Oxidation of Copper Sulfides in Aqueous Ammonia. II* Electrochemical Aspects

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Abstract

The oxidation of covellite, CuS, to copper(II) and sulfur or sulfate ions in aqueous ammonia is slowed by the formation of an equilibrium thickness of a copper polysulfide Cu_yS ($y < 1$). The polysulfide is thermally and electrochemically unstable when in contact with CuS. A surface coating of sulfur, although formed, is not responsible for the semi-passivation of CuS during oxidation. Cyclic voltammetry, controlled potential electrolysis, linear sweep voltammetry, and various amperiometric and coulometric experiments with electrodes of pressed CuS, of carbon paste containing CuS and or a carbon ring with a CuS disc have been used to study the formation or decomposition of Cu_yS and its effect on rates of oxidation or CuS in aqueous ammonia. CuS–carbon paste electrodes offer some advantages over pressed discs of CuS for such studies.

Inroduction

The oxidation of copper sulfides by oxygen in aqueous ammonia is of interest to hydrometallurgists.[1-3] Under certain conditions, high proportions of sulfur, rather than the thermodynamically expected sulfate ions, are formed.[4] The oxidation of CuS at first follows parabolic kinetics then the kinetics of a chemically controlled shrinking sphere. Thus the oxidation slows dramatically after an initial fast dissolution of copper and elevated temperatures are required if practicable reaction rates are to be achieved.[5] The production of sulfur[4] and the slowing in rate of oxidation[5]
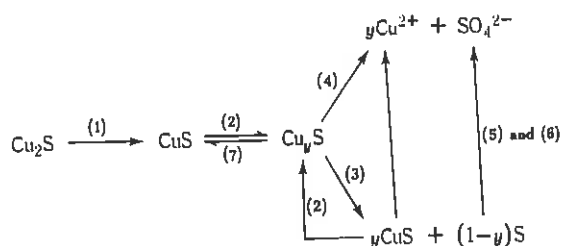
Scheme 1

* Part I, *Aust. J. Chem.*, 1979, **32**, 961.

[1] Forward, F. A., and MacKiw, V. N., *J. Met.*, 1955, **7**, 457.
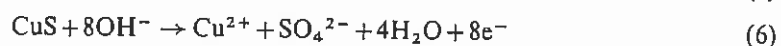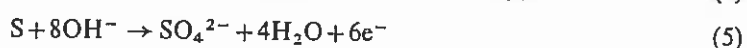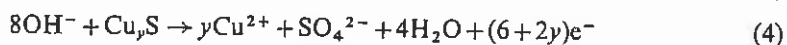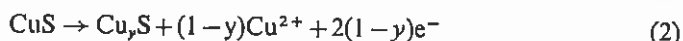[2] Kuhn, M. C., Arbiter, N., and Kling, H., *CIM Bull.*, 1974, 62.
[3] Biswas, A. K., and Davenport, W. G., 'Extractive Metallurgy of Copper' (Pergamon Press: Oxford 1976).
[4] Filmer, A. O., Parker, A. J., and Wadley, L. G. B., *Aust. J. Chem.*, 1978, **32**, 961.
[5] Filmer, A. O., Ph.D. Thesis, Murdoch University, Murdoch, W.A., 1978.

can be explained by the formation and decomposition of an equilibrium film of a copper polysulfide Cu_yS ($y < 1$), which covers CuS during oxidative leaching. Thus the oxidation of Cu_2S or CuS is thought to follow the scheme shown in Scheme 1. This scheme was deduced from factors influencing the rate of oxidation,[5] and the proportions of sulfur from oxidation[4] but without the electrochemical observations reported here, the scheme, and especially the role of the copper polysulfide, Cu_yS, is only speculative.

In Scheme 1, Cu_2S is rapidly oxidized to CuS [equation (1)] in a reaction controlled by diffusion of Cu^+ through a thickening layer of Cu_xS ($2 > x > 1$). The CuS surface is then oxidized to Cu_yS ($y < 1$) [equation (2)] and the polysulfide Cu_yS either decomposes thermally to CuS and sulfur [equation (3)][6] or is oxidized to oxysulfur anions and eventually to SO_4^{2-} [equation (4)]. The CuS formed on the surface by decomposition of Cu_yS [reaction (3)] undergoes further reactions (2) and (6). Sulfur from reaction (3) is slowly oxidized to sulfate ions [equation (5)] in a reaction which proceeds through thiosulfate ions:[7]

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^- \tag{1}$$

$$CuS \rightarrow Cu_yS + (1-y)Cu^{2+} + 2(1-y)e^- \tag{2}$$

$$Cu_yS \rightarrow yCuS + (1-y)S \tag{3}$$

$$8OH^- + Cu_yS \rightarrow yCu^{2+} + SO_4^{2-} + 4H_2O + (6+2y)e^- \tag{4}$$

$$S + 8OH^- \rightarrow SO_4^{2-} + 4H_2O + 6e^- \tag{5}$$

$$CuS + 8OH^- \rightarrow Cu^{2+} + SO_4^{2-} + 4H_2O + 8e^- \tag{6}$$

A developing film of Cu_yS on CuS slows the conversion of CuS into more Cu_yS in two ways. Firstly, diffusion of Cu^{+} [8,9] through Cu_yS is slower than through CuS and, secondly, electron transfer to some oxidants at cathodic sites is slower on Cu_yS than on CuS.[10] This slowing of the rate of oxidation regulates the formation of Cu_yS because the slowing is greater the more closely y in Cu_yS approaches zero, and the thicker the layer of Cu_yS. In conjunction with this self-stifling formation of Cu_yS there are three reactions (3), (4) and (7) which remove Cu_yS and thus allow oxidation to slowly proceed, with an equilibrium thickness and composition of Cu_yS. In reaction (7), the polysulfide Cu_yS has a more anodic potential than CuS[11] and oxidizes CuS, as Cu^+ diffuses from CuS to Cu_yS, and this, like reactions (3) and (4), tends to remove Cu_yS and maintain an equilibrium thickness and composition of Cu_yS during oxidation:

$$Cu_yS + nCuS \rightarrow nCu_{y'}S \qquad (y' \gg y, n \gg 1) \tag{7}$$
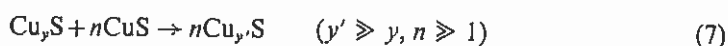
It is difficult to examine copper-deficient polysulfides like Cu_yS by optical, chemical or spectroscopic methods because they are present only as a thin film, and frequently revert to CuS and S [equation (3)] or to $Cu_{y'}S$ ($y' \approx 1$) [equation (7)] before they can

[6] Mellor, J. W., 'Comprehensive Treatise on Inorganic and Theoretical Chemistry' (Longmans Green: London 1956).

