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By I. Zaafarany & Herbert Boller

Umm Al-Qura University, Makkah Al-Mukaramha, Saudi Arabia

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Electrochemical Behaviour of a Copper Electrode in Ammonium Sulfide Solution

I. Zaafarany^α & Herbert Boller^σ

Abstract - The electrochemical behaviour of a copper electrode in ammonium sulphide solutions was studied using cyclic voltammogrammetry and potentiostatic and galvanostatic polarization techniques. The morphology and composition of the layers formed on the copper electrode were studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) and X-ray powder diffractometry. Besides different binary copper sulphide phases the ternary phases $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ and NH_4CuS_4 were observed, $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ crystallizing as needles perpendicular to the electrode surface.

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I. INTRODUCTION

Copper combines corrosion resistance with high electrical and heat conductivity, formability, machinability and strength. It has good resistance to urban, marine and industrial atmosphere and water. Being a noble metal it is not corroded by acids unless oxygen or another oxidizing agent is present. Copper and its alloys are also resistant to slightly alkaline solutions. Several authors studied the electrochemical behaviour of copper in alkaline solutions [1-5]. The presence of sulphide ions, however, enhances its corrosion. When soluble sulphides are present in potable water or sea water, a thick black, poorly adherent scale forms on a copper or brass surface [6]. This scale is composed mainly of Cu_2S although copper deficient Cu_{1-x}S , CuS and Cu_2O have also been reported [7]. There is a lack of studies of the electrochemical behaviour of copper in ammonium sulphide solutions.

There are several binary copper sulphides also occurring as minerals: Cu_2S (Chalcocite), $\text{Cu}_{1.97}\text{S}$ (Djurleite), $\text{Cu}_{1.8}\text{S}$ (Digenite), $\text{Cu}_{1.74-1.82}\text{S}$ (Roxbyite), $\text{Cu}_{1.4}\text{S}$ (Anilite) and CuS (Covellite) [8].

Two ammonium thiocuprates $\text{NH}_4\text{Cu}_7\text{S}_4$ [9] and $\text{NH}_4\text{Cu}_4\text{S}_3$ [10] and one polysulphide NH_4CuS_4 [11] have been reported and the formation of $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ and of the new compound $\text{NH}_4\text{Cu}_4\text{S}_3$ by reaction of copper with yellow ammonium sulphide solutions has been studied [10].

The present work aims to study the electrochemical behaviour of a copper electrode in

ammonium sulphide solutions using cyclic voltammograms, potentiostatic and galvanostatic polarization techniques with special emphasis on the morphology, chemical and phase composition of the layers and scales formed.

II. EXPERIMENTAL

Cyclic voltammograms (CVs), potentiostatic and galvanostatic polarization techniques were performed with the computer-controlled electrochemical measurement system Autolab (ECO Chemie) combined with the software package GPES (General Purpose Electrochemical System). A standard electrochemical cell with five holes - three holes for the electrodes and two for nitrogen inlet and outlet - was used. A commercial Ag/AgCl electrode was used as reference electrode. The counter electrode was a platinum wire. The working copper electrode was prepared from a high purity (99.98%) copper rod. A small piece of copper rod - diameter 6 mm, length 6 mm - was placed in a "Kel-F" shield, secured by epoxy resin. The bottom electrode was screwed onto a polyethylene holder with a contact wire in order to obtain good electrical contact. The electrodes were successively abraded with finest grade emery paper and degreased with acetone. Complete wetting of the surface was taken as indication of its cleanliness when rinsed with bi-distilled water. All chemicals used were of A.R. quality. The solutions were prepared using bi-distilled water; no attempts were made to de-aerate them. Most experiments were done in relatively concentrated 2.9M ($\text{pH} \approx 9$) ammonium sulphide solutions.

Cyclovoltammetric sweeping was generally between -2.0V (hydrogen evolution) to +1.0 V (oxygen evolution). All measurements were taken at 25 ± 1 °C.

The surface of the electrode and the scales formed at the electrode were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray elemental analysis (EDAX). Guinier powder photographs were used for the crystallographic phase analysis of the products.

