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Effect of some aromatic nitro compounds on the passivation of copper anodes during electrorefining

S. JIN, E. GHALI*

Department of Mining and Metallurgy, Laval University, Ste-Foy, Québec G1K 7P4, Canada

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The effect of some aromatic nitro compounds on the passivation of copper anodes during electrorefining was investigated by galvanostatic methods and by scanning electron microscopy. The results showed that the passivation delay efficiency of the tested aromatic nitro compounds depended strongly on their molecular structure: 3,5-dinitrosalicylic acid (DNSA), which is not only an oxidizing agent but also a chelating agent, inhibited the passivation of copper anodes significantly, particularly that of the pure copper anode; 3,5-dinitrobenzoic acid was also a good inhibitor of passivation of copper anodes; mononitrocompounds were ineffective and the di- or trinitrocompounds, which do not contain carboxyl groups in the molecule, did not significantly influence the passivation. The mechanism of the passivation of the copper anode and the delay mechanism of DNSA are discussed.

1. Introduction

The passivation of copper anodes has been an important problem often encountered in the electroplating and electrorefining of copper and has prohibited the industry from using higher currents through the electrodes. In some electrolytic copper refineries, the current density is below 200 A m^{-2} and some are as low as 160 A m^{-2} [1]. In order to solve this problem, several techniques have been suggested and used. For example, periodic reversal of the current allowed the current density to be raised from 165 to 330 A m^{-2} [2], while some methods involving electrolyte circulating have been developed [3].

Previous results from our group have proved that some amino acid chelating agents and inorganic and organic oxidizing agents delayed the passivation of pure and impure copper anodes to varying degrees [4, 5]. The present study concerns the influence of some aromatic nitro compounds on passivation of copper anodes during refining. The passivation delay efficiency of these compounds, as a function of their molecular structure, is examined using pure and impure copper anodes.

2. Experimental details

2.1. *Materials and sample preparation*

3-nitrobenzoic acid (3-NBA), 4-nitrobenzoic acid (4-NBA), 3,5-dinitrobenzoic acid (DNBA), 2,4,6-trinitrophenol (picric acid, PCA), 2,4-dinitrobenzenesulphonic acid (DNBSA), 2,4-dinitrophenylhydrazine (DNPZ), 3,5-dinitrosalicylic acid (DNSA) and its parent compound salicylic acid (SA) were obtained from Aldrich Chemicals Company Ltd. All other chemicals used were A.C.S. reagent grade. Deionized water was obtained using an activated carbon and ion exchange resin deionizing system. The conductivity of the deionized water was lower than 5 $\mu\Omega^{-1}$ cm^{-1}.

Three types of copper were used as anode materials: an electrolytic copper, a synthetic copper-antimony alloy and three commercial anode coppers (supplied by CCR Inc. via Noranda Research Center, Montreal). Their major impurities are shown in Table 1. The samples were short lengths of rod soldered to a PVC insulated copper wire, cast in acrylic resin, polished with emery paper down to 600 grit and washed with distillated water and alcohol. The exposed area was 0.785 cm^2. Counter electrodes were made of a 2 cm diameter copper rod, prepared in the same way.

2.2. *Experimental set-up*

The electrolytic cell was a one liter double walled cell containing 950 g (771 ml, 20° C) of electrolyte heated by a flow of thermostated water in the double wall (65 ± 0.5° C). The supporting electrolyte contained 1.66 M H_2SO_4, 0.66 M $CuSO_4 . 5H_2O$ and 0.29 M $NiSO_4 . 6H_2O$ and was stirred using a magnetic stirrer. The anode and cathode were mounted in a suitable Teflon made holder and the distance between them was fixed at 2 cm. The reference electrode was of mercurous sulphate (MSE), Hg, $HgSO_4$/sat.K_2SO_4 (0.64 V/NHE). A saturated K_2SO_4 salt bridge was used to keep the reference electrode close to the anode. All potentials are given with respect to NHE.

