

## Electrochemical behavior of copper electrode in sodium hydroxide solutions

I. ZAAFARANY<sup>1\*</sup> and H. BOLLER<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Applied Science,

Umm Al-Qura University, P.O.Box:118, Makkah Al-Mukaramha, (Saudi Arabia).

<sup>2</sup>Institute of Inorganic Chemistry, Johannes-Kepler-Universität Linz, A-4040 Linz, (Austria).

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### ABSTRACT

The cyclic voltammograms of the copper electrode in different concentrations of NaOH solutions was studied using cyclic voltammogram's (CV's) technique. In addition surface examination and morphological studies were also conducted using scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX). The four anodic peaks were found to correspond successively to the formation of a mono layer of  $\text{Cu}_2\text{O}$ , a thick layer of  $\text{CuO}$  and  $\text{CuO}_2^{2-}$  and finally the formation of a higher oxide  $\text{Cu}_2\text{O}_3$  before the evolution of oxygen. It is suggested that the  $\text{CuO}$  is formed from the oxidation of  $\text{Cu}_2\text{O}$  and/or direct oxidation of metallic copper in 5M NaOH solution. The ratio of anodic and cathodic charge was found to be about unity, indicating the quantitative reduction of solid oxidation product. The behavior of copper electrode in NaOH solutions was found to be quite complicated. Thus, no simple relation were found between the voltage scan rate and both the peak current and peak potential or between the peak K current and alkali concentration of alkali.

**Key words:** Electrochemical behavior, copper electrode, sodium hydroxide.

### INTRODUCTION

The electrochemical behaviour of copper is of considerable interest in many areas of technology, including solar cell<sup>(1)</sup>, integrated circuits<sup>(2)</sup> and heat exchangers<sup>(3)</sup>. Hence, the cyclic voltammograms of this metal has been extensively studied, particularly in alkaline solutions<sup>(4-7)</sup> which affords more resolution than the conventional galvanic technique.

The anodic behaviour of Copper in alkaline environments leads to the formation of an oxide film consisting of either  $\text{Cu}_2\text{O}$  or a duplex layer of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  depending on the electrolyte composition and electrochemical conditions<sup>(8-10)</sup>.

Pyun and Pork<sup>(11)</sup> using *insitu* spectroelectrochemical technique for identifying surface film and concluded that hydroxides of  $\text{Cu(I)}$  and  $\text{Cu(II)}$  were first formed by anodic oxidation at corresponding potentials and then they transform to oxides upon aging. Macdonald<sup>(12)</sup> studied the

cyclic voltammetry of copper in hydroxide solutions at elevated temperatures 25 to 250 °C and found that the results are consistent with the formation of both soluble  $\text{Cu}_2\text{O}_2^{2-}$  and insoluble  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  products at the metal surface. The formation and reduction of  $\text{Cu(III)}$  was found to occur near oxygen evolution region at 25 °C but not at higher temperatures due to a sharp reduction in the oxygen evolution potential with temperature.

The aim of the present investigation is to throw new lights on the characteristics of the reaction products formed on the copper surface, products performed on the copper surface in NaOH solutions. The implications of these results with references to the mechanism of the electrochemical reactions are also discussed.

### EXPERIMENTAL

The working of copper electrode was prepared from high purity (99.98 %) copper rod, diameter 6 mm, length 6 mm was placed in a "Kel-

F" shield, protected 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 are 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 bidistilled water. All chemicals used were of A.R. quality. The solutions were prepared using bidistilled water, no attempts were made to deaerate them. The electrolytic cell was of pyrex and is described elsewhere<sup>(13)</sup>.

Cyclic voltammograms curves (CV's) were obtained from an autolab. (ECO Chemie) combined with the software package GPES (General Purpose Electrochemical System). This is a computer-controlled electrochemical measurements system. It consists of data-acquisition system and a potentiostat/galvanostat. CVs were used to study the corrosion of copper in alkaline solutions sweeping from hydrogen evolution -1.8 V to 0.8 V of oxygen evolution. All measurements were taken at  $25 \pm 1$  °C.

