Electrochemical production of cuprous oxide and metallic nickel in a two-compartment cell

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The purpose of the present investigation was to develop an electrochemical process to obtain simultaneously cuprous oxide powder and metallic nickel in a two-compartment cell. Nafion® 901 bimembrane (Dupont, USA) was employed to separate the compartments to avoid the diffusion of nickel ions from the catholyte to the anolyte. A continuous addition of sodium hydroxide solution to the anodic compartment was necessary to form *in situ* the cuprous oxide by chemical reaction with the cuprous chlorocomplexes generated at the anode. As an anode system, a titanium basket filled with copper scrap wire was utilized. The anodic operating conditions were: NaCl $250\,g\,dm^{-3}$, pH 10, $80°\,C$, c.d. $6\,A\,dm^{-2}$ and current concentration $0.4\,A\,dm^{-3}$. The cathodic parameters were: $Ni^{2+}\,74\,g\,dm^{-3}$, $H_3BO_3\,30\,g\,dm^{-3}$, sodium lauryl sulphate $0.5\,g\,dm^{-3}$, coumarin $0.15\,g\,dm^{-3}$, pH 2, $50°\,C$, c.d. $6\,A\,dm^{-2}$. Good quality red–violet cuprous oxide powder, meeting ASTM specifications D912-65 to be used in antifouling paints and metallic nickel (> 99.96% Ni) was obtained.
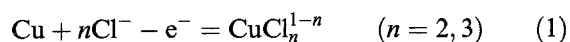
1. Introduction

The production of cuprous oxide can be achieved using different methods [1]. The electrochemical method is used to obtain cuprous oxide powder on an industrial scale, yielding a product of good purity and colour. The basic electrochemistry of the process in alkaline sodium chloride solution and the operating conditions necessary to give a product having the purity required by ASTM specification D912-65 have been studied [2–9]. Additionally, the authors have reported the use of a titanium mesh basket filled with small pieces of high-grade copper scrap (anode-support system) to replace the conventional copper sheet anode [10–12].

In this paper a proposal is described for an alternative to the conventional electrochemical process. It consists of replacing the cathode reaction (hydrogen evolution) by another electrode process (nickel deposition). The system requires a diaphragm to separate the catholyte from the anolyte and the continuous addition of a sodium hydroxide solution to the anode compartment.
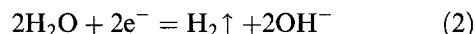
2. Principles

During the anodic dissolution of copper in alkaline concentrated sodium chloride solutions the principal reactions in the system are:
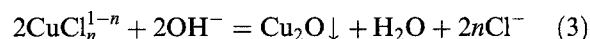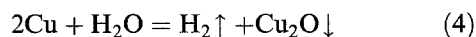Anodic reaction:

$$Cu + nCl^- - e^- = CuCl_n^{1-n} \qquad (n = 2, 3) \qquad (1)$$

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Cathodic reaction:

$$2H_2O + 2e^- = H_2\uparrow + 2OH^- \qquad (2)$$

Chemical reaction:

$$2CuCl_n^{1-n} + 2OH^- = Cu_2O\downarrow + H_2O + 2nCl^- \qquad (3)$$

Net cell reaction:

$$2Cu + H_2O = H_2\uparrow + Cu_2O\downarrow \qquad (4)$$

A secondary reaction is possible, leading to the reduction of cuprous oxide to spongy copper by contact of the finely divided powder with the cathode. This reaction can be avoided if the cathode is covered with a diaphragm or if additives are employed.

According to the chemical reaction (Equation 3) the hydroxyl ions generated at the cathode (Equation 2) are necessary for the formation of cuprous oxide. These ions pass through the diaphragm into the anodic region by migration, diffusion and convection.

The net cell reaction indicates that only copper (anode) and water are consumed in the process. The chloride concentration remains constant (Equations 1 and 3).

