (c) potential held at −250 mV for 600 s; (d) potential held at −100 mV for 600 s; (e) potential scanned between −200 mV and −620 mV for twenty cycles at 100 mV s$^{-1}$. (The spikes at the start of scans b to d are due to double-layer charging and reduction of $Cu(OH)_2$.)

less than the anodic when copper(II) oxide was formed. This indicates that some copper(II) species enter the solution phase during the positive-going scan. Loss of copper(II) occurs in borate solution even though the solubility of copper(II) hydroxide is at a minimum at this pH (~5 × 10$^{-9}$ M [17]).

Fig. 2b presents a reduction scan for a copper electrode oxidized in borate solution by holding the potential for 100 s in the region when only copper(I) oxide is formed. The cathodic peak appears at a similar potential to that in Fig. 1a for the oxide formed on a triangular potential cycle. However, when the electrode was held at higher potentials for longer periods, the cathodic peak shifted to more negative values (curves c to d). The scan shown in Fig. 2e was for an oxide formed by 'electrochemical ageing' [11] in which the potential was cycled between −0.2 V and −0.6 V twenty times at 100 mV s$^{-1}$ before the normal scan from −0.4 V was applied. The voltammogram now displays an additional peak at more negative potentials. The changes in the voltammetric profile in Fig. 2 is considered to arise from restructuring of the copper(I) oxide layer making it more difficult to reduce [11, 12]. Thus, whereas the initial copper(I) oxide can be reduced close to the reversible potential, a significant overpotential is required to reduce the reconstructed, more stable compound.

Fig. 2 also shows a voltammogram obtained for a fresh copper surface after brief exposure to air (curve a). The characteristics of this curve are similar to those in Fig. 2b and this suggests the nature of the oxide layer is the same.

### 3.2. *Oxide phases*

Fig. 3 shows potential scans in 0.1 M $Na_2B_4O_7$

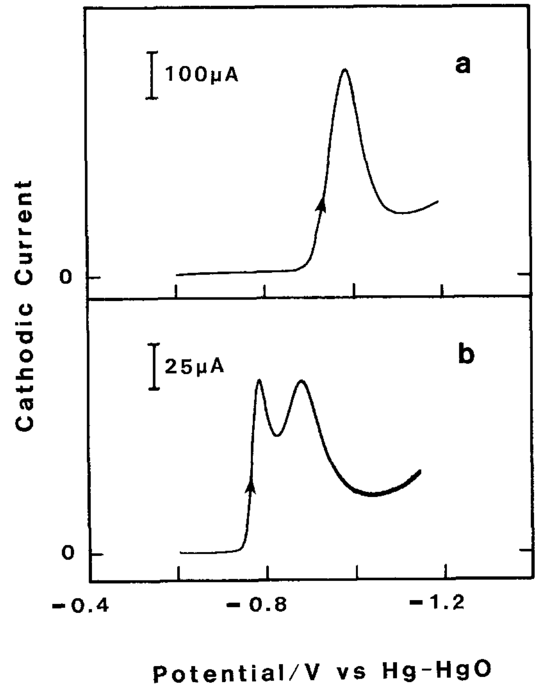

Fig. 3. Potential scans at 0.5 mV s$^{-1}$ for the reduction of copper oxide powders on a carbon paste substrate in 0.1 M $Na_2B_4O_7$. (a) $Cu_2O$ powder. (b) CuO powder.

for $Cu_2O$ and CuO powders supported in a carbon paste electrode. Reduction of $Cu_2O$ gives rise to a peak at about −0.98 V (curve a). Thus the electrochemical reduction of a bulk $Cu_2O$ phase requires a much greater overpotential than that of the thin copper(I) oxide layer formed electrochemically or on exposure to air at 25° C. The potential for the latter species was about −0.58 V (see Figs 1, 2).

The voltammogram for CuO (Fig. 3b) displays two peaks at −0.78 V and about −0.88 V indicating that, as with the electrochemically formed copper(II) oxide, two steps are involved, i.e. $CuO \rightarrow Cu_2O$ and $Cu_2O \rightarrow Cu$. Again, the reduction of the oxide phase requires a considerable overpotential compared to the electrochemical species. The second peak occurs at a more negative potential than that for $Cu_2O$ reduction in Fig. 3a. The different overpotential for the reduction of copper(I) oxide in the two situations probably reflects a difference in hydration.

