

Electrochemical synthesis of cupric oxide powder

Part II: Process conditions

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Electrosynthesis of cupric oxide powder was carried out on a laboratory scale in an electrochemical cell under various experimental conditions. The electrolysis was appraised in terms of the particle size of the cupric oxide product and the anodic dissolution of the copper electrode. Using a previously determined pH value of 7.50, the other optimum electrolysis operating conditions established were a current density of 4000 A m^{-2} , temperature of 353 K, and Na_2SO_4 concentration of 0.5 M. The optimum values of current efficiency, cell voltage and specific energy consumption for the electrochemical synthesis of cupric oxide powder were determined.

Keywords: *cupric oxide, powder, current density, temperature, sodium sulfate*

1. Introduction

Considerable differences in the optimum ranges for the operating electrolysis parameters in Cu_2O and CuO synthesis have been suggested [1–4]. In addition, the microstructure of electrochemically produced cupric oxide powder, the electrodisolution of the copper anode, the stability of the electrolysis and the effect of current density have not been well researched.

The purpose of this research was to evaluate the best operating CuO electrolysis conditions for work described previously for which an optimum pH had been determined [5]. The effects of current density, temperature and sodium sulfate concentration were analysed. The shape and grain size of the cupric oxide particles produced were also determined.

2. Experimental details

A schematic drawing of the cell is presented in Fig. 1. The cell consisted of a Pyrex glass 200 ml beaker with a water jacket which was mounted in a recirculating loop for controlling and maintaining the constant solution temperature in the cell.

An AMEL–551 galvanostat–potentiostat set-up was used in all experiments. The temperature of the electrolyte was in the range 313–363 K. Electrolysis was performed at different constant current densities of 500, 1000, 2000, 3000 and 4000 A m^{-2} . Na_2SO_4 solution in the concentration range 0.25–2.0 M was used for electrochemical synthesis of cupric oxide powder.

After electrolysis the solution containing cupric oxide powder was filtered, then washed with distilled

water and dried at 100°C for 1 h. The photomicrographs of the powder particles were made at a magnification of $\times 64$. The cupric oxide powders were also characterized by X-ray diffractometry using copper K_α radiation at a scan rate of 1 deg min^{-1} , and by transparency measurements.

3. Results and discussion

3.1. Effect of current density

Potential–time curves for electrochemical synthesis of CuO powder in 0.5 M Na_2SO_4 (pH 7.50, $T = 80^\circ\text{C}$) were obtained at several current densities. Figure 2 shows a typical set of potential–time curves. There are some remarkable differences: a substantial rise in the electrode potential to about 5 V occurs after 20 min at a current density of 2000 A m^{-2} , whereas a

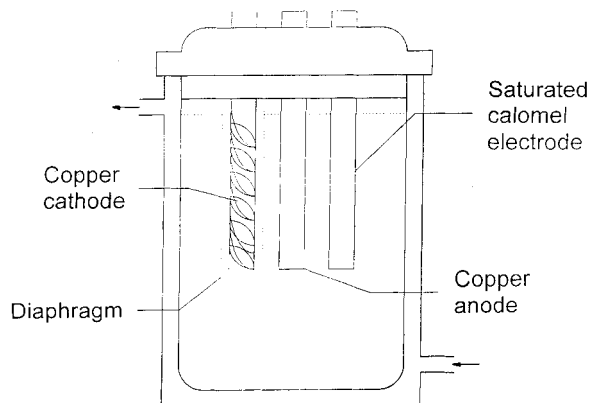


Fig. 1. Schematic diagram of the electrochemical cell.

