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Electrochemical treatment of dilute cyanide solutions containing zinc complexes by oxidation at carbon felt (Sigratherm)

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Abstract

The electrochemical oxidation of dilute solutions containing cyanide complexes of zinc using a carbon felt anode is described. The composition of the solution was determined using stability constants for particular complexes. The application of a GFA5 electrode enables the oxidation of cyanides (10 mmol dm^{-3}) in 99.2% at 0.7 V and 30 C (1.5 Q_t). Under these conditions, the electrical energy consumption is about 24 kWh (kg CN^-)$^{-1}$. Modification of the anode surface with copper oxides allows a cyanide conversion degree of 99.6% at 0.7 V and 17.5 C (0.875 Q_t) with electrical energy consumption of 17.6 kWh (kg CN^-)$^{-1}$. However, modification of the anode resulted in 75% destruction.

1. Introduction

Electroplated zinc coatings are widely used for the protection of cast iron and steel against corrosion. Alkali-cyanide baths are commonly used. Thus, cyanide complexes with zinc often occur in the plating rinsewater dispensed from electroplating plants. Electrochemical oxidation is the common method for destruction of concentrated wastewater containing cyanides. Electrochemical methods are not efficient if the cyanide concentration drops below 1 g dm^{-3}. This is due to the mass transport limitations and the resultant low current efficiency. This problem can be solved by application of electrode materials of high specific surface area together with activation by metal oxides [1–4]. A further interesting solution may be application of trickle towers with Raschig rings and feeder electrodes made of carbon cloth [5, 6]. Carbon fibre was found to be a suitable electrode material not only for electrochemical oxidation of cyanides but also for removal of copper and cadmium from their cyanide solutions [7–11].

The aim of this work was to investigate the applicability of carbon felt (Sigratherm type GFA5) for oxidation of cyanides from complexes with zinc. It was envisioned that application of carbon felt GFA5 as an electrode material in processes carried out under potentiostatic conditions would minimise energy losses due to the low concentration of substrates.

2. Experimental details

All the experiments were carried out in a cell with undivided electrode compartments under potentiostatic conditions and at room temperature. The anode was a carbon felt (Sigratherm, type GFA5). The main properties of the electrode were as follows [12]: weight per unit area 470–600 g m^{-2}; specific surface (BET method) < 1.0 m^2 g^{-1}; longitudinal resistivity 1.5–2.5 Ω mm and transverse resistivity 3–4 Ω mm.

The anode surface area was about 0.07–0.08 m^2. The cathode consisted of platinum in the form of a wire around the working electrode. Its surface area was about 8 cm^2. The potential of the working electrode was measured against a saturated calomel electrode (SCE).

Solutions were prepared using doubly distilled water and reagent-grade chemicals without further purification. A stock solution of 2.5 mmol dm^{-3} $K_2[Zn(CN)_4]$ was prepared by mixing two parts of KCN with one part of $Zn(CN)_2$ in 0.1 mol dm^{-3} NaOH. A stock solution of 3.0 mmol dm^{-3} $K_3[Cu(CN)_4]$ was prepared by mixing one part of CuCN with three parts of KCN in 0.01 mol dm^{-3} NaOH.

Changes in cyanide concentration during electrolyses were determined by square wave voltammograms recorded using a hanging mercury drop electrode (HMDE). To determine the copper ion concentration, samples of 0.2 ml of analysed solutions were added to 10 ml of 0.5 mol dm^{-3} H_2SO_4. For zinc ions, samples of 5 ml of analysed solution were added to 5 ml of 1.9 mol dm^{-3} NaOH. Solutions were purged with argon prior to recording the square wave voltammograms using the HMDE in order to remove dissolved oxygen, which can be reduced in the recorded potential range. All voltammetric measurements were carried out at a frequency of 200 Hz using an Autolab system (EcoChemie, Holland).

Modification of the anode by the deposition of copper oxides was carried out by electrooxidation in a solution of 3.0 mmol dm^{-3} $K_3[Cu(CN)_4]$ (pH 12) at a constant potential of 1.1 V and electrical charge of 0.9 Q_t (Q_t is the theoretical electrical charge for total cyanide oxidation) [9].

