JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 826–834

Electrochemical preparation of cuprous oxide powder: Part II. Process conditions

J. JI, W. C. COOPER*

Department of Metallurgical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received 30 August 1989; revised 5 December 1989

Practical electrosynthesis of cuprous oxide powder was carried out on a laboratory scale in a cell specially constructed both with and without a diaphragm under the various operating conditions guided by the authors' previous research. The electrolysis was appraised in terms of the quality of the cuprous oxide product, the electrodissolution of the copper anode, and the SEM microstructure of the cuprous oxide powder. In a cell having a diaphragm, of which nylon fabric is the best, the optimal electrolysis operating conditions are: $250\,\mathrm{g\,l^{-1}}$ NaCl, 0.1–$1.0\,\mathrm{g\,l^{-1}}$ NaOH, 500–$1500\,\mathrm{A\,m^{-2}}$, 80° C, perforated titanium sheet as the cathode, and around 3% cell volume of electrolyte circulation per minute. Under these conditions a product containing more than 97% cuprous oxide can easily be produced with very stable electrolysis and quite uniform dissolution of the copper anode. To eliminate the use of a diaphragm in the cell, the addition of sodium chromate, sodium dichromate, or calcium gluconate is effective in a sense, depending upon the requirements of the cuprous oxide product. For a product in which more than 95% cuprous oxide and no copper powder are required but a slightly higher content of chloride is allowable, sodium chromate and dichromate can be proposed for use with the former around 0.03–$0.05\,\mathrm{g\,l^{-1}}$ and the latter around 0.020–$0.025\,\mathrm{g\,l^{-1}}$, although the copper anode will not be perfectly evenly dissolved. For a product in which more than 97% cuprous oxide is demanded and a very small amount of copper powder is tolerated, calcium gluconate would be acceptable at around $4.5\,\mathrm{g\,l^{-1}}$ with quite even dissolution of the copper anode. As to the auxiliary additives, hydrazine hydrate has a negative effect on the quality of the cuprous oxide product. Sucrose can cause a small increase in the chloride content but can make the particles of cuprous oxide more compact thereby increasing sharply its apparent density. Hydroxylamine hydrochloride is the best auxiliary additive which has a positive effect on the purity of the cuprous oxide product but produces no obvious change in the microstructure on the cuprous oxide particles. Even though most work has been concentrated on the electrolytic process, the subsequent processes are equally important: 65–70° C, distilled water for washing, benzotriazole in ethanol solution for stabilization of the cuprous oxide, and 100° C at a vacuum of less than 20 mm Hg for drying seem to be satisfactory. A vacuum drying temperature of 55–60° C may be more appropriate to ensure against any oxidation of the product.

1. Introduction

Cuprous oxide powder can be produced using a variety of techniques, including electrochemical, sintering, hydrothermal, chemical and displacement processes, on which its physico-chemical properties are dependent [1]. The electrochemical technique, which has been developed since the 1940's [2], appears to be the best on an industrial scale in view of its economy, easy operation, short flowsheet, high productivity and its ability to yield a product having the required purity and colour. However, spongy metallic copper powder would often be deposited on the cathode during the electrolysis, leading to a contamination of the cuprous oxide. The solution to this problem is usually to use a diaphragm [3–7] or to use certain additives [8–12]. Although some research work in these areas has been conducted, there are considerable differences in the optimal ranges suggested for the operating electrolysis parameters. In addition, the microstructure of the cuprous oxide powder produced electrochemically, the chloride content in the product, the electrodissolution of the copper anode, the stability of the electrolysis and the washing feasibility are almost unknown for a cell using additives instead of a diaphragm.

In the flowsheet for the electrosynthesis of cuprous oxide powder [13] the electrolysis process itself is of course a very important step in the whole procedure. Yet the authors believe that the subsequent washing, stabilization and drying are equally significant as regards the physico-chemical properties and the purity

---

* Currently at the Department of Metals and Materials Engineering, The University of British Columbia, 309–6350 Stores Road, Vancouver, B.C., V6T 1W5 Canada.

of the cuprous oxide powder. Much less attention has been given to these steps than to the electrolysis itself.

The present report details the results of an extension of the previous research [14]. The purpose of this phase of the research was: to evaluate the best operating electrolysis conditions predicted in the earlier work; to study the diaphragm materials, the additives to eliminate the use of a diaphragm in the cell, the microstructure of the cuprous oxide powder; and finally to produce successfully a product containing more than 97% cuprous oxide in a cell both with and without a diaphragm.

2. Experimental details

The cell, 14.5 cm (L) × 8 cm (W) × 16 cm (H) (all inside dimensions with a wall thickness of 0.9 cm), was constructed of plexiglass with a slightly sloping bottom. The cell was divided into two chambers, one for the electrolysis with dimensions of 12 cm (L) × 8 cm (W) × 16 cm (H), and the other for the holder of overflow electrolyte with dimensions of 8 cm (W) × 1.6 cm (L) × 16 cm (H) with an overflow separator whose dimensions are 8 cm (W) × 13 cm (H) × 0.9 cm (T) to ensure a constant height of electrolyte level in the electrolysis chamber, which otherwise would change during the electrolysis due to the large evaporation of water at high temperature and to water consumption in the cathodic region. The height from the electrolyte surface to the cell cover was taken and kept constant at 3 cm during the electrolysis. There was a hot-water jacket, 19.5 cm (L) × 13 cm (W) × 19 cm (H) (all inside dimensions), which was also made of plexiglass sheet with a thickness of 0.9 cm, surrounding the cell to heat the electrolyte inside. A plexiglass cell cover was used to lessen the evaporation of water. This cover was provided with slots for introducing the anode as well as the diaphragm frames with the cathodes inside, and also with holes for introducing a feed inlet, a feed outlet, and a thermometer.