The electrochemical experiments were conducted with a Tacussel PRT-2x potentiostat; an analog X–Y recorder (Honeywell 530) and a Fisher recorder (Recordall SERIES 5000) were used for chrono-

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* To whom correspondence should be addressed

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Table 2. The name, structure and efficiency of tested aromatic nitro compounds

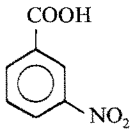
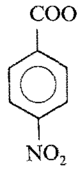
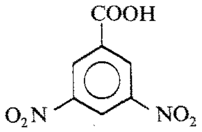
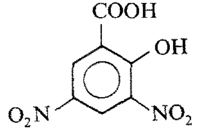
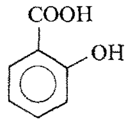
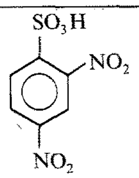
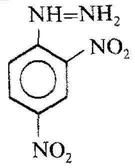
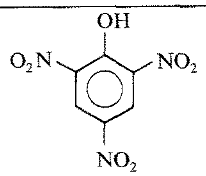
Nitro compounds			τ/τ_0 (*optimal value*)
No.	*Structure*	*Name*	
1		3-nitrobenzoic acid (3-NBA)	2.41
2		4-nitrobenzoic acid (4-NBA)	1.47
3		3,5-dinitrobenzoic acid (DNBA)	39.18
4		3,5-dinitrosalicylic acid (DNSA)	85.43
		salicylic acid (SA)	1.51
5		2,4-dinitrobenzene-sulphonic acid (DNBSA)	1.51
6		2,4-dinitrophenylhydrazine (DNPZ)	1.69
7		2,4,6-trinitrophenol (picric acid) (PCA)	1.58

Table 3. Effect of current density on the efficiency of DNSA of different concentrations (agitation: 1200 r.p.m.; NaCl: 50 p.p.m.)

DNSA concentration (p.p.m.)	*Time to passivation (s)*			
	255 mA cm^{-2}	*382 mA cm^{-2}*	*510 mA cm^{-2}*	*637 mA cm^{-2}*
0	2490	320	84	18
200	18 400	1500	150	55
400	44 070	2660	50	19
600	59 040	18 925	38	17
800	67 350	29 440	*	*

* not determined

Table 1. Major impurities of the copper anodes

Impurities (p.p.m.)	*Anode coppers*			*Pure Cu*	*Cu–Sb Alloy*
	1	*2*	*3*		
O	1360	1350	1490	224	11
As	200	350	2000		
Sb	140	50	270		550
Bi	190	70	220		
Ni	560	1400	2600		
Pb	1900	420	630		
Se	80	1040	800		
Te	20	80	60		
Ag	300	2000	2300		

potentiograms. Unless otherwise noted, the galvanostatic electrolysis experiments were performed in the following conditions: 50 p.p.m. NaCl added to the supporting electrolyte with (or without) tested compounds; 65 ± 0.5° C; stirrer rotation rate was 1200 r.p.m.; current density was 382.2 mA cm^{-2}. The SEM analyses of the electrolyzed anode surface were performed using a JEOL JSM-25s III model scanning electron microscope equipped with a TN 5700 model energy dispersive X-ray analyzer (Tracor Norther).

3. Results and discussions

3.1. *Comparison of the efficiencies of various nitro compounds*

The chronopotentiograms were obtained when galvanostatic electrolyses were carried out (Fig. 1). On the basis of these chronopotentiograms, the times before the passivation of the copper anodes in the electrolyte with or without the additive were determined as τ and τ_0, respectively. The ratio τ/τ_0 expresses the efficiency of the passivation delay using the tested nitro compound.

Table 2 shows the name, structure of the tested aromatic nitro compounds and their efficiency in delaying passivation (τ/τ_0). It can be seen that 3,5-dinitrosalicylic acid demonstrated the best passivation delay action; 3,5-dinitrobenzoic acid significantly had also an important effect on the passivation; the effects of other tested compounds were negligible. Figure 2 shows the passivation delay action of salicylic acid and 3,5-dinitrosalicylic acid. Comparing the different effects on passivation, it can be assumed that the nitro groups in the molecule of DNSA have a very important role. Moreover, the number of nitro groups and the presence of carboxyl group in the molecule are also a decisive factor. This can be confirmed by comparing the effect of DNBA and a 3-NBA, DNBSA, DNPZ and PCA (Table 2).

