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Potentiostatic Study of Ruthenium Electrodes in Acidic Media*

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Potentiostatic polarisation curves of ruthenium in solutions of nitric, sulphuric and perchloric acids have revealed two new steps at 600-800 mV and at 1200 mV which have not been observed by previous workers. Five steps were observed altogether and comparison of potential steps with those obtained by previous workers indicates the following formation potentials (mV) 450-550 RuO; 600 - 800, hydrated Ru_2O_3; 900 - 1050, Ru_2O_3 / RuO_2; 1200, RuO_2; 1300 - 1350, RuO_4.

INTRODUCTION

Whereas recent investigations have revealed that ruthenium can play an important part in hydrogenation processes (1) little in fact is known about the chemistry of ruthenium metal. The existance of such oxides as RuO and Ru_2O_3 have not yet to be established and simple salts of Ru^{++} have not yet to be found. Such electrochemistry as has been attempted has produced disagreement as to the passivity potential and the hydrogen region.

Now the properties of the other platinum group metals have been faitfully examined (2, 3, 4) by determining their behaviour as electrodes in oxyacids at different potentials. We decided to

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use this technique to study ruthenium electrochemistry. Therefore we have obtained the potentiostatic polarisation curves of ruthenium in solutions of nitric, sulfhuric and perchloric acids. The potentials at which oxides were formed and reduced were noted and their values were compared with those predicted by theory.

EXPERIMENTAL

Potentiostatic polarization curves were obtained with a Wenking Breitband Model 61 RS electronic potentiostat. Measurements were carried out in a pyrex cell having three compartments. Throughout the experiments the solutions were stirred and freed from oxygen by the bubbling of nitrogen. Potentials were changed in steps of 50 mV every fifteen seconds and the corresponding current was read at the end of each step. The counter electrode was made of platinum while saturated calomel and PbO_2 / $PbSO_4$ electrodes were used as reference. The working electrode was composed of ruthenium wire 1 mm in diameter and 3 cm in length. During the construction of this electrode thick layer of ruthenium oxides were formed which prevented reproducible current-voltage curves. The shapes of the curves took their normal forms after about 40 runs. This phenomenon is shown in figure 1. Special attention was paid to the pretreatment of the working electrode. Our pretreatment method was to oxidise the electrode for fifteen minutes after it had attained a potential of 800, 1000, 1200, 1400 or sometimes 1600 (the formation potential of the highest valency oxide) mV.

Polarisation curves were also obtained with electrodes which were reduced for 30 minutes at potentials of 300 and 400 mV. Each curve given in the present study is the result of at least three experiments.

RESULTS AND INTERPRETATION

Cathodic polarization curves obtained with oxidised electrodes are shown in figure 2a. The initial potentials correspond to the rest potentials of the electrodes under the appropriate experimental conditions. The higher the potential at which the pretreatment oxidation was carried out, the higher the number of steps which were subsequently obtained on the cathodic polarization curves. When oxidation was carried out at low potentials (curve 490) only two reduction steps between 800 and 600 and between 450 and 250 mV were subsequently obtained. The third wave was seen between 1000 and 900 mV on the curve 492 in addition to these two waves. The curve 494, obtained with the electrode oxidized at 1200 mV, exhibited the forth step appeared between 1200 and 1100 mV together with these three steps. On the curve 496 obtained with the electrode oxidised at 1340 mV a fifth step could be seen at about 1340 mV.

The well defined limiting current concerning these five steps are seen on some of the curves. For all of these curves, the step between 800 and 600 mV, exhibited a well defined limiting current region in the potential range 600 – 450 mV. Whose magnitude were the same to within ± 1 μA. The curve 154 was obtained with an electrode oxidized at 1600 mV. Unlike the previous curves, this curve showed a decrease in current at about 1000 mV and did not show the third step in this region. The fourth step at about 1100 mV was clearly defined, however.

Curve 503 in figure 2b shows the anodic polarization in 1 N H_2SO_4 with the electrode which had been reduced at 400 mV. On immmersing the electrode in the solution there was a sudden increase in potential to 500 mV, the rest potential of ruthenium electrodes in 1 N H_2SO_4. The first step to be observed, occured in the region 500-600 mV. Most of the curves showed a decrease in current at 850 mV which was presumably due to the formation of a film on the electrode. The next step was seen at 950-1100 mV. A step near 1100 mV was observed in some experiments as a limiting current region but in others as a small decrease in current. The steps seen in the previous expreriments at 1200 mV and 1340 mV were again observed. After 1400 mV there was a marked increase in current due to the violent evolution of oxygen and the simultaneous formation of RuO_4.

