COMMUNICATIONS

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

Série B: Chimie

TOME 27 ANNEE : 1981

A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

The Electrochemical Behaviour of Silver in Bichromate Solutions

Turkey

by

Melike KABASAKALOĞLU

8

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

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

---

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté.

La Revue, jusqu'a 1975 à l'exception des tomes I, II, III, était composée de trois séries:

Série A: Mathématiques, Physique et Astronomie.

Série B: Chimie.

Série C: Sciences naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1: Mathématiques
Série A_2: Physique
Série A_3: Astronomie
Série B : Chimie
Série C_1: Géologie
Série C_2: Botanique
Série C_3: Zoologie

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adrese: Fen Fakültesi Tebliğler Dergisi Fen Fakültesi, Ankara, Turquie.

DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lit by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

The Electrochemical Behaviour of Silver in Bichromate Solutions

Melike KABASAKALOĞLU

Department of Physical Chemistry, Faculty of Science; University of Ankara, Turkey.

(Received February 16, 1981: Accepted March 11, 1981)

ABSTRACT

The electrochemical behaviour of silver electrode in solutions of 1 N H_2SO_4 and 1 N H_2SO_4 containing various amounts of H_2O_2 and bichromate have been studied by obtaining anodic and cathodic current-potential curves using potentiostatic methods. Anodic polarization curves of silver in these solutions show that dissolution of silver is the first reaction. Passivity occurs with the formation of Ag_2SO_4 film. AgO is formed after oxygen evolution from the Ag_2SO_4 film. Before oxygen evolution, silver oxides can be formed only in the oxidizing solutions.

In addition, current-potential curves obtained with the reduced silver electrode in bichromate solutions of different concentrations. These curves show that the reduction rate of bichromate on silver electrode is controlled by diffusion of bichromate ion. Bichromate reduction occurs at the reduction potential of silver ion.

INTRODUCTION

In the previous studies [1–3], it was pointed out that bichromate reduction with the noble metal electrodes in acidic solutions, occurs at the same potentials where their oxides are reduced and with a less noble metal electrode, such as copper [4] occurs at the dissolution potential of metal. Bichromate oxides noble metals to metal oxides [5-6] and copper to cupric ions [4].

In the present study, the behaviour of silver which is the same group as copper in the periodic table was investigated in bichromate solutions in order to clarify the reduction mechanism of bichromate with a less noble metal electrodes.

Silver is perfectly stable in the presence of water and in aqueous solutions of all pH's free oxidizing and complexing substances. The place

Adress: Ankara Üniversitesi, Fen Fakültesi Fizikokimya Kürsüsü ANKARA Turkey.

of silver in the standart potential table and the solubility product of Ag_2SO_4 ($K=1.12.10^{-5}$) and of $Ag_2\ CrO_4$ ($K=1.1.10^{-12}$) [7] suggest that silver, first, dissolves as silver ion and then covered with the film of $Ag_2\ CrO_4$ in bichromate solutions. Further oxidation of silver to silver oxides can be thought. Anodic behaviour of silver in 1 N H_2SO_4 and 1 N H_2SO_4 containing oxidizing agents such as hydrogen peroxide and bichromate in different concentrations were studied by potentiostatic technique in order to understand whether silver oxides are produced with anodic polarization. The potential of silver anode was changed linearly with time from the rest potentials of reduced silver electrodes in the test solutions to about +2 V and vice versa. In addition cathodic polarization curves were obtained with reduced silver electrodes.

The idea about the possible reactions occur on the surface of silver in bichromate solutions can be obtained from the consideration of the standart free energy changes, $\Delta\ G,^{\circ}$ of the different reactions involving silver, bichromate and sulphuric acid. In table I a number of electrode reactions for silver in acidic bichromate solutions are formulated. Since the PK of $HCrO^-_4 \rightleftarrows H^+ + CrO^{=}_4$ reaction is 6.45 [8], equilibria involving only $HCrO^-_4$ and $Cr_2O^{=}_7$ are considered. The neccessary free energy datas for the reactions in Table I are taken from literature [7–8]. According to Table I followings can be inferred.

Dissolution of silver which occurs with the smallest increase in free energy represents a probable reaction to take place upon oxidizing silver in acidic bichromate solutions. Upon reaching the solubility product of sparingly soluble silver salts, Ag_2SO_4 or Ag_2CrO_4 forms and passivity occurs.

The physical nature of the Ag_2SO_4 or the Ag_2CrO_4 film determines the type of electrode reactions that follow. For a nonadherent film further oxidation of silver is possible. The anode has a chance to build Ag_2O and Ag O reactions. According to free energies in Table I, the oxidation of Ag_2O to AgO and Ag_2O_3 precede that of the conversion of Ag_2CrO_4 and Ag_2SO_4 to AgO. The standart potentials of these latter processes (9 and 10) 1.75 V and 1.9 V are well above upper limit of the thermodynamic stability of water. If on the other hand, the Ag_2CrO_4 or Ag_2SO_4 forms as a compact nonporous layer, blocks the electrode surface to further oxidation. The polarization curves will show only reactions 9 and 10.

Table 1. Electrode reactions for silver in bichromate and sulphuric acid solutions and their equilibrium potentials.

Electrode reaction and equilibrium potential	Kcal
1. $Ag = Ag^+ + e^-$ $E = 0.799 + 0.0591 \log a\, Ag^+$	18.43
2. $2\,Ag + SO_4^= = Ag_2SO_4 + 2e^-$ $E = 0.653 - 0.0296 \log a\, SO_4^=$	30.17
3. $2\,Ag + HCrO_4^- = Ag_2\,CrO_4 + H^+ + 2e^-$ $E = 0.786 + 0.0296 \log a\, H^+ - 0.0296 \log a\, HCrO_4^-$	36.33
4. $2\,Ag + H_3O = Ag_3O + 2H^+ + 2e^-$ $E = 1.173 + 0.0591 \log a\, H^+$	54.1
5. $Ag + H_2O = AgO + 2\,H^+ + 2\,e^-$ $E = 1.284 + 0.0591$ Log a H^+	59.29
6. $Ag_2O + H_2O = 2\,AgO + 2H^+ + 2e^-$ $E = 1.398 + 0.0591 \log a\, H^+$	64.48
7. $2\,AgO + H_2O = Ag_2O_3 + 2H^+ + 2e^-$ $E = 1.569 + 0.0591 \log a\, H^+$	72.29
8. $Ag_2O + 2H_2O = Ag_2O_3 + 4H^+ + 2e^-$ $E = 1.747 + 0.0591 \log a^2\, H^+$	80.66
9. $Ag_2CrO_4 + \frac{3}{2} H_2O = 2\,AgO + \frac{1}{2} Cr_2O_7^= + 3\,H^+ + 2\,e^-$ $E = 1.756 + 0.0296 \log a^{1/2}\, Cr_2O_7^= \cdot a^3\, H^+$	81.105
10. $Ag_2SO_4 + 2H_2O = AgO + SO_4^= + 4\,H^+ + 2\,e^-$ $E = 1.908 + 0.0591 \log a^2\, H^+ \cdot a\, SO_4^=$	88.41

