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Voltammetric evaluation of the electrode material on the oxidation of cyanide catalyzed by copper ions

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Abstract The cyanide oxidation on vitreous carbon (VC), stainless steel 304 (SS 304) and titanium (Ti) was investigated through a voltammetric study of cyanide solutions also containing copper ions. Results showed that cyanide oxidation occurs by means of a catalytic mechanism involving adsorbed species as CN^- , $\text{Cu}(\text{CN})_4^{3-}$ or $\text{Cu}(\text{CN})_4^{2-}$ depending on the electrode material. It was observed that on VC, the adsorption of $\text{Cu}(\text{CN})_4^{3-}$ controlled the oxidation rate. Instead, for SS 304 and Ti, the adsorption of CN^- controlled the global process. However, in all cases, the adsorption of $\text{Cu}(\text{CN})_4^{3-}$ on the electrode surface was required for the catalytic oxidation of CN^- . Voltammetric experiments for solutions containing cyanide oxidation products, such as cyanogen ($\text{CN})_2$ and cyanate (CNO^-), confirmed that the adsorbed species mentioned above controlled the catalytic oxidation of CN^- depending on the electrode material. A voltammetric identification of the oxidation products showed that cyanogen, ($\text{CN})_2$ tended to adsorb on VC, while the formation of cyanate, CNO^- predominated on SS 304.

Keywords Adsorbed species · Cyanide oxidation · Catalyzed oxidation · Cyano-copper ions

Introduction

In the last 20 years, several processes have been developed trying to avoid cyanide solutions during the extraction of precious metal [1–7]. However, the cyanide-leaching technology remains the most effective due to its high selectivity for gold and silver separation. On the other hand, the awareness of high toxicity of cyanide has prompted governmental regulations requiring treatment of the leaching solutions prior to disposal. An effective pre-disposal treatment for industries dealing with high concentration of cyanide is the addition of some chemicals as HClO or H_2O_2 . The principal product of these processes is the cyanate ion, CNO^- [8, 9]. In particular, the treatment with hydrogen peroxide is more efficient in the presence of heterogeneous catalyst but it tends to produce an explosive reaction [10].

Electrochemical oxidation of cyanide is an attractive alternative since no volatile toxic compounds, such as chlorine, are produced [11]. The electrolytic process also avoids any explosion risk. Furthermore, it can be used to treat concentrated cyanide solutions (>100 ppm) at lower cost [12].

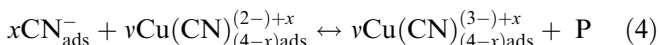
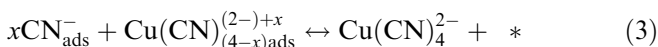
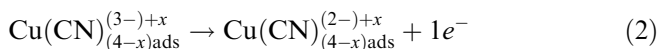
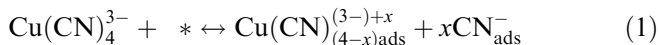
The presence of cyano-copper ions offers the possibility to deplete cyanide concentration by means of a catalytic oxidation [12, 13]. Even if the ion $\text{Cu}(\text{II})$ (cyano-copper ion) oxidizes CN^- in solution, it is well known that the catalytic heterogeneous reaction increases the velocity of cyanide oxidation [12].

About the catalytic oxidation of cyanide, the most studied case is an electrolytic process using metallic anodes covered with a thin copper oxide film [14, 15]. The cyanide oxidation mechanism, in those studies, was described as a homogeneous oxidation occurring via the cyclic reversible interchange of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$. However, the copper oxide layer (CuO), previously prepared, showed to be unstable for cyanide concentrations above 1 mM [14, 15]. In that case, the oxide layer dissolved in solution and the catalytic oxidation process was limited by the concentration of cyanide ions.

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Another case based on platinum rotating disk electrode studies in 0.2 M CN^- and Cu(I) solution proposed a heterogeneous mechanism through adsorbed cyanic species for the catalytic oxidation of cyanide [16]:



where * represents the active sites on the electrode surface, ads is the adsorbed species, ν is the stoichiometric adsorption coefficient on the electrode surface after copper oxidation and P the cyanide oxidation products. It is significant to note that reactions 3 and 4 will be in competition depending on the value of ν .

Hofseth and Chapman proposed that copper-cyanide ions such as Cu(I) = $\text{Cu}(\text{CN})_4^{3-}$ and Cu(II) = $\text{Cu}(\text{CN})_4^{2-}$ may dissociate to some degree upon adsorption; i.e., while Cu(I) and $\text{Cu}(\text{I})_{\text{ads}}$ have the same oxidation state on the central copper atom, they do not necessarily have the same number of cyanide ions coordinated in the adsorbed complex [16]. On the other hand, they avoided the formation of a copper oxide film due to $[\text{CN}^-] > 1 \text{ mM}$.

In the present study the authors propose the evaluation of the electrode material influence on the catalyzed oxidation of cyanide through cyanide and cyano-copper adsorbed ions in an industrial residue of the gold and silver extraction process. In this case, even if the copper species are initially in solution, the copper oxide formation on the electrode surface was avoided by the high cyanide concentration (0.1 M CuCN, 0.5 M KCN at pH 10).