[7] Shieh, M. C., Otsubo, H., and Okabe, T., *Bull. Chem. Soc. Jpn*, 1965, **38**, 1596.

[8] Brennet, P., Jafferali, S., Vanseveren, J. M., Vereecken, J., and Winand, R., *Metall. Trans.*, 1974, **5**, 127.

[9] Jost, W., 'Diffusion in Solids, Liquids, Gases' (Academic Press: New York 1960).

[10] Parker, A. J., Paul, R., and Nicol, M., unpublished data.

[11] Muir, D. M., Parker, A. J., and Giles, D. E., *Hydrometallurgy*, 1976, **2**, 127.

be examined.[6,12] However, electrochemical methods[13] prove most effective for studying Cu_yS and, as shown in this paper, firmly establish the reaction scheme of Scheme 1.

Experimental

CuS and Cu_2S were prepared from copper and sulfur as described previously.[4]

Copper sulfide discs were prepared from the powder ($-63\ \mu m$) as smooth pellets under a pressure of 4×10^5 kPa at $25°$. They were fitted into a sample holder to expose a geometric area of $0.5\ cm^2$. Electrical contact between the pellet and potentiostat was made by using mercury or a silver–epoxy-resin. CuS–carbon paste electrodes were 10% by weight $-63\ \mu m$ CuS in metrohm EA 267C carbon paste. The geometric area was $0.5\ cm^2$. Fresh surfaces were exposed by scraping a millimetre of paste away. Solutions were deoxygenated with nitrogen and cells were kept at constant temperature. All electrodes were connected through a P.A.R. 172A drop timer to the P.A.R. 170 electrochemistry system. Potentials were compensated for iR drop. The working electrode was platinum and the reference electrode was mercury–mercurous sulfate. Copper(II) in solution was estimated by differential pulse polarography.

The surface area of the electrodes were equated with the geometric area, assuming a surface roughness factor of unity, since the reactive nature of the carbon paste precluded the use of conventional electrochemical methods of estimating the active electrode area.

Table 1. Reduction potentials and peak potentials (s.h.e.) in the cyclic voltammetry of copper sulfides, copper and copper salt solutions in aqueous ammonia at $25°$

Solution contains 7 M ammonia and 1·5 M ammonium sulfate at pH 10·5

Process	Reaction	$E^{0\,A}$	$E_p(ox)$	$E_p(red)$
A1	$Cu_2S \rightarrow CuS + Cu(NH_3)_4{}^{2+} + 2e^-$	0·03	0·1[B,C,D]	—
	$CuS \rightarrow Cu(NH_3)_4{}^{2+} + S + 2e^-$	0·09	—	—
A2	$CuS \rightarrow Cu_yS + (1-y)Cu(NH_3)_4{}^{2+} + 2(1-y)e^-$	—	0·2[B,C]	—
A3	$CuS + 3OH^- \rightarrow Cu(NH_3)_4{}^{2+} + \frac{1}{2}S_2O_3{}^{2-} + \frac{3}{2}H_2O + 4e^-$	−0·18	1·0[B,E]	—
A4	$CuS + 8OH^- \rightarrow Cu(NH_3)_4{}^{2+} + SO_4{}^{2-} + 4H_2O + 8e^-$	−0·32	1·0[B,E]	—
C3	$yCuS + (1-y)S^{2-} \rightarrow Cu_yS + 2(1-y)e^-$	—	—	−0·12[D,C,F]
C4	$2NH_3 + Cu(NH_3)_2{}^+ \rightarrow Cu(NH_3)_4{}^{2+} + e^-$	−0·04	−0·11[E,G]	−0·20[E,G]
C2	$4NH_3 + Cu^0 \rightarrow Cu(NH_3)_4{}^{2+} + 2e^-$	−0·13	—	—
C1	$2NH_3 + Cu^0 \rightarrow Cu(NH_3)_2{}^+ + e^-$	−0·23	−0·35[G,H]	−0·55[G,H,I]

A Thermodynamic reduction potentials in this solution are calculated from $\Delta G°$ in water with all soluble species at 1 M activity adjusted by the stability constants of $Cu(NH_3)_4{}^{2+}$ and $Cu(NH_3)_2{}^+$ and the concentration of OH^- at pH 10·5 in 7 M ammonia.

B Potentials at which current maxima assigned to these processes are observed during scans at 5 mV s^{-1} of a 10% Cu_2S- or CuS–carbon paste electrode in still solutions.

C These peaks were not changed by stirring the solutions.

D Only observed with Cu_2S containing electrodes.

E These peaks were diminished significantly by stirring the solutions.

F Only observed if a CuS electrode is first scanned from 0·05 V to 0·3 V (see text).

G Observed during cyclic voltammetry at 5 mV s^{-1} of 10^{-3} M CuSO$_4$ in the solvent at a carbon paste electrode. Note copper(II) and copper(I) species are 10^{-3} M for E_p, against 1 M for the E^0 values.

H These peaks were enhanced by stirring the solutions.

I Tentative assignment to poorly defined peaks.

Results and Discussion

All potentials are presented as volts against s.h.e. As shown by the E^0 values in Table 1 for reactions (6) and (8), sulfate ion rather than sulfur is the expected product

[12] King, J. A., Ph.D. Thesis, University of London, 1966.
[13] Koch, D. F. A., 'Electrochemistry of Sulfide Minerals' in 'Modern Aspects of Electrochemistry' (Eds J. O'M. Bockris and B. E. Conway) (Plenum Press: New York 1975).

