

Electrochemical synthesis of cupric oxide powder

Part I: Influence of pH

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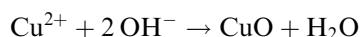
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Electrochemical synthesis of cupric oxide powder (CuO) in alkaline sodium sulfate is of technological interest. As it is known that hydroxyl ions are needed for the formation of cupric oxide, according to the principal chemical reaction:



The effect of pH (in the range from 7.50 to 10.80) on cupric oxide powder formation was investigated. Optimum conditions for cupric oxide powder synthesis, with respect to particle size, cell voltage, current efficiency and specific energy consumption were determined to be a pH 7.5 and a current density of 4000 A m^{-2} . A significant effect of pH on the particle size and aggregation of the powder was confirmed by both galvanostatic measurements and particle size determination. The lowest powder particle sizes were obtained at pH 7.5. Aggregation of powder particles at higher pH was also observed.

Keywords: *cupric oxide, pH, powder, sodium sulfate*

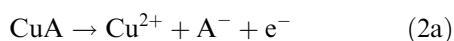
1. Introduction

Many investigations have been undertaken on the electrochemical dissolution and deposition of copper in acidified sulfate systems [1–11], but very little has been reported concerning the anodic dissolution of copper at potentials other than the corrosion potential. Recently, Balakrishnan and Venkatesan [12] reported an increased dissolution rate of copper with increased sulfate ion concentration, especially at high potentials.

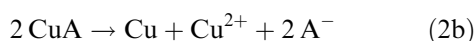
Awad *et al.* [13] carried out dissolution studies in acidified aqueous solutions of various anions using a potentiostatic method. The Tafel slopes were found to depend on the nature of the anion (chloride, nitrate or sulfate), indicating the possibility of anion participation in the anodic copper dissolution. These authors suggested a reaction mechanism involving the general anion, A^- , based on the formation of intermediate Cu^+ compounds (a fast reaction). This was then followed either by a slow electron exchange reaction or by a slow disproportionation reaction:



either



or



Recently, it has been shown that the electrochemical dissolution of copper in acidified sulfate solutions increases with increasing pH, suggesting a possible onset of a new reaction involved the diffusion of Cu^+ away from the electrode [14]. This is the expected observation as a result of the formation of Cu_2O in alkaline solution [15–17].

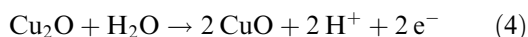
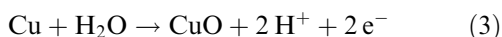
The electrolytic powder production method usually yields products of high purity which can be well pressed and sintered. Recently, it has been shown [18, 19] that by using different electrolytic procedures it is possible not only to obtain powders with a wide range of properties, but also to predict the characteristics of powders which are of vital importance for powder quality control and for specific applications. Due to the rapid increase in the significance of powder metallurgy, metal powders, as well as their oxides, are produced in large quantities, a large amount being produced by electrolysis. The effect of different parameters on metal powder preparation, especially copper [20–26], has been studied by a number of authors under various conditions with a variety of interpretations of the effects observed.

However, unlike pure copper powder, there are no systematic studies of the effect of different parameters (e.g., pH, anodic current density, temperature etc.) on the electrochemical synthesis of copper oxide powders (Cu_2O and CuO). Unlike the other procedures such as hydrothermal, sintering, chemical, and displacement processes, the electrochemical approach

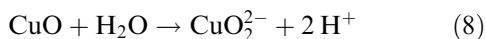
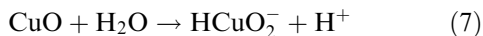
appears to be the best on a large scale in view of its short process flowsheet, easy operation, high quality product and flexible operating conditions.

A survey of the literature [27–29] about cuprous oxide powder reveals there are large differences in operating conditions, especially the concentration of sodium hydroxide and the anodic current density. Much less attention has been given to the electrochemical synthesis of cupric oxide powder (CuO) [30].

According to the potential–pH diagram [31] for the binary system Cu–H₂O at 25 °C, cupric oxide is stable in the alkaline region. Yet, the mechanism of cupric oxide powder synthesis during the electrodisolution of copper in alkaline solutions is still unknown. It is known that copper appears in different valence states and, hence, several reactions can be expected:



In addition, within the range of solubility of the solid phases, the following reactions are possible:



The purpose of the present research was to study the electrode processes on a copper anode under a broad range of variables using the galvanostatic method and thereby to establish guidelines for selecting optimum conditions for the electrochemical synthesis of cupric oxide powder in sulfate solutions. Extending the range of OH[−] concentration over four orders of magnitude allows investigation of the dependence of the rate of reaction on pH and hence of the role of hydroxyl ions on cupric oxide powder synthesis.

