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Electrochemical preparation of cuprous oxide powder: Part I. Basic electrochemistry

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The preferred process for the production of cuprous oxide powder is via the anodic dissolution of copper in an alkaline solution of sodium chloride. The principal reactions are as follows:

$$\begin{aligned} Cu + nCl^- &= CuCl_n^{1-n} \qquad (n = 2, 3) \\ 2H_2O + 2e &= H_2\uparrow + 2OH^- \\ 2CuCl_n^{1-n} + 2OH^- &= Cu_2O\downarrow + 2nCl^- + H_2O \end{aligned}$$

In the present investigation the basic electrode processes were studied systematically under a broad range of conditions using linear sweep voltammetry. Variables studied include the concentration of sodium chloride and sodium hydroxide (i.e., alkalinity), temperature of the solution, two categories of additives (an inhibitor for preventing the deposition of spongy metallic copper powder on the cathodes, and a chemical reducing agent for reducing the cupric ions to the cuprous state), and the effect of carbonate ions (resulting from the spontaneous absorption of carbon dioxide from the air by sodium hydroxide). Useful guidelines concerning the electrolysis conditions, additives, and the concentration limit of carbonate ions have been established. The proper operating conditions can be considered to be as follows: 80–85° C, NaCl 240–260 $g\,l^{-1}$, NaOH below 1 $g\,l^{-1}$. Conditions pertaining to the use of additives are the following: calcium gluconate 0–5 $g\,l^{-1}$, Na_2CrO_4 below 0.5 $g\,l^{-1}$, $Na_2Cr_2O_7$ below 0.25 $g\,l^{-1}$, $NH_2OH.HCl$ below 2.5 $g\,l^{-1}$, $N_2H_4.H_2O$ below 2.5 $g\,l^{-1}$, sucrose 0–5 $g\,l^{-1}$. Special attention must be given to eliminate or reduce the presence of carbonate ions in the electrolyte below 0.25 $g\,l^{-1}$ Na_2CO_3.

1. Introduction

Cuprous oxide powder can be produced using a variety of techniques, including electrochemical, sintering, hydrothermal, chemical and displacement processes [1], on which its physico-chemical properties are dependent. Of these five processes, the electrochemical approach appears to be the best on a large scale in view of its short process flowsheet, lower cost, easy operation, high productivity, flexible operating conditions and high quality product. Almost all of the electrochemical processes involve electrolyzing an aqueous sodium chloride solution with the addition of sodium hydroxide and using copper as the anode.

A survey of the literature [2–13] reveals that there are large differences in the operating conditions, especially the concentration of sodium hydroxide (i.e., pH) and the anodic current density, and very few conditions can ensure a product having more than 97% cuprous oxide as required in ASTM Specification D912-81. To avoid the contamination of cuprous oxide caused by the deposition of spongy copper powder on the cathode during electrolysis, diaphragms [2, 5, 7] can be used to cover the cathodes or some additives, such as, sodium nitrate [8, 9], sodium gluconate [10], potassium dichromate [11] and potassium chromate [12, 13] can be added to the electrolyte. Nevertheless, no products except those reported by Vetere and Romagnoli [8] contain more than 97% cuprous oxide produced in a cell without a diaphragm.

Based on the present situation in the electrochemical preparation of cuprous oxide powder, systematic electrochemical investigations of anodic copper dissolution in an alkaline solution of concentrated sodium chloride are still necessary. The purpose of the present research was to study the electrode processes of copper under a broad range of variables using linear sweep voltammetry and thereby to establish the guidelines required for selecting the optimum conditions for the electrochemical preparation of cuprous oxide powder.

2. Principles

According to the potential-pH diaphragms for the ternary system of Cu–Cl^-–H_2O at 25° C [14], in the case of a low concentration of sodium chloride, only

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Cu_2O and CuO are stable in the alkaline region, while Cu_2O, CuCl, $CuCl_n^{1-n}$ and $Cu_2(OH)_3Cl$ are stable in the acid region. In the case of a high concentration of sodium chloride, i.e. beyond 4 M, Cu_2O, CuO and $Cu_2(OH)_3Cl$ are stable in the alkaline region while only soluble $CuCl_n^{1-n}$ complexes are stable in the acidic region.

The dissolution-hydrolysis precipitation mechanism can reasonably be used to describe the formation of cuprous oxide powder during the electrodissolution of copper in alkaline concentrated sodium chloride solutions.

