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The Investigation of Chromate Reduction With Rhodium and Iridium Electrodes

by

M. KABASAKALOLU and S. ÜNERİ

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The Investigation of Chromate Reduction With Rhodium and Iridium Electrodes*

M. KABASAKALOĞLU and S. ÜNERİ

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

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In this work, the cathodic reduction of chromate ion with rhodium and iridium electrodes in acidic bichromate solution was investigated. For this purpose, cathodic polarization curves were obtained through an electronic potentiostat with oxidized and reduced electrodes in 1 N H_2SO_4 and together with various concentrations of $K_2Cr_2O_7$. In each electrode chromate reduction occurred at the reduction potential of the metal oxide in 1 N H_2SO_4. According to other investigators practically no chromate reduction occurs at the positive potentials and it drifts toward the negative side where the hydrogen discharge take place. In this work, a potential step which is related to the chromate reduction in the positive potential region was found. This step drifts to the negative potential when bichromate concentration is increased.

It was shown that the limiting current was proportional with the bichromate concentration in a definite region. Particularly with iridium electrode, these proportionalities are effective only around very small concentration region.

In addition, hysteresis curves were obtained with oxidized and reduced iridium and rhodium electrodes in 1 N H_2SO_4 + 7. 5.10^{-6} M $K_2Cr_2O_7$ and 10^{-3} N H_2SO_4 + 7. 5.10^{-6} M $K_2Cr_2O_7$ + 1 N Na_2SO_4 solutions.

In these studies, it was concluded that the film formed by cathodic reduction on the electrode surface and it has different composition and thickness in acidic and weak acidic solutions.

INTRODUCTION

In our previous study (1) it was shown that platinum, rhodium and iridium electrodes do not behave as noble metals in oxidizing media. Their surfaces get oxidized. In addition, chromate reduction was investigated with platinum electrode (2) it was also po-

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† Mailing adress: Ankara Üniversitesi, Fen Fakültesi, Fiziko-Kimya Kürsüsü, Ankara, Turkey.

inted out that bichromate reduction took place at the same potential with the reduction of metal oxide. Moreover, the film formed by cathodic polarization contain electrode metal oxide (2,3).

The apparatus and chemicals used in the experiments and the pretreatment of the electrodes were the same as the previous study (1,2). Current-potential curves were obtained with both oxidized and reduced electrodes.

CONCLUSION

a) Rhodium

At first the reduction potential of the oxide film formed by anodic polarization and the dependence of this reduction potential on the acid concentration were investigated. The reduction potentials of oxide film was decreased approximately 50 mV per unit pH, but the shape of the curve did not change. In addition, maximum current-intensity at the reduction potential steps was independent of pH, (Fig 1). Vetter and Bernt(4) arrived at the same

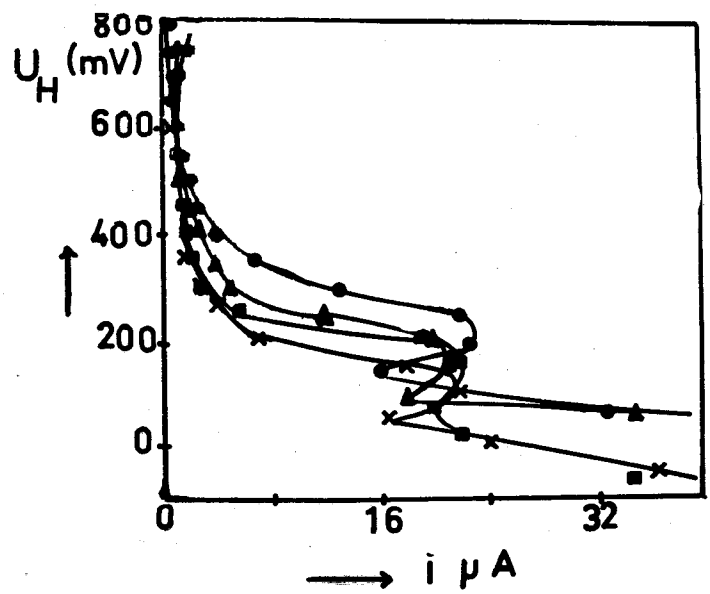

Fig. 1. Current-potential curves obtained with oxidized rhodium electrode in various H_2SO_4 concentration.

● 1 N, ▲ 0.1 N, ■ 0.01 N, × 0.001 N

conclusions for platinum, palladium and gold electrodes. Cathodic polarization curves obtained with oxidized and reduced rhodium electrodes in 1 N H_2SO_4 and acidic bichromate solutions are shown in fig 2, 2 A and in fig 3 respectively. In fig 2 A the curves of oxidized rhodium electrode between 800 and 1400 mV are shown. As is seen from fig 2 and 2 A, these curves start with 1400 mV, after the slight maximum at 1100 mV the current intensity decreases to 500 mV and it increases again to a maximum at 200 mV, then it increases very sharply around the hydrogen region. The potential step at around the 1100 mV is in good agreement with the rest potential of rhodium electrode in 1 N HNO_3 and it is also in agreement with the potential step on the potential time-curve obtained with oxidized rhodium electrode in 1 N H_2SO_4 as was indicated in our previous study (1).

From this point of view, this step should correspond to the reduction of one of the oxide of rhodium.

The potential step at 300 mV in the current-potential curve obtained in 1 N H_2SO_4 in Fig 2 also exists in the cathodic polarization curves obtained by other investigators, who exercised different methods and this step is attributed to the reduction of the oxygen film which is formed by anodic polarization (5-7). As is seen from fig 2 the shape of the curves obtained with oxidized rhodium electrode in the solution of low bichromate concentration is the same as the curve obtained with oxidized rhodium electrode in 1 N H_2SO_4, but only the current intensity increases. Therefore, the reduction of bichromate takes place at the reduction potential of rhodium oxide. While the bichromate concentration is increased, the step drifts to the negative potential as in the case of platinum (2). In the concentrated bichromate solution limiting current was not obtained in the positive potential region. This is shown with the curve obtained in 10^{-3}M $K_2Cr_2O_7$ + 1 N H_2SO_4 solution in fig 4.

