COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME : 28 ANNÉE : 1982

Formation And Reduction of Surface Oxides of Copper

by

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Formation and Reduction of Surface Oxides of Copper*

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(Received February 19, 1982: accepted May 13, 1982)

SUMMARY

Nature of the phases formed on copper electrode was investigated by cyclic voltammetry. Cu_2O was the major product during electrochemical oxidation. Cu_2O was formed by dissolution precipitation mechanism. Two different Cu_2O films existed on copper electrode and reduced at different potentials. The first $(Cu_2O)_I$ film exhibited resistance polarization to the second $(Cu_2O)_{II}$ film.

INTRODUCTION

Corrosion of copper in alkaline solution is of interest in both chemical engineering and nuclear reactor application. For this reason consecutively electrochemical formation and reduction of copper oxides is of interest. Numerous experimental investigation have been reported on electrochemical behaviour of copper anions $Cu(OH)_2^-$, or $Cu(OH)_4^{-2}$ or $Cu(OH)_n^{1-n}$, $Cu(OH)_n^{2-n}$ [1–4] and solid phases such as Cu_2O, $Cu(OH)_2$ and Cu_2O_3 [1–7] were reported during anodic polarization of copper in alkaline solutions.

But no general agreement was reached about the oxidation and reduction mechanism of these products as well as different potential values postulated for their formation. At the same time in Cu_2O formation region some investigators [1,7] observed two steps while some observed one step [2–6].

In the potential region between –700 mV and –380 mV which is the potential range of Cu_2O formation no sufficient investigation has

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* This study is the part of a thesis which was presented to the University of Ankara by G. Bereket for the fulfillment of the requirement for the Ph. degree.

been done. So in this study we wish to clarify the reactions occur between the potential range –700 mV and –380 mV.

EXPERIMENTAL TECNIQUE

For the preparation of working electrode high purity grade (Johnson–Matthey 99.9 %) copper wire was spot welded to Pt and sealed in a glass bulb. The seal was carefully extended down the copper for several mm. from the Cu / Pt weld.

Before each set of measurements the electrode was abraded with fine emery paper and immersed successively in concentrated HCl and conductance water.

Current–potential curves were obtained with electrodes which were reduced at a potential of–1400 mV (against S.C.E) until the current takes the constant value in I N NaOH after pretreated in the preceeding manner.

During the experiment the solution in the cell was kept at the same level and freed from oxygen by bubbling nitrogen before and throughout the experiment. Aqueous NaOH solutions were prepared using conductance water. Runs were conducted in a three armed glass cell. Potentials were measured v.s. S.C.E and all potentials were referred to this potential scale.

Current–potential curves were obtained using Tacussel PRT 30,01 potentiostat, UAP–3 unit and EPL2 recorder system. Several types of information were obtained with the above system. a) Sweep rate effects on the peak currents. b) The respective quantities Q_A and Q_C of anodic and cathodic charges that corresponding to the respective anodic and cathodic peaks observed for various sweep rates.

since
$$q = \int_{t_1}^{t_2} i dt = \int_{E_1}^{E_2} i \cdot \frac{dE}{v} ,$$

integration of current–potential curves or the areas under the curves give the charges. v is the potential sweep rate and E is the potential. The areas under the curves were measured with a planimeter.

RESULTS AND DISCUSSION

a) Form of the Current–Potential Curve at Copper· The typical potentiodynamic current–voltage relation (–1400 to + 250 mV v.s. S.C.E) in the anodic and cathodic directions is shown in figure 1 for 1 N NaOH. The sweep rate was 2.5 mV / see.

In the anodic direction the two main peaks were denoted by b and (c–d). In some other investigations [1,7] prior to the b region smaller pre–peak sometimes was present. This peak has been attributed to the dissolution of Cu as $Cu(OH)_2^-$ [1] or Cu (OH) film [7].

Cathodic polarization curves following each anodic polarization were severely depended on anodic scan limit (Eλ).

Figure 1, la and lb show cathodic polarization curves following different anodic polarization scan limit. Eλ values were shown on the curves. Cathodic peak (I) could not occur unless Eλ$\geqslant$ –550 mV was. Starting potential of this peak is –600 mV. This value is very close to –580 mV equilibrium potential for Cu / Cu_2O system [8]. When anodic scan limit, Eλ increases, potential of cathodic peak (I) shifts negative value and peak current increases. Figure 2 shows the variation of peak potential and peak current with Eλ. This variation can be explained by thickening of Cu_2O film with anodic polarization. Only the peak (I) resulted in cathodic region (Figure 1 and lb) if the anodic scan limit is increased up to potential region of step c.

In the potential region between –375 mV and –275 mV where step c occurs as a shoulder, new peak was not seen on the cathodic part, but only increasing of peak current of peak I was observed. The step c can be attributed to the formation of soluble specie of copper. This soluble specie is probably copper II anion. This anion can partially diffuse to solution and some of them give disproportionation reaction by the contact of the electrode surface.

$$Cu(OH)_4^{=}{}_{(surface)} \xrightarrow{dif} Cu(OH)_4^{=}{}_{(solution)}$$

$$Cu(OH)_4^{=}{}_{(surface)} + Cu \longrightarrow Cu_2O + H_2O + 2OH^-$$

The second reaction shows the formation of Cu_2O. So, this explains the increment of peak current at peak (I) in the potential region between –375 mV and –275 mV.