Scanning electron microscope (SEM) of the type (XL30) was used to examine the surface of copper in absence and presence of NaOH solutions. All micrograph of corroded specimens were taken at a magnification of (X 500). Energy dispersive analysis of X-ray examination using a Traktor TV-2000 energy dispersive spectrometer was used in this work.

## RESULTS AND DISCUSSION

### 1- Effect of alkali concentrations

The electrochemical behavior of copper in alkaline solutions was studied using cyclic voltammograms technique (CV's). Figures 1-3 show typical CV's of copper electrode in 0.1, 1 and 5M NaOH solutions traced at a voltage scanning rate of  $50 \text{ mV s}^{-1}$ , respectively. The potential was swept between hydrogen and oxygen evolution. Repeated cycling of electrode polarization gave essentially similar CV's except that the peak currents increase and the peak potential is shifted to more negative values. This could be due to electrode activation as a result of successive sweep. The excellent reproducibility is an indication of the stability of the

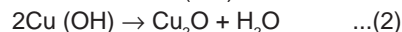
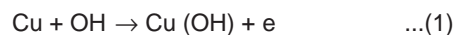
system and the reversibility of all the reaction involved.

The voltammograms are characterized by several features marked from A to D on the anodic half cycle and from E to G on the cathodic one.

### A- Anodic half cycle (forward scanning)

#### 1- Peak (A):

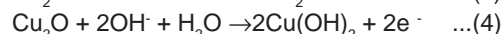
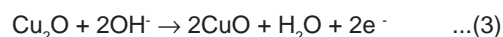
The thermodynamic consideration of different possible oxidation reaction reveals, the possibility of such transformation and helps in determining the most possible reactions like among a number of probable one. Owing to the stability of cuprous rather than cupric state in direct contact with metallic copper, it is most probable that the peak (A) corresponds to the formation of cuprous oxide according to the following equations:



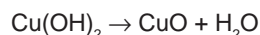
A comparison of the quantity of electricity under peak A is also reported for the formation of  $\text{Cu}_2\text{O}$ .

#### 2- Peak (B):

It appears at a more noble potential than that of peak (A). This peak is due to the oxidation of cuprous oxide to either (or both)  $\text{CuO}$  and  $\text{Cu}(\text{OH})_2$  according to the following equations:



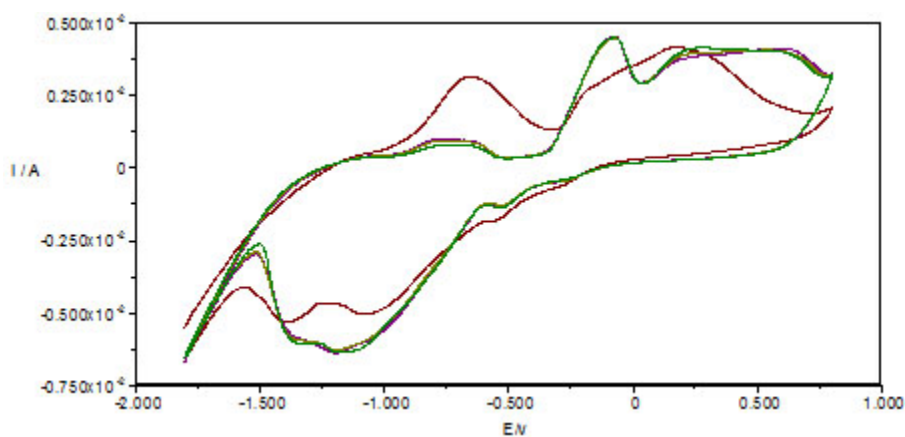
The resulting  $\text{Cu}(\text{OH})_2$  exists in the following equilibrium.



