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## ORIGINAL ARTICLE

## Corrosion of copper electrode in sodium sulfide solution

I. Zaafarany<sup>a,\*</sup>, H. Boller<sup>b</sup><sup>a</sup> Chem. Dept. Faculty of Appl. Sci., Umm Al-Qura University, Makkah Al Mukaramha, P.O. Box 118, Saudi Arabia<sup>b</sup> Institute of Inorganic Chemistry, Johannes-Kepler-Universität, Linz, A-4040 Linz, Austria

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## KEYWORDS

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**Abstract** The electrochemical reactions of a copper electrode in Na<sub>2</sub>S solutions were studied using cyclic voltammetry, potentiostatic and galvanostatic measurements. In addition surface examination and morphological studies were applied using scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX). There are three anodic peaks were found in the anodic branch of the voltammogram's. These peaks may be corresponding successively to the formation of Cu<sub>2</sub>S, CuS and Cu<sub>2</sub>O. On the other hand, the cathodic branch contains four peaks. These peaks correspond to the reduction of copper oxide and copper sulfide formed on the anodic branch.

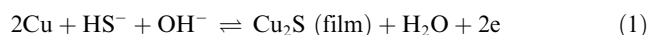
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## 1. Introduction

The sulfidation of metals is a process of practical importance as well as of theoretical interest as oxidation. From the theoretical point of view, sulfidation reactions afford important parallels and contrasts with the corresponding oxidation reactions. Films of solid reactions formed on metals and alloys constitute in general, a field of study of great importance in electrochemistry, which is still for investigations on the electrochemical behavior of copper in sulfide solutions and the formation of sulfide films on copper are relatively scarce despite their

importance in many areas of applied chemistry and electrochemistry (Gennerode De Chialvo and Arvia, 1985; Rand, 1977; Peter, 1978). Stoichiometric and non-stoichiometric copper sulfide films have been widely used in dielectric metallization (Stepanova et al., 2003), in solar cell technology (Schimmel et al., 1998) and as ion specific electrode (Zirino et al., 2002), when soluble sulfides are present in potable water or seawater, a thick black, poorly adherent scale forms on copper or brass surface (Jacobs and Edwards, 2000). This scale is composed mainly of Cu<sub>2</sub>S although CuS, Cu<sub>2</sub>O and non-stoichiometric copper sulfide species such as Cu<sub>1.8</sub>S have also been reported (McNeil et al., 1993).

Cu<sub>2</sub>S has been formed as an insoluble film on Cu electrode in aqueous sulfide solutions according to (Velasquez et al., 2001):



The aim of the present work aims to give new lights on the characteristics of the reaction products performed on the copper surface in sodium sulfide (Na<sub>2</sub>S) using cyclic voltammograms technique.

\* Corresponding author.

E-mail address: [ishaq\\_zaafarany@yahoo.com](mailto:ishaq_zaafarany@yahoo.com) (I. Zaafarany).

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## 2. Experimental

The working copper electrode was prepared from 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. These were fixed to borosilicate glass tube with epoxy resin. Electrical contact was achieved through a copper wire soldered to the end of the electrode not exposed to the solution. Before being used, the electrode surface was polished with different grade emery papers until it appeared free of scratches and other defects. Then, it was rinsed with acetone and finally washed with twice distilled water. All chemical used were of A.R. quality. The electrolytic cell was all Pyrex and is described elsewhere (Shams El-Din and Abd El-Haleem, 1973).

Cyclic voltammograms (CVs), potentiostatic and galvanostatic polarization techniques performed using autolab [ECO Chemie] combined with the software package General purpose Electrochemical System (GPES) was used. This is a computer-controlled electrochemical measurements system. It consists of data-acquisition system and a potentiostat/galvanostat. CV was used to study the corrosion of copper in sodium sulfide solutions ( $\text{Na}_2\text{S}$ ) sweeping from  $-1.8$  to  $0.8$  V. All measurements were taken at  $25 \pm 1$  °C.

