JOURNAL OF APPLIED ELECTROCHEMISTRY 24 (1994) 953–964

Factors affecting the electrochemical behaviour of copper anodes under simulated electrorefining conditions

E. A. KUCHARSKA-GIZIEWICZ, D. J. MACKINNON

Mineral Sciences Laboratories, CANMET, Department of Natural Resources Canada,
555 Booth Street, Ottawa, Ontario, Canada, K1A OG1

Received 24 September 1993; revised 23 February 1994

Cyclic voltammetry (CV) was used to characterize the behaviour of copper anodes during electrorefining. The method involved cycling the anode potential at a rate of $2\,\mathrm{mV\,s^{-1}}$ between the open circuit potential of $-0.35\,\mathrm{V}$ and $0.0\,\mathrm{V}$ vs mercury/mercurous sulphate (MSE) reference electrode. Reproducible electrochemical characteristics for pure copper anodes of different shapes, sizes and configurations (vertical vs horizontal) were determined. Passivation time measurements indicated a strong correlation between the CV profile and the ease of anode passivation. The size, shape and geometrical configuration of the anode impact significantly on the electrochemical dissolution and passivation of pure copper. An IBM compatible computer equipped with a data acquisition board was used to acquire, examine, compare, and catalogue the electrochemical data which were presented in the form of a potential–current–time spectrum rather than a conventional cyclic voltammogram. This format enhanced the clarity and readability of the results.

1. Introduction

Anode passivation during copper electrorefining is a serious problem which is sometimes encountered in all refineries. It is believed that various impurities or combinations of impurities contained in the copper anodes have a significant effect on anode passivation and on the morphology and composition of the anode slimes. The problems associated with anode impurities are expected to intensity as anodes become dirtier through expansion of custom smelting activities and the processing of impurity-rich concentrates. Hence, the primary objective of this work was to establish a body of fundamental knowledge on anode passivation that could lead to a passivation index, and hopefully, to a method of analysis of commercial anodes to predict their behaviour during electrorefining. Prior knowledge of the electrochemical characteristics of a particular batch of anodes would allow the adjustment of the electrorefining parameters (current density, temperature, etc.) to lower the energy demand.

Despite the large volume of work already reported on the properties and electrochemical behaviour of copper anodes in acidic copper sulphate solutions, the mechanism of copper anode passivation is still subject to speculation. Some researchers think that the crystallization of nonconductive copper sulphate on the anode surface is the prime cause of anode passivation [1], whereas others conclude that the passivation is due to the formation of a cuprous oxide film [2]. Furthermore, it was reported [3] that the simultaneous formation of $CuSO_4.5H_2O$, $CuCl$, Cu_2O and CuO with other slime components contributes to anode passivation. Chen and Dutrizac recently carried out mineralogical studies [4] of passivated and nonpassivated anodes. The surfaces of the nonpassivated anodes consisted mostly of bare copper metal. Although masses of $CuSO_4.5H_2O$ and tiny particles of Cu_2O were commonly present, they did not cover a large fraction of the anode surface. The anode slimes formed on passivated pure copper consisted of a mixture of copper powder and Cu_2O, and both phases might contribute to the passivation. Although copper powder was a prominent constituent of the anode slimes formed on pure copper, it was generally absent from commercial anode slimes. The copper powder probably formed by the disproportionation of cuprous ions according to the following:

$$2Cu^+ \longrightarrow Cu^0 + Cu^{2+} \qquad (1)$$

Cu_2O was the product of another reaction:

$$2Cu^+ + H_2O \longrightarrow Cu_2O + 2H^+ \qquad (2)$$

Many of the anodes examined were clearly passivated by a thin layer of Cu_2O on the anode surface. The morphology of the Cu_2O layer indicated that it formed during electrolysis and that it was not just the accumulation of the spheroidal Cu_2O particles present in the anode copper. Furthermore, the thickness of the Cu_2O layer seemed to increase when the anode was held in the passivated state for a prolonged time. This observation correlates with the results of Abe and Goto [2] who showed that the formation of Cu_2O is inhibited as long as the pure copper anode continues to dissolve. Garneau *et al.* [5] noticed that the Cu_2O phase became detectable after multiple cyclic voltammetry sweeps, conducted between −0.34 V and +0.5 V at a speed of $50\,mV\,s^{-1}$. The surfaces of most passivated commercial copper anodes [4] were extensively covered either by a thick layer of $CuSO_4.5H_2O$ or by a thin continuous layer of Cu_2O. The morphological observations indicated that the copper sulphate crystallizes directly on the surface of the copper metal during electrolysis [6]. The above discussion shows that some uncertainty still exists as to the causes of copper anode passivation and that further study is needed. Hence, the objectives of the present work were:

(i) To develop a reproducible technique using cyclic voltammetry to characterize the behaviour of copper anodes during electrorefining.
(ii) To establish reproducible electrochemical characteristics, using this technique, for pure copper anodes of different sizes, geometries and configurations that could be used later, as a standard, in comparing copper anodes containing different and various amounts of impurities.
(iii) To correlate these electrochemical characteristics with the tendency of the copper anode to passivate.

2. Experimental details

Copper rods measuring 20 cm long by 5 cm in diameter and containing various amounts of oxygen, silver, selenium and nickel were prepared for CANMET by the Noranda Technology Centre. Samples of commercial anodes were obtained from Noranda's CCR Division, from Falconbridge's Kidd Creek Division and from the Hudson Bay Mining and Smelting Co. (HBMS). A listing of the synthetic and commercial anodes used in this study is presented in Table 1. Typical impurity concentrations of the commercial anodes are presented in Table 2. Additional pure copper rods were prepared at CANMET by melting hydrogen-reduced pure cathode copper in vacuum-sealed silica tubes. These rods were 8 cm in length and 1.6 cm in diameter. Twenty-two pure copper anodes of different sizes and geometries were examined, ranging from a thin wire (surface area $0.05\,cm^2$) to a circular anode with a surface area of $2.27\,cm^2$. A listing of the pure copper anodes of different shapes, surface areas and configurations is presented in Table 3.

Table 1. Anodes characterized by cyclic voltammetry in this study

* Pure Cu
* Cu–0.1% Ag
* Cu–0.1% Se
* Cu–0.1% O
* Cu–0.1% Ag + 0.1% Se
* Cu–1.0% Ag
* Cu–1.0% Se
* Cu–1.0% O
* Cu–0.3% Ni + 0.3% O
* CCR Commercial Anode
* Kidd Creek Commercial Anode
* HBMS Commercial Anode

Table 2. Typical concentrations of major impurities contained in the commercial anodes used in this study

Element	*Weight percent in anode*		
	CCR	*Kidd Creek*	*HBMS*
Ag	0.29	0.17	—
Se	0.12	0.22	0.096
O	0.13–0.15	0.13–0.15	0.13–0.15
As	0.02–0.07	0.004	0.011
Pb	0.066	0.27	0.011

Anodes were prepared either by cutting rectangular sections from the cast rods or by slicing the laboratory rod samples into round pieces. The copper anodes were mounted in acrylic such that only a single face was exposed to the electrolyte. Electrical contact was achieved by drilling through the back of the acrylic mount into the copper. A brass rod was threaded into the copper and this served as the external electrical contact. The brass rod was insulated from the electrolyte by a tight-fitting sleeve of Tygon tubing which was sealed into the acrylic mount using silicone rubber. Most of the anodes were assembled in a vertical configuration although some were also mounted horizontally such that the slimes produced during electrorefining stayed on the surface of the anode. Thus the effect of these slimes on the electrochemical behaviour of the anode could be determined.