3.2. *Effect of current density on the efficiency of DNSA*

Table 3 shows the results obtained for different current densities and different concentrations of DNSA. It seems that there is a critical current between 350 and 400 mA at which DNSA loses its passivation delaying effect, even with vigorous stirring and high concentrations of DNSA. This means that at the critical current, the production rate of cuprous ions Cu^{+} and cupric ions Cu^{2+} is so high that the added DNSA cannot inhibit effectively the formation and accumulation of copper powder, the solubility product of copper sulphate is reached; the anode surface is quickly covered by copper powder and copper sulphate crystals, the anode potential rises rapidly without oscillation and the anode becomes passive. Therefore, the anodic current density has a limit under given conditions and cannot be increased indefinitely.

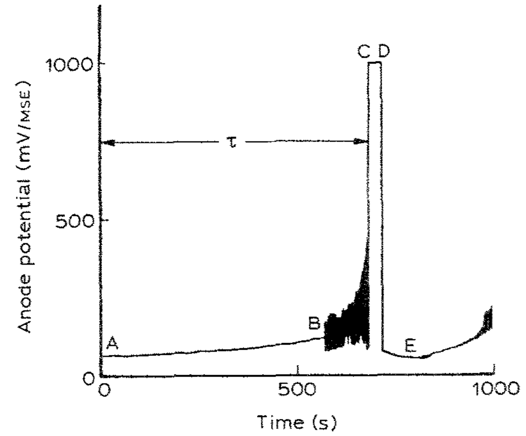


Fig. 1. A typical schematic chronopotentiogram of copper anode electrolyzed in the supporting electrolyte added with 50 p.p.m. NaCl under the standard experiment condition (382.2 mA cm^{-2}, 65 ± 0.5° C, 1200 r.p.m.).

3.3. *Effect of agitation on the efficiency of DNSA*

Figure 3 shows the relationship between the stirring rate and the time to passivation of the pure copper anode and industrial copper anode at a current density of 2000 A m^{-2}. It can be seen that strong agitation allows the DNSA to perform better.

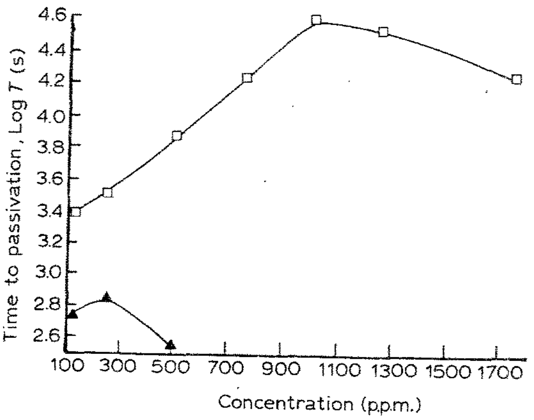


Fig. 2. Time to passivation against concentration of (□) 3,5-dinitrosalicylic acid (DNSA) and (▲) salicylic acid (SA) for pure copper anodically dissolved at a constant current of 382.2 mA cm^{-2} in the supporting electrolyte added with 50 p.p.m. NaCl. Temperature: 65 ± 0.5° C. Stirring rate: 1200 r.p.m..

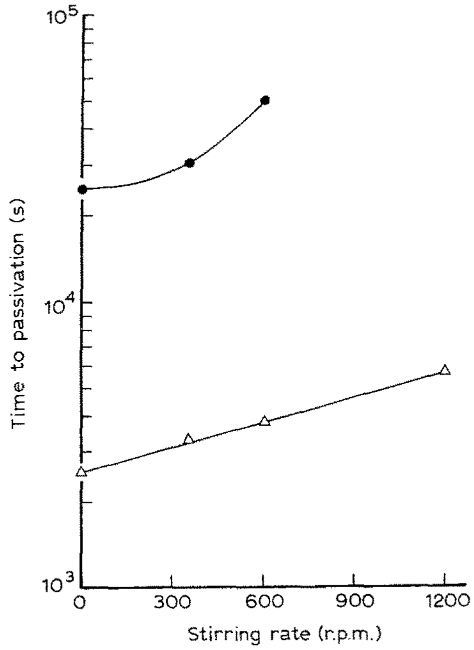


Fig. 3. Dependence of the passivation delay action of DNSA on stirring rate of the electrolyte. NaCl: 50 p.p.m. Anode current density: 200 mA cm^{-2}. DNSA concentration: 1000 p p m. Temperature 65 ± 0.5° C. (●) Pure copper, (△) anode copper 1.