Since the heterogeneous catalytic oxidation involves adsorbed species in all steps, the substrate plays a fundamental role in the process. For this reason, voltammetric studies of cyanide electrochemical oxidation on vitreous carbon (VC), stainless steel 304 (SS 304) and titanium (Ti) were carried out using 0.1 M CuCN, 0.5 M KCN at pH 10. These materials were selected because they are commonly used as electrodes in industrial electrolytic processes. Using the last three different materials, we determined the influence of the substrate on a heterogeneous reaction mechanism presented in Eqs. 1, 2, 3 and 4. Additionally, this study let to establish a criterion to select the most convenient material for the oxidation of cyanide by means of an electrogenerated catalyst.

The products formed from the catalyzed cyanide oxidation were also identified by voltammetric measurements on the three different substrates, using prepared solutions of $(\text{CN})_2$ and CNO^- .

Materials and methods

The voltammetric experiments were carried out in a typical three-electrode cell with inert atmosphere (nitrogen). The counter electrode was an isolated graphite rod (Alfa AESAR 99.99% purity) and the reference was a saturated calomel electrode (SCE). The working electrode was fabricated with rods of different materials: Vitreous Carbon (VC), Stainless Steel 304 (SS 304) and Titanium (Ti). The electrodes area were 0.20 cm^2 for VC (of Electrosynthesis Company), 0.03 cm^2 for SS 304 (C 0.08% wt, Si 1% wt, Mn 2% wt, Cr 19% wt and Ni 9% wt) and 0.12 cm^2 for Ti (98.8% of purity). Prior to experiments, each working electrode was polished to a mirror finish with 0.3 μm alumina, rinsed with deionized water, submitted to an ultrasonic bath during 5 min to remove traces of alumina, and finally rinsed with deionized water.

The surface characterization of each working electrode was performed in 0.6 M KOH, pH 10 and 0.6 M KCN, pH=10 by a cyclic potential scan. This test showed any possible passivation or oxide film formation on the electrode surface, before the cyanide oxidation.

Cyanide oxidation was performed in three solutions: (1) 0.15 M CuCN and 0.45 M KCN (CN/Cu=4); (2) 0.12 M CuCN and 0.48 M KCN (CN/Cu=5) and (3) 0.1 M CuCN and 0.5 M KCN (CN/Cu=6). The pH was fixed at 10 for all solutions. The solution with CN/Cu=6, (main interest for this study) ensures the predominance of $\text{Cu}(\text{CN})_4^{3-}$ [17]; this ratio was similar with that considered on a study of cyanide decomposition in a packed-bed electrochemical reactor [13]. Under this consideration, it was assumed that the concentration of free CN^- for this work was 0.2 M.

In order to characterize the cyanide oxidation products, a cyanogen solution was prepared mixing 0.1 M CuSO_4 and 0.2 M KCN, according to a well-known procedure [18]. The 1 M cyanate solution was prepared dissolving KCNO (Aldrich, A.R.) in deionized water (18 $\text{M}\Omega\text{-cm}^{-1}$). To change the surface adsorption preferences of cyanide species, Triton 100X (Merck, A.R.) was used as surfactant. This experimental series was also performed at pH 10 (adjusted with NaOH) and 25°C.

All solutions were de-oxygenated by bubbling nitrogen 10 min prior to each experiment. During the experiments, the nitrogen flow was maintained at the solution surface. A potentiostat/galvanostat PARC 273 EG & G commanded with software M270 was used for all the experiments.

Results and discussion

Predominant chemical species in the solution

For solution containing 0.1 M CuCN and 0.5 M KCN, CN/Cu=6 at pH 10, the thermodynamic diagram of the

system Cu(II)/Cu(I)/CN/H₂O [12, 17] predicts the formation of Cu(CN)₄³⁻ species as the predominant species of Cu(I) in solution [17]. For Cu(II) formed in the interface, the predominant species could be Cu(CN)₄²⁻. The free cyanide concentration in all solutions was greater than 1 mM, thus the formation of CuO film on the electrode surfaces was not expected [19].

Substrate influence in CN⁻ oxidation

Non catalyzed oxidation

Cyclic voltammograms on VC and SS 304 are presented in Fig. 1a, b, respectively for aqueous solutions at pH 10 without cyanide (curve i) and with cyanide (curve ii). The voltammetric curves show that on VC (Fig. 1a(ii)), the cyanide oxidation (without copper) took place at a potential range from $E=0.3$ V vs. SCE to $E=1.2$ V vs. SCE in view of a greater current density. However, for SS 304 (Fig. 1b) the oxidation process can not be directly attributed (from $E=0.3$ V vs. SCE to $E=0.7$ V vs. SCE) to the cyanide degradation because SS 304 substrate is also liable to be corroded in contact with cyanide solutions [11].