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based on thermodynamic considerations,[14] when CuS is oxidized in 7 M aqueous ammonia at pH 10·5. Despite the thermodynamic predictions of Table 1, over 60% of sulfur is produced as a kinetic product when CuS is oxidized at 30°

$$CuS \xrightarrow[H_2O]{NH_3} Cu(NH_3)_4{}^{2+} + S + 2e^- \tag{8}$$
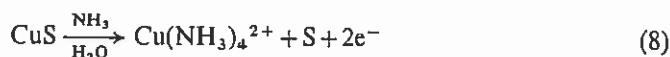
with oxygen in 7 M ammonia at pH 10·5.[4]

Formation of S and $SO_4{}^{2-}$

Sulfate formation [equation (6)] is easily distinguished by electrochemical techniques from formation of sulfur [equation (8)] or of Cu_yS [equation (2)] because the ratio (n) of the number of electrons in sulfate formation per Cu^{2+} produced is 8. The ratio (n) is 2 if S or Cu_yS is formed. If thiosulfate is formed [equation (9)]:

$$2CuS + 6OH^- \rightarrow S_2O_3{}^{2-} + 2Cu^{2+} + 3H_2O + 8e^- \tag{9}$$
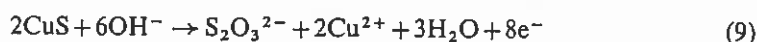
then four electrons are produced per Cu^{2+}. Chemical analysis of the moles of Cu^{2+} oxidized by a known quantity of coulombs from a CuS disc electrode at a fixed potential, gives n, and this indicates the proportion of sulfur, sulfate and thiosulfate produced during oxidation. Measurement of the currents, at a rotating CuS disc electrode being oxidized at a mixed anodic potential and at a surrounding glassy carbon ring electrode held at $-0·45$ V, gives n. The carbon ring reduces Cu^{2+} from the disc to Cu^0. Allowance for the collection efficiency of the ring must be made.

Table 2.   Oxidation of CuS disc and CuS–carbon paste electrodes in aqueous ammonia at 25°. Effect of disc potential (s.h.e.) on the number of electrons per copper(II) ion
Solution is 4 M NH_3 plus 1·5 M $(NH_4)_2SO_4$, at pH 10·3

Disc E (V)	Ring–disc n^A	D.p.p. n^B	Ring–C paste n^C	Disc E (V)	Ring–disc n^A	D.p.p. n^B	Ring–C paste n^C
1·25	5·1	5·1	5·7	0·55	2·3	2·2	—
0·95	4·8	5·1	—	0·35	2·3	—	—
0·75	2·6	2·5	—	0·15	2·0	—	2·0

A n is the number of electrons per Cu^{2+} produced at a CuS disc or a CuS–carbon paste electrode as determined by the ring–disc method. A CuS disc electrode surrounded by a glassy carbon ring held at $-0·45$ V was electrolysed at the potentials E shown, while rotated at 1000 r.p.m. The collection efficiency of the ring at $-0·45$ V for $Cu^{2+} + e \rightarrow Cu^0$ (Table 1) was estimated by assuming that n was 5·1 at $E = 1·25$ V. This value of n was obtained as described in footnote B.
B n is the number of electrons per Cu^{2+} produced at the CuS disc in a still solution as estimated by differential pulse polarography (d.p.p.) at a dropping mercury electrode of the copper(II) ions in solution after electrolysis at the potential E shown for 10–30 min with a known current (i.e. $it \times 96500 \times 1/Cu^{2+} = n$).
C A CuS–carbon paste electrode surrounded by a glassy carbon ring at $-0·95$ V ($Cu^{2+} \rightarrow Cu^0$) was electrolysed as in footnote A. The collection efficiency was estimated by assuming that n was 2·0 at $E = 0·15$ V.

Table 2 gives values of n measured in both ways, when a stationary and a rotating CuS disc and a CuS–carbon paste electrode with and without a carbon ring electrode was oxidized at various fixed potentials in 4 M ammonia containing 1·5 M ammonium sulfate at pH 10·2 at 25°. The number of electrons required to produce one Cu^{2+}

[14] Pourbaix, M., 'Atlas D'Équilibres Electrochimiques' (Gauthier, Villars & Co.: Paris 1963).

ion is $5 \cdot 1$ when the CuS disc is between $0 \cdot 95$ and $1 \cdot 25$ V. This suggests that the sulfur-containing products are not only sulfate ($n = 8$) at these very high potentials, but also are thiosulfate ($n = 4$) [equation (9)], Cu_yS ($n = 2$) [equation (2)] or sulfur ($n = 2$) [equation (8)]. At lower disc potentials, n is only slightly above 2 which is consistent with oxidation of CuS to Cu_yS [equation (2)] or sulfur [equation (8)]. There is very little oxidation of CuS or Cu_yS to sulfate [equation (4)] or thiosulfate ions at potentials below $0 \cdot 55$ V. It is thought that sulfate formation by equation (4) from Cu_yS only becomes competitive with the thermal decomposition of Cu_yS [equation (3)] to sulfur as the potential of the CuS disc becomes higher than about $0 \cdot 60$ V.

