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The effect of impurities on the anodic process in an industrial pyrophosphate copper bath

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The galvanic pyrophosphate copper bath is long-lasting, reliable, easy to run and produces a good quality deposit even in continuous operation. It is therefore widely used in industry both for the protection of ferrous materials and in the manufacture of brass-plated cords for radial tyres. However, this type of bath is particularly sensitive to impurities. This paper presents the results of a voltammetric study on the effects of chloride, sulphate, nitrate and phosphate anions and ammonia on the anodic process in an industrial pyrophosphate copper bath.

1. Introduction

Steel may be protected from corrosion by electrodeposition of successive layers of different metals. Owing to problems connected with the dilatation thermal coefficients, the layer in direct contact with the steel should preferably be copper. The copper coating of steel wires is of industrial importance in the manufacture of brass-plated cords for radial tyres and for high pressure pipes in plastic materials. In such industrial processes the pyrophosphate copper bath is most commonly used because it gives a good quality deposit, is reliable, durable and easy to operate. This well-known bath has been the subject of recent studies [1, 2], but the operating conditions employed were different from those used in industry. More recent studies have concentrated on the morphological characteristics of the copper deposit [3] in relation to determining the optimum composition of the bath (Tables 1, 2). The different operating parameters used in industry are also reported in Table 1.

Although very reliable, the pyrophosphate bath is sensitive to the presence of impurity ions; the most common of these are chloride, sulphate and phosphate ions, deriving respectively from improperly demineralized waters, from previous sulphur pickling and from the hydrolytic degradation of the pyrophosphate ion, according to the reaction

$$P_2O_7^{4-} + H_2O \longrightarrow 2HPO_4^{2-}$$

Preliminary tests demonstrated that Fe^{3+} and Pb^{2+} can be detrimental to the quality of the electrodeposited copper. The effects of these ions will be discussed in another paper. As far as the effect of chloride ion is concerned, experimental observations have indicated that it causes cavitation with violet spots.

In the present paper the influence of phosphate, sulphate and chloride anions and of ammonia and nitrates on the dissolution process of the copper anode has been studied. For a bath to be run for a long time (2 or more years), electrolysing continuously, the efficiency of the anodes must be close to 100% and never lower than that of the cathode. It is therefore imperative to prevent passivation of the anodes.

2. Experimental details

2.1. *Instruments*

Experiments were carried out using an AMEL

0021-891X/86 $03.00 + .12

Table 1. Composition and characteristic operating conditions of a standard pyrophosphate bath (SPB) for the copper coating of steel

Composition of SPB	*Mol* l^{-1}
$Cu(P_2O_7)_2^{6-}$	0.455
$P_2O_7^{4-}$	0.13
$HP_2O_7^{3-}$	0.13
$CuH(P_2O_7)_2^{5-}$	traces
$CuP_2O_7^{2-}$	traces
$H_2P_2O_7^{2-}$	traces

Operating conditions in industry: t = 20–50° C; pH = 8.8 ± 0.1; current density = $10-20\,A\,dm^{-2}$; cathodic efficiency > 95%; bath density = $1.35-1.45\,kg\,l^{-1}$.

apparatus (consisting of models 550, 564, 560, 667) and equipped with a Perkin Elmer recorder (mod 023) and a MGW–Lauda thermostat.

2.2. *Electrodes*

The cell [5] consisted of a three-electrode system:

Working electrode: copper 99.999%, area $1\,cm^2$, mounted in resin, polished with emery paper No. 220–No. 1000 and diamond paste $1.0-0.26\,\mu m$, degreased with alcohol and dried with ethanol.

Reference electrode: saturated calomel electrode (SCE)(all reported potential values are referred to this electrode).

Counter electrode: two bars of graphite placed symmetrically on each side of the copper electrodes.