The curves obtained with reduced rhodium electrode in 1 N H_2SO_4 and acidic bichromate solution are shown in Fig. 3. In Fig 5 and 6 current-concentration curves are shown, for oxidized and reduced rhodium electrode. For this plot, the current in 1 N H_2SO_4 is subtracted from the current read at each potential and these

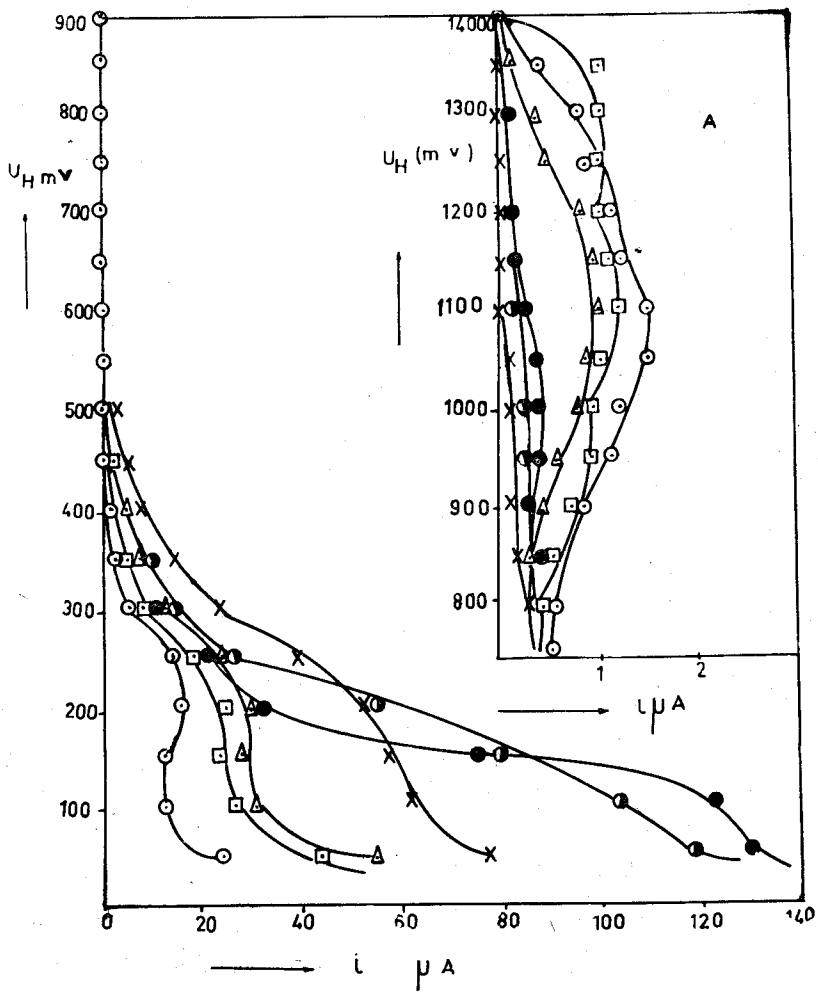

Fig. 2. Cathodic polarization curves obtained with oxidized rhodium electrode in N H_2SO_4 and in addition of various concentration of bichromate.

Fig. 2. A. The curves of oxidized rhodium electrode between 800 and1400mV. ⊙ 1 N H_2SO_4, ⊡ 1 N H_2SO_4 + $7.5.10^{-6}$M $K_2Cr_2O_7$, △ 1 N H_2SO_4 + 10^{-5}M $K_2Cr_2O_7$, × 1 N H_2SO_4 + $2.5.10^{-5}$M $K_2Cr_20_7$, ◑ 1 N H_2SO_4 + 4.10^{-5}M $K_2Cr_2O_7$ ● IN H_2SO_4 + 6.10^{-5} M $K_2C_2O_7$

values are plotted at the ordinate versus bichromate concentration.

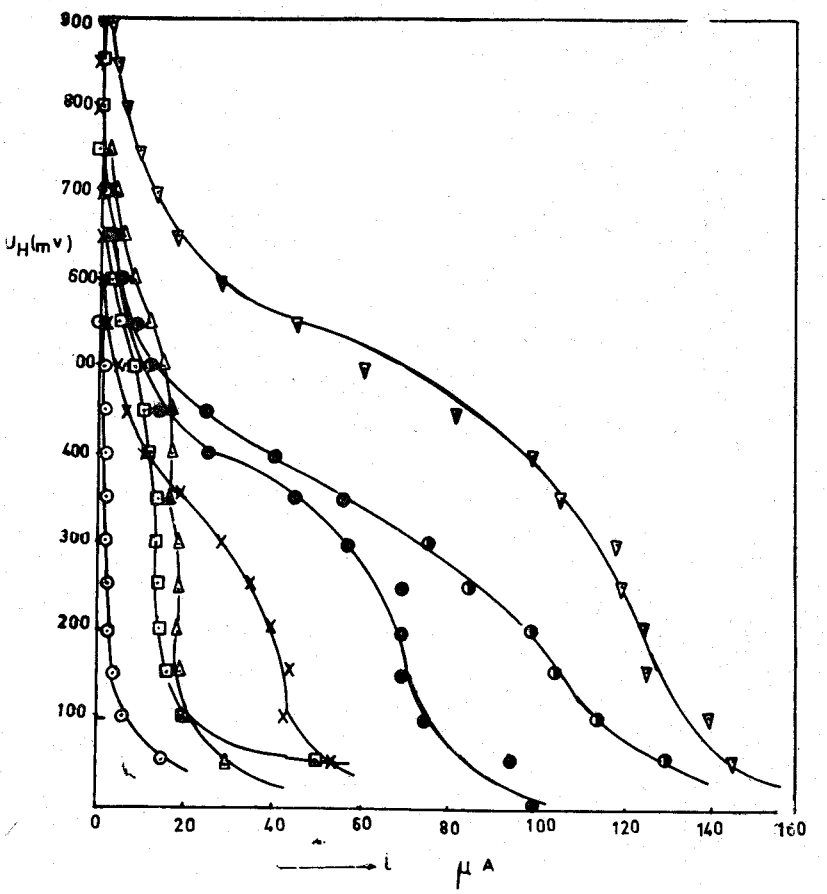

Fig. 3. Cathodic polarization curves obtained with reduced rhodium electrode in 1 N H_2SO_4 and in addition of various concentration of bichromate.

