Anodic behaviour of alkaline solutions containing copper cyanide and sulfite on the graphite anode

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Abstract

Sulfite may be added to copper cyanide solutions to reduce cyanide oxidation at the anode during copper electrowinning. Anodic sulfite oxidation is enhanced in the presence of copper cyanide. Sulfite also suppresses the oxidation of copper cyanide. The effect of sulfite on the oxidation of copper cyanide decreases with increasing mole ratio of cyanide to copper. This is related to the shift in the discharged species from $Cu(CN)_3^{2-}$ to $Cu(CN)_4^{3-}$ with increasing mole ratio of cyanide to copper. Sulfite is oxidized to sulfate. At $[Cu^+]$ = around 1 M, CN:Cu = 3.0–3.2, $[OH^-]$ = 0.05–0.25 M, $[SO_3^{2-}]$ = 0.4–0.6 M and the temperature = 50–60 °C, the anodic current efficiency of sulfite reached 80–90%. With further increase in sulfite concentration beyond 0.6 M, the current efficiency of sulfite oxidation will not be increased significantly. Further increase in CN:Cu mole ratio will result in decrease in the anodic current efficiency.

1. Introduction

Cyanide leaching has been widely accepted as an excellent economical method to recover gold and silver. However, the cyanidation of copper–gold ores containing the common oxide and secondary sulfide copper minerals results in cyanide degradation and copper dissolution as cuprous cyanide complexes. In conventional gold processing, the copper and complexed cyanide are not recovered after the gold is removed from solution. This leads to a significant economic penalty in excess cyanide consumption, loss of a valuable copper byproduct and a significant cost in cyanide destruction during effluent treatment. Therefore, the recovery of copper and associated complexed cyanide from leach solutions has been approached in a variety of ways such as acidification–volatilization–regeneration (AVR), ion exchange and electrolysis [1–11].

However, generally these processes suffer from the following drawbacks: incomplete recovery of cyanide and copper, low-value copper products (e.g., CuCN, CuSCN and Cu₂S) and complicated flowsheets. To overcome the above drawbacks, a solvent extraction-electrowinning process has been developed to recover copper and cyanide from gold mining effluents [12]. In summary, copper cyanide is extracted using a guanidine-based extractant (XI7950) or a mixed strong base extractant with nonylphenol (XI78), stripped with strong alkaline electrolyte and finally electrolysed in a membrane cell to produce copper metal and a bleed stream for AVR to recover cyanide. The use of a membrane (Nafion®) in the copper electrowinning cell is necessary to prevent cyanide oxidation at the anode. Unfortunately, the use of a membrane is expensive and the membrane may be subject to mechanical damage by the growing metal deposit. To eliminate the use of a membrane, the possible inclusion of sulfite as a sacrificial species was tested in some proof-of-concept electrowinning experiments and was shown to be promising [13]. With sulfite addition, the cell chemistry becomes:

$$Na_2Cu(CN)_3 + \tfrac{1}{2}Na_2SO_3 + NaOH$$
$$\rightarrow Cu + 3\,NaCN + \tfrac{1}{2}Na_2SO_4 + \tfrac{1}{2}H_2O \tag{1}$$
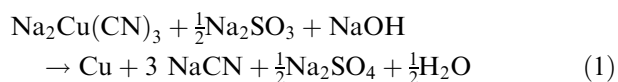
Accordingly, the objective of the present research was to understand the anodic oxidation of copper cyanide and then limit the anodic consumption of cyanide by the use of the sulfite as a sacrificial species during electrowinning. This contribution summarizes the detailed study of the anodic behaviour of the solutions of the Cu^+–CN^-–SO_3^{2-}–OH^- system. Previous studies have been conducted on the anodic oxidation of sulfite [14] and copper cyanide [15]. So far there have been no published reports regarding the anodic behaviour of mixed copper cyanide and sulfite solutions.

2. Experimental details

2.1. Equipment

Impregnated NE-150 graphite rod from National Electric Carbon Co. was used to make a graphite rotating disc. The graphite was machined to 4 mm diameter and surrounded tightly with a plastic shield of 10 mm in diameter. Another sample of graphite rod having a 25 mm diameter was fashioned as a rotating disc for coulometric measurements.

The rotating disc electrode system was an EG&G PARC (model 636) electrode rotator. The potentiostat used was Solartron (model 1286) electrochemical interface. An EG&G water-jacketed electrolytic cell was used. An argon gas purge was used to protect copper cyanide species from possible oxidation by air.

2.2. Reagents

Reagent grade chemicals and ultrapure deionized water were used throughout the investigation.

2.3. Experimental procedure

100 cm^3 of the solution of the required composition were added to the electrolytic cell. The experiments were carried out under an argon atmosphere. The ohmic drop between the working electrode and the reference electrode was compensated using the current interruption technique. For each experiment, the electrode surface was first renewed using 600 grit sandpaper, polished with 4000 grit silicon carbide sandpaper and then soft tissue paper. Finally the disc surface was checked under a microscope for smoothness. To obtain a stable electrode condition and reproducible results, the electrode was first treated by cyclic voltammetry between 0 and 0.60 V vs SCE at 100 mV s^{-1} in the solution containing 0.25 M NaOH and 1 M Na$_2$SO$_4$ for 0.5 h and polarized repeatedly at 1 mV s^{-1} until the electrode reached a stable condition. The liquid junction potential was not considered since the concentration of hydroxide is not very high and the mobilities of the ions of sulfate, sulfite and the copper cyanide species are close to that of the sodium ion. The thermal liquid junction potential was measured using two calomel reference electrodes.

2.4. Chemical analysis

To analyse solutions, the sample was treated by addition of BaCl$_2$ to precipitate BaSO$_3$. The BaSO$_3$ precipitate was filtered and washed. Determination of the total cyanide in solution involved: (i) distillation of cyanide as HCN at a mildly acid pH of 4 in the presence of EDTA, (ii) absorption of HCN in 0.25 M NaOH solution, and (iii) titration with silver nitrate. The copper concentration in solution was determined by EDTA titration method. The BaSO$_3$ precipitate was first dissolved by addition of HCl and then immediately analysed by adding an excess of standard iodine solution followed by back titration with standard thiosulfate solution.

3. Results and discussions

3.1. Coulometric measurements

Coulometric measurements were conducted using controlled potential and controlled current methods to investigate the anodic current efficiencies of cyanide and copper oxidation in the presence of sulfite.

Table 1 lists the anodic current efficiencies of cyanide, copper(I) and sulfite (assuming sulfite was oxidized to sulfate) using the controlled current method. The sum of the anodic current efficiencies of cyanide (CN$^-$ → CNO$^-$), copper(I) (Cu$^+$ → CuO) and sulfite (assuming SO$_3^{2-}$ → SO$_4^{2-}$) was very close to 100%. Thus sulfite was oxidized to sulfate. In the presence of 0.4–0.5 M sulfite, the anodic current efficiency decreased from 86% to about 10% for cyanide and from 13% to 3% for Cu(I) at [OH$^-$] = 0.25 M. With decreasing hydroxide concentration (tests 9–20), the anodic current efficiency of Cu(I) decreased because the formation of copper oxide was not favoured at low hydroxide concentration from the kinetic and thermodynamics viewpoints and more Cu(II) was reduced by sulfite or cyanide. The anodic current efficiency of cyanide was not affected very much due to the change in the hydroxide concentration while the anodic current efficiency of sulfite increased slightly. With increasing CN:Cu mole ratio, the anodic current efficiency of Cu(I) was decreased (tests 1–8, 9–12 and 21–32) since Cu(II) was stabilized to prevent the formation of copper oxide and also reduced by cyanide in the cyanide rich environment [15].