EXPERIMENTAL

In these experiments great care was taken to see that all chemicals were chemically pure and solutions were prepared with conductivity water. The electrode used was composed of silver wire (99.999 % Johnson Matthey and Co ltd. London) of 0.5 mm diameter and 3 cm in lenght. Silver wire were spot welded to platinum and sealed in a glass tube. The seals were carefully extended down the silver for several mm from the Ag/Pt weld.

Before each set of measurements the electrode was abraded with fine emery paper and oxidized for five minutes under a current of 10 mA in 1 N NaOH. Then it was reduced at –750 mV (N.H.E) using po-

tentiostat for 15 minutes in 1 N NaOH under a flow of nitrogen (reduced electrode). The electrode was washed with conductivity water before the experiment. Each set of experiment was carried out with newly pretreated electrode using fresh solutions. Curves in 1 N H_2SO_4 and 1 N H_2SO_4 containing hydrogen peroxide were obtained both in stirred and unstirred solutions. In stirred solutions the solutions in the cell were kept at the same level and mixed continuously with a magnetic stirrer. Nitrogen was bubbled through the solution for 30 minutes before and throughout the experiment. In unstirred solutions nitrogen was bubbled only prior to experiment. Measurements were carried out in a three armed pyrex cell. The first arm was the anode; the second was the cathode compartment. The reference calomel electrode was dipped within the third arm. The stopcocks between the arms were kept close during the experiments.

Polarization curves were obtained with a Wenking Breitband model 61 RS electronic potentiostat. Potential was changed by Wenking scanning potentiometer Model SMP 69 at the rate of 200 mV/minute and 100 mV/minute.

RESULTS AND DISCUSSION

a. Anodic polarization curves obtained in 1 N H_2SO_4

In Fig.1, curve 1 and 2 show the anodic polarization curves obtained in stirred and unstirred 1 N H_2SO_4 solutions respectively. In curves, the potential of silver electrode was made to vary linearly from the rest potentials of silver in deareted solutions towards to +2V at a rate of 200 mV/ minute. The curves showed a well developed active region and active passive transition. The potential range of the active region and the maximum current (18 m A) did not vary greatly in stirred and unstirred solution. In active region, the anodic dissolution of the silver in 1 N H_2SO_4 occurs. The accumulation of the Ag^+ ions in the vicinity of the electrode surface leads to saturation and deposition of Ag_2SO_4 on with the blocking of the surface and fall of current to lower values. Stirring affects the phenomena on the electrode surface after passivation. In stirred solution, the increase of current at 0.85 V and the oscillating region on the curve may be described by the nonadherent porous nature of the film. Convection and increasing polarization cause the film spills