⊙ 1 N H_2SO_4, ⊡ 1 N H_2SO_4 + $7.5.10^{-6}$M $K_2Cr_2O_7$, △ 1 N H_2SO_4 + 10^{-5}M $K_2Cr_2O_7$, × 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 $K_2Cr_2O_7$

The slopes of the various lines for different concentrations are listed in Table I with the values of platinum electrode (2) for comparison. As the potentials decreases, the slopes of the lines are increased and proportionality becomes wider as in the case of

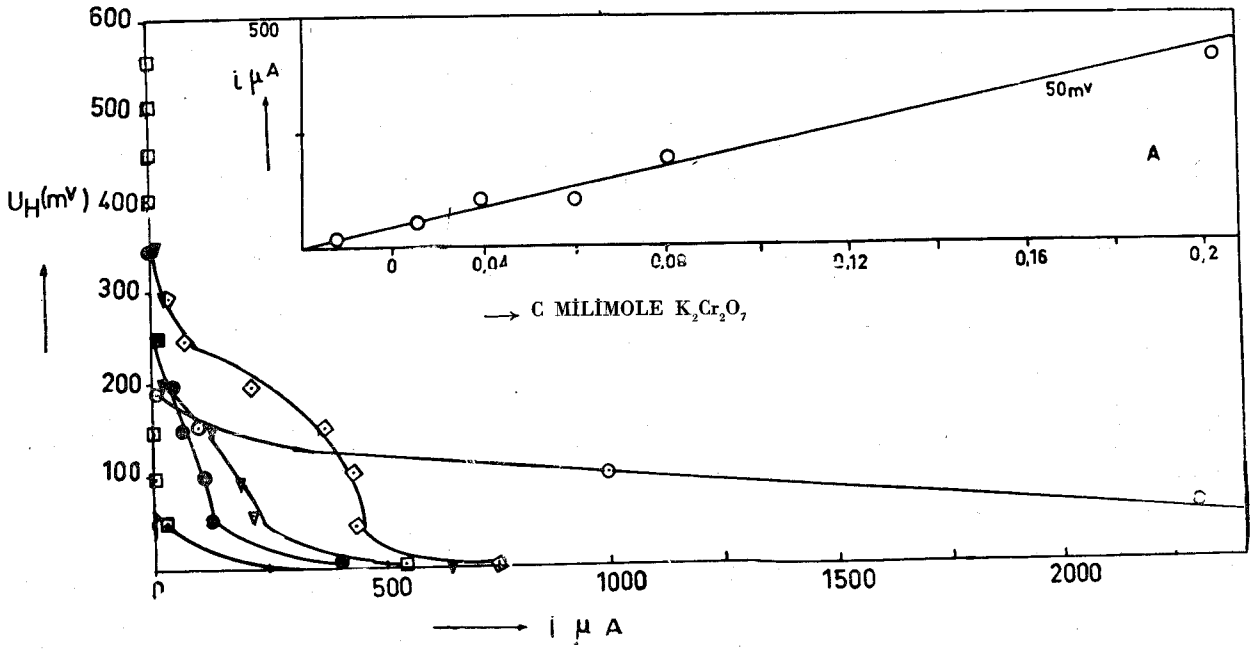

Fig. 4.Cathodic polarization curves obtained with oxidized rhodium electrode in concentrated bichromate solution.
□ 1 N H_2SO_4 + 10^{-5}M $K_2Cr_2O_7$, ● 1 N H_2SO_4 + 6.10^{-5}M $K_2Cr_2O_7$, ▽ 1 N H_2SO_4 + 8.10^{-5}M $K_2Cr_2O_7$, ◈ 1 N H_2SO_4 + 2.10^{-3}M $K_2Cr_2O_7$, ⊙ 1 N H_2SO_4 + 10^{-3}M $K_2Cr_2O_7$

Fig. 4. A. Limiting current- concentration curve for oxidized rhodium electrode at 50 mV.

platinum. The agreement of K values for platinum and rhodium shows that the same reactions take place at both electrodes. Feigl, Kandler and Reinhold (8) established that current intensity is proportional with the chromic acid concentration of 0 .24 molar at the second step on the current-potential curves obtained with gold electrode of which the calculated K value is 2.0 mA/cm² milimole CrO_3. Whilst in our study it was found that the K values for platinum and rhodium at the second step are 4.2 mA/cm² milimole $K_2Cr_2O_7$ is in agreement with the value for gold electrode, (2.1 mA/cm² milimole CrO_3).

TABLE I.