The curves shown in figure 3a were obtained in 1 N $HClO_4$ with electrodes oxidised at 800, 1000, 1200 and 1600 mV. The pretreatment of the electrode was carried out in a second vessel which was also filled with 1 N $HClO_4$. There was no apparent difference between these curves and those obtained in 1 N H_2SO_4 under the same conditions, the only discrepancy being that whilst curve 639 (figure 3a) was obtained with an electrode which was preoxidised at 1400 mV and started from its rest potential of 1200 mV, curve 496 (figure 2a) was obtained with an electrode preoxidised at 1340 mV, started from a rest potential of about this value. Examination of figure 3a reveals steps at about 1200, 1000 - 900, 800 - 600 and 450 - 300 mV and a well defined limiting current region between 600 and 450 mV as on the curves in figure 2 a.

Curves 371 and 372 (Figure 3b) were obtained with electrodes which had been reduced at 300 and 400 mV respectively. Both curves have the same shape and show steps at about, 450-500, 700, 950, 1050 and 1200 mV. There is also decrease in current at about 850 mV, as on the curves in figure 2b.

Figure 4 shows curves obtained in 1 N HNO_3 with electrodes reduced at 800, 1000 and 1600 mV. The steps were observed at 1300, 1000 - 950, 600, 400 and 200 mV. Comparison of curves 185 and 569 shows that they both possess poorly defined limiting current regions but the magnitudes of these currents are very different. The limiting current region at 600 - 450 mV in figures 2a and 3a corresponds to that shown between 400 and 500 mV in figure 4.

Figure 5 displays the hysteresis curves obtained in H_2SO_4, HNO_3 and $HClO_4$ all curves show increases of current at approximately the same potentials. The curves show clearly that anodic and cathodic steps appeared at identical potentials, that is there was no overpotential.

CONCLUSION

Table 1 lists the step potentials obtained from all the curves discussed above. Those potentials can be grouped into five ranges. 1) 450-550, 2) 600 - 800, 3) 900 - 1050, 4) 1200-1300, 5) 1300-1350 mV and in addition, most curves show an increase in current between 200 and 350 mV. This increase corresponds to the step quoted in the literature (1,5) or occurring between 220 and 300 mV due to the adsorption or desorption of hydrogen. Although ruthenium has a greater ability to adsorb hydrogen than the other platinum group metals, the bonding energy of hydrogen with the metal surface is less. Thus the desorption of hydrogen from ruthenium ceases at a lower potential than in the case of platinum and the adsorption of hydrogen by ruthenium during cathodic polarization begins at a higher potential (6). Stoyanovskaya, Khomchenko, Vovchenko (7) studied the anodic charging curves of ruthenium electrodes in a solution of 1 N H_2SO_4 and identified a step at 800 mV as indicating the beginning of stable oxygen adsorbtion and anodic oxidation. On the other hand, Llopis and Coworkers (8, 9, 10) found that the adsorption of oxygen began to occur at 500 to 600 mV depending on the solution being studied. In our experiments the start of oxidation corresponded to the first step observed at 450 to 550 mV in reasonable agreement with the work of Llopis et al.

Nekrasov and Kruscheva (11) divided the layers obtained on ruthenium electrodes in alkaline solutions into two groups and proposed that the layers formed below 1000 mV were due to chemisorbed oxygen. Thus the layer formed between 450 and 550 mV in our experiments was RuO formed from chemisorbed oxygen. In the literature only Stoyanovskaya and Coworkers (7) has mentioned the step between 600 and 800 mV in their studies. But this potential region was represented as the beginning of stable oxygen adsorption. The Pourbaix diagram (12) shows that potentials of 600-800 mV lie in the Ru $(OH)_3$ region. The diagram also shows that the 900-1050 mV step falls in the domain of RuO_2. $2H_2O$ but it is also possible to see the effect of Ru_2O_3 in this region. In the study of Llopis and coworkers (8) this value was obtained as 1050 mV and interpreted as the formation potential of RuO_2. In the same study, according to the results obtained with the electrode pretreated at 1150 mV, formed layer at this potential was mentioned as a non-stokiometric oxide film and taken into account as a mixed oxide of RuO_2 and Ru_2O_3.