During all electrolyses the solutions were purged with argon in order to remove dissolved oxygen which can oxidize Cu(I). Experiments with the non-modified anode were carried under the same conditions. The flow rate of argon was such that further increase did not bring about an increase in the current value at the specified potential. Purging with argon also achieved stirring of the solution, which caused a decrease in concentration gradients in the pores of the working electrode.

3. Results and discussion

3.1. *Distribution of zinc and cyanide ions in complexes*

During electrooxidation of $K_3[Cu(CN)_4]$ solution (0.5 mol dm^{-3} NaOH), the content of copper cyanide and hydroxide complexes changed [9, 13, 14]. This was caused by different rates of cyanide ion oxidation and copper ion reduction. Similar changes can be expected in the content of cyanide complexes with zinc during electrooxidation.

A composition of the $K_2[Zn(CN)_4]$ solution (0.1 mol dm^{-3} NaOH) was calculated using stability constants of particular cyanide and hydroxide complexes with zinc [15, 16]. Results of equilibrium calculations are presented in Figures 1 and 2. The content of zinc ions in various cyanide and hydroxide complexes was as follows:

$$Zn^{2+} = 0.00\% \qquad Zn(OH)_2 = 1.36\%$$
$$[Zn(CN)_3]^- = 0.10\% \qquad [Zn(OH)_3]^- = 12.90\%$$
$$[Zn(CN)_4]^{2-} = 7.99\% \qquad [Zn(OH)_4]^{2-} = 38.79\%$$
$$[Zn(CN)_3(OH)]^{2-} = 36.40\% \qquad [Zn(CN)_2(OH)]^- = 2.45\%$$

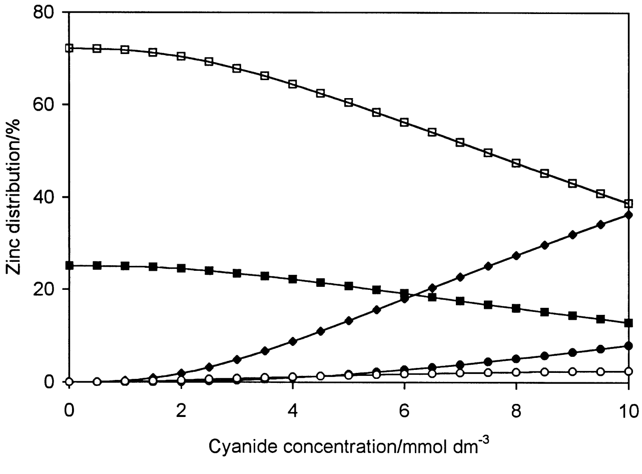

Fig. 1. Distribution of zinc ions in cyanide, hydroxide and mixed complexes in a solution of 2.5 mmol dm^{-3} $K_2[Zn(CN)_4]$ at pH 13; (●) $[Zn(CN)_4]^{2-}$, (◆) $[Zn(CN)_3(OH)]^{2-}$, (○) $[Zn(CN)_2(OH)]^-$, (■) $[Zn(OH)_3]^-$, (□) $[Zn(OH)_4]^{2-}$.

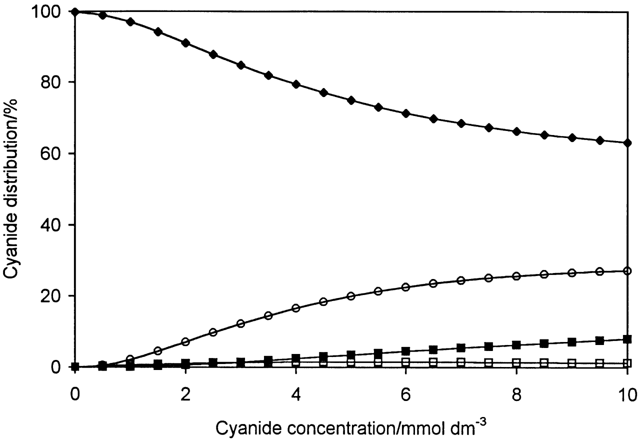

Fig. 2. Distribution of cyanide ions in zinc complexes in a solution of 2.5 mmol dm^{-3} $K_2[Zn(CN)_4]$ at pH 13; (◆) CN^-, (■) $[Zn(CN)_4]^{2-}$, (○) $[Zn(CN)_2(OH)]^{-2}$, (□) $[Zn(CN)_2(OH)]^-$.

