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by

S. ÜNERİ and M. KABASAKALOĞLU

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The Rest Potentials of Gold, Palladium, Platinum, Rhadium and Iridium Electrodes in Various Oxidizing Media *

S. ÜNERİ and M. KABASAKALOĞLU

Department of Physical Chemistry, Faculty of Science,
University of Ankara, Turkey†.
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The reduced and oxidized gold and palladium electrodes were alternately dipped into the solutions of 1 N H_2SO_4, 1 N HNO_3, 1 N H_2SO_4 + 1/8 M $K_2Cr_2O_7$, 1 N HNO_3 + 1/8 M $K_2Cr_2O_7$, 1/4 M CrO_3, 1 N H_2SO_4 + 10^{-2}M H_2O_2, 1 N H_2SO_4 + 10^{-2} M $KMnO_4$, 1 N H_2SO_4 + 10^{-2}M Ce (IV) SO_4, 1 N NaOH, 1 N NaOH + 1/8 M $K_2Cr_2O_7$. The potentials with respect to time were measured against a calomel electrode, (rest potentials).

The rest potentials of the oxidized and reduced electrodes were soon reached the same value. The electrodes were pretreated in one of the two following ways.

I. The electrodes were first anodically oxidized at 10 mA for five minutes. Then they were reduced (reduced electrodes) using a potentiostat, until the oxidized layer of the anodic polarization was removed to the extent where hydrogen adsorption di l not yet start.

II. The electrodes prepared according to the above procedure were again oxidized, anodically, for five minutes under a current of 10 mA, (oxidized electrodes).

The curve relating the variation of potentials with respect to time, contained distinct steps corresponding to the normal potentials given in the literature for the oxidized states of gold, palladium, platinum, rhodium and iridium. In this work, it was found that the rest potentials of these electrodes in the same oxidizing solutions were different from each other.

INTRODUCTION

The purpose of this work is to show that iridium, rhodium, platinum, gold and palladium electrodes that come first in the

order of thermodynamic nobility [1] are oxidized in various oxidizing media. These metals show different potential steps in this media. In this work, it is indicated that these potential steps correspond to the equilibrium potential of the corresponding metal oxides.

EXPERIMENTAL

In these experiments great care was taken to see that all chemicals were chemically pure and solutions were prepared with conductance water and the glass ware was made of pyrex glass. Variations of cathode potential with time in various oxidizing solutions were measured against a saturated calomel electrode and apparatus used to determine the potential was Knick-messverstärker (Berlin).

The solution in the cell was kept at the same level and mixed continuously with a magnetic stirrer during the experiment. The electrodes used were iridium, rhodium, platinum, gold and palladium wires in 0.5 cm diameter and 3 cm lenght.

As is indicated before [2] potential time curves change in accordance with the pretreatment of the electrodes. In order to get reproducible curves, electrodes are treated in the following manner before the experiment.

Reducing the electrodes: The electrode was dipped into 1 N H_2SO_4 solution as anode and a current of 10 mA was passed for five minutes. Then they were inserted in a cell which contained 1 N H_2SO_4 solution through which nitrogen gas was passed continuously. The potential of gold and palladium electrodes held stable with the potentiostat (Wenking Breitband Model 61 RS) at 0.300 V and 0.700 V respectively and waited until the current fell to zero μ A. According to Will and Knorr [3] oxygen adsorption on gold in 4 M H_2SO_4 cannot take place at potentials lower than + 0.85 V, while hydrogen absorption occurs below + 0.15 V (nhe). Therefore, for this metal 0.300 V was accepted as a potential that in this potential the oxide layer produced with anodic polarization was first removed but hydrogen adsorption had not yet begun.

It was already known that palladium adsorbed a lot of hydrogen. In order to find the potential that electrode freed from oxide layer and adsorbed hydrogen, palladium electrode were reduced using a potentiostat at various potentials in the above manner. In addition, these reduced electrodes were oxidized, anodically, for five minutes under a current of 10 mA and then the rest potentials of these oxidized and reduced electrodes were determined in 1 N H_2SO_4 solution through which nitrogen gas was passed. All the curves obtained with electrodes that reduced below 0.700 V showed sharp minimums between 0.250 and 0.350 V that were attributed to the annihilation of adsorbed hydrogen.