No previous worker appear to have observed the step at 1200 mV which can be attributed to the formation and reduction of RuO_2 (without involving Ru_2O_3).

The Pourbaix diagram (12) shows that the step at 1350 mV corresponds to the reduction potential of RuO_2 / RuO_4 and thus 1350 mV is the formation potential of RuO_4. Other investigators (13,6) also observed 1350-1400 mV to be the formation potential of RuO_4.

Table 1 summarises this discussion. It gives the formation potentials of the ruthenium oxides based on our studies and theoric and experimental data in the literature.

TABLE 1

Potential interval	Corresponding oxide
450 – 550 mV	Ru–O
600 – 800 mV	Hydrated Ru_2O_3
900 –1050 mV	Ru_2O_3 /RuO_2
1200 mV	RuO_2
1300 –1350 mV	RuO_4

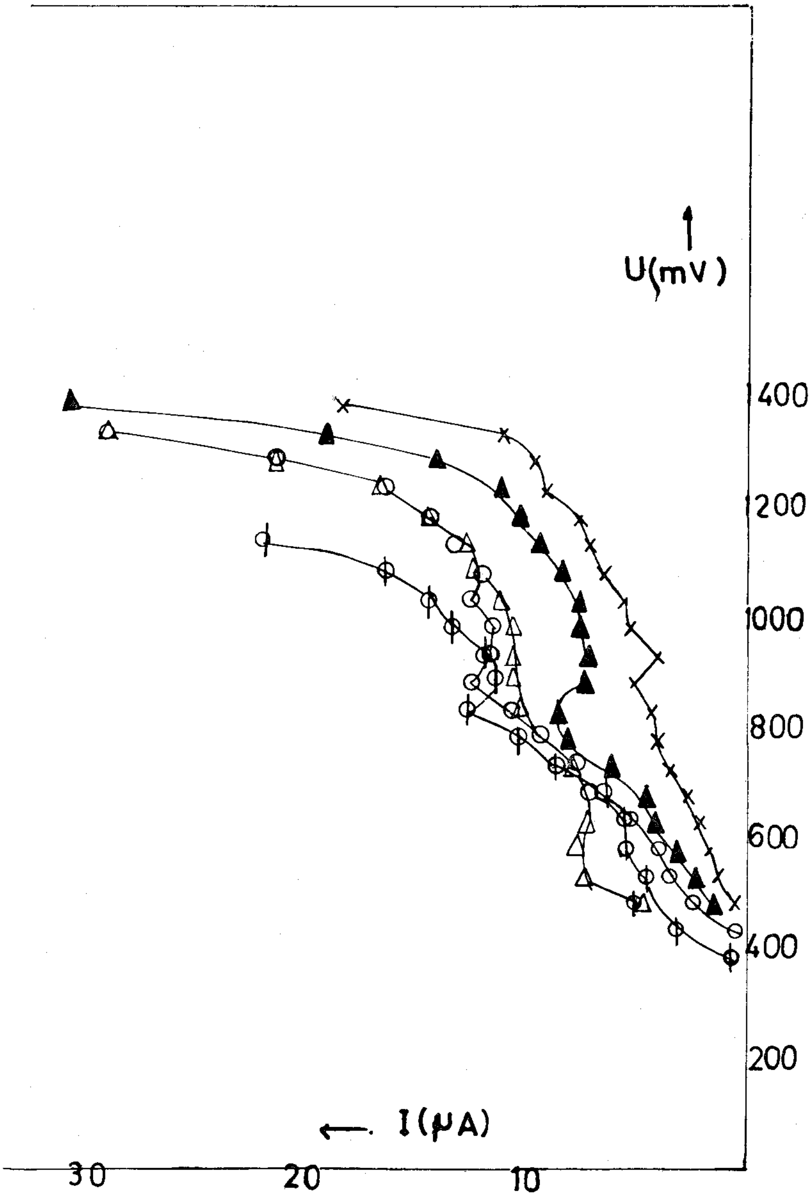

Fig. I. The shapes of the curves after the construction of ruthenium electrode: x Curve 245; O Curve 348; Δ Curve 358; Φ Curve 365; ▲ Curve 372

