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von

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The Investigation Of Chromate Reduction On Platinum Electrode*

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In this work the cathodic reduction of bichromate was investigated with a potentiostatic method to the hydrogen discharge potential. Current - potential curves were obtained both oxidized and reduced platinum electrodes. It was shown that the reduction of bichromate on platinum electrode occurs on the same reduction potential of metal oxide. Limiting current at the steps which are seen in the positive potential are proportional with bichromate in low concentration region. As concentration was increased these steps drift to the negative potential and limiting current decreased in the first step.

In addition, hysteresis curves were otained in 1 N H_2SO_4 and acidic bichromate solutions with reduced and oxidized platinum electrode. From these studies it was shown that the film formed on the electrode does not prevent the chromate reduction in acidic medium and changes its sturucture during cathodic reduction.

INTRODUCTION

In our previous studies (1,2) we have indicated that rhodium, platinum and iridium electrodes surfaces are oxidized and coated with a film when they are inserted in various oxidizing media. Due to such a film of oxide bichromate reduction is produced not in the equilibrium potential of $Cr_2O_7^{=}/Cr^{3+}$ but in the same potential where their oxides are reduced. In this study current – potential curves were determined in various concentrations of bichromate solutions and the nature of the film formed on the electrodes were investigated.

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EXPERIMENTS

Current – potential curves were obtained with Wenking Breitband potentiostat Model 6IRS (Göttingen), in which potential was changed 50 mV every 15 second. In the cell used for this experiment cathode compartment was separated with a porous cup. Nitrogen gas was passed though the solution for one hour, prior to each experiment. Hydrogen electrode was used as a reference electrode. The solution in the cell was continuously kept at the same level and mixed with a magnetic stirrer during the experiment.

The same procedure(1) was used for the pretreatment of platinum electrode. Current - potential curves were obtained both with oxidized and reduced electrodes (1).

CONCLUTIONS

Current – Potential curves obtained with platinum electrode in various concentration of bichromate solutions are shown in figure 1 and 2 for oxidized platinum electrode and in figure 3 for reduced platinum electrode. Cathodic polarization curves obtained with oxidized platinum electrode are begun around 1500 mV (the rest potentials obtained in 1 N $H_2SO_4 + 10^{-2}$ M Ce (IV) SO_4). The curves have two potential steps one is between 800 and 550 and the other is between 300-200 mV. Current rose rapidly around the hydrogen region after these steps.

The first potential step which is seen on the current – potential curves obtained in 1 N H_2SO_4 is shown from other investigators (3–9) by various methods and that it is related to the reduction of platinum oxides. The steps in the first two curves which are obtained in the solutions of low bichromate concentration (7.5 10^{-6} ; 10^{-5}) is the same as the steps on the curve obtained in 1 N H_2SO_4 except the fact that current intensity is increased in the former. So bichromate reduction must take place at the reduction potential of the platinum oxide in 1 N H_2SO_4. At the first step current intensity increased with concentration to $6\text{x}10^{-5}$ molar bichromate. As concentration was increased further current intensity decreased in the first step and drift to the negative po-