Principal anodic reaction (anodic dissolution of copper):

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

Principal cathodic reaction (hydrogen evolution):

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

Principal chemical reaction (hydrolysis precipitation):

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

Thus the net cell reaction is the summation of Equations 1–3, that is:

$$2Cu + H_2O \longrightarrow H_2\uparrow + Cu_2O \quad (4)$$

The hydroxyl ions necessary for the formation of cuprous oxide, according to the principal chemical reaction, are generated in the cathodic reaction and arrive at the anodic compartment by migration, diffusion and convection. Reduction of cuprous oxide to metallic copper by contact with the cathode is avoided with a diaphragm or by using certain additives such as potassium dichromate. The finely divided cuprous oxide is then removed from the cell (usually from the cell bottom) continuously or discontinuously.

The initial chloride in the electrolyte cell, which provides for the formation of cuprous chlorocomplex anions, is regenerated in the chemical reaction step (Equation 3). Thus it is evident from the net cell reaction (Equation 4) that the only consumptions in the electrolysis are water and the metallic copper which serves as the anode, nothing else. The pH of the electrolyte and the chloride concentration should not change with the electrolysis if the above stoichiometry is obeyed.

3. Experimental details

All of the chemicals used in the experiments were C.P. grade supplied by BDH Chemicals Co., Toronto, Canada. The working electrode was a 6 mm diameter copper rod which was coaxially inserted in a Teflon bar with a 12 mm diameter so as to fix the area of the working electrode and to insulate it from the solution. The counter electrode was a 7 cm × 8 cm sheet of titanium and the reference electrode was a saturated calomel electrode (SCE). All the potentials quoted in this paper, unless otherwise noted, are given with respect to this reference electrode. The cell consisted of a Pyrex glass 500 ml beaker with a water jacket which was mounted in a recirculating pump loop for controlling and keeping constant the temperature of the solution inside the cell. The position of the electrodes and the 3 mm space between them were fixed with a plexiglass frame.

All of the experiments were conducted using a PAR Model 170 Electrochemistry System. Accessory apparatus included a thermostat and a pH meter.

For each run of experiments, the working electrode was first mechanically polished to a mirror surface. Afterwards, the electrode was chemically degreased with acetone and subsequently rinsed with distilled water. Finally, the electrode was dried with a filter paper and immediately put into the solution. According to Vetere and Romagnoli [9], the polarization curves are virtually the same whether the solution is deaerated or not. Thus for simplicity the solution was not deaerated by bubbling an inert gas. The cell was covered to prevent evaporation of the solution and to inhibit the absorption of oxygen and carbon dioxide from the air. The scanning rate was $10\,mV\,s^{-1}$ for both anodic and cathodic measurements. All of the polarization curves were measured in unstirred solution.

4. Results and discussion

4.1. *Effects of sodium hydroxide concentration*

The effect of the sodium hydroxide concentration on the electrode process was investigated under the conditions of $250\,g\,l^{-1}$ NaCl, 80° C, $0–10\,g\,l^{-1}$ NaOH and without agitation of the solution. The anodic polarization curves were drawn at a scan rate of $10\,mV\,s^{-1}$ from −0.6 to 0.2 V, while the cathodic polarization curves covered the range −0.4 to −1.9 V. All the potentials were against the SCE. The results obtained are shown in Fig. 1. Six parameters were taken into account, i.e., the anodic peak current density (i_p), the anodic limiting current density (i_l), the anodic peak potential (φ_p), the cathodic current density at a potential of −1.8 V ($i_{\varphi=-1.8V}$), the cathodic current density at a potential of −1.6 V ($i_{\varphi=-1.6V}$), and the cathodic decomposition potential (φ_D). The reason for selecting the cathodic current densities at potentials of −1.6 and −1.8 V lies in the fact that these two potentials correspond approximately to the cathodic current density range of $500–2000\,A\,m^{-2}$ for most processes reported in the literature.

Fig. 1 demonstrates that the peak and limiting current densities and the peak potential decrease with the increase in the concentration of sodium hydroxide, indicating that sodium hydroxide inhibits the anodic process of copper dissolution. These observations are in agreement with the data of Vetere and Romagnoli [9]. These authors interpreted their findings as a result of the curpous oxide becoming more adherent to the anode with increasing sodium hydroxide concentration. Thus it can be inferred that an electrolyte with a high concentration of sodium hydroxide should be

