

Application of Polarisation Curves to the Study of the Electrochemical Process for Producing Cuprous Oxide

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Polarisation curves are useful for establishing the optimum experimental conditions for producing electrolytic cuprous oxide. They provide a reasonable means of determining the influence of each variable on cuprous oxide formation at an electrode surface. In this work, a sodium chloride solution was electrolysed, and sodium hydroxide and sodium nitrate (in several concentrations) were added in successive stages to determine the behaviour of the resultant systems. Finally, the effect of the presence of cuprous oxide on the cathodic behaviour of the electrode was studied. The working electrode was of copper and the experiments were conducted at different temperatures. The polarisation curves were obtained without agitating the liquid and with aerated and deaerated solutions. The passage of nitrogen during 30 min removed oxygen from the electrolyte.

Keywords: polarisation; cuprous oxide; oxidation; dismutation.

1. Introduction

The references concerning the process for producing cuprous oxide are both restricted and ancient,^{1–3} although a laboratory method has recently been mentioned.⁴ Almost all processes consist of electrolysing solutions of halides from alkaline metals, i.e. sodium chloride with addition of sodium hydroxide. Different concentrations have been used. The electrodes are generally made of copper, although iron cathodes have been proposed. The current density and temperature also vary in the different methods. Most of the processes use diaphragms and require a predetermined electrolyte flux rate on the electrode. The performances are generally low. Some protective colloids such as glue or gelatine are used to avoid oxidation and dismutation of the cuprous oxide obtained.

One of the best known processes⁵ employs a cell made of ceramic or chemical clay. Electrodes are of copper, and the current density is 6–7 A dm⁻². The electrolyte consists of a solution of sodium chloride, or potassium chloride (20% by wt) with an alkalinity from 0.1 to 9 g dm⁻³ in sodium oxide; 0.1% of glue is added as colloid, the working temperature may vary between 50 and 100°C and the potential drop is of 1.5 to 4 V. The diaphragm used is made of asbestos or of synthetic fibre cloth.

The purpose of this work is to establish the experimental conditions needed to obtain electrolytic cuprous oxide, by means of polarisation curves of copper systems in solutions of sodium chloride-sodium hydroxide-sodium nitrate, in different proportions and at diverse temperatures. The variables involved in the production of cuprous oxide are optimised from the results obtained.

2. Experimental

The most important variables relative to the method employed were studied.

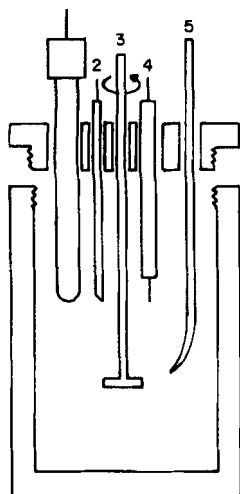


Figure 1. Electrolytic cell. 1, Reference electrode; 2, working electrode; 3, stirrer; 4, counterelectrode; 5, nitrogen bubbler.

2.1. Electrolytic cell

The design of the cell is presented in Figure 1. The cell is made in Pyrex glass; the working electrode is a 0.2 cm diameter electrolytic copper wire (Figure 2) inserted in a Teflon bar of 1.5 cm diameter. The electrode is transversally cut at 45° so as to allow quick evacuation of the gases formed on the surface. The reference electrode is made of calomel saturated in potassium chloride and the counter electrode is a platinum wire.

The electrode is previously mechanically polished and afterwards chemically degreased by means of alkaline substances. Copper is then electrolytically deposited on the electrode from a 0.2M copper sulphate solution, with an acidity 2M in sulphuric acid, at a current density of 8 mA cm^{-2} , during 5 min, at room temperature. Finally, the electrode is washed with distilled water.

2.2. Working temperature

Three temperatures were taken into account: 25, 50 and 80°C. To obtain them a thermostatic bath was used, operating with an accuracy of $\pm 0.1^\circ\text{C}$.