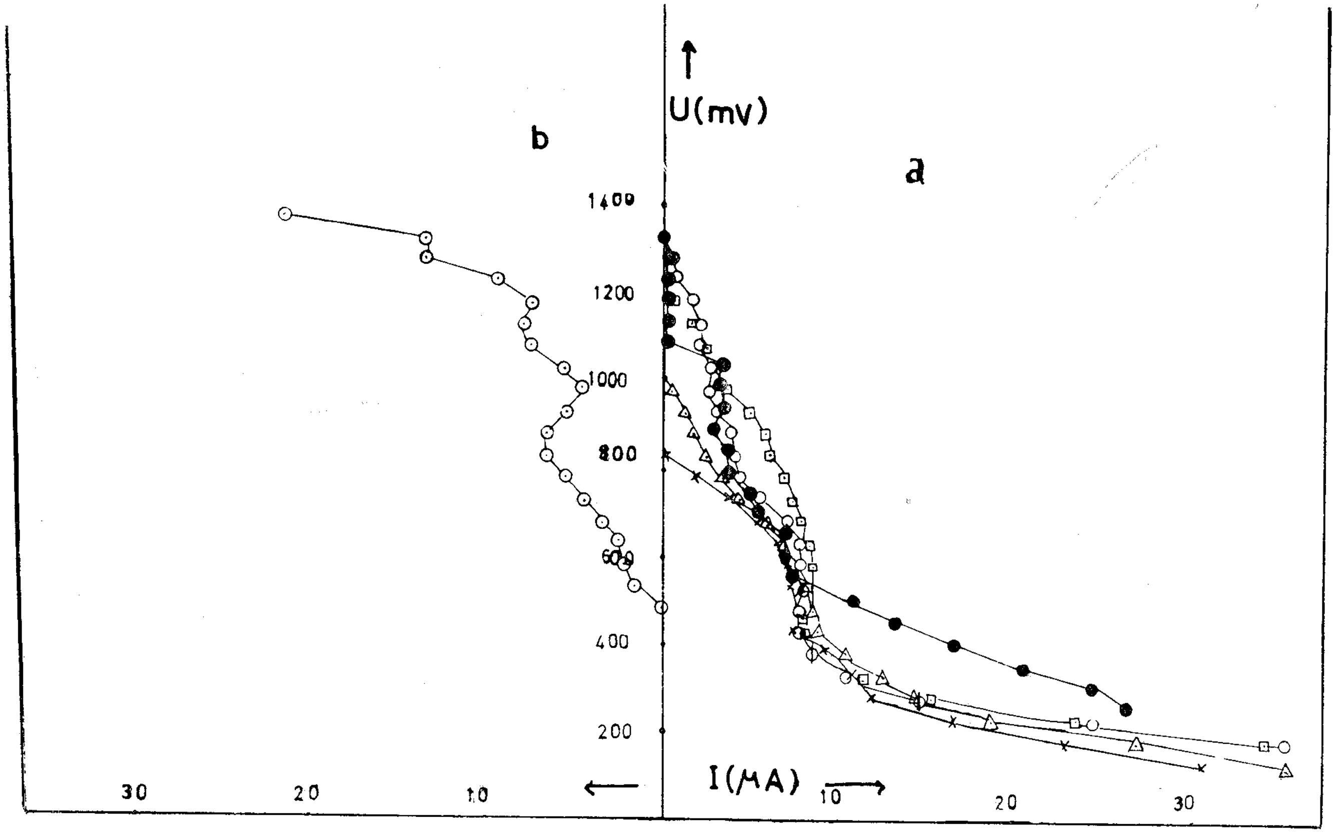

Fig. II a) Reduction curves with the oxidized ruthenium electrode: x Curve 490 with the electrode oxidized at 800 mV; △ Curve 492 at 1000 mV; ○ Curve 494 at 1200 mV; ⊡ Curve 496 at 1340 mV; ● Curve 154 at 1600 mV b) ⊙ Curve 503 anodic polarization of ruthenium electrode reduced at 400 mV.