2. Experimental details

1.5 M Na₂SO₄ solution was used for electrochemical cupric oxide powder synthesis. Solutions with appropriate pH values (in the range from 7.50 to 10.80), were obtained by adding H₂SO₄ and NaOH. A vertical stationary spiral copper wire (dia. 1.0 mm, length 40 cm) served as cathode. Reduction of cupric oxide to metallic copper by contact with the cathode was avoided by use of a diaphragm. A sheet of electrolytic refined copper (1 cm wide × 4 cm long) served as anode and the reference electrode was a saturated calomel electrode (SCE). All the potentials quoted in this study are given with respect to this reference electrode.

An ‘AMEL-551’ set-up was used as a galvanostat in the galvanostatic experiments. The temperature of the electrolyte was 80 °C and electrolysis was performed at a constant current density of 4000 A m^{−2}.

After electrolysis the solution containing cupric oxide powder was filtered, then washed with distilled water and dried at 100 °C for 1 h. The photomicro-

graphs of the powder particles were made at a magnification of ×64.

To determine the approximate powder grain size obtained at different pHs, transparency measurements of CuO powder suspensions were carried out as a function of time. All suspensions were made up of 0.1 g of CuO powder in 5 cm³ distilled water. The powder and the liquid phase together with two glassy bolls were shaken in a colorimeter tube for 30 min and then, using a photocolormeter, the transparency was registered at time intervals of 15 min. The cupric oxide powders were also characterized by X-ray diffractometry using copper K_α radiation, at 30 kV accelerating voltage.

3. Results and discussion

The changes in the electrode potential of the copper anode with time, for cupric oxide powder synthesis, in 1.5 M Na₂SO₄ solution were determined for several pH values: 7.50, 8.64, 8.96, 9.62, 10.55 and 10.80. A typical change in the electrode potential of the copper anode with time at pH 8.96 is shown in Fig. 1. A substantial and rapid rise in the electrode potential up to a potential of 5 V occurs during the first 10 min, with a slight fall at the end of the process. A curve of similar shape to that presented in Fig. 1 was obtained at the other pH values. In the investigated pH range, the potentials changed with time from 1.0 to 5.8 V. At pH 7.50, the initial potential was the lowest.

It should be noted, however, that for electrode processes, including the dissolution of the copper electrode, the presence of an insoluble film on the electrode surface can affect its kinetics. For this reason the anodic copper dissolution was probably inhibited (during the initial stage, Fig. 1) by local passivation leading to the overly high current density at the dissolution-active sites. This was followed by the local saturation of the concentration of cupric ions. Similar behaviour of the anodic potential of copper has been previously noticed by Ji and Cooper [29], for cuprous oxide powder synthesis in alkaline chloride solution in the presence of different additives.

The average electrode potential of the anode, calculated as the mean value of all experimental points between the first stage and the last measurement, were plotted as a function of pH. A straight line of slope 78.6 mV, as illustrated in Fig. 2, was obtained, although considerable scatter was observed in the data.

An example of the relationship between cell voltage and time for cupric oxide powder synthesis from 1.5 M Na₂SO₄ solution (pH 8.96) is shown in Fig. 3. As was the case for the other pH values, after the initial period cell voltage increased steeply reaching a stable value (about 10 V) after about 20 min. In the investigated pH range (7.50 to 10.80), the cell voltages changed with time from 6 to 12 V.