One copper anode, 4 cm (W) × 5 cm (H) × 0.29 cm (T), and two titanium cathodes, 4 cm (W) × 5 cm (H) × 0.1 cm (T), perforated with rows of small holes whose diameter was 0.254 cm, were used. The distance between the holes was 0.5 cm. The titanium cathodes were placed inside the diaphragm frames or put directly in the electrolyte in the presence of certain additives. One anode was positioned between two cathodes, and the space between the anode and the cathode was 4 cm. The frames for supporting the diaphragms and cathodes were also made of plexiglass and their dimensions were 5 cm (L) × 2 cm (W) × 12.2 cm (H) (all inside dimensions). The diaphragms were fixed on both sides of the frames with nylon screws. The distance of the lower edges of the cathodes towards the bottoms of the frames was 1 cm, while the gap between the side edges of the cathodes and the side inner walls of the frames was 0.5 cm. According to the above dimensions of the electrodes, the diaphragm frames and the cell, a large free space in the lower part of the cell was preserved to hold the cuprous oxide slurry formed during the electrolysis. The heights from the lower edges of the anode and the diaphragm frames to the cell bottom were 8 cm and 6.1 cm, respectively. A schematic drawing of the whole experimental apparatus is presented in Fig. 1.

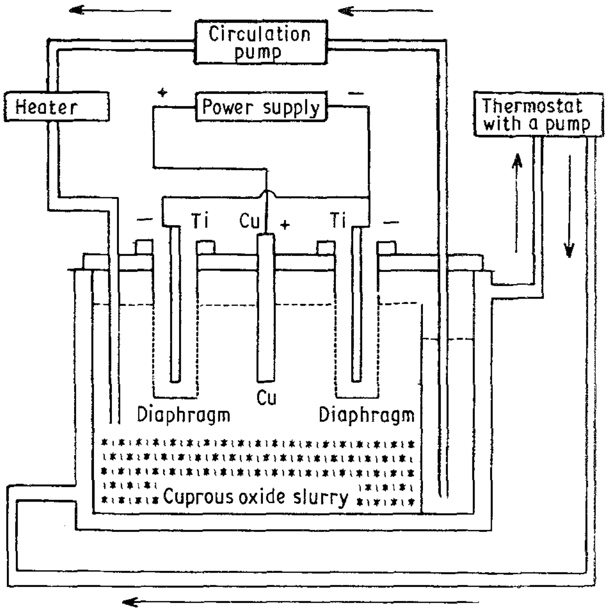

Fig. 1. Schematic drawing of the experimental apparatus.

The operating electrolytic conditions were chosen from those suggested to be optimal in the previous paper [14]. All of the chemicals used in the present experiments were C.P. grade. The electrolyte was circulated at about 3% cell volume per minute, and the duration of electrolysis corresponded to 4500 Ah m^{-2} (i.e., 4.5 h at 1000 A m^{-2}, 2.25 h at 2000 A m^{-2}) for most cases with no interval brushing of the anode for cleaning, during which about 82% $\{=(2.371 \times 4500 \times 2)/(8.96 \times 10000) \times 100/0.29\}$ of the copper anode would be dissolved.

The following parameters were taken into account to assess comprehensively the electrolysis process:

(a) chemical analyses of the cuprous oxide product*, including:
  - total reducing power as cuprous oxide
  - metallic copper
  - cuprous oxide
  - total copper, calculated as copper
  - chloride, calculated as Cl^-;

(b) current efficiency calculated on the basis of the weight of the final dry cuprous oxide powder;
(c) power yield;
(d) electrodissolution of the copper anode, i.e., the appearance of the copper anode after electrolysis;
(e) feasibility of washing;
(f) SEM microstructure of the cuprous oxide powder.

---

* Standard analytical methods refer to: (i) National Standard Specification for Curpous Oxide Powder GB 1620-79 (People's Republic of China); (ii) Standard Methods of Chemical Analysis of Dry Curpous Oxide and Copper Pigments, ASTM 283-84.

3. Results and discussion

3.1. *Electrolytic processes in a diaphragm cell without any additives*

It has been ascertained from the literature that there are considerable differences as to what are considered to be the best electrolytic conditions, especially for the anodic current density and the concentration of sodium hydroxide (i.e., pH). It is difficult to assess properly these so-called best conditions in a cell of different dimensions without first-hand knowledge. These large differences are caused possibly by different cell designs, different electrode shapes and dimensions, and different hydrodynamics of the electrolyte during the course of electrolysis. So it is necessary to investigate these two crucial variables (anodic current density and alkalinity) systematically in a cell with specific dimensions and electrode arrangement in order to get a better insight into the optimal range of operating parameters. Diaphragm materials which have been used include canvas [3], polypropylene [5, 7], and asbestos [15]. The detailed lifetimes of these materials are almost unknown, since their effectiveness over a short period of time cannot usually be guaranteed over the long run. Nonetheless, unlike the ionic diaphragm, the diaphragm used here is only some kind of fabric which can prevent the penetration of cuprous oxide particles, and whose desired key property is to be highly resistant to strongly alkaline solutions at high temperature. Several fabrics have been tested as diaphragms in the present research.