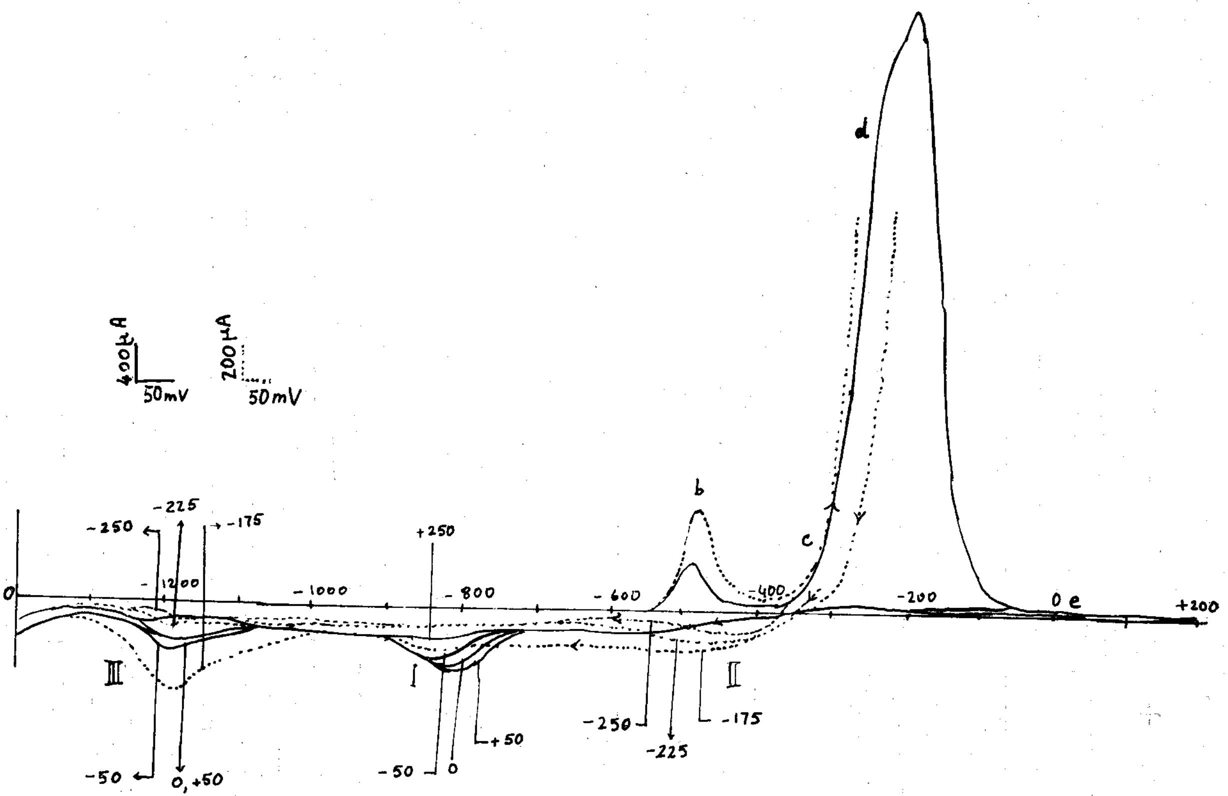

Fig. 1. Potentiodynamic i / v curves for copper oxidation and oxide reduction processes in 1 N NaOH. Scanning potential limits were shown on the reduction curves. Sweep rate was 2.5 mV / sec.

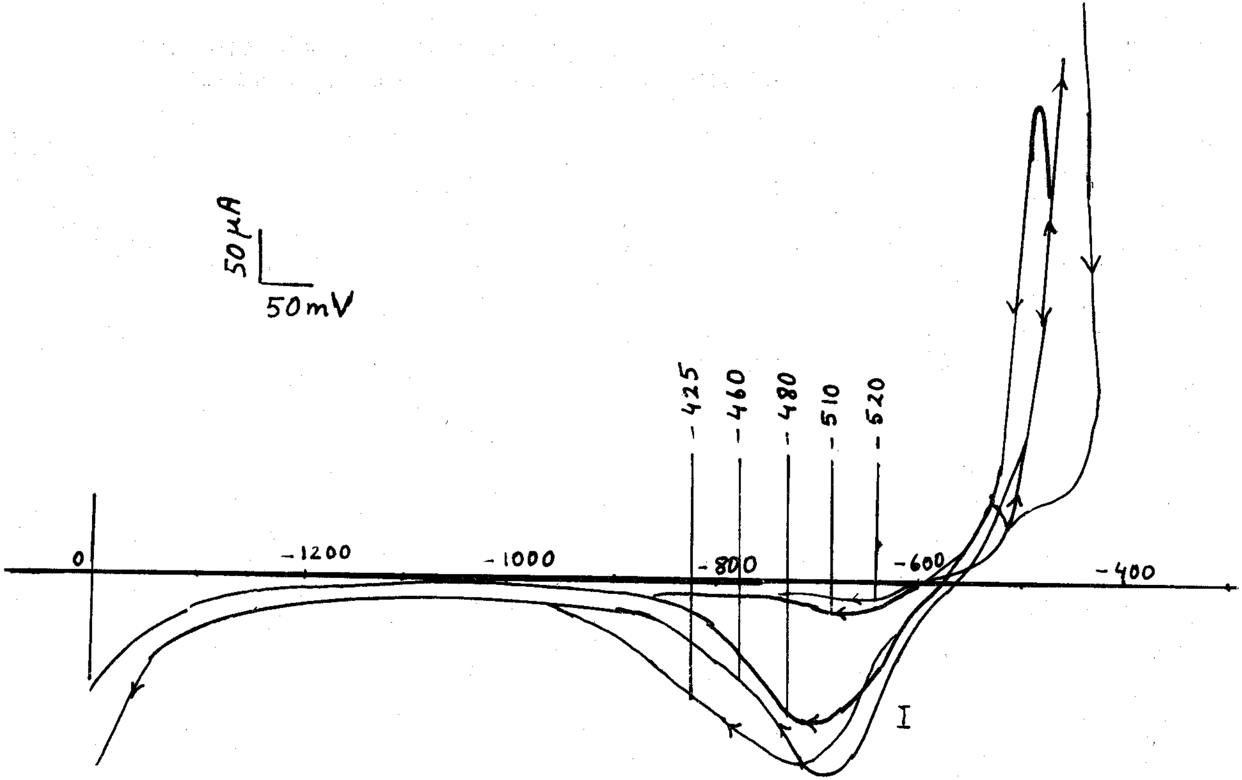

Fig. 1 a Cyclic voltammograms at 2.5 mV/sec in IN NaOH when anodic scan limit is changed betveen –520 mV and –425 mv.