The content of cyanide ions in various complexes with zinc ions were as follows:

$$CN^- = 63.74\% \qquad [Zn(CN)_3(OH)]^{2-} = 27.30\%$$
$$[Zn(CN)_4]^{2-} = 7.99\% \qquad [Zn(CN)_2(OH)]^- = 1.23\%$$

These ion distributions demonstrate that more than half the cyanide ions in the solution are not involved in formation of complexes. The remaining ions mainly form a mixed complex with three cyanide ligands and one hydroxide ligand. Also, zinc ions form hydroxide complexes. Knowledge of the distributions of complexes is important during analysis of simultaneous cyanide electrooxidation and zinc ion reduction.

3.2. *Electrooxidation of cyanides at non-modified carbon felt*

3.2.1. *The effect of applied potential*

Cyclic voltammograms recorded on GFA5 carbon felt in a solution of 2.5 mmol dm^{-3} $K_2[Zn(CN)_4]$ are presented in Figure 3. Electrooxidation of cyanides at GFA5 starts at a potential of 0.4 V and is irreversible. Electroreduction of zinc ions from complexes present in the solution starts at a potential of -1.47 V.

The dependence of the degree of cyanide conversion on anode applied potentials was determined at constant electrical charge (Figure 4).

In the potential range 0.7–0.8 V, the cyanide conversion is almost constant and close to 82%. A further increase in anode potential causes a significant decrease in cyanide conversion to about 50%. Presumably this is due to a competitive reaction of oxygen adsorption and evolution on the carbon felt. Therefore, current efficiency also decreases to 50%.

Cyanide electrooxidation in alkaline media can yield the following oxidation products [1]:

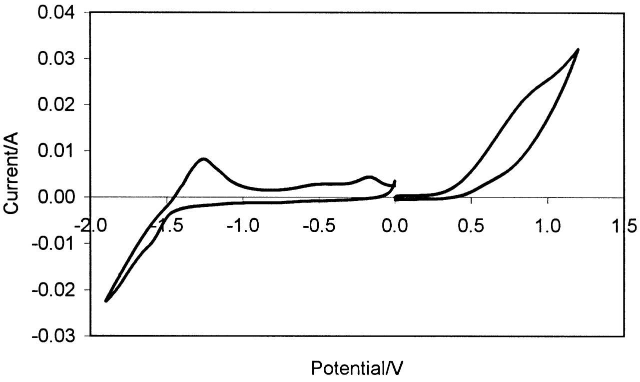

Fig. 3. Cyclic voltammograms on GFA5 carbon felt in a solution of 2.5 mmol dm^{-3} $K_2[Zn(CN)_4]$ for oxidation and reduction; $v = 0.01$ V s^{-1}.

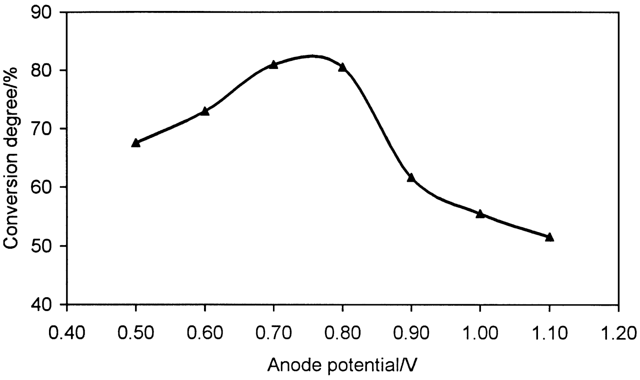

Fig. 4. Dependence of cyanide conversion on anode potential at constant electrical charge $Q_t = 20$ C.