The experimental results are listed in Tables 1 and 2 and in Figs 2 and 3. It can be seen from Table 1 that when the concentration of sodium hydroxide is in the range of 0.02–1.5 $\mathrm{g\,l^{-1}}$ (pH = 10.1–12.3) under constant other variables of 250 $\mathrm{g\,l^{-1}}$ NaCl, 80° C and 1000 $\mathrm{A\,m^{-2}}$, it has a small effect on the quality of the cuprous oxide product. These conditions maintain a product having more than 97% cuprous oxide with a bright red color and well dispersed. There was a uniform electrodissolution of the copper anode except in the case of 1.5 $\mathrm{g\,l^{-1}}$ NaOH. Here there was a slightly uneven dissolution in the upper part of the copper anode. As regards the anodic current density, it has a fairly large effect on both the quality of the product and the dissolution of the copper anode. Higher anodic current density increases linearly the rate of electrodissolution of the copper anode, and its continued increase would possibly cause the mass-transfer rate of complex cuprous ions to be exceeded, resulting in the precipitation of insoluble cuprous chloride on the anode surface. Because of this, the copper anode was dissolved very unevenly at higher anodic current density, especially when the anodic current was beyond 2000 $\mathrm{A\,m^{-2}}$. To make matters worse, some spongy metallic copper powder was found to be on and between the diaphragm in the case of a current density of 2500 $\mathrm{A\,m^{-2}}$. Even though the exact cause of this phenomenon is not well understood, it seems that double polarity of the diaphragm produced by the clogging of its pores with cuprous oxide particles may be responsible. Since insoluble cuprous chloride precipitated on the anode surface, it would drop to the cell bottom and mix with the cuprous oxide slurry. Therefore, the chloride content in the final product would be higher than usual.

From the SEM photomicrographs in Fig. 2 it can be seen that the particles of the cuprous oxide powder exhibit an octahedral shape, and each component is an elongated square pyramid. The particle is very small, only a few microns in diameter. Here it is noteworthy that the chloride content in several cuprous oxide products exceeds the 0.5% limit which is specified in ASTM D912-81. As can be seen from the SEM photomicrographs of the cuprous oxide powder in Fig. 2,

*Table 1. The effect of NaOH concentration in a diaphragm cell without any additives**

NaOH (gl^{-1})	*0.02*†	*0.1*†	*0.25*‡	*0.5*†	*0.75*‡	*1.0*‡	*1.5*‡
RP (%); Cu_2O (%)	98.9	97.9	99.1	99.0	98.6	98.9	97.9
Cu° (%)	0	0	0	0	0	0	0
Cu_T (%)	88.1	87.9	88.6	88.3	88.1	87.8	87.5
CuO (%)	0.3	1.1	0.7	0.4	0.6	0	0.7
Cl^- (%)	0.35	0.57	0.41	0.50	0.34	0.49	0.39
C.E. (%)	96.9	98.3	97.9	96.7	95.3	93.5	96.4
P.Y. ($\mathrm{kWh\,kg^{-1}}$ Cu_2O)	1.02	1.03	1.08	1.05	1.08	1.10	1.10
Final product	red and dispersed	red and dispersed	red and dispersed	red and dispersed	red and dispersed	red and dispersed	red and dispersed
Anode dissolution	even and stable	even and stable	even and stable	even and stable	even and stable	even and stable	a bit uneven and stable
Product washing	easy	easy	easy	easy	easy	easy	easy

* Other constant conditions: 250 $\mathrm{g\,l^{-1}}$ NaCl, 80° C, 1000 $\mathrm{A\,m^{-2}}$, perforated Ti cathodes and 3% cell volume circulation of electrolyte per minute.

† Using two-layered polyester diaphragm.

‡ Using four-layered nylon diaphragm.

RP: reducing power calculated as cuprous oxide.

C.E.: current efficiency calculated on the basis of the weight of the final cuprous oxide powder (%).

P.Y.: power yield ($\mathrm{kWh\,kg^{-1}}$ Cu_2O).

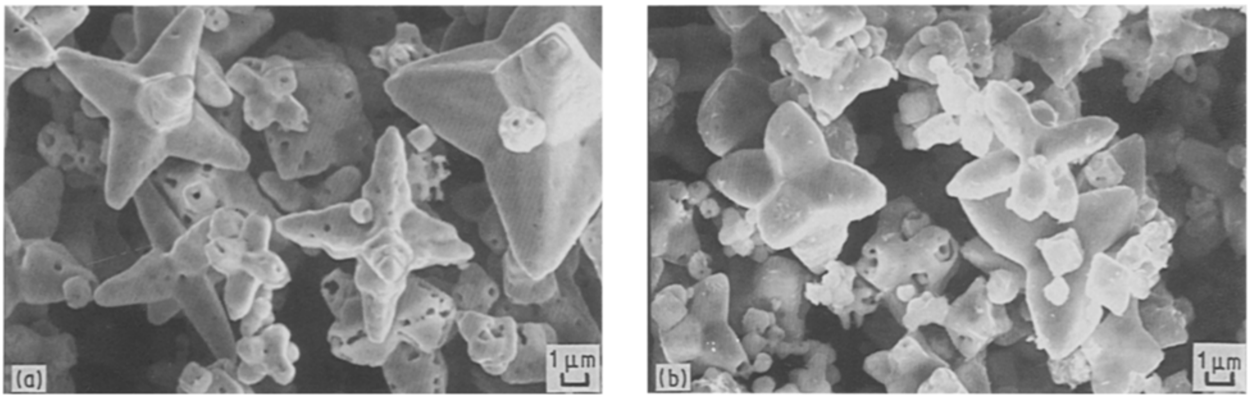

Fig. 2. SEM photomicrographs of the cuprous oxide powder produced electrochemically in a diaphragm cell without any additives under the conditions of: (a) 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 1000 A m^{-2}; (b) 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 500 A m^{-2}.

there are many small pores in the cuprous oxide particles. These small pores entrap the sodium chloride solution during the course of the formation of the cuprous oxide crystals. Because of the extremely small size of these pores, it is difficult to release the chloride during washing. If the time for washing is prolonged, a much lower chloride content in the cuprous oxide product would be expected.