At [CN$^-$] = 0.05 M, the anodic current efficiency of cyanide did not change very much with increasing CN:Cu from 3 to 4 (tests 1–8). However, at [Cu$^+$] = 1 M, the anodic current efficiency of cyanide increased significantly with increasing CN:Cu mole ratio from 3 to 4 (tests 9–12 and 21–32). At a CN:Cu mole ratio of 3 and a constant of current, the anodic current efficiency of cyanide did not change very much with increasing cyanide concentration from 0.05 to 3 M. However, at a CN:Cu mole ratio of 4 and constant current, the anodic current efficiency of cyanide increased significantly with increasing cyanide concentration from 0.05 to 4 M. The above phenomena are probably related to the distribution of copper cyanide. At CN:Cu mole ratio 3, the distribution of copper cyanide changes only slightly with increasing cyanide concentration and over 97% of Cu(I) exists in the form of Cu(CN)$_3^{2-}$ [16] and Cu(CN)$_3^{2-}$ was the dominant discharged species [15]. At CN:Cu mole ratio 4, the dominant species is Cu(CN)$_3^{2-}$ for 0.05 M CN$^-$ solution and Cu(CN)$_4^{3-}$ for 4 M CN$^-$ solution respectively [16]. The dominant discharged species is Cu(CN)$_4^{3-}$ for both 0.05 and 4 M CN$^-$ solutions [15]. With increasing [CN$^-$] from 0.05 to 4 M, the concentration of Cu(CN)$_4^{3-}$

Table 1. Current efficiency for copper (2), cyanide and sulfite using controlled-current coulometric at 100 rpm 1 M Na_2SO_4 of supporting electrolyte was used for tests 1–8

Test	Composition	Controlled current /A m^{-2}	Temperature /°C	Current efficiency for SO_3^{2-} /%	Current efficiency for CN /%	Current efficiency for Cu$^+$ /%
1	0.05 M CN$^-$	250	50	87	13	3
2	0.0167 M Cu$^+$(CN:Cu = 3)	250	60	88	10	2
3	0.4 M SO_3^{2-}	500	50	86	12	1.6
4	0.25 M OH$^-$	500	60	89	10	1.8
5	0.05 M CN$^-$	250	50	–	13	0
6	0.0125 M Cu$^+$(CN:Cu = 4)	250	60	–	11	0
7	0.4M SO_3^{2-}	500	50	–	15	–
8	0.25 M OH	500	60	–	12	–
9	3 M CN$^-$	250	50	83	14	2.2
10	1 M Cu$^+$ (CN:Cu = 3)	250	60	86	13	2.4
11	0.5 M SO_3^{2-}	500	50	84	15	2.5
12	0.25 M OH$^-$	500	60	86	12	2.6
13	3 M CN$^-$	250	50	–	13	0
14	1 M Cu$^+$ (CN:Cu = 3)	250	60	–	12	0
15	0.5 MSO_3^{2-}	500	50	–	12	0
16	0.10 MOH$^-$	500	60	–	11	0
17	3 M CN$^-$	250	25	88	15	0
18	1 M Cu$^+$ (CN:Cu = 3)	250	40	88	14	0
19	0.5 M SO_3^{2-}	250	50	89	10	0
20	0.05 M OH$^-$	250	60	87	09	0
21	3.2 M CN$^-$	250	50	–	13	0
22	1 M Cu$^+$ (CN:Cu = 3.2)	250	60	–	12	0
23	0.5 MSO_3^{2-}	500	50	–	15	0
24	0.25 M OH$^-$	500	60	–	14	0
25	3.5 M CN$^-$	250	50	–	19	0
26	1 M Cu$^+$ (CN:Cu = 3.5)	250	60	–	18	0
27	0.5 MSO_3^{2-}	500	50	–	22	0
28	0.25 M OH	500	60	–	21	0
29	4 M CN$^-$	250	50	–	40	0
30	1 M Cu$^+$ (CN:Cu = 4)	250	60	–	39	0
31	0.5 M SO_3^{2-}	500	50	–	45	0
32	0.25 M OH	500	60	–	46	0

increased greatly and the discharge speed of $Cu(CN)_4^{3-}$ became faster than that of SO_3^{2-}. $Cu(CN)_4^{3-}$ was oxidized to $Cu(CN)_4^{2-}$, which was probably not effectively reduced by SO_3^{2-} in the cyanide-rich environment. Therefore, sulfite did not effectively limited the cyanide oxidation when both cyanide concentration and CN:Cu mole ration were high.

Table 2 lists the current efficiencies for cyanide, copper and sulfite using controlled potential method. At 0.3/0.25 V vs SCE, the anodic current efficiencies of sulfite for the solutions containing 0.05 and 3 M CN$^-$ were very close to each other. At 0.6 V vs SCE where the current reached a limiting value, the anodic current efficiency of sulfite for the solution containing 0.05 M CN$^-$ decreased slightly while the anodic current efficiencies for the solution containing 3 M CN$^-$ increased significantly. That means that at a low potential, sulfite would decrease the anodic current efficiency of cyanide for both dilute and concentrated cyanide solution. At 0.6 V vs SCE, the anodic current efficiency of sulfite for

0.05 M CN$^-$ was still high because the limiting current was approximately the sum of sulfite and copper cyanide and the former limiting current was much higher than the latter one while in the case of 3 M CN$^-$ the current was much larger than the sulfite limiting current (as shown in the following two Sections) and so the current efficiency of sulfite was lower.

3.2. *Anodic behaviour of dilute copper cyanide solution with sulfite*

The anodic oxidation of mixed sulfite and copper cyanide has been studied as a function of temperature, CN:Cu mole ratio and sulfite and hydroxide concentrations.

3.2.1. *Effect of temperature*
Figure 1 shows the polarization curves of the solution with 0.05 M CN$^-$, a CN:Cu mole ratio of 3, 0.4 M Na_2SO_3, 0.25 M NaOH and 1 M Na_2SO_4 at 25 and 60 °C.