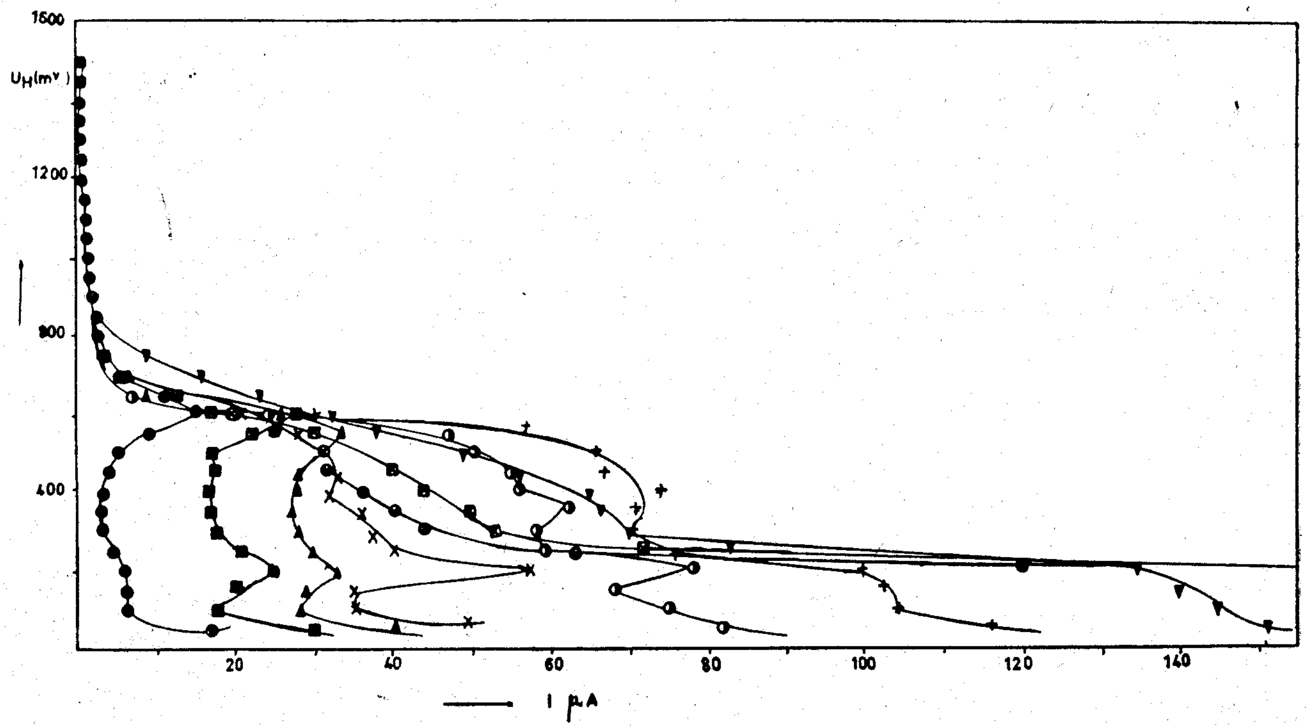

Fig. 1. Current - potential curves obtained with oxidized platinum electrode in H_2SO_4 and acidic bichromate solutions
● 1 N H_2SO_4, ■ 1 N H_2SO_4 + 7.5×10^{-6} M $K_2Cr_2O_7$, ▲ 10^{-5} M $K_2Cr_2O_7$ + 1 N H_2SO_4, X 1 N H_2SO_4 + 2.5×10^{-5} M $K_2Cr_2O_7$, ◑ 1 N H_2SO_4 + 4×10^{-5}M $K_2Cr_2O_7$, + 1 N H_2SO_4 + 6×10^{-5} M $K_2Cr_2O_7$, ▼ 1 N H_2SO_4 + 8×10^{-5}M $K_2Cr_2O_7$, ⊠ 2×10^{-4}M $K_2Cr_2O_7$ + 1 N H_2SO_4, ⊗ 10^{-3} M $K_2Cr_2O_7$ + 1 N H_2SO_4.