3.2. *Electrolytic processes in a cell without a diaphragm*

Several additives, viz., potassium dichromate [8], potassium chromate [10, 11], calcium gluconate [9], and sodium nitrate [12, 15], were studied for the purpose of eliminating the diaphragm in the cell. Apart from the work of Vetere and Romagnoli [12], there is no literature which demonstrates clearly that a product containing more than 97% cuprous oxide can be obtained in a cell without a diaphragm when using additives. Little is known regarding the stability of electrolysis and the smoothness of the copper anode dissolution which the authors believe to be very important in the electrochemical production of cuprous oxide. On account of the prevention of copper powder deposition in the case of chromate and dichromate, it is preferable to use sodium chromate or dichromate as an additive in the sodium chloride system. Comprehensive electrolytic results are given in Table 3 and the SEM photomicrographs of the cuprous oxide particles are shown in Fig. 3.

First of all, concerning the sodium chromate additive, as can be seen from Table 3, the addition of sodium chromate is very effective in preventing the deposition of copper powder on the cathodes, there being no copper powder in the product at all. But the sodium chromate hardly ensures more than 97% cuprous oxide in the product prepared in a cell without a diaphragm. Although a product having 98.0% cuprous oxide was obtained in the case of 0.025 g l^{-1} Na_2CrO_4, this product was contaminated by a small amount of copper powder which had deposited on the cathodes due to the gradual consumption and ultimate exhaustion of chromate as the electrolysis progressed. This copper powder then dropped to the cuprous oxide slurry in the cell bottom. Chemical analyses in Table 3 demonstrate that with a decrease in the concentration of sodium chromate, the content

*Table 2. The effect of anodic current density in a diaphragm cell**

i (Am^{-2})	*500‡*	*750‡*	*1000§*	*1500‡*	*2000†*	*2500†*
RP (%); Cu_2O (%)	97.5	97.8	99.0	98.4	96.4	96.4
Cu° (%)	0	0	0	0	0	0
Cu_T (%)	86.8	87.0	88.3	87.8	86.1	86.8
CuO (%)	0.4	0.2	0.4	0.1	0.5	1.5
Cl^- (%)	0.87	0.63	0.50	0.37	2.03	1.14
C.E. (%)	92.7	94.7	96.7	94.6	93.9	85.3
P.Y. (kWh kg^{-1} Cu_2O)	0.88	1.03	1.03	1.29	1.57	1.86
Final product	red and dispersed	red and dispersed	red and dispersed	red and dispersed	red and dispersed	red and dispersed
Anode dissolution	even and stable	even and stable	even and stable	even and stable	very uneven and stable	severely uneven and stable
Product washing	easy	easy	easy	easy	slightly uneasy	slightly uneasy

* Other constant conditions: 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, perforated Ti cathodes, and 3% cell volume circulation of electrolyte per minute.
† Using four-layered nylon diaphragm.
‡ Using two-layered polypropylene diaphragm.
§ Using two-layered polyester diaphragm.

*Table 3. The addition of sodium chromate, dichromate, or calcium gluconate in the cell without a diaphragm**

Na_2CrO_4 ($g\,l^{-1}$)					$Na_2Cr_2O_7$ ($g\,l^{-1}$)			Calcium gluconate ($g\,l^{-1}$)			
	0.5	*0.1*	*0.05*	*0.025*	*6*	*4.5*	*2.5*	*0.25*	*0.05*	*0.025*	*0.02*
RP (%); Cu_2O (%)	88.7	94.1	96.5	99.7†	95.3	99.0	99.1	91.8	95.4	96.7	97.3
Cu^o (%)	0	0	0	0.75	0	0	0	0	0	0	0
Cu_T (%)	84.2	86.3	86.4	87.8	84.7	88.4	88.8	85.3	86.4	86.6	86.7
CuO (%)	8.0	3.5	0.9	0	0.2	0.5	0.8	4.7	2.1	0.9	0.3
Cl^- (%)	1.48	1.49	1.26	0.51	3.39	0.57	0.47	1.73	1.40	1.20	1.29
C.E. (%)	72.0	89.6	99.3	96.5	90.2	92.1	91.9	79.9	94.0	97.8	96.2
P.Y. (kWh kg^{-1} Cu_2O)	1.61	1.19	1.06	1.09	1.10	1.00	0.97	1.40	1.15	1.06	1.09
Final product	deep red and agglomerated	deep red and a bit agglomerated	red and dispersed	red and dispersed	orange-red and dispersed	red and dispersed	red and dispersed	deep red and agglomerated	red and a bit agglomerated	red and dispersed	red and dispersed
Anode dissolution	severely uneven and unstable	very uneven and unstable	uneven and unstable	uneven and a bit unstable	even and stable	even and stable	even and stable	severely uneven and unstable	very uneven and unstable	uneven and unstable	uneven and a bit unstable
Product washing	extremely difficult	difficult	somewhat difficult	easy	very difficult	somewhat difficult	somewhat difficult	extremely difficult	difficult	somewhat difficult	somewhat difficult

* Other constant conditions: 250 $g\,l^{-1}$ NaCl, 0.5 $g\,l^{-1}$ NaOH, 80° C, 1000 A m^{-2}, perforated Ti cathodes and 3% cell volume circulation of electrolyte per minute.