We have measured a mixed potential of $0 \cdot 35$ V, which slowly changes to $0 \cdot 03$ V, when a fresh rotating CuS disc is immersed in 7 M ammonia at 25° and pH $10 \cdot 5$ under oxygen at atmospheric pressure for several hours. From the n values in Table 2, we would expect a very high proportion of sulfur from an oxidation of CuS at $0 \cdot 03$–$0 \cdot 35$ V, and this has been found for oxidation of CuS with oxygen in this solvent.[4]

Anodic Processes

Fig. 1 shows a linear sweep voltammogram, i.e. the current in mA cm^{-2} which flows when stationary electrodes of 10% by weight Cu_2S, CuS or sulfur powders in a silicone paste with carbon are oxidized by slowly scanning to higher potentials (anodically) at 5 mV s^{-1} in stirred 7 M aqueous ammonia containing $1 \cdot 5$ M ammonium sulfate at pH $10 \cdot 5$ and 25°. Much less clearly defined, but detectable maxima at similar peak potentials E_p for current maxima were observed when discs of compressed CuS or Cu_2S powders replaced the carbon paste electrodes. Table 1 shows potentials for the current maxima, together with processes assigned to these maxima and standard potentials for the processes in this solvent.
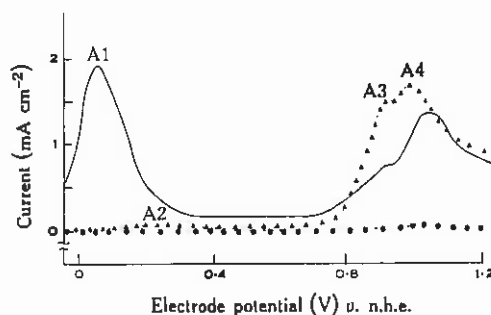

Fig. 1. Scan of Cu_2S, CuS, S electrodes as 10% by weight powders in carbon paste at 25° in 7 M ammonia and $1 \cdot 5$ M $(NH_4)_2SO_4$ at pH $10 \cdot 5$. Scan speed 5 mV s^{-1} in unstirred solution. Current peaks $i_p(A1)$–$i_p(A4)$ are as assigned in Table 1. ▲ CuS; ● S.

For the Cu_2S–carbon paste electrode, three current maxima A1, A3 and A4 (Table 1) are observed. For CuS–carbon paste, no A1 is observed but a small peak A2 plus large A3 and A4 current maxima appear. The sulfur–carbon paste electrode generates only a very small current and only above $0 \cdot 8$ V, i.e. electrochemical oxidation of sulfur mixed with carbon paste is very slow under these conditions.

The large current, peaking at $E_p(A1)$, which is observed during oxidation of Cu_2S, is not observed during oxidation of CuS or of sulfur and is assigned to oxidation of Cu_2S to CuS [equation (1)];[15] $E_p(A1)$ is only 70 mV higher than the standard e.m.f. for oxidation of Cu_2S to CuS [equation (1)] in 7 M ammonia at pH $10 \cdot 5$.

[15] Hepel, M., and Hepel, T., *J. Electroanal. Chem.*, 1977, **81**, 161.

Neither the maximum current flowing $i_p(A1)$ at $E_p(A1)$ nor $E_p(A1)$ in the still solution was changed when the solution was vigorously stirred. The polarization causing the current maximum is thus unlikely to be a solution diffusion involving copper ions, but is consistent with solid state diffusion-controlled formation of a solid species Cu_xS ($2 > x > 1$) which slows diffusion of Cu^+ to the solid–liquid interface.[5] The large current $i_p(A1)$ suggests that such diffusion is quite fast.

The value of $E_p(A2)$ is $0\cdot2$ V which is only a little higher than the standard e.m.f. ($0\cdot09$ V) for oxidation of CuS to sulfur in 7 M ammonia [equation (8)]. However, for reasons to be discussed below, we do not believe that process A2 is oxidation of CuS to sulfur but rather is oxidation of CuS to Cu_yS [equation (2)].

The current $i_p(A1)$ for oxidation of Cu_2S to CuS is nearly 2 mA cm^{-2} as a carbon paste. This is 200 times greater than $i_p(A2)$ for the oxidation of CuS to Cu_yS [equation (2)]. Since the Cu_2S and CuS carbon pastes are of the same weight percentage composition and the CuS used is of greater surface area than Cu_2S,[5] the much greater $i_p(A1)$ against $i_p(A2)$ shows that, electrochemically speaking, oxidation of Cu_2S to CuS is much faster than oxidation of CuS to Cu_yS at mixed potentials in the region of $0\cdot1$–$0\cdot3$ V. The rate difference is 150 when Cu_2S and CuS are chemically oxidized with oxygen.[5] The slower reaction of CuS is because Cu_yS ($y < 1$) is more effective at partially passivating CuS than is Cu_xS ($2 > x > 1$) at partially passivating Cu_2S.[5]

$E_p(A2)$ was 300 mV anodic of E_p for oxidation of $Cu(NH_3)_2{}^+$ to $Cu(NH_3)_4{}^{2+}$ on carbon paste (Table 1) so A2 is not that solution process. Like process A1, the peak current, $i_p(A2)$, and peak potential $E_p(A2)$ was unchanged by vigorously stirring the solutions. Thus polarization by a film of solid Cu_yS on CuS which restricts diffusion of Cu^+ and only allows a chemically controlled[5] oxidation is more likely as the source of $i_p(A2)$ than is a solution polarization involving copper ions. As noted in Table 2, oxidation of CuS at $0\cdot1$–$0\cdot35$ V was a two-electron process per Cu^{2+} which agrees with oxidation to Cu_yS or to sulfur, rather than to $SO_4{}^{2-}$.

Very similar processes A3 and A4 appear at E_p values near 1 V whether oxidation is of CuS or of Cu_2S–carbon paste electrodes in 7 M aqueous ammonia at pH $10\cdot5$. Values of $E_p(A3)$ and $E_p(A4)$ are in a region where n is $5\cdot1$ (Table 2). Such a value of n is consistent with at least 50% formation of sulfate ions [equation (4)] and 50% Cu_yS [equation (2)] or with 33% sulfate formation and 66% thiosulfate formation. Further studies are needed before A3 and A4 are characterized more definitively. The peak currents for A3 and A4 increased and $E_p(A3)$, $E_p(A4)$ varied, when the solutions were stirred. This differed from A1 and A2 and suggested that solution polarization is the cause of the current peaks. These thiosulfate–sulfate-forming processes were not studied further, because our aim was to study the effects of formation of Cu_yS at potentials close to the mixed potentials ($0\cdot1$–$0\cdot3$ V), which operate during chemical oxidation of copper sulfides with oxygen in aqueous ammonia. It is noteworthy that $E_p(A3)$ and $E_p(A4)$ show very large overpotentials, being more than $1\cdot2$ V higher than the standard potentials for reactions (6) and (9) in 7 M ammonia at pH $10\cdot5$.