Table 2. Equilibrium constants of a standard pyrophosphate bath (SPB) for the copper coating of steel

	Equilibrium constants at 25° C [4]
$H_4P_2O_7/H_3P_2O_7^-$	0.85
$H_3P_2O_7^-/H_2P_2O_7^{2-}$	1.49
$H_2P_2O_7^{2-}/HP_2O_7^{3-}$	5.77
$HP_2O_7^{3-}/P_2O_7^{4-}$	8.22
$Cu(P_2O_7)_2^{6-}/Cu(P_2O_7)^{2-}$	2.3
$Cu(P_2O_7)^{2-}/Cu^{2+}$	6.7

2.3. *Reagents*

All reagents used were analytical grade. A stock solution was prepared from $K_4P_2O_7 \cdot 3H_2O$ and $Cu_2P_2O_7 \cdot 5H_2O$ (standard pyrophosphate bath, SPB) with the composition specified in Table 1. The required amount of each of the anions studied was added to a known volume of SPB immediately before every measurement and the pH was adjusted to 8.8 ± 0.05 by adding $H_4P_2O_7$.

2.4. *Measurements*

The measurements at 25 ± 0.1° C were carried out under a N_2 atmosphere with continuous stirring of the solutions for a maximum amplitude of no more than 1 V at the following scanning rates: 2, 5, 10 and $20\,mV\,s^{-1}$. Each measurement was repeated for four consecutive cycles.

2.5. *XPS–Spectra*

The experiments were performed at the 'ESCA–Service Center' of the National Council of Research (CNR) in Rome using a VG ESCA-3 MK-II spectrometer equipped with a hemispherical electrostatic analyser. Oil diffusion pumps fitted with cold traps produced a vacuum of 5×10^{-10} Torr. Al–$K_{\alpha 1,2}$-radiation ($h\nu$ = 1486.6 eV) was employed to record the spectra. The binding energies were calibrated with the binding energy of the Au $4f_{7/2}$ electrons of gold (83.8 eV).

3. Results and discussion

3.1. *Preliminary measurements*

The voltammogram obtained using 0.1 M pyrophosphate electrolyte at pH = 8.8 (scan rate = $2\,mV\,s^{-1}$) was characterized by a broad region of anodic dissolution with weakly pronounced current peaks, Fig. 1. The shape of this voltammogram is similar to that reported in the literature [6] for electrolytes containing citrate, borate or phthalate buffers.

The cyclic voltammograms obtained using 1.2 M pyrophosphate (curve a, $2\,mV\,s^{-1}$) and the SPB (curve b, $2\,mV\,s^{-1}$) are shown in Fig. 2.

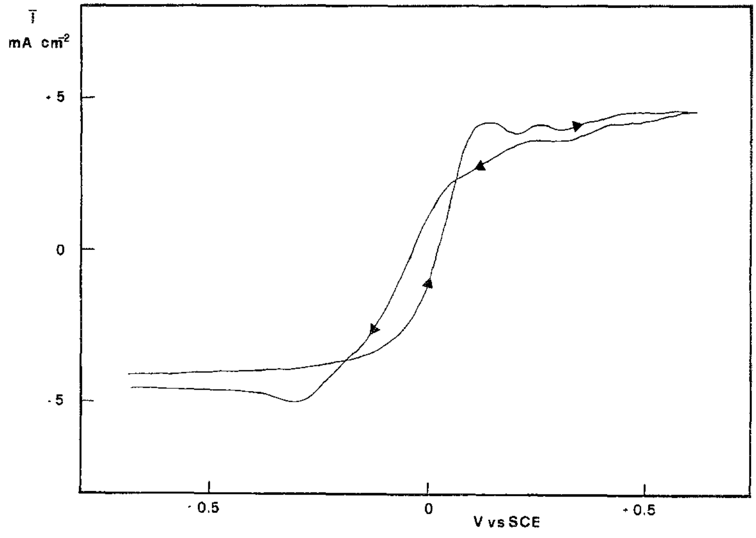

Fig. 1. Voltammogram of copper in 0.1 M $P_2O_7^{4-}$ solution (pH = 8.8; t = 25° C; scan rate = 2 mV s^{-1}; 1st cycle).

Although both solutions have approximately the same total concentration of pyrophosphate ion, 0.9 M pyrophosphate is complexed with copper ion in the SPB. In spite of this, both the voltammograms shown in Fig. 2 are similar but they are quite different from that in Fig. 1.

The voltammograms shown in Fig. 2 are characterized by the fact that only the copper oxidizing processes are present. It can also be observed that the peaks occurring at the more positive potentials in the forward scan (peak IV) and the reverse scan (peak V) shift as shown in Table 3 in going from curve a (1.2 M pyrophosphate) to curve b (SPB).