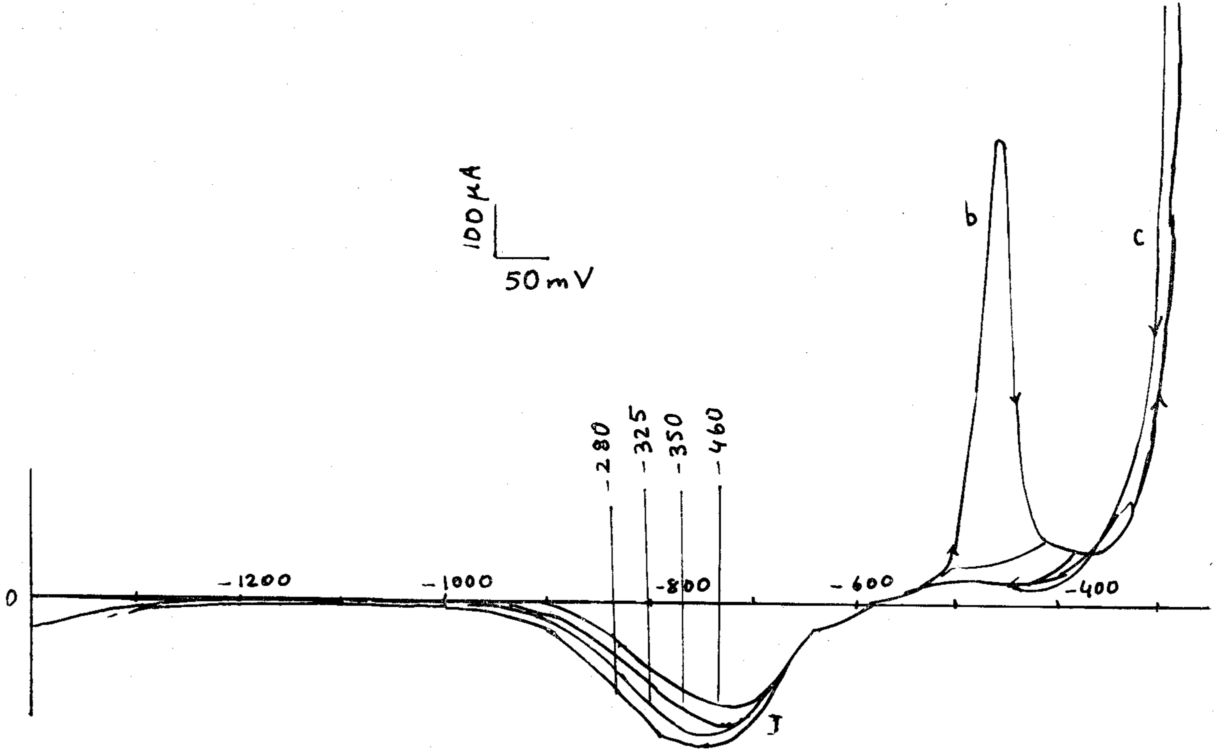

Fig. 1 b Cyclic voltammograms at 2.5 mV / sec in 1 N NaOH when anodic scan limit is changed between –460 mV and –280 mV.

When E$\lambda \gg -275$ mV (Figure 1 and 1b) in addition to peak I, peak II and peak III appear. As anodic scan limit is increased between –275 mV and –50 mV, peak current of peak II and III also increased (Fig. 1).

The ratio of the volume of the solution to the electrode surface was rather high. So we can neglect the reduction current of soluble species which formed in the anodic region. If three different cathodic peaks are observed, three different reduction process should take place on the surface. Starting potential of peak II is –380 mV and this potential is equal to equilibrium potential of CuO / Cu_2O referred to S.C.E [8].

Peak II can be explained by the reduction of CuO to Cu_2O which was produced by the increment of current density. This is consistent with the result of investigators who detected the formation of CuO on the surface depending on current density [2]. The area under the curve is a magnitude proportional with the electric charge. In the potential range between –275 mV and –50 mV anodic area under the curve is much greater than the cathodic area, so greater portion of the current produces soluble species designated as Cu $(OH)_4^{=}$. These species can form amorf $Cu(OH)_2$ by the following reaction.

$$Cu(OH)^{=}_4 \longrightarrow Cu(OH)_2 + 2\ OH^-$$

Reduction of amorf films needs considerable high overpotential [9]. So peak III can be explained by reduction of $Cu(OH)_2$ to Cu.

Region"e" in figure 1 is the passivity region. But as the anodic scan limit is increased in this region, peak II becomes less pronounced and reproducibility of cathodic voltammograms decrease. This is the result of disselution process leading loosely bounded films. At long polarization periods the probability of falling of films increase. But it is evidently true that for E$\lambda \leq 100$ mV, the main film on the surface is Cu_2O.

Examination of figure 2 shows two different plateau in Ep_1 –Eλ and I_p – Eλ curves. These changes suggest that two different types of Cu_2O films are formed on the electrode surface. The first one formed between –540 mV to –275 mV and the peak potential changes between –650 mV to –740 mV. The second one formed for E$\lambda \gg -275$ mV and the peak potential is about –830 mV. We have suggested formation of $Cu(OH)_2$ when Eλ is greater than –275 mV. The second