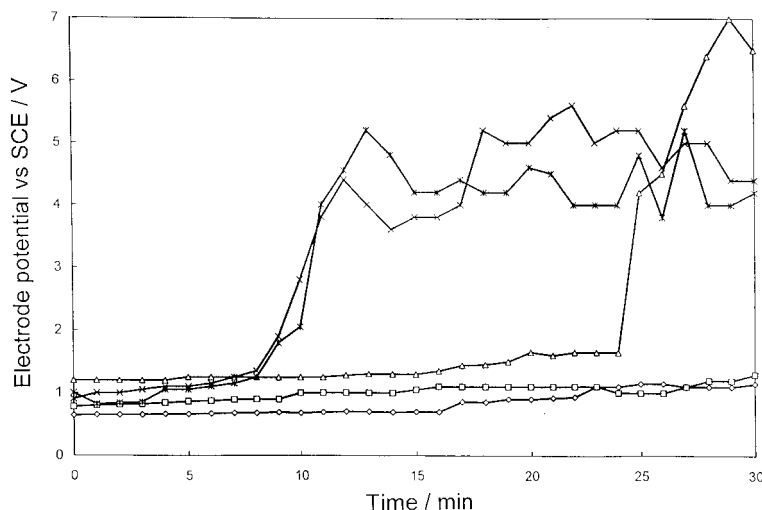


Fig. 2. Influence of current density on copper anode potential during electrochemical synthesis of CuO powder in 0.5 M Na₂SO₄ solution. pH = 7.50, $T = 353$ K. Current densities, j : (\diamond) 500, (\square) 1000, (\triangle) 2000, (\times) 3000 and ($*$) 4000 A m⁻².

potential jump to 4 V appears after only 10 min at current densities of 3000 and 4000 A m⁻². These potential profiles show that the metal dissolution reaction was inhibited by the formation of an insoluble passive layer of CuO. As stated in Part I of this investigation [5], the basic mechanism of CuO powder synthesis can be described by the principal chemical reaction:



At higher current densities, however, the anodic overpotential is shifted to more positive values when oxygen evolution can be expected. Hence, at the copper anode surface, the reaction is



It can be assumed that the product of Reaction 2 is the primary reason for the passivity of the copper anode and the shift in electrode potential to higher values.

Figure 3 shows the influence of current density, in the range 500–4000 A m⁻², on the average copper

anode potential and the average cell voltage. Both, the average electrode potential and the cell voltage were calculated as mean values of all points from the first to the last stage of the synthesis. As shown in Fig. 3, an increase in current density to about 3000 A m⁻² leads to increases in the average electrode potential and cell voltage (0.3–3.0 V and 10–16 V, respectively). Further increase to 4000 A m⁻² apparently decreases the average cell voltage quite notably. The possible explanation for the decreasing of cell voltage at 4000 A m⁻² may be the following: high current density leads to local increase in temperature and to consequent drop in electrolyte resistance.

The transparencies of the samples were determined each minute over a period of 15 min. Transparency data are shown in Fig. 4. A gradual increase in transparency with time, for samples in the current density range 500–3000 A m⁻², occurs. This suggests that the particles of cupric oxide powder synthesized at different current densities are almost of the same size. Therefore, 100% transparencies could not be reached during the measurement period (15 min).

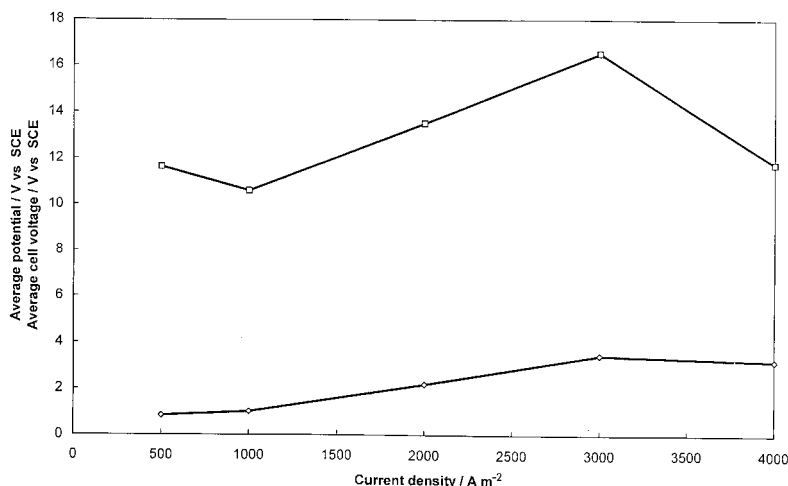


Fig. 3. Dependence of average anode potential (\diamond) and cell voltage (\square) on current density for CuO synthesis in 0.5 M Na₂SO₄ solution. pH 7.50, $T = 353$ K.