Table 2. Current efficiency for copper (1), cyanide and sulfite using controlled-potential coulometry at 100 rpm 1 M Na_2SO_4 of supporting electrolyte was used for tests 1–10

Test	Composition	Controlled potential /V vs SCE	Temp. /°C	Current efficiency for CN /%	Current efficiency for Cu^+ /%	Current efficiency for SO_3^{2-} /%
1	0.05 M CN^-, 0.0167 M Cu^+	0.3	60	11	2.2	87
2	0.4 M SO_3^{2-}, 0.25 M OH^-	0.5	60	13	2.9	84
3	0.05 M CN^-, 0.0125 M Cu^+	0.4	60	10	1.3	85
4	0.4 M SO_3^{2-}, 0.25 M OH^-	0.6	60	13	2.8	83
5	0.05 M CN^-, 0.0167 M Cu^+	0.25	60	9	0	89
6	0.4 M SO_3^{2-}, 0.05 M OH^-	0.6	60	11	0	90
9	0.05 M CN^-, 0.0125 M Cu^+	0.25	60	11	0	89
10	0.4 M SO_3^{2-}, 0.05 M OH^-	0.6	60	13	0	88
11	3 M CN^-, 1 M Cu^+	0.3	60	13	2.3	87
12	0.5 M SO_3^{2-}, 0.25 M NaOH	0.6	60	52	0	47
13	3 M CN^-, 1 M Cu^+	0.3	60	11	0	87
14	0.5 M SO_3^{2-}, 0.05 M NaOH	0.6	60	48	0	57

At 25 °C (Figure 1(a)), the current first increased and then decreased sharply to a minimum value with the formation of copper oxide on the anode. With further increase in potential, the current increased again. At a

Fig. 1. Polarization curves at (a) 25 and (b) 60 °C. Electrolyte: 0.05 M CN^-, 0.0167 M Cu^+ (CN:Cu mole ratio = 3), 0.25 M NaOH, 0.4 M Na_2SO_3 and 1 M Na_2SO_4. Key: (1) 100, (2) 400 and (3) 1600 rpm.

potential less than about 0.8 V vs SCE, some gas bubbles were observed on the anode and believed to be due to oxygen evolution. The passivation is probably due to the precipitation of copper oxide and the adsorption of oxygen. A very thin layer of copper oxide was precipitated on the graphite but not on the outer insulator. The XPS analysis showed that the precipitated copper oxide was cupric oxide.

In our previous work [15], when only copper cyanide was present in the solution, copper oxide was precipitated both on the graphite and the outer insulator with the amount of copper oxide being much larger. Therefore, sulfite can reduce cupric ions to cuprous ions and decrease the extent of copper oxide formation.

At 60 °C, the polarization curves (Figure 1(b)) became different. At 100 and 400 rpm, the current increased to a limiting value, which was approximately the sum of copper cyanide and sulfite limiting currents when they are present separately in the solution. At 1600 rpm, the current first increased to a peak value and then decreased to a minimum value with the precipitation of copper oxide and finally rose sharply to a limiting value. At a potential more than 1.0 V vs SCE, bubbles were observed and the current decreased sharply. Oxygen evolution passivated the electrode surface. This dependence of the anodic behaviour on the rotational speed is due to the difference in the composition on the electrode surface at different rotational speeds. The difference in the compositions of the electrolyte can affect the precipitation of copper oxide and evolution of oxygen and finally the electrochemical properties. The dependence of the anodic behaviour on the temperature is due to the change in the catalytic properties of copper oxide. The copper oxide precipitated at a higher temperature has a relatively higher catalytic effect on the anodic oxidation of copper cyanide and sulfite from the anodic behaviour of copper cyanide and sulfite on the copper oxide coated electrode
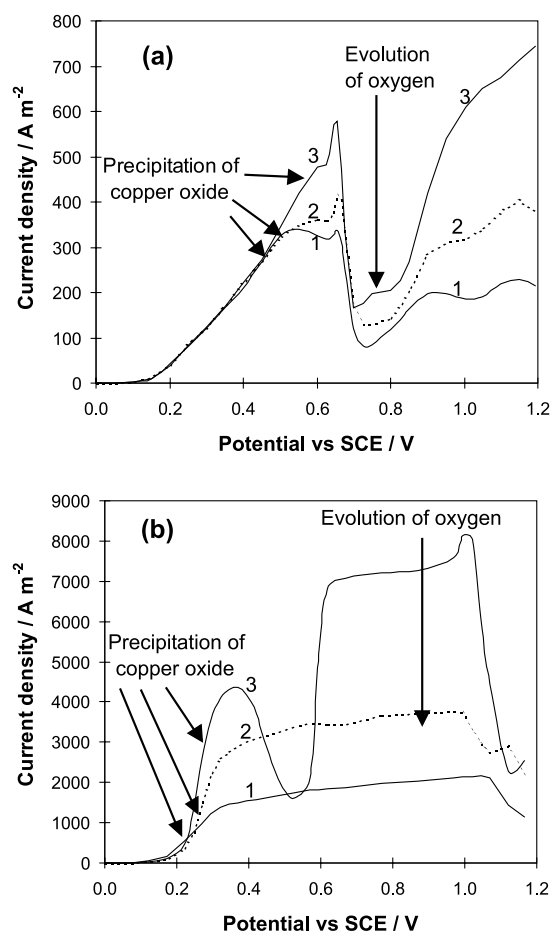
when they were separately present in the solution. The anodic behaviour of mixed copper cyanide and sulfite was somewhat similar to that for copper cyanide [15]. However, the copper oxide precipitated in the solution containing both copper and cyanide has a much lower catalytic effect on the anodic oxidation of sulfite and copper cyanide than that precipitated in the solution containing only copper cyanide. The catalytic effect was further decreased when both sulfite and copper cyanide were present in the solution. In a certain potential region, the copper oxide precipitate had significant inhibiting effect on sulfite oxidation as shown in Figure 1. This inhibiting effect was dependent on the temperature and the solution composition. With increasing potential scanning rate, there is less inhibiting effect observed since less copper oxide was precipitated.

In comparing three polarization curves respectively for (i) mixed sulfite and copper cyanide, (ii) sulfite and (iii) copper cyanide (Figure 2) at 400 rpm and 60 °C, the anodic oxidation of sulfite was enhanced in the presence of copper cyanide. The current efficiency of sulfite oxidation was 85–90% over the potential range 0.2–0.8 V vs SCE. At 0.8 V vs SCE, the total anodic current for the mixture of sulfite and copper cyanide was approximately the sum of those for sulfite and copper cyanide when they were present separately.