The curves obtained with electrodes that reduced at, 0.700 V did not show this minimum. The curves obtained with oxidized electrodes that were reduced before below 0.400 V, showed also sharp minimums between, 0.350 and 0.400 V that were attributed to the annihilation of adsorbed hydrogen (Fig. 1).

In this work the gold and palladium electrode that reduced at 0.300 V and 0.700 V respectively are called "reduced electrodes".

Oxidizing the electrode: The electrodes that were reduced in the above procedure are again oxidized, anodically, for five minutes under a current of 10 mA. These electrodes are called "oxidized electrodes".

The pretreatment of platinum, rhodium and iridium electrodes were the same as has been explained in the previous work [2].

RESULTS

The potential time curves obtained with the oxidized and reduced gold and palladium electrodes in various oxidizing media are shown in figures 2–4. The potentials that were measured against calomel electrode are shown against nhe in figures. In order to indicate the upper section of the curves in Fig. 3, upper section is shown again in Fig. 2.
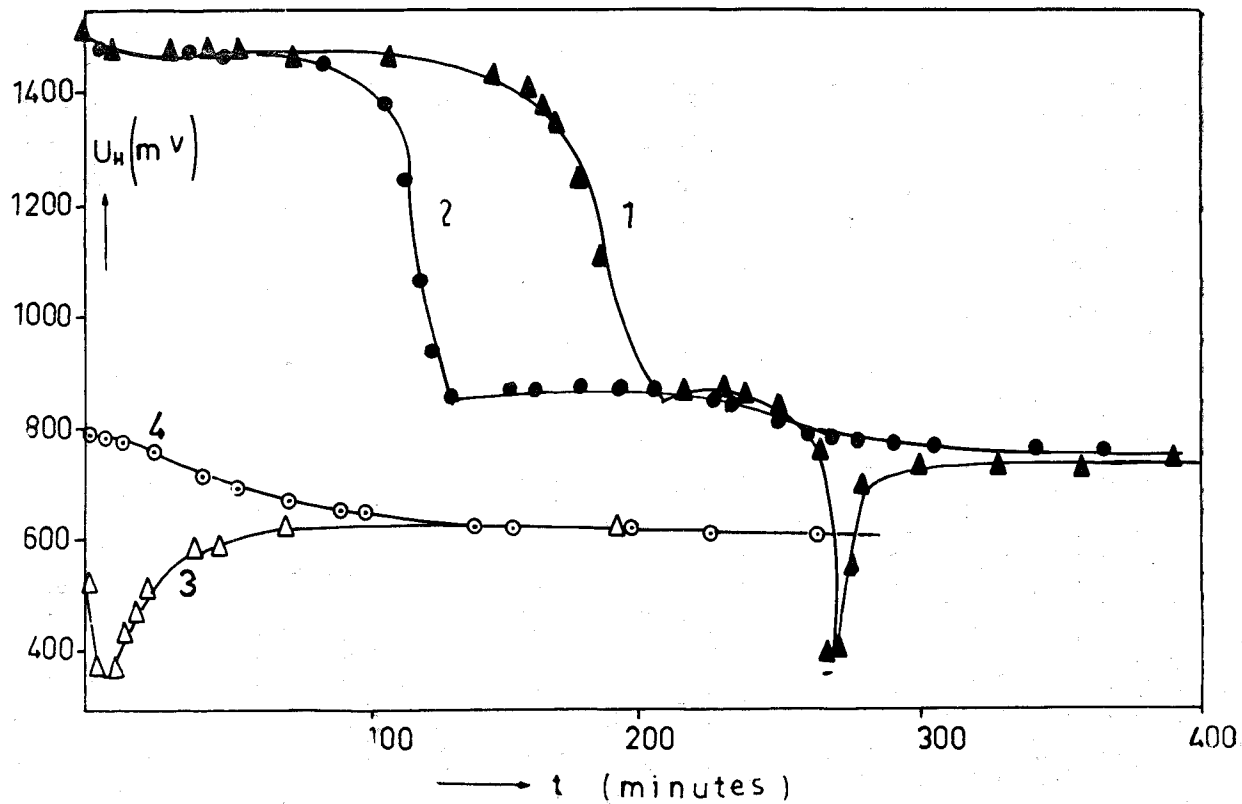
Fig 1. The rest potentials obtained with palladium electrode in 1 N H_2SO_4 through which nitrogen gas was passed. Curve 1 ▲ reduced to 0.350 V before treated anodically, Curve 2 ● reduced to 0.400 V before treated anodically, Curve 3 △ and 4 ⊙ reduced electrodes (0.650 and 0.750 V respectively)
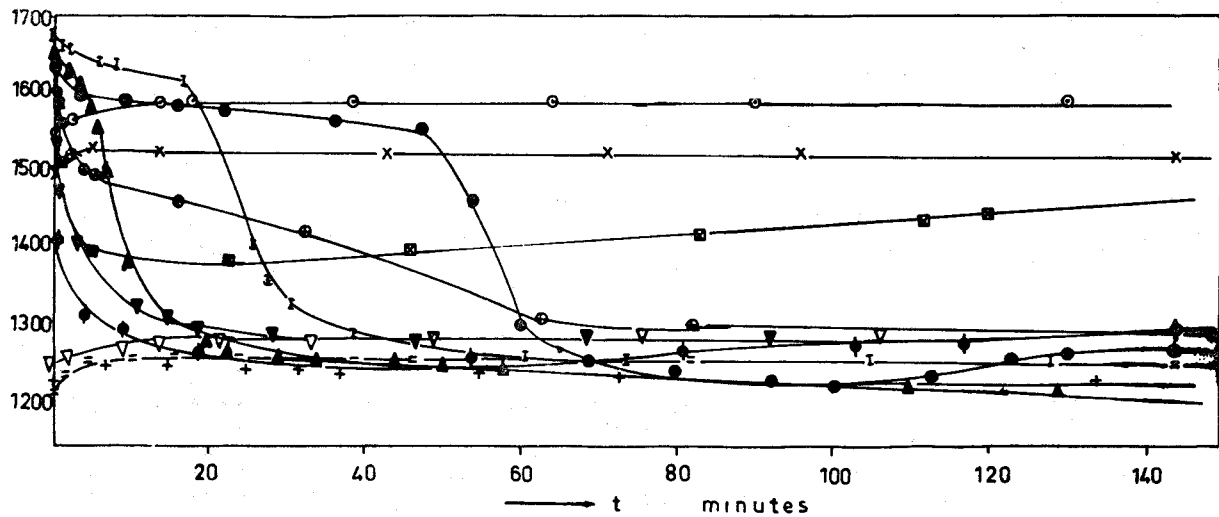
Fig 2. The rest potentials of gold electrode in various media, filled figures for oxidized, open figures for reduced electrodes.