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

mV	Platinum oxidized	Electrode reduced	Rhodium oxidized	Electrode reduced
600	—	0.7		
550	2.2	—		
500	2.7	1.2		
400	3.2	1.4		
300	3.5	1.9	1.5	—
250			2	2.8
200	4.2	2.5	2.9	3.2
150	4.2	2.5	3.4	3.2
100	4.2	2.8	4.4	3.2
50	—	—	4.5	—

DISCUSSION

As it can be observed in fig 2 A, the current intensity at the potential step at 1100 mV is not proportional with the bichromate concentration and it also diminishes. Probably the rhodium oxide which is formed on the rhodium electrode during the anodic polarization is reduced to the oxide with the lower oxidation state on the one hand, on other hand the reduction products of bichromate reduced at the same time with the oxide cover the electrode surface. So, the current decreased intensity increases again at 400 mV and reaches to a maximum value at the 250 mV. At this second step, also electrode surface covered by the thin film which is more convenient for the bichromate reduction, after the reduction of other oxide continues the bichromate reduction. In addition, as it is seen in table I the calculated slope of the oxidized

platinum electrode (2) between (550-300 mV) is in agreement with the calculated slope of the oxidized rhodium electrode between 250-200 mV. As is shown in one of the previous works (3) by using radioactive H_2SO_4, the film formed at the reduction potential of platinum electrode at 550 mV. As in the case of rhodium, between 250-200 mV, a film composed with metal oxide and bichromate reduction products is formed. Also, the calculated slope between 300 and 400 mV for the oxidized platinum electrode is in agreement with the calculated slope of the oxidized rhodium electrode between 200 and 150 mV. Considering the agreement of the K values, we can conclude that the some reaction occurres between 200 and 150 mV at the platinum electrode and between 100 and 50 mV at rhodium electrode.

As is seen in fig 3 the current begins to increase at the higher potentials in the curves of the reduced rhodium electrode with respect to the oxidized rhodium electrode curves. Because the oxide film formed on the electrode surface by dipping the reduced electrode into the bichromate solution gets thinner then the one which is formed by anodic polarization and it requires less overthe voltage for reduction (10).

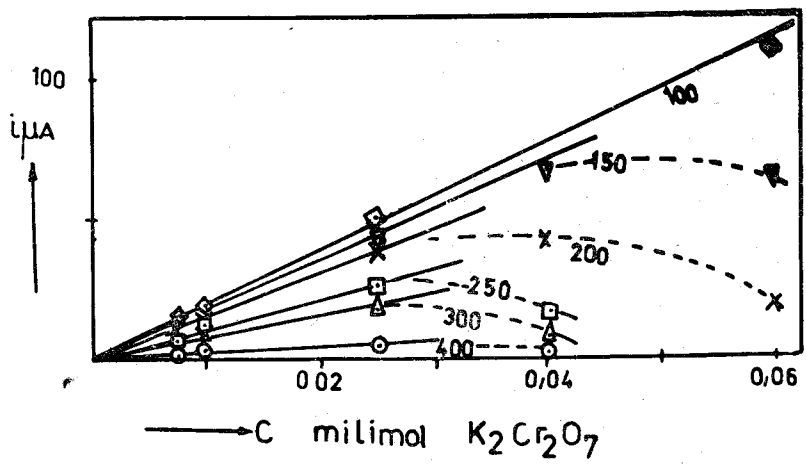

Fig. 5. Current-concentration curve for oxidized rhodium electrode at various potentials.

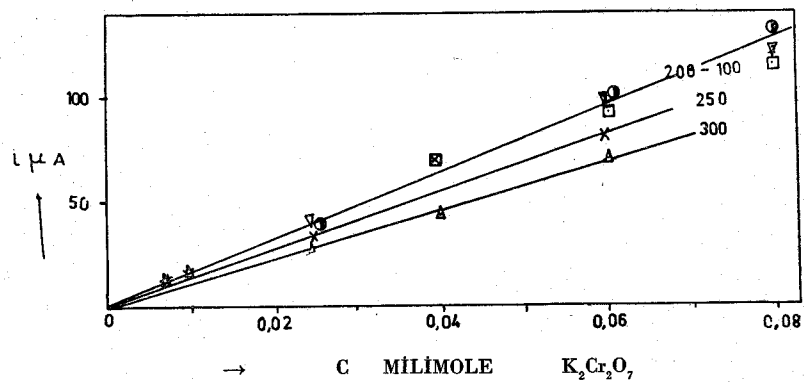

Fig. 6. Current-concentration curve for reduced rhodium electrode at various potentials.

b. Iridium

The curves obtained with oxidized and reduced iridium electrodes are shown in figures 7 and 8 respectively. The 1400-700 mV interval of the curves in fig 7 are shown again in fig 7 A. These curves start with 1400 mV and exibit two small maximums at 1100 mV and 900 mV respectively. The current begins to increase after 700 mV and makes a limiting current around 300 mV and again increases in hydrogen region. These potential steps which are seen on the current potential curves in fig 7 are seen in the cathodic polarization curves obtained with others (5-7) in H_2SO_4 and $HClO_4$. The steps in the first curves obtained in low bichromate concentrations (4.10^{-6}, 6.10^{-6}, $7.5.10^{-6}$) are 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. Therefore bichromate reduction must take place at the reduction potential of the iridium oxides in 1 N H_2SO_4.

In fig. 9 limiting current-concentration curve is shown for oxidized iridium electrode at 300 mV. Current intensity is proportional with bichromate for low conncentration region. The current does not increase further by bichromate concentration in the iridium electrode as it is in platinum (1) and rhodium electrodes case. When bichromate concentration is increased further the shape of the curve changes and the limiting current is not seen at the second step. The curve obtained in 10^{-3} M $K_2Cr_2O_7$ +

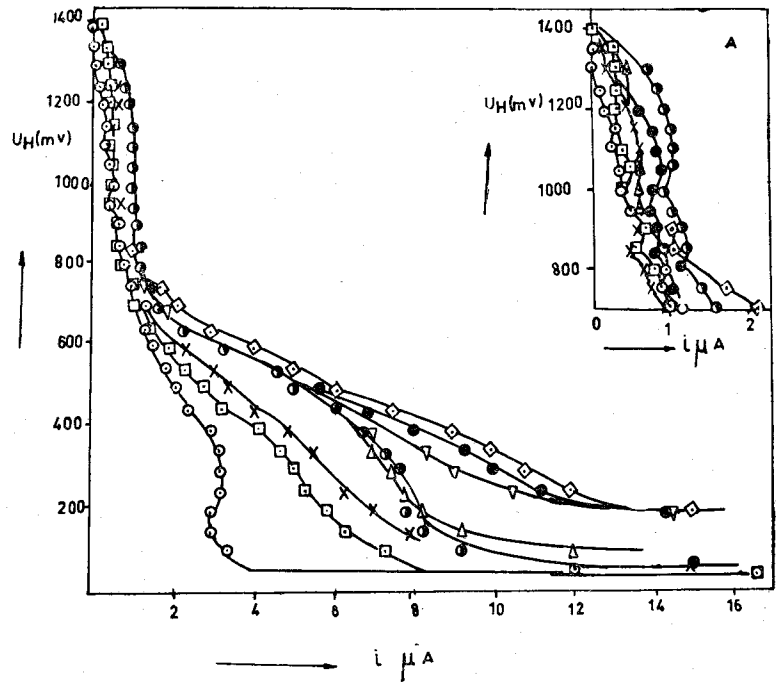

Fig. 7. Cathodic polarization curves obtained with oxidized iridium electrode in 1 N H_2SO_4 and in addition of various concentration of bichromate