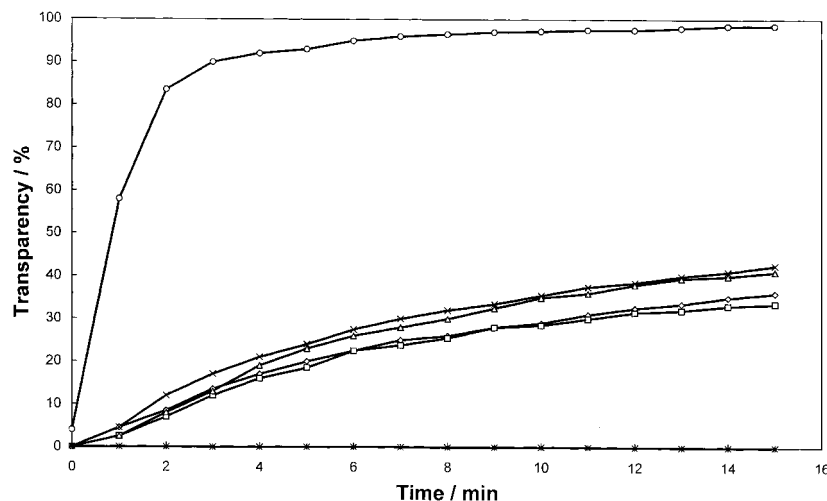


Fig. 4. Transparency of CuO powder suspension as a function of time at different current densities for CuO synthesis in 0.5 M Na₂SO₄ solution. pH 7.50, $T = 353$ K. Current densities, j : (\diamond) 500, (\square) 1000, (\triangle) 2000, (\times) 3000 and ($*$) 4000 A m⁻²; (\circ) reference curve.

This means that the particles in suspension are very small (less than 1×10^{-6} m). Transparency of 100% could not be achieved even after 24 h. Moreover, at a current density of 4000 A m⁻², a constant transparency value of 0% was obtained. This was expected, because at this current density, the suspension of cupric oxide powder contained very small particles (of a few nanometres). This observation was confirmed by the X-ray diffraction measurements.

The photomicrographs showed that the particles had a spheroidal shape. A certain degree of aggregation was observed, especially at higher current densities (4000 A m⁻²). It should be noted, however, that the aggregation could be easily dispersed by handling. Over the whole current density range the cupric oxide powder had a characteristic black colour.

The X-ray diffraction patterns of the cupric oxide powder obtained from 1.5 M Na₂SO₄ solution in the current density range 500–4000 A m⁻² are shown in Fig. 5. It is clear that all diffraction lines correspond to CuO, indicating very high purity of the powders in all cases. Also, the shape of the diffraction peaks (high and dispersed) suggests that the cupric oxide powder consists of very fine particles. The most important experimental result, relevant to the discussion on the optimal conditions of CuO powder synthesis, is the fact that the diffraction patterns presented in Fig. 5, (e) have the lowest peak heights. This means that the smallest cupric oxide particles were obtained at a current density of 4000 A m⁻². The last peak, at a diffraction angle of 15°, corresponds to the Na₂SO₄ phase.