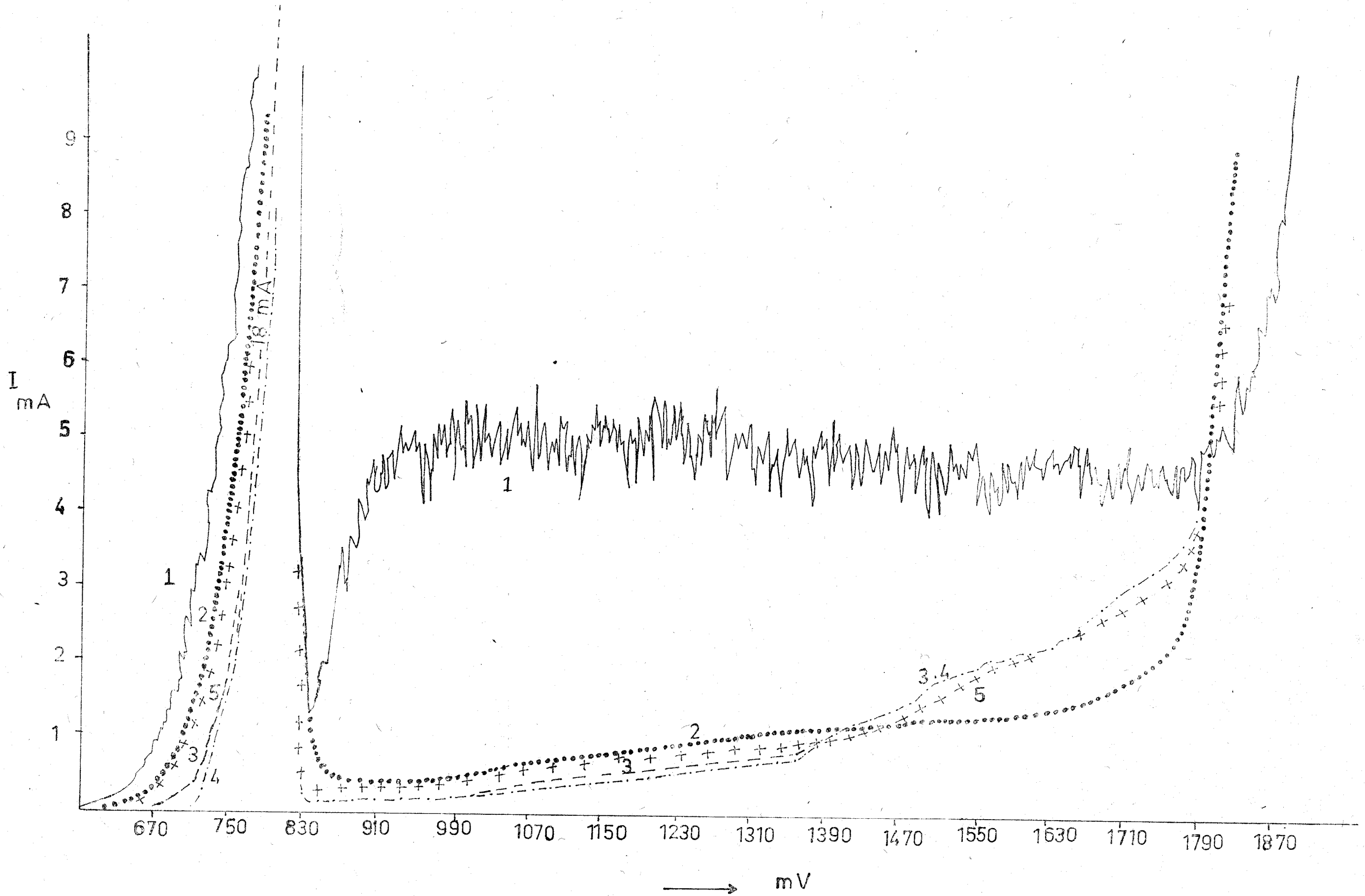


Figure 1. Anodic polarization curves obtained in 1 N H_2SO_4 and with the addition of various amounts of H_2O_2. Curve 1) (———) in stirred 1 N H_2SO_4. Curve 2) ..... in unstirred 1 N H_2SO_4. Curve 3) — — — — 1 N H_2SO_4 + 2.65 10^{-3} M H_2O_2. Curve 4) —.—. 1 N H_2SO_4 + 5.3 10^{-3} M H_2O_2. Curve 5) ++++ 1 N H_2SO_4 + 0.106 M H_2O_2 Curves (2–5) were obtained in untirred solutions.

off the surface. Renewal of the Ag_2SO_4 film causes the passage of oscillating current up to the oxygen evolution potential. In unstirred solution, oscillating region was not observed (curve 2). Oxygen evolution occurs at 1.8 V. It is referred that the $Ag_2SO_4 + H_2SO_4$ system has displayed a behaviour remarkably analogous to that of the $Pb + H_2SO_4$ system [9].

In lead, after passivation by $PbSO_4$ film the formation of PbO and $Pb(OH)_2$ occur [10, 11].

In silver, polarization curves (1, 2) obtained in 1 N H_2SO_4 have no steps attributed to the known silver oxides.

b. Anodic polarization curves obtained in acidic H_2O_2 solutions.

In order to see whether silver oxides can be formed by the help of the oxidizing agents, anodic polarization curves obtained in acidic H_2O_2 and bichromate solutions. Curves (3, 4, 5) in Fig.1 obtained in unstirred acidic H_2O_2 solutions. Curves in Fig.2. obtained in stirred solutions. In Fig.2a, the potential region of the curves between 1.2V and 1.6V are shown in a large scale. There are potential steps at 1.35 V on the curves 3.4.5 in Fig.1 obtained in the unstirred solutions and at 1.41 V on the curves in Fig.2a and Fig.2 obtained in stirred solutions. These potential steps can be attributed to the silver/silver oxides equilibrium (the reactions 4 or 5 in Table I) delayed by the presence of Ag_2SO_4 film. After oxygen evolution at 1.8V, another potential steps occur at about 1.9V and 2 V. Both oxygen evolution and the mentioned two steps moved to more positive potential as the concentration of H_2O_2 is increased. According to the Table I, the first step at about 1.9 V can be related to the convertion of Ag_2SO_4 to AgO. Wales and Burbank [12] proposed that silver sulphate is the first product formed in the anodic oxidation of silver in sulphuric acid. The silver sulphate is then oxidized to black argentic oxide with simultaneous evolution of oxygen. This argentic oxide is further oxidized to silver oxysulphate and then electrode is almost passivated. X ray diffraction studies of Briggs, Dugdale and Wynn-Jones [13] showed that the anodic oxide film formed on silver in H_2SO_4 solutions thickens considerable during continuous polarization and that both AgO and Ag "peroysulphate" are formed. In the present study the curve obtained in sulphuric acid solution has any step at 1.35 V or 1.41 V which can be attributed to the silver oxides. However silver oxides can be formed by the help of the H_2O_2 before evolution of oxygen.

c. Anodic polarization curves obtained in bichromate solutions.

Figure 3, and 3a show the polarization curves obtained in 1 N H_2SO_4 with the addition of various concentration of bichromate at the sweeprate of 200 mV/ minutes as the same way in figures (1,2). Up-to the concentration of 3.10^{-2} M $K_2Cr_2O_7$, curves are almost the same as the curve obtained in 1 N H_2SO_4. In Figure 3 a the potential regions between 650 and 900 mV in fig. 3 were shown. Up to the concentration of 3.10^{-2}M bichromate, current begins to rise at the same potential as in the curve obtained in 1N H_2SO_4. The increase of the peak current with increase of bichromate concentration shows the increase of anodic oxidation rate of silver with bichromate. The forms of the curves show that the first reaction is the dissolution of silver and passivity occurs with the formation of Ag_2SO_4 up to the concentration of 3.10^{-2}M $Cr_2O_7^=$. Up to this concentration, Ag_2SO_4 film does not protect the metal surface and the second active dissolution begins at about 0.85 V–0.9V by inereasing polarization and by the help of oxidizing power of the bichromate. Oxygen evolution occurs at 1.8V. After 3.10^{-2}M $Cr_2O_7^=$ all the curves begin at the same potential 0.79 V, the equilibrium potential of Ag / Ag_2CrO_4 system according to the Table 1. and the electrode surface is covered with a reddish brown layer by the immersion of the electrode in the solutions.

The polarization curve obtained in 3.10^{-2} M $Cr_2O_7^=$ has two passivation peaks. The first one begins at, 0.79 V, the equilibrium potential of $Ag / Ag_2 CrO_4$ system, shows the passivation mainly by $Ag_2 CrO_4$ film. However the film formed in 3.10^{-2}M. bichromate solution is probably thin cannot protect the surface from the second active dissolution. By increasing polarization dissolution of silver ion is increased and the second layer of $Ag_2 CrO_4$ film is formed and then the second passivation peak at 1.1 V occurs. After 3.10^{-2} M bicromate, corrosion current is low and oxygen evolution begins at higher potential because of the thick $Ag_2 CrO_4$ film.