3.2.2. *Effect of sulfite concentration*
With decreasing sulfite concentration to 0.2 M (the other composition were kept constant), more copper oxide was precipitated and the current was decreased over the potential range 0–0.5 V vs SCE. However, the current increased and reached almost the same value as for the solution containing 0.4 M sulfite over the potential range 0.6–1.0 V vs SCE due to the evolution of more oxygen. When sulfite concentration was further decreased to 0.1 M, the evolution of oxygen became dominant at the
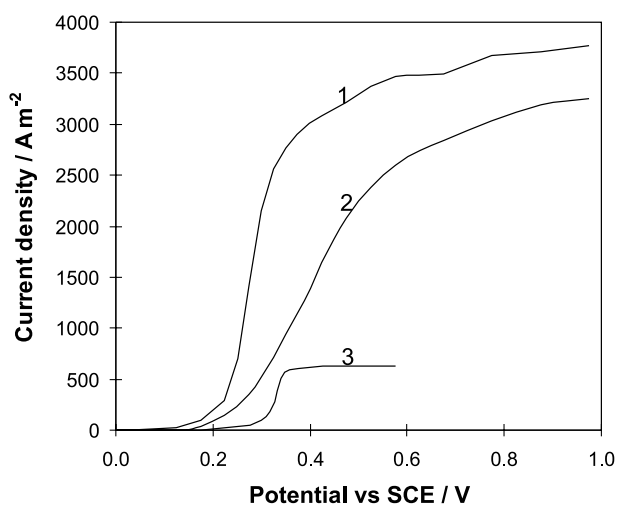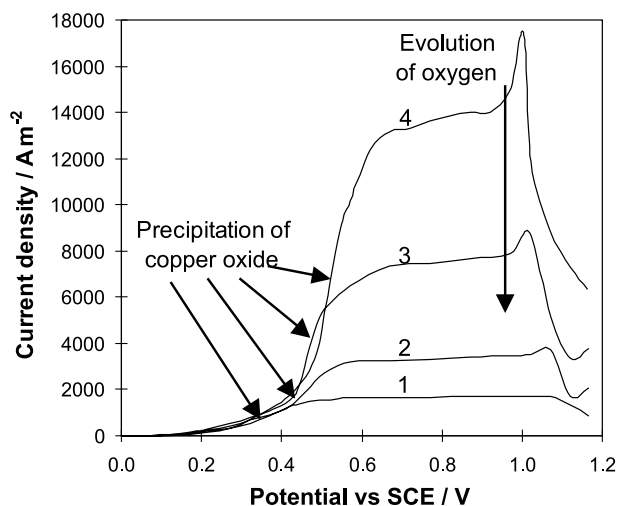

Fig. 3. Polarization curves at 60 °C. Electrolyte: 0.05 M CN$^-$, 0.0125 M Cu$^+$ (CN:Cu mole ratio = 4), 0.25 M NaOH, 0.4 M Na$_2$SO$_3$ and 1 M Na$_2$SO$_4$. Key: (1) 100, (2) 400 rpm, (3) 1600 and (4) 4900 rpm.

potential >0.6 V vs SCE, which was similar to that observed in the solution containing copper cyanide, but no sulfite [15].

3.2.3. *Effect of mole ratio of cyanide to copper*
When the mole ratio of cyanide to copper increased from 3 to 4 ([Cu$^+$] decreased from 0.0167 to 0.0125 M) at [CN$^-$] = 0.05 M, the polarization curves were different (comparing Figures 1(b) and 3). The current rose to a limiting value at a higher potential for CN:Cu = 4 than that for CN:Cu = 3. In the case of CN:Cu = 4, the current did not decrease after reaching a limiting value at a rotational speed $\geqslant$1600 rpm in the potential range 0–0.9 V vs SCE. A lower concentration of Cu(I) resulted in a lower catalytic effect on cyanide and sulfite oxidation and in the formation of less copper oxide. Therefore, no passivation was not observed in the potential region at 1600 rpm and CN:Cu mole ratio of 4.

3.2.4. *Effect of concentration of hydroxide*
The precipitation of copper oxide affected the anodic oxidation of sulfite and copper cyanide. The concentration of hydroxide was decreased to 0.05 M to investigate its effect on the anodic behaviour of sulfite and copper cyanide. The anodic behaviour of the solution containing copper cyanide and sulfite (curve 1), sulfite (curve 2) and copper cyanide (curve 3) are shown in Figure 4. From curve 1, the current first increased to a peak value, decreased, then increased slightly and finally decreased slightly with further increasing potential. No visible copper oxide was formed and no oxygen evolution was observed.

Comparing curves 1 and 2 in Figure 4, at a potential about or less than 0.30 V vs SCE, the sulfite oxidation did not seem to be catalyzed by the oxidation of copper cyanide. However, at a potential about or more than 0.3 V vs SCE, the current increased rapidly and the sulfite oxidation was enhanced in the presence of copper
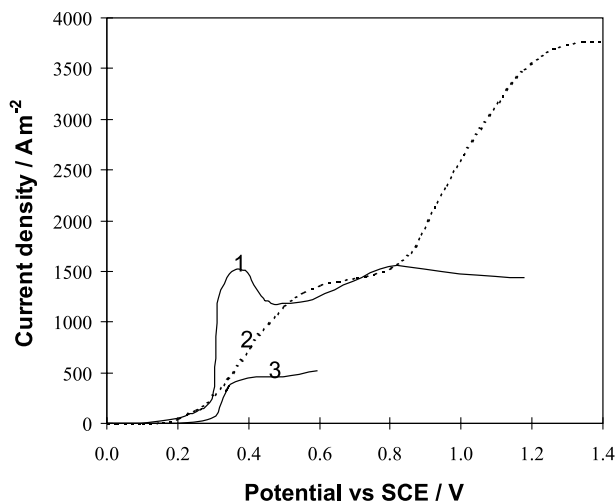

Fig. 2. Polarization curves for (1) 0.05 M CN$^-$, 0.0167 M Cu$^+$ (CN:Cu mole ratio = 3) and 0.4 M Na$_2$SO$_3$, (2) 0.4 M Na$_2$SO$_3$ and (3) 0.05 M CN$^-$ and 0.0167 M Cu$^+$ at 400 rpm and 60 °C. Supporting electrolyte: 0.25 M NaOH and 1 M Na$_2$SO$_4$.

Fig. 4. Polarization curves for (1) 0.05 M CN⁻, 0.0167 M Cu⁺ (CN:Cu mole ratio = 3) and 0.4 M Na₂SO₃, (2) 0.4 M Na₂SO₃ and (3) 0.05 M CN⁻ and 0.0167 M Cu⁺ at 400 rpm and 60 °C. Supporting electrolyte: 0.05 M NaOH and 1 M Na₂SO₄.

cyanide. The potential for the sharp increase in the current for mixed sulfite and copper cyanide is almost the same as that for copper cyanide (curve 3). The current for the direct oxidation of sulfite (curve 2) reached the first limiting value at a potential about 0.7 V vs SCE and then the second one at 1.4 V vs SCE. The first limiting current increased with the concentration of OH⁻ and was proportional to the square root of the rotational speed, but was not proportional to the sulfite concentration. The second one was proportional to the concentration of sulfite and the square root of the rotational speed but not the hydroxide concentration. At [OH⁻] = 0.25 M, there was only the second limiting current but not the first one as shown in Figure 2. This indicates that the first limiting current was limited by OH⁻ diffusion while the second one was limited by sulfite diffusion. At a potential more than 0.6 V vs SCE, the current for curve 1 was proportional to the square root of the rotational speed and increased with hydroxide concentration. This indicates that the current for curve 1 at a potential less than 0.6 V vs SCE was limited by hydroxide diffusion. At a potential more than 0.6 V vs SCE, the pH on the electrode would be below 7 and the dominant sulfite species shifted to HSO_3^- or further SO_2 [14]. The maximum anodic current of the mixture of sulfite and copper cyanide (curve 1) was only about the first limiting current of the oxidation of sulfite (curve 2). Therefore, at a potential less than 0.6 V vs SCE, the oxidation of sulfite (HSO_3^- or SO_2) was not enhanced in the presence of copper cyanide possibly because the anodic oxidation of copper cyanide would be limited due to the low pH on the anode as observed in the copper cyanide solution [15], or due to the passivation of the anode.