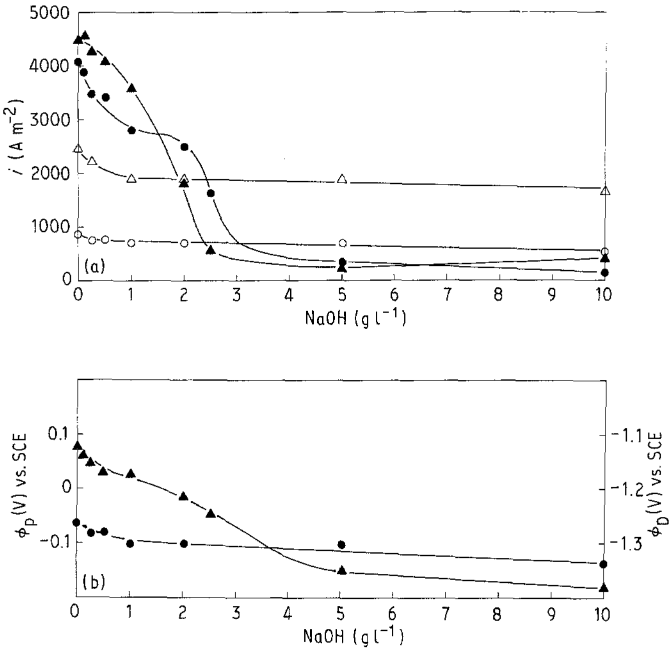

Fig. 1. (a) The effect of sodium hydroxide concentration on the electrode current densities. ▲ i_p: anodic peak current density; ● i_l: anodic limiting current density; △ $i_{\varphi=-1.8\,V}$: cathodic current density potential −1.8 V (vs SCE); ○ $i_{\varphi=-1.6\,V}$: cathodic current density at potential −1.6 V (vs SCE). (b) The effect of sodium hydroxide concentration on the electrode potentials. ▲ φ_p: anodic peak potential corresponding to the anodic peak current; ○ φ_D: cathodic decomposition potential.

chosen to produce a cuprous oxide product with a high density. However, the current density chosen for the electrolysis should be below the limiting current density; otherwise, other electrode reactions, such as cuprous oxide oxidizing to cupric ions, and oxygen evolution, would take place, thereby making the cuprous oxide product impure. As can be seen from Fig. 1, beyond 5 g l^{-1} NaOH the limiting current density is very small. This has been proven by Ermakova and Puzakov [11] who showed that when the concentration of sodium hydroxide exceeds 7 g l^{-1}, a black area (i.e., CuO) appears on the anodes and the cuprous oxide product contains large amounts of cupric oxide.

The observed influence of the sodium hydroxide concentration on the cathodic process is also in agreement with Vetere and Romagnoli [9] in that the decomposition potential becomes more negative as the sodium hydroxide concentration increases. Compared with the anodic process, the effect of the sodium hydroxide concentration on the cathodic process is much smaller, especially beyond 1 g l^{-1} NaOH.

4.2. *Effect of sodium chloride concentration*

The anodic polarization curves for the effect of sodium chloride concentration were made under the conditions of 0.5 g l^{-1} NaOH, 140-300 g l^{-1} NaCl, 80° C and without agitation of the solution. The peak and limiting current densities are presented in Fig. 2. Under these conditions the peak potential did not change greatly, the range being 0.06 ± 0.01 V.

Fig. 2 reveals that a high concentration of sodium chloride facilitates the anodic dissolution of copper. This can be explained through reference to the anodic dissolution of copper in acidic chloride solutions [15–21] and in neutral and alkaline chloride solutions [22, 23]. The higher concentration of sodium chloride initially favours the formation of soluble cuprous chlorocomplex anions $CuCl_n^{1-n}$ ($n = 2, 3$). However, when the concentration of sodium chloride surpasses 260 g l^{-1}, the peak and limiting current densities drop slightly probably due to the attainment of a saturation concentration of sodium chloride, thereby leading to the precipitation of sodium chloride crystals on the anode. The existence of the residual sodium chloride crystals was observed in the case of 300 g l^{-1} NaCl solution.

According to Fu and Zheng [14] the stable region of solid cuprous chloride (CuCl) disappears beyond 240 g l^{-1} NaCl. On the basis of this information and the aforementioned experimental results, it can be recommended that the appropriate range of sodium chloride concentration should be between 240 and 260 g l^{-1}.

4.3. *Effect of temperature*

The selection of temperature depends mainly upon the dehydration of cuprous hydroxide and the grain size of cuprous oxide. Besides, some attention should be paid to the evaporation of the solution and the corrosion resistance of the cell materials. In the present study the authors examined only the magni-

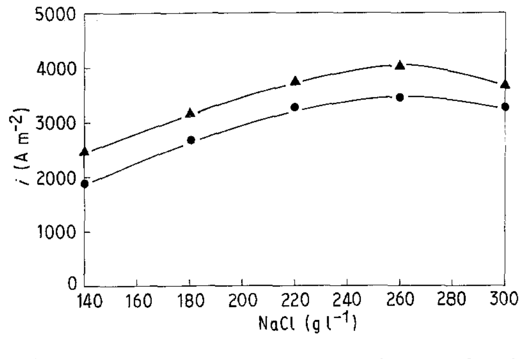

Fig. 2. Anodic peak and limiting current densities as a function of sodium chloride concentration. ▲ i_p, ● i_l.