As seen from the figures polarization current has irregular fluctuations. Short-term changes of the thickness of diffusion layer can be the cause of the fluctuations(14). As seen from the curves 6 and 7 in Fig. 3, these current fluctuations disappear because of the steady thick $Ag_2Cr O_4$ film formed in 10^{-1} and 0.25 M $Cr_2O_7^=$ solutions. It is impossib-

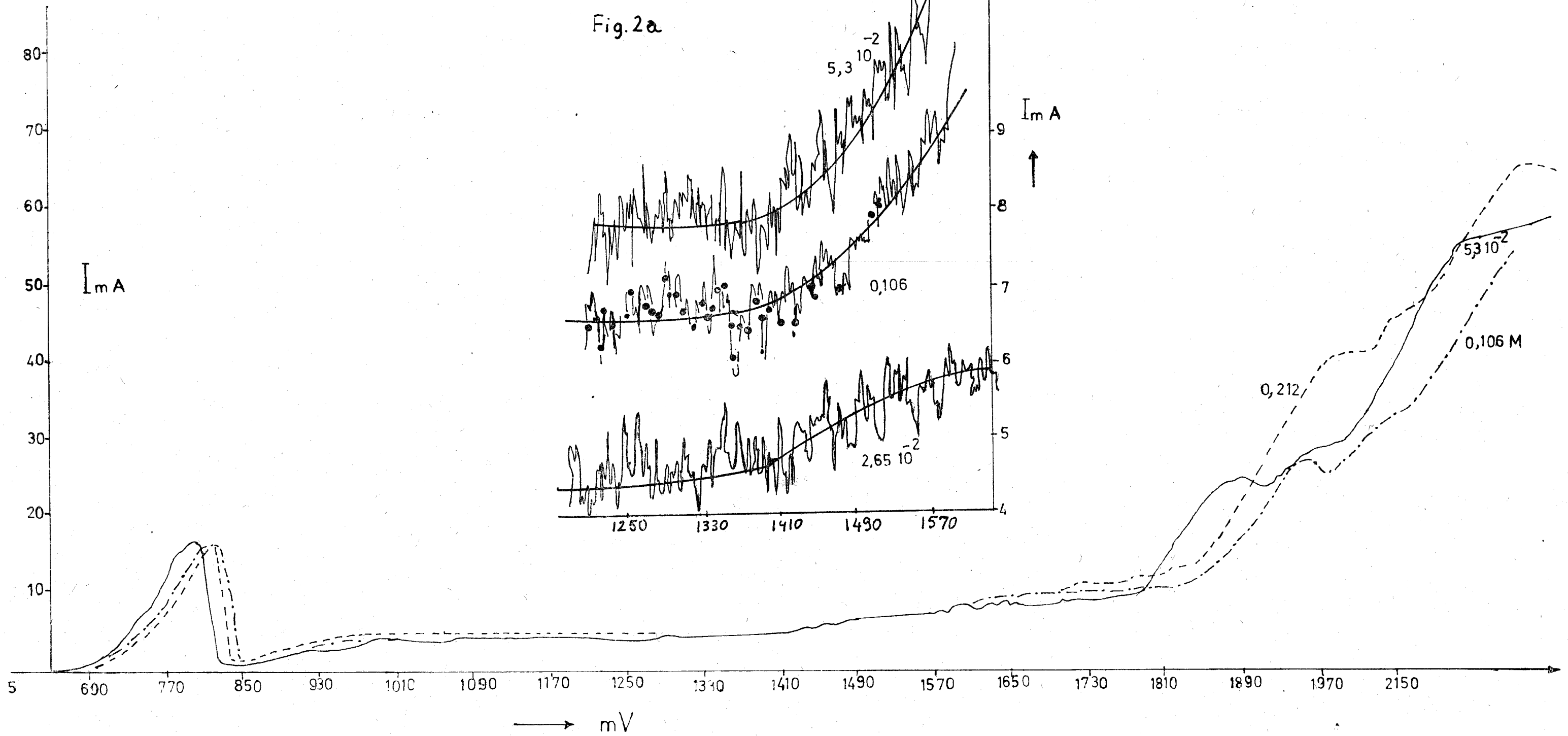


Figure 2. Anodic polarization curves obtained in stirred 1 N H_2SO_4 with the addition of various amounts of H_2O_2.
——— 5.3 10^{-2} M H_2O_2; —.—.— 0.106 M H_2O_2; — — — — 0.212 M H_2O_2 Figure 2a. Shows the potential regions of the curves between 1.2 and 1.6 V. Dark line shows the mean current.

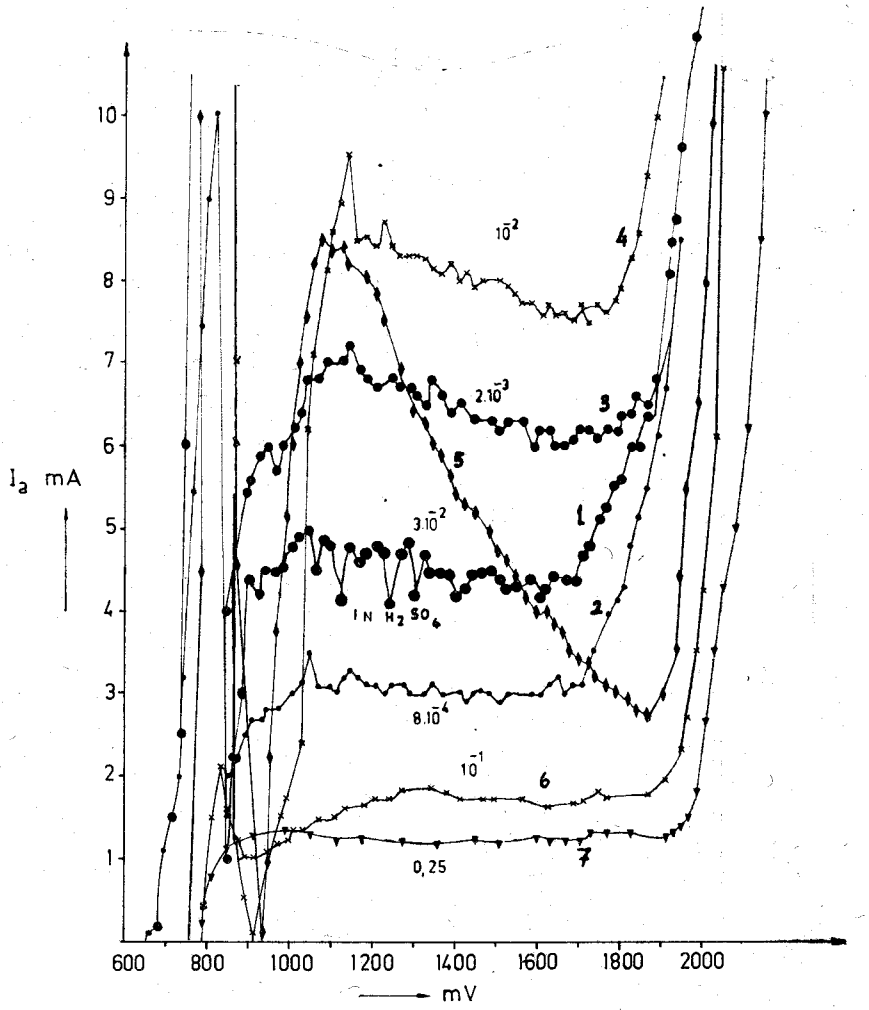


Figure 3. Polarization curves obtained in 1) 1 N H_2SO_4 with the addition of bichromate in various concentration, 2) 8.10^{-4}; 3) $2\ 10^{-3}$; 4) 10^{-2}; 5) $3\ 10^{-2}$; 6) 10^{-1}; 7) 0.25 M.