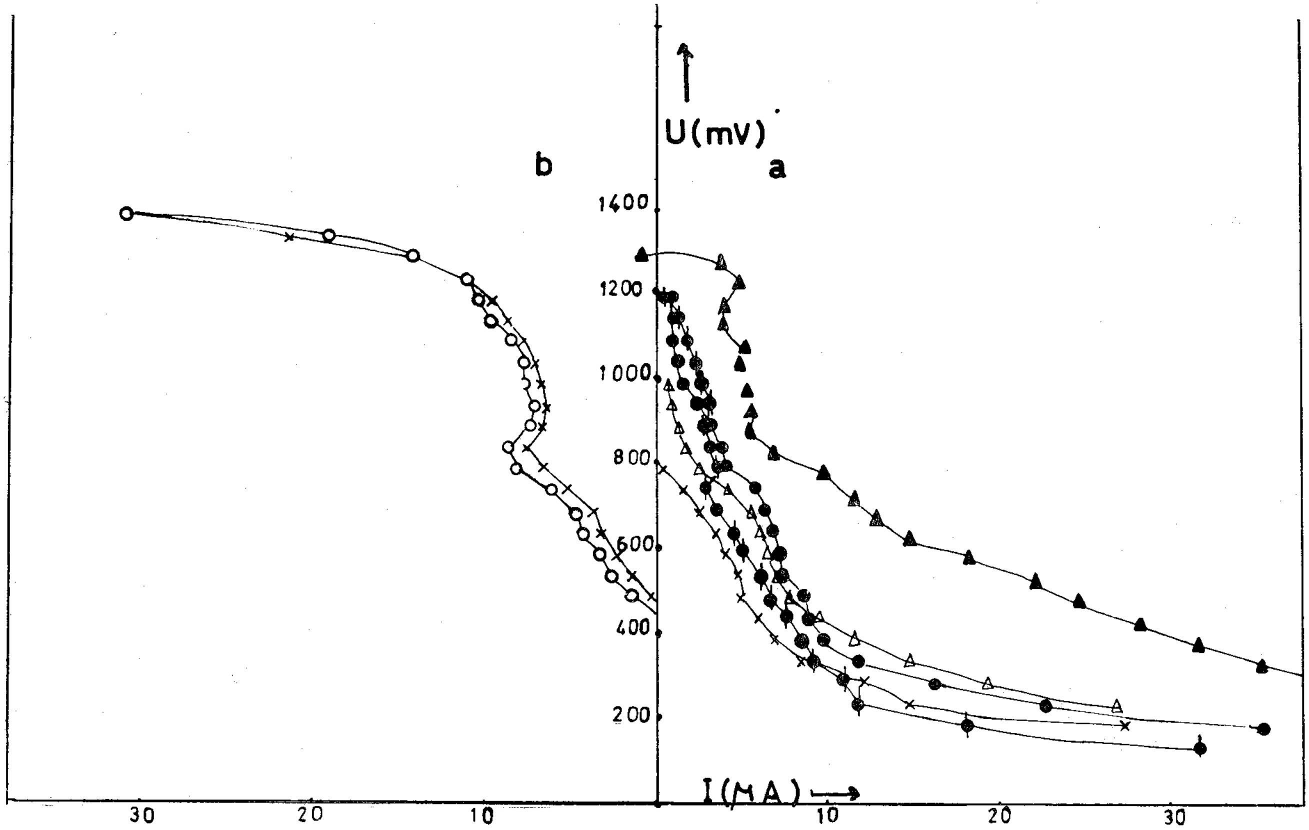

Fig. III a) Cathodic polarization curves in 1 N $HClO_4$ solution: x Curve 633 with the ruthenium electrode oxidized at 800 mV; △ Curve 368 at 1000 mV; Φ Curve 639 at 1400 mV; ● Curve 370 at 1200 mV; ▲ Curve 240 at 1600 mV. b)- Anodic polarization curves in I N $HClO_4$ solution: x Curve 371 the electrode reduced at 400 mV; ○ Curve 372 at 300 mV