● ◐ ○ 1 N H$_2$SO$_4$ + 10^{-2} M Ce (IV) SO$_4$,   ⊠   X 1 N H$_2$SO$_4$ + 10^{-2} M KMnO$_4$, ▼ ▽ 1 N HNO$_3$ + 0.125 M K$_2$Cr$_2$O$_7$, ⊕ + 0.25 M CrO$_3$, I = 1 N H$_2$SO$_4$ + 0.125 M K$_2$Cr$_2$O$_7$, ▲ 1 N HNO$_3$, ● 1 N H$_2$SO$_4$.
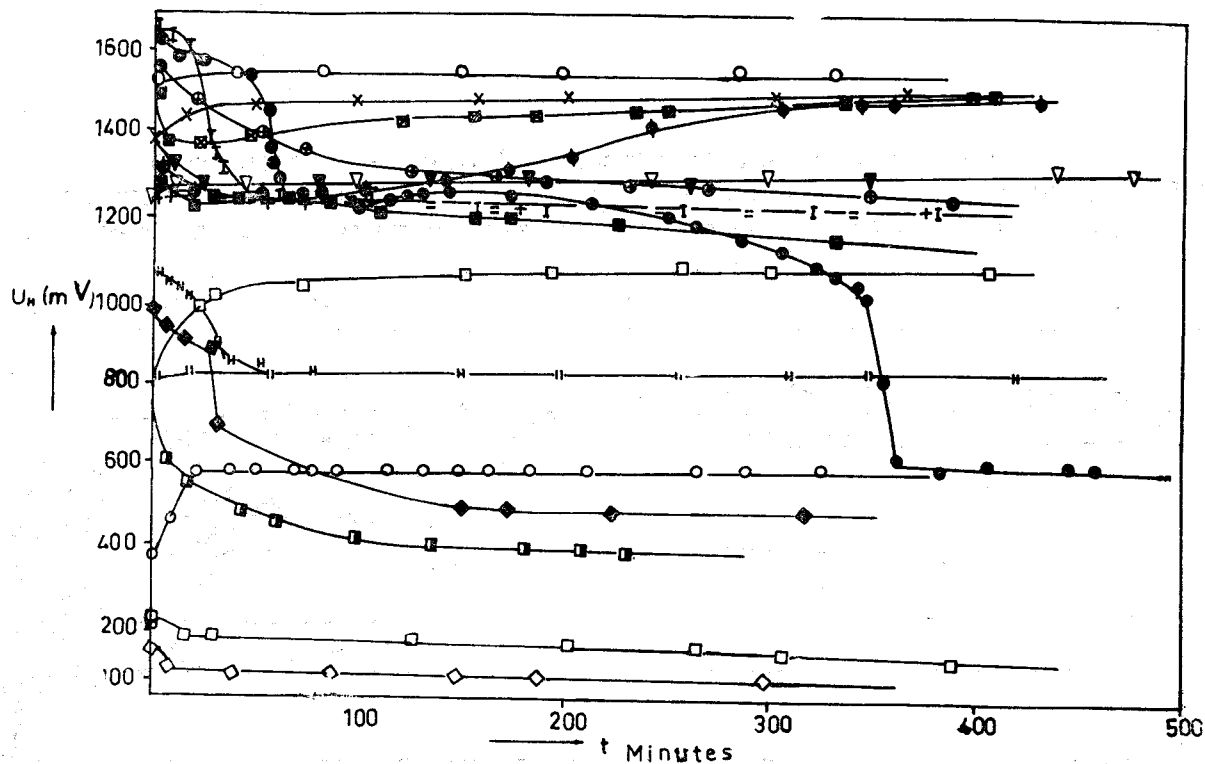
Fig 3. The rest potentials of gold electrode in various media, filled figures for oxidized open, figures for reduced electrodes.