Cyclic voltammetry (CV) studies were performed using a conventional water-jacketed cell with a copper working electrode, a platinum counter electrode and a mercury/mercurous sulphate reference electrode. A Luggin capillary, the tip of which was set at a distance of 1 cm from the surface of the working electrode, was used to minimize uncompensated resistance effects. This configuration gave reproducible cyclic voltammograms and thus objective (i) of this study was achieved. A PAR 173 potentiostat-galvanostat, equipped with plug-in module M376, was used as a potentiostat allowing the anode to be maintained at various programmed potentials with respect to the reference electrode. A PAR 175 universal programmer provided various potentiodynamic voltage vs time programs. Initially the I/V profiles were recorded using a Hewlett–Packard X–Y recorder. Later, the I/V profiles were recorded via an analog to digital Keithley MetraByte DAS-16 board. The acquired data were analysed, graphically examined, directly compared and presented as plotter-generated graphs.

Most of the CV experiments were conducted in aqueous solutions containing $40\,g\,dm^{-3}$ Cu as $CuSO_4$ and $160\,g\,dm^{-3}$ H_2SO_4 at 65 °C as these conditions approximate those used in commercial electrorefining operations. The effect of copper ion concentration on the electrochemical characteristics

Table 3. Geometry and configuration of pure copper anodes used in this study

Anode	*Shape*	*Configuration*	*Surface area/cm^2*	*Dimensions/cm*
Cu 1	rectangular	vertical	1.10	1.1 × 1.0
Cu 2	rectangular	vertical	1.10	1.1 × 1.0
Cu 3	rectangular	vertical	1.10	1.1 × 1.0
Cu 4	rectangular	vertical	0.90	0.95 × 0.95
Cu 5	rectangular	vertical	0.90	0.95 × 0.95
Cu 6	rectangular	vertical	0.81	0.95 × 0.85
Cu 7	rectantular	horizontal	0.81	0.95 × 0.85
Cu 8	rectangular	vertical	0.39	0.3 × 1.3
Cu 9	rectangular	vertical	0.98	0.7 × 1.4
Cu 10	rectangular	vertical	1.26	0.9 × 1.4
Cu 11	rectangular	vertical	1.54	1.1 × 1.4
Cu 12	rectangular	vertical	1.68	1.2 × 1.4
Cu 13	round	vertical	2.01	$r = 0.80$
Cu 14	rectangular	vertical	1.96	1.4 × 1.4
Cu 15	round	vertical	2.27	$r = 0.85$
Cu 16	round	vertical	0.71	$r = 0.475$
Cu 17	round	vertical	0.05	$r = 0.125$
Cu 18	round	vertical	0.05	$r = 0.125$
Cu 19	round	vertical	0.05	$r = 0.125$
Cu 20	round	horizontal	2.27	$r = 0.85$
Cu 21	rectangular	vertical	2.09	1.55 × 1.35
Cu 22	round	horizontal	2.27	$r = 0.85$

of a copper anode was determined by conducting some of the measurements in a solution consisting only of 160 g dm^{-3} H_2SO_4. The cell electrolyte was heated and maintained at the desired temperature using a circulation water bath. Experiments were performed in an air atmosphere and the electrolyte was not stirred. The surfaces of the copper anodes were prepared by grinding on a diamond wheel (45 μm). Just before an experiment, a quick grind at 100 μm was done, followed by a rinse with doubly distilled water. Polishing was not done, as it was discovered that polishing gave less reproducible results, probably due to the required initial 'attack' to dissolve the polished surface.

The copper anodes were subjected to a controlled number of continuous potential cycles ranging between −0.35 and 0.0 V at a scan speed of 2 mV s^{-1}. The scan speed of 2 mV s^{-1} was chosen after establishing that the potentials at which the peaks form are scan dependent. This speed seemed low enough to accommodate second peak formation without unduly lengthening the experiment. The potential range of −0.35 to 0.0 V was chosen because of the distinct differences in the electrochemical behaviour displayed by copper electrodes with various impurity contents in this potential region. The anodes were always disconnected at the 'cathodic end' of the sweep (at −0.35 V), and usually after 30 cycles. The computer was programmed to read the experimental data at 5 points per second, equivalent to 1750 points per cycle.

In other experiments, passivation times were determined for selected anodes by maintaining the anodes at constant current and monitoring the potential–time profiles. A PAR 362 potentiostat/galvanostat was used as a galvanostat allowing the anode to be maintained at a constant current. The onset of passivation was signalled by an abrupt increase in the anode potential. A constant current, equivalent to 900 A m^{-2} current density, and a temperature of 45 °C were chosen to ensure that impurity-containing anodes, which will be investigated in a subsequent study, would passivate in a reasonable time period. Commercial copper electrorefining is normally carried out at a current density of 250 A m^{-2} and a temperature of 65 °C.

3. Results and discussion

3.1. *Cyclic voltammetry*

In the initial phase of this study, copper anodes containing various impurities (Table 1) were characterized by cyclic voltammetry. Reproducible and consistent results were obtained when the anode potential was cycled at a rate of 2 mV s^{-1} between the open circuit potential of −0.35 and 0.0 V vs MSE. For example, the shape of the CV changed with continuous cycling depending on the concentration of silver in the copper anode. As a result of continuous cycling, the anodic current decreased dramatically due to the formation of a slimes layer on the anode surface. This slimes layer consisted of a mixture of copper and silver powders, or exclusively of silver powder for high-silver anodes. The presence of the slimes layer on the anode surface also resulted in the formation of a second peak during the forward scan of the CV. The ease of formation of this second peak was dependent on the silver content of the anode suggesting that the number of continuous cycles needed to form this peak might be correlated to the ease of anode passivation.

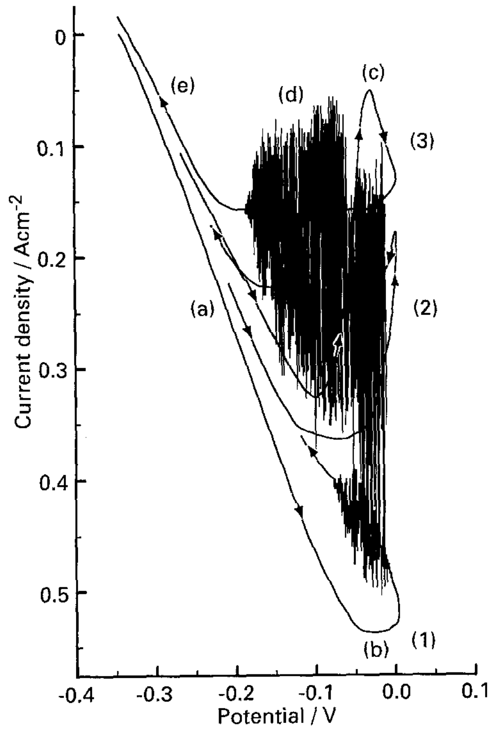

Fig. 1. Cyclic voltammograms showing the formation of peaks during the cycling of a Cu–0.1% Ag anode where: (1) 1st cycle, (2) 4th cycle and (3) 23rd cycle.