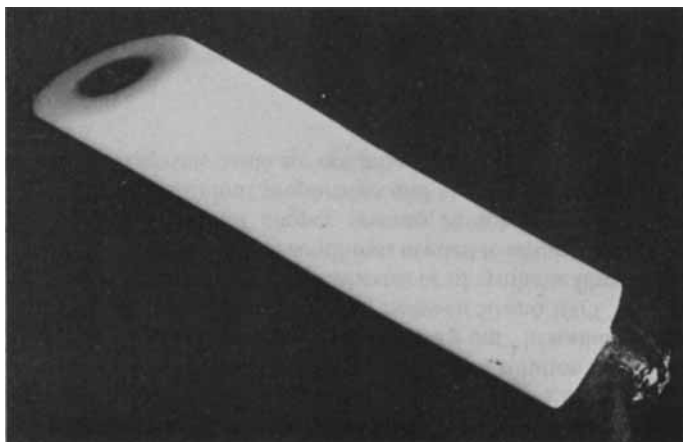


Figure 2. Working electrode

2.3. Electrolytes

Aqueous solutions of sodium chloride (15%) with sodium hydroxide contents of 0.1, 1 and 5% (wt/vol) respectively, were prepared in order to study the effect of alkalinity on cuprous oxide formation.

Once an adequate concentration of sodium hydroxide had been selected, sodium nitrate was added to the system, to obtain a concentration of 5% (wt/vol). Thus, it was possible to determine the influence of the nitrate anion.

The polarisation cathodic curves were made with the systems sodium chloride 15%, sodium hydroxide 0.1% and sodium nitrate 5%, in the presence of cuprous oxide added expressly in one case, or generated *in situ* in the other (by anodic dissolution of a copper wire electrode).

These trials allowed the determination of the effect of the presence of cuprous oxide on the cathodic reaction. Working temperatures were 25 and 80°C. Curves were obtained without agitating the system. In all cases the voltagrams were done both in aerated solutions and in deaerated solutions using purified nitrogen, bubbled for 30 min before measurement.

3. Results and discussion

3.1. Effect of sodium hydroxide concentration

The effect of the alkali concentration on the electrode reactions was studied using a solution of sodium chloride at 15% (wt/vol) with sodium hydroxide contents of 0, 0.1, 1 and 5% (wt/vol), at temperatures of 25, 50 and 80°C.

The corrosion potentials measured varied between -250 and -360 mv vs. saturated calomel electrode and they became more negative as the temperature and the concentration of sodium hydroxide increased.

3.1.1. Anodic curves

The anodic sweep was done from the corrosion potential. It presents a voltagram with only one peak corresponding to the formation of cuprous oxide. In the case of the solutions without sodium hydroxide or with the addition of 0.1% of this reagent, the product obtained was not adherent and maintained a considerable current which varied with the temperature (Table 1, Figure 3).

However, when the sodium hydroxide content was 1 or 5%, the above-mentioned peaks appear and the electrodes became passive owing to the formation of an adhesive coat of cuprous oxide. This can be seen from Table 1 and Figure 3.

3.1.2. Cathodic curves

Starting from the corrosion potential in direction of the cathode, it is possible to observe a small peak corresponding to the reduction of the film of a copper compound formed on the electrode, owing to a

Table 1. Anodic curves

NaOH (%)	Temperature (°C)	E_p (mv vs. SCE)	i_p (A dm ⁻²)	$i_{p'}$ (A dm ⁻²)
0	25	-100	12	10
	50	-40	28	22
	80	-10	37	30
(Curve no. 1) 0.1	25	-60	10	9
	50	-50	15	14
	80	-100	24	22
(Curve no. 2) 1	25	-170	1	0.4
	50	-220	1.2	0.5
	80	-240	1.6	0.6
(Curve no. 3) 5	25	-260	2.7	1.0
	50	-300	2.9	1.2
	80	-350	3.6	1.4

E_p = peak potential; i_p = peak current density; $i_{p'}$ = current density after peak.