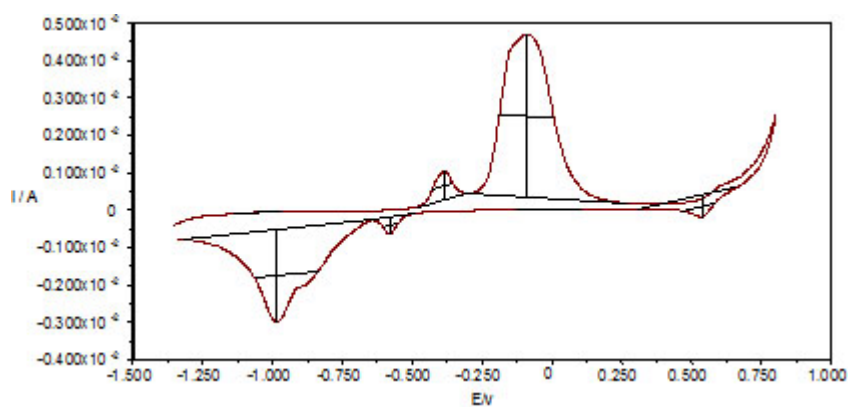
Abd El-Haleem *et al.*<sup>(14)</sup> assumed the formation of a multilayer film of  $\text{CuO}$  under peak B in contrast to the monolayer of  $\text{Cu}_2\text{O}$  under peak A. The formation of a multilayer oxide results from three dimensional nucleation processes.

#### 3- Region (C):

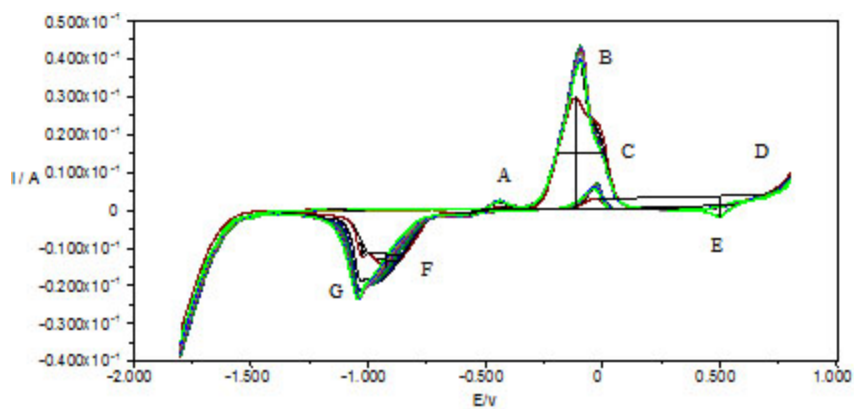
Region (C) appears only below 1M alkali concentration and at higher concentrations. This is due to the direct dissolution of copper as cuprite



**Fig. 1: Cyclic voltammogram of copper in Sodium Hydroxide solution concentration 0.1M at sweep rate 50mv/s.**

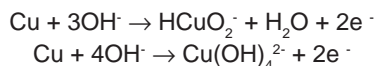


**Fig. 2: Cyclic voltammogram of copper in Sodium Hydroxide solution concentration 1M at sweep rate 50mv/s.**

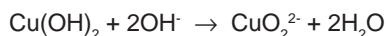


**Fig. 3: Cyclic voltammogram of copper in Sodium Hydroxide solution concentration 5M at sweep rate 50mv/s.**

ions according to either (or both) of the following electrochemical reactions:



and/or from  $\text{Cu(OH)}_2$  through chemical reaction:



#### 4- Region (D):

It is thought to be due to the formation of a higher oxide. Some authors<sup>(5,15)</sup> reported that this oxide may be copper sesquioxide  $[\text{Cu}_2\text{O}_3]$ .

Latimer<sup>(16)</sup> is also of the opinion that  $\text{Cu}_2\text{O}_3$  is formed only when copper dissolves as cuprite  $\text{HCuO}_2^-$ . However, Al-Kharafi and El-Tanawy<sup>(17)</sup> argue that the source of this oxidation peak is the possible formation of  $\text{Cu(OH)}_2$  on the oxide surface.