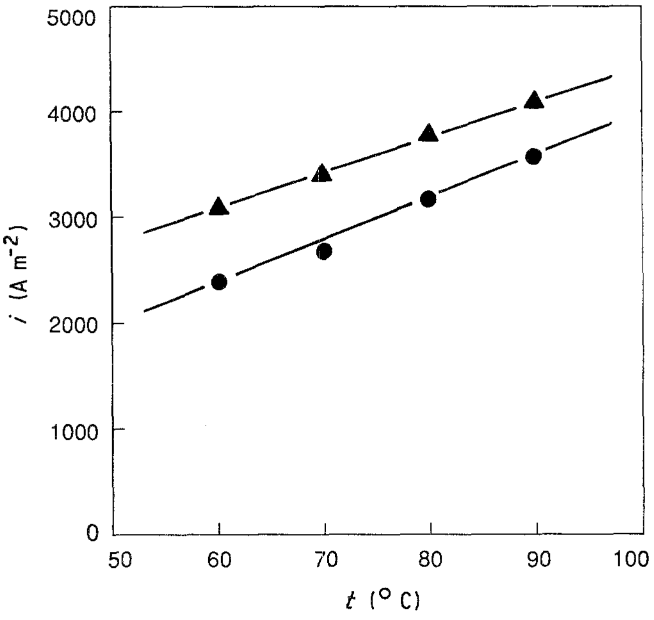

Fig. 3. Anodic peak and limiting current densities as a function of temperature. $\varphi_p = 0.05\,\mathrm{V}$: ▲ i_p, ● i_l.

tudes of the peak and limiting current densities in the temperature range of 60–90° C under the constant conditions of $250\,\mathrm{g\,l^{-1}}$ NaCl, $0.5\,\mathrm{g\,l^{-1}}$ NaOH and without agitation of the solution.

In the light of Fig. 3 alone, the higher the temperature, the better the results, since higher temperature raises the mass transfer rate and the speed of cuprous hydroxide dehydration. However, we must consider other problems which can arise at higher temperatures. When the temperature is close to the boiling point of water, not only can a large evaporation of water from the electrolyte take place, but also oxidation of the cuprous oxide which is suspended in the electrolyte may occur due to the rise of the steam bubbles from the cell bottom. According to numerous references [2, 4, 7, 8, 12, 13] and the above results, it is better that the temperature be held in the range of 80–85° C.

4.4. *Effect of additives*

There are two categories of additives which have different actions. The first category, called an inhibitor, is a chemical reagent which has the ability to prevent the reduction of cuprous oxide to copper powder on the cathode. Through reference to several papers [10–13] and in view of the sodium chloride system, the authors chose to study the effects of calcium gluconate, sodium chromate and sodium dichromate as additives on the anodic and cathodic processes. The

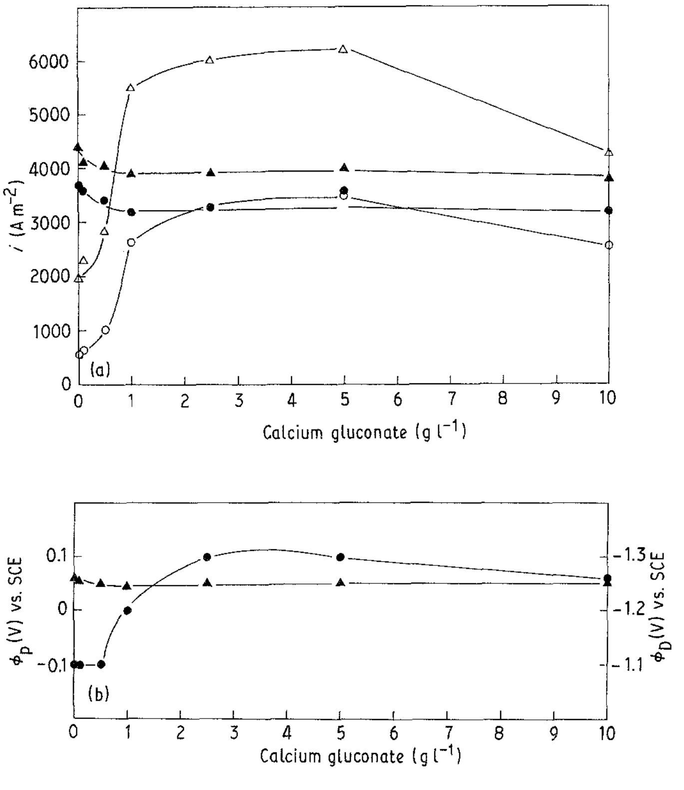

Fig. 4. (a) The effect of calcium gluconate on the cathodic current densities. ▲ i_p, ● i_l, △ $i_{\Phi=-18\,\mathrm{V}}$, ○ $i_{\varphi=-1.6\,\mathrm{V}}$. (b) The effect of calcium gluconate on the electrode potentials. ▲ φ_p, ● φ_D.