The pH of the electrolyte may either decrease or increase depending on the generation of secondary products, such as $Cu_2(OH)_3Cl$ or $CuCl_2\cdot3Cu(OH)_2$ [12]. Additionally, the pH decreases during the electrolysis because of CO_2 absorption.

The alternative system proposed in this work consists in replacing the cathodic process (Equation 2) by the electrochemical production of metallic nickel, from a nickel chloride solution, maintaining the same anodic reaction.
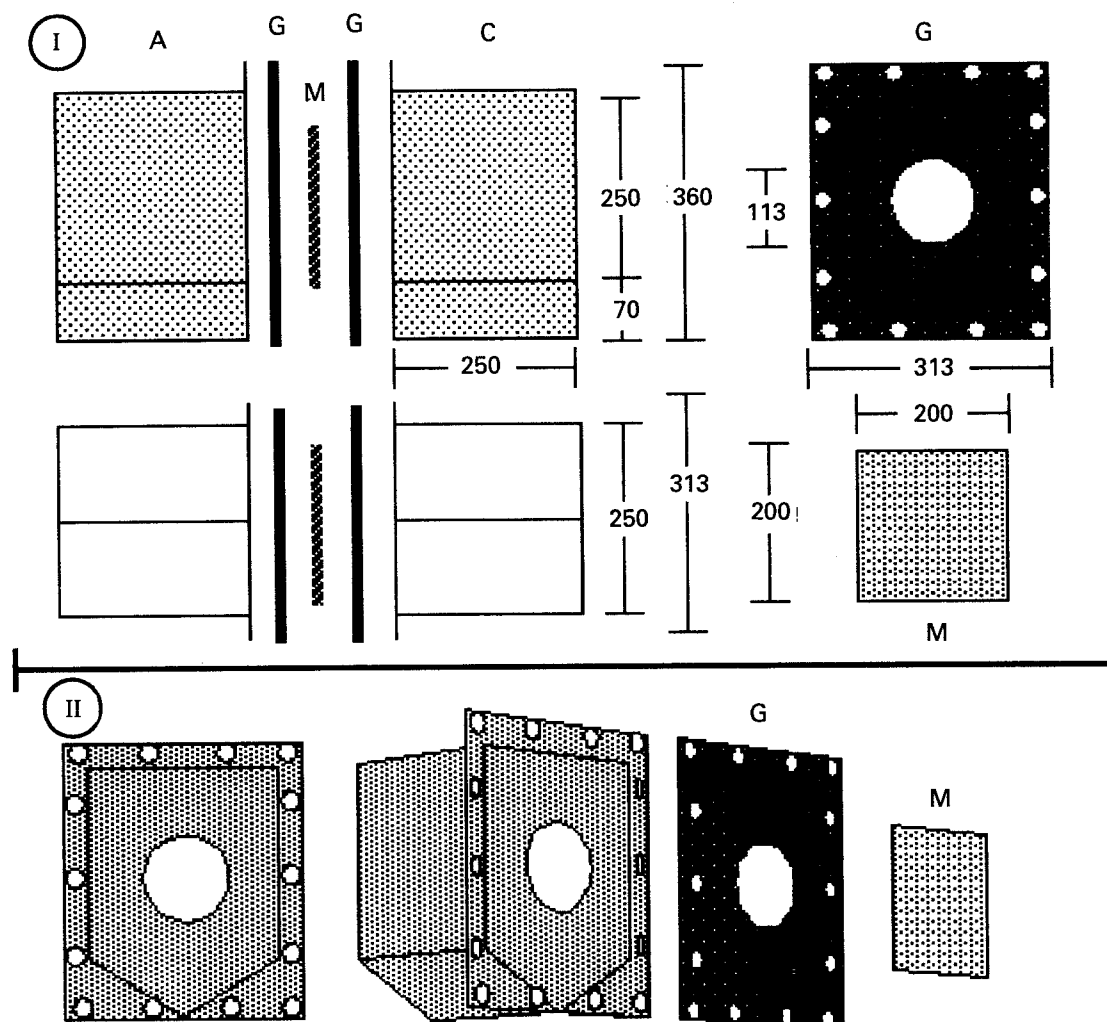
Fig. 1. 40 dm³ coated steel cell for Cu₂O and metallic nickel production (all measures in mm). A,C: anode and cathode compartments. M: Nafion® membrane, G: rubber gasket. I: Section and plan view. II: Half-cell details.