III. RESULTS AND DISCUSSION

a) Cyclic Voltammogram Curves

Figure 1 represents the cyclic voltammogram of a Cu electrode in 2.9M ammonium sulphide solutions between -2.0V and 1.0V at a voltage scan rate 50mV sec^{-1} . Inspection of this figure reveals that there are three

^{Author^α} : Chem. Dept, Faculty of Appl. Sci, Umm Al-Qura University, Makkah Al-Mukaramha, Saudi Arabia.

E-mail : ishaq_zaafarany@yahoo.com

^{Author^σ} : Institut für Anorganische Chemie, Johannes-Kepler-Universität Linz, Austria.

anodic peaks (A, B, C). A corresponds to the formation of the copper sulphide layer Cu_{2-x}S while the peaks B and C are related to the formation of CuS and some Cu_2O [12]. The reverse scanning shows three cathodic peaks namely, D, E and F. The cathodic peak D corresponds to the partial reduction of CuS , while the cathodic peak E is associated with the reduction of the sulphide layer formed in region A - B. The study was then restricted to the potential range where the processes associated with A, B, and E take place, since the aim of this work was to elucidate the formation of the sulphide layer. Such a voltammogram is shown in Figure 2. The layer does not passivate the surface, and the fact that the ratio of Q_a/Q_c was found to be close to 1 (where Q_a and Q_c are the anodic and cathodic charges) indicates that no appreciable dissolution of the electrode or of the layer takes places in this potential region.

b) Potentiostatic Polarization Measurements

Figure 3 (a, b and c) shows the potentiostatic polarization ($i - t$) curves for the copper electrode in 2.9M ammonium sulphide solution at different potentials. The general shape of the transients is characteristic of a nucleation and growth process. At very short times double layer charging takes place, followed by an increase of current due to the formation and growth of nuclei. The current reaches a maximum and starts to decrease rapidly because of the layer growth controlled by mass transport till a steady state is reached. Although the initial current increases are usually too fast to be seen in the potentiostatic current-time curves, it is clearly shown in Figure 3b.

c) Galvanostatic Polarization Measurements

Figure 4a represents the galvanostatic polarization curves of the copper electrode in 2.9M ammonium sulphide solution at zero current. The shape of the transient is characteristic of a nucleation process. Sand's equation seems to be obeyed in the region between the minimum (1sec) till the end of the experiment

The main contribution of the peak observed during the galvanostatic polarization experiment is that of the nucleation process. The potential decreases rapidly to less negative potentials arriving at a steady state at -0.975V probably corresponding to chalcocite formation.

Figure 4b represents the galvanostatic polarization curves of a copper electrode in 2.9M of ammonium sulphide at current = 1A. No steady state is reached within the measuring time. The discontinuities in the transient indicate mechanical ruptures during layer formation.

d) The Composition And Nature Of Anodically Formed Layers

The layers formed on the copper electrode in 2.9M ammonium sulphide solution under potentiostatic

conditions at different potentials were investigated by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and X-ray powder diffraction.

Dependent on the experimental conditions layers with different morphologies and compositions are observed (Table 1). EDAX analyses indicate that oxygen contents are generally very low. Besides binary copper sulphide phases two ternary compounds, $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ and NH_4CuS_4 , are formed. The morphology of $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ is drastically different from that of Chalcocite. The layer is felt-like with thin packages of needles growing perpendicularly to the electrode surface (Figure 5a). By increasing time the needles become a little thicker and longer without changing their orientation.

Two reaction paths are feasible:

- in situ reaction of anodically formed Cu^+ with S^{2-} and NH_4^+
- consecutive reaction of anodically formed Cu_2S with S^{2-} and NH_4^+

Reaction path a) appears to be more probable in view of the oriented crystal growth. Cu^+ ions are supposed to travel through the channels existing in the quasi-one-dimensional crystal structure of $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ along the needle axis (c-axis). Hollow needles were also observed (Figure 5b). In this case the Cu^+ ions can also travel along the macroscopic channels inside the needles.

Figure 5c shows a typical micrograph of apparently well crystallized NH_4CuS_4 .

Scales formed under cyclo-voltammetric conditions correspond to irreversible processes. Therefore they are different from those formed under potentiostatic conditions. Thus by cycling between -0.8 V- to positive potentials of +0.2 to 0.8 V dark grey layers of Djurelite ($\text{Cu}_{-1.96}\text{S}$) were obtained, while under potentiostatic conditions at comparable positive potentials dark blue layers of Covellite (CuS) are formed.