$$CNO^- + H_2O + 2\,e^- \rightarrow CN^- + 2\,OH^- \qquad E^\circ = -0.97\,V \qquad (1)$$

$$CO_2 + 0.5\,N_2 + 2\,H^+ + 5\,e^- \rightarrow CN^- + 2\,OH^- \qquad E^\circ = -0.49\,V \qquad (2)$$

$$C_2N_2 + 2\,e^- \rightarrow 2\,CN^- \qquad E^\circ = -0.18\,V \qquad (3)$$

$$CO_3^{2-} + NO_3^- + 6\,H^+ + 10\,e^- \rightarrow CN^- + 6\,OH^- \qquad E^\circ = +0.14\,V \qquad (4)$$

Electrochemical oxidation of cyanide complexes with heavy metals such as copper, cadmium and zinc can proceed in a very similar way and at similar rate to free cyanides [17]. However, this oxidation must be preceded by dissociation of complexes. It was envisioned that this dissociation would proceed quickly enough not to limit the rate of the overall process. However, it was also discovered that cyanide complexes with copper can be directly anodically oxidized [18].

During electrolyses under the above conditions, zinc ions were not reduced at the cathode. The voltage between the electrodes during electrolysis at 1.1 V was about 2.6 V, which means that the cathode potential must have been higher than −1.5 V. The cathode potential at this level is too low for zinc reduction. During electrooxidation of cyanide complexes with copper and cadmium, both metals were cathodically deposited [8, 9, 11].

3.2.2. *Effect of applied electrical charges*

Electrolyses at various electrical charges (higher than Q_t) were carried out at a constant anode potential of 0.7 V vs SCE. The dependence of cyanide conversion on electrical charges is presented in Figure 5. The highest conversion (above 99.2%) was obtained with an electrical charge 1.5 times higher than Q_t. However, under this condition the current efficiency decreased to about 65%. The electrical energy consumption was relatively high, about 24.3 kWh (kg CN^-)$^{-1}$.

Comparison of selected results with results obtained at WRW5 carbon fibre in electrooxidation of the same dilute cyanide solutions containing zinc complexes [13] are summarized in Table 1. The geometric surface area of WRW5 (specific surface area 2.5 m^2 g^{-1}) was similar to the GFA5 surface. Table 1 shows that although the WRW5 anode has a higher specific area, the yield of cyanide electrooxidation is much lower than at the GFA5 anode. Electrooxidation at 1.5 Q_t causes the cyanide conversion to be twice as high as in similar processes performed at the WRW5 anode. Moreover, the current efficiency at GFA5 is almost twice as high

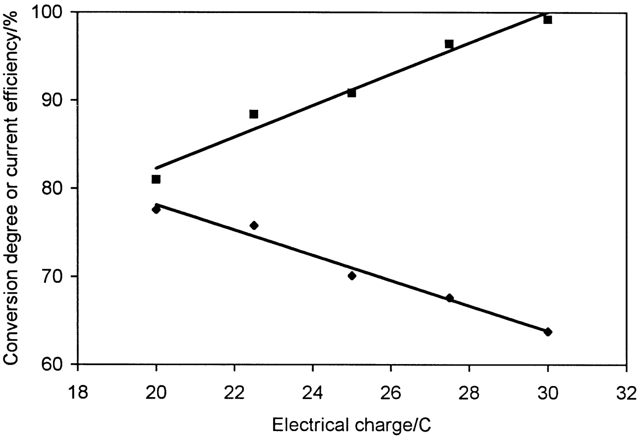

Fig. 5. Dependence of cyanide conversion and current efficiency on the electrical charge during electrolyses at anode potential of 0.7 V; (■) conversion degree, (◆) current efficiency.