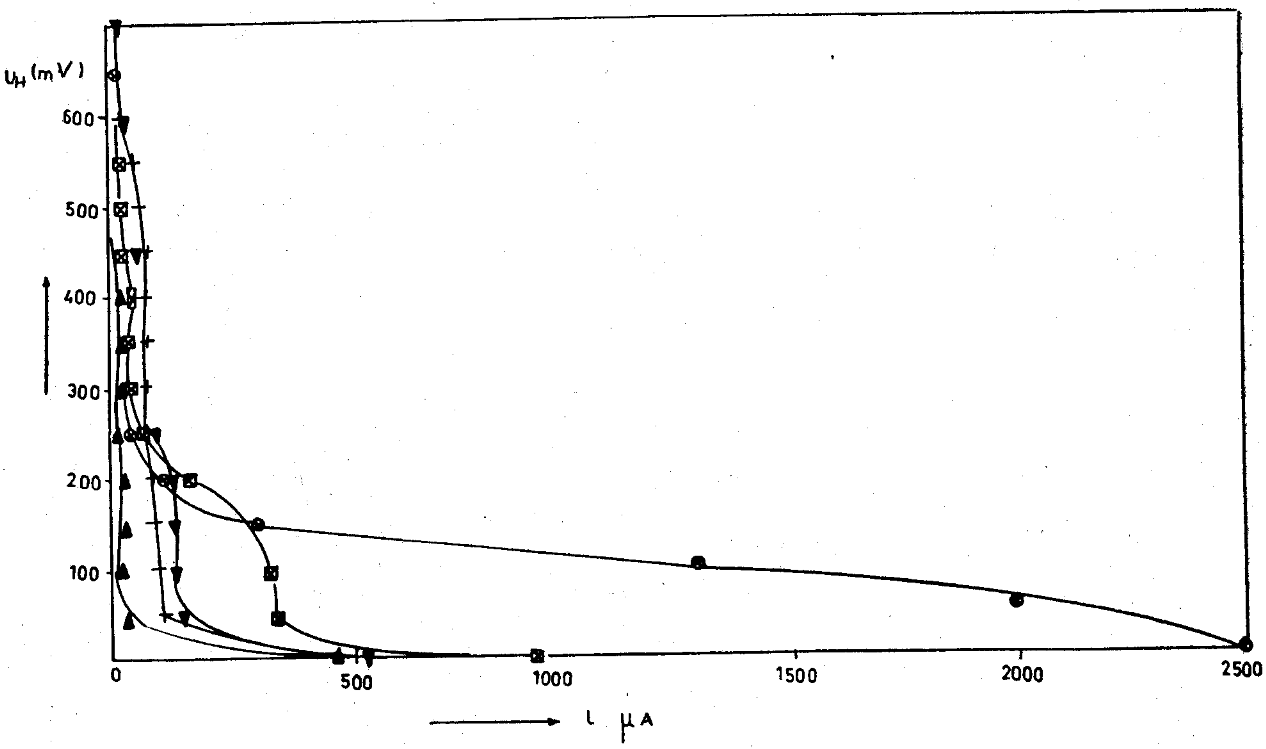

Fig. 2. Current - potential curves obtained with oxidized platinum electrode in acidic bichromate solutions for high bichromate concentrations ▲ 10^{-5} M $K_2Cr_2O_7$ + 1 N H_2SO_4, + $6x10^{-5}$ M $K_2Cr_2O_7$ + 1 N H_2SO_4, ▼ $8x10^{-5}$ M $K_2Cr_2O_7$ + 1 N H_2SO_4, ⊠ $2x10^{-4}$M $K_2Cr_2O_7$ + 1 N H_2SO_4, ⊗ 10^{-3} M $K_2Cr_2O_7$ + 1 N H_2SO_4.