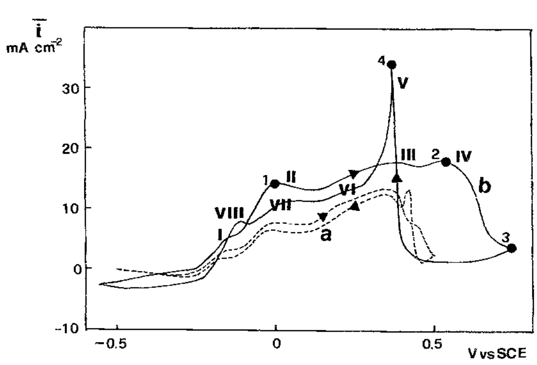

Fig. 2. Voltammograms obtained with: (a) 1.2 M $P_2O_7^{4-}$ solution; (b) standard pyrophosphate copper bath (SPB), as in Table 1 (scan rate = 2 mV s^{-1}; 1st cycle). Roman numerals are used to denote the different peaks while arabic numerals indicate those samples examined by XPS spectrometry.

Of the different peaks, those labelled IV and V are the most affected by variations in the free pyrophosphate concentration. Peak IV is probably due to the interaction of the pyrophosphate ion with the surface. In order to confirm this hypothesis ESCA measurements were performed on samples polarized for 10 min in the SPB for a variety of potential values, as shown in curve b in Fig. 2. In the study of the copper surfaces the peaks Cu 2p 3/2 (signal barycentre BE 933.0 ± 1 eV), Cu_{LMM} (KE 918.3 ± 0.4 eV), K 2p 3/2 (BE 293.3 ± 0.6 eV), P 2p (BE 133.7 ± 0.5 eV), O 1s (BE 531.7 ± 0.8 eV) and C 1s were examined. The preliminary results are reported here. Binding energies were measured relative to the Au 4f 7/2 line (83.8 eV) while the C 1s line (285.0 eV) (due to the vacuum system contamination) was used as internal standard for the charging effect corrections. The deconvolution of the C(1s) signal indicates the presence of carbonate (traces, 288.8 ± 0.7 eV) on the surface and, after sputtering with argon ion, of carbide (284 ± 0.7 eV) [7].

Table 3. Comparison of peaks (mV versus SCE) in curves a and b as seen in Fig. 2

	Curve a	*Curve b*
Peak IV	450	520
Peak V	520	360

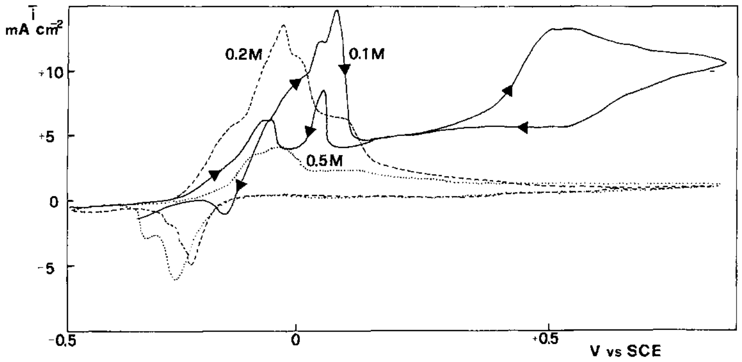

Fig. 3. Cyclic voltammetry in the presence of chloride ion (pH = 8.8; t = 25°C; scan rate = 2 mV s^{-1}; 1st cycle).

A preliminary test carried out on a polished copper mirror dipped for 48 h in SPB showed, surprisingly, the presence of potassium and phosphorus up to a depth of about 11 000 Å. (The amounts of material erased (in Å) were evaluated using the following formula: Å = 0.35 $I(\mu A)$ E(KeV) t(min), where the factor 0.35 is that used for our instrument with argon ion bombardment.)

The atomic ratio (evaluated from the area values and sensitivity factors) [8] between copper and phosphorus in this sample is in the range 1 to 10, increasing with depth; at about 11 000 Å it is of the order of magnitude of 100.

With regard to the oxidation state of copper, the chemical shift between Cu_2O and CuO is only 1.0 eV [9]; therefore the shake-up peak at 934.4 ± 0.8 eV, which is only observed in paramagnetic substances, is used for identification of copper(II) oxide or hydroxide on the metal surface. Moreover, it should be pointed out that Cu_2O and Cu metal cannot be distinguished from the Cu 2p (3/2) signal but only through both the shape of the Cu_{LMM} and O(1s) signals [10–13].