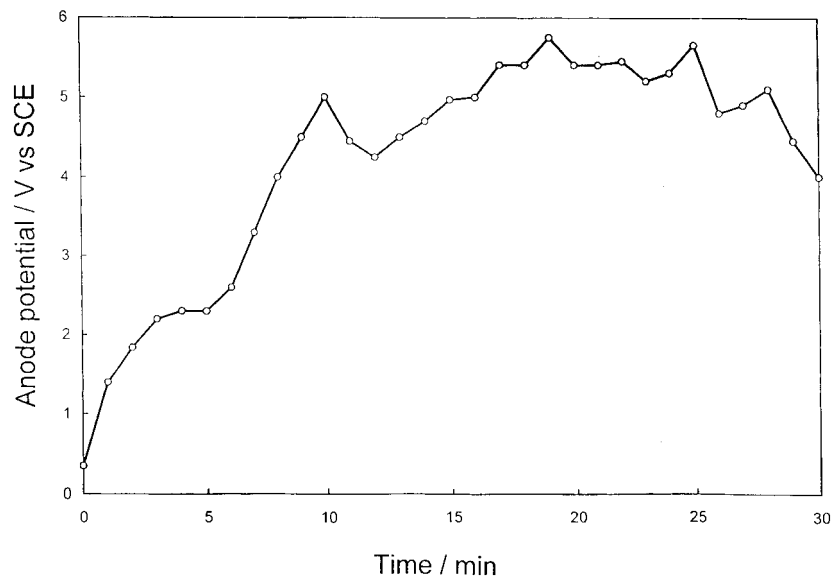


Fig. 1. Change in electrode potential with time for cupric oxide powder synthesis in 1.5 M Na_2SO_4 solution at pH 8.96. $i = 4000 \text{ A m}^{-2}$; $t = 80^\circ\text{C}$.

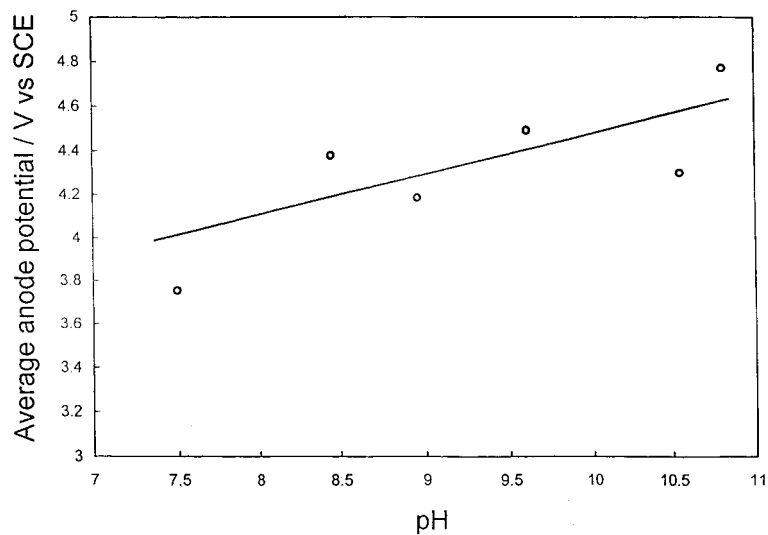


Fig. 2. Relationship between average electrode potential and pH for cupric oxide powder synthesis in 1.5 M Na_2SO_4 solution. $i = 4000 \text{ A m}^{-2}$; $t = 80^\circ\text{C}$.

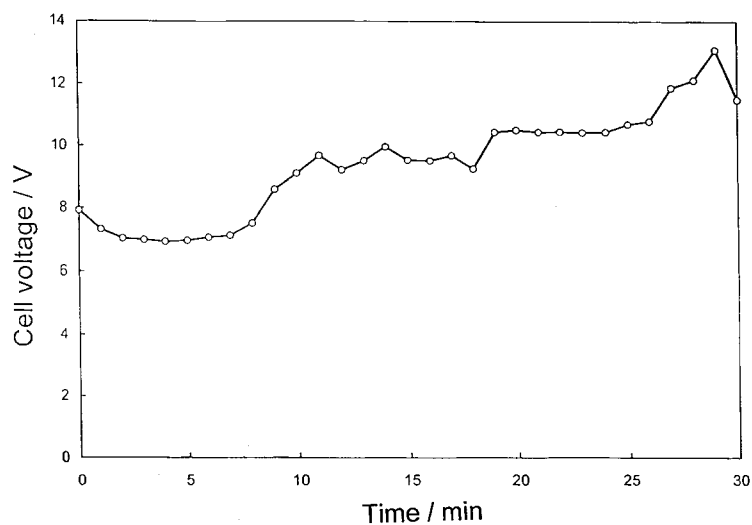


Fig. 3. Change in cell voltage with time for cupric oxide powder synthesis in 1.5 M Na_2SO_4 solution at pH 8.96. $i = 4000 \text{ A m}^{-2}$; $t = 80^\circ\text{C}$.