The average crystallite size depends on current density. Table 1 summarizes the data obtained from the line broadening analysis of the first three peaks in

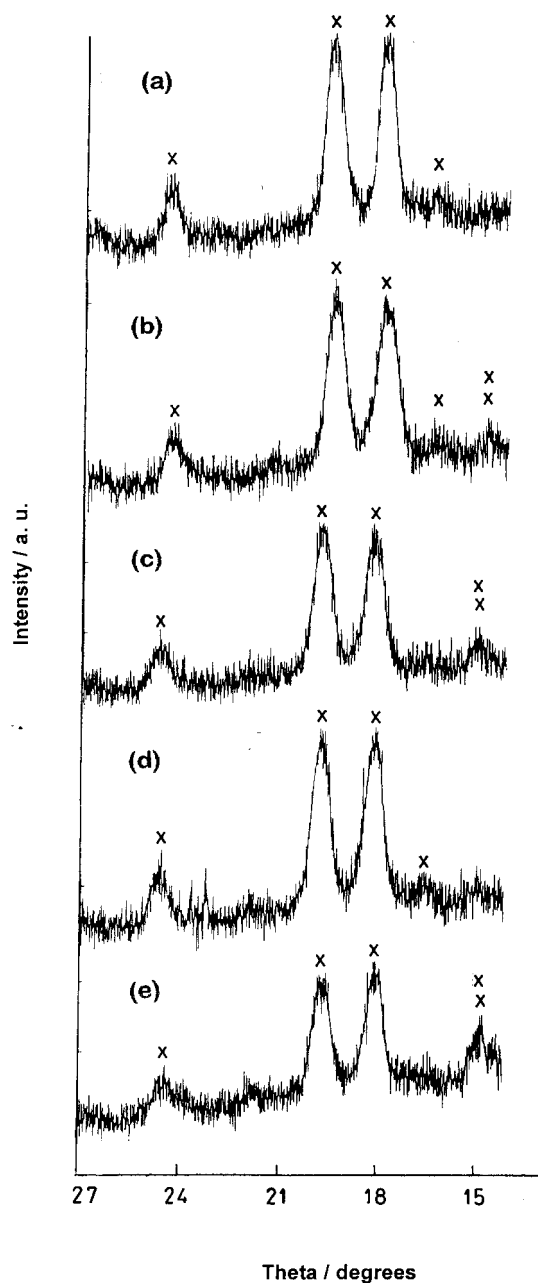


Fig. 5. X-ray diffraction patterns of CuO powder produced electrochemically in 0.5 M Na₂SO₄ solution at various current densities. pH 7.50, $T = 353$ K. Current densities, j : (a) 500, (b) 1000, (c) 2000, (d) 3000 and (e) 4000 A m⁻².

Table 1. Values of average crystallite sizes of CuO powder obtained at difficult current densities

| Current density /A m ⁻² | Average crystallite size /nm |
|---------------------------------------|---------------------------------|
| 500 | 45 |
| 1000 | 149 |
| 2000 | 167 |
| 3000 | 186 |
| 4000 | 422 |

the X-ray diffraction patterns as a function of current density.

It is clear that the anodic current density has an effect on both the product particle size and the copper anode dissolution. Higher anodic current density increases the rate of anodic electrodisolution linearly.

From the energy point of view it is convenient to carry out CuO synthesis at a current density of 4000 A m⁻², since at this current density, and pH 7.5, temperature 353 K and 1.5 M Na₂SO₄, the specific energy consumption is the lowest ($W = 5.9$ kWh (kg CuO)⁻¹).

It is difficult to compare the values for the optimum current densities determined by different authors. The differences are normally due to varying experimental parameters, such as different cell designs, different electrode shapes and dimensions, and different hydrodynamics. The present results were obtained under laboratory conditions, but further investigations will be carried out on a semi-industrial scale.