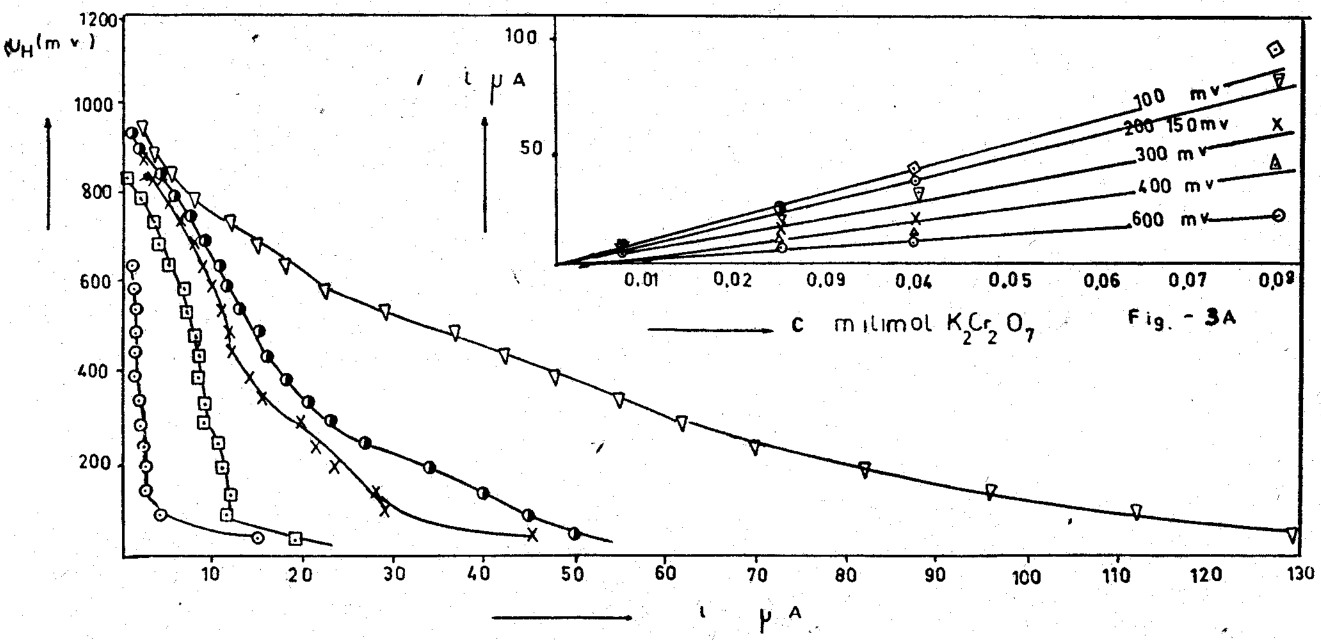

Fig. 3. Current - potential curves obtained with reduced platinum electrode in H_2SO_4 and acidic bichromate solutions ⊙ 1 N H_2SO_4, ⊡ 7.5×10^{-6} M $K_2Cr_2O_7$ + 1 N H_2SO_4, X 2.5×10^{-5} M $K_2Cr_2O_7$ + 1 N H_2SO_4, ◑ 4×10^{-5} M $K_2Cr_2O_7$ + 1 N H_2SO_4, ▽ 8×10^{-5} M $K_2Cr_2O_7$ + 1 N H_2SO_4.

Fig. 3. A. Limiting Current - concentration curves at various potentials for reduced platinum electrode

tential. But in the second step it continued to increase. If bichromate concentration was increased further this second step also drift to negative potential and a limiting current is not seen in the positive potential (figure 2).

Weiner (10), Müller (11) and Knorr (12) could not find out the potential steps with platinum electrode in the chromic acid solution, that have been indicated in this paper. The reason why they could not find out the potential steps is that they used concentrated chromic acid solution.

In the curves obtained with reduced platinum electrode in figure 3 current intensity and the begining potentials of the curves increased as the bichromate concentration is increased. This showed that the electrode is oxidized when it is inserted into the solution. In these curves there are two regions as in the oxidized platinum case. Between 650 and 300 mV current intensity increased a little with bichromate concentration. Between 300 and 100 mV it increased much more than the first. As the bichromate concentration increased, the transient of the potential from one region to another was gradual as in the case of oxidized platinum electrode. At each potential current intensity read from the current – potential curves that corrected for the portion of 1 N H_2SO_4 showed at the ordinate; and the concentration of bichromate as milimol in the apsisca in figure 4 and 3 A for oxidized and reduced electrodes respectively. As it is seen, current intensity is proportional with bichromate concentration in a short region between 650 and 300 mV ($6x10^{-5}$ M $K_2Cr_2O_7$). At less negative potentials the slopes of the lines are increased and proportionality becomes wider.

Hysteresis curves are obtained with reduced and oxidized electrodes in 1 N H_2SO_4 solution in order to indicate the properties of the film that formed on the electrode surface with cathodic reduction in bichromate solutions. Therefore, first oxidized and reduced electrodes polarized cathodically in 1 N H_2SO_4 from positive potential to the hydrogen discharge potential in the usual way all along the curve a, then without inturrupted the current, potential increased with the same speed and returned to the beginning potential all along the curve b.