† Cu_2O 98.0%.

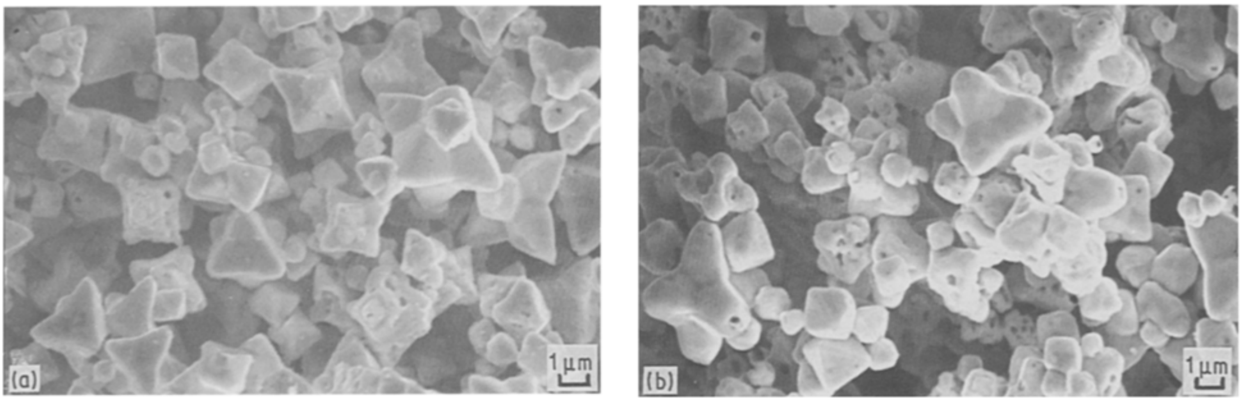

Fig. 3. SEM photomicrographs of the cuprous oxide powder produced electrochemically in the cell without a diaphragm under the conditions of: (a) 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 1000 A m^{-2}, 0.02 g l^{-1} $Na_2Cr_2O_7$; (b) 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 1000 A m^{-2}, 4.5 g l^{-1} calcium gluconate.

of cuprous oxide increased, and the contents of cupric oxide and chloride declined accordingly. Nevertheless, the copper anodes were electrodissolved always unevenly and unstable electrolysis took place in all cases, especially at high concentrations of sodium chromate. The rough dissolution of the copper anode can be explained by the formation of insoluble cuprous chromate on the anode surface. Because of this insoluble film on the anode surface, the electrodissolution of the copper anode was inhibited greatly, causing local passivation and thus leading to the overly high current density at the dissolution-active sites. This was followed by the local saturation of the concentration of cuprous ions and the precipitation of insoluble cuprous chloride. The net effect was that the anode potential increased beyond the equilibrium potential of the cupric ion formation. This can be proven with the data in Table 3 which show that there are considerable amounts of cupric oxide in the cuprous oxide product when using a high concentration of sodium chromate. The high chloride content can be ascribed to the existence of insoluble cuprous chloride and the surface tension of the particles, since it was found that it was difficult to wash the cuprous oxide slurry clean in this case.

As to the mechanism by which sodium chromate prevents the spongy metallic copper powder from depositing on the cathodes, as pointed out in the authors' previous paper [14], the chromate is first reduced to form an insoluble chromium hydroxide film on the cathode. This film is conductive, hydrogen continuing to evolve. However, it can inhibit the reduction of cuprous oxide. At the end of each experiment, a dense, deep green film was usually observed on the surface of the titanium cathodes.

As expected, sodium dichromate behaved almost exactly the same as sodium chromate, since the dichromate hydrolyzes to the chromate in alkaline solution. The minor difference between them is that sodium dichromate would be consumed at a slower rate than sodium chromate. Thus there was still sodium dichromate in the electrolyte which contained initially 0.02 g l^{-1} $Na_2Cr_2O_7$ (which is about equivalent to $0.02 \times 161.97 \times 2/262.04 = 0.025$ g l^{-1} Na_2CrO_4) and no copper powder deposition on the cathodes after 4.5 h of electrolysis. An SEM photomicrograph of the cuprous oxide powder produced with the addition of sodium dichromate is shown in Fig. 3a. Compared with the photomicrographs in Fig. 2, Fig. 3a reveals some modification in the particle morphology and the particle size, but the structure remains basically the same, being octahedral in shape.

So here it can be understood that sodium chromate and dichromate are not perfect additives. However, if a product having 95% cuprous oxide is still acceptable, they may also be recommended for use.

Gluconate appears to be a mysterious additive. According to Yang *et al.* [9], sodium gluconate should be superior to other gluconate salts. However, to the author's great surprise, sodium gluconate and calcium gluconate behave so differently that the former has virtually no inhibiting effect on the deposition of spongy copper powder on the cathodes. There were always large amounts of copper powder on the cathodes in the case of 2–6 g l^{-1} sodium gluconate, and the final dry cuprous oxide product was contaminated by copper powder in an amount approaching 30%. On the other hand, calcium gluconate can prevent effectively the deposition of copper powder. Not only can a satisfactory cuprous oxide product be obtained, but also the copper anode is dissolved quite evenly, in spite of the existence of very small nodules on its upper surface. Higher concentrations of calcium gluconate, such as 6 g l^{-1}, although resulting in almost no copper powder formation, cause extreme difficulty in washing the cuprous oxide slurry, for it does not settle readily. It was found in experiments that there was already a very small amount of copper powder attached to the upper edges of holes on the titanium cathode after electrolysis. Since calcium gluconate cannot inhibit completely the deposition of copper powder, it is recommended for use in a cell without a diaphragm when a very small amount of copper powder in the product can be tolerated. It is certain that the product produced with the addition of calcium gluconate in the cell without a diaphragm can contain more than 97% cuprous oxide. Fig. 3b reveals the SEM photo-