#### B- Cathodic half cycle

The reverse scanning shows three reduction peaks namely E, F and G. The first cathodic peak E, that occurs at the most positive potential is presumably corresponds to the reduction of (or part of) the anodic product  $\text{Cu}_2\text{O}_3$  in the anodic region (D). The area under the cathodic peak was slightly greater than that under the anodic one because of the reduction of dissolved oxygen. However, when the potential scan is reversed after peak B. Two well defined cathodic peaks were recorded (peaks F and G). These two main steps would be expected to be attributed to the reduction of  $\text{Cu(OH)}_2$  and  $\text{Cu}_2\text{O}$  formed in the corresponding three main anodic steps (A, B and C).

Peak F is a well defined peak with a relatively small area. It could be mostly attributed to the partial reduction of  $\text{Cu(OH)}_2$ . On the other hand, Peak G is well defined peak with a relatively large area, greater than any of the corresponding anodic step areas. Accordingly, peak (G) could be attributed to the reduction of the remaining  $\text{Cu(OH)}_2$  which was not reduced under peak (F), along with the reduction of  $\text{Cu}_2\text{O}$  formed under anodic step (A). In other words, peak (G) is a complex (composite) peak which corresponds to the either parallel or series processes. However, there are evidence<sup>(18)</sup> to indicate that reduction of  $\text{Cu}_2\text{O}$  and remaining

$\text{Cu(OH)}_2$  do not proceeds as it would be expected  $\text{Cu(OH)}_2 \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$  but rather  $\text{Cu}_2\text{O} \rightarrow \text{Cu}$  and  $\text{Cu(OH)}_2 \rightarrow \text{Cu}$ .

The reaction occurring during this peak (G) is however complex since, the system is unstable being directly transferred to the corresponding  $\text{Cu}_2\text{O}$  /  $\text{Cu(OH)}_2$  /  $\text{OH}^-$ .

#### Charge consideration

A comparison of the quantity of charge under the anodic ( $Q_A$ ) and cathodic ( $Q_C$ ) peaks is sometimes useful in detecting the formation of soluble reaction products. Figs. (4 & 5) and Tables (1 & 2) show the relation between the number of multicycles on the anodic charge capacity and the cathodic charge copper electrode in 5M NaOH from -1.8 to 0.8 V at a scan rate 50 mVs<sup>-1</sup> respectively.

The values of  $Q_A/Q_C > 1$ . This may be due to either of the following:

- (i) A soluble reaction product is produced in the anodic halfcycle and diffuses away from the electrode surface, and hence is not recovered in the cathodic half cycle.
- (ii) Only partial reduction of the oxidation products. Under this condition, repeated cycling should result in lower anodic reaction rates and hence lower peak currents due to the restricting effect of the unreduced oxidation products remaining on the electrode surface.

**Table 1: The multicycles effect on the layer of the cyclic voltammogram for copper electrode in 5M-sodium hydroxide from -1.8 to 0.8V, scan rate 50 mv/s**

Number of cycles	Total Anodic Charge ( C )
1	2.330E-01
2	2.755E-01
3	2.922E-01
4	2.955E-01
5	2.914E-01
6	2.860E-01
7	2.799E-01
8	2.736E-01
9	2.667E-01
10	2.597E-01

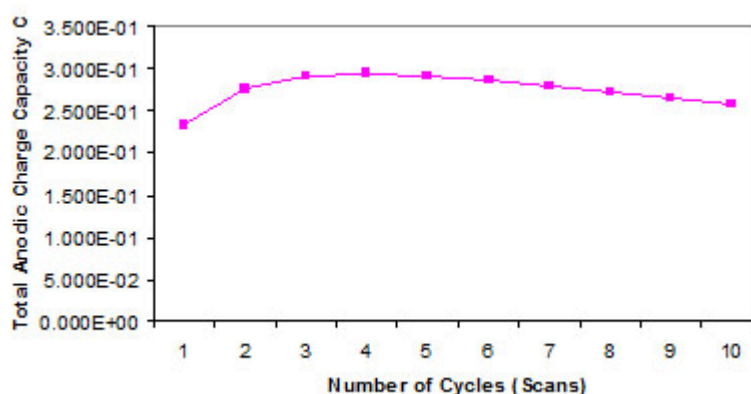
**Table 2: The multicycles effect on the layer of the cyclic voltammogram for copper electrode in 5M-sodium hydroxide from -1.8 to 0.8V, scan rate 50 mv/s**