For the Ti substrate (Fig. 2), two different behaviors were presented: one for the first potential scan and the other for the subsequent potential scans. Figure 2a shows an oxidation process in the presence and absence of cyanide. However, the oxidation potential in the solution of KOH (Fig. 2a(i)) is more positive than that in cyanide solution ($\Delta E = 0.3$ V vs. SCE, Fig. 2a(ii)). This means that the cyanide may improve the oxidation process only in the first potential scan. On the sub-

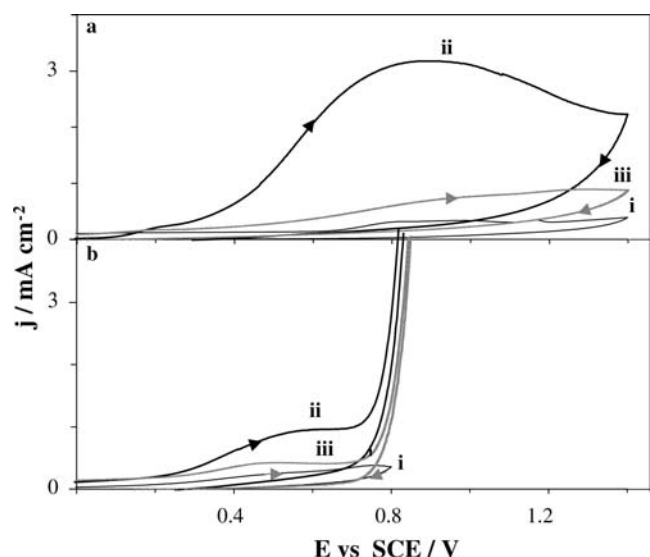


Fig. 1 Typical cyclic voltammograms (scan rate 20 mVs⁻¹) obtained from aqueous solution containing: i) 0.6 M KOH, ii) 0.6 M KCN and iii) 0.6 M KCN and 900 ppm of Triton 100X at pH 10. The substrates were: **a** Vitreous Carbon electrode and **b** Stainless Steel 304 electrode

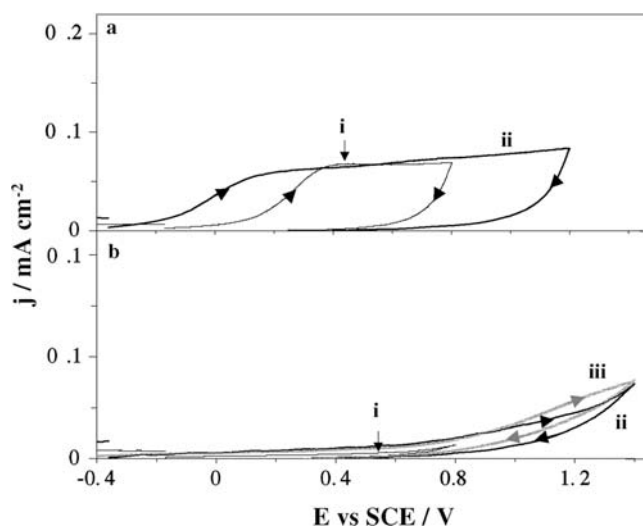


Fig. 2 Typical cyclic voltammograms (scan rate 20 mVs⁻¹) obtained from aqueous solution containing: i) 0.6 M KOH, ii) 0.6 M KCN and iii) 0.6 M KCN and 900 ppm of Triton 100X at pH 10 on Ti electrode. **a** First potential scan and **b** subsequent potential scans

sequent scans, titanium surface was passivated (see Figs. 2a, b). From these results, it was established that titanium substrate was oxidized under alkaline conditions (pH 10) during the first potential scan and that cyanide oxidation may occur within the range of $E=0.2$ V vs. SCE to $E=0.8$ V vs. SCE.

Catalyzed oxidation

To study the influence of Cu(I) in solution, two experiments were compared. Figure 3 shows the contrast between solutions without Cu(I) (Fig. 3(i)) and with Cu(I) (Fig. 3(ii)). It is clear that the presence of Cu(I) improved the oxidation current density. In this case, there is, likely, a catalytic EC process for CN⁻ oxidation due to the cyclic conversion of Cu(II) (appeared after oxidizing CN⁻) to Cu(I) [16]. Additionally, voltammetric curves on VC (Fig. 3a) and SS 304 (Fig. 3b) show the maximum current density at $E_{p_{ox}}=0.72$ V vs. SCE and $E_{p_{ox}}=0.55$ V vs. SCE, respectively. Given the form of these two voltammograms, the oxidation process may occur by three different paths: adsorbed electroactive species, mass transfer limitation of the electroactive species, or passivation of the electrode subsequent to the oxidation process. Meanwhile the oxidation processes on Ti (Fig. 3c), did not attain any maximum of current density confirming a passivation of the electrode.

The differences between current density scales and the voltammograms by themselves in Fig. 3 indicate, as expected, that the substrate plays an important role in the catalytic oxidation of cyanide. The catalytic oxidation current density for cyanide is higher on SS 304 (Fig. 3b(ii)) than on VC (Fig. 3a(ii)), whereas the catalytic oxidation rate on Ti (Fig. 3c (ii)) is considerably lower than on VC.

To elucidate a possible oxidation of SS 304, a lab experiment with two plates of SS 304 was performed. One of them was immersed in cyanide solution and the other one in copper cyanide solution. After 2 days, the SS 304 did not show any corrosion effect and moreover its voltammetric behavior remained the same. This fact confirmed that the oxidation process in the Fig. 3b(ii) was not attributed to the SS 304 corrosion.

In order to determine between mass transport limitation or adsorbed species phenomena, the study of CN^- catalytic oxidation on the three different substrates (VC, SS 304 and Ti) was done changing the switching potential (E_s) in the positive scan. All the experiments were repeated for the three substrates with stirring and without stirring (Fig. 4).