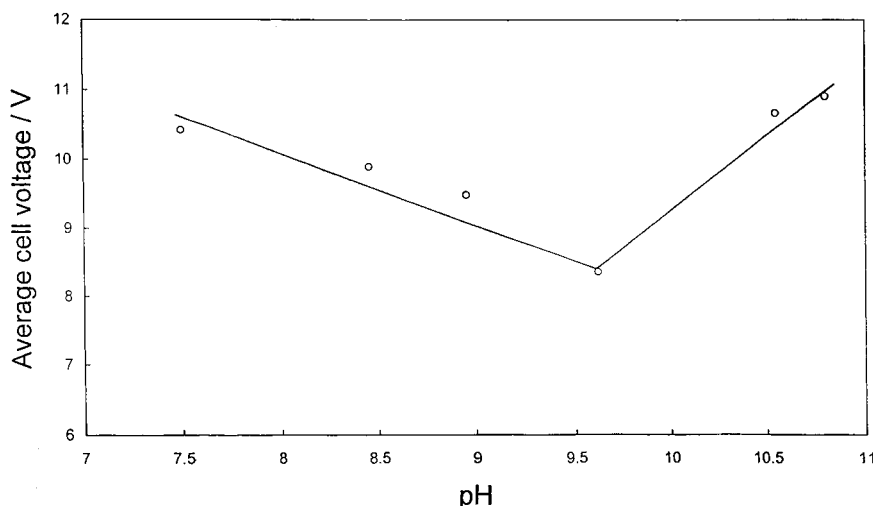


Fig. 4. Relationship between average cell voltage and pH for cupric oxide powder synthesis in 1.5 M Na_2SO_4 solution. $i = 4000 \text{ A m}^{-2}$; $t = 80^\circ\text{C}$.

The overall cell voltage, U , may be expressed as a sum of the reversible potential, U_o , the ohmic voltage drop between the anode and the counter electrode, ΔU_{ohm} , the overpotentials, η , and the voltage drop through the diaphragm, $\Delta\phi$. Thus,

$$U = U_o + \Delta U_{\text{ohm}} + \eta_{\text{A,a}} + \eta_{\text{C,c}} + \Delta\phi \quad (9)$$

The average cell voltage, expressed as the mid-value of all experimental points, may be plotted against pH. This is illustrated in Fig. 4. Two different cell voltage trends can be identified; a decrease from 11.0 to 8 V at lower pH and an increase from 8 to 11.5 V at higher pH. The transition occurs between pH 9.5 and 10. The observed minimum can be explained by the effect of pH on the solubility of CuO and $\text{Cu}(\text{OH})_2$ (Fig. 5). The experimental results presented in Fig. 4 are in a good agreement with the revised Pourbaix diagram for the copper–water system at 75°C [32] (Fig. 5).

To investigate the approximate grain size of cupric oxide powder, obtained at different pHs and with other conditions constant, transparency measurements for suspensions of CuO powders in distilled water were carried out as a function of time. The transparencies of the samples were measured every minute up to 15 min. These data are presented in graphical form in Fig. 6. The curve marked reference was obtained for copper powder particles (0.1 g , $(45\text{--}50) \times 10^3 \text{ nm}$) suspended in distilled water (5 cm^3).

The curves shown in Fig. 6 have a characteristic shape with gradual increase in transparency with time in the first few minutes. Another important experimental result, relevant to the discussion of the particle size, is that the curves did not completely level off, even after 15 min. This suggests that powder particles of a smaller size exist in suspension after 15 min. The lowest transparency values were obtained at pH 7.50. Since the transparency depends directly on particle diameter, it is clear that the smallest particles are obtained at pH 7.50. The diameter of the CuO powder particles was calculated by using the

simple relation $T_1/T_2 = r_1/r_2$, where T_1 is the transparency from the reference curve, T_2 is the transparency for the CuO suspension, r_1 is the known diameter of copper powder particles ($\sim 45 \times 10^3 \text{ nm}$), from which the reference transparency curve is obtained, and r_2 is the diameter of the CuO particles investigated.

The average transparency, calculated as a mean value of all the experimental points is plotted as a function of pH in Fig. 7. Two different transparency ranges were noted depending on pH. Unlike the data in Fig. 5, where a pronounced minimum was noted, here a maximum appears. Again, the change-over occurs between pH 9.5 and 10. Clearly, the transparency data confirm the electrochemical measurements.