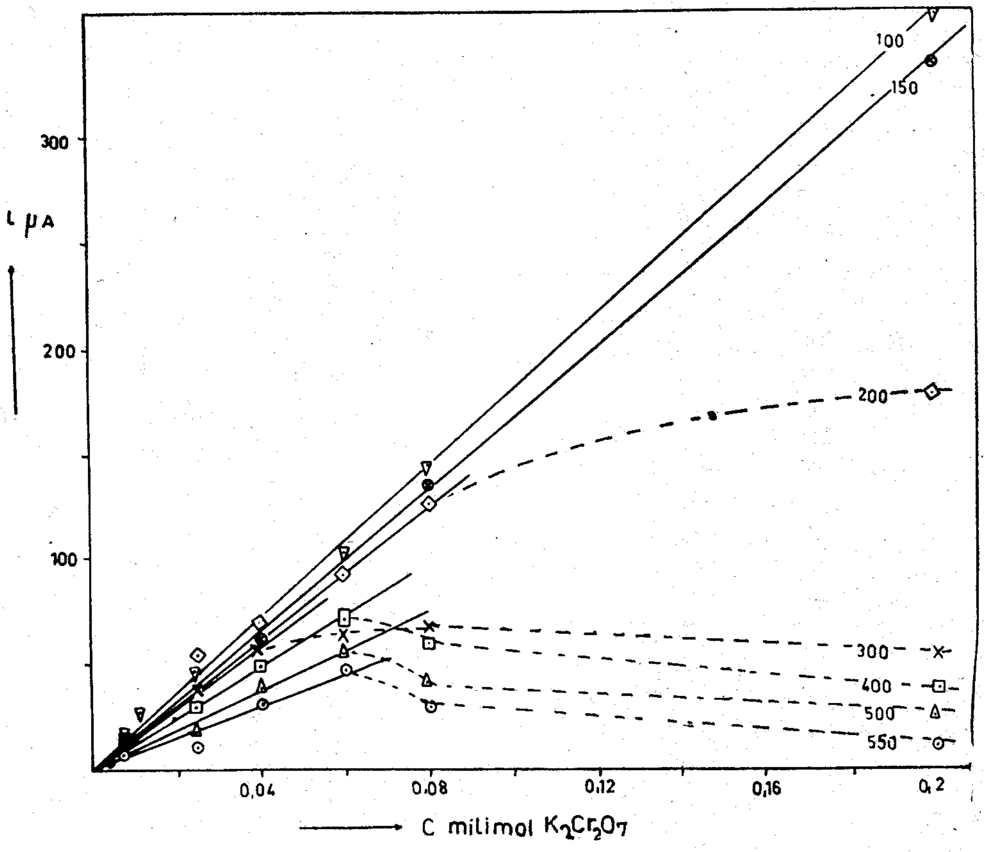

Fig. 4. Limiting current - concentration curve at various potentials for oxidized platinum electrode