Very similar results were obtained if the electrolyte was 0.1 M $Na_2CO_3$. (Both peak and reference potentials shifted by the same amount when the electrolyte was changed.)

When thicker coatings of oxide were investigated, broad ill-defined peaks were seen shifted by varying amounts to more negative potentials. The two peaks for CuO were not resolved when high scan rates were used or thick films investigated.

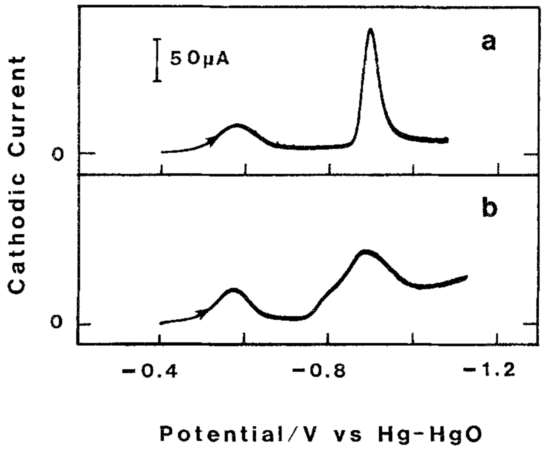

Fig. 4. Potential scans at 0.5 mV s$^{-1}$ for the reduction of copper oxide powders on a copper substrate in 0.1 M $Na_2B_4O_7$. (a) $Cu_2O$ powder. (b) CuO powder.

Fig. 4 shows voltammograms for the reduction of $Cu_2O$ and CuO supported on a copper substrate. The cathodic peaks arising from the reduction of these oxides are similar to those observed with the carbon paste electrode; $Cu_2O$ gave a peak at about −0.9 V and CuO a doublet at about −0.78 V and about −0.88 V. However, an additional peak at −0.58 V is evident on the scans for both oxides. This is due to the reduction of the oxide layer already present on the copper substrate (see Fig. 2a).

### 3.3. *Oxidation of copper deposited on glassy carbon*

A known amount of copper was deposited on a glassy carbon electrode, oxidized in air at 600° C for varying lengths of time and the resulting oxide layer reduced on a potential scan. A 30 mC charge was passed in the deposition. Assuming a 100% current efficiency for deposition, a reduction charge of 15 mC would be expected if the copper had been converted to $Cu_2O$, and 30 mC if CuO was the product (a slightly lower charge

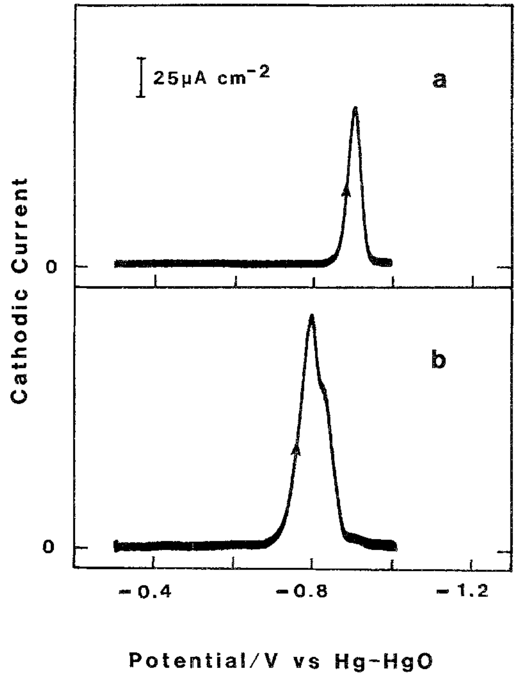

Fig. 5. Potential scans at 0.5 mV s$^{-1}$ in 0.1 M $Na_2B_4O_7$ for the reduction of copper oxides formed by oxidation of a thin film of copper on glassy carbon. (a) $Cu_2O$ formed by oxidation in air at 600° C for 15 s. (b) CuO formed by oxidation in air at 600° C for 180 s.

will be observed since the depositon charge includes contributions from double layer charging etc.).