Alternative cathodic reaction:

$$Ni^{2+} + 2e^- = Ni \qquad (5)$$

The proposed system has the economic advantage of replacing the generation of two mols of hydroxyl ions by the production, in the same cell, of one mole of a metal with good commercial value, maintaining the production of cuprous oxide.

To achieve this goal it is necessary that the cell has an appropriate diaphragm to separate the anolyte from the catholyte and to minimize the diffusion and convection of some species, namely the cuprous chlorocomplexes, towards the cathode compartment and the nickel ions toward the anode compartment. Furthermore, it is essential to add continuously sodium hydroxide solution to the anolyte to maintain its concentration between 0.1 and $1.0\,g\,dm^{-3}$ [2, 3].

It is advisable to use a nickel chloride solution as catholyte to avoid the presence in the system of other anions such as sulphate or nitrate. This solution must be added continuously to the cathodic compartment to keep the nickel ion concentration within an adequate range. The nickel chloride solution can be obtained in the course of recovering the metal from wastes such as the catalyst used in fish oil hydrogenation [13, 14].

3. Experimental details

Electrolyses were carried out in a 40 dm³ cell with two compartments of equal dimensions separated by a 5 dm² circular diaphragm. The cell, 500 mm (L) × 250 mm (W) × 320 mm (H) inside dimensions, was constructed of 3 mm thick steel covered with epoxy resin, with the compartments having a slightly sloping bottom (Fig. 1). When it was necessary to replace the diaphragm, both compartments were completely separated.

An anode-support system (AS), developed by the authors, was used to replace the conventional copper sheet anode [15–20]. In this process a 120 mm × 100 mm AS having the form of a basket with a 35 mm wide mouth was employed. The manufacturing details of this basket have been described [12]. The basket was filled with chopped wire copper scrap (2–4 mm diameter) with the AS acting only as an electrical contact between the external current source and the particulate copper material to be dissolved. The parallel sides were made of 0.7 mm thick titanium mesh (Imperial Metal Industries, UK) having elongated horizontal perforations to prevent the chopped copper from falling to the bottom of the cell as the particle size decreased. The bottom

Table 1. Electrolyte composition and operating parameters

	Anode compartment	Cathode compartment
Electrodes	Basket Ti/Cu	Ni sheet
Electrolyte (g dm^{-3})	NaCl (250)	Ni^{2+} (74)
		H$_3$BO$_3$ (30)
		Na-LS (0.5)
		Coumarin (0.15)
Density (22° C) (g cm^{-3})	1.16	1.16–1.18
pH	10 ± 0.3	2–5 ± 0.3
Temperature (° C)	80 ± 2	20–60 ± 2
Current density (A dm^{-2})	1–12	1–12
Electrode area (dm^2)	1.2 (*)	0.7–1.7
Current conc. (A dm^{-3})	0.1–0.5	0.2–0.6
Electrolyte flow (dm^3 min^{-1})	0.5	0.1–3.0
Continuous filtration	yes	no

* The area of one of the flat sides of the basket is considered in the case of the anode-support.

and the narrow sides of the basket were made of U-shaped unperforated 0.7 mm thick titanium sheets riveted to a 2 mm thick copper support bar (150 mm × 20 mm).

A 0.5 mm thick nickel sheet was used as cathode ('starting sheet'). These thin sheets were obtained by stripping from a 3 mm stainless steel AISI-316 cathode, making use of an ancillary cell containing Watts solution at 55–57° C, using a 5 mm thick nickel anode and a 4 A dm^{-2} current density.