Analyzing the results of the previous experimental series, the mass transfer control of electroactive species before the peak potential ($E_{p_{\text{ox}}}$) has been discarded. The evidence was a higher current density for the unstirred over the stirred solution (Figs. 4a(i), 4b(ii), respectively)

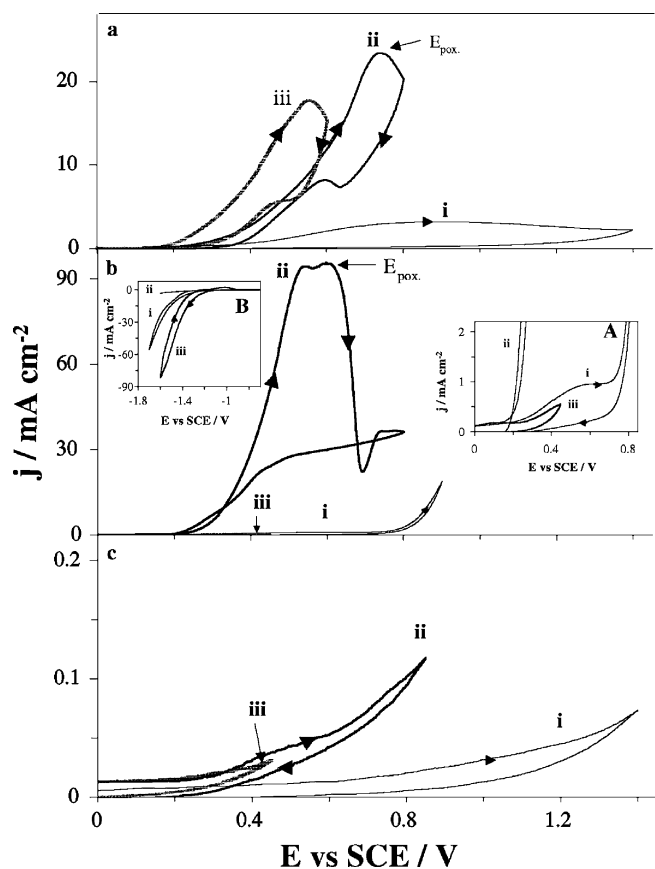


Fig. 3 Typical cyclic voltammograms (scan rate 20 mVs^{-1}) obtained from aqueous solution containing 0.6 M of total CN^- at $\text{pH } 10$ on different electrodes **a** Vitreous Carbon, **b** Stainless Steel 304 and **c** Ti electrodes. The voltammograms were obtained (i) without Cu(I) , (ii) in the presence of 0.1 M Cu(I) and (iii) in the presence of 0.1 M Cu(I) and 900 ppm of Triton 100X. The inset shows: (A) anodic and (B) cathodic part of the voltammograms for the SS304 electrode

when $E_s < E_{p_{\text{ox}}}$ on VC and SS 304. Moreover, the stirred solution did not present any displacement of the oxidation process to more positive potentials. On the other hand, a variation of the current density peak, on VC and SS 304 electrodes, versus the scan rate indicated strong adsorption of the electroactive species (experimental data not included) [20]. Dipping into the analysis of the voltammetric curves, we assume that the current density decrease, under stirred conditions (Fig. 4b(ii)) at potentials near to $E_{p_{\text{ox}}}$, could be associated to the change of the CN^-/Cu molar ratio on the electrode surface as have been observed by Lu et al. [21].

To support the hypothesis of adsorbed species on the electrode, voltammetric curves of the oxidation process were obtained for different CN^-/Cu molar ratios (the total cyanide concentration was fixed to 0.6 M) on VC, SS 304 and Ti electrodes. In Fig. 5, the VC electrode (Fig. 5a) presented a shifting of the oxidation potential to more positive values as the CN^-/Cu molar ratio increased. At the same time, the current density decreased for a selected potential (see Figs. 5a(i–iii)). These results are in agreement with a study of the anodic oxidation of copper cyanide on graphite [21]. In contrast, on SS 304 and Ti electrodes (Figs. 5b, c), the increase of the CN^-/Cu molar ratio shifted the oxidation potential to less positive values and the current density values increased for a constant potential (Figs. 5b(i–iii) and c(i–iii)).

Based on the heterogeneous mechanism presented in Eqs. 1, 2, 3 and 4, we attempted to determine how each electrode material changes the reaction path. It is important to remember that the charge transfer step (Eq. 2) was always considered the most rapid and irreversible process due to the applied overpotential. In addition, reactions 3 and 4 must be in competition depending on the stoichiometry of $\text{Cu(II)}_{\text{ads}}$.

The preferential adsorption of CN^- on VC implied greater mol number of CN^-_{ads} in Eq. 1, thus the inhibition of $\text{Cu(I)}_{\text{ads}}$ and consequently the avoidance of $\text{Cu(II)}_{\text{ads}}$ produced by Eq. 2. When diminishing CN^-/Cu ratio (with constant CN^- concentration) greater amount of $\text{Cu(I)}_{\text{ads}}$ was favored, then production of Cu(II) through reaction 3 is preferred over reaction 4. Moreover, the formation of Cu(II) is reflected on the current density decrease at a constant potential (see Fig. 5a), i.e., the regeneration of $\text{Cu(I)}_{\text{ads}}$ was stopped. A confirmation of this fact was an EPR spectrum of the resulting solution after an anodic electrolysis on VC showing the presence of Cu(II) in solution (i.e., the catalyst $\text{Cu(I)}_{\text{ads}}$ was not completely regenerated).