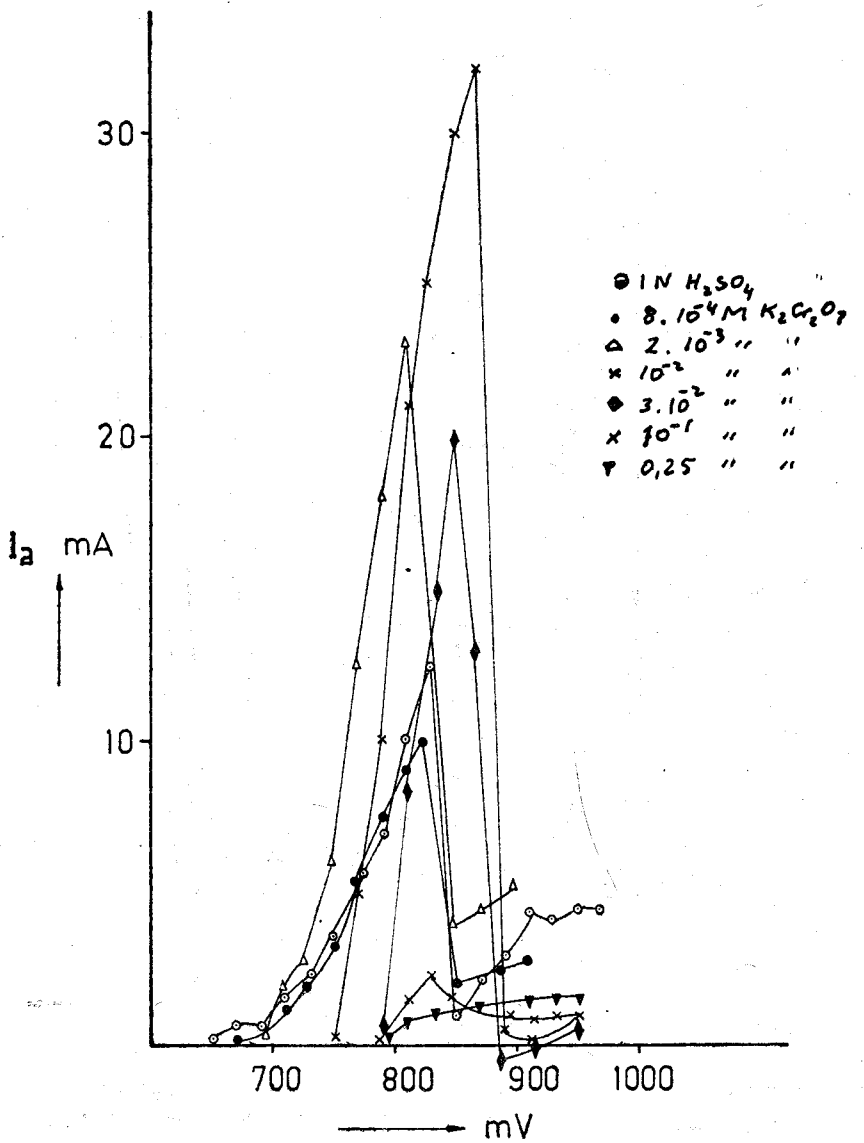


Figure 3a. The potential regions between 0.65 and 0.9 V in Fig 3.