### Electrochemical Characteristics of Cu_yS

Our assignment of $i_p(A2)$ (Fig. 1) to oxidation of CuS or Cu_yS rather than oxidation of CuS to sulfur, oxy anions of sulfur or to oxidation of $Cu(NH_3)_2{}^+$ is justified as follows. As noted in Table 2, $i_p(A2)$ is in a potential region where oxidation of CuS has been shown to involve two electrons per Cu^{2+} ion solubilized, so that electro-

chemical reactions producing sulfur oxy anions ($n = 4$ or 8) are not occurring in this potential region.

A disc of CuS and a CuS–carbon paste electrode were partially passivated when electrolysed at $0 \cdot 3$ V in 7 M ammonia containing $1 \cdot 5$ M $(NH_4)_2SO_4$ at pH $10 \cdot 5$ at 25°. The *same rate* of partial passivation of both types of electrode was observed whether the solutions were *still* or *stirred*. This suggests that the slowing of the oxidation of CuS is a solid-state rather than a solution effect. In the case of the CuS disc (not shown) at first application of $0 \cdot 3$ V a very large anodic current of 500 mA cm^{-2} flowed, but this dropped rapidly to a steady current of 20 mA cm^{-2} over about 1 min.

Of more interest is the behaviour of a 10% CuS–carbon paste electrode during the same electrolysis in the same solvent as shown in Fig. 2. Comparable behaviour was observed for the CuS disc. The initial current is less and it drops more rapidly to a constant value in less time than with the CuS disc. If the CuS–carbon paste electrode, having reached the constant current, was switched to open circuit (i.e. no electrolysis current) for 1 min, then electrolysed again at $0 \cdot 3$ V, a large current flows again, but rapidly decreases to the same constant value. If open circuit is then for 2 min, an even larger current flows. When electrolysis is recommenced after 48 min on open circuit, the electrolysis current at $0 \cdot 3$ V is almost equal to the original current for a fresh CuS–carbon paste electrode. This behaviour is shown in Fig. 2, and as noted, similar effects, with larger overall currents, were observed for the CuS disc.

Fig. 2. Chrono-amperogram of 10% by weight CuS powder in carbon paste electrode electrolysed at $0 \cdot 3$ V in 7 M ammonia, $1 \cdot 5$ M $(NH_4)_2SO_4$ at pH $10 \cdot 5$ at 25°. The same curve is obtained in still or stirred solutions. The electrode was open circuited for the periods shown, before resuming electrolysis.
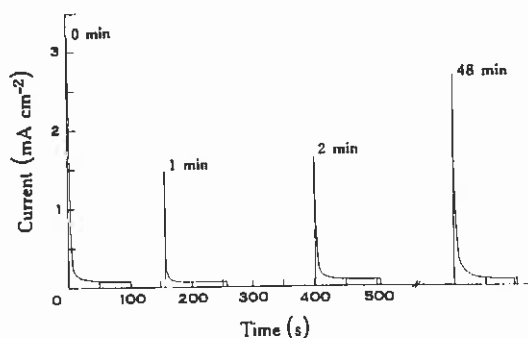
The time-dependent semi-passivation then time-dependent partial reactivation of both types of CuS electrode, when changed from electrolysis to open circuit (Fig. 2), shows that the semi-passivating material cannot be normal sulfur. Sulfur as S_8 is kinetically stable over several hours at 25° in 7 M ammonia at pH $10 \cdot 5$.[4] It is not soluble in solution and it adheres to the electrode. Thus a film of sulfur, even if capable of semi-passivating the CuS, would not allow partial reactivation over a few minutes on open circuit.

Fig. 3 shows a plot of i^{-2} against time. This is equivalent to the parabolic growth law of metal oxidation,[16] with growth limited by ionic diffusion in the solid and current decreasing as film thickness increases. If a semi-passivating film is growing on a fresh surface, then the plot should be linear with an intercept of zero. Such behaviour is shown in the early stages of the reaction (Fig. 3a), but as reaction proceeds, i^{-2} approaches a constant value (Fig. 3b), which is maintained for the bulk of the electro-

[16] Kubaschweki, O., and Hopkins, B. E., 'Oxidation of Metals and Alloys' (Butterworths: London 1953).

lysis. Fig. 3 shows the electrolysis of a CuS–carbon paste electrode in 7 M ammonia containing 1·5 M ammonium sulfate at 0·3 V. The same behaviour was observed in stirred or unstirred solutions. The behaviour is consistent with growth of a film of Cu_yS on CuS until the Cu_yS reaches an equilibrium thickness and composition, where its decomposition matches its rate of formation.
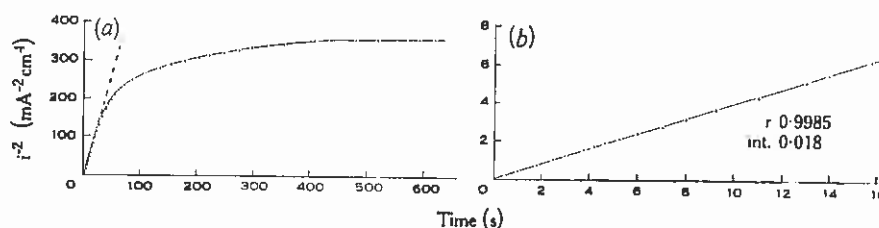

Fig. 3. Plots of i^{-2} against different time bases, (a) and (b), for electrolysis at 0·3 V of a 10% by weight CuS paste electrode in 7 M NH_3, 1·5 M $(NH_4)_2SO_4$ at pH 10·5 at 25°.

This electrochemical behaviour matches our kinetic observations[5] on the rates of oxidation of CuS by oxygen in similar solutions. These followed parabolic kinetics with the increase in copper concentration being proportional to $t^{1/2}$.