On the other hand, for SS 304 and Ti, the preferential adsorption of $\text{Cu(I)}_{\text{ads}}$, thus production of $\text{Cu(II)}_{\text{ads}}$ by Eq. 2, points out that reaction 4 was favored; however, because of the less amount of CN^-_{ads} , the current density decreases involving less quantity of oxidation products (see Figs. 5b, c).

The previous results indicated that the catalytic EC oxidation of cyanide on all the substrates is certainly limited by adsorbed species CN^-_{ads} , $\text{Cu(I)}_{\text{ads}}$ and/or $\text{Cu(II)}_{\text{ads}}$ (see Eqs. 1, 2, 3 and 4).

Changing the interfacial adsorption phenomena by means of a surfactant

Considering that EC catalytic oxidation of cyanide involves different adsorbed species, the same procedure discussed above was performed adding Triton 100X (900 ppm) to the testing solutions. It is well known that surfactants change the adsorption phenomena on an electrode surface, thus the copper–cyanide system would show remarkable differences in presence of Triton 100X.

The first potential scans were done at the same potential range considered before but using a free cyanide solution 0.6 M KOH at pH 10 with and without surfactant. This study showed a non-electrochemical response for the three substrates in both solutions (results not shown). In order to determine the action of the surfactant on the adsorbed species, a voltammetric sequence for the three electrodes in solution 3, containing 0.6 M KCN was performed. The presence of Triton 100X provoked a considerable decrease on the current density of electrochemical cyanide oxidation (Figs. 1, 2). It was noticed that current density decreases when the CN^- was not adsorbed on the surfaces of the VC and SS

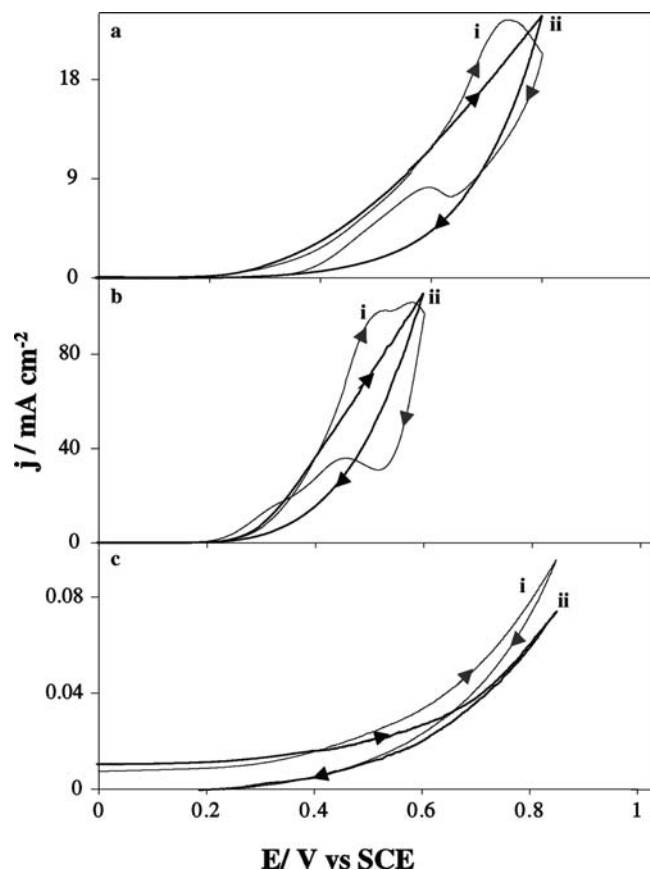


Fig. 4 Typical cyclic voltammograms (scan rate 20 mVs^{-1}) obtained from aqueous solution containing 0.6 M total CN^- and 0.1 M Cu(I) at pH 10 when switching potentials (E_s) were more positive than $E_{p_{ox}}$ on different electrodes **a** Vitreous Carbon, **b** Stainless Steel 304 and **c** Ti electrodes. The voltammograms were obtained in: (i) unstirred solution and (ii) stirred solution

304 (Fig. 1a(iii), b(iii)); being more important the decrease on the VC surface; whereas titanium surface did not show any important difference between those voltammograms (Fig. 2b(iii)).

The presence of surfactant in a solution containing 0.6 M KCN and 0.1 M Cu(I) on VC provoked a higher current density, at the same potential as observed for the surfactant-free solution (Fig. 3a(ii, iii)). This is due to the decrease of adsorbed cyanide species involved in the heterogeneous mechanism of the catalytic oxidation (Eqs. 1, 2, 3 and 4) and the consequent decrease of CN/Cu molar ratio analyzed in Fig. 5a.