Sample 1, polarized in SPB at 0 mV versus SCE for 10 min. The surface is covered by a very thin film of CuO and Cu_2O; only traces of phosphorous are found.

Sample 2, polarized in SPB at + 520 mV versus SCE for 10 min. A thick film of CuO is formed (the Cu metal appears at a depth of about 7000 Å). The atomic ratio Cu : P varies over the range 2 : 1 to 10 : 1 in the outer 30 Å, while at greater depths the phosphorous is present only in traces.

Sample 3, polarized in SPB at + 730 mV versus SCE for 10 min. Copper is present on the surface as copper(II) and is completely coated with a continuous potassium pyrophosphate film (from two to four phosphorous atoms for each copper atom). The copper metal signal appears at a depth of about 8600 Å.

Sample 4, polarized in SPB at + 460 mV in the reverse scan for 10 min. On the surface the copper is present as CuO, while only traces of potassium and phosphorous are detected; the Cu-metal Auger signals appear immediately after a cleaning sputtering (about 10 Å erased).

These findings appear to support the hypothesis that the peaks occurring at more positive potential values are due to the interaction of pyrophosphate salt with the surface.

3.2. *Chloride ion*

The cyclic voltammogram obtained for SPB with the addition of 0.1, 0.2 and 0.5 M chloride ion are shown in Fig. 3. Examination of the curve obtained for $[Cl^-]$ = 0.1 M revealed: (a) anodic current density is always greater than zero both in the forward and reverse scans; (b) between − 100 and + 100 mV, various peaks of anodic current are present; (c) for potential values between + 100 and + 400 mV the current density is relatively constant, beyond this potential range a maximum current value occurs at + 550 mV; (d) in the reverse scan there are two anodic peaks (+ 55 and − 60 mV) as well as a cathodic current peak at − 160 mV.

Comparison of the three curves shows that: (a) for $[Cl^-] > 0.1$ M the peak at + 550 mV disappears and in the range + 100 to + 400 mV the current density is virtually zero; (b) in the reverse

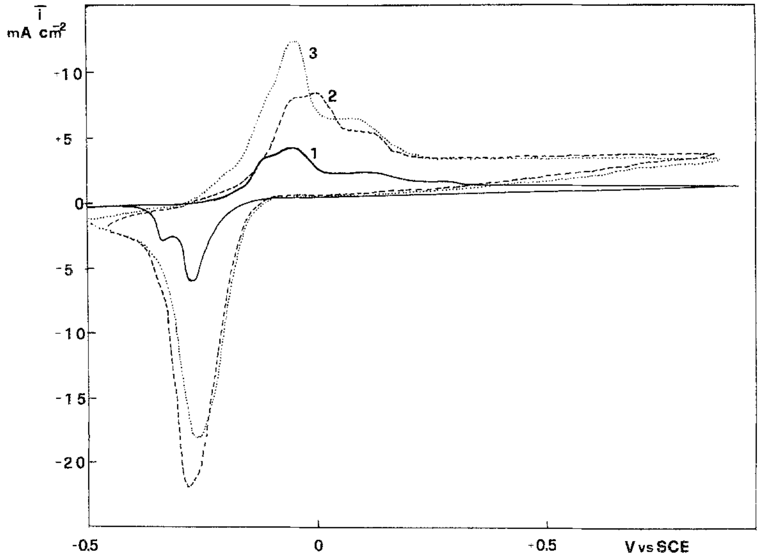

Fig. 4. Cyclic voltammetry in the presence of 0.5 M Cl^- ion: effect of three immediately successive cycles (pH = 8.8; t = 25°C; scan rate = $2\,mV\,s^{-1}$).

scan the current density is always zero and the anodic peaks are absent while the cathodic peak is more intense; (c) on increasing the chloride ion concentration to 0.5 M the cathodic peak shifts toward a more negative potential and splits, thus indicating two different stages of copper ion reduction.

If the peak at +550 mV can be attributed to the interaction between anode surface and pyrophosphate, then the fact that it is also present when $[Cl^-]$ = 0.1 M shows that under such conditions the Cl^- ion and the $P_2O_7^{4-}$ ion compete to occupy the active sites of the anode surface. The co-presence of oxidation and reduction peaks in the reverse scan suggests that the surface is only partially depolarized by the free pyrophosphate present. The relation between the anodic and cathodic current regions indicates that with increasing Cl^- concentration the anodes become much less soluble in the $P_2O_7^{4-}$–Cl^- system and the oxidized superficial film stabilizes.