Fig. 7 A. The curves of oxidized iridium electrode between 700 and 1400 mV.

⊙ 1 N H_2SO_4 , ⊡ 1 N H_2SO_4 + 4.10^{-6}M $K_2Cr_2O_7$, × 1 N H_2SO_4 + 6.10^{-6}M $K_2Cr_2O_7$, ◑ 1 N H_2SO_4 + $7.5.10^{-6}$M $K_2Cr_2O_7$, △ 1 N H_2SO_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 + 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 is almost equal to the curve obtained in 8.10^{-5}M $K_2Cr_2O_7$ + 1 N H_2SO_4 , as is seen in the curve in fig 8 obtained by reduced iridium electrode, while bichromate concentration is increased, the difference in the second step between oxidized and reduced iridium electrode disappeares. The shape of the curve after 800 mV obtained in 1 N H_2SO_4 + 10^{-3} M $K_2Cr_2O_7$ with oxidized electrode is identical with the curve for reduced iridium electrode in the same solution.

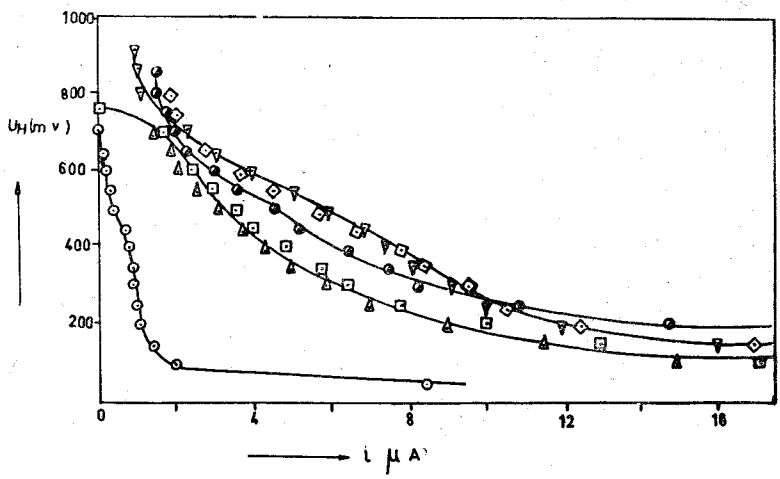

Fig. 8. Cathodic polarization curves obtained with reduced iridium electrode in 1 N H_2SO_4 and in addition of various concentration of bichromate.

⊙ 1 N H_2SO_4, ⊡ 1 N H_2SO_4 + $7.5.10^{-6}$ M $K_2Cr_2O_7$, △ 1 N H_2SO_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 + 2.10^{-4} M $K_2Cr_2O_7$, ▽ 1 N H_2SO_4 + 10^{-3}M $K_2Cr_2O_7$

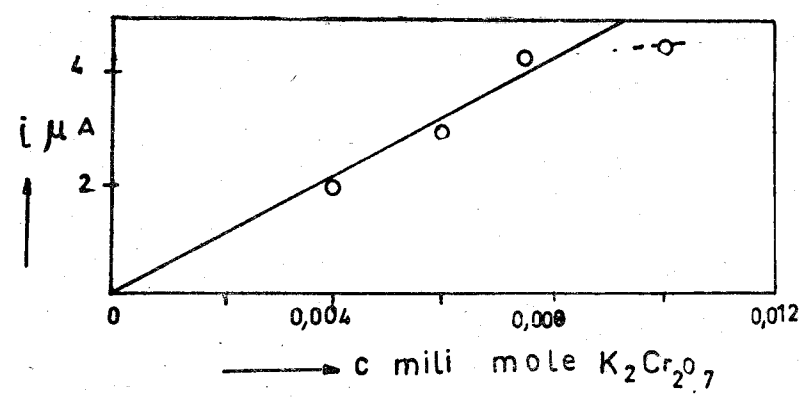

Fig. 9. Current-concentration curve obtained for oxidized iridium electrode at 300 mV

As is seen in the curves in fig 8 obtained by the reduced iridium electrode the current does not change too much by the bichromate concentration.

DISCUSSION

According to Will and Knorr (5) and Boeld and Breiter (6) who determined the maximums of the curves of the anodic oxidation and cathodic reduction at the same potential, in H_2SO_4 and $HClO_4$, the formation and the reduction of the oxide layer on iridium electrode are reversible. As is seen in fig 7 and 7 A the current began to increase from 1275 mV; this potential is the rest potential of the iridium electrode in 1 N H_2SO_4+0.125 M $K_2Cr_2O_7$.