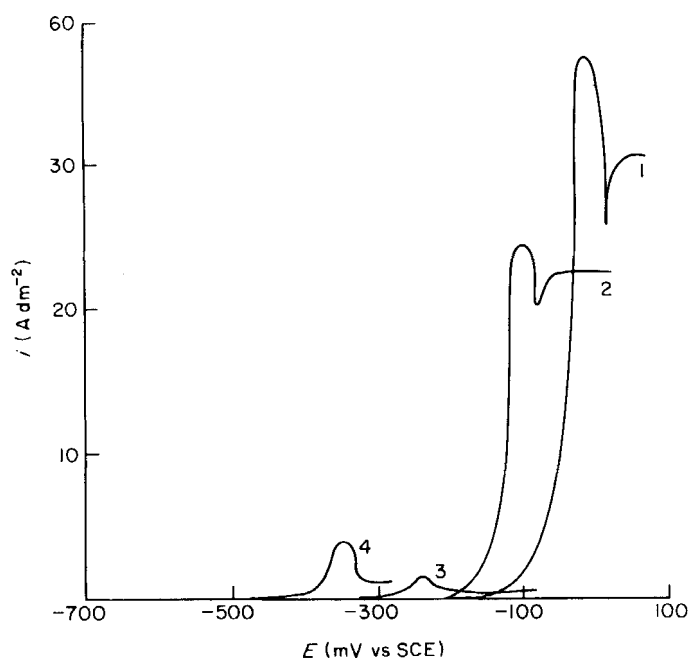


Figure 3. Anodic curves. Voltagram with only one peak, which corresponds to the formation of cuprous oxide.

spontaneous corrosion process. Afterwards, hydrogen evolution is seen at much more negative potentials.

The decomposition voltage becomes more negative as sodium hydroxide concentration increases and as the temperature decreases (Table 2, Figure 4).

3.2. Effect of sodium nitrate addition

The incorporation of sodium nitrate in the solution does not significantly modify the characteristics of the anodic curves, but it considerably reduces the decomposition voltage of the cathodic curves. This is due to the reduction of nitrate ion, and this reaction occurs before the evolution of hydrogen. Under the given hydrodynamic conditions this curve shows a limiting current which is proportional to the nitrate concentration and has a value of about 10 A dm^{-2} for nitrate concentrations of about 5%, at room temperature (Table 2).

Table 2. Cathodic curves.

NaOH (%)	NaNO ₃ (%)	Temperature (°C)	V_D (mv vs. SCE)	i_l (A dm ⁻²)
0.1	5	25	-850	10
		80	-850	15
0	0	25	-1400	
		50	-1360	
		80	-1220	
0.1	0	25	-1500	
		50	-1400	
		80	-1290	
1	0	25	-1520	
		50	-1430	
		80	-1370	
5	0	25	-1540	
		50	-1470	
		80	-1400	

V_D = Decomposition voltage; i_l = Limiting current density of the nitrate.

It was determined that the nitrate reduction leads to the formation of hydroxylamine when preparing a matrix solution composed of sodium chloride at 15%, sodium hydroxide at 0.1% and sodium nitrate at 5%, and working with three portions of 70 cm³ each. The first portion was electrolysed with a copper electrode similar to that used in the preparation of cuprous oxide, but separating the anode from the cathode. To the second was added 25 cm³ of hydroxylamine hydrochloride (0.1M), and the third portion was used as a reference. The three samples were diluted to the same final volume (100 cm³). Aliquots of each solution were titrated with a standardised solution of potassium dichromate in excess and this was back titrated with a ferrous solution of known concentration. Thus, the number of electrons involved for each system was calculated, in the first two cases being four. As hydroxylamine reduces cupric to cuprous compounds its presence in the system is considered very favourable.

3.3. Effect of the presence of cuprous oxide

The presence of cuprous oxide in the system, as can be seen from the polarisation curves obtained (Figure 4) did not significantly affect the above mentioned reactions. The current for copper reduction is almost negligible compared with the values for current relative to the process of nitrate anion reduction, even when the solution was agitated.