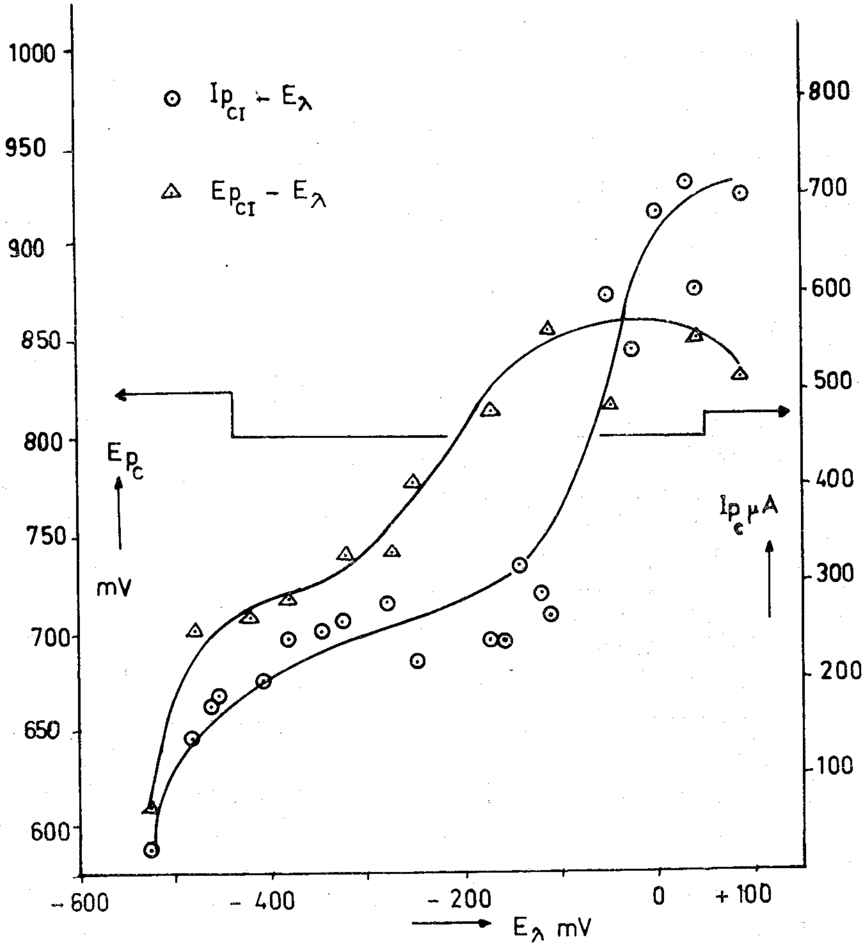

Fig. 2. Variation of peak potential and peak current of cathodic peak I with scan limit Eλ.

Cu_2O film can be formed by two ways: From $Cu(OH)_2$ by the following reaction.

$$Cu + Cu(OH)_2 \longrightarrow Cu_2O + H_2O$$

and the reduction of CuO to Cu_2O.

b) Curves Obtained at Different Sweep Rates in 1 N NaOH; Cyclic voltammograms in I N NaOH obtained at different sweep rates plotted in figure 3. The beginning of the sweep range was –1400 mV. The anodic scan limit was adjusted in such a way that it was the ending potential of peak b but not entering the region "c" shown in figure 1.

At high sweep rates current passed on the reversal scan (fig. 3) was greater than the current passed on forward scan in the anodic region. This shows that at high sweep rates, surface was not completely covered by Cu_2O film. If dissolution takes place and surface films are produced from the precipitation of the soluble species, anodic and cathodic charge should be the function of sweep rate. Table I shows the value of $Q_{A\ (forward)}$, $Q_{A\ (reverse)}$, Q_{total} and Q_C as a function of sweep rate ν. $Q_{A\ (forward)}$ is the charge passed between the potential where anodic current starts to pass and the anodic scan limit. $Q_{A\ (reverse)}$ is the charge between the potential of anodic scan reversal and the potential where cathodic current begins to pass. Q_{total} is the sum of $Q_{A\ (forward)}$ and $Q_{A\ (reverse)}$. Q_C is the cathodic charge.

Table I Anodic and Cathodic Charges as a Function of Sweep Rate.

mV / s	$Q_a(f)$ mC	$Q_a(r)$ mC	$Q_a(T)$ mC	Q_c mC	$\frac{Q_a(f)}{Qc}$	$\frac{Q\ a\ (T)}{Qc}$	$\frac{Q_a(T)-(Q_c)}{Q_a(T)}$ = loss%
100	1.16	1.55	2.71	1.5	0.77	1.8	44.6
50	2.0	1.1	3.1	2.0	1.0	1.5	35.5
25	3.0	0.9	3.9	3.56	0.84	1.09	8.7
10	4.6	1.0	5.6	5.0	0.92	1.1	10.0
5	6.3	1.3	7.6	7.0	0.85	1.08	7.8
2.5	9.0	2.0	1.1	1.4	0.7	0.8	—

In figure 4 $Q_{A\ (forward)}$, $Q_{A\ (reverse)}$, Q_{total} and Q_C were shown as a function of sweep rate. Q values depend severely on the sweep rate. At small sweep rates Q_A and Q_C values are high, and decrease as the sweep rate is increased. This shows that dissolution precipitation reaction is a slow process.

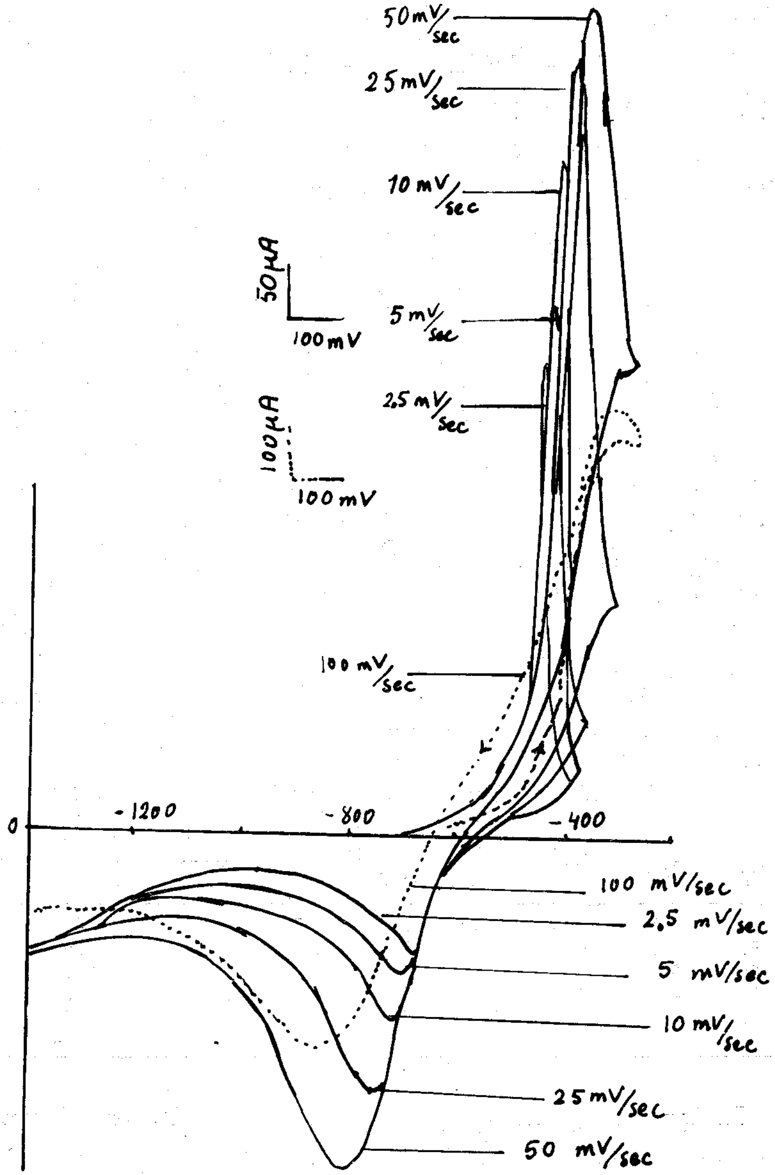

Fig. 3. Cyclic voltammograms obtained at different sweep rate in IN NaOH.