IV. CONCLUSIONS

The electrochemical processes in the studied system are complex. Scale formation is governed by nucleation and growth and is characterized by concurrent reversible and irreversible reactions. Scales formed at cyclo-voltammetric conditions are different from those formed under potentiostatic conditions, where also the ternary phases $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ and NH_4CuS_4 are formed. $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$ is growing as fine needles perpendicular to the electrode surface suggesting an in situ reaction of anodically formed Cu^+ ions travelling from the electrode through the scale with $[\text{NH}_4]^+$ and S^{2-} ions in the solution.

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Table 1

Anodically formed layers under potentiostatic conditions
(electrolyte concentration 2.9M)

-0.73 to -0.53V	dark grey layer	chalcocite (Cu_2S)
-0.67 to -0.60V	needles + polycrystalline substrate	$\text{NH}_4\text{Cu}_7\text{S}_4$ + chalcocite(Cu_2S)
-0.4 to -0.3V	black layer	digenite (Cu_{1-x}S)
-0.3 to +0.2V	brown layer	NH_4CuS_4 + chalcocite
+0.4 to +0.6V	black blue layer	Covellite (CuS)

Figure Captions

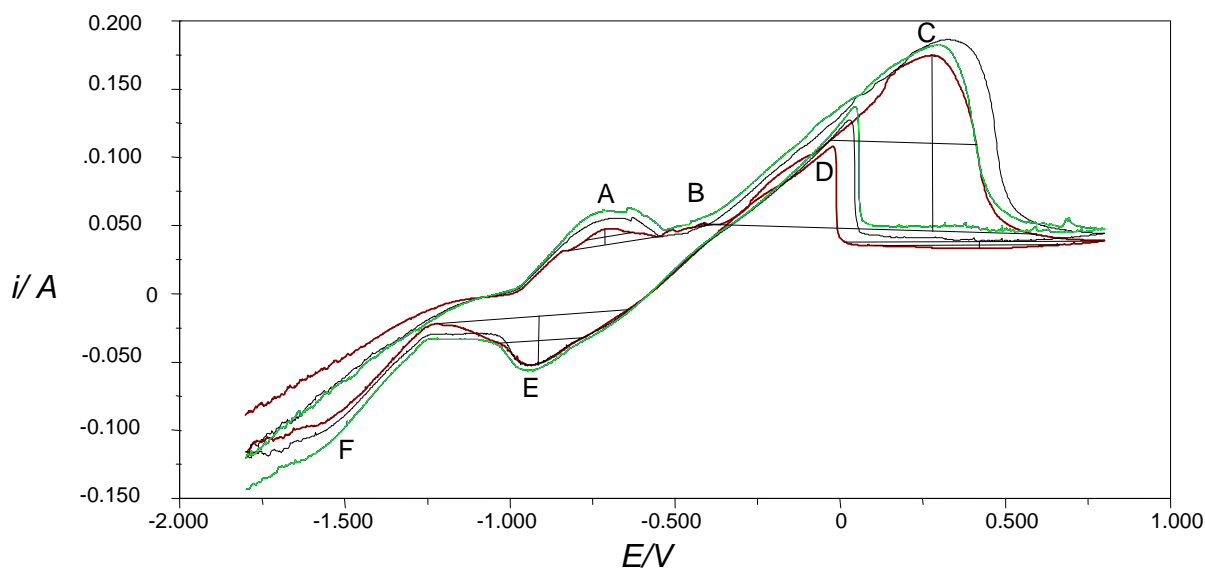


Figure 1 : Cyclic voltammogram of copper in 2.9 M ammonium sulphide solution at a sweep rate of 50mV/s.