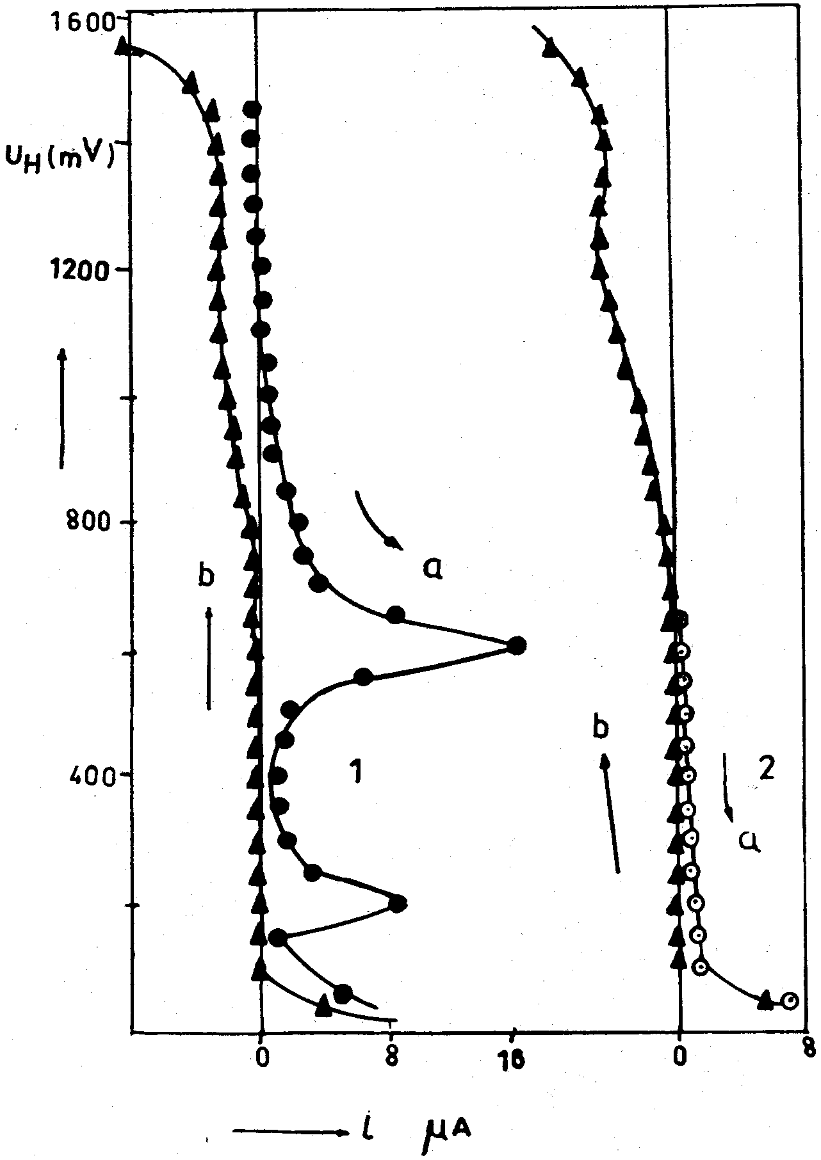

Fig. 5. Hysteresis curves obtained with oxidized (curve 1) and reduced (curve 2) platinum electrode in 1 N H_2SO_4 solutions

Fig (5) shows hysteresis curves otained in 1 N H_2SO_4 solution with reduced and oxidized platinum eletrode and also figure 6 and 7 show the curves obtained with oxidized and reduced platinum electrode in $7.5x10^{-6}$ M $K_2Cr_2O_7 + 1$ N H_2SO_4 respectively that returned from various potentials.As expected the return of the curves obtained with reduced electrode is almost the same as the curves of oxidized electrode.

The difference between oxidized and reduced electrode was removed going down to the zero mV with cathodic reduction. As it is seen from the curves as returned from the less positive potential the return of the curves overcomes the curve a. The reason for this may be the film formed by cathodic reduction changes the sturucture or electrode freed from oxide film. In less positive potentials the film on the electrode surface is to be convenient to penetrate current. If the hysteresis curves in figure 6 and 7 compared with the hysteresis curves obtained in 1 N H_2SO_4 solution that the film formed on electrode surface with cathodic reduction unhindered the chromate reduction. Because, the return of the curves obtained in sulfuric acid the passing current is zero μ A but in the case of bichromate solution it is 8 μ A. In this case, current rises only with bichromate reduction.

DISCUSSION

Feigl, Kandler and Reinhold (13) established that current intensity is proportional with the chromic acid concentration to the 0.24 molar at the second step on the current – potential curves obtained with gold electrode the calculated K value is 2.0 mA /cm^2 mili mol CrO_3 for limiting current. From the figure 4, K value for the limiting current for platinum at the second step is 4.2 mA / cm^2 mili mol $K_2Cr_2O_7$ is agreed with the value for gold electrode (2.1 mA / cm^2 mili mol CrO_3). From the agreement of K values we can say that the same phenomena occurred at the second step for both electrodes.

According to the above curves the beginning of the reduction potential of electrode metal oxides (550 - 500 mV) must be the film formation potential. The reason for limiting current is not pro-