Number of cycles	Total Cathodic Charge ( C )
1	1.763E-01
2	1.958E-01
3	2.003E-01
4	1.997E-01
5	1.978E-01
6	1.955E-01
7	1.935E-01
8	1.909E-01
9	1.879E-01
10	1.852E-01

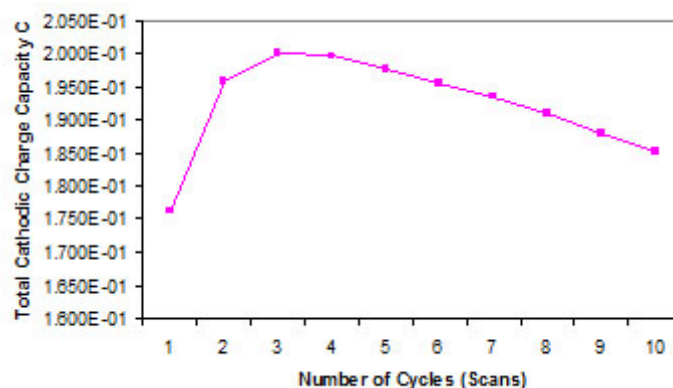
It is interesting to note that these dissolution reaction occur only at potential beyond that of peak (B), i.e. above + 0.275 V (S.C.E.). This is because the charge ratio for the second cyclic voltammogram in Fig. (3) was < 0.95 V in 5 M NaOH solution while the reversal potential was 0.275 V.

### Surface Analysis

The thin layer formed after immersion of copper electrode in 5M NaOH solution was investigated by scanning electron photomicrographs energy dispersive analysis of X-ray (EDAX). The anodic current decreases under potentiostatic conditions (Figs. 4 and 5) at -0.094 V and -1.049 V corresponding to the peaks B and G, respectively, in Fig. 5. (The electrode was covered by the dark layer.) Analysis of the surface by SEM indicate the



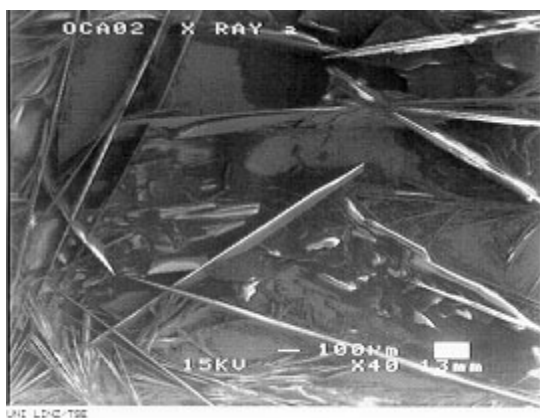
**Fig. 4: Effect of multicycles on the anodic charge capacity for copper electrode in 5M-sodium hydroxide from -1.8 to 0.8V, scan rate 50mv/s**



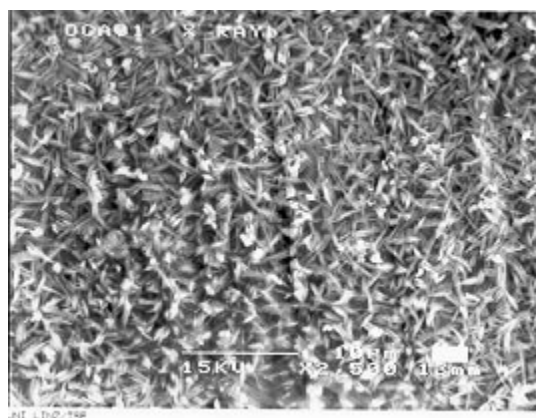
**Fig. 5: Effect of multicycles on the cathodic charge capacity for copper electrode in 5M-sodium hydroxide from -1.8 to 0.8V, scan rate 50mV/s**

formation of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , Fig. 6 (A, B and C). EDAX helped to determine oxygen together with other elements in the layers formed under different conditions, Fig. 7 (A-C) shows that the dark layer formed by CV contains copper, oxygen and sodium salt.