A typical reproducible CV profile (current density against potential plots) obtained during the continuous potential cycling of a silver-containing copper anode is shown in Fig. 1. In the first cycle (1), there is a long gradual slope, which ends in a gradual curve showing some oscillations in the reverse scan. After several cycles (2), the CV profile shows a firmly rounded current maximum (first peak). A small sharp current minimum is formed followed by very heavy oscillations in the reverse scan. As the cycling continues, the transformation of the curve progresses (3). The curve now ends in a very well defined current maximum (first peak) approximately in the areas of the oscillations of the first cycle. The line then rises to form a well defined current minimum (second peak), before turning around at the beginning of the reverse scan. The oscillations move towards more negative potentials, and when silver content is > 0.5%, they disappear altogether.

Examination of Fig. 1 demonstrates that the CV profile of a copper electrode containing silver consists of five distinct regions, which are marked (a) to (e) on the Figure:

(a) copper dissolution where the current is proportional to the voltage;

(b) formation of the first peak; i.e. a current maximum resulting from the accumulation of the reaction products on the anode surface;

(c) a second peak; i.e. a current minimum develops with time, as more slimes accumulate on the electrode surface. At the same time, the first peak shifts towards more negative potentials;

(d) oscillations which are related to loosening of the surface layer; and

(e) regular dissolution curve reestablished along the same slope as the initial dissolution (a).

As a result of continuous cycling, the anodic current decreases dramatically. The surface of the anode is covered with a mixture of copper and silver powders, or exclusively with silver powder for high-silver electrodes.

Similar CV profiles were obtained for the electrodes listed in Table 1 except that certain changes occurred depending on the type and concentration of impurity contained in the copper anode. These changes include a decrease in the maximum current for copper dissolution (first peak), a broadening of the hysteresis that occurs on the reverse scan, changes in the intensity of the oscillations that occur (mostly during the reverse scan) and the formation of a second peak featuring a minimum current. The shape of the second peak is related to the nature and composition of the

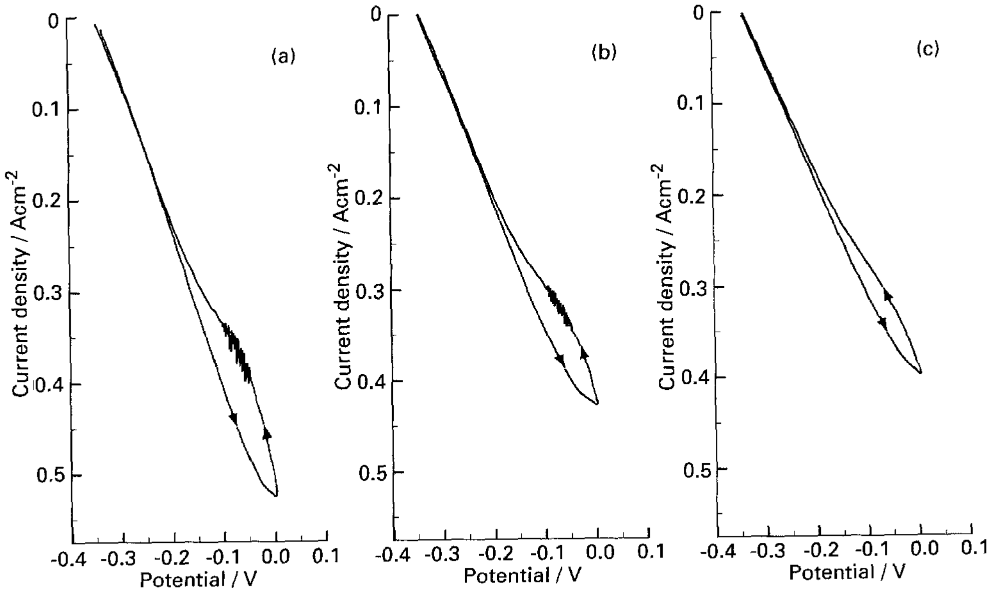

Fig. 2. Cyclic voltammograms obtained for a pure copper anode: (a) 1st cycle, (b) 4th cycle and (c) 23rd cycle.

product layer formed on the anode surface during the continuous cycling of the potential.

In the case of a pure copper anode, the CV profiles, Fig. 2, indicate that the second peak (current minimum) does not form and that even the oscillations disappear as the number of cycles increases. This behaviour is attributed to the fact that many copper flakes separated from the anode surface every time the cycle passed through the oscillation stage.

3.2. *Electrochemical spectrum*

In subsequent work, the CV experimental data were collected by computer. This allowed the results to be displayed as an electrochemical spectrum, the clarity of which is clearly superior to the conventional cyclic volammogram. This is advantageous as copper anodes sometimes display heavy oscillations, usually on the reverse scan, Fig. 1. The advantage of presenting the data as an electrochemical spectrum is illustrated in Fig. 3. Figure 3(a) and (b) show the electrochemical behaviour of a copper anode containing 0.1% Ag during the sixth consecutive cycle. Figure 3(a), the electrochemical spectrum, clearly shows a well defined second peak followed by heavy oscillations. The potential at which it appears is readily discernible. Figure 3(b) shows the same CV profile presented in the traditional manner. In this case, it is impossible to distinguish where the second peak forms as the heavy oscillations during the reverse scan mask the true shape of the curve.

Because of the superior clarity of the electrochemical spectrum, this technique was used to investigate the electrochemical behaviour of pure copper anodes. These results will be used as a basis for comparison with the electrochemical spectra obtained for the impurity-containing copper anodes (listed in Table 1) that will be presented in a subsequent report. The electrochemical spectra were obtained for a large number of pure copper anodes (Table 3) of various geometries, configured both vertically and horizontally in the electrochemical cell. The results refer either to the first 10 consecutive cycles of the 30 cycles to which the anode was subjected, or to the full 30 cycles.

Figure 4(a), (b) and (c) display the electrochemical spectra of three rectangular, vertically mounted, copper anodes having surface areas of 0.39 cm^2, 0.81 cm^2 and 2.09 cm^2. Figure 5(a), (b) and (c) show the electrochemical spectra of three vertically mounted round copper anodes with surface areas of 0.05 cm^2, 0.71 cm^2 and 2.01 cm^2. The circular anode with the smallest surface area (Fig. 5(a)) showed a high current density during the first cycle followed by the clear formation of the second peak. This result was surprising as the previously obtained CV profiles for pure copper anodes indicated that the second peak does not form and that the oscillations disappear as the number of cycles increases (cf. Fig. 2). Figures 4 and 5 also illustrate that small-area electrodes show a higher current density response and more oscillations than larger anodes.