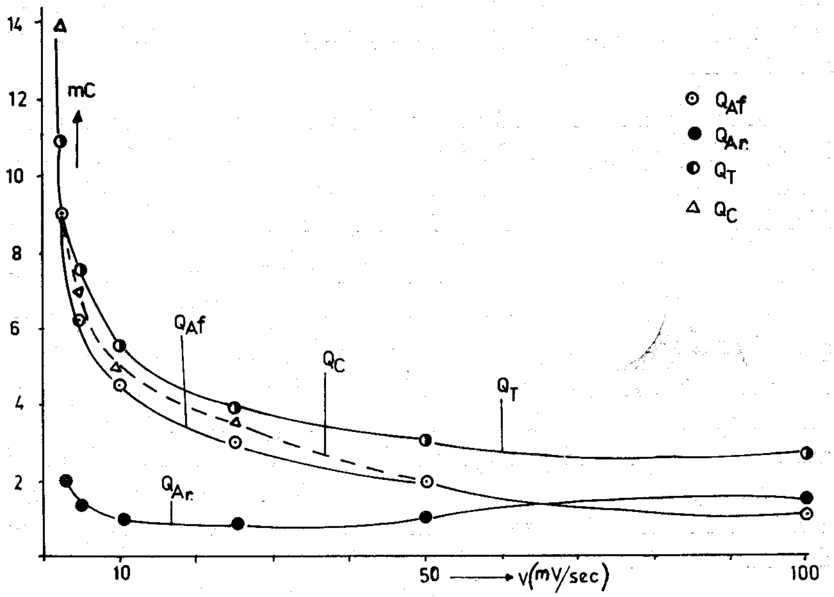

Fig. 4. Anodic charge (Qa) and cathodic chage (Qc) as a function of sweep rate.

In figure 5. the ratios of $Q_{A\ total}/Q_C$, $Q_{A\ (ferward)}/Q_C$ and $\frac{Q_{total}-Q_C}{Q_{total}}.100$ = loss % were shown as a function of sweep rate. $Q_{A\ (forward)}/Q_C$ has a value little beat smaller than one and not much depended on sweep rate. Thus large part of surface film formed during forward sweep. Q_{total}/Q_C is little beat higher than one. Up to 25mV / sec, charge loss by dissolution is about 10 %. At low sweep rates soluble species has the opportunity of precipitation at the surface to form surface film.

At sweep rates $\upsilon > 25$ mV / sec loss by dissolution approaches to 50 % and $Q_{A\ (forward)} = Q_C$ for all sweep rates. So, anodic current after sweep reversal is used for dissolution at high sweep rates.Surface film has pore like structure and could not prevent dissolution.

c) Dependence of Anodic and Cathodic Current Peaks on Sweep Rate: Variation of Ip_a and Ip_c as a function of $\sqrt{\upsilon}$ were plotted in Figure 6. Variation of Ip_c with $\sqrt{\upsilon}$ is a straight line while variation of Ipa with $\sqrt{\upsilon}$ is two broken lines. For the formation of monolayer adsorbed species, it was shown that Ip_a and Ip_c should change linearly with υ [10]. The charge required for the reduction of the oxide film was much greater than that the charge required to form monolayer film. Since formation of Cu_2O was not monolayer, linear relationship between Ip and υ was not expected.

There are two cases for the linearity of Ip – $\sqrt{\upsilon}$ plots.

1– Growth of the film is controlled by the solution resistance in the pores of the film [11]. For this situation E_p v.s. $\sqrt{\upsilon}$ should be linear as well as anodic and cathodic charges should be independent of the sweep rate. For copper anodic and cathodic charges depended on sweep rate, so this model was not valid.

2– Film growth is controlled by ion diffusion at low field. For this case the following equation was given [12].

$$I = K\bar{E}$$

$$I_p = \frac{n\ F\ K}{V_m}\sqrt{\upsilon}$$

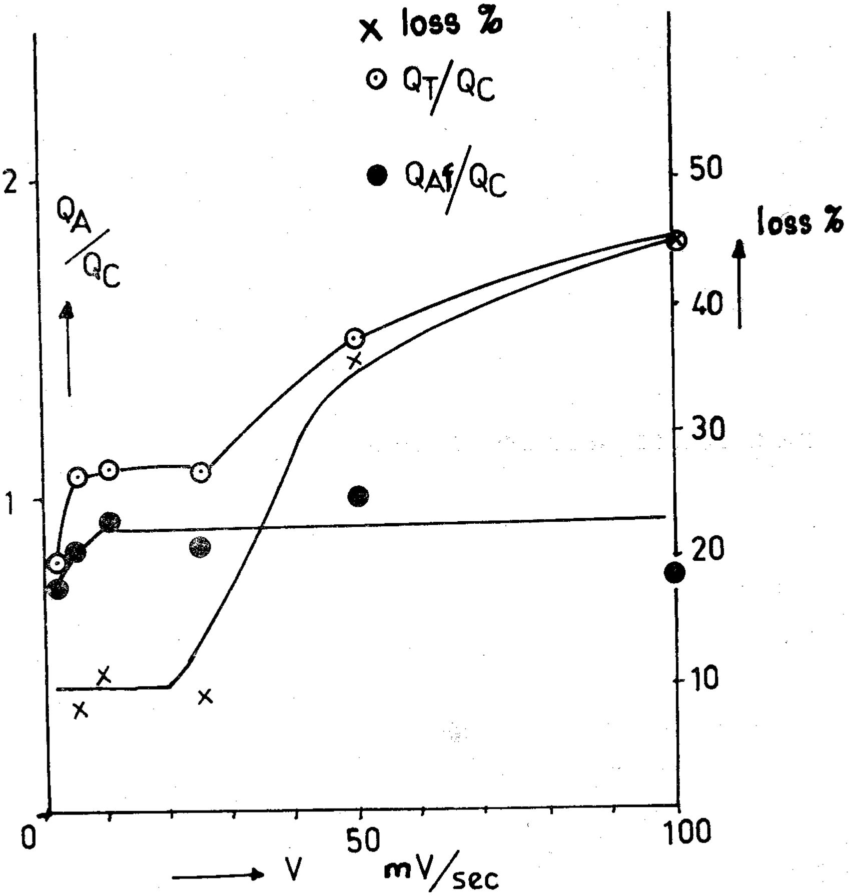

Fig. 5. QA Total / QC, QA forward / QC, loss % as a function of sweep rate.