Table 1. Comparison of selected results of 2.5 mmol dm^{-3} $K_2[Zn(CN)_4]$ electrooxidation at WRW5 and GFA5 (electrolyses at 0.7 V and electric charge Q_t)

Parameter	Anode type	
	WRW5	GFA5
Cyanide conversion degree/%	43	81
Current efficiency/%	42	78
Electrical energy consumption/kWh (kg CN^-)$^{-1}$	35.79	21.71

Table 2. Selected results of two-step electrolyses

Parameter	Process	
	Cyanide electrooxidation I step	Zinc electroreduction II step
Potential/V	0.7	−1.7
Electrical charge/C	1.5 Q_t	3 Q_t
Conversion degree/%	99.6	>99.6
Current efficiency/%	66.6	31.9

and the electrical energy consumption is about 14 kWh (kg CN^-)$^{-1}$ lower than at WRW5.

Since zinc ions are not reduced on the cathode during the cyanide electrooxidation, treatment of plating rinse-water containing cyanide and zinc ions should be carried out in two steps: first by cyanide electrooxidation followed by zinc reduction. Two-step electrolyses were carried out on the GFA5 carbon felt in the same cell under optimum parameters for cyanide oxidation and zinc reduction. The same electrode (GFA5) was initially used as anode and subsequently as cathode. Selected results are presented in Table 2. The electrical energy consumption calculated for the two-step electrolysis is about 3.58 kWh (kg $K_2[Zn(CN)_4]$)$^{-1}$.

3.3. *Electrooxidation of cyanides on modified carbon felt*

Modification of carbon fibre with copper oxides brings about an increase in the cyanide conversion and a substantial decrease in the electrical energy consumption in the electrooxidation of cyanide complexes with copper or cadmium [8, 9, 11]. Therefore, similar results could be expected for electrooxidation of cyanide complexes with zinc.

3.3.1. *The effect of applied electrical charges*

The dependence of cyanide conversion on electrical charge (Figure 6) was determined at a constant potential (0.7 V) of the modified anode which appeared to be the best for the non-modified electrode. The highest conversion (above 99.6%) was obtained at an electrical charge lower than the theoretical charge (20 C) for the total cyanide oxidation. This was due to the catalytic effect of the Cu(III)–Cu(II) redox couple (probably CuO(OH)–CuO) present at the modified anode surface [1]. Within the range 16–18 C, the difference between the experimental and theoretical conversion calculated on the basis of the electrical charge, becomes slightly lower. This is probably due to longer durations of electrolyses and, in consequence, higher destruction of the anode modification. The destruction of the anode modification is caused by chemical dissolution in cyanides, especially at concentrations higher than 1 mmol dm^{-3} [1].

Electrochemical oxidation of cyanides on the modified GFA5 anode proceeds simultaneously with zinc ion reduction on the cathode. The dependence of the degree of zinc removal on electrical charge was determined at constant anode potential (Figure 7). During cyanide electrooxidation at a potential of 0.7 V and at an electrical charge ranging from 15 to 17.5 C, zinc ions were remove with only 20% yield. This low yield was a result of the low voltage between the electrodes which was about 2.4 V. This means that the cathode potential must have been higher than −1.7 V. Our investigation of the zinc ion electroreduction suggests that the optimum potential is −1.7 V [19]. Simultaneously with the reduction of zinc ions, reduction of copper ions was observed. Copper ions were present in the solution due to degradation of the anode modification. The concentration of copper ions was quite low (0.5 mmol dm^{-3}) and constant within the investigated range of electrical charges.

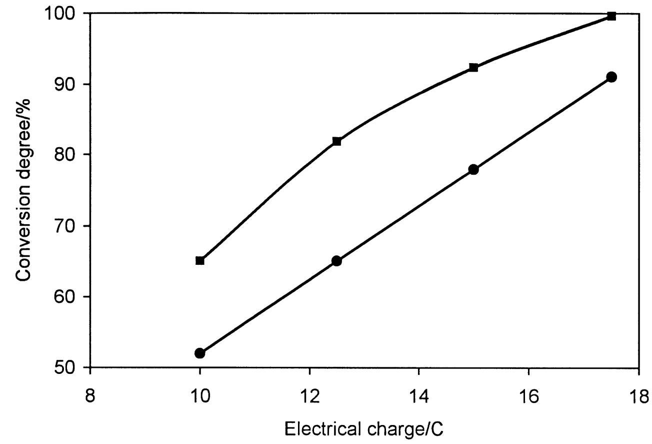

Fig. 6. Dependence of the cyanide conversion at the modified electrode on the electrical charge at an anode potential of 0.7 V; (■) experimental degree, (●) theoretical degree.