The differences in the electrochemical behaviour exhibited by the small and large anodes may be

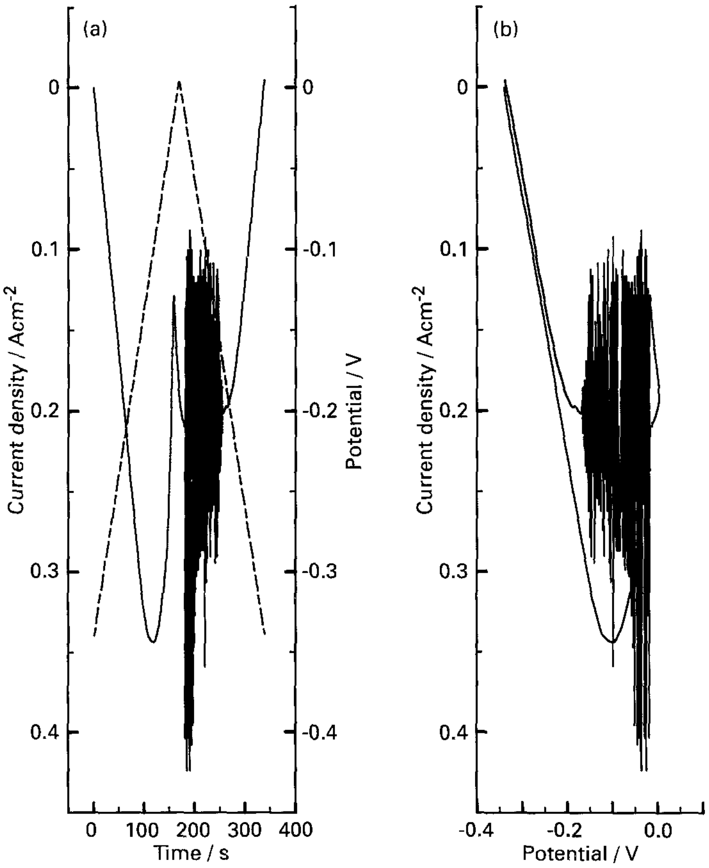

Fig. 3. The comparison between the electrochemical spectrum (a) and the cyclic voltammogram (b).

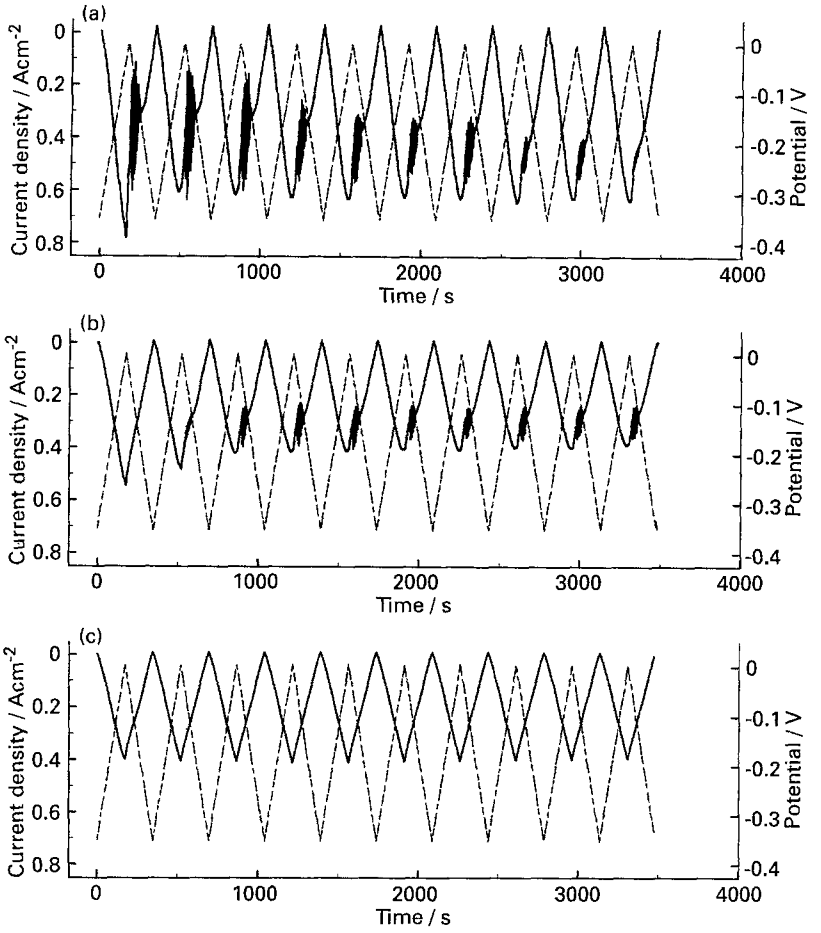

Fig. 4. The electrochemical spectra of ten continuous cycles (cycle 1–cycle 10) recorded for the rectangular pure copper anodes, configured vertically, with surface areas of: (a) 0.39 cm^2, (b) 0.81 cm^2, and (c) 2.09 cm^2.

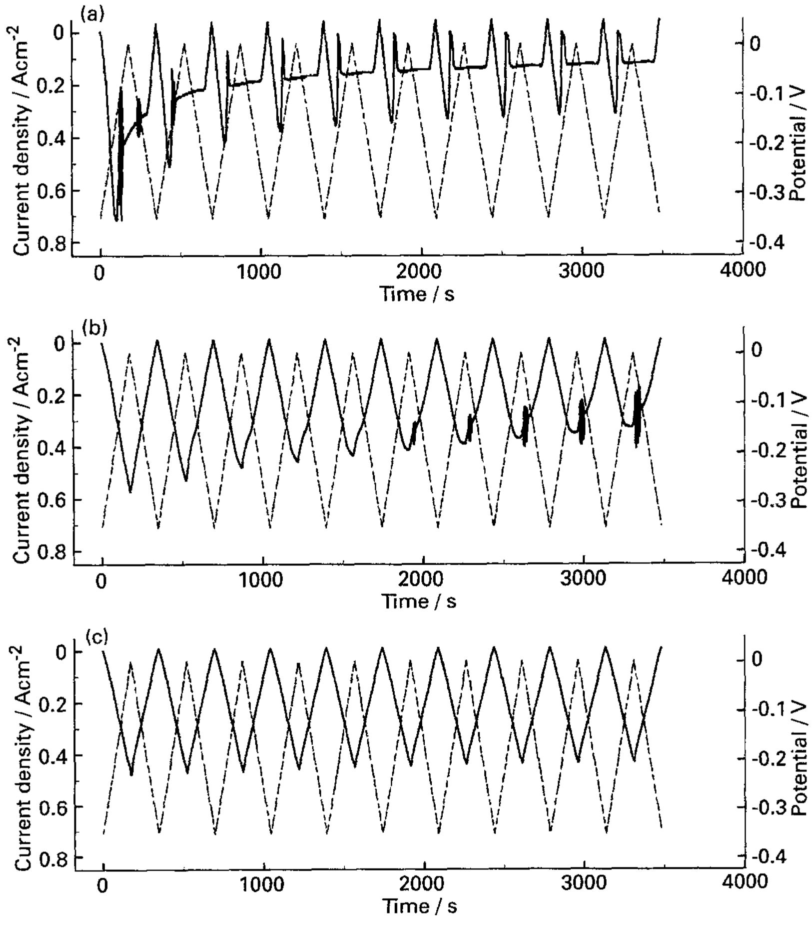

Fig. 5. The electrochemical spectra of ten continuous cycles (cycle 1–cycle 10) recorded for the round pure copper anodes, configured vertically, with surface areas of: (a) 0.05 cm^2, (b) 0.71 cm^2, and (c) 2.01 cm^2.

explained in terms of edge effects. The anodes produce high current densities along the edges. As the electrode surface is increased, the ratio of edges to the remaining surface decreases, thus resulting in a decrease in the average current density. As the electrode surface area increases, the oscillations disappear completely. This suggests an orderly dissolution of the copper anode, with virtually no copper powder accumulation on the surface. The ability of the tiny anode to produce the second peak can be explained as follows. When a small copper anode dissolves, a deep hole is created in the surrounding mounting medium wherein the reaction products are trapped. This blocks the surface and impedes the transport of copper ions from the anode. As the electrode surface increases, the second peak disappears, the oscillations decrease and the flaking stops (Figs 4 and 5).