As shown in Fig. 4, on passing from the first to the third cycle in the 0.5 M Cl^- solution, all peaks appear more pronounced. Therefore the maximum value of the anodic current appears to be controlled by the following factors:

(i) it decreases when the Cl^- concentration increases

(ii) it increases with scan rate

(iii) it increases with a series of successive cycles.

For SPB to which 0.5 M Cl^- was added, the correlation between the maximum value of the anodic current density (+100 mV) and the square root of the scan rate (Fig. 5) results in a straight line through the origin. This shows that at low scan rates the anodic product is soluble and the process is controlled by diffusion. No conclusive remarks can, however, be made regarding the chemical composition of this superficial film.

Earlier literature [14–16] on the anodic behaviour of copper anodes in chloride solution, reported results obtained in acid or neutral sys-

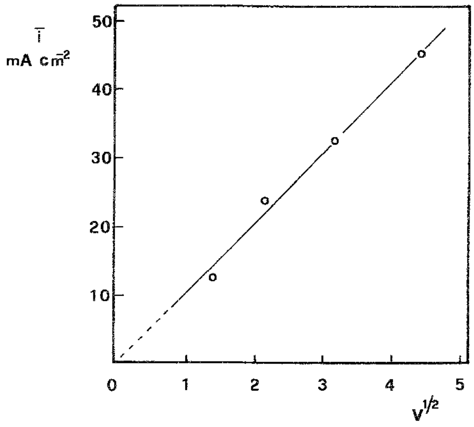

Fig. 5. Correlation between the maximum anodic current density (+100 mV versus SCE) and the scan rate in the presence of 0.5 M chloride ion (1st cycle).

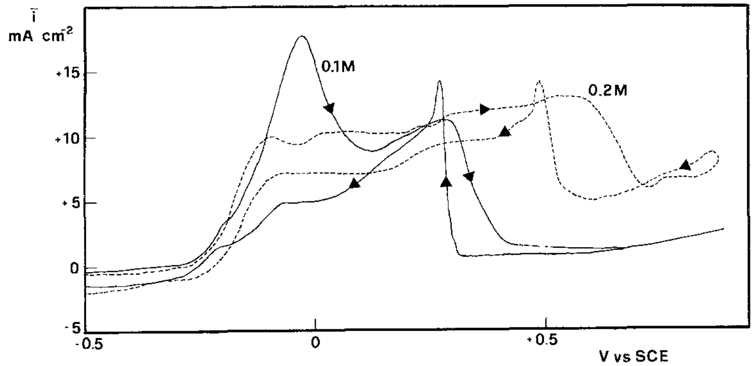

Fig. 6. Cyclic voltammetry in the presence of sulphate ion (pH = 8.8; t = 25° C; scan rate = $2\,\mathrm{mV\,s^{-1}}$; 1st cycle).

tems with the electrolyte either in static conditions or forced to flow between the anodes. These studies have shown the formation of a cuprous chloride film (at $-100\,\mathrm{mV}$) that grows to a considerable thickness. Copper is dissolved as complex ions partly as copper(I) and partly as copper(II). Moreover, it has already been proven [17] that the chloride ion does not always promote corrosion of the copper anodes but in some cases may retard it; such an ion produces radical changes in the dissolution kinetics and the growth of the superficial film. These changes have been interpreted in terms of a transition from a general corrosion to a localized one.

However, the system studied here, because of its complexity, is very different from those reported in the literature. In order to determine the nature of the films that interfere with the copper dissolution in the range $+200$ to $+900\,\mathrm{mV}$ for $[\mathrm{Cl^-}] > 0.1\,\mathrm{M}$, surface analysis methods must be conducted. However, when the chloride concentration is 0.1 M, the anodes are still sufficiently soluble.

3.3. *Sulphate ion*

SPB is saturated by the sulphate ion at a concentration of about 0.3 M. The measurements were therefore carried out in 0.1 and 0.2 M solutions at scan rates of 2, 5, 10 and $20\,\mathrm{mV\,s^{-1}}$.