Again we would not expect behaviour as in Fig. 3 if passivation was due to a continuously growing film of porous sulfur and liquid diffusion of ions in the pores. A growing film of sulfur is formed, but it is not this which decreases the current, because sulfur would continue to decrease the current as it thickened. One might expect that stirring would at least slightly enhance diffusion through the solution in the porous sulfur. An electrochemically active Cu_yS, capable of decomposing by reactions (3) or (7), and capable of slowing solid state diffusion of copper(I) through it, is more consistent with the passivation–reaction of Fig. 2 and the i^{-2} against t behaviour of Fig. 3.

Table 3. Effect of temperature on the rate of removal of Cu_yS from a CuS–carbon paste electrode

A fresh 10% CuS–carbon paste electrode in a still solution of 4 M NH_3 plus 1·5 M $(NH_4)_2SO_4$ at pH 10·2 was scanned at 5 mV s^{-1} from 0·05 to 0·45 V, to determine $i_p(A2)$, then held at open circuit for the time shown and rescanned from 0·05 to 0·45 V to determine $i_{p'}(A2)$. The peak A2 was observed near 0·2 V (Table 1)

Time[A] (min)	$i_{p'}/i_p(A2)$ 25°	50°	Time[A] (min)	$i_{p'}/i_p(A2)$ 25°	50°
0	0·14	0·22	20	0·35	0·50
5	0·28	0·32	60	0·44	0·59
10	0·25	0·45	120	0·61	0·64

[A] This is the time the electrode was held on open circuit after scanning to 0·45 V and before rescanning.

Table 3 indicates the rate of removal of Cu_yS [equation (3)] or its reduction [equation (7)] on the 10% CuS–carbon paste electrode at 25° and 50° on open circuit. In this experiment, a fresh electrode in a still solution of 4 M ammonia containing 1·5 M

ammonium sulfate at pH 10·2 was swept from its rest potential of from 0·05 V to 0·45 V at 5 mV s^{-1}. The peak current i_p(A2) for process A2 [equation (2)] was noted. Upon reaching 0·45 V the electrode was placed on open circuit (i.e. no electrolysis) for various times t noted in Table 3. It was then swept from 0·05 V to 0·45 V and a now smaller peak current $i_{p'}$(A2) was measured. Values of $i_{p'}/i_p$ are in Table 3, where it is apparent that the semi-passivated current peak $i_{p'}$(A2) was not restored to its first sweep value [i_p(A2)] even after 2 h on open circuit at 50°. Values of $i_{p'}/i_p$ increase the longer the electrode was held on open circuit after oxidation. The rate of increase is faster the higher the temperature. This is consistent with formation and slow removal of a semi-passivating layer of Cu_yS by decompositions (3) and Cu^+ migration during redox reaction (7).

Table 4. Effect of temperature on the initial rate of process A2 [equation (2)] and on the removal of Cu_yS from a CuS–carbon paste electrode over 5 min

A fresh 10% CuS–carbon paste electrode in a still solution of 4 M NH_3 plus 1·5 M $(NH_4)_2SO_4$ at pH 10·2 at temperature T (°C) was scanned at 5 mV s^{-1} from 0·05 to 0·45 V to determine i_p(A2) (μA cm^{-2}), then held on open circuit for 5 min and rescanned from 0·05 to 0·45 to determine $i_{p'}$(A2). The peak A2 was observed near 0·2 V (Table 1) and was unchanged by stirring the solution

T	i_p(A2)	$i_{p'}/i_p$(A2)	T	i_p(A2)	$i_{p'}/i_p$(A2)
0	100	0·21	40	320	0·30
15	150	0·25	45	420	0·35
25	180	0·28	50	500	0·32
35	220	0·28	55	560	0·40

Table 4 indicates the effect of temperature on i_p(A2) and on the rate of reactivation of a Cu_yS-coated CuS–carbon paste electrode, when held on open circuit. The behaviour was the same in still or stirred solutions. The experiment was as for Table 3, at various temperatures, except that after the first sweep to 0·45 V and measurement of i_p(A2), the electrode was held on open circuit for 5 min, then $i_{p'}$(A2) was measured. The initial peak current [i_p(A2)] increased from 100 μm cm^{-2} at 0° to 560 μA cm^{-2} at 55°. The greater current i_p(A2) at higher temperatures is due in part to faster diffusion of Cu^+ through a given thickness and composition of Cu_yS and to faster breakdown [equation (3)] of Cu_yS at the higher temperatures[5,6] during the scan. Ratios of $i_{p'}/i_p$ increase from 0·21 at 0° to 0·40 at 55°, showing again (Table 3) that open circuiting for 5 min only partly reactivates the electrode for process A2 but that the reactivation of Cu_yS coated CuS on open circuit is fastest at the highest temperature. This is in accord with thermal decomposition of Cu_yS [equation (3)] being faster at higher temperatures.[6,11]

As noted above, the concept of a thermally unstable [equation (3)] equilibrium film of semi-passivating but electrochemically and chemically active Cu_yS, capable of being reduced by CuS while on open circuit,[11] explains Table 3 and 4, and Fig. 2 much more satisfactorily than does the concept of semi-passivation by a thickening layer of sulfur.

Further evidence as to the nature of Cu_yS is in Table 5. A potential sweep of CuS–carbon paste was performed as for Table 3, from $0 \cdot 05$ V to $0 \cdot 45$ V but then the CuS–carbon paste electrode was immediately swept back to the rest potential of $0 \cdot 05$ V. Values of $i_p(A2)$ at $0°$, $25°$ and $50°$ (Table 4) were noted. The Cu_yS coated CuS–carbon paste electrode was then switched to open circuit (no electrolysis) for various times, during which, as for Tables 3 and 4, Cu_yS was decomposed in accordance with reactions (3) and (7). The decomposition was to an extent determined by the temperature and the time on open circuit as discussed for Tables 3 and 4. The electrode was then scanned to lower potentials at 5 mV s^{-1} from $0 \cdot 05$ V. A cathodic peak current $i_{p,r}(C3)$ was detected at $-0 \cdot 12$ V. Unlike reduction of Cu^{2+} or Cu^+ on carbon paste (Table 1) the peak current and peak potential were unchanged by stirring the solution.