Scanning electron microscope (SEM) of the type (XL 30) was used to examine the surface of copper in absence and presence of  $\text{Na}_2\text{S}$  solution. All micrograph of corroded specimens were taken at a magnification of (X500). Energy dispersive analysis of X-ray [EDAX] examination using a Trakton TV 2000 energy dispersive spectrometer was used in this work.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

The electrochemical behavior of copper electrode was studied in normally aerated  $0.8$  M aqueous sodium sulfide solution using cyclic voltammogram's technique. Fig. 1 represents the CVs of Cu electrode in  $0.8$  M  $\text{Na}_2\text{S}$  recorded in three successive sweeps at  $25$  °C and at voltage sweep rate  $50$  mV/s. The observed difference in the curves can be attributed to different initial state of the electrode surface and can be recognized a long both the anodic and cathodic branches of the cyclic voltammograms. The initial state of the electrode surface

determines to an important extent the shape of the resulting cyclic voltammograms.

It is of interest to remark that the second and third sweeps give essentially similar voltammograms which differ from that the first sweep in some significant characteristics. Inspection of curves of Fig. 1 reveals that three peaks (A–C) in the anodic branch of voltammograms and four peaks, in the cathodic branch [D–G]. It is also note that there is no passivation is observed, the current rises steadily.

#### 3.1.1. Peak (A)

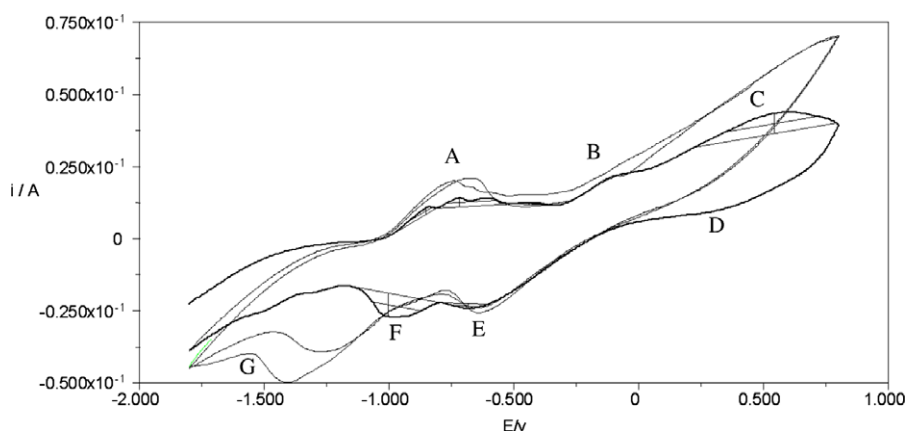
Peak (A) is a well-defined peak appears at about  $-0.7$  V<sup>-</sup> and in the contrast to this peak there are two steps are observed in the cathodic branch of the scan indicating that the anodic peak (A) is composite peak, the anodic peak (A) is supported by two electron transfer reaction.

There seems to be a general agreement between different authors that when copper electrodes comes in contact with sulfide ions in solution, the corrosion product, developing spontaneously is mostly cuprous sulfide which thicken on anodic polarization. This process can be looked upon as occurring through the ionization of Cu metal followed by combination of cuprous ions and sulfide with the precipitation of a porous black-scale of cuprous sulfide on the surface.



The mechanism of the film formation under peak (A) can be explained, on the basis of specific adsorption of  $\text{OH}^-$  and  $\text{S}^{2-}$  (or  $\text{HS}^-$ ) on the metal surface. Two alternatives can be thought of surface film formation under peak (A).

- (i) The initially thin film forms on the copper surface when immersed in sulfide solution is  $\text{Cu}_2\text{S}$ . The  $\text{S}^{2-}$  (or  $\text{HS}^-$ ) ions which are adsorbed on the metal oxide will ultimately produce islands of  $\text{Cu}_2\text{S}$ . The non-stoichiometric  $\text{Cu}_2\text{S}$  will induce the outward diffusion of  $\text{Cu}^{2+}$  ions to the film solution interface and allows cuprous sulfide scale growth on the top of the oxide film. The  $\text{OH}^-$  ions at the boundary between oxide film and sulfide film may react with the anodically formed  $\text{Cu}^+$  ion and allow some growth of the oxide film or even if not previously



**Figure 1** Cyclic voltammogram of copper in  $0.8$  M  $\text{Na}_2\text{S}$  at sweep rate  $50$  mV/s.

formed. The oxide film may or may not doped with sulfur content never approach that of  $\text{Cu}_2\text{S}$  scale that grows on top of it then an oxide-type may begin to grow beneath the sulfide film as suggested by More and Baccharia (1975).