3.4. *Effect of DNSA on the passivation mechanism of pure copper anode*

According to the chronopotentiograms (Fig. 1 shows a typical example), the anodic passivation can be divided into four stages:(1) the active dissolution stage of the copper anode (A–B segment); (2) the potential oscillation stage (B–C segment); (3) the anode passivation stage (C–D segment); and (4) the anode reactivation stage (D–E segment). In the first stage, the principal reaction which takes place on the anode is:

$$Cu = Cu^{2+} + 2e \qquad (E^0 = 0.34\,V) \qquad (1)$$

the secondary reaction is:

$$Cu = Cu^{+} + e \qquad (E^0 = 0.522\,V) \qquad (2)$$

Table 4. Change of anode potential with anodic current

Current (*mA*)	*Current density* ($A\,m^{-2}$)	*Anode potential instantaneous values* (*mV/NHE*)
100	1274	394
150	1911	435
200	2548	475
250	3185	516
300	3822	560
350	4459	600
400	5096	642
500	6369	730

From Table 4 it can be seen that the higher the current applied through the electrodes, the more positive is the anode potential. It is conceivable that when the current exceeds 250 mA, the rate of formation of cuprous ions increases and so does the proportion of cuprous ions to the total amount of copper anodically dissolved. The latter is reflected by the increase of the anodic current efficiency. It has been reported that the concentration of cuprous ions in a similar electrolyte was of the order of 10 mg l^{-1} while in the nitrogen flushed solution the values reached 70 mg l^{-1} (25° C) and 700 mg l^{-1} (80° C), respectively [6].

Since the cuprous ions in the electrolyte are governed by thermodynamic equilibria, when their concentration exceeds 10^{-6} M, the following disproportionation reaction takes place [7]:

$$2Cu^{+} = Cu^{2+} + Cu \qquad (3)$$

The copper powder formed during this reaction covers the anode surface as layer of anodic slime and hinders the diffusion of copper ions. Thus the anode potential increases and more cuprous ions are formed. As a result, the slime layer thickens rapidly and forms a barrier which hinders the cupric ions from diffusing into the bulk electrolyte. This leads to the precipitation of copper sulphate crystals on the anode and still further to the formation of cuprous oxide, and finally to the anode passivation. In case of industrial

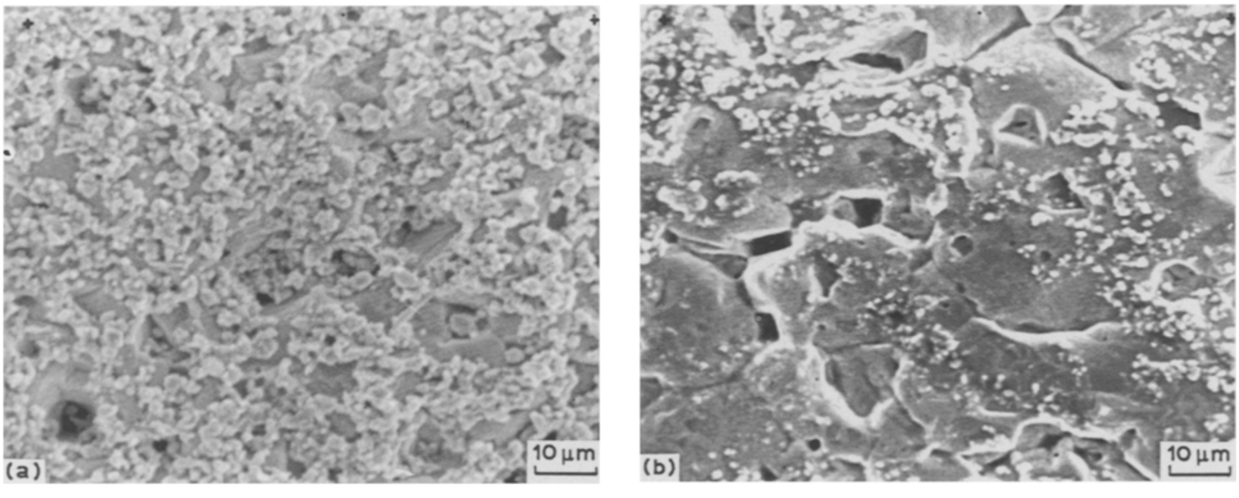


Fig. 4. Scanning electron micrographs of the pure copper anode electrolyzed for 300 s in the supporting electrolyte without (a) and with (b). 550 p.p.m. DNSA at current density of 382.2 mA cm^{-2}.