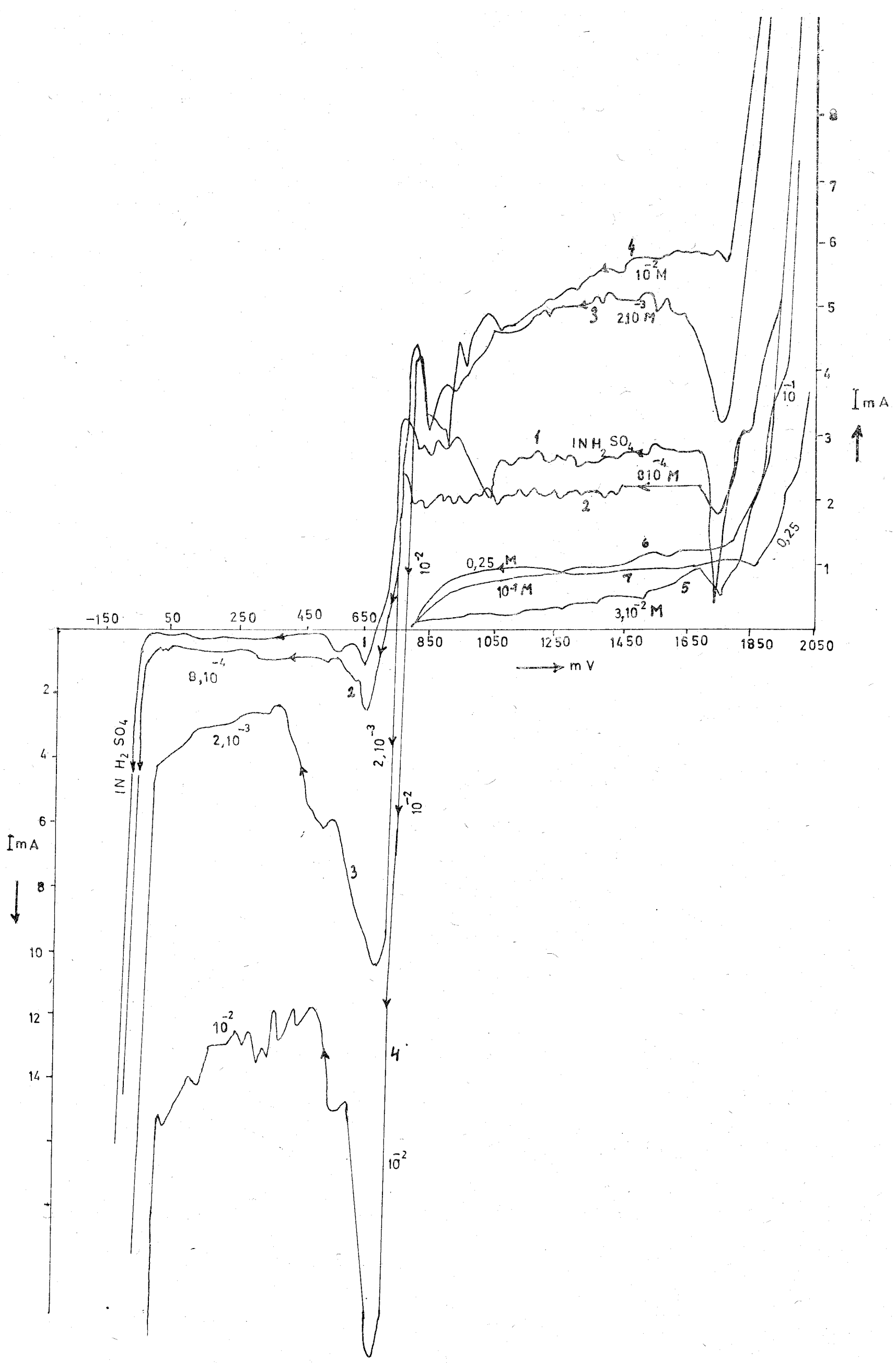


Figure 4. Anodic and cathodic current regions of the curves in Fig.3 after potential reversal at oxygen evolution.

le to see any step attributed to the silver oxides in anodic polarization region.

d. Cathodic polarization curves obtained in bichromate solutions.

In Fig. 4, anodic and cathodic current region of the curves in Fig. 3 after potantial reversal were shown. In anodic region all the curves show minimum at 1.7 V which is related to the reduction of oxygen in the pores of the Ag_2SO_4 or Ag_2CrO_4 film. Up to the concentration of 3.10^{-2} M $Cr_2O_7^{=}$ after potential reversal anodic current is almost the same as the curves in Fig.3. When the potential reaches to 0.85 V, dissolution of silver appears again. After this concentration the curves do not show the dissolution of silver after potential reversal and the current is low. In these curves, cathodic current begins to pass from the dissolution potential of silver. First curve is obtained in 1 N H_2SO_4. The step which shows maximum at 0.65 V is related to the reduction of silver ions. After the first silver reduction peak; there is a shoulder step which can be attributed to the reduction of Ag_2SO_4 to silver. The curves obtained in bichromate solutions are the same as the curve obtained in 1 N H_2SO_4 only the peak currents are increased. This is expected, because as the bichromate concentration is increased, the concentration of silver ions which pass to the solution during anodic polarization are increased. After 3.10^{-2} M $Cr_2O^{=}_7$ cathodic current regions of the curves can not be obtained. If the potential is increased further in the cathodic direction, potentiostat system does not work because of the thick film (Ag_2CrO_4) formed on the electrode surface.

Fig. 5 shows the cathodic polarization curves obtained in bichromate solutions with reduced silver electrode. The rate of potential change was 100 mV/minute. First curve is obtained in 1 N H_2SO_4. Cathodic current begins at 0.2 V and hydrogen evoalution begins at –0.050 V. As the bichromate concentration is increased, the beginning potentials and the limiting currents of the curves are increased. The limiting current goes proportional with bichromate concentration up to the 2.10^{-3} M $Cr_2O_7^{=}$. The proportionality coefficient between 0.6 – 0.4 V is 2.6 miliampere milimole^{-1} lt.

It is seen from the curves that limiting current has irregular fluctuations and these fluctuations increase as the bichromate concentration is increased. After 10^{-3} M $Cr_2O_7^{=}$ two limiting current regions can

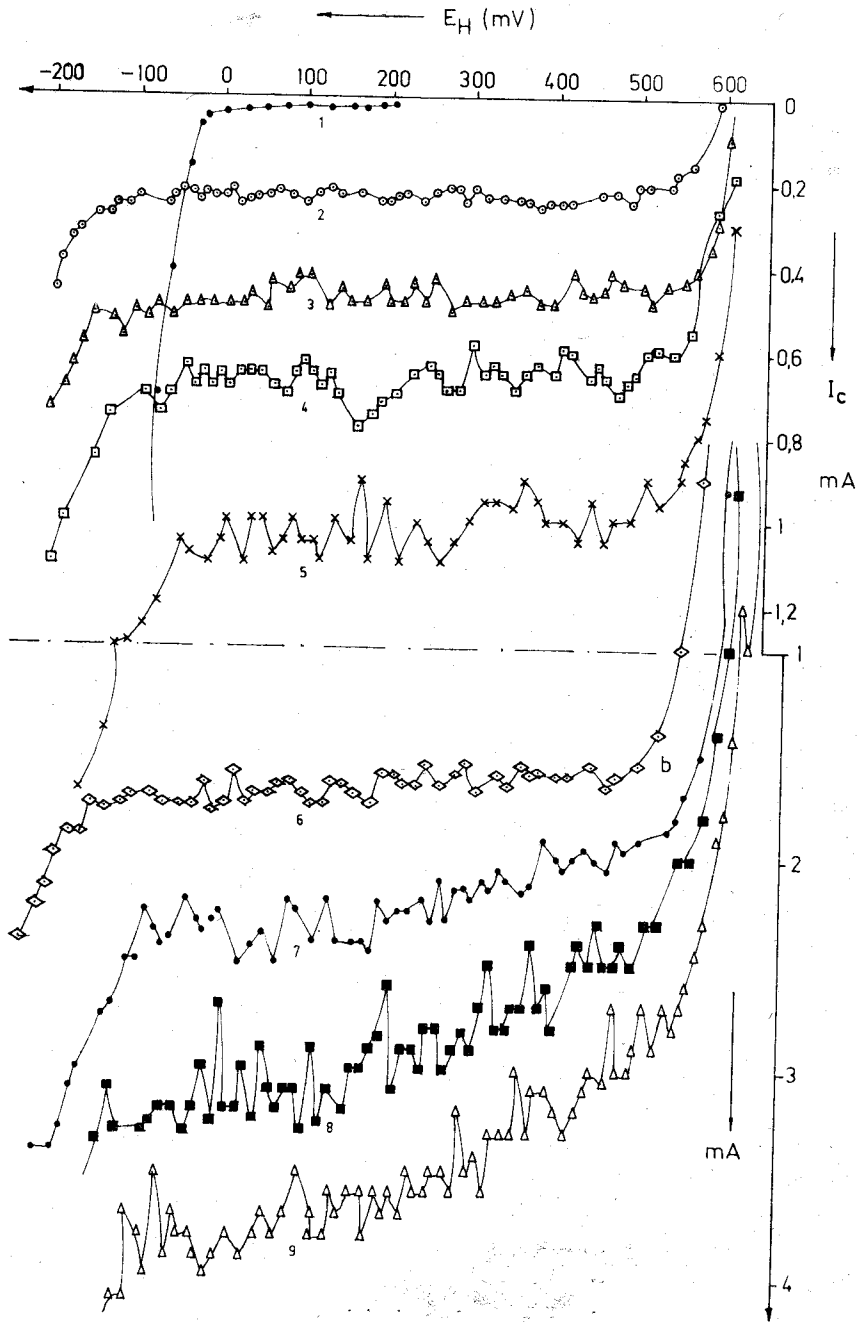


Figure 5. Cathodic polarization curves obtained in 1 N H_2SO_4 and with the addition of various amounts of bichromate.