The anolyte and catholyte composition and the operating parameters are indicated in Table 1.

Both electrolytes were heated in the cell by means of two 1.5 kW heaters with a thermoregulator and the water lost by evaporation was replenished continuously with distilled water.

The agitation, continuous filtration and recirculation of the catholyte was provided by means of a Sethco filtration system model LPM-30.

The anolyte was agitated by bubbling nitrogen and a sodium hydroxide solution was dripped continuously using a syringe system, Braun Melsungen AG. Recirculation of the electrolyte was provided by a Cole–Parmer peristaltic pump by the bottom-top system. The anolyte was continuously centrifuged with a 451/ IEC chemical centrifuge under nitrogen atmosphere to recover the cuprous oxide powder. Following filtration the washed product was suspended in distilled water at 80° C (rendered alkaline to pH 10 with NaOH) for 10 min under bubbling nitrogen. Decantation and further washing took place until the supernatant solution was free of chloride ions. The solid was then agitated for 20 min in a 0.2% alcoholic solution of benzotriazole to stabilize the cuprous oxide. After standing for 10–12 h, the supernatant liquor was decanted, the slurry filtered, and cuprous oxide dried in a vacuum oven at 70–80° C and 25 cm Hg. The powder was screened through a 325 Tyler mesh screen (44 μm) and kept under a nitrogen atmosphere.

Different types of polypropylene cloth (Reicotex, Chile) and Nafion® membranes (Dupont, USA) were utilized as diaphragms between the compartments.

A modified Leed & Northrup System was utilized to measure the influence of the diaphragms on the internal resistance of a two-compartment 0.5 dm^3 cell with platinum electrodes and KCl 0.02 N solution.

A stabilized power supply (12V, 30A) was used and the electrical charge was measured with an LYP-Electronica digital coulometer.

Chemical analysis of the cuprous oxide powder and the nickel deposit was carried out by atomic absorption spectrophotometry, and the morphology of the powder was examined with a scanning electron microscope, JEOL model JSM-6400, with an X-ray microprobe to determine the presence of chloride and nickel.

4. Results and discussion

4.1. Diaphragm

The main objective of using a diaphragm in this electrolytic process was to control the diffusion of the nickel ions from the cathodic to the anodic compartment so that contamination of the cuprous oxide was avoided. Additionally, it was important to prevent the passage of the cuprous compound toward the cathode compartment to avoid its loss. Therefore, different types of polypropylene/polyethylene, polyester and polyamide cloth (Reicotex, Chile) were employed as diaphragm, under the operating conditions indicated in Table 1. Unfortunately, the main condition of the diaphragm was not achieved and the nickel ions passed through the cloths contaminating the cuprous oxide.

Consequently, four types of Nafion® cation permselective membranes (324, 417, 423 and 901, Dupont) were employed as diaphragm [21, 22]. For all these types, practically the main mass transport process is the passage of sodium ions through the membrane from the anolyte to the catholyte. As indicated above, the sole purpose of the membrane was to prevent the diffusion of nickel ions toward the anolyte. In this case, the property of OH$^-$ ion and Cl$^-$ ion rejection on the cathode face of the membrane is not important.

Table 2 shows the contamination of the NaCl solution with nickel ions after 24 h at different temperatures, using the solution indicated in Table 1, without polarization of the system. Both solutions

*Table 2. Amount of nickel (mg) in the anodic compartment after 24 h without polarization of the system**

Nafion® type	Temperature (° C)		
	20	40	60
	Nickel amount/mg		
324	232	318	641
417	445	470	918
423	343	499	849
901	< 50	< 50	< 50