When the electrode was heated for 15 s, a single peak at about −0.9 V was observed on the voltammogram (Fig. 5a) and the cathodic charge passed was 9.4 mC. We assign this peak to the reduction of $Cu_2O$. When the electrode was heated for 90 s or more, a doublet was observed (Fig. 5b) and the charge passed was 25 mC. The peak potentials were about −0.79 and about −0.82 V. This doublet is assigned to the reduction of CuO. Thus for both copper(I) and copper(II) oxides formed by thermal treatment of copper, the cathodic peaks appear at similar potentials to those observed for copper oxide powders supported on carbon paste and copper electrodes.

### 3.4. *Surface oxidation of copper sheet*

A voltammogram observed for the reduction of the oxide layer formed when copper sheet was heated in air at 125° C for 16 h is shown in Fig. 6. It has been reported for X-ray diffraction (XRD) and other studies [18–21] that $Cu_2O$ is the ultimate product at this temperature. Indeed, a large cathodic peak is apparent at about −0.9 V and this peak corresponds closely to that formed for the reduction of bulk $Cu_2O$ and of $Cu_2O$ formed by thermal oxidation of copper deposited on glassy carbon. In addition, a minor peak is evident at about −0.54 V which is in the potential region in which reduction occurs of the thin copper(I) oxide formed on exposure of copper to air at 25° C. This suggests that the $Cu_2O$ bulk phase developed in patches on the metal surface and that a thin, more readily reducible oxide layer covered the remaining surface.

Investigations were also carried out on copper sheet heated in a furnace held at 600° C. Voltammograms for samples placed in the furnace for short times were similar to those observed for electrochemical oxidation (Fig. 2), the cathodic peak due to reduction of the oxide layer occurring at more negative potentials as the exposure time increased. This suggests a similar mechanism, namely a reconstruction or dehydration of the oxide making it more difficult to reduce.

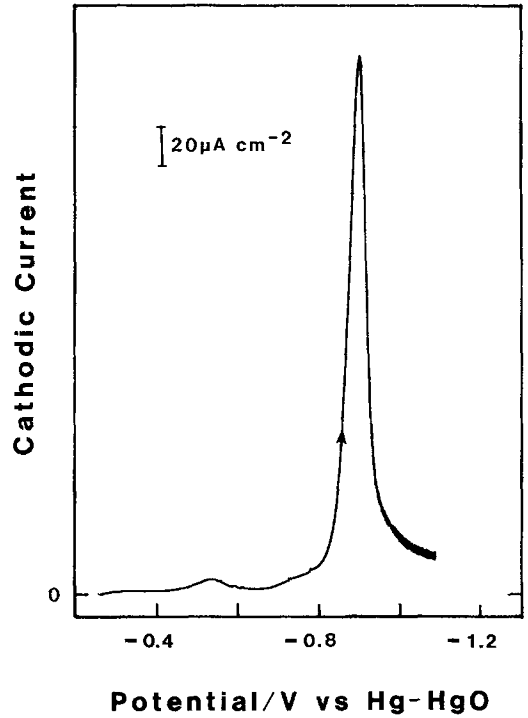

Fig. 6. Potential scan at 0.5 mV s$^{-1}$ in 0.1 M $Na_2B_4O_7$ for the reductin of $Cu_2O$ formed by heating copper sheet in air at 125° C for 16 h.

For exposure times ⩽25 s, the reduction peak split into two components and a $Cu_2O$ phase nucleated and grew rapidly on the surface giving rise to a major peak at about −0.9 V (Fig. 7a). The peak corresponding to the initial thin copper(I) oxide layer (−0.58 V in Fig. 7a) is no longer evident after exposure times ⩾70 s (Fig. 7c and d) and a doublet now appears in the potential region expected for CuO. Identification of the doublet with the presence of CuO is supported by the fact that the copper surface appeared black when it was heated for 70 s or longer. Copper(II) oxide is the stable phase for copper in air at temperatures above 200° C but forms only a thin outer layer because the growth of an inner $Cu_2O$ layer is favoured by the greater rate of diffusion of copper ions via copper vacancies in $Cu_2O$ [22]. X-ray diffraction analysis confirmed that the bulk of the oxide was $Cu_2O$. The charge passed in the reduction of the oxide layers in Fig. 7a and d indicate that the oxide thickness was 112 nm and 915 nm, respectively.