At a potential more than 0.9 V vs SCE, the current for the solution containing copper cyanide and sulfite did not increase as expected from the further direct oxidation of sulfite species (HSO_3^- or SO_2) as observed in the solution containing only sulfite (curve 2). The direct oxidation of sulfite (HSO_3^- or further SO_2) was suppressed in the presence of copper cyanide at a potential less than 0.9 V vs SCE possibly due to the passivation of the electrode. In the potential range 0.2–0.8 V vs SCE, the anodic current efficiency of sulfite was essentially maintained about 85%.

3.3. *Anodic behaviour of concentrated copper cyanide solution with sulfite*

3.3.1. *Effect of temperature*
The polarization curves for the solution with 3 M CN⁻, 1 M [Cu⁺] and 0.5 M Na₂SO₃ and 0.25 M NaOH are shown in Figure 5. At 25 °C, the current first increased and then decreased slightly with precipitation of copper oxide. At a potential more than about 0.52 V vs SCE, the current increased to a peak value and decreased rapidly. The second passivation is probably due to oxygen adsorption. At 40 °C, the polarization curves at 400 and 1600 rpm were similar to those at 100 rpm and 25 °C. However, at 100 rpm and 40 °C, the current reached a limiting value and became independent of potential. The oxide formed in the potential range 0.38 to 0.5 V vs SCE was dissolved when the current was at its limiting value. This is why the current did not decrease with potential after the current sharply increased to a limiting value.

This dependence of the anodic behaviour on the rotational speed is related to the composition of the reactive species on the surface of the electrode. At a potential more than 0.5 V vs SCE, the current increased sharply with increasing potential and was almost independent of the rotational speed. Therefore, the concentration of hydroxide on the electrode surface decreased with decreasing rotational speed. At 100 rpm, the concentration of hydroxide was so low that the formation of copper oxide was not favoured. Even copper oxide was more readily reduced by sulfite ions and dissolved. Therefore, a second passivation was not observed. At 400 and 1600 rpm, the concentration of hydroxide on the surface was still high and the formation of copper oxide was still favoured. With increasing potential, the second passivation appeared probably due to the adsorption of oxygen.

At 50 °C and 100 rpm, the current increased continuously to a limiting value and no copper oxide was formed on the electrode. At 400 rpm, the anodic behaviour of current against potential was similar to that at 100 rpm and 40 °C. At 1600 rpm, the anodic behaviour was still similar to that at 40 °C.

At 60 °C and a rotational speed of 100 or 400 rpm, the current increased continuously to a limiting value and became independent of the potential. The anodic behaviour at 1600 rpm was similar to that at 100 rpm and 40 °C over the potential 0–0.5 V vs SCE.

Figure 6 shows the plots of the current vs time at different potentials at 400 rpm and 25 °C, At 0.4 V vs SCE, the current first decreased rapidly and then slowly
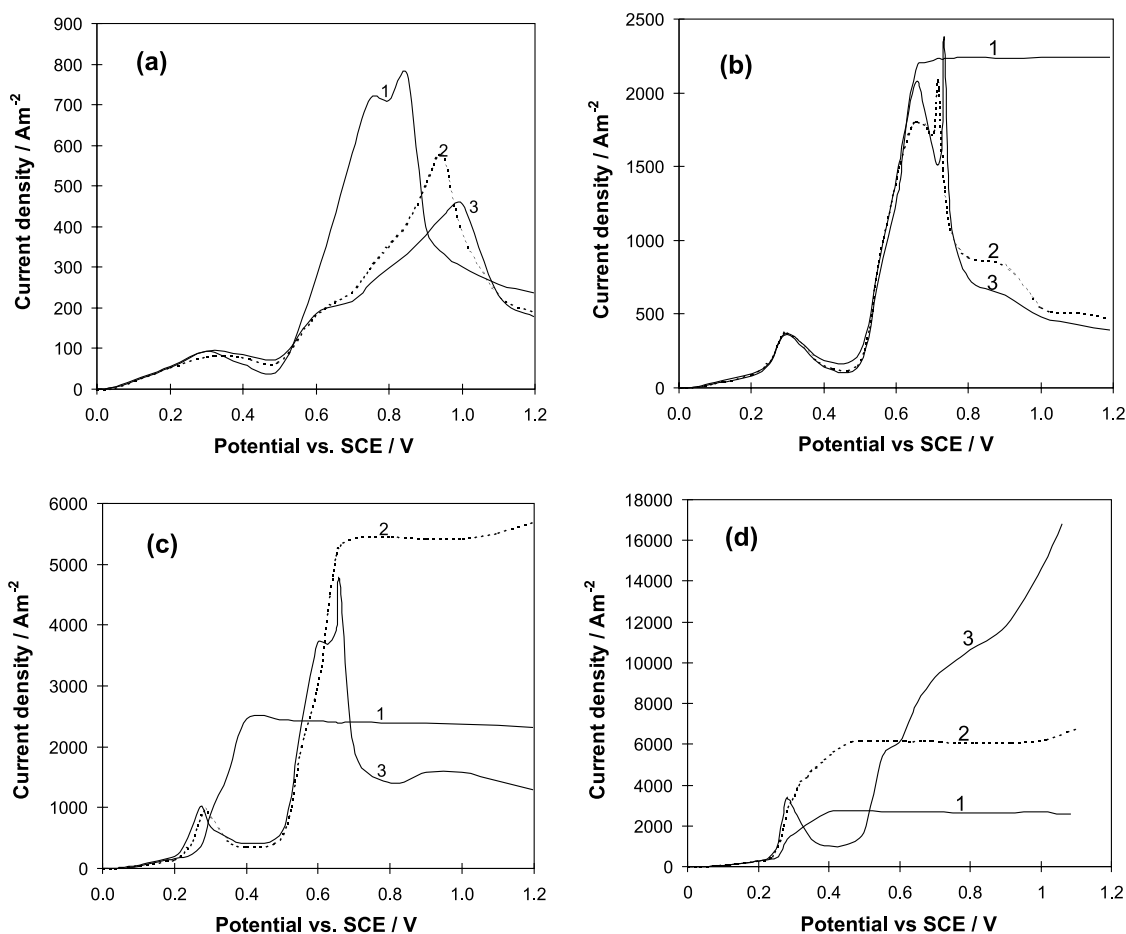
Fig. 5. Polarization curves at (a) 25, (b) 40, (c) 50 and (d) 60 °C. Electrolyte: 3 M CN⁻, 1 M Cu⁺, 0.25 M NaOH, 0.5 M Na₂SO₃. Key: (1) 100, (2) 400 rpm and (3) 1600 rpm.

and finally became stable. A thin layer of copper oxide was precipitated on the anode. At 0.60 V vs SCE, the current increased to a certain value and then became stable. No copper oxide was precipitated on the electrode. At 0.80 V vs SCE, the current decreased to a limiting value and became stable with no copper oxide appearing on the anode. It should be noted that at 25 °C and 0.80 V vs SCE, the current densities in Figure 5(a)
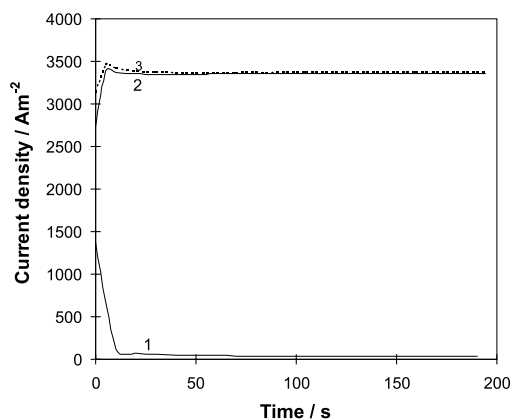
Fig. 6. Current density against time at constant potential, 400 rpm and 25 °C. Electrolyte: 3 M CN⁻, 1 M Cu⁺, 0.25 M NaOH, 0.5 M Na₂SO₃. Key: (1) 0.2, (2) 0.6 and (3) 0.8 V vs SCE.