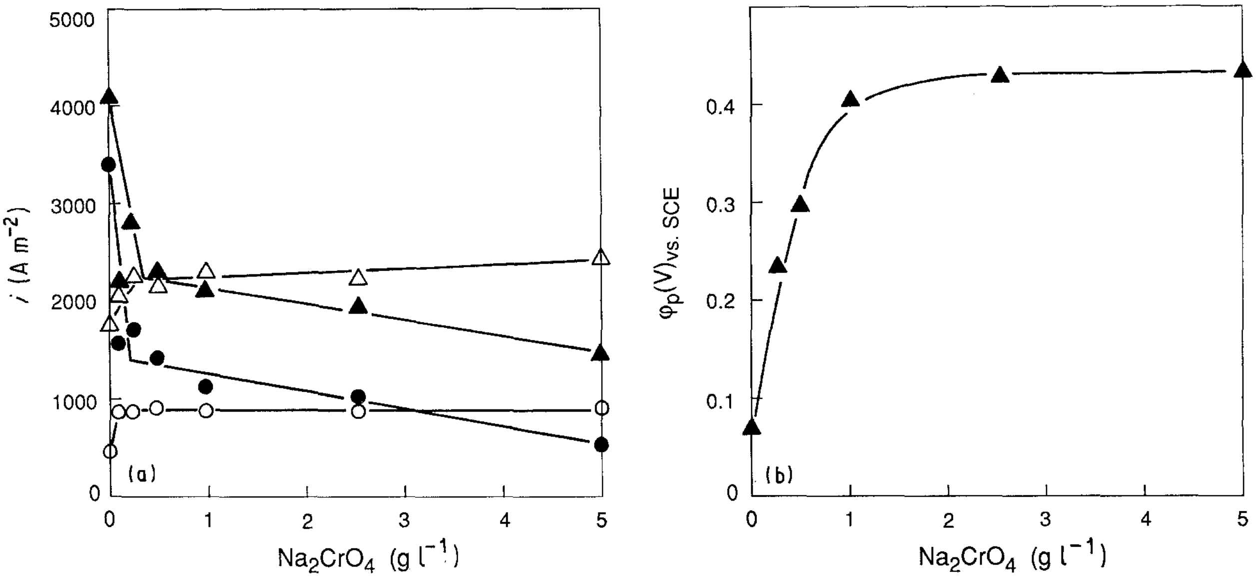

Fig. 5. (a) The effect of sodium chromate on the electrode current densities (0.5 g l^{-1} NaOH for anodic curves; 1.0 g l^{-1} NaOH for cathodic curves). ▲ i_p, ● i_l, △ $i_{\varphi=-1.8V}$, ○ $i_{\varphi=-1.6V}$. (b) The effect of sodium chromate on the anodic peak potential $\varphi_D = -1.28 \pm 0.02$ V.

second category of additives is in fact a chemical reducing agent with medium reducing power such that it can reduce cupric ions only to the cuprous state rather than to metallic copper. The selection of these additives should be considered from amongst the reagents which have already been used as reducing agents in the chemical preparation of cuprous oxide in aqueous solution. A literature survey has shown that appropriate reducing agents are invert sugar (equimolecular mixture of glucose and fructose) [8], sucrose [8], hydroxylamine [9], and hydrazine [8]. The authors examined all of these reagents except invert sugar.

All of the polarization curves were drawn under the constant conditions of 250 g l^{-1} NaCl, 0.5–1.0 g l^{-1} NaOH, 80° C and without agitation of the solution. The results for the effects of above two categories of additives on the electrode processes are shown in Figs 4–8 inclusive.

Fig. 4 shows that the addition of calcium gluconate to the solution has only a little effect on the anodic dissolution of copper in the concentration range of 0–10 g l^{-1}. The anodic peak and limiting current densities do not change considerably with the calcium gluconate concentration. The peak potential is also almost unchanged around 0.05 V. On the other hand, as can be seen from Fig. 4(a), the existence of calcium gluconate in the solution can depolarize the evolution of hydrogen gas when its concentration is below 5 g l^{-1}. The cathodic current densities decrease beyond 5 g l^{-1}, since the calcium gluconate has a low solubility in the solution and much suspended matter was observed in the case of 10 g l^{-1} calcium gluconate.