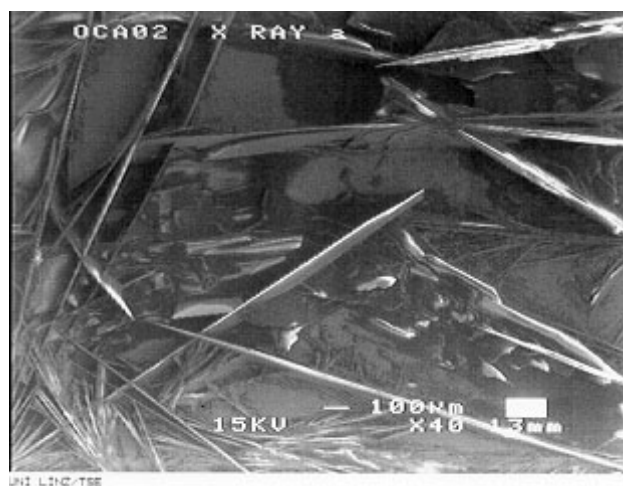
Analysis of the surface by SEM showed two distinctive areas. Most of the electrodes look covered with a dry looking layer for which the elemental composition was consistent with  $\text{Cu}_2\text{O}$ . Therefore, copper should be expected to corrode activity. Producing cuprous oxide  $\text{Cu(I)}$ . In fact, this is the most common product found. As the electrode surface appeared completely covered by a dark layer, Fig. 6 (A,B and C).



**Fig. 6.A:** Scanning electron photomicrographs of Cu electrode in NaOH 5M (CV) -1.8 to 0.8V.  $\text{Cu}_2\text{O}$



**Fig. 6.B:** Morphology of copper oxide after anodic oxidation for 1h in NaOH 5M CA at -0.094V. ( $\text{CuO}$ )



**Fig. 6.C:** Scanning electron photomicrographs of Cu in NaOH 5M CA -1.044V. ( $\text{Cu}_2\text{O}$ )



EDAX analysis of the surface showed amounts of oxygen and copper except for some shallow needles and very small amorphous deposits, where the needles were consistent with a cupric oxide composition. During the anodic scan, the current decreases slowly with time. this suggest a competition between passivation and active dissolution.

EDAX analysis of the surface showed concentration of sodium and found some shallow needles Fig. 7 (A-C), which were found to be copper and oxygen. It had been suggested that in some cases non-crystalline deposits are a necessary precursor to the formation of the SEM analysis is not completely conclusive in the sense that it can not positively identify different copper hydroxide or complex phases, the results of these experiments strongly indicate that it is related to the formation of  $\text{Cu}(\text{OH})_2$  under the conditions of the SEM (high vacuum, electron bombardment  $\text{Cu}(\text{OH})_2$  loses certainly water to form  $(\text{CuO})$  cupric oxide.

PCONTEC EDWIN WinTools OCA02B 13.06.2000 (14:25)  
Version: 3.1 deu Eo:15.0 keV (AW:35.0 MW:12.0)

\*\*\* PZaf Ergebnisse \*\*\*  
Elem/Linie P/U R F c c(Atom) Vertr. h  
O K-ser 1.00000 1.00000 8.91 21.96 +- 1.85 n  
Cu K-alpha 282.1 1.05696 1.04318 91.57 78.04 +- 7.96  
standardfrei 100.49 100.00 [1s]

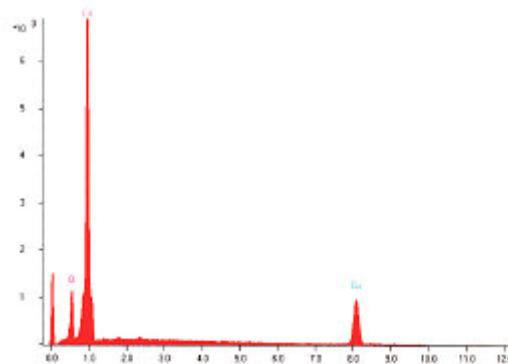


Fig. 7(b): SEM pattern and EDAX profile of the layer form at potential -0.094V during 1h in Sodium Hydroxide solution.