In contrast for SS 304 in a solution containing Triton 100X, the cyanide oxidation was energetically less favorable (inset A of the Fig. 3b(iii)). The oxidation current density value was similar to those obtained in the voltammetric response of the free copper solution (see Fig. 3b(i) and inset A on Fig. 3b(iii)). When the potential scan varied toward negative potential values (shown in Fig. 3 inset B), surfactant had a very significant effect on hydrogen evolution, e.g., by modifying the adherence of bubbles to the electrode. This behavior indicated that the cyanide oxidation could also diminish because the presence of Triton 100X. For the SS 304 surface the adsorption of Cu(I) is more important than that of CN^- , avoiding the cyanide oxidation through

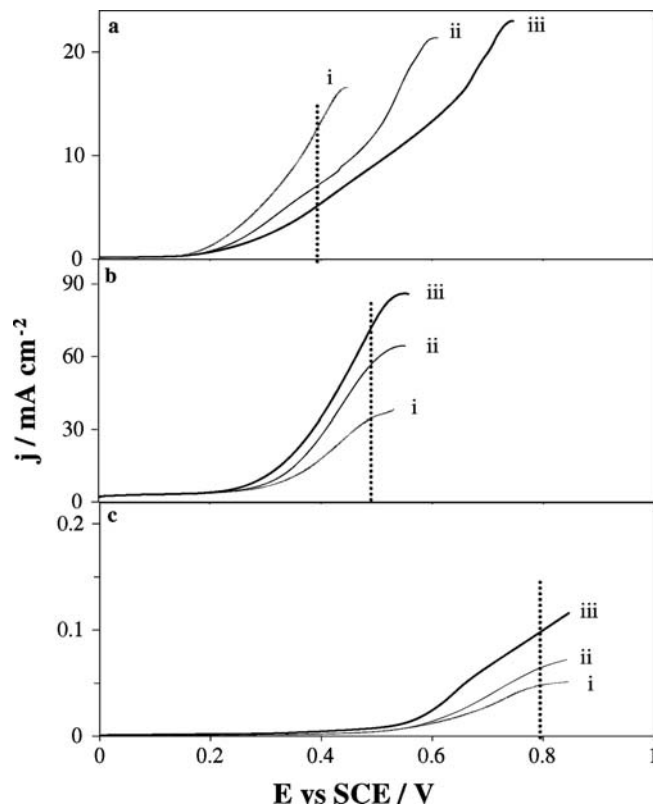
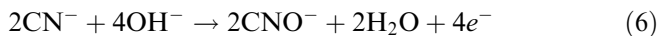


Fig. 5 Typical voltammograms (scan rate 20 mVs^{-1}) obtained from aqueous solutions, pH 10 and containing different $\text{CN}^-/\text{Cu(I)}$ ratios (i) $\text{CN}^-/\text{Cu(I)} = 4$, (ii) $\text{CN}^-/\text{Cu(I)} = 5$ and (iii) $\text{CN}^-/\text{Cu(I)} = 6$ on different electrodes **a** Vitreous Carbon, **b** Stainless Steel 304 and **c** Ti

heterogeneous mechanism (Eqs. 1, 2, 3 and 4) (necessarily involving Cu(I) species) and favoring an homogeneous mechanism described by the Eqs. 5 or 6:



Once again, we confirmed that the adsorbed species limiting catalytic cyanide oxidation are different on VC than on SS 304. $\text{Cu(I)}_{\text{ads}}$ or $\text{Cu(II)}_{\text{ads}}$ are easily adsorbed on SS 304, but the cyanide adsorbed species, CN^-_{ads} , is the controlling factor for the catalytic cyanide oxidation rate. Meanwhile, on VC, the CN^-_{ads} species was preferentially adsorbed, but the $\text{Cu(I)}_{\text{ads}}$ or $\text{Cu(II)}_{\text{ads}}$ species control the catalytic cyanide oxidation rate.

Additionally, SS 304 and Ti electrodes showed similar behavior. The current density, in the presence of surfactant (Fig. 3c(iii)), was smaller than the current density in surfactant-free solution (Fig. 3c(ii)). This means that the heterogeneous cyanide oxidation process is probably controlled by the same adsorbed species for these two electrode materials. Finally, the identification of the oxidation products, P, was done using the linear potential scan technique.

Characterization of CN^- oxidation products

Reports of cyanide oxidation in solutions containing copper have shown that the main oxidation product is cyanogen $(\text{CN})_2$ [12, 16, 19], whose stability depends on pH. These studies, carried out with copper modified electrodes, established that cyanogen in alkaline pH reacts rapidly with hydroxide to form CNO^- and CN^- [14, 15]. In studies using metals other than copper, the direct product of cyanide oxidation was cyanate, CNO^- [11, 23]. This suggests that the product of the heterogeneous reaction mechanism will also depend on the electrode material.

To generate the cyanide oxidation products by an EC mechanism, an electrolysis experiment was performed for each electrode material applying an anodic pulse for 120s.

Figure 6a(i), b(i) and c(i) shows the voltammograms obtained just after each electrolysis. Assuming that the oxidation products were at the electrode surface and they did not change, considerably, their concentration during the scan time ~ 90 s, these curves were compared with those obtained for $(\text{CN})_2$ on VC (Fig. 6a(ii)), and CNO^- (Fig. 6b(iii) and 6c(iii)) on SS 304 and Ti.

The voltammograms comparison suggested that the oxidation product on VC electrode is cyanogen $(\text{CN})_2$ (see Fig. 6a(i), 6a(ii)) even the current density difference and the potential shift of the cyanogen reduction. To support this fact, different switching potentials towards positive E_{λ} values in a stirring copper cyanide solution were performed. Those experiments showed that $(\text{CN})_{2\text{ads}}$ species produced during the oxidation process have remained adsorbed on the VC surface (results not shown). The formation of $(\text{CN})_{2\text{ads}}$ indicated that CN^- adsorption

onto VC was, indeed, stronger than onto the other substrates, supporting our previously stated hypothesis.