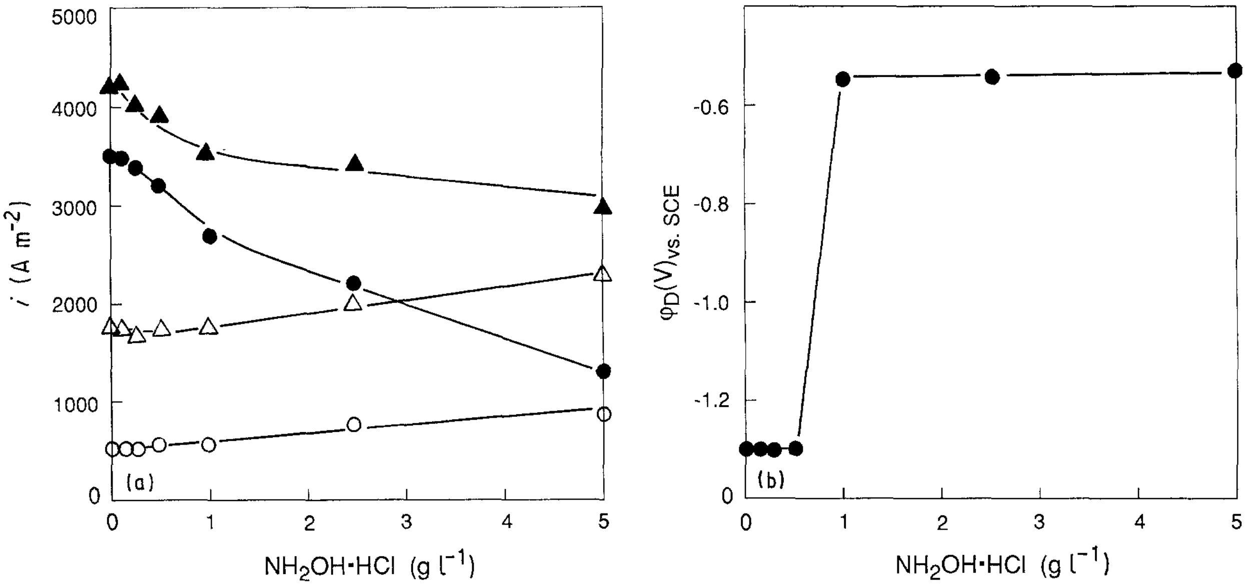

Fig. 6. (a) The effect of hydroxylamine hydrochloride on the electrode current densities (0.5 g l^{-1} NaOH). ▲ i_p, ● i_l, △ $i_{\varphi=-1.8V}$, ○ $i_{\varphi=-1.6V}$. (b) The effect of hydroxylamine hydrochloride on the cathodic decomposition potential $\varphi_p = 0.05 \pm 0.015$ V.

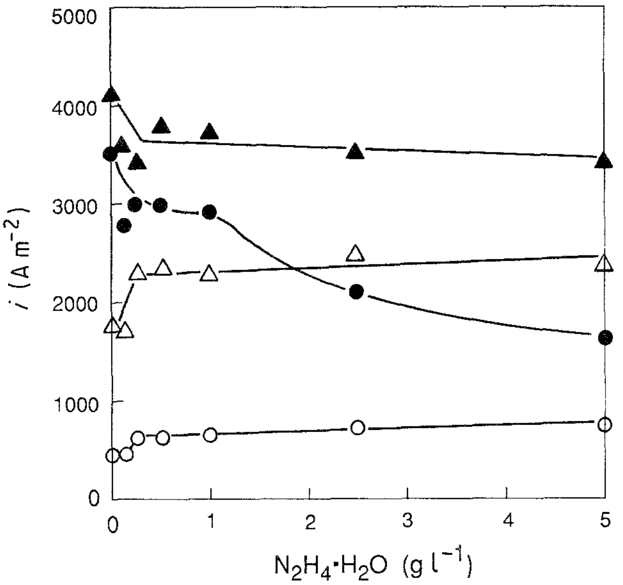

Fig. 7. The effect of hydrazine on the electrode current densities (0.5 g l^{-1} NaOH). $\varphi_p = 0.055 \pm 0.015$ V; $\varphi_D = -1.31 \pm 0.03$ V. ▲ i_p, ● i_l, △ $i_{\varphi=-1.8\text{V}}$, ○ $i_{\varphi=-1.6\text{V}}$.