PCONTEC EDWIN WinTools OCA01E 13.06.2000 (14:09)  
Version: 3.1 deu Eo:15.0 keV (AW:35.0 MW:16.0)

\*\*\* PZaf Ergebnisse \*\*\*  
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O K-ser 1.00000 1.00000 75.88 78.09 +- 6.26 n  
Cu K-alpha 226.6 1.03190 1.13286 36.02 21.9 +- 1.4  
standardfrei 111.90 100.00 [1s]

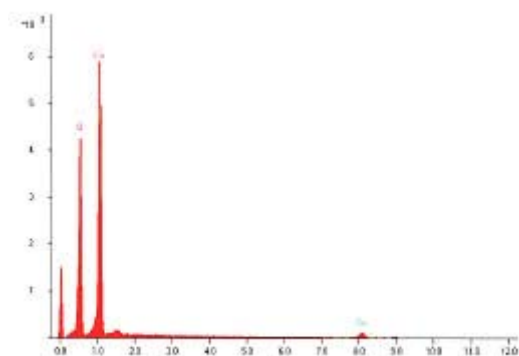


Fig. 7(a): SEM pattern and EDAX profile of the layer form at potential -1.044V during 1h in Sodium Hydroxide solution.

PCONTEC EDWIN WinTools OCV01A 13.06.2000 (14:26)  
Version: 3.1 deu Eo:15.0 keV (AW:35.0 MW: 0.0)

\*\*\* PZaf Ergebnisse \*\*\*  
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Cu K-alpha 226.6 1.05036 1.04872 49.63 25.23 +- 2.97  
Na K-ser 130.8 1.00948 1.00095 26.91 37.82 +- 3.62 \*  
standardfrei 94.83 100.00 [1s]

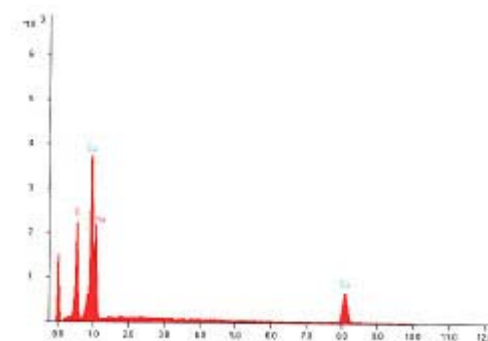


Fig. 7(c): SEM pattern and EDAX profile of the layer form at potential -1.8 to 0.8V in Sodium Hydroxide solution by cyclic voltammetry.

### CONCLUSION

The cyclic voltamograms of the copper electrode were obtained in NaOH solution as a function of the electrolyte concentration and voltage range. A correlation was made between three well-defined anodic peaks and their corresponding cathodic ones. The anodic peaks were found to correspond successively to the formation of a monolayer of  $\text{Cu}_2\text{O}$ , while the formation of a thick multilayer composed of CuO and finally  $\text{Cu}_2\text{O}_3$  upon

which  $\text{O}_2$  is evolved. It is suggested that the CuO is formed from the oxidation of  $\text{Cu}_2\text{O}$  and/or direct oxidation of metallic copper in 5M NaOH. The ratio of anodic and cathodic charges was found to be about unity, indicating the quantitative reduction of solid oxidation products. The behaviour of copper electrode in NaOH was found to be quite complicated. Thus, no simple relations were found between the voltage scan rate and both, the peak current and peak potential or between the peak current and alkali concentration.

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