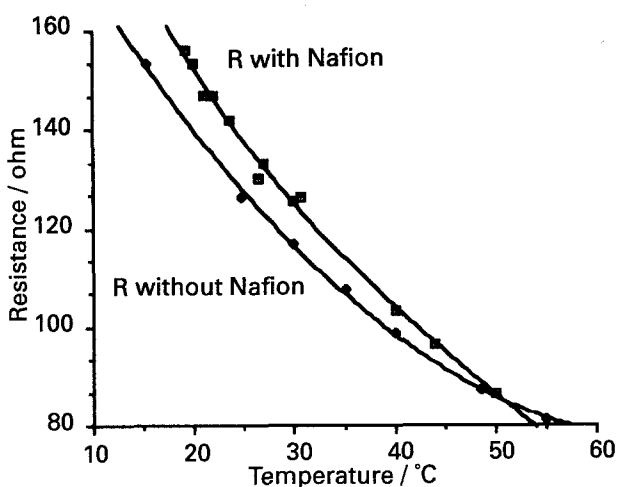* Operating conditions indicated in Table 1.

Fig. 2. Cell resistance as a function of temperature in systems with and without Nafion® 901 diaphragm. KCl 0.02 N solution and platinum electrodes.

had the same density to avoid the generation of hydrostatic pressure in the system.

Clearly, the most efficient membrane was the Nafion® 901, because it practically avoided the contamination of the anolyte with nickel. When electrolyses were carried out for 24 h, with Nafion® 901 previously 'swollen', no nickel contamination of the cuprous oxide was detected. This behaviour was expected, because the polarization of the system contributed to maintain the nickel ion in the cathode compartment.

The effect of the use of a Nafion® 901 diaphragm on the internal resistance of the system was studied at different temperatures. Figure 2 shows that the use of Nafion® 901 at 20° C produced an increase of ∼ 10% in the resistance with respect to the system without a diaphragm. On the other hand, at 50° C the resistance was the same in both cases. This behaviour can be explained because the hydrophobic fluorocarbon component of the membrane and the hydrophilic ionic groups are incompatible. Therefore, some degree of phase separation occurs, leading to the formation of interconnected hydrated ionic
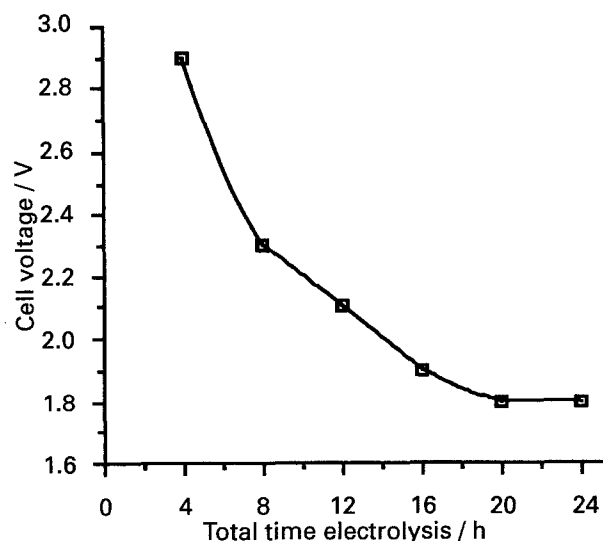
clusters which determine the electrochemical properties of the polymer. As the temperature is increased, these restraining forces are weakened, and the fluorocarbon chains develop enough mobility to adjust to a more highly swollen state. For this reason, it is important to swell the membrane before use.

Figure 3 shows the variation in the cell voltage, when an electrolysis was carried out for 24 h, with anodic c.d. 1 A dm^{-2}, cathodic c.d. 6 A dm^{-2}, at 25 ± 1° C, without previous swelling treatment of the Nafion® 901. Initially the voltage was 2.9 V, which remained practically constant at 1.8 V after 16–20 h. The last value was achieved immediately if the membrane was previously swollen in a sodium hydroxide solution (3 g dm^{-3}) for 24 h.