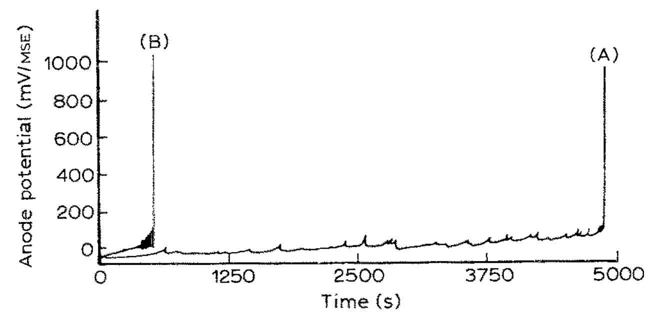


Fig. 5. Chronopotentiogram of pure copper anodes electrolyzed in the supporting electrolyte added with 50 p.p.m. NaCl at a current density of 382.2 mA cm^{-2}. (A) with 350 p.p.m. DNSA, (B) without DNSA.

anode coppers, the slime layer is composed also of the anode impurities which accelerates the processes of passivation.

The aromatic nitro compounds such as DNSA and DNBA in the electrolyte remarkably delayed the passivation of pure copper anodes (Table 3). This passivation inhibition can be related to their effect on the copper powder formation. Figure 4 shows the morphology of pure copper anodes electrolyzed in the electrolyte with and without 550 p.p.m. DNSA. It can be seen that in the presence of this additive, the quantity and the size of the copper powders on the anode surface are much smaller than in its absence. This could be explained as follows: as an organic oxidizing agent, DNSA and DNBA could oxidize the cuprous ions into cupric ions while they themselves are reduced to nitrohydroxylamino compounds [8]. So, most of the cuprous ions formed on the anode were transformed into the cupric ions and the formation rate of the copper powder on the anode was reduced remarkably. As a result, the passivation of the copper anode was delayed dramatically. Moreover, cuprous ions can be chelated by the organic molecules and the chelation makes the oxidation of the cuprous ions easier. Therefore, dinitrobenzoic acids and dinitrosalicylic acids are double function compounds in that they are both oxidizing and chelating agents. If there is a hydroxy group in the ortho-position to the carboxyl group, the chelating action becomes more important. So DNSA displays a more outstanding passivation delaying effect than DNBA.

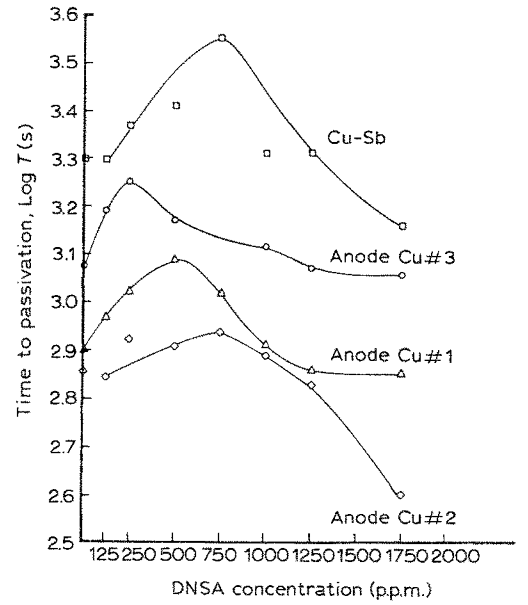
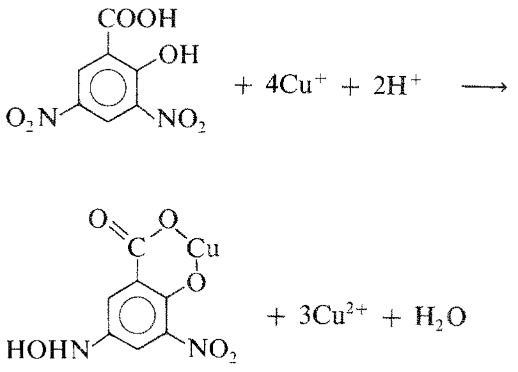


Fig. 6. The effect of DNSA on the passivation of industrial copper anodes and antimony-containing copper anodes (Cu–Sb alloy) showing a lower passivation inhibition efficiency of DNSA for high selenium anode copper (anode Cu #2, see Table 1).