As to the additions of sodium chromate and sodium dichromate, these two additives behave similarly in both the anodic and cathodic processes. As shown in Fig. 5 the peak and limiting current densities drop drastically and the peak potential rises considerably as the concentration of sodium chromate increases. As for the cathodic process, the addition of sodium chromate or dichromate at first raises the cathodic current, but subsequently has almost no continued action on the cathodic current beyond a concentration of about 0.3 g l^{-1}.

It is important to examine the reason why sodium chromate and dichromate drastically decrease the anodic current and drastically increase the anodic overpotential. First it is noteworthy that the dichromate anion decomposes partially to the chromate anion in the alkaline solution, $Cr_2O_7^{2-} + 2OH^- = 2CrO_4^{2-} + H_2O$. Hence it is reasonable that sodium chromate and dichromate behave similarly in the alkaline electrolytes. The drastic drops in the peak and limiting current densities and the marked rise of peak potential are very probably attributable to the formation of insoluble precipitates of cuprous and cupric chromate as the copper dissolution progresses. The cathodic reduction of chromate ions has even been considered [11]. The chromate is first reduced to the chromium hydroxide on the cathode, i.e.,

$$CrO_4^{2-} + 4H_2O + 3e = Cr(OH)_3\downarrow + 5OH^- \quad (5)$$

This film of chromium hydroxide formed on the cathode is conductive, hydrogen continuing to evolve, but can inhibit the reduction of cuprous oxide to copper powder.

In comparing the behaviour of gluconate and dichromate in the electrode processes, it can be concluded that the dichromate as an additive would give rise to a higher energy consumption than gluconate at the same current density. This was confirmed by Yang *et al.* [10]. At present on the basis of the experimental data, it is the authors' opinion that it is preferable to use calcium gluconate rather than sodium chromate or dichromate as an additive to prevent the deposition of spongy metallic copper powder on the cathode.

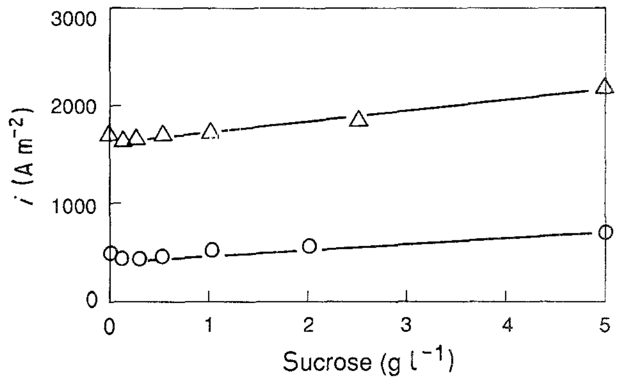

Fig. 8. The effect of sucrose on the cathodic current densities of (0.5 g l^{-1} NaOH). $i_p = 4200 \pm 100$ A m^{-2}, $\varphi_p = 0.05 \pm 0.01$ V. $i_l = 3550 \pm 150$ A m^{-2}, $\varphi_D = -1.32 \pm 0.02$ V. △ $i_{\varphi=-1.8\text{V}}$, ○ $i_{\varphi=-1.6\text{V}}$.

Concerning the second category of additive, i.e., the chemical reducing agent, the effects of this type of additive on the electrode processes are summarized in Figs 6–8 inclusive. Figures 6 and 7 show that both hydroxylamine and hydrazine inhibit the anodic dissolution of copper. From the cathodic polarization curves, it is known that hydroxylamine would be reduced partially before the evolution of hydrogen, and that its decomposition potential corresponds to the point where a large jump takes place (Fig. 6b). The product of hydroxylamine hydrochloride reduction may be hydrazine ($2NH_2OH + 2e = N_2H_4 + 2OH^-$) since, as can be seen from Fig. 7, the cathodic current densities are nearly unchanged except for the small initial portion. Thus the amount of hydroxylamine hydrochloride would be consumed gradually as the electrolysis proceeds. Why hydroxylamine hydrochloride and hydrazine affect more the limiting current density than the peak current density cannot be explained at this stage. Hydroxylamine can reduce the cupric oxide to cuprous oxide ($4CuO + 2NH_2OH = 2Cu_2O + N_2O + 3H_2O$). But the cuprous oxide will be reduced to metallic copper when boiled with an excess of hydroxylamine ($Cu_2O + 2NH_2OH = 2Cu + N_2 + 3H_2O$).

Sucrose does not change the shape of the anodic polarization curves, the values of the peak and limiting current densities and the peak potential. In addition, it can depolarize a little the evolution of hydrogen (Fig. 8) but is itself not reduced.

In the light of the above results and discussion for these three reducing agents, it is suggested that all can be tried as additives to the solution during electrolysis. The concentrations of hydroxylamine hydrochloride and hydrazine should be below 2.5 g l^{-1}.