However during the passage of the current, the oxide film on the iridium electrode formed by anodic polarization is reduced at its formation potential on the one hand, bichromate is reduced on the other hand. Therefore a film is formed and it prevents the further increase of the current. Since the reduction of the oxide layer on the platinum and the rhodium requires overvoltage, bichromate reduction takes place at the more negative potential where the metal oxide begins to reduce. As in the case of iridium bichromate reduction starts at the value close to the equilibrium potential of the bichromate. The current maximums are seen between 1300-800 mV in fig 7 A. These should be related to the reduction of the iridium oxides which correspond to the rest potentials around 1250 mV and 1070 mV obtained by iridium electrode in the previous work (1). Probably, while the oxide layer is reduced by the reduction of the bichromate, the film should be formed at these potentials. The current increases again after 800 mV by the beginning of the reduction of the oxide at the potential which corresponds to the rest potential of iridium electrode in 1 N H_2SO_4. But the proportionality range of the current by the bichromate concentration is small with respect to platinum and rhodium. In this region bichromate is reduced electrolitically while it is reduced by oxidation of metal surface. At the same time the oxide which is formed by the effect of the oxidation of the bichromate on the metal surface can be reduced. As is seen from figure 7 the current goes proportionally with bichromate concentration around 300 mV until $7.5.10^{-6}$ molar bichromate.The current remains constant instead of increasing further probably the reduction rate of metal oxide is higher than the oxidation rate of the bichromate of the electrode surface.

In the curves obtained with reduced iridium electrode in figure 7, the achieved potential of the iridium electrode by dipping into the bichromate + H_2SO_4 solutions are around 800 mV which is close to the equilibrium potential of the Ir/IrO system. While bichromate concentration is increased, the increase of these potentials show that the electrode is oxidized.

The event which takes place at the reduced iridium electrode should be identical with the one which takes place at the oxidized iridium electrode after 700 mV. As is seen clearly from figures 7 and 8 both of them attain the same state after 700 mV.

HYSTERESIS CURVES

Hysteresis curves were obtained in order to indicate the proporties of the film which is formed in the rhodium and iridium electrodes in acidic and less acidic media. For this purpose oxidized and reduced rhodium and iridium electrodes polarized cathodically until zero mV in 1 N H_2SO_4. After this point without interrupting the current, potential was increased at the same rate and returned to the starting point.Fig 10A and B are obtained with oxidized and reduced rhodium electrodes in 1 N H_2SO_4 respectively. Fig 11 and 12 are obtained with oxidized and reduced rhodium electrodes in 1 N H_2SO_4 + 7.5 .10^{-6}M $K_2Cr_2O_7$ respectively and show the returns of the curves from various potentials. As is expected the returns of the reduced electrodes curves are the same as the returns of the oxidized electrode curves. In addition, the lower the potentials from which the returns made, the higher the returns of the curves are. The reason of this can be attributed to the change of the sturucture of the film. While going down to the lower potential, the film on the electrode surface becomes more available to the reduction of bichromate. Gerischer (10) established that film which is formed on gold electrode changes its structure with potential. Weiner and his coworkers (11,12) found that two kinds of films are present on the electrode and it is composed with electrode metal, metal oxide and Cr_2O_3. Their results support our view that bichromate reduction takes place at the reduction potential of metal oxide.

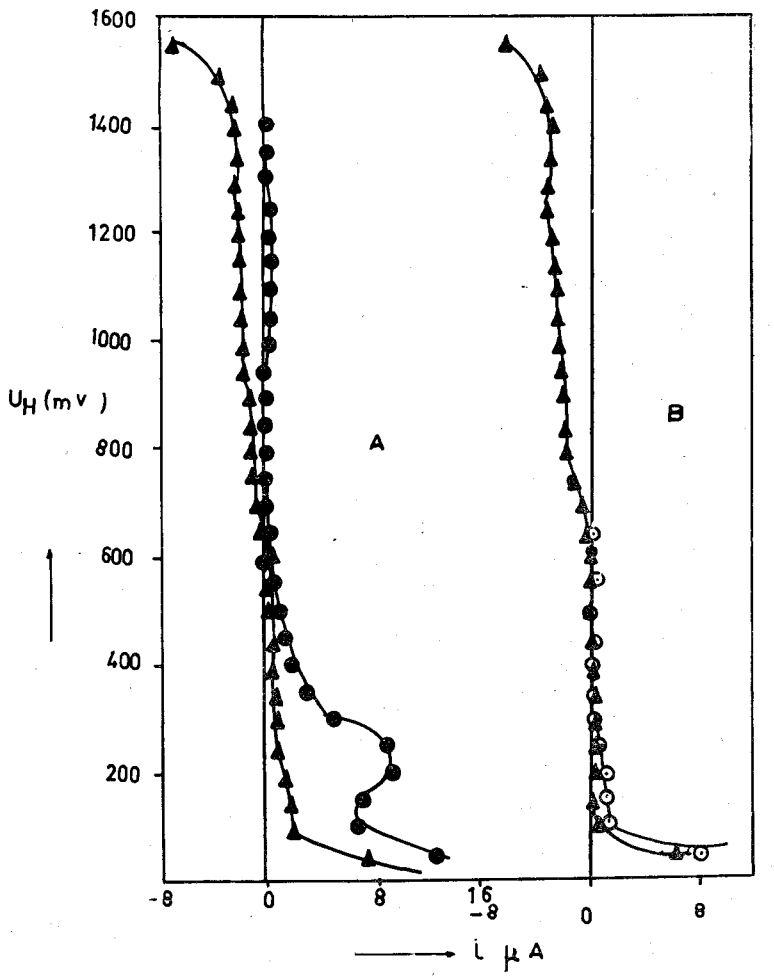

Fig. 10. Hysteresis curves obtained for rhodium electrode in 1 N H_2SO_4. A and B are for oxidized and reduced electrodes respectively.