(4)

It is not yet known if the hydroxylamino group formed in the process takes part in the complexation.

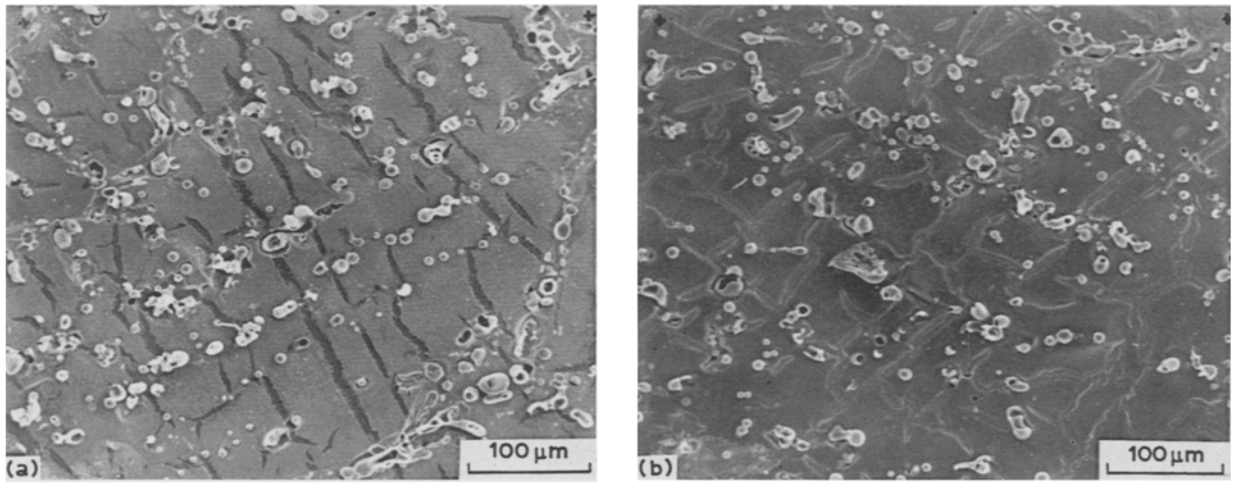


Fig. 7. Morphologies of the No. 2 industrial copper anode after 200 seconds electrolysis in the supporting electrolyte added with 50 p.p.m. NaCl under the standard electrolysis condition. (A) without DNSA, (B) with 1000 p.p.m. DNSA.

It is of interest to note that when NaCl is added to the supporting electrolyte, once the potential oscillation occurs, the potential increase and anode passivation tends to be irreversible, but the addition of DNSA can change this irreversible tendency and change the shape of the chronopotentiogram (Fig. 5). This could be due to the changed property of the slime layer by DNSA, causing local slime layer to fall off from anode surface and the potential to decrease.

3.5. *Effect of nitro compounds on passivation of the industrial copper anodes*

Some industrial anode coppers were electrolyzed under the same standard conditions. The results showed that the nitro compounds, such as DNSA, increased the time to passivation by about 50% (Fig. 6, anode Cu #3). However, the increased value for anodes containing more selenium was only 20% (Fig. 6, anode #2). SEM analysis showed that the DNSA addition in the electrolyte did not change the morphology of the industrial copper anodes very much during anodic dissolution (Fig. 7). These results indicate clearly that the parameters which influence passivation of the pure copper anode are not the same for impure copper anode. In fact, after 300s electrolysis of the industrial anode copper No. 2 in the electrolyte containing 50 p.p.m. NaCl, only fine silver powders and cuprous selenides were observed (Figs. 8 and 9). For high lead copper anode (No. 1), besides silver powders and selenide, many thorn shaped lead sulphate crystals were formed on the selenide cores (Fig. 10). It can be said that the silver and selenium compounds in the anode are the principal factors resulting in the anode passivation of the industrial anode coppers examined while the formation of copper powders on the anode surface is the most important cause for pure copper anode passivation.