4.5. *Effect of carbonate impurity*

It is well known that solutions of sodium hydroxide

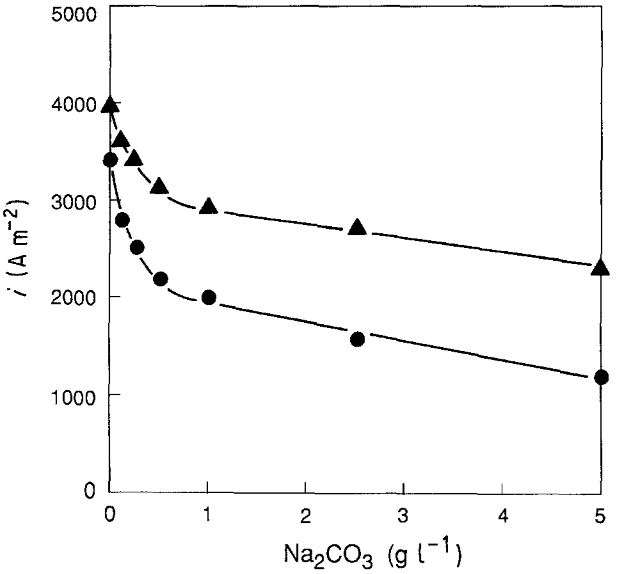

Fig. 9. The effect of sodium carbonate on the anodic current densities. $i_{\varphi=-1.8\,V} = 1700 \pm 250\,A\,m^{-2}$, $\varphi_D = -1.35 \pm 0.05\,V$. $i_{\varphi=-1.6\,V} = 440 \pm 130\,A\,m^{-2}$, $\varphi_p = 0.045 \pm 0.015\,V$. ▲ i_p, ● i_l.

absorb carbon dioxide from the air with the formation of sodium carbonate. The existence of carbonate would cause the passivation of the anode. The effect of carbonate on the electrode processes under the constant conditions of 250 g l^{-1} NaCl, 0.5 g l^{-1} NaOH (for anodic curves) and 1.0 g l^{-1} NaOH (for cathodic curves), 80° C and without agitation of the solution, is presented in Fig. 9. Figure 9 demonstrates that the presence of carbonate ions in the solution is very harmful to the anodic dissolution of copper. The considerable drop in anodic current densities can be ascribed to the increase in the activation polarization due to the adsorption of carbonate ions on the anodes. The incorporation of sodium carbonate in the electrolyte does not modify significantly the characteristics of the anodic polarization curves. In order to maintain an anodic current density of 2000 A m^{-2}, the concentration of sodium carbonate should be controlled below 1 g l^{-1}. On account of the presence and gradual accumulation of carbonate in the solution, it is suggested that the electrolyte be examined regularly for carbonate and be purified of carbonate after a period of time, possibly through precipitation by the addition of barium chloride. On the whole, the carbonate has only a very small effect on the cathodic process.

5. Conclusions

(1) The basic conditions for the electrochemical preparation of cuprous oxide powder are as follows: NaOH below 1 g l^{-1}, NaCl 240–260 g l^{-1}, and temperature 80–85° C. Under these conditions, the limiting current density can reach as high as 2800 A m^{-2}.

(2) As for the inhibitors, calcium gluconate is the best since it can not only keep a very high limiting current density around 3400 A m^{-2} in the concentration range 0–5 g l^{-1}, but also depolarize greatly the evolution of hydrogen. Sodium chromate and dichromate behave similarly. Their addition to the electrolyte is not favourable since they increase drastically the anodic polarization and thereby decrease markedly the limiting current density. The concentrations of sodium chromate and dichromate should not exceed 0.5 g l^{-1} and 0.25 g l^{-1}, respectively. Even so at these concentrations the peak and limiting current densities drop to about 2300 A m^{-2} and 1400 A m^{-2}, respectively.

(3) The reducing agents hydroxylamine hydrochloride, hydrazine, and sucrose can be added to the solution during electrolysis. In the light of the limiting current density, the addition of sucrose is the most favourable because it cannot change the limiting current density in the concentration range 0–5 g l^{-1}. Although hydroxylamine hydrochloride and hydrazine are not perfect from the viewpoint of the electrode processes, in order to maintain a limiting current density of 2000 A m^{-2} their concentrations should not exceed 2.5 g l^{-1}.

(4) Carbonate can be very harmful, decreasing greatly the limiting current density. In order to get a limiting current density of 2000 A m^{-2}, the carbonate concentration should be below 1 g l^{-1}. To obtain a high limiting current density of 2500 A m^{-2}, its concentration must not exceed 0.25 g l^{-1}.

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