4.2. Anodic production of cuprous oxide powder

Several 24 h electrolyses were carried out in the 40 dm^3 cell with a Nafion® 901 diaphragm, under the conditions indicated in Table 1. The electrolyte concentration, pH and temperature were selected in accordance with the best values obtained by the authors in previous work [11, 12]. The pH 10 ± 0.3 was maintained by the dropwise addition of a 40 g dm^{-3} sodium hydroxide solution. It was possible to keep the volume of the anolyte between 17.5 and 18.5 dm^3, because the continuous addition of solution permitted the replacement of water lost by evaporation.

Figure 4 indicates the quality of the cuprous oxide powder as a function of the current density (c.d.) and the current concentration (CI), which expresses the current (A) per unit volume of electrolyte (dm^3). Both factors, c.d. and CI, have been shown to be very important parameters in cuprous oxide production, especially with respect to a possible scale-up of the system [12]. In this work, the factors CI and c.d.
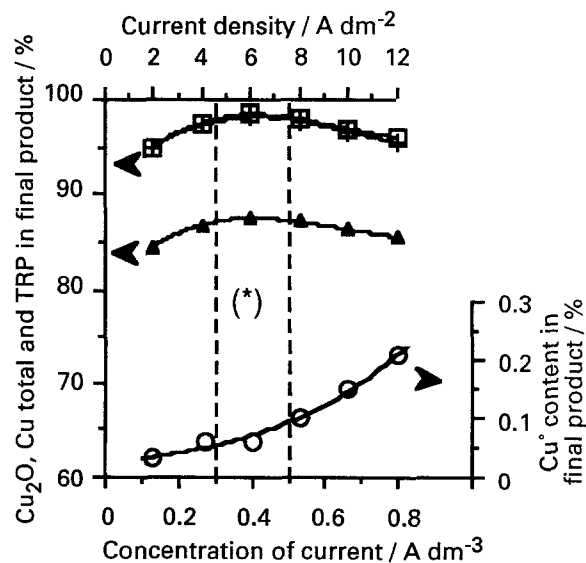

Fig. 3. Cell voltage as a function of electrolysis time, under the operating conditions indicated in Table 3.

Fig. 4. Quality of Cu$_2$O powder as function of the concentration of current (CI) and the current density (c.d.) in 24 h electrolyses under the operating conditions indicated in Table 3. Key: (□) Cu$_2$O; (▲) Cu metal; (+) TRP; (○) Cu^0. (*) Range of CI where the Cu$_2$O meeting ASTM specification D912-65.
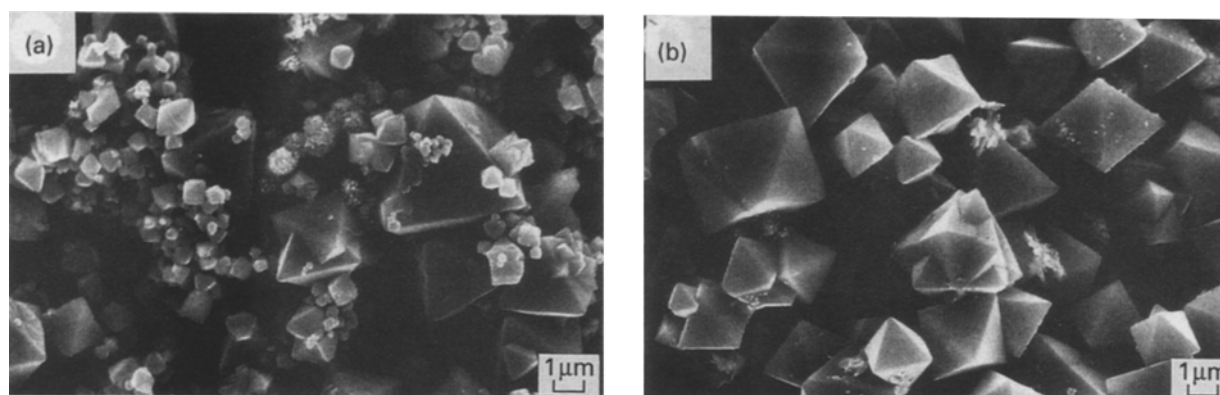
Fig. 5. SEM photomicrographs of Cu_2O obtained under the operating conditions indicated in Table 3. (a) Yellow–orange product, with c.d. $2\,A\,dm^{-2}$; (b) red–violet product, with c.d. $6\,A\,dm^{-2}$.