● ◯ 1 N H₂SO₄ + 10⁻² M Ce (IV) SO₄,   ⊠   X 1 N H₂SO₄ + 10⁻² M KMnO₄, ▼ ▽ 1 N HNO₃ + 0.125 M K₂Cr₂O₇,
⊕ + 0.25 M CrO₃, I ＝ 1 N H₂SO₄ + 0.125 M K₂Cr₂O₇, ▨ ☐ 1 N HNO₃, H ⦀ 1 N H₂SO₄ + 10⁻² M H₂O₂, ◕ ◯ 1 N H₂SO₄,
◨ ☐ 1 N NaOH,   ◆ ◇ 1 N NaOH + 0.125 M K₂Cr₂O₇,

The theoretical and the experimental values of different gold and palladium oxides are collected in table I and II.

The potential steps and the rest potentials that are obtained for gold, palladium, platinum, rhodium and iridium electrodes in various media are given in table III.

a) Gold:

In figures 2 and 3 the rest potentials of reduced and oxidized gold electrodes are shown in various oxidizing media. The potential step around 1.6 V in the curve which is obtained in 1 N H_2SO_4 with oxidized gold electrode may be related to the AuO_2. This oxide is formed at the anode during high anodic polarization with oxygen evolution on gold electrode and the equilibrium potential for Au/AuO_2 system [4,5] was given as 1.75 V. The same potential step was seen in the curves of oxidized gold electrode that were obtained in 1 N HNO_3, 1 N H_2SO_4+ 0.125 M $K_2Cr_2O_7$. Only potential remained fixed at this values for a rather short time in these solutions. AuO_2 is an unstable substance and decomposed [1] spontaneously to Au_2O_3 and O_2. The curves obtained with oxidized and reduced gold electrodes in 1 N H_2SO_4+ 10^{-2} M $KMnO_4$ and in 1 N H_2SO_4+ 10^{-2} M Ce (IV) SO_4 got fixed also around this potential step.