Table 5. Cyclic voltammetry on a CuS–carbon paste electrode in aqueous ammonia. Detection of Cu_yS by reduction and thermal removal of Cu_yS

In 7 M NH$_3$, $1 \cdot 5$ M (NH$_4$)$_2$SO$_4$ at pH $10 \cdot 5$. The still solution was scanned at 5 mV s^{-1} from $0 \cdot 03$ to $0 \cdot 45$ V to measure $i_p(A2)$, then from $0 \cdot 45$ to $0 \cdot 05$ V. It was then held on open circuit for the time shown, then scanned cathodically to $-0 \cdot 30$ V to measure $i_p(C3)$

Temperature (°C)	$i_p(C3)/i_p(A2)$			
	0 min[A]	2 min[A]	5 min[A]	10 min[A]
0	0·82	0·69	0·67	0·59
25	0·65	0·52	0·47	0·37
50	0·32	0·15	0·10	0·05

[A] Electrode was held at open circuit for this time (see text).

Ratios of $i_{p,r}(C3)/i_p(A2)$ for various times t spent on open circuit after formation of Cu_yS, at various temperatures are in Table 5. The ratio decreases from $0 \cdot 82$ at $0°$, with no time spent on open circuit, but some time spent scanning, to $0 \cdot 05$ at $50°$ after the Cu_yS coated electrode had been held for 10 min on open circuit. As noted in Tables 3 and 4, Table 5 confirms that the Cu_yS is decomposed more extensively the higher the temperature and the longer the period on open circuit.

Further support for our assignment of A2 to oxidation of CuS to Cu_yS and of C3 to reduction of Cu_yS to CuS [equation (10)] comes from the interdependence of $i_p(A2)$ and $i_p(C3)$ and their independence of stirring (Table 1):

$$2(10y)e^- + Cu_yS + (1-y)H_2O \rightarrow yCuS + (1-y)HS^- + (1-y)OH^- \qquad (10)$$
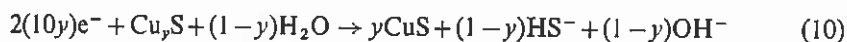
More significantly, $i_p(C3)$ is *not* observed at $-0 \cdot 12$ V when a fresh surface of a 10% CuS–carbon paste electrode is scanned to lower potentials from the rest potential, *without* any prior excursion to higher potentials. This is shown in Fig. 4, which contains cyclic voltammograms of a CuS–carbon paste electrode in 7 M ammonia containing $1 \cdot 5$ M ammonium sulfate at pH $10 \cdot 5$. An initial fast scan to higher potentials and an initial fast scan to lower potentials from the rest potential are shown. Process C3, the reduction of Cu_yS to CuS, only appears if the electrode is first oxidized at higher potentials to generate Cu_yS from CuS by reaction (2).

Table 6 shows the effect on i_p(A2) of removing Cu_yS by electrochemical reduction [equation (10)] to CuS rather than by reactions (3) or (7). As noted (Table 3) for a succession of scans of a CuS electrode between 0·05 and 0·30 V, i_p(A2) is much less on the second scan than on the first scan of a fresh CuS electrode. This is because Cu_yS is formed on the first scan. However, if after scanning to 0·30 V the disc is scanned to −0·25 V, so as to include the Cu_yS removing process [equation (10)], rather than simply to 0·05 V, the peak anodic current for process A2 on the next scan to 0·30 V is considerably greater than i_p(A2) measured on the second scan when
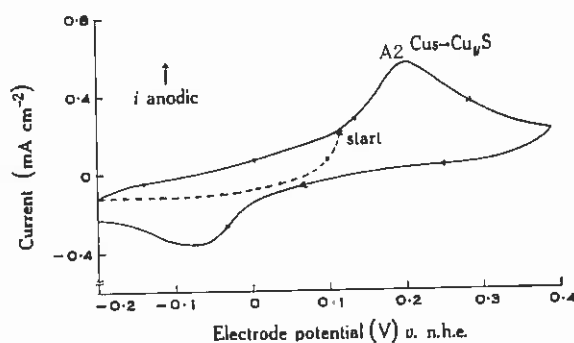

Fig. 4. Cyclic voltammogram of a 10% CuS–carbon paste electrode in 7 M ammonia and 1·5 M $(NH_4)_2SO_4$ at pH 10·5. Initial scans from the rest potential at 5 mV s^{-1} are shown. Stirred and unstirred solutions gave the same plot.

Table 6. Cyclic voltammetry (5 mV s^{-1}) on a CuS–carbon paste electrode in aqueous ammonia. Passivation of CuS oxidation by Cu_yS and removal of Cu_yS by reduction

In 7 M ammonia plus 1·5 M $(NH_4)_2SO_4$ at pH 10·5, still solution

Temperature (°C)	i_p A	$i(A2)$ ($\mu A\ cm^{-2}$)		
		$i_{p'}$ B	$i_{p,c}$ C	$i_{p,c'}$ D
0	200	30	90	160
25	320	57	160	300
50	660	130	800	800

A Peak current for process A2 during first scan on fresh electrode from 0·05 to 0·30 V, to 0·05 V.

B Peak current for process A2 on second scan, following that in footnote A, from 0·05 to 0·30 V.

C Peak current for process A2 on second scan of a fresh electrode after the sweep sequence 0·05 to 0·30 to −0·25 to 0·30 V, i.e. a cathodic scan incorporating C3 is introduced.

D Peak current for process A2 on the second scan of a fresh electrode after the sweep sequence 0·05 V to 0·30 V to −0·25 V (hold 5 min at −0·25 V) to 0·30 V.

scanning is only between 0·05 and 0·30 V. This behaviour is presumably because Cu_yS is reduced [equation (10)] when the scan is taken to −0·25 V but is not removed by simply cycling from 0·30 V to 0·05 V. This reactivation of a Cu_yS-coated CuS electrode, by reduction of the Cu_yS, is even more effective when Cu_yS is formed by an initial oxidation by scanning a fresh CuS electrode from 0·05 V to 0·30 V, then scanning from 0·30 V to −0·25 V and electrolysing at −0·25 V for 5 min to remove Cu_yS by process C3. When the electrode is rescanned to 0·03 V, process A2 is observed as a peak current, at the usual peak potential. The current is almost as great as the

value of $i_p(A2)$ for the first anodic scan of a fresh CuS electrode. As shown in Table 4, 5 min at $25°$ is insufficient time to remove all Cu_yS by the open circuit reactions (3) and (7), so that the almost complete reactivation after electrolysis for 5 min at -0.25 V must be by a reduction like (10).