- (ii) Initially thin films of cuprous oxide and cuprous sulfide could be formed on the surface in random fashion. Both compounds are cation deficient and that both thickening occur by inducing the outward diffusion of Cu ions to the film/solution interphase. The build up of these films is rather complex. The deviation from stoichiometry of  $\text{Cu}_2\text{O}$  is different from that  $\text{Cu}_2\text{S}$  and consequently rate of thickening will be different. Beside the cuprous oxide is a nonporous film while the cuprous sulfide is porous film. As mentioned above, the porous structure of the sulfide film allows the solution to come in direct contact with the copper electrode and  $\text{Cu}_2\text{O}$  is obtained at the metal/electrolyte interface at the bottom of  $\text{Cu}_2\text{S}$  film.

Thus, peak (A) could be attributed to the formation of duplex corrosion product on copper electrode. The available evidence would indicate that the surface of the electrode is covered with a thick optically black and porous scale which is primarily  $\text{Cu}_2\text{S}$ . This black-scale is separated from the metal by a thin, subscale which is primarily protective, nonporous

cuprous oxide doped with elements from solution (sulfur doped, oxide scale).

### 3.1.2. Peak (B)

The second anodic peak (B) appears at nearly  $-0.1$  V. This peak is thought to correspond to the partial transformation of the thick corrosion product  $\text{Cu}_2\text{S}$ , formed under peak (A) to  $\text{CuS}$ :

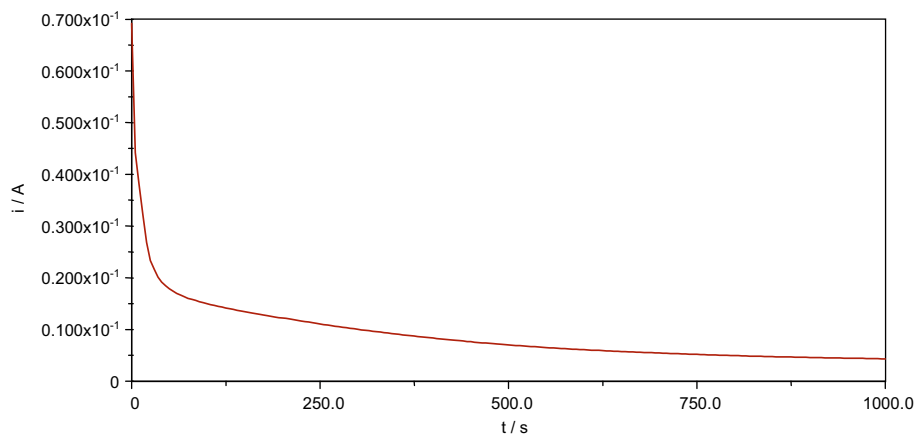
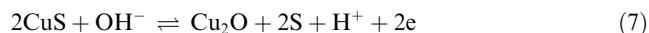


Some  $\text{CuS}$  may also be formed by the direct combination between  $\text{Cu}^{2+}$  ions and sulfide ions which could block some pores in the sulfide-type film.