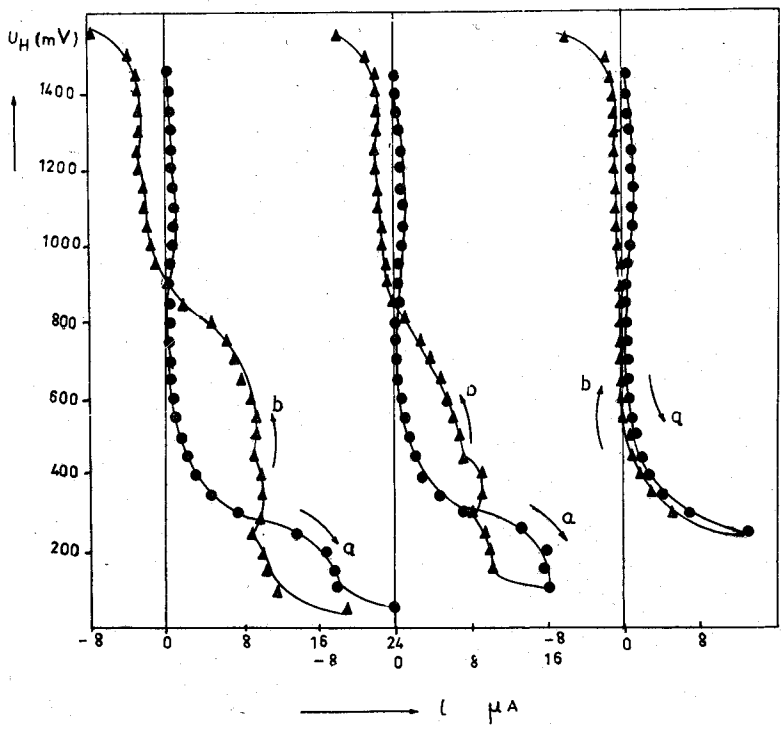

Fig. 11. Hysteresis curves obtained for oxidized rhodium electrode in 1 N H_2SO_4+7.5 10^{-3}M $K_2Cr_2O_7$ that show the returns of the curves from various potentials. Curve 1 from zero, curve 2 from 100, curve 3 from 300 mV.

If figures 11 and 12 are compared with figure 10, it is seen that the film is formed on the electrode surface in acidic medium by cathodic reduction, can not prevent the reduction of bichromate. In the case of bichromate the current is bigger while the current is around zero μ A at the returns of the curves obtained in 1 N H_2SO_4. At the return, the increase of the current can only be obtained by the reduction of bichromate. In order to investigate the proporties of the film formed in less acidic media, current potentials curves are obtained in 10^{-3}M H_2SO_4 + 7.5 10^{-6}M $K_2Cr_2O_7$ + 1 N Na_2SO_4. The proporties of the film depend on both foreign ion and acid concentration. For this reason the sulphate

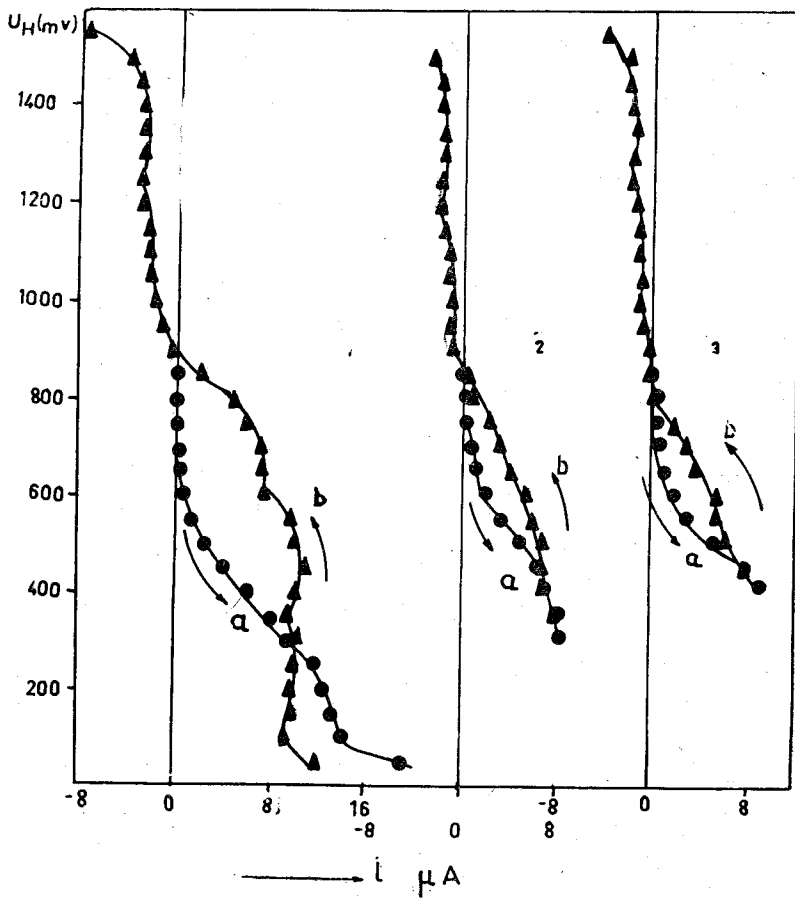

Fig. 12. Hysteresis curves for reduced rhodium electrode in 1 N H_2SO_4 + $7.5.10^{-5}$M $K_2Cr_2O_7$ that show the returns of the curves from various potentials.

Curve 1 from zero, curve 2 from 300, curve 3 from 400 mV.

ion concentration is kept constant fig 13. If these curves are compared with fig 11 and 12 it is clearly seen that they are different. All of the hysteresis curves, the return of the curve (b) goes lower than the normal polarization curve (a) and it shows obviously that the film formed in less acidic bichromate solution is not