Table 7. Proportions of sulfur formed from CuS during oxidation at $30°$. Relationship with $i_p(A2)$ with oxygen in aqueous ammonia
With 210 kPa oxygen and 4 g CuS per 300 ml solution

| (NH_3) (M)	$(NH_4)_2SO_4$ (M)	pH	S^A (%)	$i_p(A2)^B$ (mA cm^{-2})	$E_p(A2)^C$ v. s.h.e.
7	1·5	10·5	59	0·27	0·15
4	1·5	10·2	—	0·12	0·20
1	1·5	9·9	38	0·06	0·35
0·25	1·5	9·5	2	<0·06	—
4	0	12·1	<1^D	0·11	0·22

^{A} Percentage of the total of oxidized sulfate which appears as elemental sulfur in the reaction product (see ref. 4).
^{B} Peak current or process A2 (Table 1) for a 10% CuS–carbon paste electrode during first anodic scan at 5 mV s^{-1} (Fig. 5) at $25°$.
^{C} Peak potential for process A2 (Table 1) for a 10% CuS–carbon paste electrode during first anodic scan at 5 mV s^{-1} (Fig. 5) at $25°$.
^{D} Sulfur is kinetically unstable at this pH at $30°$ (see ref. 4).

Fig. 5. Effect of ammonia concentration and pH on the peak current and peak potential for anodic process A2 of a 10% CuS–carbon paste electrode at $25°$. Scan rate 5 mV s^{-1} in a still solution. A, 10 M NH$_3$, pH 11·0; B, 7 M NH$_3$, pH 10·5; C, 4 M NH$_3$, pH 10·2; D, 1 M NH$_3$, pH 9·9; E, 4 M NH$_3$, pH 12·1. [(NH$_4$)$_2$SO$_4$ 1·5 M in A–D; Na$_2$SO$_4$ 0·5 M in E.]
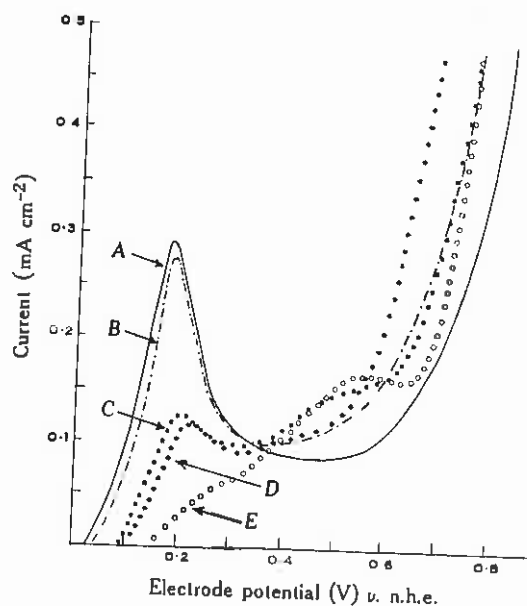
Effect of pH and Ammonia Concentration on Cu_yS Formation

We have noted[4] that the ammonia concentration and the pH of the solution have a very profound influence on the proportion of sulfur formed during the oxidation of CuS with oxygen in aqueous ammonia. At a pH above 12, or below 9·5, very little sulfur is formed. In the absence of a high proportion of ammonia to copper(II), very

little sulfur is formed and the reaction is slow.[5] Table 7 shows typical proportions of sulfur produced during oxidation of CuS with oxygen in aqueous ammonia.

Fig. 5 shows that process A2 [equation (2)] is most clearly defined as a current peak $i_p(A2)$ in 7–10 M ammonia containing 1·5 M ammonium sulfate at 25° and at pH 10·5–11·0. This is also the solution which gives the highest proportion of sulfur from oxidation of CuS with oxygen.[4] With less (1–4 M) ammonia at pH 9·9–12·1, the first current peak $i_p(A2)$ at 0·2 V with a fresh CuS–carbon paste electrode is much smaller and much less clearly defined with respect to other processes in the potential region 0·3–0·5 V. At pH 12·1, in the absence of ammonium sulfate in 4 M ammonia, processes A3 and A4 [equations (4) and (9)], which lead to sulfate and thiosulfate ions, produce large currents at potentials nearly 0·1 V cathodic of the potentials at which similar large currents are observed at pH 10·2 in 4 M ammonia. Process A2 is, however, unaffected. This shift of potential with pH is a little less than predicted by the cathodic 80 mV per decade of increased OH⁻ concentration for reaction (4) ($y = 0$). Fig. 5 shows that the peak current $i_p(A2)$ for formation of Cu_yS from CuS is greater and occurs at lower potentials the greater the ammonia content of the solution. 'Chemical oxidations' of CuS by oxygen occur at mixed potentials near 0·2 V and are faster the greater the concentration of ammonia.[5] Yields of sulfur are also greater the greater the proportion of ammonia to copper(II) ions (Table 7).[4] Fig. 5, in conjunction with those observations,[4,5] suggests that sulfur is formed through Cu_yS which is formed in a process A2 taking place near 0·2 V. The species Cu_yS is only formed at high pH (near 10) if there is a high proportion of ammonia to copper(II). In < 1 M ammonia, very little Cu_yS (Fig. 5) or sulfur (Table 7) is formed at pH 9–10 and the major oxidation is formation of sulfate and thiosulfate from CuS and Cu_yS. In high concentrations of ammonia, formation of Cu_yS is extensive (Fig. 5) and so formation of sulfur, at the expense of sulfate and thiosulfate, is substantial.