Photomicrographs showed that the particles of cupric oxide powder exhibit spheroidal shape. A certain degree of aggregation was noticed, especially

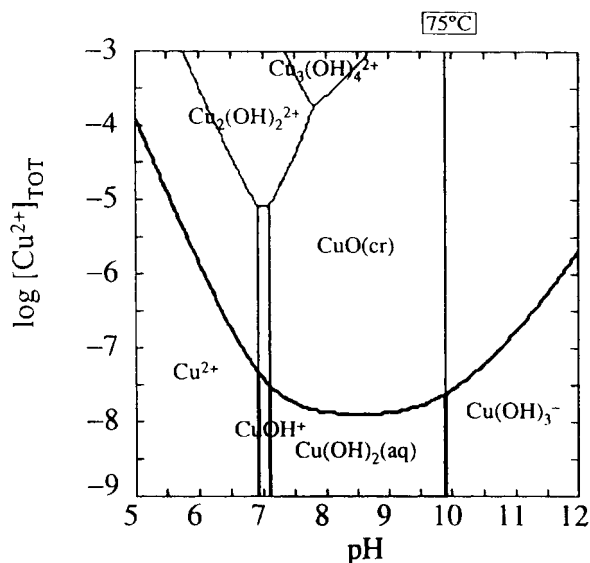


Fig. 5. Influence of pH on the solubility of CuO and $\text{Cu}(\text{OH})_2$ at 75°C in aqueous solution [32].

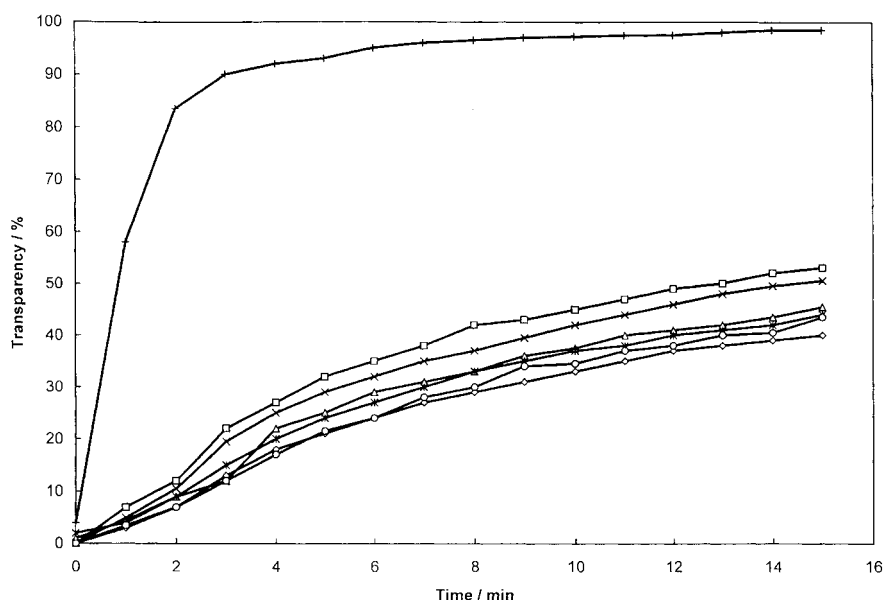


Fig. 6. Change in transparency of CuO powder suspensions with time at different pH in 1.5 M Na₂SO₄ solution. $i = 4000 \text{ A m}^{-2}$; $t = 80^\circ \text{C}$. Key for pH: (\diamond) 7.50, (\square) 8.64, (\triangle) 8.96, (\times) 9.62, ($*$) 10.55, (\circ) 10.80 and (—+) reference curve.

at higher pH. However, it should be noted that the aggregation product could easily be destroyed by handling. In the whole pH range a characteristic black color for the cupric oxide powder was obtained.

The X-ray diffraction patterns of the cupric oxide powder obtained in 1.5 M Na₂SO₄ solution, in the pH range from 7.5 to 10.80, are shown in Fig. 8. The first four diffraction lines correspond to a CuO phase with cubic thenorite structure. The shape of the diffraction peaks (high and dispersed) also suggest that the cupric oxide powder consists of very fine particles. However, the last peak appearing at a diffraction angle of 15° corresponds to Na₂SO₄.