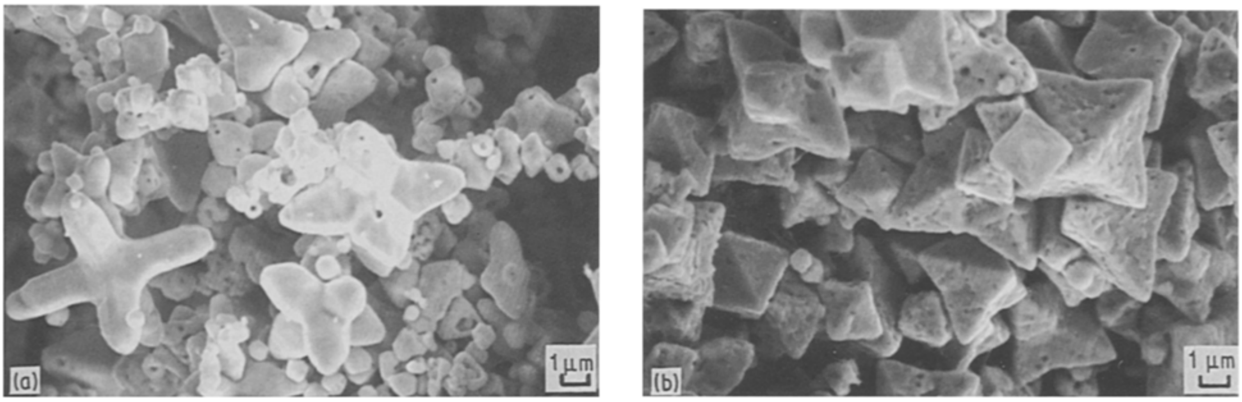

Fig. 4. (a) SEM photomicrographs of the cuprous oxide powder produced electrochemically in a diaphragm cell with (a) hydroxylamine hydrochloride additive under the conditions of: 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 1000 A m^{-2}, 0.5 g l^{-1} $NH_2OH.HCl$. (b) Sucrose additive under the conditions of: 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 1000 A m^{-2}, 0.5 g l^{-1} sucrose.

micrograph of the cuprous oxide powder produced using an addition to the electrolyte of 4.5 g l^{-1} calcium gluconate. It will be noted that there is a small change in the particle morphology and size.

As regards the mechanism of the inhibiting effect of calcium gluconate, the effect cannot be interpreted simply as the result of the adsorption of gluconate ions on the cathode so as to eliminate the direct contact of cuprous oxide with the cathode surface. Based on the present experimental results, the inhibition of copper powder deposition by the calcium gluconate is created possibly by the joint action of calcium ions and gluconate ions, with calcium ions adsorbed inside, directly contacting the cathode surface, and gluconate ions outside, chemically combined with the adsorbed calcium ions. On the other hand the reduction of cuprous oxide could be prevented by a thin film of calcium hydroxide.

3.3. *Electrolytic processes in a diaphragm cell with auxiliary additives*

Table 4 summarizes the experimental data, and Fig. 4 exhibits the SEM photomicrographs of the cuprous oxide powder. Hydroxylamine hydrochloride, in accordance with the experimental results, is the best auxiliary additive, having a positive effect on the quality of the cuprous oxide product. Not only was the copper anode dissolved uniformly, but also a very pure product reaching as high as 99% cuprous oxide with nearly no cupric oxide was obtained. As hydroxylamine hydrochloride is a mild reducing agent, it can reduce the cupric oxide to cuprous oxide ($2NH_2OH + 4CuO = 2Cu_2O + N_2O + 3H_2O$). The SEM photomicrograph of the cuprous oxide powder produced with the addition of hydroxylamine hydrochloride is presented in Fig. 4a. Because hydroxylamine hydrochloride appears acidic, sodium hydroxide solution must be added to bring the pH to the same value as in the initial electrolyte. The addition of hydroxylamine hydrochloride to the electrolyte would not cause any extra difficulty in removing the chloride during the washing of the cuprous oxide slurry. A comparison of the SEM photomicrograph in Fig. 4a with those in Fig. 2, shows that hydroxylamine hydrochloride will not create any obvious modification in the microstructure of the cuprous oxide particles.

Sucrose also has a positive effect on decreasing the content of cupric oxide (Table 4), makes the cuprous oxide particles more compact (Fig. 4b) and will not

*Table 4. The addition of hydroxylamine hydrochloride or sucrose in a diaphragm cell**

	$NH_2OH.HCl$ (g l^{-1})†		*Sucrose (g l^{-1})‡*		
	0.5	*2.5*	*0.5*	*2.5*	*5.0*
RP (%); Cu_2O (%)	99.3	99.2	97.1	97.4	97.4
Cu° (%)	0	0	0	0	0
Cu_T (%)	87.9	87.8	86.5	86.5	86.4
CuO (%)	0	0	0.3	0	0
Cl^- (%)	0.49	0.38	1.84	2.20	1.87
C.E. (%)	92.6	94.8	85.9	88.4	92.1
P.Y. (kWh kg^{-1} Cu_2O)	1.22	1.14	1.31	1.27	1.21
Final product	red and dispersed	red and dispersed	red and dispersed	red and dispersed	red and dispersed
Anodic dissolution	even and stable	even and stable	even and stable	even and stable	even and stable
Product washing	easy	easy	difficult	difficult	difficult

* Other constant conditions: 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH, 80° C, 1000 A m^{-2}, perforated Ti cathodes and 3% cell volume circulation of electrolyte per minute.