had a direct relation, because the volume of the electrolyte and the surface of the anode remained constant.

In the CI range $0.3-0.5\,A\,dm^{-3}$ (c.d. $4.5-7.5$ $A\,dm^{-2}$) good quality products were obtained conforming to the ASTM specification D912-65 for use in antifouling paints ($Cu_2O > 97\%$, $Cu_{tot} > 86\%$, TRP $> 97\%$). The best result was achieved with $0.4\,A\,dm^{-3}$, corresponding to a current density of $6\,A\,dm^{-2}$. For low c.d. values ($2-3\,A\,dm^{-2}$) a yellow–orange final product was obtained, similar to that achieved when the electrolyses were carried out maintaining the pH in the 8–9 range.

The presence of a small amount of metallic copper was detected in the final product. Obviously, the use of a two-compartment cell separated by a Nafion® membrane during the electrolytic process does not permit the generation of copper metal either by chemical or electrochemical reduction. Therefore, the presence of metallic copper can only be explained considering that during the anodic dissolution of scrap in the titanium mesh basket small particles of copper might fall to the bottom of the cell as anode slime. This explanation is supported by the fact that the amount of metallic copper in the Cu_2O increased when the current density rose from 2 to $12\,A\,dm^{-2}$. When the c.d. was higher than $8\,A\,dm^{-2}$ it was necessary to reload the basket with chopped wire scrap to maintain the level of the particulate copper in the anode-support system. If the amount of copper scrap in the basket was adjusted so as not to fall below 3/4 of a full load, the cell voltage could be maintained within a 6–7% fluctuation. During the reload operation it was possible that small particles could pass through the perforated titanium walls falling to the bottom of the cell, because the basket was not covered with a cloth.

The amount of cupric oxide in the final product fluctuated in the range 0.01–0.1%, without any correlation with CI, so it is postulated that this oxide was generated during the filtration and drying processes.

Figure 5 shows SEM photomicrographs of the yellow–orange and red–violet cuprous oxide powders produced electrochemically in the $40\,dm^3$ cell under the conditions indicated in Table 3. Both types of powder exhibit an octahedral bipyramidal shape, but

the red–violet Cu_2O has a more homogeneous crystal size than the yellow–orange one. In both cases X-ray microanalysis detected the presence of chloride in some areas. No contamination with nickel was noted. In relation to the SEM photomicrographs obtained by Ji and Cooper [3] a notable difference can be observed. In fact, in that study many small pores in the octahedral shaped particles of cuprous oxide could be seen. These small pores could entrap the sodium chloride solution during the formation of the cuprous oxide crystals. Because of the small size of these pores, it is difficult to remove the chloride during washing. The main difference between the aforementioned study and the present work are two operating conditions. In the Ji and Cooper study the current density ($10\,A\,dm^{-2}$) and particularly the current concentration ($2.6\,A\,dm^{-3}$) were higher than those used in this work.

4.3. Cathodic production of nickel

To establish the optimal operating conditions for the cathodic process, several 1 h electrolyses were carried out using the electrolyte indicated in Table 1.