The crystallite size, D (nm), was calculated for several reflections in a given X-ray pattern, for each pH value, from the Scherrer equation [33]:

$$D_{hkl} = 0.9 \lambda / (\beta \cos \theta) \quad (10)$$

where λ is the wavelength of the X-rays, θ is the diffraction angle and β is the corrected full width at half maximum of the peak given by

$$b^2 = b_m^2 - b_s^2 \quad (11)$$

where b_m is the measured halfwidth and b_s is the half width of a standard silicon powder (NIST SRM 640b). Equation 11 was used to correct the X-ray peaks for instrumental broadening, since the peaks were observed to have a near-Gaussian shape [32].

The average crystallite size of the electrochemically prepared powders was influenced by the solution pH. Table 1 summarizes the data obtained from the line

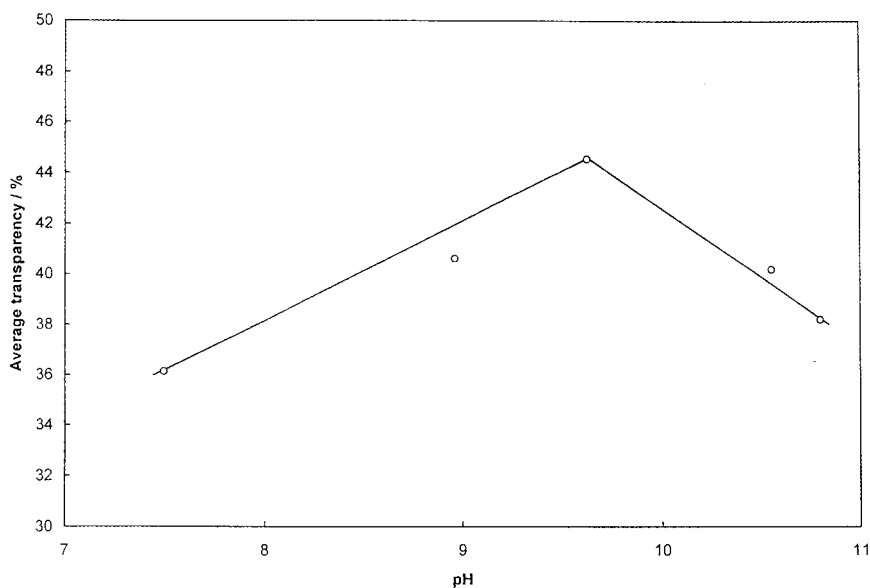


Fig. 7. Relationship between average transparency and pH for cupric oxide powder obtained at different pH in 1.5 M Na₂SO₄ solution. $i = 4000 \text{ A m}^{-2}$; $t = 80^\circ \text{C}$.