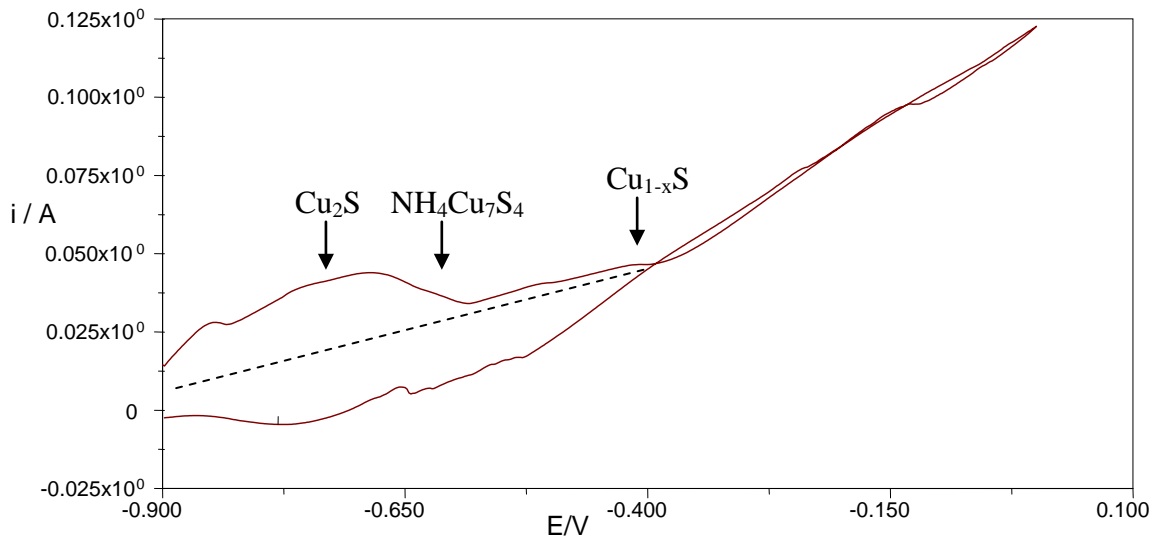
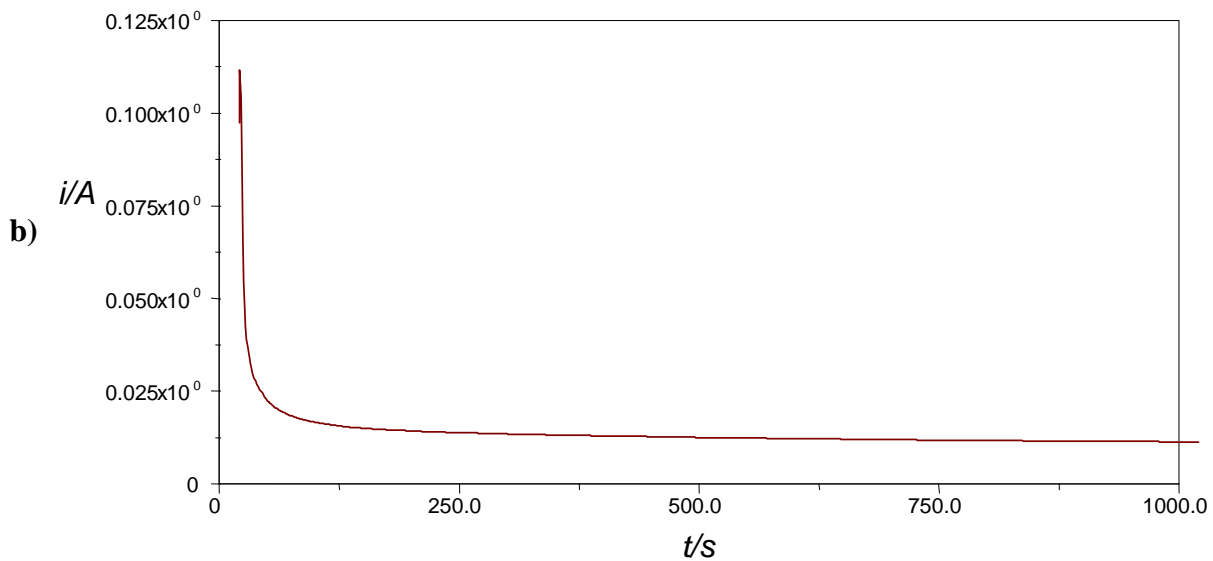
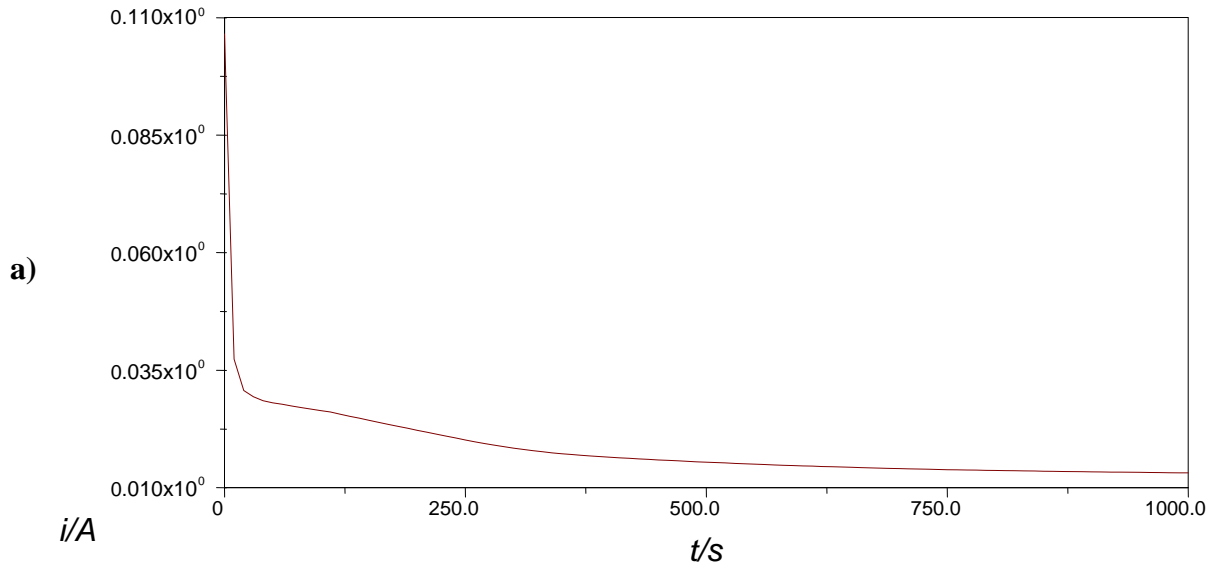