3.2. Effect of temperature

The selection of temperature depends mainly upon the dehydration of cupric hydroxide and the grain size of the cupric oxide powder. Consideration must also be given to the evaporation of the solution and the corrosion resistance of the cell materials. Figure 6 shows the change in the anode potential with time over a wide temperature range (313–363 K). The

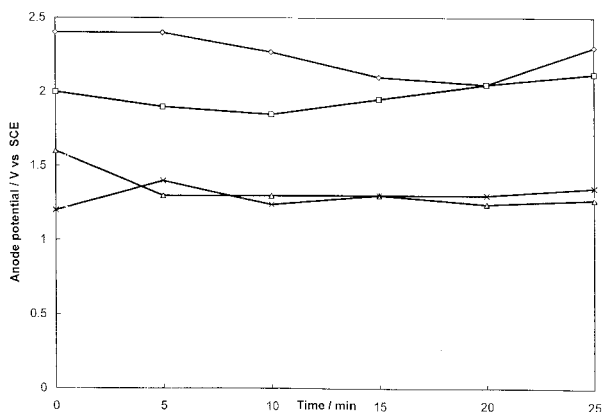


Fig. 6. Effect of temperature on the copper anode potential with time. 0.5 M Na₂SO₄ solution, pH 7.50, $j = 4000$ A m⁻². Temperatures, T : (◇) 313, (□) 333, (△) 353 and (×) 363 K.

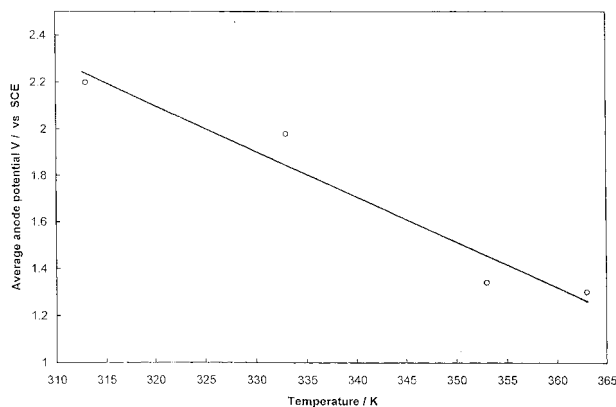


Fig. 7. The average electrode potential of the copper anode as a function of temperature. 0.5 M Na₂SO₄ solution, pH 7.50, $j = 4000$ A m⁻².

anode potential, expressed as the mean value, shows a linear dependence on temperature as shown in Fig. 7.

Figure 8 presents the specific energy consumption as a function of temperature. The lowest value (5.9 kWh (kg CuO)⁻¹) occurs at 353 K. Higher temperatures would be expected to favour CuO synthesis. However, some difficulties occur at higher temperatures, for instance a possible change in the nature and size of the gas bubble at the electrode surface due to the increase in water vapour content. Hence, according to other studies [1–3] and the present results, it is better to keep the temperature in the range 353–358 K.

3.3. Effect of sodium sulfate concentration

Figure 9 illustrates the cell voltage change with time when the Na₂SO₄ concentration was varied in the range 0.25–2 M with other conditions constant: pH 7.50, $i = 4000$ A m⁻² and $T = 353$ K. The anode potentials at all Na₂SO₄ concentrations, except 2.0 M, showed a fairly stable value. The difference in the case of 2.0 M Na₂SO₄ may be attributed to partial surface crystallization of Na₂SO₄ on the anode.

The dependence of CuO specific energy consumption at 4000 A m⁻² on the Na₂SO₄ concentra-

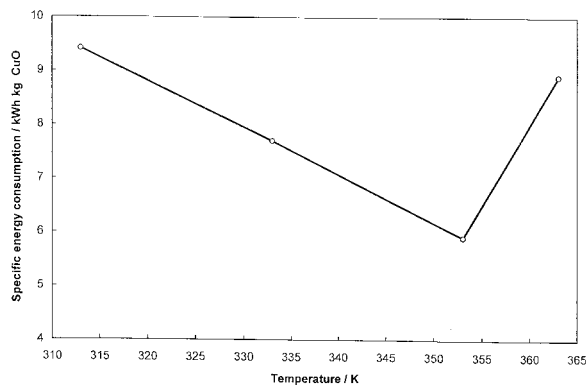


Fig. 8. Specific energy consumption for CuO powder synthesis in 0.5 M Na₂SO₄ solution as a function of temperature. pH 7.50, $j = 4000$ A m⁻².