In general, fine and adherent deposits were obtained in all experiments in the pH range studied (2–5). The colour of the nickel deposit changed from light grey (pH 2–3) to dark grey (pH 5). This behaviour could be attributed to the coevolution of hydrogen, the corresponding increase of the pH in the diffusion layer and the hydrolysis and formation

Table 3. *Optimal electrolytic operating conditions*

	Anode compartment	Cathode compartment
Electrodes	Basket Ti/Cu	Ni sheet
Electrolyte ($g\,dm^{-3}$)	NaCl (250)	Ni^{2+} (74)
		H_3BO_3 (30)
		Na-LS (0.5)
		Coumarin (0.15)
pH	10	2
Temperature (°C)	80	50
Current density ($A\,dm^{-2}$)	6	6
Current conc. ($A\,dm^{-3}$)	0.4	0.4

of basic salts on the surface of the cathode. When the pH of the electrolyte solution was lower than 3 this phenomenon was avoided. The pH increased slowly with deposition time because of the continuous evolution of a small amount of hydrogen. Therefore, a continuous dropwise addition of 5% hydrochloric acid was necessary to maintain the pH in the appropriate range (± 0.3).

The sodium chloride concentration increase in the catholyte after 24 h electrolysis (173 Ah) was 53 mg dm^{-3}. This is according to the mass balance of the system considering the amount of nickel deposited.

Good quality nickel deposits were obtained when electrolyses were carried out over a wide range of current density (1 to 12 A dm^{-2}) if the electrolyte temperature was maintained at an acceptable value. For instance, good c.d./T relations were 2–6 A dm^{-2} at 20–45° C and 6–12 A dm^{-2} at 45–60° C.

A series of 24 h electrolyses were carried out at 50–55° C 6.7 A dm^{-2}, and pH 2 $\pm$ 0.2, to study the effect of some additives on the electrodeposits (> 2 mm thick). Sodium lauryl sulphate (Na–LS) (0.2–1.0 g dm^{-3}) was added as surface active agent to avoid the pitted deposit generated by the slow evolution of small hydrogen bubbles on the cathode surface. With 0.5 g dm^{-3} of this antipitting agent the surface tension of the solution was reduced to 30–31 dynes cm^{-1} (25° C) and the cathodes were obtained free of pits.

Coumarin and 2-butyne-1,4 diol were utilized separately to favour the production of fine nickel deposits without nodules. The use of butyne-diol in the 100–1000 mg dm^{-3} concentration range gave fine deposits, but with a strong contractile type internal stress which bent the nickel cathode after a few hours of electrolysis. When 100–1000 mg dm^{-3} of coumarin was added to the electrolyte, fine light grey deposits were achieved, with no visible cathode bending. The best nickel deposits were obtained with 150–250 mg dm^{-3} of coumarin, with an electrolyte flow range of 0.1–0.2 dm^3 min^{-1} below the cathode. When high flow rates were used, the nickel crystallization was less homogeneous, especially when the solution entered in front of the cathode face.

Microanalysis of the nickel deposits by atomic absorption and X-ray indicated no contamination with copper or other heavy metals. Deposits with more than 99.96% nickel were obtained.

5. Conclusions

This study has shown that it is feasible to use a two-compartment electrolytic cell to obtain cuprous oxide powder and good quality metallic nickel (simultaneously) in the same operation.

To achieve this goal it is fundamental to separate the compartments with a diaphragm such as bimembrane Nafion® 901 to avoid the diffusion of nickel ions to

the anolyte. Furthermore, the continuous addition of sodium hydroxide solution to the anode compartment is necessary to form *in situ* the cuprous oxide by reaction of the cuprous chlorocomplexes generated at a titanium anode-support system filled with copper scrap wire. It is advisable that both the anolyte and the catholyte have the same density to avoid the effect of hydrostatic pressure on the membrane.

Under the recommended operating conditions indicated in Table 3 it is possible to obtain red–violet cuprous oxide powder meeting the D912-65 ASTM specification for use in antifouling paints and nickel cathodes containing > 99.96% nickel.

The electrolyte process can be carried out with a cell voltage of 2.0 V, with a 0.8 kWh (kgCu$_2$O)$^{-1}$ power requirement.

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