† Two-layered polypropylene diaphragm.

‡ Four-layered nylon diaphragm.

result in an uneven dissolution of the copper anode. However, as can be seen from the SEM photomicrograph of Fig. 4b, the particles of cuprous oxide have a very rough surface, which is a direct reason for the high chloride content in the cuprous oxide product (Table 4).

Hydrazine hydrate, perhaps due to its strong reducing power, failed to be an effective additive, since a medium amount of copper powder was produced during the electrolysis.

3.4. *Washing*

The washing of the cuprous oxide slurry after its withdrawal from the cell is a very important step in the process. It is necessary to effect the fast and thorough removal of impurities, especially chlorides, and to prevent the oxidation of cuprous oxide. Vetere and Romagnoli [12] recommended that the cuprous oxide slurry be treated with a solution of neutralized invert sugar (equimolecular mixture of dextrose and levulose) at 3% concentration for 10 min before washing in order to reduce the tendency towards oxidation during washing and drying. Palanisamy and coworkers [3] suggested that the cuprous oxide slurry be separated from the electrolyte within 12 h to avoid the formation of a greenish copper oxychloride layer. The slurry should always be covered with distilled water during washing and before stabilization. The following washing procedures were observed in the present research.

After the cuprous oxide slurry, together with the electrolyte, was withdrawn from the cell, the precipitate of cuprous oxide was allowed to settle. As soon as a good settling of the cuprous oxide was reached, as much of the clear electrolyte as possible was decanted. Afterwards, the cuprous oxide powder was washed repeatedly with 65–70° C distilled water through the cycles of stirring settling and decanting for 6 to 9 times, or until no precipitation occurred in the supernatant solution upon the addition of a few drops of silver nitrate solution. Suction filtration was not used during washing on account of the possible entrapment of chloride in the cuprous oxide particles, and the possible oxidation of the wet, unstabilized cuprous oxide when the air passes through it on suction.

It is noteworthy that it is nearly impossible to wash the cuprous oxide entirely free of chlorides using only mechanical washing, since as can be seen from the aforementioned SEM photomicrographs of the cuprous oxide powder, there are many small pores in the particles of cuprous oxide, and there are some chlorides which are combined chemically in the insoluble copper compounds, such as, $CuCl \cdot 3CuO \cdot 4H_2O$ [1], $CuCl_2 \cdot 3Cu(OH)_2$ [16], $CuCl_2 \cdot 3Cu(OH)_2 \cdot 3H_2O$ [16], CuCl [17], and $Cu_2(OH)_3Cl$ [17].

3.5. *Stabilization*

Due to the high activity of the wet, freshly prepared cuprous oxide, the cuprous oxide must be passivated from oxidation. The goal of stabilization with 0.1–0.25% glue, gelatin or linseed oil is to make a lyophilic adsorption coat on the surface of the cuprous oxide particles [3], while with 0.2% benzotriazole (BTA), the objective is to form a compact multilayer complex film of $Cu(I)\text{–}C_6H_4N_3$ on the surface of the cuprous oxide particles so as to keep the cuprous oxide from oxidizing during drying and storage [18].

$$Cu_2O + 2HC_6H_4N_3 \longrightarrow 2Cu(I)\text{–}C_6H_4N_3 + H_2O$$

Since benzotriazole has been used successfully in preventing the tarnishing of metallic copper on exposure to the air and the corrosion of metallic copper on immersion in sodium chloride solution, it is reasonable to expect that prevention of the oxidation of cuprous oxide to cupric oxide would be realized when benzotriazole is employed in the case of cuprous oxide.

The stabilizing solution was prepared by dissolving 2 g of benzotriazole in 1000 ml of 95% ethanol at room temperature. When stabilizing the cuprous oxide, decant the clear supernatant water as much as possible, and then add the stabilizing solution according to the following ratio:

$$Cu_2O\,(kg) : \text{Benzotriazole}\,(kg) = 1000 : 2$$

Stir for half an hour, and then allow the slurry to stand still overnight at room temperature. Just before drying, dehydrate the cuprous oxide with suction or centrifugal filtration to remove the solution as much as possible.

3.6. *Drying*

Vacuum or an inert atmosphere should be used for drying to prevent the cuprous oxide from oxidizing. A stationary vacuum oven was used in the present experiments under the following conditions:

80° C	for 2 h
100° C	for 6 h
vacuum	less than 20 mm Hg

To ensure that no black CuO is formed during vacuum drying a temperature of 55–60° C may be preferable. In production on a commercial scale, the use of a rotating drum-style vacuum oven with a very slow rotation speed would need to be considered to accelerate the drying process and to avoid a local high pressure of steam inside the lumps of the cuprous oxide, possibly causing the oxidation of cuprous oxide. The drying was considered to be complete if the vacuum inside the oven did not drop down any further within one hour after stopping the vacuum pump. In the present research, most products except a few were found to be slightly agglomerated after drying but to be well-dispersed through gentle grinding.

3.7. *Packing and storage*

Vacuum packing should be required in the commercial production of cuprous oxide so as to eliminate the air inside the powder and thus to avoid its oxidation. The packing room should be air-conditioned to control the humidity and temperature, and to ensure the absence of harmful dust in the atmosphere. The cuprous oxide should preferably be packed in plastic such as polyethylene bags under vacuum, and then placed in a metal drum.