Figure 2 : Cyclic voltammogram of copper in 2.9 M ammonium sulfide solution in the range of Cu_{2-x}S layer formation at sweep rate 50mV/s.



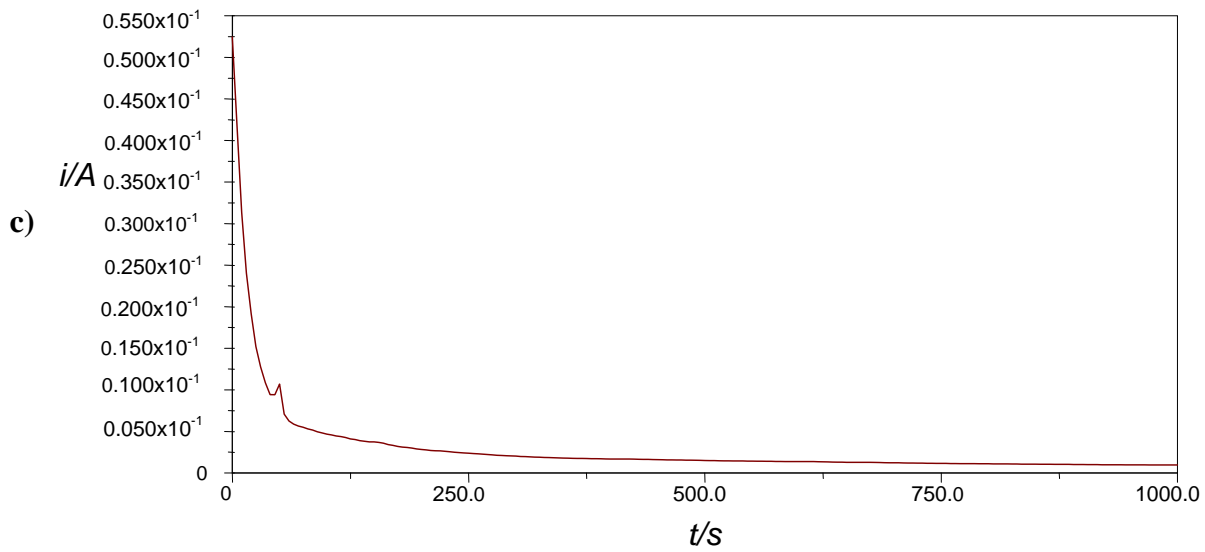
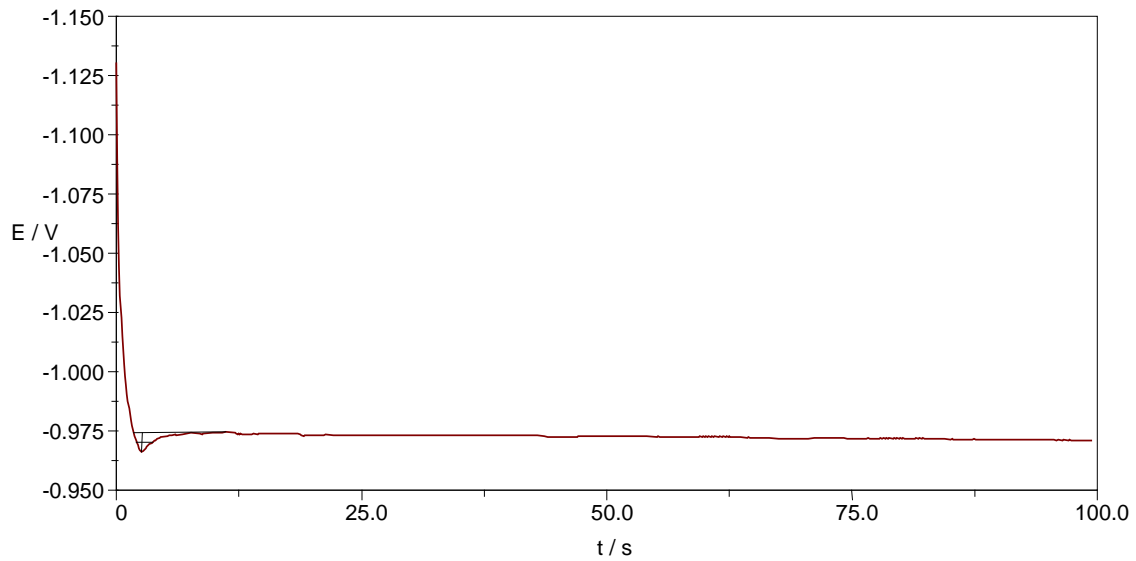
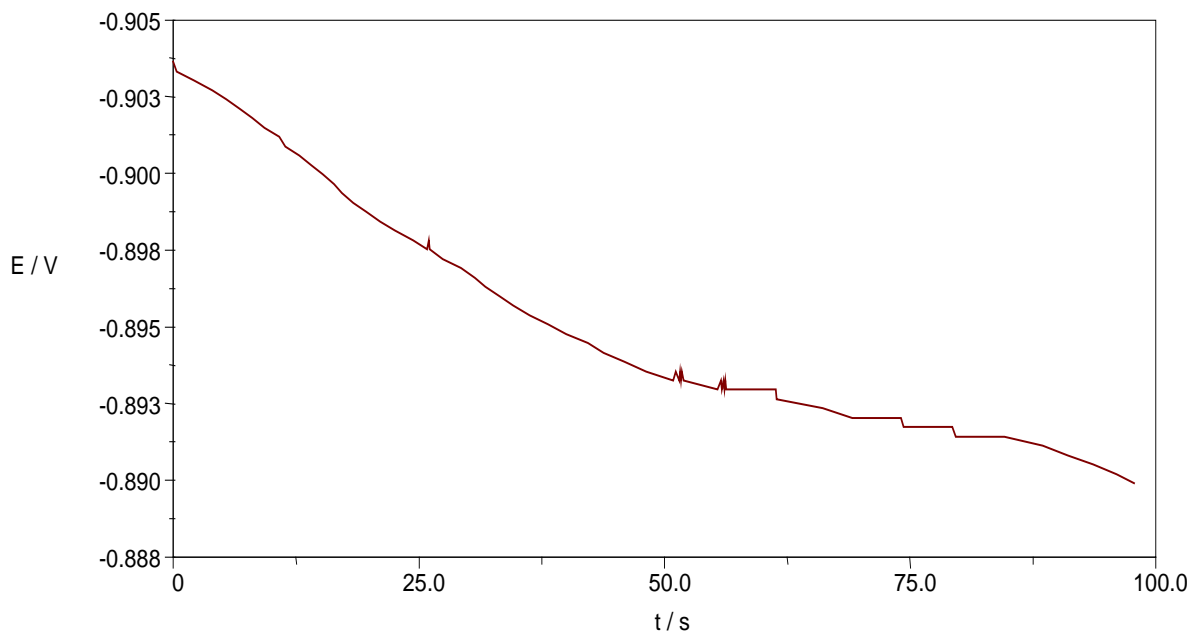