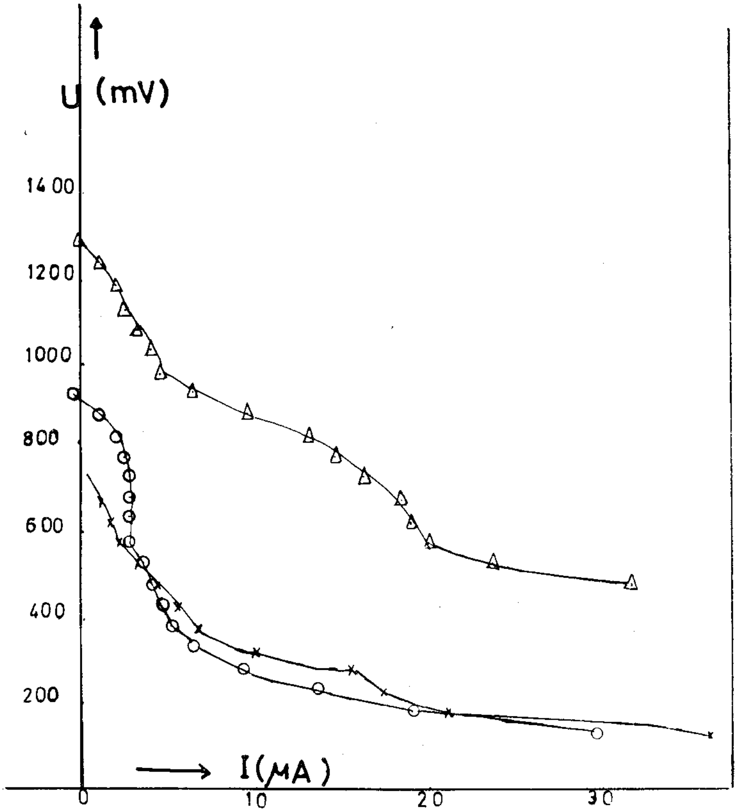

Fig. IV. Cathodic polarization curves in 1 N HNO_3 solution; △ Curve 185 ruthenium with the electrode oxidized at 1600 mV; x Curve 567 at 800 mV; ⊙ Curve 569 at 1000 mV.

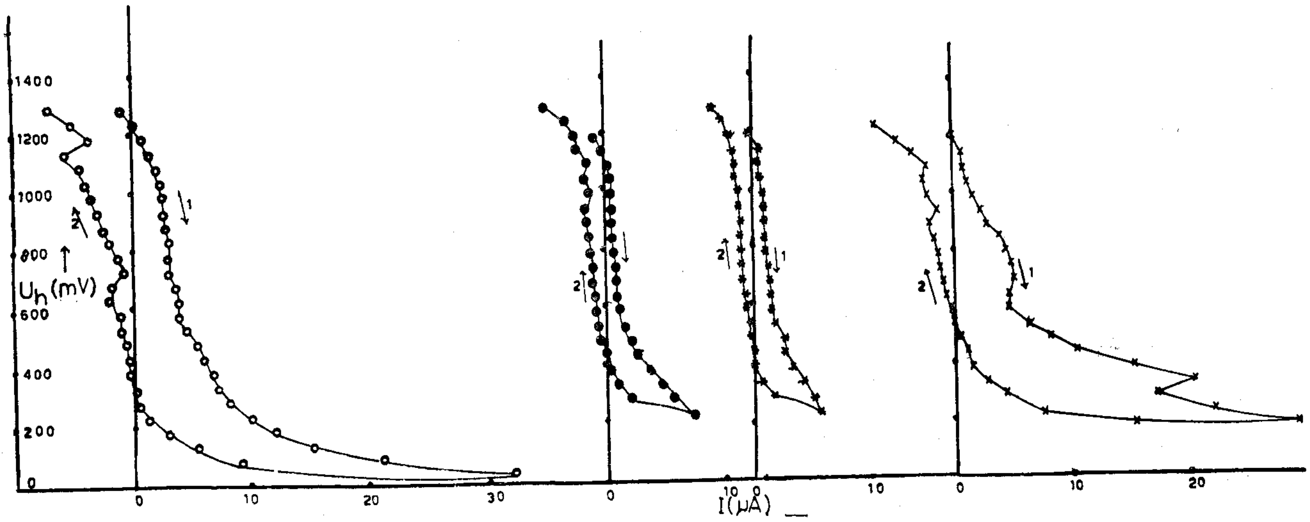

Fig. V Hysteresis curves in various media: ⊙ Curve 63 in 1 N H_2SO_4 with the ruthenium electrode oxidized at 1600 mv; ● Curve 83 in 1 N $HClO_4$ at 1200 mV; * Curve 371 in 1 N $HClO_4$ at 1600 mV; x Curve 67 in 1 N HNO_3 at 1600 mV;

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ÖZET

Rutenyum elektrodun nitrik, sülfürik ve perklorik asitler içerisinde potansiyostatik polarizasyon eğrileri elde edilmiştir. Bu eğrilerde saptanan basamaklardan 600-800 mV arasındaki ve 1200 mV daki iki basamak bundan önceki araştırmacılar tarafından gözlenememiştir. Bunlar bu çalışmada ortaya konan iki yeni basamaktır. Eğrilerdeki diğer basamaklar literatürdekilerle karşılaştırıldığında şu oksit potansiyelleri görülmektedir:

450-550 mV RuO; 600-800 mV hidratize Ru_2O_3; 900-1050 mV Ru_2O_3 / RuO_2; 1200 mV RuO_2; 1300-1350 mV RuO_4.

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