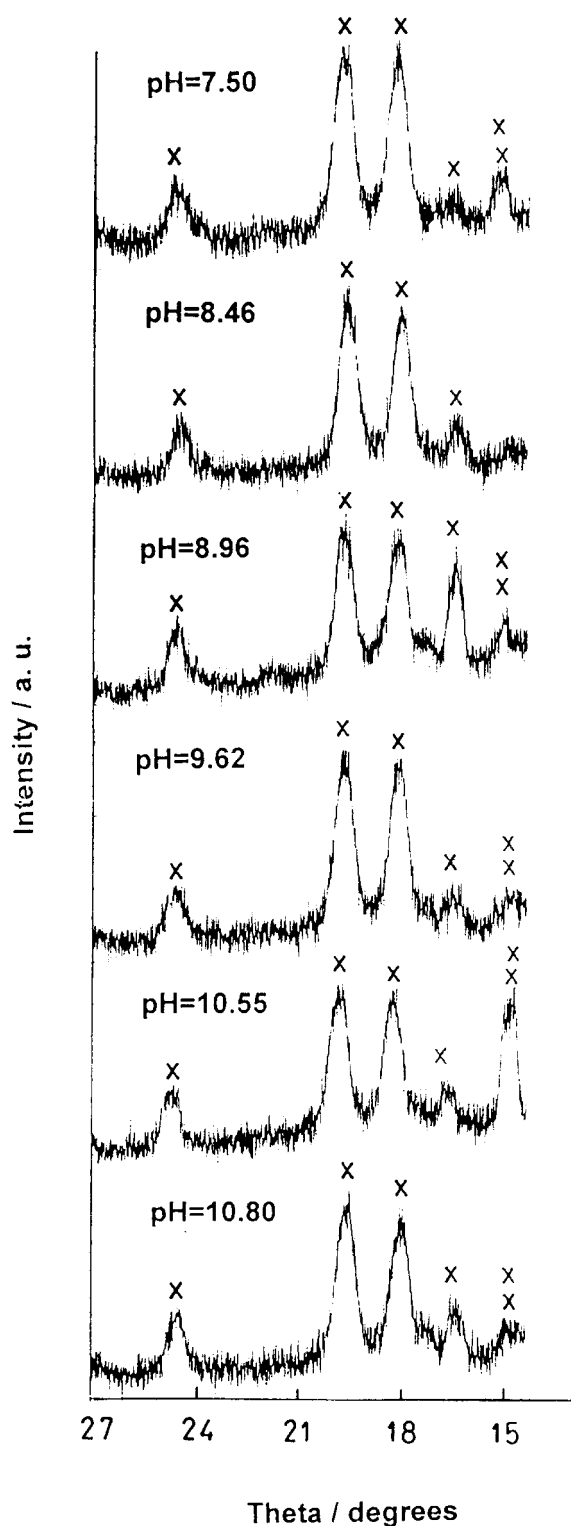


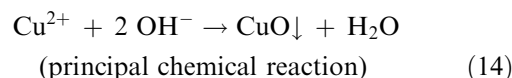
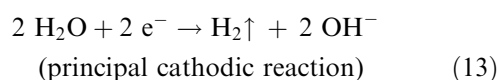
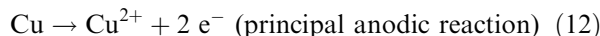
Fig. 8. X-ray diffraction patterns of the cupric oxide powder produced electrochemically in 1.5 M Na₂SO₄ solution, at current density of 4000 A m⁻²; at *t* = 80 °C and at different pH.

broadening analysis of the first three peaks in the X-ray diffraction patterns as a function of pH. The average crystallite size increased from 125 nm at pH 7.50 to 290 nm at pH 9.62. Moving to higher pH values (up to 10.80), the crystallite size decreased. The average crystallite size from X-ray line broadening and the particle size from transparency measurements are in good agreement.

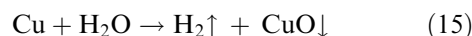
Table 1. Values of average crystallite sizes of CuO powder obtained at different pH

pH	Average crystallite size/nm
7.50	125
8.64	258
9.62	292
10.50	241
10.80	162

Clearly, pH has a significant role in the synthesis of CuO. It can be assumed that the reaction pathway is as follows:



Thus, the net cell reaction is the summation of Equations 12–14, that is:



The hydroxyl ions necessary for the formation of cupric oxide, according to the principal chemical reaction, are generated in the cathodic reaction and arrive at the anodic compartment by migration, diffusion and convection. From Equation 15 it is evident that the only substances consumed in the electrolysis are water and the metallic copper which serves as the anode. The pH of the electrolyte should not change during electrolysis according to the above stoichiometry. This was verified by pH measurements.

Being anodically dissolved in sulfate solutions, copper is ionized to a divalent state in a multistage process [34]. In chloride solutions, copper is ionized to the univalent state within a single stage, and Cl⁻ ions are assumed [35] to participate in a charge transfer reaction through a specific adsorption step. Hence, by varying the anionic composition of the electrolyte, the role played by the anion in the anodic dissolution mechanism can be elucidated.

It has been shown elsewhere [30] that the current efficiency for cupric oxide powder electrosynthesis in 0.5 M Na₂SO₄ solutions (*i* = 4000 A m⁻²; *t* = 80 °C) had a highest value of 95% at pH 7.50. A specific energy consumption of 6.0 kWh (kgCuO)⁻¹ at pH 7.50 was calculated. However, at pH 9.0 the specific energy consumption increased to 9.00 kWh (kgCuO)⁻¹ [30].

4. Conclusions

(i) Two different ranges of potential change, depending on pH, have been observed: from 11.00 to 8.00 V (at lower pH) and from 8.00 to 11.50 V (at higher pH). It has been established that the transition occurred between pH 9.50 and 10.00. This transition is related to the change in copper speciation in the

solution in accordance with the E_h -pH diagram for the Cu-H₂O system.

(ii) The lowest cupric oxide particle sizes were obtained at pH 7.5. This was confirmed by transparency measurements since the transparency depends directly on particle diameter.

(iii) On the basis of diffractograms obtained in the pH range from 7.50 to 10.80, it can be stated that in all cases powder of a purity of about 97% cupric oxide was electrochemically synthesized. The lowest value of average crystallite size (125 nm) was obtained at pH 7.50, whereas the highest value of 290 nm was obtained at pH 9.62.

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