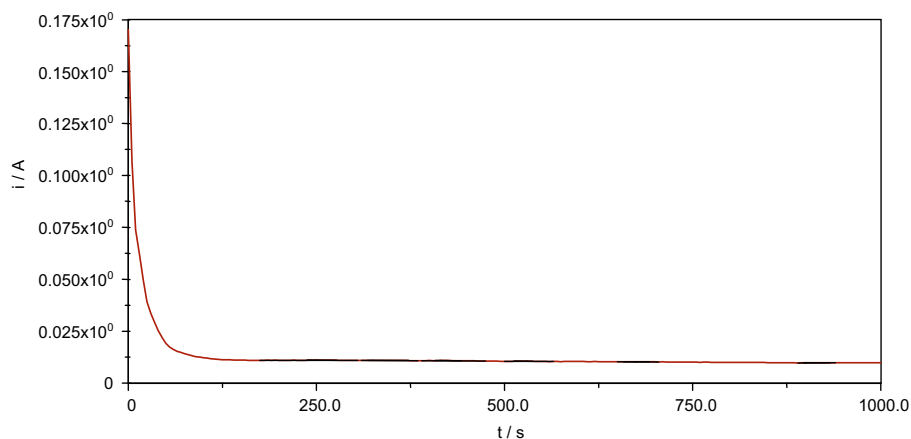


### 3.1.3. Peak (C)

The third anodic peak (C) at about  $0.5$  V, correspond to the thick cuprous sulfide scale is transformed to copper oxide, elemental sulfur is produced. Nevertheless, the electronic and ionic conduction of the growing film decrease because of the low  $\text{S}^{2-}$  ion content (Bates and Popplewell, 1975).



**Figure 2** Potentiostatic current–time curve of copper electrode in  $\text{Na}_2\text{S}$  0.8 M at potential  $-0.722$  V ( $\text{Cu}_2\text{S}$  formation, peak I in Fig. 1).



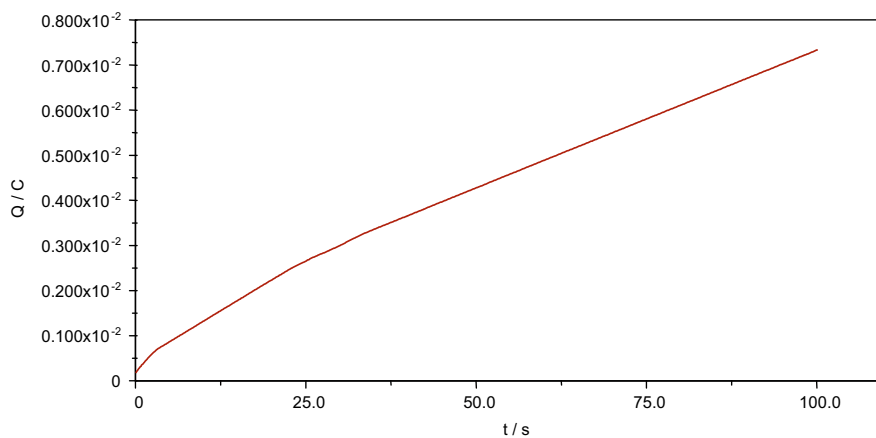
**Figure 3** Potentiostatic current–time curve of copper electrode in  $\text{Na}_2\text{S}$  0.8 M at potential  $0.1$  V ( $\text{CuS}$  formation, peak II in Fig. 1).

### 3.1.4. Cathodic peaks

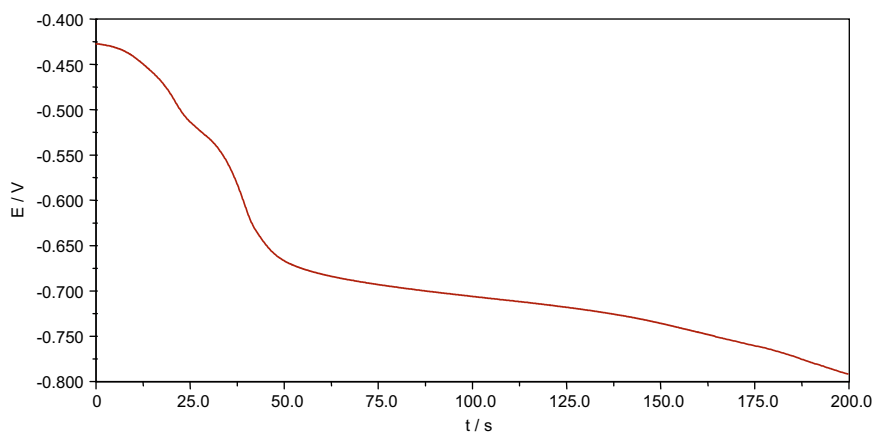
When, however, the potential scan is reversed after the third anodic peak (C), the four cathodic peaks (D–G) and (E) could be attributed to the successive reduction of the copper oxide layer giving eventually metallic copper. On the other hand, the two cathodic peaks (H) and (G) could be attributed to the reduction of copper sulfide.