The final cuprous oxide product should be stored in a dry and well-ventilated room at room temperature in the absence of any oxidants.

4. Conclusions

(1) A product with more than 97% cuprous oxide can be electrosynthesized in a cell both with and without a diaphragm.

(2) In the cell with a diaphragm, the best diaphragm material is nylon fabric, and the optimal operating electrolytic conditions are:

sodium chloride	250 g l^{-1}
sodium hydroxide	0.1–1.0 g l^{-1} (pH = 11.1–12.1)
temperature	80° C
anodic current density	500–1500 A m^{-2}
cathode	perforated titanium sheet
circulation	around 3% of the cell volume per minute

(3) In the cell without a diaphragm, sodium chromate, sodium dichromate and calcium gluconate are all effective additives in preventing the deposition of copper powder on the cathodes.

Sodium chromate or dichromate can prevent effectively the deposition of copper powder on the cathodes, and their concentrations should be as low as possible, the former around 0.03–0.05 g l^{-1}, and the latter around 0.02–0.025 g l^{-1}. Although the anode is dissolved unevenly, these two additives can still be considered for use when a slightly higher chloride content is allowable and a content of cuprous oxide down to 95% is acceptable.

Sodium gluconate is not an effective additive, but calcium gluconate proved to be very positive, although its use did not eliminate completely the deposition of spongy copper powder on the cathodes. If a very small amount of copper powder can be tolerated in the cuprous oxide product, calcium gluconate is a very good additive for the purpose of eliminating the use of a diaphragm in the cell. The appropriate concentration is around 4.5 g l^{-1}.

(4) In the cell with a diaphragm, as to the auxiliary additives, hydroxylamine hydrochloride is the best additive, having a positive effect on the purity of the cuprous oxide product and giving rise to no obvious modification in the microstructure of the cuprous oxide particles. Sucrose makes the particles of cuprous oxide more compact, resulting in a product having a high apparent density. Also the product contains slightly more than 97% cuprous oxide, despite a little higher content of chloride. Hydrazine hydrate is an unfavourable additive.

(5) Washing the cuprous oxide slurry with 65–70° C distilled water will not cause a visible oxidation of cuprous oxide. Benzotriazole in ethanol solution is an effective stabilizer in avoiding the oxidation and tarnishing of the cuprous oxide during drying and storage. Vacuum drying at 55–60° C is appropriate.

Acknowledgements

This work was sponsored by the International Development Research Centre (IDRC), Ottawa, Canada. The authors express their grateful thanks to Professor Shiguan Chen of the Shanghai University of Technology, People's Republic of China, for providing useful literature, to Kashmir Gill at Queen's University for preparing the SEM photomicrographs, and to Joseph H. Dobrosielski in Amoco Fabrics and Fibers Ltd., Pointe Claire, Quebec, Canada, for recommending the use of nylon fabric as a diaphragm.

References

[1] S. S. Naboichenko, A. B. Lebed, L. L. Ermakova and E. Z. Kharitid, *Tsvetn. Met.* (1987) (9) 30.

[2] L. C. Hurd, U.S. Pat. 2273643 (February 1942).

[3] R. Palanisamy, K. C. Narasimham, R. Viswanathan and H. V. K. Udupa, *Indian Journal of Technology* **22** (1984) 319.

[4] K. Sugasaka, T. Kobayashi, S. Kato and J. Mizuguchi, *Denki Kagaku* **36** (1968) 250.

[5] L. C. Cahue and S. M. Castro, *Bol. Soc. Chil. Quim.* **27** (1982) 337.

[6] Z. Stankovic, V. Zlatkovic, M. Pjescic, P. Zivkovic, Z. Matic and S. Zivic, *Tehnika (Belgrade)* **32** (7–8) (1977) 16.

[7] R. E. Gana, Research Report on Electrochemical Production of Cuprous Oxide Powder in Anode-Support System, Universidad Catolica de Chile, Santiago, Chile (March 1988).

[8] L. L. Ermakova and V. V. Puzakov, *Tsvetn. Met.* (1986) (10) 25.

[9] C. Y. Yang, J. L. Zhao, S. Wang, B. K. Liu, Z. W. Kong, D. S. Shi, W. F. Jin, Y. J. Wang, J. S. Xia and Y. Luo, *Huaxue Shijie* **23** (3) (1982) 66; *Chemical Abstracts* **100** (1984) 93378a.

[10] A. G. Sokolovskii, I. B. Markov, V. Ya. Aleksandrov, E. V. Sokolovskaya and B. P. Matseevskii, *Khim. Tekhnol. Khim.* (1974) 102.

[11] *Idem, ibid.* (1974) 108.

[12] V. F. Vetere and R. Romagnoli, *Ind. Eng. Chem. Prod. Res. Dev.* **23** (1984) 656.

[13] L. L. Ermakova, V. V. Puzakov and A. D. Lanskikh, *Tsvetn. Met.* (1986) (7) 35.

[14] J. Ji and W. C. Cooper, *J. Appl. Electrochem.* **20** (1990) 818.

[15] V. F. Vetere and R. Romagnoli, *J. Chem. Tech. Biotechnol.* **34A** (1984) 335.

[16] M. Drogowska, L. Brossard and H. Henard, *Corrosion* **43** (1987) 549.

[17] C. Y. Fu and D. J. Zheng, *J. Central-South Inst. Mining and Metallurgy* (People's Republic of China) (3) (1980) 12.

[18] C. H. Huang, *Plating and Surface Finishing* **73** (6) (1986) 96.