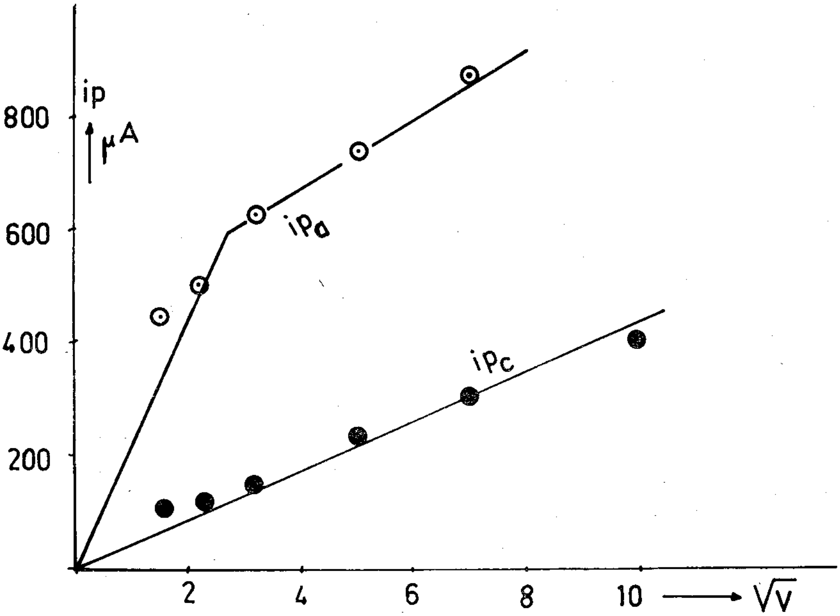

Fig. 6. Ip_a and Ip_c as a function of sweep rate.

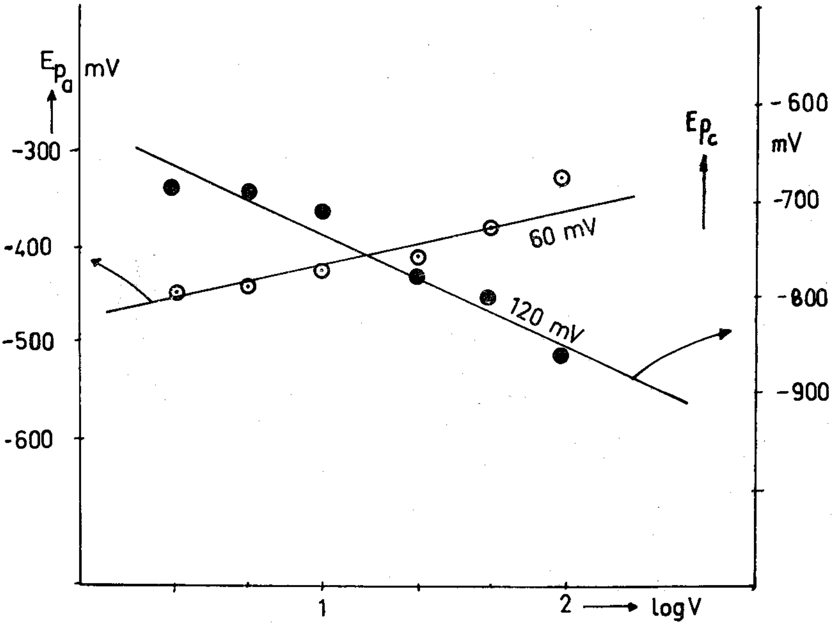

Fig. 7. Ep_a and Ep_c values v.s. log sweep rate.

We proposed the growth of Cu_2O film is controlled by ion diffusion at low field.

For oxide films formed on Ni and Ag linear relationship for Ip v.s. $\sqrt{\upsilon}$ was observed (18]. At high sweep rates for Ag_2O film $I_p - \sqrt{\upsilon}$ line was broken. Ip v.s. $\sqrt{\upsilon}$ linear relationship was also observed for Fe electrode in alkali solution [14].

d) Dependence of E_{pa} and E_{pc} on log ν:

For the adsorbed films formed on various metal surface, emprical and theoretical equations between peak potentials and sweep rate were investigated. Oxidation and reduction peak potentials of adsorbed films formed on various metals like Au [15]. Pt [16–18] and Ag [19] were found to change linearly with the logaritm of the sweep rate. The slope of Ep–logυ was equal to the Tafel slope 2,303 $\frac{RT}{\alpha\, nF}$ for all cases. For copper, at the formation and reduction region of Cu_2O film, E_{pa} v.s. logυ and E_{pc} v.s. logυ were linear (fig. 7). The anodic slope was 60 mV and the cathodic was 120 mV. From the anodic slope $\alpha n = 1$ was found. Assuming $\alpha = 0.5$, the transfered electron number was found to be equal to 2. This is consistent with the two electron transferred reaction for the formation of Cu_2O.

For the cathodic region, $\alpha\, n = 0.5$ was calculated from the slope. The number of the electron transferred in the anodic reaction should be equal to the number of electron transferred in the corresponding cathodic reaction. So, if we assumed $n = 2$, then $\alpha = 0.25$ was found for the cathodic reaction. Conway [20], proposed two energy barrier for the case $\alpha = 0.25$. Effective symmetry factor α_e was described by the equation

$$\alpha_e = \frac{\alpha_1 \,.\, \alpha_2}{\alpha_1 + \alpha_2}$$

If $\alpha_1 = \alpha_2 = 0.5$, then $\alpha_e = 0.25$ is found. If it is true, two different types of Cu_2O films should be formed during anodic oxidation. Two different Cu_2O films cause two different energy barriers during reduction.

e) Evidence for the Existance of Two Different Cu_2O Films.

Figure 8 illustrates voltammograms obtained at different anodic scan limit (Eλ). The sweep rate was 2.5 mV / sec at anodic oxidation and 50 mV / sec at cathodic reduction. For Eλ = – 500 mV, one reduction peak at $E_{pc} = -800$ mV, and for Eλ > – 500 mV, two reduction peaks at $E_{pc1} = -800$ mV and $E_{pc2} = -1050$ mV were observed.