### 3.2. Potentiostatic measurements

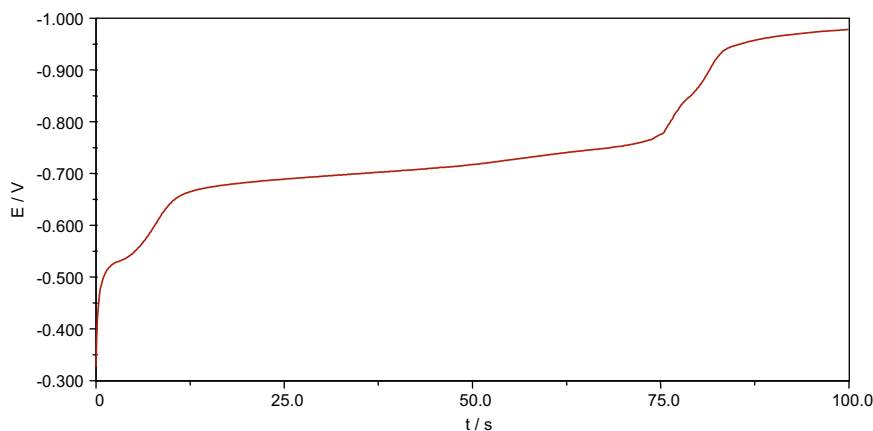
The potentiostatic measurements were performed at different potentials between  $-0.8$  and  $+0.8$  V. Studies were performed with the same copper electrode in different concentration ranges as in the voltammetric study. Same shapes of potentiostatic current transit curves were observed for



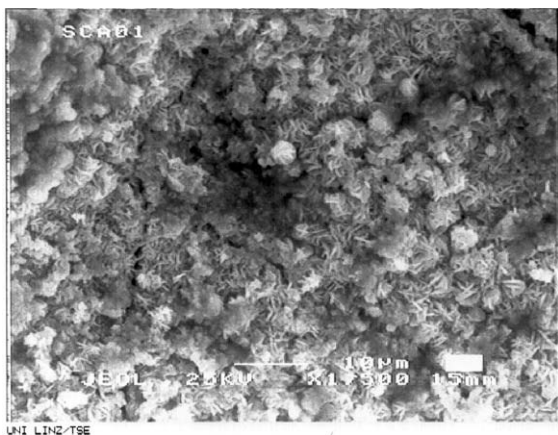
**Figure 4** Charge capacity of copper electrode at potential  $-1.033$  V  $\text{Na}_2\text{S}$   $0.8$  M.



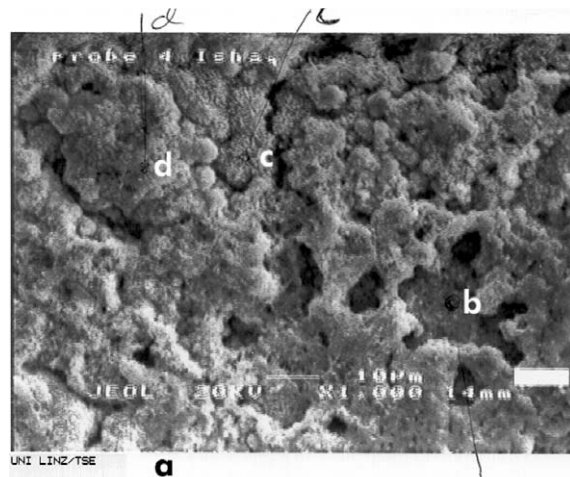
**Figure 5** Galvanostatic curve recorded for copper electrode in  $0.8$  M  $\text{Na}_2\text{S}$  constant current  $1$  A.