An examination of the surfaces of the various anodes after 30 continuous cycles under an optical microscope or scanning electron microscope (SEM) revealed a definite cavity between the copper and the acrylic mount. The cavity was created by the accelerated dissolution along the edges of the copper. This narrow cavity then trapped the nonconductive copper sulphate and slimes. The accelerated edge dissolution resulted in an increase in the observed current density for the smaller anodes. Examination of the surfaces of the reacted pure copper anodes showed the presence of copper powder and crystallized copper sulphate. No Cu_2O was detected.

Figure 6 compares the electrochemical spectra generated for the same rectangular anode examined in both the vertical and horizontal configurations. There are some oscillations in the vertical position (Fig. 6(a)). The horizontal electrode, however, clearly displays the second peak and heavy oscillations as the slimes are trapped on the anode surface (Fig. 6(b)). Although the horizontally-mounted anode forms the second peak, the reverse scan oscillations appear at approximately the same potential for both anode configurations suggesting the same dissolution mechanism. In the vertically configured anode, oscillations precede the flaking whereby the anode surface is reconditioned and the dissolution process starts again as the slimes fall from the surface. In the case of a horizontally placed anode, the oscillations preceding the flaking are also present. Because the slimes accumulate on the surface of the anode, however, they trap even more of the nonconductive copper sulphate, and the second peak continues to grow.

Figure 7 illustrates the electrochemical spectra of a large, round copper anode corroded in both the vertical and horizontal configurations. The ideal dissolution of the vertically placed anode, with no oscillations, no second peak and no spalling is apparent (Fig. 7(a)). By contrast, the horizontally configured anode forms a second peak with heavy oscillations and no flaking (Fig. 7(b)). Although there are large differences in the two electrochemical spectra, the currents before the second peak is formed and after the oscillations subside follow the same curve.

These experimental results suggest that the formation of a strongly adhered slimes layer results in a well-defined second peak appearing at a lower potential than if the slimes are weakly adherent. Figure 8 compares the electrochemical spectra of the third consecutive cycle of the previously shown horizontally-mounted rectangular and circular anodes with surface areas of $0.81\,\mathrm{cm}^2$ (curve (a)) and $2.27\,\mathrm{cm}^2$ (curve (b)). Visual *in situ* observation of these anodes showed that the slimes layer on the surface of the horizontally configured rectangular anode was adherent, thicker and denser than that formed on the surface of the large circular anode. The diffusion of copper ions to and from the rectangular anode surface was seriously inhibited, and this resulted in a higher second peak at a less anodic potential. Slimes produced during the electrolysis of the large horizontally mounted circular anode did not adhere well to the centre of the anode although the slime did adhere

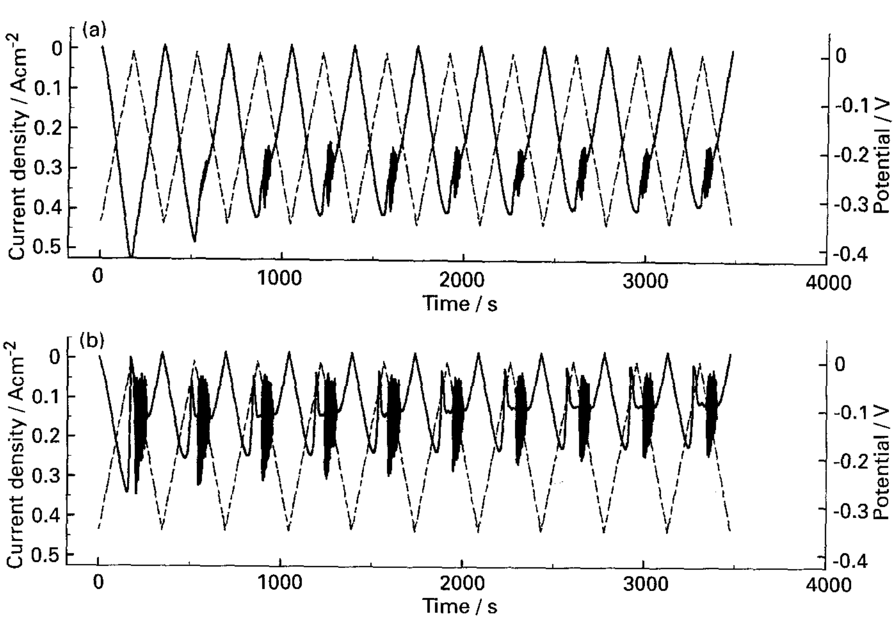

Fig. 6. The electrochemical spectra of ten continuous cycles (cycle 1–cycle 10) recorded for a rectangular pure copper anode, surface area $0.81\,\mathrm{cm}^2$, configured: (a) vertically, (b) horizontally.

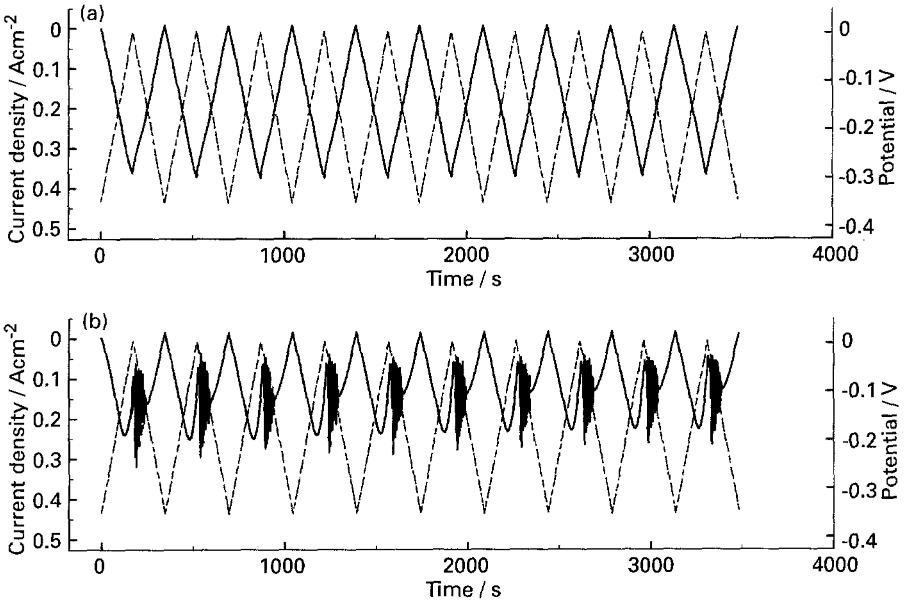

Fig. 7. The electrochemical spectra of ten continuous cycles (cycle 1–cycle 10) recorded for a circular pure copper anode, surface area 2.27 cm^2, configured: (a) vertically, (b) horizontally.

around the edges. Careful examination of the surface of the round anode after it was removed from the cell showed that its edges were preferentially dissolved. The smaller rectangular anode with dense, adhering slimes produced a distinct second peak, during the forward scan, at a potential of −0.048 V. The large circular anode with uneven slime coverage produced a much smaller second peak, during the reverse scan, at a potential of −0.009 V.