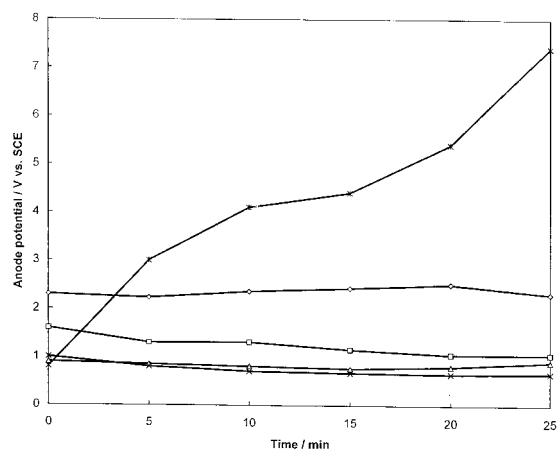


Fig. 9. Change in electrode potential of copper anode with time at different concentrations of Na_2SO_4 . pH 7.50, $j = 4000 \text{ A m}^{-2}$ and $T = 353 \text{ K}$. Concentrations, C: (\diamond) 0.25, (\square) 0.50, (\triangle) 1.50 and (\times) 2.00 M.

tion is shown in Fig. 10. A minimum is attained at 1.5 M ($W = 3.0 \text{ kWh (kg CuO)}^{-1}$). However, a CuO current efficiency of almost 100% was obtained at two Na_2SO_4 concentrations: 0.5 and 1.5 M. On the basis of these results, a Na_2SO_4 concentration of 0.5 M can be considered preferable for cupric oxide powder synthesis because considerably smaller quantities of this compound are required for the process.

4. Conclusions

The following conclusions may be drawn from the present study:

- (i) There is a strong dependence of grain size and cupric oxide powder purity on current density. A current density of 4000 A m^{-2} may be suggested for successful CuO powder synthesis, other conditions being as follows pH 7.5, 353 K and 1.5 M Na_2SO_4 . The smallest sized (a few nanometers) CuO particles were obtained at a current density of 4000 A m^{-2} . The average crystallite size increased from 45 nm (at a current density of

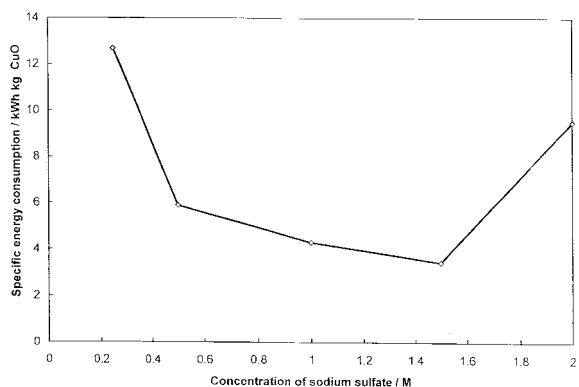


Fig. 10. Effect of Na_2SO_4 concentration on CuO specific energy consumption. pH 7.50, $j = 4000 \text{ A m}^{-2}$ and $T = 353 \text{ K}$.

500 A m^{-2}) to 400 nm (at a current density of 4000 A m^{-2}). According to CuO suspension transparency measurements, which showed a decrease in powder particle size with increasing current density, higher current densities lead to less pronounced aggregation.

- (ii) The optimum temperature for cupric oxide powder synthesis is 353 K.
- (iii) An optimum value of Na_2SO_4 concentration of 0.5 M was established. Although a minimum in specific energy consumption of $3.0 \text{ kWh (kg CuO)}^{-1}$ is attained with 1.5 M Na_2SO_4 , this is not suggested as the optimum operating parameter. An optimum value of sodium sulfate concentration of 0.5 M is proposed due to considerably smaller quantities of the compound required.

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