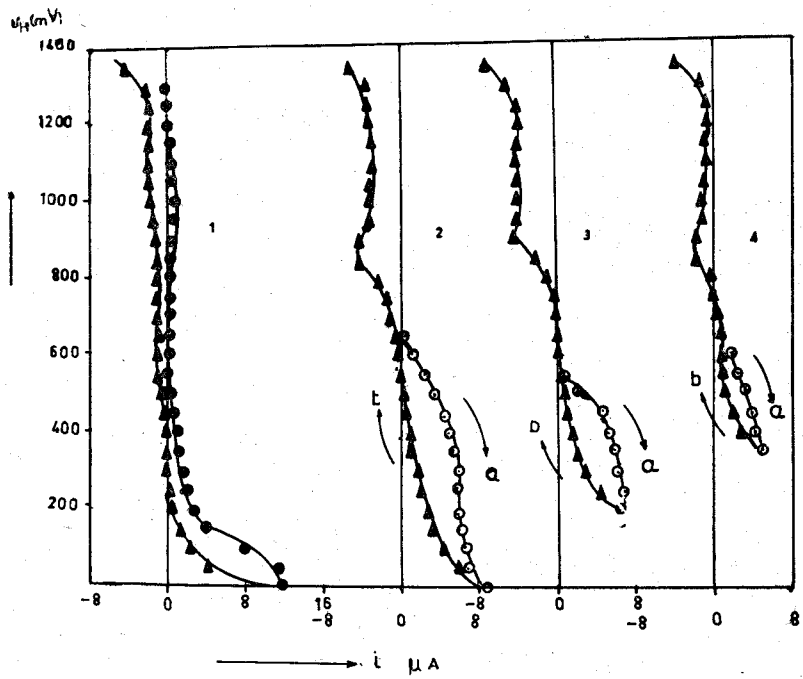

Fig. 13. Hysteresis curves for rhodium electrode in 0.001 N H_2SO_4 + 1 N Na_2SO_4+7.5 10^{-5} M $K_2Cr_2O_7$.

Curve 1 for oxidized electrode that returned from zero mV, curve 2, 3 and 4 for reduced electrode that returned from zero, 200 and 400 mV respectively.

convenient to transfer the current. Therefore the sturucture of the film depends on the pH. Same results are also obtained by other investigators. While the figures of hysteresis curves obtained with iridium electrode are different from rhodium, similar results can be deduced from these obtained figures.

CONCLUSIONS

1. The reason for the reduction of bichromate can not take place of the reduction potential of $Cr_2O_7^{=}$ / Cr^{3+} is that as the carbon electrode is a metal electrode covered by an oxide film in bichromate solution. That is, electrode becomes passive in bichromate solution.

2. If the results obtained with platinum, rhodium and iridium electrodes are compared, it is seen that iridium behaves differently from others. This can be explained by the fact that iridium is more noble than platinum and rhodium. The reduction of the oxide film formed on platinum and rhodium by anodic polarization requires over voltage, but iridium does not. Some investigators (5,14) have pointed out that the oxide layer formed by anodic polarization on each three metals are monomolecular. Therefore the reason of the reduction of oxide layer on iridium electrode does not require over voltage; this can be explained by the lower affinity of the iridium to oxygen with respect to other metals. Llopsis and Vazquez (15) have noticed that the iridium is more resisting to the corrosion than the platinum and rhodium.

3. If the reduction of bichromate takes place through the reduction of electrode metal oxide, current must be highest on the rhodium which is most easily oxidized. If bichromate reduction on reduced rhodium, platinum and iridium in the same concentrations are compared fig 14, it is seen that the current is the highest in the rhodium and the lowest in the iridium.

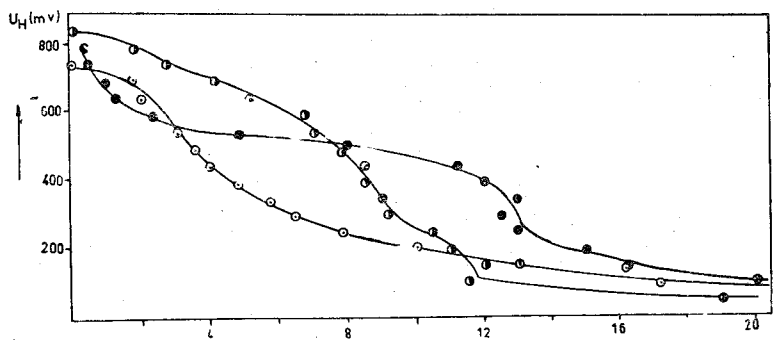

Fig. 14. Current-potential curves obtained with reduced ⊙ iridium, ◑ platinum and ● rhodium electrodes.

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ÖZET

Bu çalışmada rodyum ve iridyum elektrotlarla asitli bikromat çözeltisi içinde kromat iyonunun katodik redüksiyonu incelenmiştir. Bu maksatla oksitli ve redüklenmiş rodyum ve iridyum elektrotlarla 1 N H_2SO_4 de muhtelif konsantrasyonda bikromat ilâve ederek elde edilen çözeltiler içinde katodik polarizasyon eğrileri elde edilmiş, her iki elektrotta da metal oksitlerinin H_2SO_4 içindeki redüksiyon potansiyelinde kromatın redüklendiği gösterilmiştir. Daha önce başka araştırıcılara göre rodyum ve iridyum elektrotlarla pozitif potansiyellerde kromat redüksiyonunun pratik olarak cereyan etmediği doğruca hidrojen basamağına atladığı görülmekte iken bu çalışma küçük akım şiddetlerinde bir basamak elde edilebileceğini göstermiştir. Bu basamaklar fazla bikromat konsantrasyonu ile daha negatif potansiyele kaymaktadır. Pozitif potansiyelde gerek oksitli ve gerekse redüklenmiş elektrotlarla, sınır akımının belirli bir konsantrasyon bölgesine kadar kromat konsantrasyonu ile orantılı olarak arttığı gösterilmiştir. Bu orantılılık sınırı iridyum elektrotla çok küçük bir konsantrasyon bölgesinde sona ermektedir. Ayrıca 1 N H_2SO_4, 1 N H_2SO_4 + 7, 5.10^{-6} M $K_2Cr_2O_7$, 10^{-3} N H_2SO_4 + 7, 5.10^{-6} M $K_2Cr_2O_7$ + 1 N Na_2SO_4 çözeltileri içinde oksitli ve redüklenmiş elektrotlarla muhtelif potansiyellerden geri dönüş eğrileri elde edilmiştir.

Bu incelemelerden, az asitli ve çok asitli ortamlarda elektrot yüzeyinde teşekkül eden filmin kalınlığının ve bileşiminin farklı olduğu sonucu çıkarılmıştır.

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