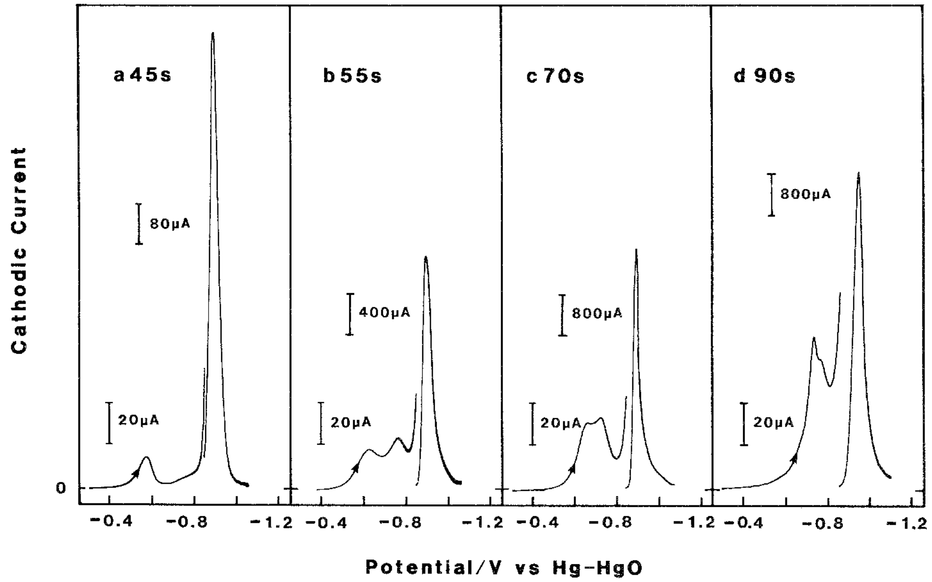

Fig. 7. Potential scans at 0.5 mV $s^{-1}$ in 0.1 M $Na_2B_4O_7$ for the reduction of oxides produced by heating copper sheet in a furnace at 600° C for the times shown. Note changes in current scales (each bar is current per $cm^2$).

Ethanol is used in the production of copper rod for wire production to protect the metal surface from oxidation. To simulate the effect of this treatment, copper sheet was placed in the furnace at 600° C for 70 s and then plunged into absolute ethanol. Fig. 8 shows voltammograms for two samples after this procedure. The charge associated with the reduction peaks was much less than that observed after 70 s in the furnace (Fig. 7c), demonstrating that reduction of the oxide occurred during quenching in ethanol.

The colour of the sample before Fig. 8a was recorded was identical to that of a freshly cleaned copper surface, confirming that the bulk of the oxide had been removed. A couple of dark spots could be seen on the sample giving rise to Fig. 8b after it had been removed from the ethanol, indicating that some bulk oxide was still present.

The peak at about −0.9 V in Fig. 8a and b can confidently be assigned to bulk $Cu_2O$. A minor peak is evident at about −0.7 V in Fig. 8b and this is indicative of a small amount of CuO remaining on the surface. In both Fig. 8a and b