Comparison of the first cycles of the runs performed with two different sulphate concentrations at the same scan rate of $2\,\mathrm{mV\,s^{-1}}$ (Fig. 6) shows:

(i) The curve obtained with 0.2 M $\mathrm{SO_4^{2-}}$ is very similar to that for the 'impurity free' SPB (i.e. curve b, Fig. 2).

(ii) The peaks IV and V shift as shown in Table 4 (with respect to SPB potential values).

(iii) In the case of 0.1 M $\mathrm{SO_4^{2-}}$ the anodic peaks II and V are more pronounced; furthermore, after peak IV the anodic current approaches zero and remains near zero on the reverse scan until peak V occurs.

(iv) In the case of 0.2 M $\mathrm{SO_4^{2-}}$ the anodic current after peak IV decreases only to $5\,\mathrm{mA\,cm^{-2}}$ (at about 600 mV) and does not fall below this value until peak V occurs.

A series of four successive cycles ($2\,\mathrm{mV\,s^{-1}}$, 0.2 M $\mathrm{SO_4^{2-}}$) does not produce significant changes in the curve shape but only a small shift of the I, IV and V peaks towards more positive potential values (Table 5).

Comparison of the first cycles (Fig. 7) of the runs carried out at different rates with the same 0.1 M $\mathrm{SO_4^{2-}}$ concentration indicates an absence of significant changes in the shape of the voltammograms for the 2 and $5\,\mathrm{mV\,s^{-1}}$ scans and an increase of the peak current density to more positive values of the potential. The disappearance of the 300 mV peak is noted in the reverse of the 10 and $20\,\mathrm{mV\,s^{-1}}$ scans. The current density values steadily approach zero in the reverse scan, until the potentials attain the characteristic values of oxidation.

Table 4. Comparison of peaks (mV versus SCE) IV and V for two different sulphate concentrations

	Peak IV	*Peak V*
SPB	520	360
0.1 M $\mathrm{SO_4^{2-}}$	305	289
0.2 M $\mathrm{SO_4^{2-}}$	575	494

Table 5. Comparison of peaks I, IV, V and VIII for four successive cycles

	Forward scan				*Reverse scan*			
	Peak I		*Peak IV*		*Peak V*		*Peak VIII*	
	mV	*mA cm^{-2}*	*mV*	*mA cm^{-2}*	*mV*	*mA cm^{-2}*	*mV*	*mA cm^{-2}*
1st	−103	10	600	12.7	494	14.0	−81	7.2
2nd	−29	11	599	12.0	502	13.5	−71	7.2
3th	−18	11	605	12.0	514	12.7	−68	7.3
4th	−18	11	610	11.8	517	12.3	−73	7.0

A similar comparison as above, but for $[SO_4^{2-}] = 0.2$ M, reveals a behaviour similar to that at 0.1 M; the current density, however, does not drop to zero but remains at about 7 mA cm^{-2} both in the forward and in the reverse scans. For the first cycles at scan rates of 10 and 20 mV s^{-1} the peak does not appear at more positive potential values and the copper ion reduction peak occurs in the curve at 20 mV s^{-1}.

For the solutions with $[SO_4^{2-}] = 0.1$ M and 0.2 M at the same scan rate, a shift towards more positive potentials is exhibited by the peaks as the number of cycles increases. For the solutions containing chloride ions the current densities were generally higher than those for the solutions with sulphate ions.

3.4. *Ammonia and Nitrates*

In industry, ammonia is added at a concentration of about 3 g l^{-1} (or more) and is kept constant by compensating losses due to alkalinity in association with temperature and stirring. This reagent is used because it gives a smooth and bright deposit (the use of less volatile amines does not yield positive results). Our measurements have shown that no anode passivation phenomena are evident up to a concentration of 0.1 M ammonia, although they appear at higher concentrations. This fact agrees with literature reports [18]. However, higher concentrations of ammonia are very well tolerated by SPB in association with the nitrate ion which has a strong depolarizing effect. A subsequent series of voltammetric cycles carried out in the presence of NH_3 and NO_3^- at concentrations of 3 and 6 g l^{-1}, respectively (Fig. 8), shows high anodic current density values over the entire potential range for the first and second cycle. Moreover, the cathodic reduction peaks are not present and the electrode always appears depolarized. However, for the third and fourth cycles the current versus potential curve closely resembles that obtained in SPB, the main difference consisting of a marked shift of the anodic peak towards