In order to indicate the upper section of these curves (in Fig. 3) this section is shown again in Fig. 2. The potential maximum at 1.27 V in the curve of oxidized gold electrode obtained in 1 N H_2SO_4 (Fig. 2) can be related to the Au_2O_3. The potential of Au/Au_2O_3 electrode is given as 1.36 V by other investigators [6–8] (See Table II). Other curves also show this potential step in this region as follows: The curves obtained with oxidized and reduced gold electrode in 1 N H_2SO_4+ 0.125 M $K_2Cr_2O_7$, 0.25 M CrO_3, 1 N HNO_3+ 0.125 M $K_2Cr_2O_7$, and oxidized gold electrode in 1 N H_2SO_4+ 10^{-2} M Ce (IV) SO_4, 1 N HNO_3. The potential values given in parenthesis at table III are the calculated values which correspond to the pH = 0.3, that is 1 N acid solutions as the other's, (the pH of 0.25 M CrO_3 solution is 1.08).
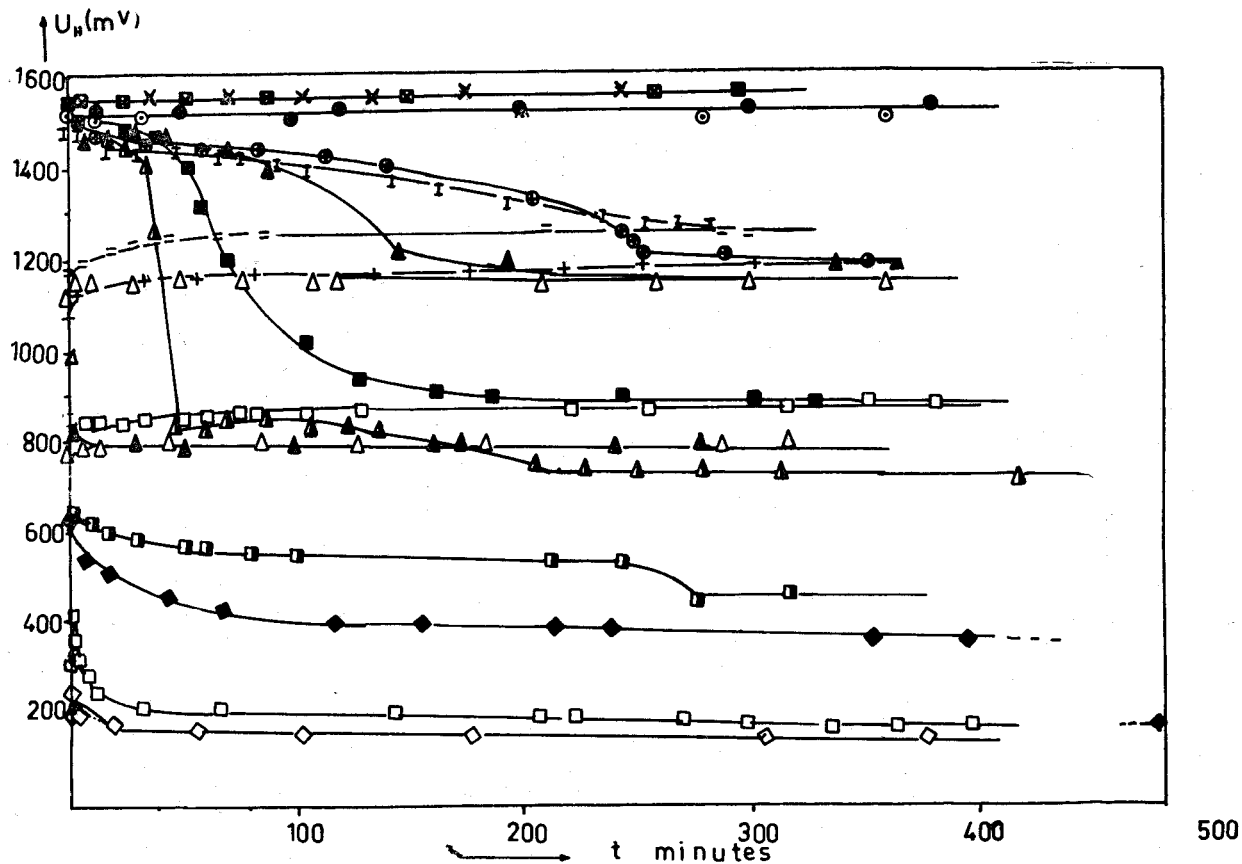
Fig 4. The rest potentials of palladium electrode in various oxidizing media, filled figures for oxidized, open figures for reduced electrodes.