To examine the effect of copper concentration on the electrochemical behaviour of pure copper, one experiment was carried out in a solution containing only H_2SO_4. The results of this experiment are presented in Fig. 9. After the large circular, horizontally configured anode was examined in a solution containing 40 g dm^{-3} Cu^{2+} + 160 g dm^{-3} H_2SO_4 (Fig. 9(a)), the anode was removed and reground. The same anode was then reexamined in a solution containing only 160 g dm^{-3} H_2SO_4. During the course of this experiment, the sulphuric acid solution became light blue indicating the presence of copper ions from the electrochemical reaction of the copper anode as well as from the dissolution of the copper powder formed on the anode surface. The electrochemical spectrum (Fig. 9(b)) does not show the second peak; there is just a small shoulder in the potential range where the reverse scan oscillations occurred in the $CuSO_4 + H_2SO_4$ medium, Fig. 9(a). The second peak did not form because the diffusion of copper ions into solution was not inhibited by high concentrations of copper ions in the anode vicinity. Although there was copper powder on the surface, no second peak formed as copper sulphate did not precipitate. There are slight oscillations and a shoulder is noticed (Fig. 9(b)) in the potential region where oscillations occurred in the $CuSO_4 +$ H_2SO_4 electrolyte; this is due probably to copper powder desorption. Another reaction which probably occurred in this system was the dissolution of the copper powder in the acid solution. This process occurs more rapidly in the absence of high concentrations of copper ions.

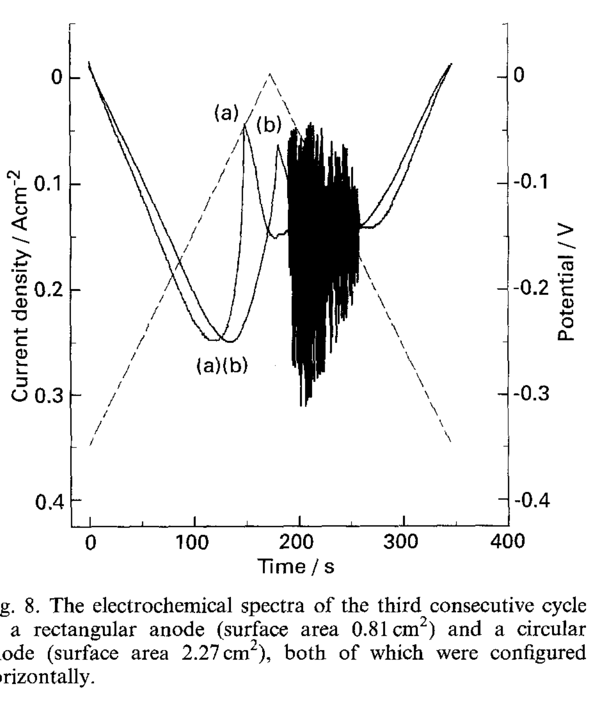

Fig. 8. The electrochemical spectra of the third consecutive cycle of a rectangular anode (surface area 0.81 cm^2) and a circular anode (surface area 2.27 cm^2), both of which were configured horizontally.

Although pure copper does not readily passivate under typical electrorefining conditions, a slimes layer consisting of copper powder and copper sulphate forms on the anode surface. Copper powder formation is thought to occur according to Reactions 3 and 4:

$$Cu_{(anode)} \longrightarrow Cu^{+} + e^{-} \quad (3)$$

$$2Cu^{+} \longrightarrow Cu^{0} + Cu^{2+} \quad (4)$$

$$Cu^{2+} + SO_4^{2-} + 5H_2O \longrightarrow CuSO_4.5H_2O \downarrow \quad (5)$$

As excess Cu^{2+} builds up near the anode surface, $CuSO_4.5H_2O$ precipitates forming a nonconducting layer on the anode surface, Reaction 5. Although some authors [2–5] mention Cu_2O as a possible passivation species, Cu_2O was never detected on the surfaces of the pure copper anodes in the course of

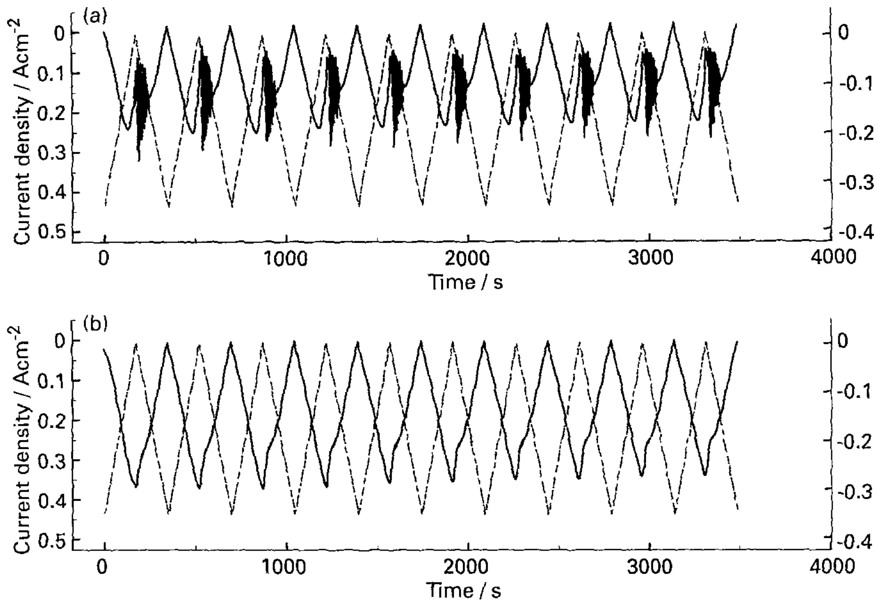

Fig. 9. The electrochemical spectra of ten continuous cycles (cycle 1–cycle 10) recorded for a circular pure copper anode, configured horizontally (surface area 2.27 cm^2), in solutions: (a) $CuSO_4 + H_2SO_4$, (b) H_2SO_4.

this research. By contrast $CuSO_4.5H_2O$ was detected after the examined anodes were carefully washed to remove any adhering electrolyte.