Figure 5a. 1) 1 N H_2SO_4; 2) 10^{-4}; 3) 2.10^{-4}, 4) 3.10^{-4}, 5) 4.10^{-4} 6) 6.10^{-4}; 7) 8.10^{-4}; 8) 10^{-4}; 9) $1.2.10^{-3}$;

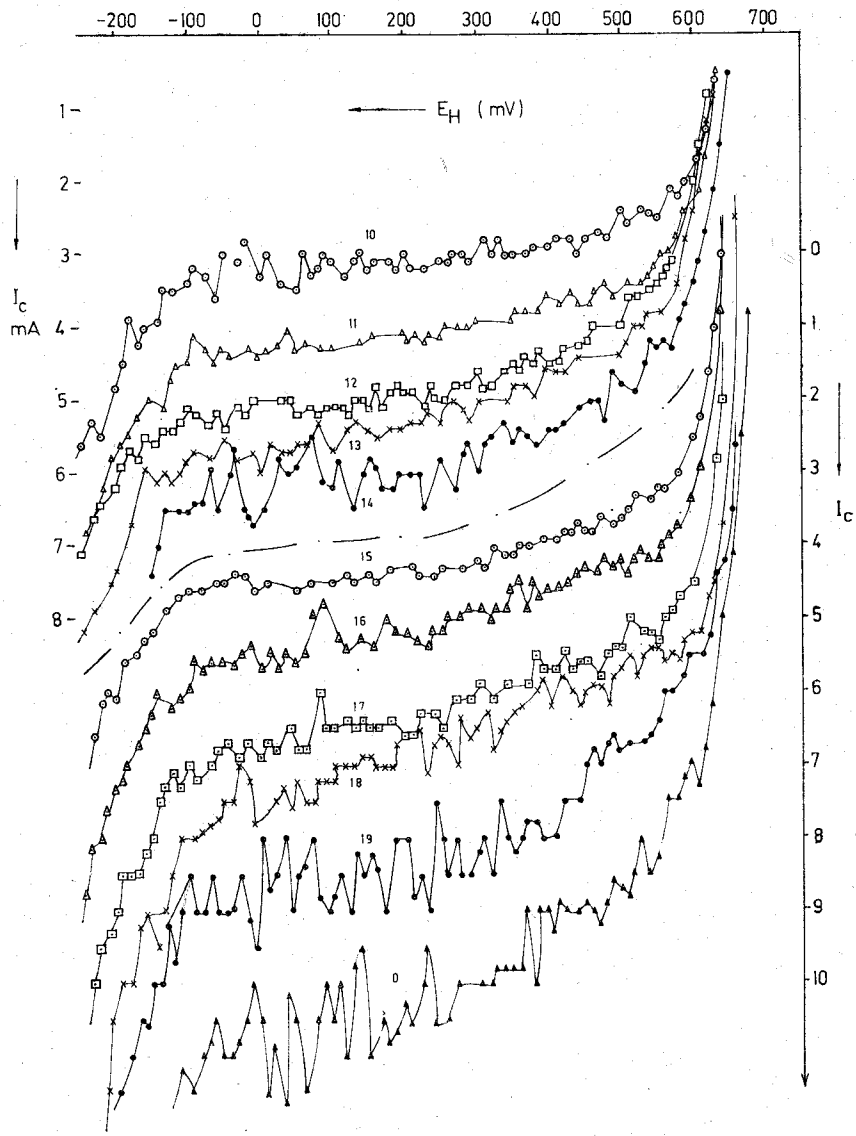


Figure 5b. 10) $1.1.10^{-3}$; 11) $1.3.10^{-3}$; 12) $1.5\ 10^{-3}$; 13) $1.6.10^{-3}$; 14) $2.3.10^{-3}$ 15) $1.4.10^{-3}$; 16) $1.7.10^{-3}$; 17) 2.10^{-3}. 18) $2.6.10^{-3}$. 19) 3.10^{-3}; 20) $3.5.10^{-3}$ Molar.

be distinguished. One is between 0.65 and 0.45 V, the other is between 0.35 and −0.100 V. In the second region cathodic current is also proportional with bichromate concentration and proportionality coefficient is 3.2 miliampere milimole^{-1} lt.

After 2.10^{-3} M bichromate limiting current-concentration line (Fig 6) shows a minimum and deviation from linearity found as in the copper [4].

CONCLUSION

The curves obtained both in 1 N H_2SO_4 and in acidic bichromate solutions show that silver first dissolves as Ag^+ ions (Fig 1.2 and 3). Passivation occurs with the formation of Ag_2SO_4 and Ag_2CrO_4 films in dilute and concentrated solutions of bichromate respectively. Silver oxides can be formed anodically only in the oxidizing solutions by the protecting effect of the Ag_2SO_4 film.