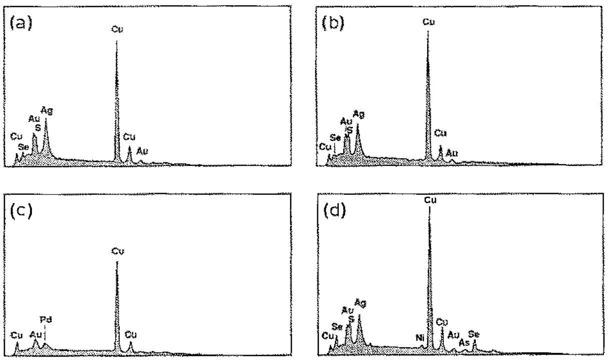


Fig. 9. EDX spectra of the species on the surface of industrial anode copper No. 2 shown in Fig. 8. (A) silver grain, (B) silver powder layer on the copper substrate, (C) silver powder layer rift (i.e. copper substrate), (D) selenide inclusion.

The selenium in the industrial anode coppers exists mainly in form of cuprous selenide in the boundaries. When the coppers are dissolved anodically, the selenide inclusions are released. Moreover, a selective dissolution of copper around the inclusions was observed (Fig. 11). It was also noticed that after electrochemical dissolution, the selenide inclusions became porous (Fig. 12). This may be caused by the dissolution of cuprous oxide and/or copper contained in these inclusions.

The behaviour of silver during copper electrorefining has been investigated by some researchers [9, 10]. A plausible mechanism of the formation of the silver powder layer has been suggested: silver exists as a solid solution with copper in the copper matrix; during electrolysis, copper and silver are ionized and the formed silver ions react with metallic copper or cuprous ions producing very fine silver powders according to the equations:

$$Ag^+ + Cu^+ = Ag + Cu^{2+} \qquad (5)$$

$$2Ag^+ + Cu = 2Ag + Cu^{2+} \qquad (6)$$

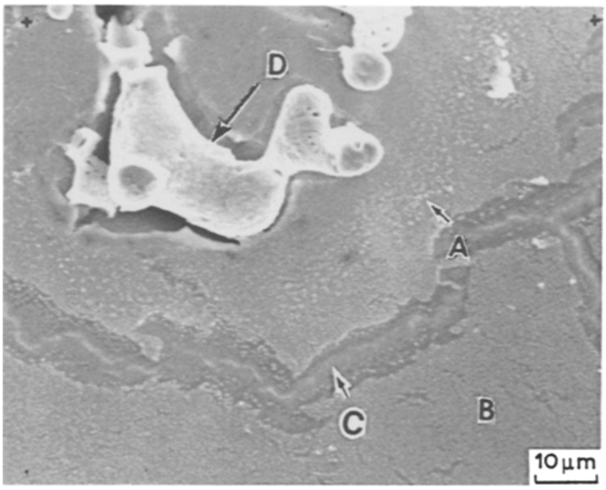


Fig. 8. Scanning electron micrograph showing the detailed morphology of industrial copper anode No. 2 electrolyzed for 300 s in supporting electrolyte with 50 p.p.m. NaCl and 50 p.p.m. DNSA under the standard electrolysis condition. Element analyses by EDX (see Fig. 9) show that the anode slime layer mainly consists of silver powder and copper selenide.

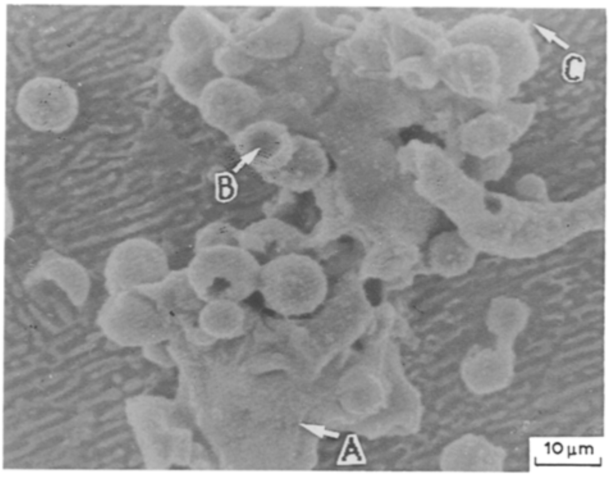


Fig. 10. SEM micrograph of the anode surface of industrial copper anode No. 1 after 300 s electrolysis in the supporting electrolyte showing that silver, cuprous selenide and lead sulfate are the principal components of the anode slime layer (A) silver powder, (B) cuprous selenide, (C) lead sulphate crystal.