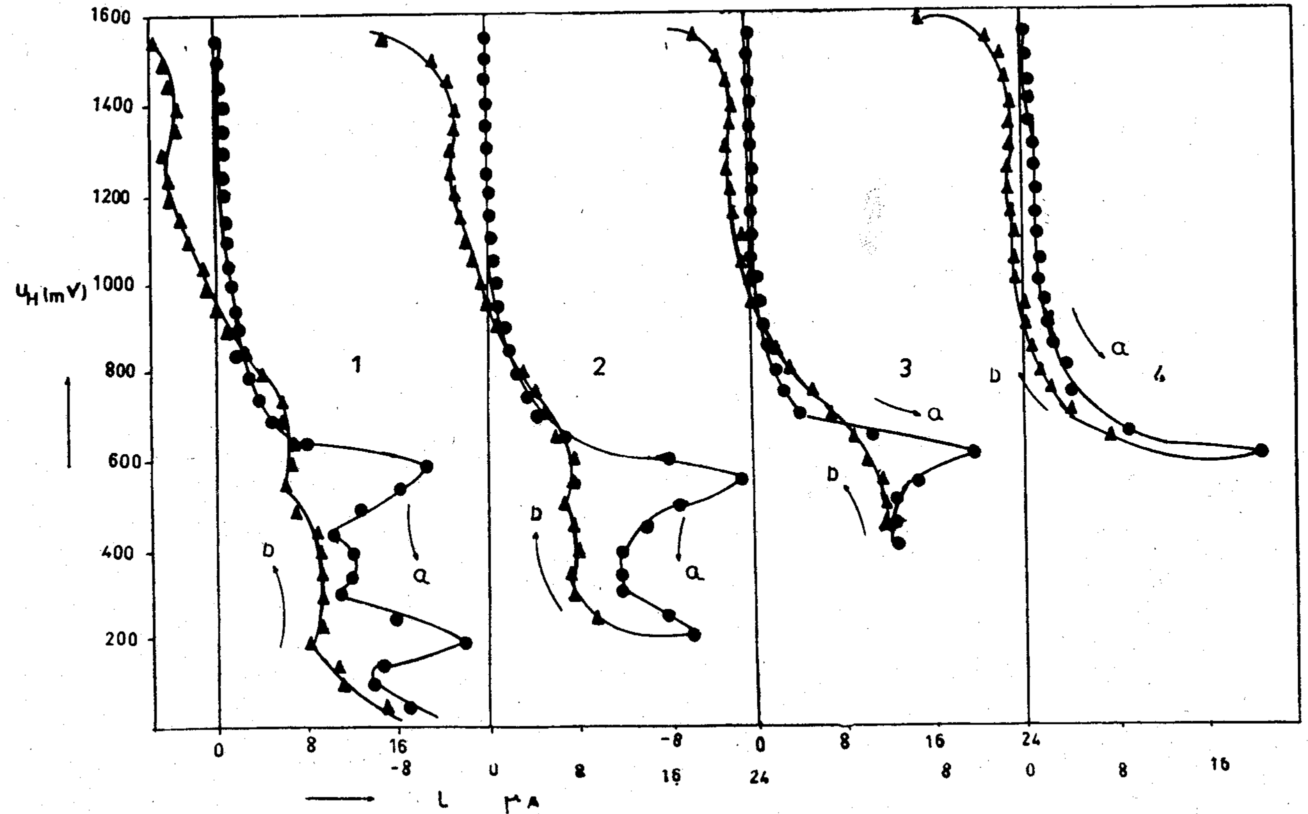

Fig. 6 Hysteresis curves obtained in 1 N H_2SO_4 + 7.5×10^{-6} M $K_2Cr_2O_7$ solution with oxidized platinum electrode that returned from various potentials: Curve 1 from zero, curve 2 from 200, curve 3 from 400, curve 4 from 600 mV