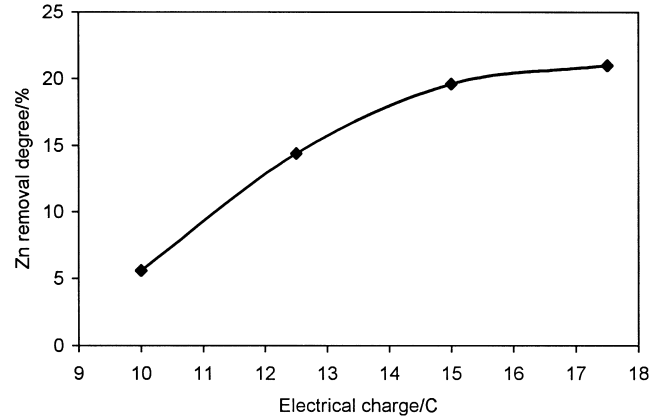

Fig. 7. Effect of electrical charge on the removal of zinc ions during cyanide electrooxidation at a constant anode potential of 0.7 V.

3.3.2. *Effect of the applied potential*

Degradation of the anode modification with copper oxides depends on the applied anode potential. The effect of applied potential on cyanide conversion was determined at a constant electrical charge of 0.5 Q_t. This electrical charge was chosen because the cyanide con-

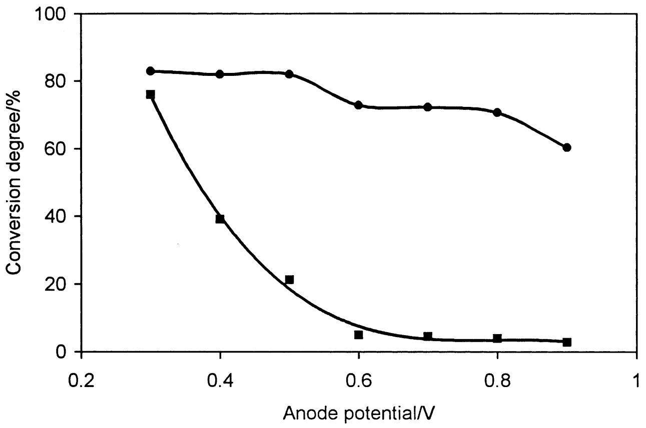

Fig. 8. Dependence of cyanide conversion and zinc removal on anode potential at constant electrical charge of 0.5 Q_t; (●) cyanide conversion degree, (■) zinc removal degree.

version obtained during electrolyses at 0.7 V and 0.875 Q_t was very high (99.6%). The dependence of cyanide conversion on anode potential is presented in Figure 8. The highest conversion (about 80%) was achieved within the potential range 0.3–0.5 V. An increase in potential above 0.5 V brought about a decrease in conversion to 60%. The decrease in the cyanide conversion does not support a mechanism of cyanide electrooxidation on electrodes modified with copper oxides [1]. This mechanism involves anodic conversion of Cu(II) to Cu(III), starting at a potential above 0.2 V, and formation of hydroxide radicals at Cu(III) sites. That is,

$$S + OH^- \rightarrow S(^{\bullet}OH)_{ads} + e^- \quad (5)$$

$$S(^{\bullet}OH)_{ads} + CN^- + OH^- \rightarrow S + CNO^- + H_2O + e^- \quad (6)$$

$$\text{net} \quad CN^- + 2\,OH^- \rightarrow CNO^- + H_2O + 2\,e^- \quad (7)$$

We expected that the increase in anode potential would cause higher cyanide conversion, due to the increase in the amount of hydroxide radicals formed.