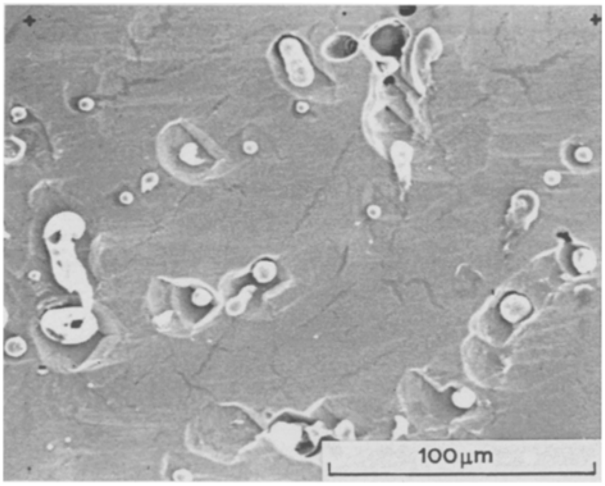


Fig. 11. SEM micrograph showing selective dissolution of copper and released selenide inclusions on the surface of the industrial copper anode (No. 2) electrolyzed for 200 s in the supporting electrolyte.

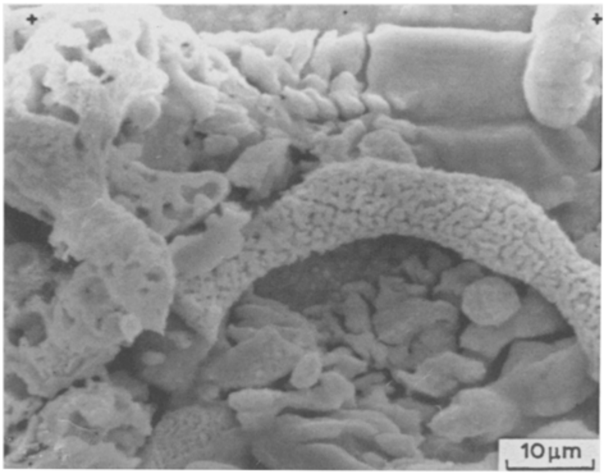


Fig. 12. SEM micrograph of an industrial copper anode after passivation showing that the selenide inclusions became porous.

The silver powder layer and porous cuprous selenide, soaked with $CuSO_4$–H_2SO_4 solution, act as a barrier to copper ions diffusion and makes the copper ion concentration in the solution absorbed by the slime layer very high, so the copper sulphate crystallizes and the anode potential rises.

Because of the stable chemical properties of silver and selenide to the tested aromatic nitro compounds, the latter do not exert a noticeable influence on the formation and the accumulation of the anode slime layer consisting of silver powder and the selenide inclusions on the surface of the industrial copper anodes. Therefore they do not effectively delay the passivation of these anodes. It is important for a future study to search for compounds which may inhibit or reduce the formation and accumulation of the silver powder layer, selenides and lead sulphate.

4. Conclusions

(1) Some aromatic nitro compounds such as 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid can effectively delay the passivation of a pure copper anode under good convection. Their effects on the passivation are attributed to their inhibition of the formation and accumulation of copper powders on the anode surface by oxidizing the cuprous ions into cupric ions.

(2) The other tested aromatic nitrocompounds such as trinitrophenol, dinitrophenylhydrazine, dinitrobenzenesulphonic acid and mononitrobenzoic acids do not delay the anode passivation significantly.

(3) The effect of nitro compounds such as DNSA and DNBA on the passivation depends not only on their oxidation capacity but also on their ability to complex with cuprous ions and this depends on the molecular structure of the nitro compounds.

(4) The passivation delaying effect of DNSA at current densities of less than $400\,\mathrm{mA\,cm^{-2}}$ is quite marked for pure copper anodes. Between 450 and $500\,\mathrm{mA\,cm^{-2}}$, there is a critical current above which DNSA is ineffective.

(5) Industrial anode coppers show a different passivation mechanism to pure copper anodes. The released selenide inclusions and the formed silver powder layer on an industrial copper anode surface during anodic dissolution are the principal cause of anode passivation. The tested nitro compounds do not influence the accumulation of the silver powders and selenides, therefore they cannot effectively delay the anode passivation.

Acknowledgements

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