**Figure 6** Galvanostatic curve recorded for copper electrode in  $0.8$  M  $\text{Na}_2\text{S}$  current =  $0$ .



**Figure 7** Scanning electron photomicrographs of Cu in 0.8 M Na<sub>2</sub>S. CA 0.1 V. (CuS) and CV -1.8 to 0.2 V.



**Figure 8** Scanning electron photomicrographs of Cu in 0.8 M Na<sub>2</sub>S. CV -1.8 to -0.8 V. (Cu<sub>2</sub>S) Roxbyite.

different concentration and potentials, indicating that the copper electrocrystallization process proceeded by the same mechanisms.

Potentiostatic curves for different potentials are presented in Figs. 2 and 3. The initial current decreases quickly indicating the formation of a primary dense layer.

At conditions of the chronocoulometric measurement Fig. 4. The formation starts with an initial charge of 2.10–4 C, which corresponds to a charge density of 0.7 mC cm<sup>-2</sup> taking into account the area of the electrode of 0.28 cm<sup>2</sup>. This very small charge is due to a very thin initial layer. With time,

three regions with decreasing steepness can be discerned: 0–4, 4–24 and 24 s – end of measurement (100 s). The third part is almost linear. The first step increase is probably due to the formation of a thin primary layer followed by a steady slower growth of an intermediate and of a final layer.

3.3. Galvanostatic measurements

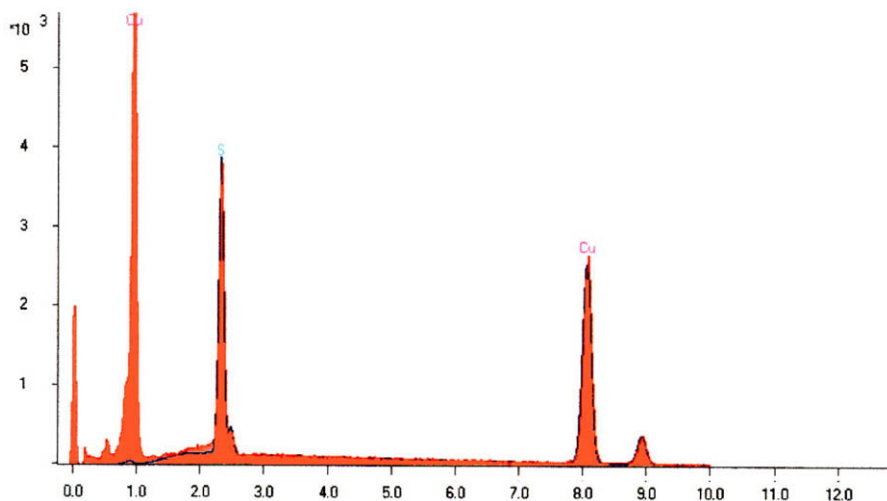
Figs. 5 and 6 represent the galvanostatic curves recorded in 0.8 M Na<sub>2</sub>S solution at constant current. The diagram at zero

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Cu K-alpha	@410.8	1.05432	1.04239	73.54	65.74	+ - 5.66	
S K-ser	@133.9	1.02392	1.01208	19.34	34.26	+ - 2.71	
standardfrei				92.88	100.00		[2s]