Figure 6b(i) and c(i) shows reduction peaks at the potential interval -0.4 to -1.25 V vs. SCE on SS 304 and -1.3 to -1.5 vs. SCE on Ti. These peaks could be attributed to the reduction of the products formed by the catalytic oxidation of cyanide. These curves were compared with the voltammetric responses for the reduction scan of a 0.1 M CNO^- solution (Fig. 6b(iii) on SS 304 and c(iii) for Ti). For SS 304 both curves presented one peak in the same potential range, indicating that the reduction process should be the same. Nevertheless, the expectation of greater current density for greater CNO^- concentration and the lack of experimental references about the reduction of CNO^- to CN^- suggest the performance of in situ UV spectra to elucidate the cyanate reduction phenomena.

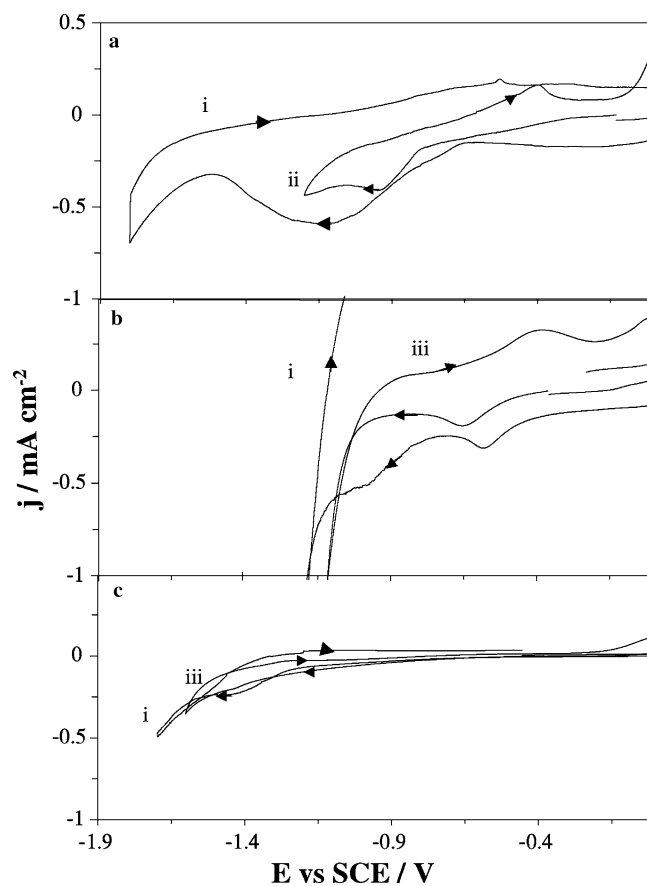


Fig. 6 Typical cyclic voltammograms (scan rate 20 mVs^{-1}) obtained on different electrodes: **a** Vitreous Carbon, **b** Stainless Steel 304 and **c** Ti. The voltammograms were obtained from aqueous solution at pH 10, containing different compounds: (i) 0.6 M total CN^- and 0.1 M Cu(I) , (ii) cyanogen (in VC) and (iii) 0.1 M cyanate (in SS 304 and Ti). Curves (i) were obtained after imposing a potential pulse (0.6 , 0.85 and 0.7 V vs. SCE on VC, SS 304 and Ti, respectively) during 120 s. The scan potential for curves (ii) and (iii) were initiated in the cathodic direction from open circuit potential

The previous results suggest that the catalytic cyanide oxidation product is also $(\text{CN})_2$ on SS 304 and Ti. However it immediately disproportionates:



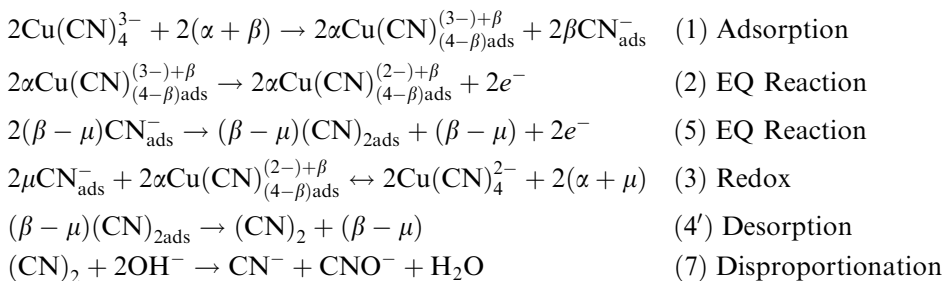
Thus, the corresponding reduction process was not observed. All these facts confirmed that the adsorption of CN^-_{ads} controls the heterogeneous catalytic cyanide oxidation on SS 304. The greater adsorption of Cu(I) or Cu(II) species on SS 304 surface seems to inhibit the adsorption of formed $(\text{CN})_2$ (favors its desorption). In that case, it may abandon the interfacial space to come into the solution and facilitate its disproportionation. For the Ti surface, we could not establish the same expectation because, as it was demonstrated, the surface is passivated into the alkaline medium.

Conclusions

The oxidation of CN^- catalyzed by Cu(I) is an heterogeneous process where the electrode material plays a crucial role. We have shown that CN^- adsorbs preferentially on the VC electrode, while on SS 304 it was either the Cu(I) or Cu(II) electrogenerated during the catalytic process.