⊠ X 1 N H_2SO_4 + 10^{-2} M Ce (IV) SO_4, ● ○ 1 N H_2SO_4 + 10^{-2} M $KMnO_4$, I ▬ 1 N H_2SO_4 + 0.125 M $K_2Cr_2O_7$, ⊕ + 0.250 M CrO_3

▲ △ 1 N HNO_3 + 0.125 M $K_2Cr_2O_7$, (around 1200 mV), ■ □ 1 N HNO_3, ▲ △ 1 N H_2SO_4 + 10^{-2} M H_2O_2, (around 800 mV),

⬔ 1 N H_2SO_4, ⬓ □ 1 N NaOH, ◆ ◇ 1 N NaOH + 0.125 M $K_2Cr_2O_7$.
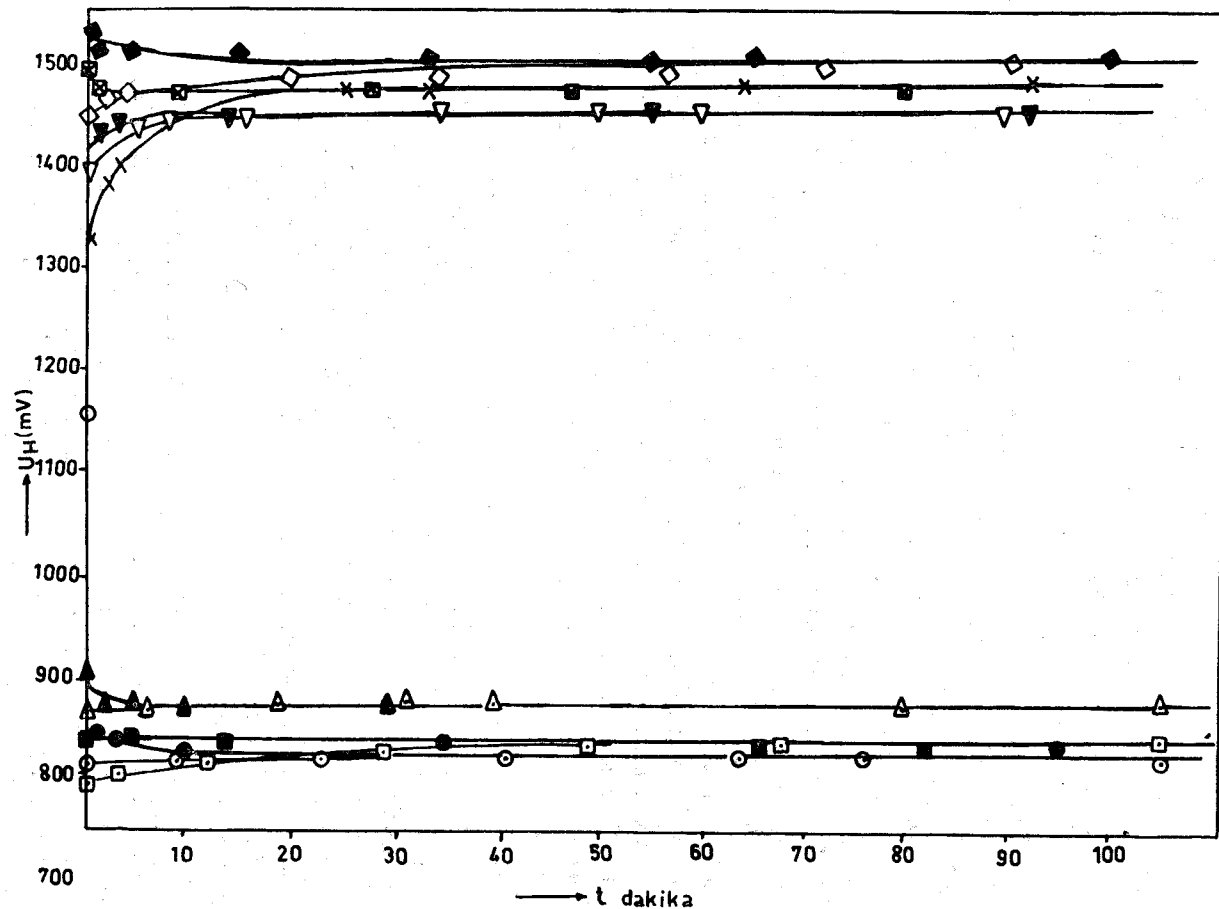
Fig. 5 The rest potentials of platinum ◇ ◆ , rhodium ⊠ X and iridium (▼ ▽) electrodes in $1 \ N \ H_2SO_4 + 10^{-2} \ M \ KMnO_4$ and in $1 \ N \ H_2SO_4 + 10^{-2} \ M \ H_2O_2$ with platinum (▣ ☐), rhodium (● ○) and iridium (▲ △) electrodes. Filled figures for oxidized and open figures for reduced electrodes.