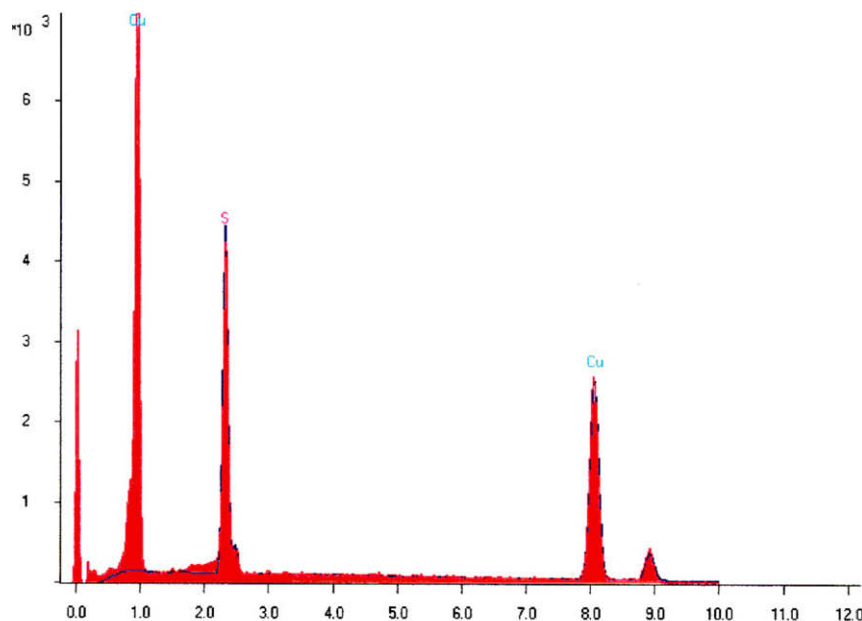


**Figure 9** SEM pattern and EDAX profile of the layer form by CV from -1.8 to -0.8 V at sweep rate 50 mV/s in 0.8 M Na<sub>2</sub>S.

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RÖNTEC EDWIN WinTools          NCA02_1  19.01.2000 (15:43)
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S  K-ser    @194.1  1.02257 1.00986  26.81    53.73   +- 1.78
Cu  K-alpha @272.7  1.05126 1.04657  45.77    46.27   +- 2.54
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standardfrei                    72.58    100.00   [1s]

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**Figure 10** SEM pattern and EDAX profile of the layer form by CV from  $-1.8$  to  $+0.2$  V at sweep rate  $50$  mV/s in  $0.8$  M  $\text{Na}_2\text{S}$ .

current (Fig. 6) is most interesting, after switching off the current, the potential rapidly increase towards more negative values, as a consequence of active Cu dissolution. The first potential arrest, which is believed to correspond solely to the monolayer of Cu(I) sulfide is denoted as the nucleation potential ( $E_0$ ). The potential plateau reached thereafter at approximately  $-0.7$  V, corresponding to the peak potential in cyclic voltammetry measurements as shown in Fig. 1. This potential is denoted as the formation potential  $E_f$ . The period of time corresponding to the potential plateau are denoted as transition time (Southampton Electrochemical Group, 1990).

After the plateau is completed, the potential begins to increase again with time, indicating the further growth of another sulfide layer. The second step in phenomenological similar to the first one. Thus, the formation of two well-defined layers is indicated.

### 3.4. Surface analysis

The corrosion product formed after immersed the copper electrode in  $0.8$  M  $\text{Na}_2\text{S}$  solution was investigated by scanning electron photomicrograph (SEM) and energy dispersive analysis of X-ray (EDAX). Fig. 7 shows the scanning electron photomicrograph of Cu electrode in  $0.8$  M  $\text{Na}_2\text{S}$  often cyclic voltammetry from  $-1.8$  to  $0.2$  V. The layer of CuS is clear but Fig. 8 shows the same micrograph it potential from  $-1.8$  to  $-0.8$  V the layer of  $\text{Cu}_2\text{S}$  is clear.

Figs. 9 and 10 show EDAX profile of the layer formed on the surface of copper often the CV from  $-1.8$  to  $-0.8$  V and  $-1.8$  to  $0.2$  V, respectively, at sweep rate  $50$  mV/s. EDAX analysis of the surface showed amounts of sulfur Cu and oxygen. This is consistent with above discussion of the layers formed on copper dissolution in  $\text{Na}_2\text{S}$ .

## 4. Conclusion

The electrochemical behavior of copper in sodium sulfide solutions are very complex and involve different processes depending in the potential range considered. The formation of Roxbyite  $\text{Cu}_{2-x}\text{S}$  and Covellite CuS has been observed. The evidence from CV and CA for anodic copper sulfide layer growth model that is compositionally heterogeneous has been verified XRD and SEM. Additionally the probe has shown the presence of an initial layer electrodisolution step involving the oxidation of Cu to the Cu(I) state. Nucleation and chemical sulfidization of the copper has been shown to be an important layer growth pathway.

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