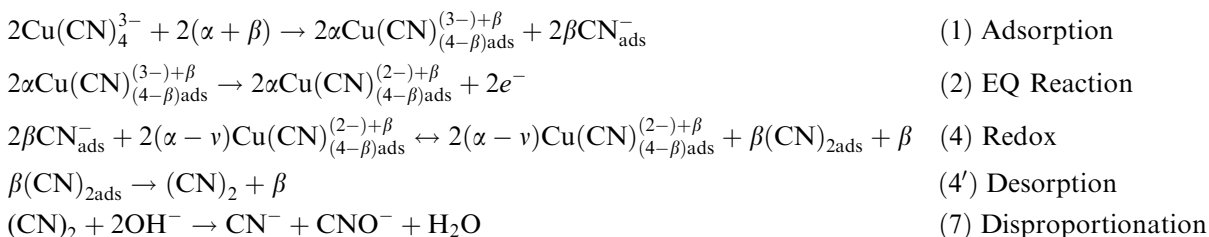
Based on the mechanism of Hofseth and Chapman (Eqs. 1, 2, 3 and 4), the working electrode is supposed as a surface with certain number of adsorption sites *. Considering that those sites can be differentiated between those occupied by cyano-copper ions (α) and those occupied by cyanide (β), then $* = \alpha + \beta$. The proposal now is a reaction pathway depending on the electrode material.

For VC ($\alpha \leq \beta$):



(steps 4' and 7 have low probability of occurrence).

For SS 304 ($\alpha > \beta$):



For this reason, the species controlling the catalytic oxidation on VC were the $\text{Cu(I)}_{\text{ads}}$ and/or $\text{Cu(II)}_{\text{ads}}$; while on SS 304 and Ti electrodes the controlling species is the CN^-_{ads} . Although the voltammetric study contains sufficient information to sustain these conclusions, in-situ spectrometric techniques would be useful to confirm the species participating on the mechanism.

According to the heterogeneous EC mechanism (Eqs. 1, 2, 3 and 4), cyanogen $(\text{CN})_2$ is the product, initially formed in catalyzed CN^- oxidation on unmodified electrodes. On the SS 304 and Ti electrodes, the cyanogen species quickly reacts with hydroxide to form the CNO^- species as a final product (Eq. 7), while the adsorption of $(\text{CN})_2$ on the VC electrode avoids disproportionation.

Even if CN^- is a chemical species that favors the SS 304 corrosion, we have demonstrated that in the presence of copper-cyanide, corrosion was not expected.

Regarding the Ti surface, we have noticed that it was passivated, in all cases, after the first voltammetric scan.

In the characterization of CN^- oxidation products, we could suggest that the CNO^- species is the final product, as mentioned before.

The results of this work show that toxic cyanide solutions from the metallurgical industry can be converted to low toxicity solutions using unmodified electrodes taking advantage of the catalytic effect of electrogenerated $\text{Cu(II)}_{\text{ads}}$ (see the proposed mechanisms). These results show that SS 304 is the most convenient material for the electrolytic process.

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References

- Oropeza MT (1991) M.Sc. Thesis, Universidad Autónoma Metropolitana-Iztapalapa, México
- Han KN, Xinghui M (1992) US Patent 5114687
- Palomar ME (1992) B.Sc. Thesis, Universidad Autónoma Metropolitana-Iztapalapa, México
- Oropeza MT, González I and Palomar ME(1991) Mexican Patent 9101212
- Lamb FE (1982) US Patent 4342592
- Wang XH (1992) In: Woods R, Richardson PE (eds) *Electrochemistry in mineral and metal processing III*. Electrochemical Society, Pennington, p 452
- Dadgar A, Howarth J (1992) In: Woods R, Richardson PE (eds) *Electrochemistry in mineral and metal processing III*. Electrochemical Society, Pennington, p 478
- Ramaldo RS (1983) *Introduction to wastewater treatment processes*, 2nd edn. Academic, New York, p 533
- Eckenfelder, Wesley W (1989) *Industrial water pollution control*, 2nd edn. McGraw-Hill, New York, p 303
- Park, Chang W (1997) *Environ Tech* 18:557
- Tissot P, Fragnière M (1994) *J Appl Electrochem* 24:509
- Hofseth CS, Chapman TW (1999) *J Electrochem Soc* 146:199
- Ho SP, Wang YY, Wan CC (1990) *Water Res* 24:1317
- Wels B, Johnson DC (1990) *J Electrochem Soc* 137:2785
- Hofseth CS, Chapman TW (1992) *J Electrochem Soc* 139:2525
- Hofseth CS, Chapman TW (1991) *J Electrochem Soc* 138:2321
- Zhang Y, Fang Z, Muhammed M (1997) *Hydrometallurgy* 46:251
- Cotton FA, Wilkinson G (1976) *Química Inorgánica Avanzada*. Limusa, México, p 325
- Katagiri A, Yoshimura S, Yoshizawa S (1981) *Inorg Chem* 20:4143
- Bard AJ, Faulkner LR (1980) *Electrochemical methods*. Wiley, New York, p 529
- Lu J, Dreisinger DB, Cooper WC (2002) *J Appl Electrochem* 32:1119
- Reyes-Cruz V (1980) M.Sc. Thesis, Universidad Autónoma Metropolitana-Iztapalapa, Mexico
- Feng J, Johnson DC (1990) *J Appl Electrochem* 20:116