Second reduction peak should also be the reduction of second Cu_2O film. Because, up to the –380 mV only one oxidation peak, oxidation of copper to Cu_2O was obtained (Fig.1). So during anodic polarization both formation of Cu_2O film and dissolution as $Cu(OH)_n^{1-n}$ ion should occur simultaneously. On increasing anodic scan limit the amount of soluble anion $Cu\ (OH)_n^{1-n}$ was increased and the second Cu_2O film was formed from the precipitation of this anion.

$$Cu + nOH^- \longrightarrow Cu(OH)_n^{1-n} + e^-$$
$$2\ Cu\ (OH)_n^{1-n} \longrightarrow Cu_2O + H_2O + (2n-2)\ OH^-$$

When the anodic and the cathodic sweeps were made with the same sweep rate, only one reduction peak observed in the cathodic region (Fig. 3). When anodic sweep rate was slow but the cathodic sweep rate was high, two reduetion peaks were obtained. In order to clarify this discrepancy following procedure was done. Anodic oxidation wascarried at 2.5 mV / sec and then at the reverse scan sweep rate was increased to 50 mV / sec at different potentials. Figure 9 illustrates voltammograms obtained for Eλ = – 435 mV by this procedure. Curve I in figure 9 shows potentiodynamic voltammogram obtained at 2.5 mV / sec both in anodic and cathodic direction. Single reduction peak at the cathodic region was resulted. However when the sweep rate was increased to 50 mV / sec at different potentials in the reverse scan, two peaks were obtained. Peak current of the second peak was increased until the potential where sweep rate was changed to 50 mV / sec at the reverse scan approaches to –600 mV. This is the potential where cathodic current starts to pass. This shows that at the reverse scan between the potentials of anodic scan limit (Eλ) and –600 mV the main procedure is dissolution and then the formation of the second film. The peak current at –800 mV and–1050 mV start to decrease when the potential sweep rate change to 50 mV / sec was done after –600 mV in the reverse scan. This indicates that both the first and the second films are reduced

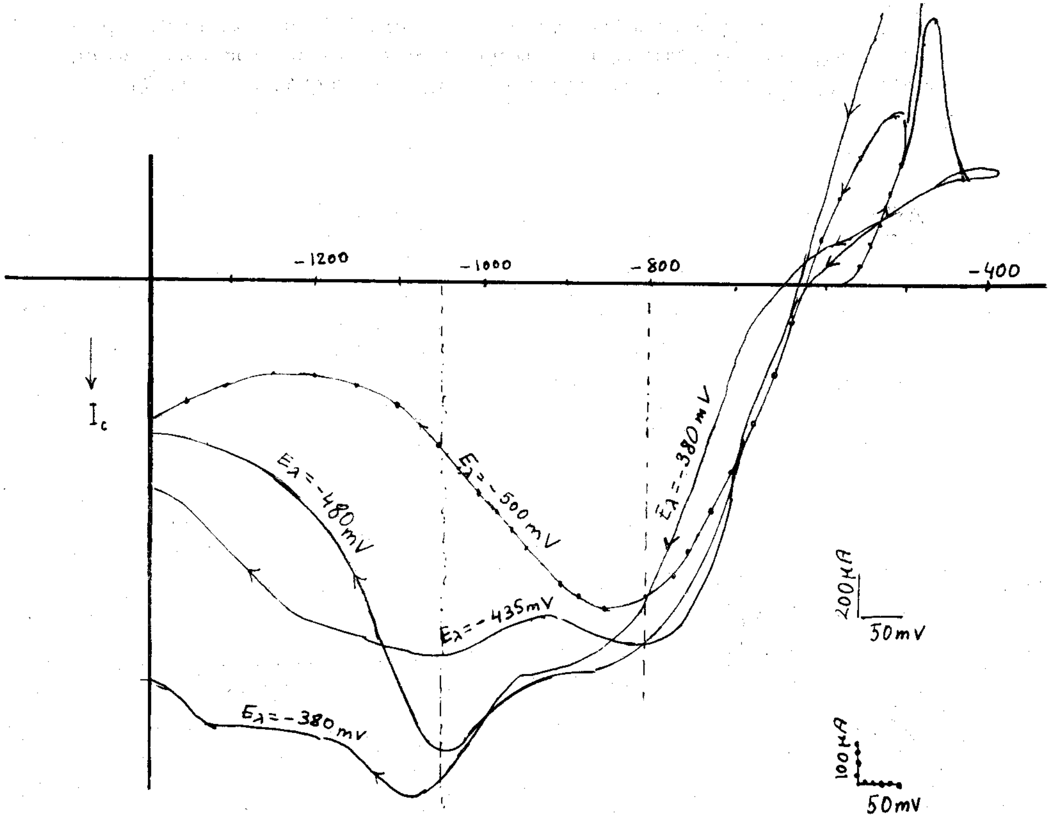

Fig. 8. Cathodic reduction curves obtained at different scan limit Eλ where oxidation was carried at 2.5 mV / sec and at sweep reversal sweep rate was increased to 50 mV / sec.