(curve 2) do not match those in Figure 6. This can be explained by: (i) the current obtained in Figure 6 was obtained using the controlled potential method. When the potential was applied, the instantaneous current reached a value where the concentration of hydroxide on the electrode surface was low so that copper oxide was not formed and the current was stabilized at a limiting value; (ii) the current in Figure 5(a) was generated by a potential scan at 1 mV s⁻¹ and so the current never reached a value at which copper oxide was readily reduced and dissolved. Hence, it passivated the electrode surface. The results at 40 and 50 °C are similar to that at 25 °C. However, at 400 rpm and 60 °C, the current obtained by the controlled potential method was close to that by the potential scanning method (curve 2 in Figure 5(d)). The copper oxide precipitated at 60 °C had a much better catalytic effect on sulfite and cyanide oxidation. Before the onset of the passivation like curve 3 (1600 rpm) in Figure 5(d), at 400 rpm (curve 2), during the potential scanning, the current reached a value (the maximum current for 0.25 M NaOH to keep the pH above 7 was about 3000 A m⁻² estimated by the anodic oxidation of sulfite) where the pH on the electrode became so low due to consumption of hydroxide ions that no copper oxide was precipitated and therefore no passivation was observed. Thus the current
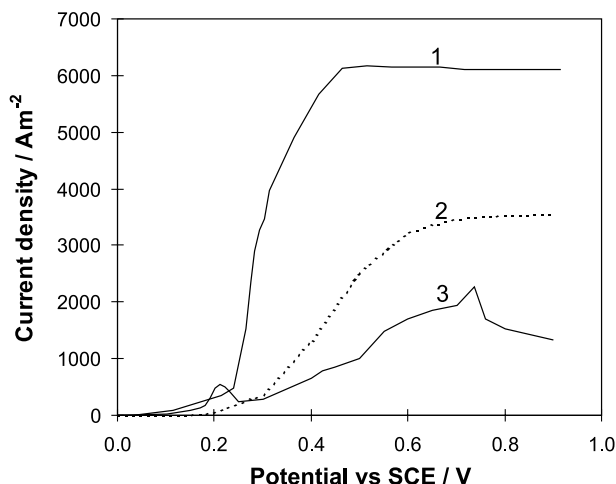
Fig. 7. Polarization curves for (1) 3 M CN⁻, 1 M Cu⁺ (CN:Cu mole ratio = 3), 0.25 M NaOH and 0.5 M Na$_2$SO$_3$, (2) 0.5 M Na$_2$SO$_3$, 0.25 M NaOH and 1 M Na$_2$SO$_4$ and (3) 3 M CN⁻, 1 M Cu⁺, 0.25 M NaOH and 0.5 M Na$_2$SO$_4$ at 400 rpm and 60 °C.
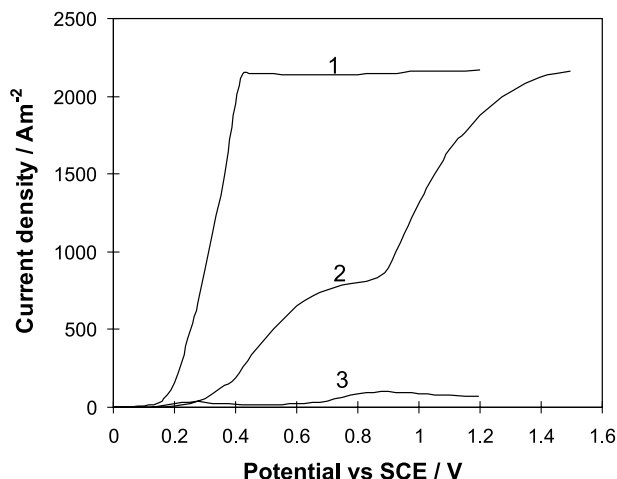

Fig. 8. Polarization curves at 400 rpm and 25 °C for (1) 3 M CN⁻ + 1 M Cu⁺ + 0.4 M Na$_2$SO$_3$ + 0.1 M Na$_2$SO$_4$, (2) 0.4 M Na$_2$SO$_3$ + 1 M Na$_2$SO$_4$ and (3) 3 M CN⁻ + 1 M Cu⁺ + 0.5 M Na$_2$SO$_4$ at [NaOH] = 0.05 M.

obtained by the potential scanning method matched that by the controlled potential method.

Figure 7 shows the polarization curves for mixed sulfite and copper cyanide solution, sulfite solution and copper cyanide solution with 0.25 M NaOH at 60 °C. At 0.3 V vs SCE, the anodic current efficiency for sulfite was about 85%. Compared to curve 2, the anodic current for sulfite in the presence of both sulfite and copper cyanide was much higher than that in the presence of only sulfite. Sulfite oxidation was enhanced in the presence of copper cyanide. At 0.6 V vs SCE, the anodic current efficiency for cyanide was about 50%, and so the anodic current for cyanide was higher than that in the presence of only copper cyanide. The oxidation of copper cyanide also seems to be affected by sulfite. At a low potential (around 0.3 V vs SCE), the oxidation of sulfite was dominant. At a high potential (>0.4 V vs SCE), the current was much higher than the limiting current of sulfite and the oxidation of copper cyanide became important.

3.3.2. *Effect of concentration of hydroxide*
The precipitation of copper oxide affected the anodic behaviour. Hence, the concentration of hydroxide was decreased to 0.1 and 0.05 M while the other compositions were kept constant to investigate the effect of pH on the anodic behaviour. At [OH⁻] = 0.2 and 0.1 M, with increasing potential, the current increased to a limiting value and became stable over the temperature range 25–60 °C and no copper oxide was precipitated on the anode and therefore no passivation was observed.