3.4. Effect of oxygen in air

Oxygen in air does not significantly modify the anodic and cathodic curves. To determine the chemical nature of the substances formed on the electrode, either by a spontaneous corrosion process, or by the cathodic polarisation effect, the following steps were carried out: a copper plate of

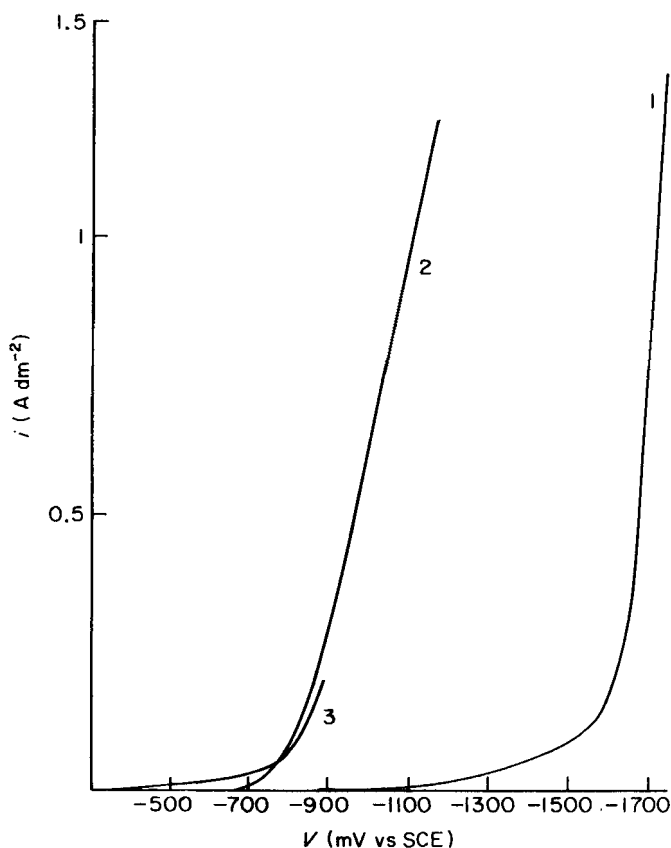


Figure 4. Cathodic curves. 1, Curve of hydrogen evolution (electrolyte NaCl 15% NaOH 0.1%); 2, curve of nitrate anion discharge (electrolyte NaCl 15% NaOH 0.1% NaNO₃ 5%); 3, curve of nitrate anion discharge in the presence of cuprous oxide (solution of similar characteristics).

$3 \times 3 \times 0.1$ cm was put at the corrosion potential, or at the studied peak potential (see E_p values in Table I), during a period long enough to obtain the recovery of the electrode (about 3 h). The products formed were isolated from the plate and identified by the application of current analytical techniques. It was possible to determine that the film formed by corrosion is of cuprous chloride, while the one formed at the peak potentials corresponds to cuprous oxide.

4. Conclusions

From the analysis of polarization curves it is possible to establish that:

- (a) The optimal sodium hydroxide concentration is about 0.1%, and the maximum anodic current density varies between 10 A dm^{-2} at room temperature and 20 A dm^{-2} at 80°C . When the sodium hydroxide content is greater than 1% the electrode passivises.
- (b) At room temperature a yellow product was obtained, while at 80°C red cuprous oxide was formed. This difference is due to the different particle size of the product obtained in each case.⁶
- (c) The addition of sodium nitrate avoids hydrogen evolution on the cathode (hydrogen is a reductor of cuprous compounds); for this reason a diaphragm was eliminated in cell design, and thereby the ohmic drop in the system was reduced.
- (d) The hydroxylamine formed as a consequence of the nitrate ion reduction, reduces the cupric compound to cuprous, in this way decreasing the oxidation effect of the oxygen in air and stabilising the cuprous oxide (diminishing the tendency to dismutation).
- (e) The cathodic current density must not be above the nitrate limiting current (10 A dm^{-2} at 25°C , and 15 A dm^{-2} at 80°C), in order to avoid simultaneous hydrogen evolution.
- (f) The use of sodium nitrate for cathodic depolarising and as a stabilising agent in the production of cuprous oxide was clearly established.

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