Generally, pure copper anodes do not show a second peak unless unusual circumstances prevail. Such unusual circumstances include an anode with a very small surface area or an anode configured horizontally. With a small-area anode, the reaction products become trapped between the edges of the anode and the acrylic mount. In the case of the copper wire, a narrow 'tunnel' is actually created in the mount as the copper dissolves; this traps copper slimes and impedes diffusion to and from the anode. This suggests that the second peak is formed only if the slimes adhere to the surface of the anode. As shown in Fig. 8, a more compact slimes layer inhibits the diffusion of copper ions and induces the second peak to form sooner.

Oscillations are a phenomenon which appears when the slimes layer formed on the surface ruptures and restores itself. The oscillations depend on the thickness, porosity and adhesion of the slimes layer to the surface. For an average size vertically configured anode ($\sim$ 1 cm^2), the slimes layer spalls from the anode surface and copper dissolution continues. The observed oscillations stop before the slimes fall from the anode surface. Large anodes ($>$ 2 cm^2) do not exhibit any oscillations or spalling.

Figure 10 shows a typical electrochemical spectrum of one cycle obtained for a horizontally configured pure copper anode. The spectrum consists of seven distinct regions, which are marked (a) to (g). These are:

(a) Copper dissolution, where the current is proportional to the voltage. Reactions 3 and 4 take place, copper powder forms on the surface, and copper ions diffuse from the anode surface.

(b) Formation of the current maximum (first peak). The point is reached where the concentration of copper ions in the vicinity of the anode reaches saturation and $CuSO_4.5H_2O$ starts to crystallize on the surface of the anode (Reaction 5). As the non-conductive copper sulphate precipitates, the current decreases. When the layer of slime (copper powder + copper sulphate) is more compact, diffusion of copper ions from the anode becomes more difficult.

(c) A current minimum (second peak) starts to develop as copper sulphate accumulates on the surface of the anode, progressively inhibiting the diffusion of copper ions into the solution; the current decreases until it reaches a minimum.

(d) Current increases as the potential is reached where copper powder precipitated on the surface of the anode starts to spall, there is an increased diffusion of copper ions into the bulk solution.

(e) Passivation; the potential changes but the current remains constant.

(f) Oscillations. Copper powder and copper sulphate spall from the surface.

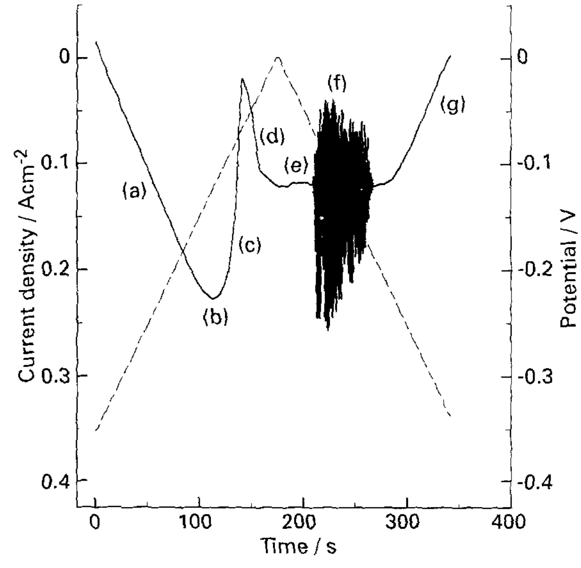

Fig. 10. The typical electrochemical spectrum of a horizontally configured pure copper anode during one CV cycle.

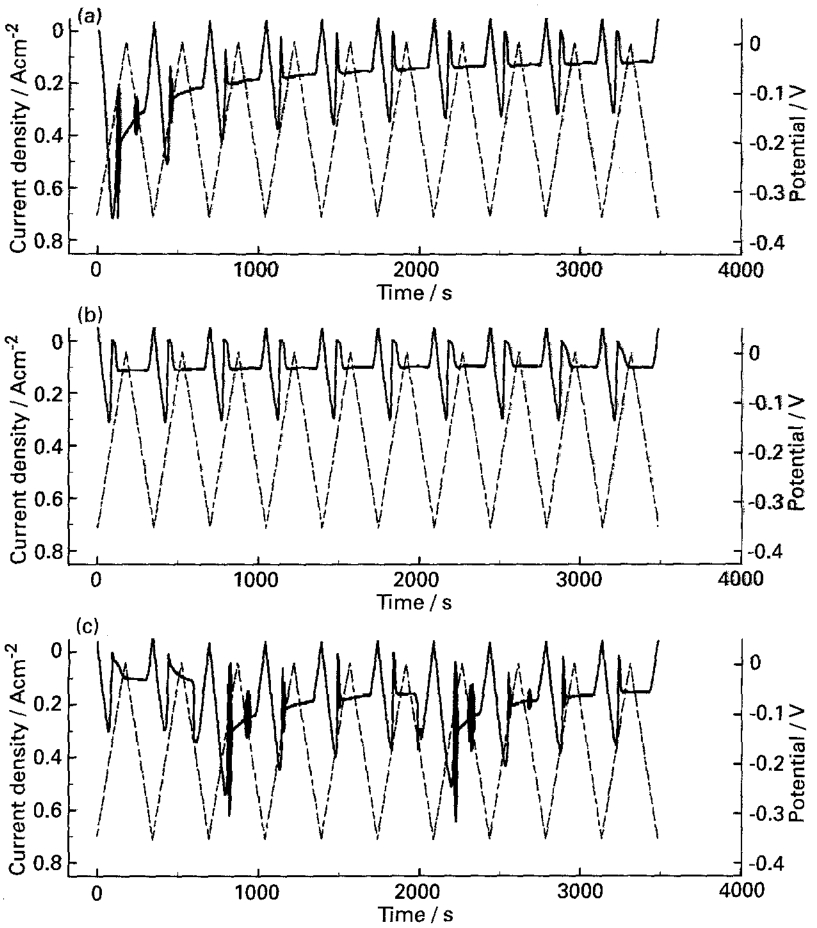

Fig. 11. The electrochemical behaviour of a circular pure copper anode (surface area $0.05\,\mathrm{cm}^2$), configured vertically, during 30 continuous cycles: (a) cycle 1–cycle 10, (b) cycle 11–cycle 20, and (c) cycle 21–cycle 30.

(g) Copper dissolution continues. The current is proportional to the voltage until the rest potential is reached.