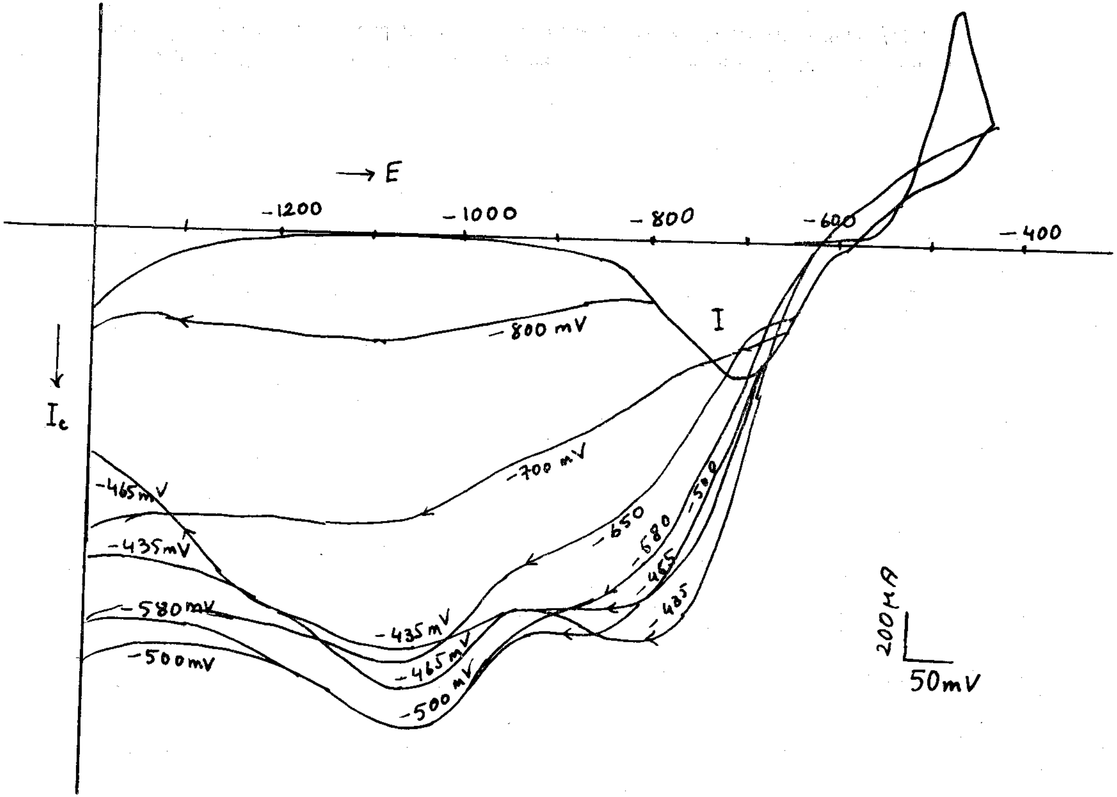

Fig. 9. Curves obtained for Eλ = – 435 mV. Oxidation was carried at 2.5 mV / sec. Sweep rate was increased to 50 mV / sec at different potential on sweep reversal. The potentials on the curves show where the sweep rate changesto 50 mV / sec. was done.

at the slow sweep rate in the same potential region. For instance, in experiments where sweep rate change was done at –800 mV at reverse scan, reduction current at the second peak is very low. Because all of the first film and some part of the second film were reduced between –600 mV and –800 mV. The remainder of the second film reduced at – 1050 mV. This can be explained by the resistance polarization effect of the first film for the second. When the sweep rate is high, as a result of resistance polarization effect of the first film, reduction of the first and the second film are obtained at two different potentials. As the change of the sweep rate to 50 mV / sec on the reverse scan is made at more negative potential, the greater part of the first film is reduced. Resistance polarization effect of the first film for the upper second film dissappears due to the reduction of the first film. Thus, the second film is reduced at the same potential as the first film. The charge for the first and the second peaks can be calculated from the curves in Fig. 9. These charges plotted as a function of potential where the sweep rate changes were made (Figure 10). Charge associated to the first peak has a constant value about 7.5–6 mC until the sweep rate change potential reached to–600 mV. The charge associated to the second peak increases until –600 mV and then decreases.

So, reactions associated with the formation of the second film takes place from the anodic sweep reversal potential to the potential where cathodic current begins to pass When cathodic current passes first $(Cu_2O)_1$ film reduces and then the second Cu_2O film starts to reduce at these empty places.

Q_{total} which is the sum of Q_1 and Q_2 charges increases slowly with the potentials where sweep rate changes were made. This shows the time effect on the formation of the second $(Cu_2O)_{11}$ film. If the sweep rate is low, Cu $(OH)_n^{1-n}$ ions continue to build $(Cu_2O)_{11}$ film on the reverse scan. If the sweep rate is high, $Cu(OH)_n^{1-n}$ ions have no time to build Cu_2O film on the reverse scan.

As a result, two kinds of Cu_2O films are formed in the potential region of b in Fig. 1. First film is formed from direct anodic oxidation and the second Cu_2O film is formed from the precipitation of soluble Cu(1) anions. Soluble Cu (II) anions can also form Cu_2O film [1,2]. Various kinds of Cu_2O films must be formed on the copper surface during anodic polarization.

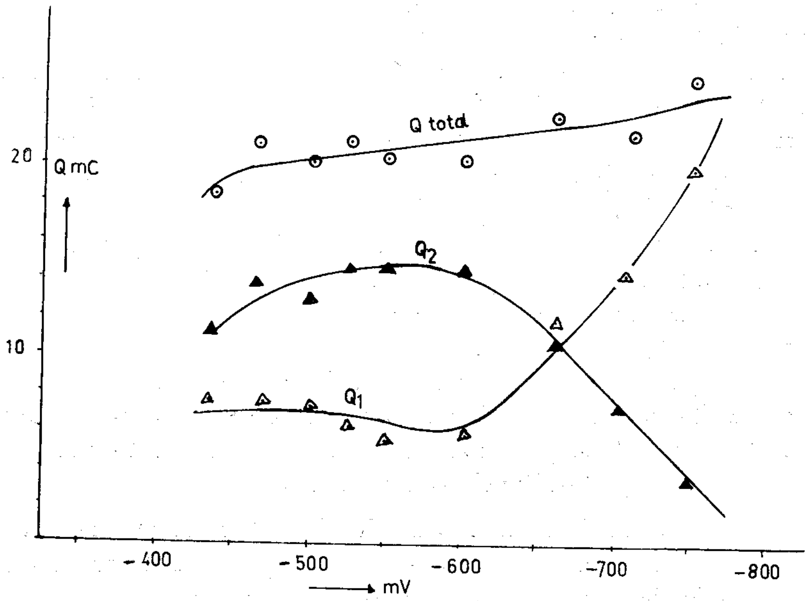

Fig. 10. The variation of cathodic charges associated to the first (△) and the second (▲) peaks on the curves in Fig. 9 wifh the potentials where the sweep rate changes to 50 mV / sec was done.

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ÖZET

Bu çalışmada bakır elektrot üzerinde oluşan fazların özellikleri dönüşümlü voltametri yöntemiyle incelenmiştir. Cu_2O çözünme çökme mekanizmasıyla oluşur. Bakır elektrot üzerinde iki farklı Cu_2O filmi vardır. Bunlar farklı potansiyellerde redüklenirler. Birinci film ikincisi için direnç polarizasyonu gösterir.