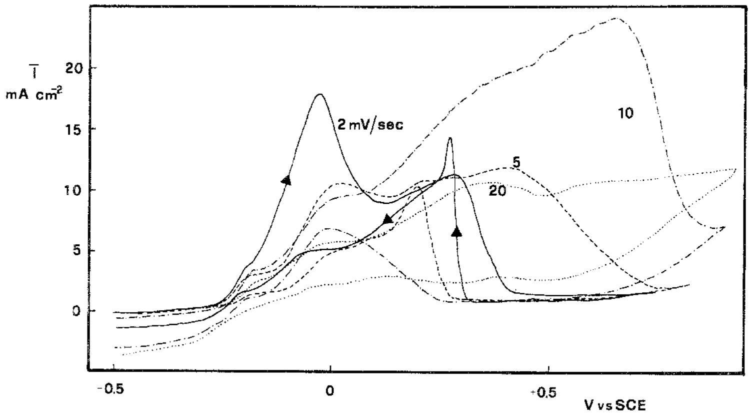

Fig. 7. First cycle voltammetry in the presence of 0.1 M SO_4^{2-} (pH = 8.8; 25° C) at various scan rates.

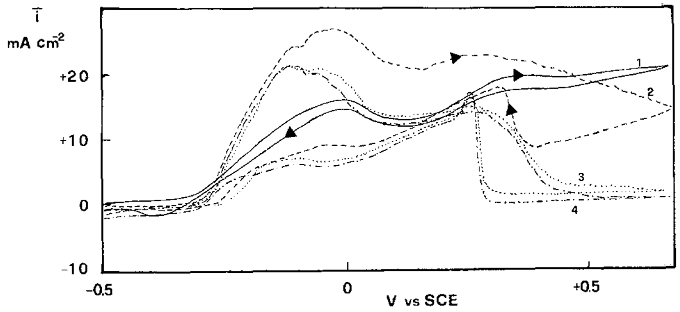

Fig. 8. A successive series of voltammetric cycles in the presence of NH_3 (3 g l^{-1}) and NO_3^- (6 g l^{-1}) (scan rate = 2 mV s^{-1}).

more negative potentials, similar to the case for 0.1 M SO_4^{2-} (Fig. 5).

3.5. *Phosphate ion*

The phosphate ion derives from the hydrolytic acid-catalysed reaction of the pyrophosphate ion. By keeping the pH above 8.6 this process is strongly retarded. However, since the average life of a pyrophosphate bath is more than one year, there is inevitably an accumulation of the PO_4^{3-} ion according to the dissociation equilibria at pH = 8.8. The voltammetric measurements taken with 10 and 50 g l^{-1} of phosphate have given current versus potential curves similar to those of SPB, thus indicating that PO_4^{3-} concentrations at these levels have no detrimental effect on the dissolution of copper.

4. Conclusions

The voltammetric study and the preliminary results of an XPS investigation on copper samples pretreated with SPB, with or without polarization at the appropriate potential value, have shown that the peak (IV) at the more positive potential might be attributable to the interaction of the pyrophosphate ion with the surface. Moreover, the presence of potassium and phosphorous in a copper mirror dipped for 48 h in SPB was detected at an estimated depth of about 1 μm. The high stability and solubility of the copper–pyrophosphate complex causes the oxide and hydroxide films to be unstable at less positive potentials. Therefore, in the absence of impurities and SPB is capable of keeping the anodes depolarized, thus guaranteeing a very high anodic current efficiency.

The chloride ion appears to be a particularly harmful impurity in industrial practice even in relation to the anodic process; however, it can be tolerated at concentrations lower than 0.1 M and with vigorous stirring of the bath.

Analysis of the voltammograms obtained in the presence of the sulphate ion revealed a partial inactivation of the copper surface, particularly for 0.1 M SO_4^{2-}.

The co-presence of ammonia and nitrate ion used as brightening and depolarizing agents, respectively, is not dangerous in industrial concentrations but, since the nitrate ion is very quickly reduced, it must be reintegrated through a continuous analytical check.

Finally, the presence of phosphate ion at concentrations of 10 or 50 g l^{-1} seems to be completely tolerable for industrial purposes.

Acknowledgements

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