Figure 8 (curve 1) shows the anodic behaviour of the mixture of copper cyanide and sulfite when the hydroxide was 0.05 M. Comparing those for the solutions containing only sulfite (curves 2) and only copper cyanide (curve 3), the anodic oxidation of sulfite and copper cyanide was affected by each other. At 0.3 V vs SCE, the anodic current efficiency for cyanide was about

20%, the net current for the oxidation of sulfite was much higher than that for the solution containing only sulfite. This means that sulfite oxidation was enhanced in the presence of copper cyanide. At 0.6 V vs SCE, the anodic current efficiency of cyanide was around 50% at 0.6 V vs SCE (curve 1) and so the net oxidation current for cyanide oxidation was 50 times that for the solution containing only copper cyanide (curve 2). So the oxidation of cyanide was also enhanced in the presence of sulfite ions. The anodic current efficiency of sulfite was about 50% at 0.6 V vs SCE and the net oxidation current of sulfite was about half its limiting current. The current did not further increased with increasing potential due to the further direct oxidation of sulfite, which was also observed in Figure 4. This could be due to the same reason as discussed in Section 3.2.4.

3.3.3. *Effect of mole ratio of cyanide to copper*
When the concentration of cyanide increased from 3 to 3.5 M and the concentrations of the other species were maintained constant, no copper oxide was precipitated and no passivation was observed. At 25 °C, the current increased with increasing potential and then reached a limiting value and became independent of the potential. At a temperature of 40 °C or more there was no limiting current and the current continuously increased with increasing potentials. At 60 °C, when the potential exceeded 0.4 V vs SCE, a significant amount of bubbles was observed at 100 and 400 rpm. The bubbles were rapidly dissolved in two seconds after turning off the current. The graphite was not corroded. At such a high current, sulfite only limited a part of the cyanide oxidation and pH on the electrode surface was so low that the rate of production of (CN)$_2$ was higher than the rate of the reaction between (CN)$_2$ and OH⁻. Therefore, (CN)$_2$ bubbles were evolved.

Figure 9 shows the polarization curves for the solutions containing both sulfite and copper cyanide (curve

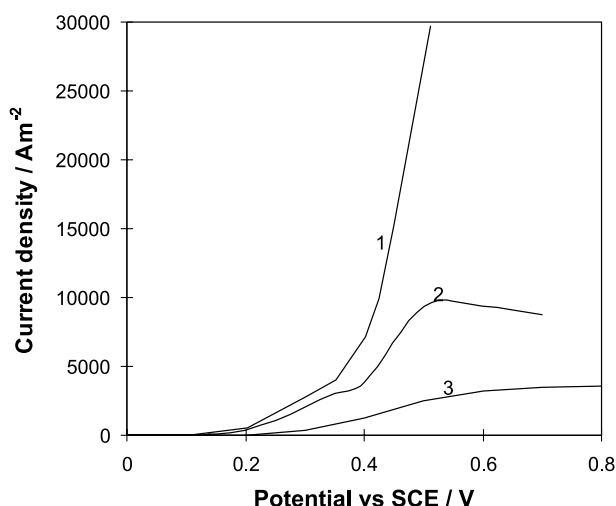*Fig. 9.* Polarization curves for (1) 3.5 M CN⁻, 1 M Cu⁺, 0.25 M NaOH and 0.5 M Na₂SO₃, (2) 3 M CN⁻, 1 M Cu⁺, 0.25 M NaOH and 0.5 M Na₂SO₄ and (3) 0.5 M Na₂SO₃, 0.25 M NaOH at 400 rpm and 60 °C.

Fig. 10. Polarization curves for (1) 4 M CN⁻ + 1 M Cu⁺ + 0.25 M NaOH + 0.5 M Na₂SO₃, (2) 0.5 M Na₂SO₃ + 0.25 M NaOH + 1 M Na₂SO₄ and (3) 4 M CN⁻ + 1 M Cu⁺ + 0.25 M NaOH + 0.5 M Na₂SO₄ at 400 rpm and 60 °C.

1), copper cyanide (curve 2) and sulfite (curve 3). The current for mixed copper cyanide and sulfite was higher than that for copper cyanide or sulfite. The anodic current efficiency for cyanide was about 20% at 0.2–0.3 V vs SCE and increased with increasing potential.

While the concentration of cyanide increased from 3 to 4 M and the concentrations of the other species were maintained constant, no copper oxide was precipitated and the current increased continuously with increasing potential over the temperature range 25 to 60 °C. When the current exceeded a certain value (depending on the rotational speed), a layer of bubbles was formed on the graphite. With increasing potential, the bubbles became larger and had a significant effect on the mass transfer.

Figure 10 shows the polarization curves for the solutions containing both sulfite and copper cyanide (curve 1), copper cyanide (curve 2) and sulfite (curve 3). The current for mixed copper cyanide and sulfite was a little higher than that for copper cyanide. The anodic current efficiency for cyanide was around 50% at 0.2–0.3 V vs SCE and increased with increasing potential. So the oxidation of cyanide was dominant. At CN:Cu = 4, the discharge of $Cu(CN)_4^{3-}$ was dominant and the main initial product was $Cu(CN)_4^{2-}$ [15]. The discharge of $Cu(CN)_4^{3-}$ would be faster than that of SO_3^{2-} and $Cu(CN)_4^{2-}$ would not be reduced effectively by sulfite. Thus the oxidation of sulfite was not dominant.

3.4. Possible anodic reactions

The anodic behaviour of mixed copper cyanide and sulfite solution is a function of hydroxide, sulfite and cyanide concentrations, the mole ratio of cyanide to copper, temperature and rotational speed. The current for mixed copper cyanide solution is not just the sum of the currents of copper cyanide and sulfite when they are present s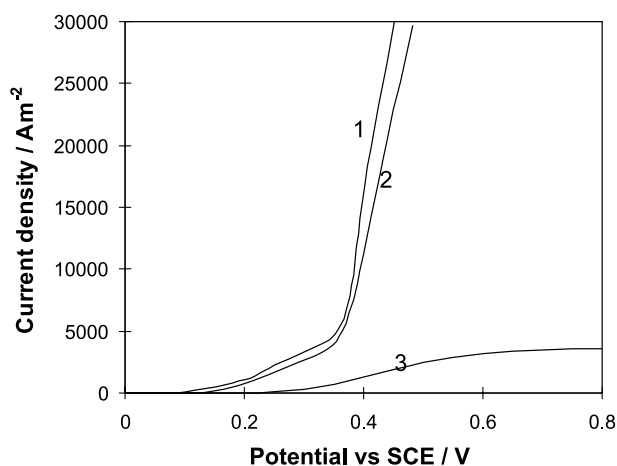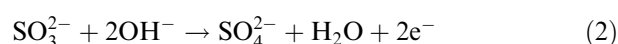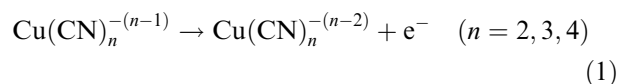eparately in the solution. Sulfite oxidation was affected significantly by the oxidation of copper cyanide. Copper cyanide oxidation was also affected by sulfite ions. Comparing Figures 7, 9 and 10, the higher the mole ratios of cyanide to copper, the less the effect on the oxidation of copper cyanide and sulfite. This may be related to the distribution of copper cyanide species. At CN:Cu = 3, the dominant discharged species is $Cu(CN)_3^{2-}$ while at CN:Cu > 3.5–4, $Cu(CN)_4^{3-}$ became the dominant discharged species [15]. Probably the discharge of $Cu(CN)_4^{3-}$ is less affected by sulfite. So sulfite has a smaller effect on the oxidation of cyanide. The oxidation of $Cu(CN)_3^{2-}$ is more affected by sulfite. So sulfite has a greater effect on the oxidation of copper cyanide. One effect of sulfite is to reduce the precipitation of copper oxide and so affects the oxidation of copper cyanide. At a concentration of hydroxide below a certain level, sulfite completely suppresses the precipitation of copper oxide. Comparing the anodic behaviour of sulfite [14] and copper cyanide [15] and their mixture, the main anode reactions are:
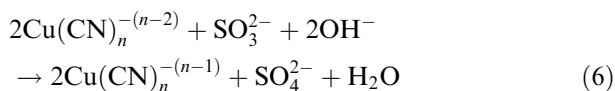
$$Cu(CN)_n^{-(n-1)} \rightarrow Cu(CN)_n^{-(n-2)} + e^- \quad (n = 2, 3, 4) \tag{1}$$