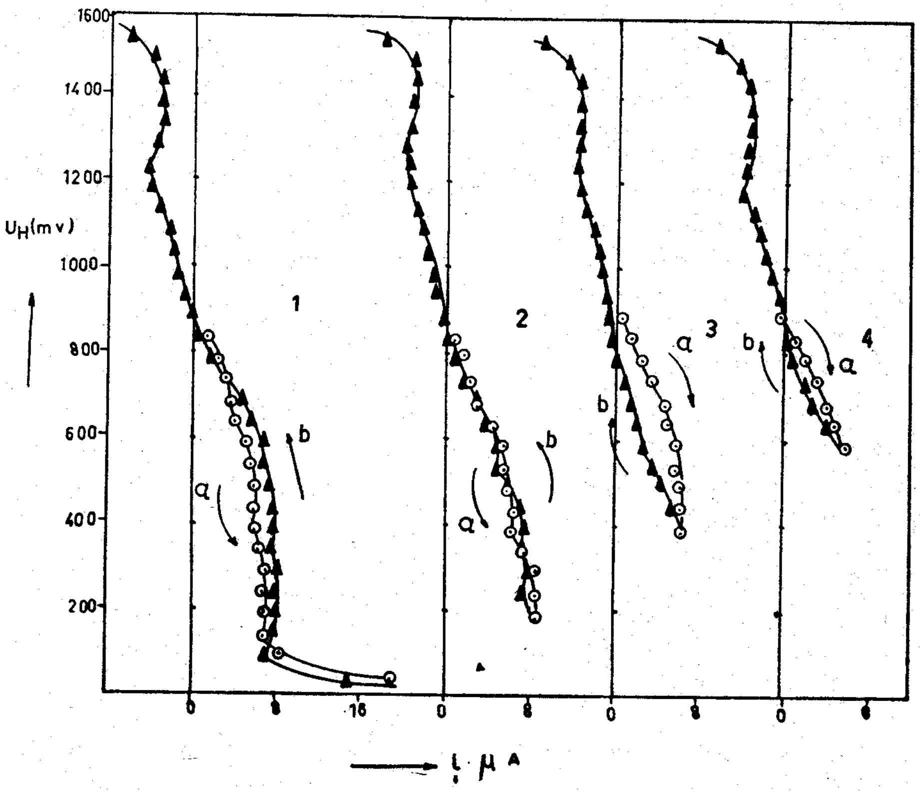

Fig. 7. Hysteresis curves obtained with reduced platinum electrode in 7.5×10^{-6}M $K_2Cr_2O_7$ + 1 N H_2SO_4 that returned from various potentials. Curve 1 from zero, curve 2 from 200, curve 3 from 400, curve 4 from 600 mV.

portional with bichromate concentration to high values , may be probably that during the bichromate reduction, reduction products and the metal oxides cover the electrode surface. One of our studies (14) showed that the film formed at the reduction potential of the metal oxide with experiments made in bichromate solutions contain radioactive H_2SO_4.

It was shown that film is to be convenient to penetrate current in less positive potentials then that in positive potentials.The slope of the lines increased (figure 4) and proportionality became wider. The reason may be that the metal oxides that covers the electrode surface with reduction products of bichromate reduced as it drops towards negative potential. The same results can be seen from the hysteresis curves. As can be seen at table (1) K values between 550 and 200 mV increases as the potential decreases, but between 200 and 100 mV it is stable.

According to Will and Knorr (15) hydrogen adsorption begins after 400 mV on platinum electrode, therefore, the oxide film does not present on the electrode from this potential. Then the film may be mixed, with metal oxides to the 400 mV and between 200 and 100 mV composed only bichromate reduction products. Film changes its sturucture between 400 and 200 mV. Gerischer(16) determined with electron diffraction that the film formed on electrode with cathodic polarization changes its sturucture. Weiner and Schiele (17, 18) discovered from the electron micrographs that two kinds of film are present at the same time on the electrode and one film can be change to another one. In addition Weiner (19) investigated the film with electron difraction and found from the difraction lines that the film composed with electrode metal, metal oxides and Cr_2O_3. So,these findings supported our conception that chromate reduction takes place at the reduction potential of metal oxide.

The phenomena that takes place on the reduced platinum electrode is the same as on the oxidized platinum electrode. The reason that the curves differ from each other is that the oxide film that is formed on the electrode surface by anodic polarization is thicker then the film formed by dipping electrode in bichromate solution (20). With reduced platinum electrode current intensity began to rise more positive potential the oxidized platinum electrode case. Therefore the oxide film is thin and wants less overtention than the anodically oxidized platinum electrode case. In the reduced platinum electrode case as in the oxidized state K values increased between 600 and 300 mV and got stable between 200 and 100 mV, (table 1).

Table 1

K Values (mA/cm² milimole $K_2Cr_2O_7$) in various potentials for oxidized and reduced platinum electrode

mV	oxidized	reduced
600	—	0.7
550	2.2	—
500	2.7	1.2
400	3.2	1.4
300	3.5	1.9
200	4.2	2.5
150	4.2	2.5
100	4.5	2.8

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ÖZET

Bu çalışmada bikromatın katodik redüksiyonu hidrojen çıkışı potansiyeline kadar, potonsiyostatik olarak incelenmiştir. Akım potanşiyel eğrileri hem redüklenmiş hem de oksitli elektrotlarla elde edilmiştir. Platin elektrot üzerinde bikromat redüksiyonunun platin oksidin redüksiyonu potansiyelinde cereyan ettiği gösterilmiştir. Pozitif potansiyel bölgesinde görülen basamaklardaki sınır akımları, düşük konsantrasyonlarda bikromat konsantrasyonu ile orantılıdır. Konsantrasyon arttıkça basamaklar daha negatif potansiyellere kaydığı gibi, limit akımı da birinci basamakta azalmaktadır.

Ayrıca, 1 N H_2SO_4 ve asitli bikromat çözeltilerinde redüklenmiş ve oksitli platin elektrot ile histerizis eğrileri elde edilmiştir. Bu çalışmalardan, elektrot üzerinde teşekkül eden filmin asitli ortamda kromat redüksiyonunu önleyemediği ve katodik redüksiyon esnasında yapısını değiştirdiği neticesi çıkarılmıştır.

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