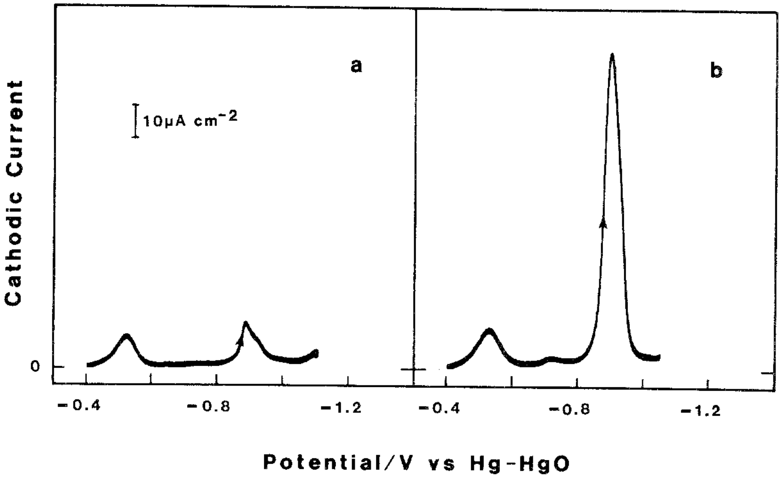

Fig. 8. Potential scans at 0.5 mV $s^{-1}$ in 0.1 M $Na_2B_4O_7$ for copper sheet heated at 600° C for 70 s and then immediately plunged into ethanol. (a) Surface identical in appearance to a fresh surface. (b) Visible small dark spots on surface.

there is a peak at about −0.5 V. This peak corresponds to reduction of the thin copper(I) oxide layer formed on exposure to air at 25° C. This species most likely arises from air oxidation of the copper surface that had been freed from bulk oxides by the treatment in ethanol.

## 4. Conclusions

The potentials at which copper(I) and copper(II) oxides are reduced varies with oxide thickness and with formation conditions. However, it is generally possible to identify the different species present on a copper surface from the characteristics of reduction.

The initial product of oxidation of copper on exposure to air is a thin copper(I) oxide layer that is reduced close to the reversible potential of the $Cu_2O$–Cu couple. Thick oxide layers are produced by thermal treatment and the reduction of these bulk phases requires significant overpotentials. When the thermal oxides completely cover the copper surface, the reversible copper(I) oxide is absent.

Our results show that, contrary to the hypothesis of Pops and Hennessy [4], CuO is reduced before the $Cu_2O$ phase on excursions to negative potentials. It is apparent that the reduction of CuO takes place in two stages, the reverse of Reaction 2 followed by the reverse of Reaction 1. The second step is usually completed before the underlying $Cu_2O$ layer is reduced, but may overlap with the latter process.

The appearance of two reduction peaks on a voltammogram (or two plateaux on a galvanostatic transient) does not necessarily indicate the presence of both copper(I) and copper(II) oxide species. Two peaks are observed when bulk $Cu_2O$ is present on part of a copper surface and the remainder is covered wih the reversible copper(I) oxide. In this case the first reduction process occurs close to the reversible $Cu_2O$–Cu potential. Three peaks are observed when CuO is present as well as the two copper(I) species.

It is possible that the reversible copper(I) oxide is present on industrial copper rod produced for wire manufacture. Bare metal sites could result from such processes as reduction by the alcohol used to protect the copper during drawing and these sites would react to form the reversible oxide on subsequent exposure to air. However, the thickness of this species is restricted to the order of 4 nm [8].

Pops and Hennessy interpreted data obtained from the reduction of oxide layers formed on copper wire during annealing for 5 s at different temperatures (see Table 2 of [4]) as indicating that the thickness of CuO increased from 3.7 nm at 93° C to 202 nm at 496° C. They concluded that a $Cu_2O$ layer was also present and its thickness was 2–4 nm below 300° C, zero between 300 and 400° C and then increased with temperature to reach 76 nm at 496° C.

The results of our studies suggest that the oxide layer identified by Pops and Hennessy as CuO arises from the presence of a $Cu_2O$ phase. This interpretation is supported by studies [22–24] that show $Cu_2O$ to be the major oxide species formed on copper in the early stage of oxidation at temperatures below 400° C.

The low temperature layer assigned by Pops and Hennessy to $Cu_2O$ probably arises from the presence of the reversible copper(I) oxide. Their example of a charging curve (see Fig. 3 of [4]) shows that the initial arrest commences at about −0.5 V versus SCE, which is equivalent to −0.53 V on the reference scale used in our work. This is in the potential region we find the reversible copper(I) oxide to be reduced. It is possible that the layer they assigned to $Cu_2O$ for treatments above 400° C should be identified as CuO.

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