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \tag{2}$$

Some of the cupric cyanide would decompose to produce $(CN)_2$, which would react with hydroxide to form cyanate [15]:

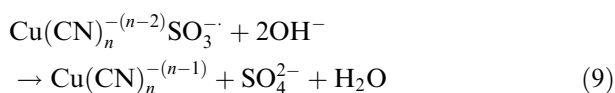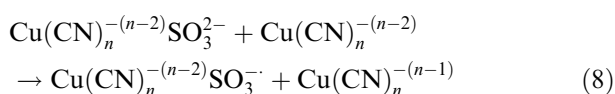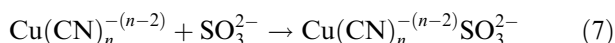$$2Cu(CN)_n^{-(n-2)} + 2CN^- \rightarrow Cu(CN)_n^{-(n-1)} + (CN)_2 \tag{3}$$

$$(CN)_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \tag{4}$$
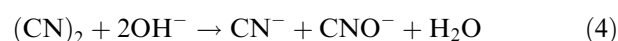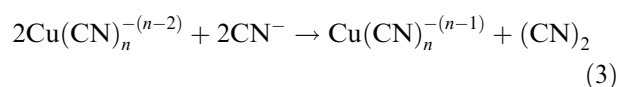
Some of the cupric cyanide would react with hydroxide to form copper oxide:

$$Cu(CN)_n^{-(n-2)} + 2OH^- \rightarrow nCN^- + Cu(OH)_2$$
$$(or\ CuO + H_2O) \tag{5}$$
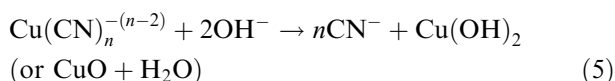
The rest of the cupric cyanide would be reduced by SO_3^{2-}:

$$2Cu(CN)_n^{-(n-2)} + SO_3^{2-} + 2OH^-$$
$$\rightarrow 2Cu(CN)_n^{-(n-1)} + SO_4^{2-} + H_2O \tag{6}$$

Reaction 6 might undergo the following steps similar to the reaction between ferricyanide and sulfite [17]:

$$Cu(CN)_n^{-(n-2)} + SO_3^{2-} \rightarrow Cu(CN)_n^{-(n-2)}SO_3^{2-} \tag{7}$$

$$Cu(CN)_n^{-(n-2)}SO_3^{2-} + Cu(CN)_n^{-(n-2)}$$
$$\rightarrow Cu(CN)_n^{-(n-2)}SO_3^{\cdot -} + Cu(CN)_n^{-(n-1)} \tag{8}$$

$$Cu(CN)_n^{-(n-2)}SO_3^{\cdot -} + 2OH^-$$
$$\rightarrow Cu(CN)_n^{-(n-1)} + SO_4^{2-} + H_2O \tag{9}$$

With decreasing pH, Reactions 4 and 5 were suppressed. Therefore, more Cu(II) was stabilized in the solution and reduced by sulfite and cyanide and the amount of precipitated copper oxide decreased. When pH was below a certain value, the rate of the production of $(CN)_2$ (Reaction 3) was much higher than the consumption rate for Reaction 4 and so $(CN)_2$ was evolved. With increasing CN:Cu mole ratio, Reaction 5 was suppressed and so the precipitation of copper oxide was suppressed since Cu(II) was stabilized and reduced in the cyanide rich environment [15]. If Reaction 6 follows the procedure expressed by Reactions 7–9 and Reaction 9 is not the rate-determining step, when pH is not so low that sulfite species shift from SO_3^{2-} to HSO_3^- or further SO_2, the rate of Reaction 6 is not affected by pH. Therefore, with decreasing pH, more Cu(II) can be reduced resulting in the precipitation of less copper oxide. When pH become so low that sulfite species shift from SO_3^{2-} to HSO_3^- or further SO_2, the rate of Reaction 6 may decrease with decreasing pH. At a high CN:Cu mole ratio (e.g., 1 M Cu, 4 M CN^-), $Cu(CN)_4^{3-}$ was the dominant charge species [15] and the anodic current efficiency of sulfite was low. $Cu(CN)_4^{2-}$ was probably not efficiently reduced by sulfite ions.

From Figures 7 and 8, Reaction 1 is enhanced by sulfite ions when $n = 3$. Since cuprous ions can form the mixed copper cyanide with other ligands such as $Cu(CN)_3^{2-}\ SCN^-$ [16], perhaps some of SO_3^{2-} might be bound to $Cu(CN)_3^{2-}$ and form $Cu(CN)_3^{2-}\ SO_3^{2-}$ which might be discharged faster than $Cu(CN)_3^{2-}$. So the oxidation of sulfite and copper cyanide is significantly catalysed. With increasing mole ratio of cyanide to copper, the concentration of $Cu(CN)_3^{2-}$ is decreased and $Cu(CN)_4^{3-}$ became the dormant discharged species. Therefore, it is less affected by sulfite ions.

4. Summary

The anodic behaviour of mixed sulfite and copper cyanide is not just the sum of sulfite and copper cyanide when they are present separately in the solution. Sulfite oxidation is enhanced by the oxidation of copper cyanide.

The effect of sulfite on the oxidation of copper cyanide decreases with increasing mole ratio of cyanide to copper. This is related to the shift in the discharged species from $Cu(CN)_3^{2-}$ to $Cu(CN)_4^{3-}$ with increasing mole ratio of cyanide to copper. Sulfite ions affect the discharge of $Cu(CN)_3^{2-}$ more than that of $Cu(CN)_4^{3-}$.

Sulfite is oxidized to sulfate. At [Cu] = around 1 M, CN:Cu = 3–3.2, $[OH^-]$ = 0.05–0.25 M, $[SO_3^{2-}]$ = 0.4–0.6 M and the temperature = 50–60 °C, the anodic current efficiency of sulfite reached 80–90%. The above condition is suitable for obtaining a good copper deposition current efficiency and therefore for industrial application conditions. With further increase in sulfite concentration, the anodic current efficiency of sulfite will not be increased, but the cost of sulfite will increase. Further increase in CN:Cu mole ratio will result in a decrease in the anodic current efficiency of the anodic oxidation of sulfite and also in copper deposition current efficiency.

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