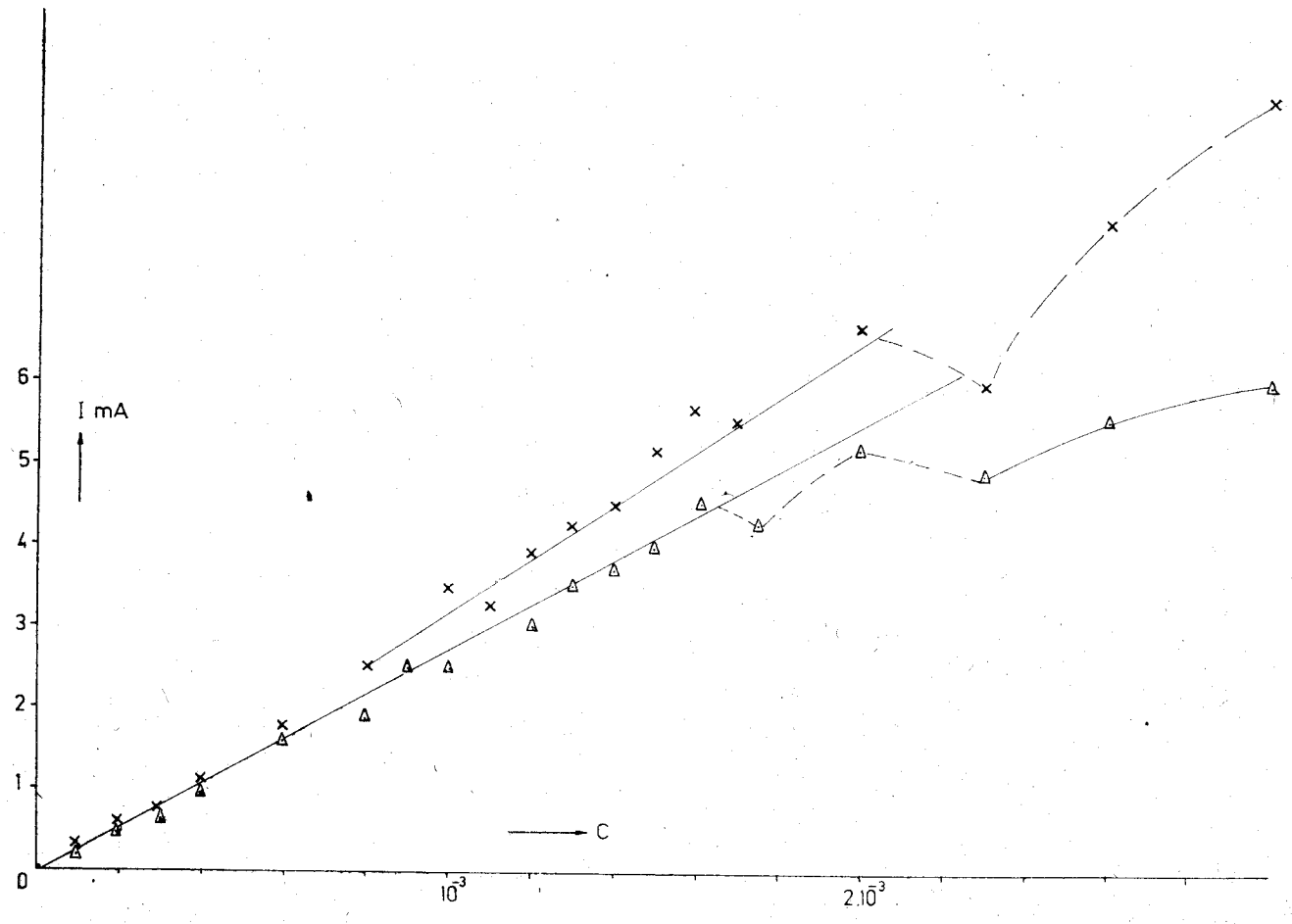
In bichromate solutions, the rest potentials of the reduced silver electrodes increase as the bichromate concentration increases, because the concentration of silver ions which pass to the solution increases. Cathodic current begins to rise from these rest potentials.

According to the present study, the reduction of bichromate on silver electrode occurs as on copper electrode [4].

Bichromate ions which come to the electrode surface by diffusion are reduced at the electrode surface both by oxidizing electrode metal chemically and electroliticaly. At the same time, the reduction of dissolved silver ions should also be taken into account. For this reason bichromate reduction does not take place at the equilibrium potential of $Cr_2O_7^{=}/Cr^{3+}$ system but take place at the reduction potential of silver ions.

As the bichromate ion concentration is increased also dissolved silver ion concentration increases and then the solubility product of Ag_2SO_4 and Ag_2CrO_4 can be reached on the surface.

Weiner and Schiele [14] showed by electron microscopy that cathode film formed on silver in chromic acid contains silver, Ag_2O and Cr_2O_3.



Fifure 6. The variation of limiting currents of the curves in Figure 5 with bichromate concentration: curve △ between 0.65–0.4 V; curve x between 0.350 and −0.050 V.

During the reduction, catholyte pH increases due to the bichromate reduction require high hydrogen ion concentration. This facilitates the formation of silver and chromium oxides in the pores of Ag_2SO_4 or Ag_2CrO_4 films.

Up to the 2.10^{-3} M bichromate concentration film formation does not occur on reduced silver electrode or the film layer does not prevent the reduction of bichromate ions and diffusion rate of bichromate controls the reduction rate of it. For higher concentrations linear dependency disappears. This suggests that the film formed at concentrations higher than $2.5\ 10^{-3}$ M covers the electrode surface and prevents partly the reduction of bichromate reduction.

Acknowledgement- The author wishes to thank to Prof.Dr. S. Üneri for her help and encouragement.

REFERENCES

1- **S. Üneri,** Commun. Fac.Sci. Üniv. D'Ankara Seri B Chim. 7, 31, 59 (1962).

2- M. Kabasakaloğlu and S. Üneri, Ibid Tome 14 B 59, (1967) - Tome 15 B, 6 (1968).

3- **İ. Ödün and S. Üneri,** Ankara Ecz. Fak. Mec. 4, 1 (1974).

4- **M. Kabasakaloğlu,** Chim. Acta Turc. 4, 97 (1976).

5- **M. Kabasakaloğlu and S. Üneri,** Commun. Fac. Sci. Üniv. D'Ankara Serie B Chim. Tome XIV 23 (1967) - Tome XVI 1 (1969).

6- **İ. Ödün,** Thesis of Ph. degree (1971).

7- Handbook of Chemistry and Physics. CRC press (1972-1973).

8- **M. Pourbaix,** Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press (1966).

9- **P. Jones and H.R. Thirsk,** Trans. Farad. Soc., 50, 732 (1954).

10- **A.A. Abdul Azim and M.M. Anwar.** Corr. Sci. 9, 245 (1969).

11- **T.M.H. Saber and A.M. Shams El Din,** Electrochim. Acta., 13, 937 (1968).

12- **C.P. Wales and J. Burbank,** J. Electrochem. Soc., 106, 855 (1959).

13- **G.W.D. Briggs,** I. Dugdale and W.F.K. Wynne Jones, Electrochim. Acta., 4, 55 (1961).

14- Electrochemical Kinetics. Klaus J. Vetter. Academic Press New York (1967). P. 400.

15- **R. Weiner and C. Schiele,** Zeit. Phys. Chem. Neue Folge, 26, 3/4 (1960).

Prix de l'abonnement annuel

Turquie: 15 TL; Étranger: 30 TL.
Prix de ce numéro : 5 TL (pour la vente en Turquie).
Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi, Ankara - 1982