Figure 3 : Potentiostatic current-time curve of copper electrode in 2.9M ammonium sulfide solution at

- a) potential at -0.463V (formation of Cu_2S , Digenite).
- b) potential at -0.568V (formation of $\text{NH}_4\text{Cu}_{7-x}\text{S}_4$).
- c) potential at -0.704V (formation of Cu_2S , Chalcocite).



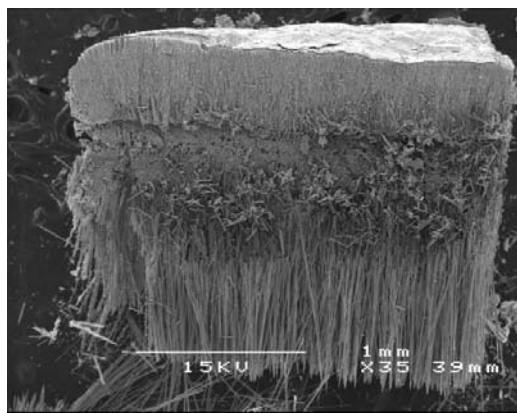
a
Galvanostatic curve recorded for copper electrode in 2.9M ammonium sulfide solution at current = 0



b
Galvanostatic curve recorded for copper electrode in 2.935M ammonium sulfide solution at current = 1A.

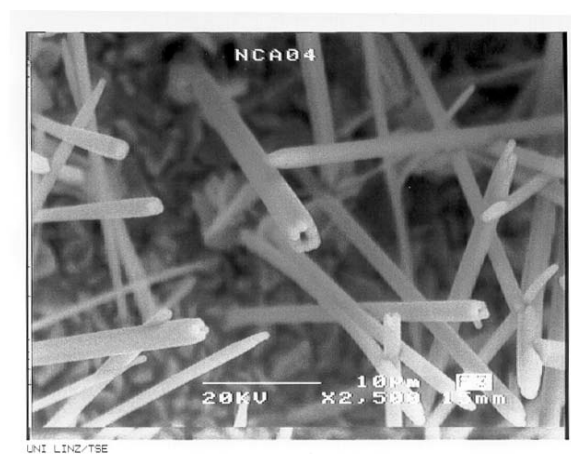
Figure 4 : Galvanostatic curve recorded for a copper electrode in 2.9M ammonium sulfide solution at

- a) current = 0
- b) current = 1A



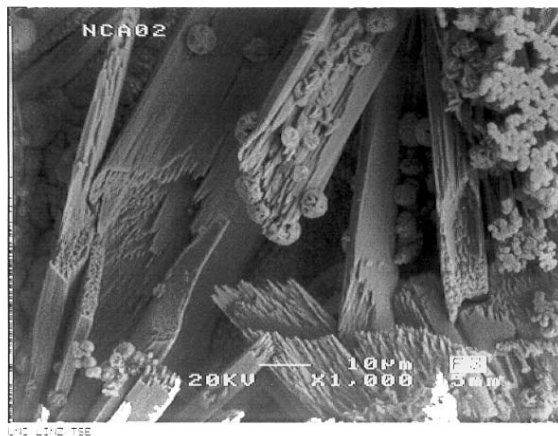
a

Scanning electron micrograph of a layer formed in 2.9M ammonium sulfide solution at potential $-0.63V$ ($NH_4Cu_7S_4$).



b

Scanning electron micrograph of $NH_4Cu_7S_4$ needles formed at the same conditions.



c

Scanning electron micrograph of a layer formed in 2.935M ammonium sulfide solution at potential 0V (NH_4CuS_4).

Figure 5 : SEM micrographs of electro crystallized $\text{NH}_4\text{Cu}_7\text{S}_4$ and NH_4CuS_4

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