Figure 11 presents the electrochemical behaviour of a pure copper, vertically mounted, anode with the smallest surface area ($0.05\,\mathrm{cm}^2$) during 30 continuous CV cycles. Because the slimes become trapped in the 'tunnel' formed in the acrylic mount by the dissolving copper, the second peak forms very quickly (third cycle) and the process persists through the next 19 cycles. Cycle 22 releases a large flake of accumulated slimes. Accordingly, the current density increases during the 23rd cycle and slimes formation starts again. The heavy oscillations indicate that the slimes layer is still breaking and reforming periodically. During cycle 26, the anode again releases a chunk of the slimes, and consequently the current density increases during the next cycle. Because the slimes buildup continues (in the

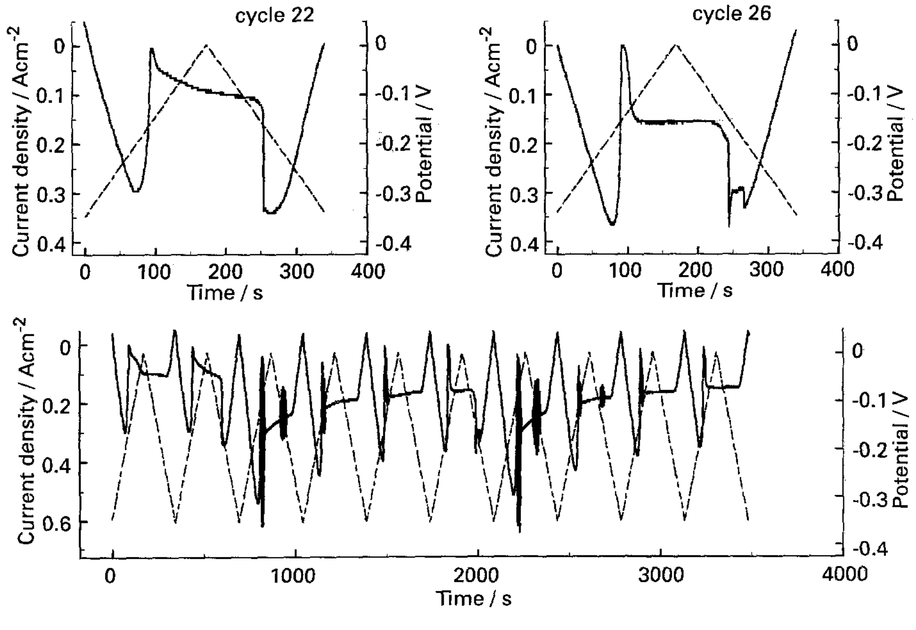

Fig. 12. The electrochemical spectra of ten continuous cycles (cycle 21–cycle 30) recorded for a vertically configured circular pure copper anode (surface area $0.05\,\mathrm{cm}^2$) with cycles 22 and 26 zoomed-out.

'tunnel' left by the dissolution of the copper), the second peak forms and the process continues. The electrochemical spectra, concentrating on cycles 21–30 with cycles 22 and 26 zoomed-out, are presented in Fig. 12. The electrochemical behaviour of this anode clearly suggests that anode slimes breakage influences the behaviour shown in region (d) (Fig. 10). The big chunks of slimes released from the electrode during cycles 22 and 26 are clearly not a consequence of heavy oscillations in the preceding cycles.

3.3. *Passivation*

Studies were done to determine if the tendency of the copper anode to passivate could be correlated to the electrochemical observations described in the previous section of this paper. The emphasis was on the hypothesis that the ease with which a particular copper anode forms the second peak is an indication of its tendency to passivate during electrorefining. Accordingly passivation times were determined for a variety of different pure copper anodes under the conditions given in Section 2.

Vertically configured, average size ($< 1\,\mathrm{cm}^2$) rectangular anodes, which display oscillations followed by spalling on the reverse scan of the cyclic voltammetry cycle, initially passivate after approximately 8 h of electrolysis. Permanent passivation takes place after 15 h. The large ($> 2\,\mathrm{cm}^2$), vertically configured anode (no oscillations and no flaking on the cyclic voltammogram) does not passivate during approximately 24 h of electrolysis, although there is an indication that it is beginning to passivate after 22 h. The horizontally configured copper anode exhibits a well formed second peak during the first cycle of cyclic voltammetry and then, as cycling continues, a growing second peak and diminishing oscillations. This anode passivates in approximately 12–15 min. These observations suggest a direct correlation between second peak formation and passivation time.

There was an interesting passivation response with the smaller circular anodes. The smallest anode shows a well defined second peak very early in the cyclic voltammetry experiments. At the same time, heavy flaking of the slimes trapped in the narrow 'tunnel' of acrylic was observed (Figs 11 and 12). This anode passivated initially after 4 h, at which time a thick flake of slime fell from the surface. The anode then reactivated and the copper dissolution process continued. Another circular electrode ($0.71\,\mathrm{cm}^2$) also showed sudden flaking during the cyclic volammetry process, although it never developed a second peak. This anode behaved in a similar way during the passivation study. Basically it never passivated permanently during 28 h at constant current, but displayed bursts of oscillations followed by brief passivation (2–4 min) and immediate depassivation.

These studies also indicated that anodes of circular shape do not passivate as quickly as rectangular anodes having the same surface area.

4. Conclusions

A correlation between the electrochemical behaviour of pure copper anodes subjected to cyclic voltammetry with their tendency to passivate was established. Reproducible electrochemical characteristics for pure copper anodes of different shapes, sizes and configurations were acquired, catalogued and extensively examined. The results confirmed that the formation of the second peak was associated with the anode slimes which remained attached to the anode surface. The causes of the second peak formation were rationalized but need further investigation to establish if copper powder is the only entity responsible for trapping copper sulphate on the surface and to determine how impurities contained in copper anodes influence the production and retention of the slimes on the anode surface.

Passivation time measurements confirmed a strong correlation between the above electrochemical behaviour of the anodes with their tendency to passivate.

The electrochemical behaviour was affected by the size and shape of the anode which influenced the dissolution pattern and hence the tendency of the anode to retain the slimes layer. It was also discovered that circular anodes do not passivate as quickly as rectangular anodes of the same size, at least for the range of sizes studied in this work. Thus, future work should be done using large anode specimens ($> 2\,\mathrm{cm}^2$) so that the observed effects are more relevant to industrial copper electrorefining.

The fully computerized data acquisition system proved superior to the formerly used setup utilizing an X–Y recorder. It was possible to see oscillations which were never suspected previously because they were masked by the filtering devices built into the X–Y recorder. Current density values were obtained by the computerized system making it possible to compare directly the electrochemical characteristics of the various copper anodes. Experimental data were presented in the form of an electrochemical spectrum rather than the conventional cyclic voltammogram, and this format enhanced the clarity and readability of the results.

Acknowledgements

Thanks are due to J. E. Dutrizac, CANMET, for many helpful discussions and to the Noranda Technology Centre for preparing some of the anode material.

References

[1] S. Abe, B. W. Burrow and V. A. Ettel, *Can. Metall. Q.* **19** (1980) 289.

[2] S. Abe and S. Goto, *J. Mining Metall. Institute of Japan* **97** (1121) (1981) 549.

[3] S. Jin and E. Ghali, 'XAES Study on Passivation of Copper Anodes', *in* 'Emerging Separation Technologies for Metals and Fuels', (edited by V. I. Lakshmanan, R. G. Bautista and P. Somasundaran), Minerals,

Metals & Materials Society, Warrendale, PA (1993) pp. 169–183.

[4] T. T. Chen and J. E. Dutrizac, 'A Mineralogical Study of Anode Passivation in Copper Electrorefining', *in* 'Hydrometallurgy and Electrometallurgy of Copper', (edited by W. C. Cooper, D. J. Kemp, G. E. Lagos and K. G. Tan), Pergamon Press, New York (1991) pp. 369–389.

[5] S. Garneau, E. Ghali, M. Girgis and R. G. Barradas, *Metall. Trans. B* **22** (1991) 623.

[6] S. Abe and S. Goto, *J. Mining Metall. Institute of Japan* **97** (1123) (1981) 951.