Simultaneously with cyanide electrooxidation at an anode potential of 0.3 V, zinc ions were deposited on the cathode in 76% during the electrolysis. An increase in anode potential causes a significant decrease in zinc removal to about 4% at 0.9 V. Zinc ions in alkali-cyanide baths can be reduced from their zincate ions on a cathode while the following equilibria exist in a solution [20, 21]:

$$[Zn(CN)_4]^{2-} + 4\,OH^- = [Zn(OH)_4]^{2-} + 4\,CN^- \quad (8)$$

$$[Zn(CN)_3(OH)]^{2-} = Zn(OH)^+ + 3\,CN^- \quad (9)$$

Partial dissociation of the mixed cyanide-hydroxide complexes (Reaction 9) proceeds very slowly. In the next step an addition of OH^- ion to $Zn(OH)^+$ proceeds quickly:

$$Zn(OH)^+ + 2\,OH^- = [Zn(OH)_3]^- \quad (10)$$

According to Bockris [22], the electrochemical reduction of zinc ions in alkaline solutions proceeds in four steps:

$$[Zn(OH)_4]^{2-} = [Zn(OH)_3]^- + OH^- \quad (11)$$

$$[Zn(OH)_3]^- + e^- = [Zn(OH)_2]^- + OH^- \quad (12)$$

$$Zn(OH)_2^- = Zn(OH) + OH^- \quad (13)$$

$$Zn(OH) + e^- = Zn + OH^- \quad (14)$$

The second step (Reaction 12) determines the overall rate of the process. The significant decrease in the removal of zinc ions during electrolyses performed at higher potentials was brought about by the simultaneous evolution of hydrogen on the cathode and/or very slow reaction (9).

In addition to zinc ions, copper ions (resulting from the degradation of the anode modification) were also reduced on the cathode. The amount of copper ions in solution after electrolyses was nearly constant (about 0.5 mmol dm^{-3}) and independent of anode potential. The amount of copper ions deposited on the cathode was also nearly constant (about 0.5 mg). This means that the modification of the anode surface was degraded by approximately 75% during experiments at various anode potentials.

The electrical energy consumption during electrolyses at 0.7 V and 0.875 Q_t at the GFA5 anode modified with copper oxides was about 6.7 kWh $(kg\ CN^-)^{-1}$ lower than at the anode without modification. Under the above conditions, normalized volumetric power consumption calculated for 90% CN^- conversion per unit volume reactor according to Walsh et al. [23] was 5.93 kW m^{-3}.

4. Conclusions

The results clearly demonstrate that carbon felt of Sigratherm type GFA5 can be used as an effective electrode material in electrooxidation of dilute cyanide solutions (10 mmol $(dm^3\ CN^-)^{-1}$) containing complexes with zinc. The optimum parameters for cyanide electrooxidation are an anode potential of 0.7 V and an electrical charge of 1.5 Q_t. Using such parameters the electrical energy consumption is about 24.3 kWh $(kg\ CN^-)^{-1}$ and the current efficiency is 64%. Under such conditions, zinc ions are not deposited on the cathode due to its low potential. Therefore, treatment of plating rinsewater containing cyanide and zinc ions should be carried out in two steps: first by cyanide electrooxidation followed by zinc electroreduction. Results of the cyanide electrooxidation on the GFA5 anode are significantly better than results obtained at the WRW5 anode, even though the specific surface area of

GFA5 is 2.5 times smaller than that of WRW5. Most importantly, the cyanide conversion and current efficiency are almost twice as high as for conversion at WRW5 under the same conditions.

Modification of GFA5 with copper oxides enables a higher cyanide conversion to be achieved. This is caused by the catalytic effect of the Cu(II)—Cu(III) redox couple. Simultaneously, the zinc ion reduction is observed on the cathode. The modification of the anode surface also helps decrease the electrical energy consumption to 17.6 kWh (kg CN^-)$^{-1}$.

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