However, the potential of oxidized gold electrode in 1 N H_2SO_4, 1 N HNO_3 and 1 N $H_2SO_4 + 10^{-2}$ M Ce (IV) SO_4 was not stable at this value. As in the case of 1 N H_2SO_4 and 1 N HNO_3 potential decreased to 1.0 V in 5.5 hours and in one day respectively. The potentials rose up to 1.5 V in 5 hours in Ce (IV) SO_4 solutions.

The reason for the potential was not stable at 1.27 V in the 1 N H_2SO_4 and 1 N HNO_3 can be explained through Au_2O_3 is not being stable compound in aqueous solutions, it is reduced to gold with oxygen evolution [1]. In fact it was noticed that electrode became black after the potential reached to 1.23 V. Hoare [6] pointed out that Au/Au_2O_3 electrode returned to Au/AuO electrode with time and it became black with a separation of colloidal gold. 1.0 V is in good agreement with the equilibrium potential of reaction 7 and electrode 10 in table I (Au /AuO). This potential step is also seen as the first step on the curve which is obtained in 1 N $H_2SO_4 + 10^{-2}$ M H_2O_2 solutions with the oxidized gold electrode. The fixed potential of oxidized and reduced gold electrode in 1 N $H_2SO_4 + 10^{-2}$ M H_2O_2 is in good agreement with the rest potential of gold electrode in acidic H_2O_2 solution found by other investigators [13, 14].

The reason of the minimums seen on the curves obtained in 1 N $H_2SO_4 + 10^{-2}$ M Ce (IV) SO_4 and in 1 N $H_2SO_4 + 10^{-2}$ M $KMnO_4$ with oxidized electrodes can be attributed to the mixed potential of AuO_2 and Au_2O_3. The potential fixed for a while at this potential then the electrode surface is oxidized by Ce (IV) SO_4 and $KMnO_4$ to the high valance oxide with time. As in the case of reduced electrode, the electrode surface is free from the oxide, the potential rises immediately to the equilibrium value in these media.

The fixed potential of 0.6 V in 1 N H_2SO_4 obtained with reduced and oxidized gold electrode is in good agreement with the potential measured by other investigators [6, 7] in H_2SO_4 solutions with gold and gold oxide electrodes. This step may be related to the low valance of gold oxide. The equilibrium potential of Au/Au_2O electrode is given almost 0.4 V in sulphuric acid solution [7, 8]. The potential of reduced gold electrode in

1 N H_2SO_4 is around 0.4 Volt at first, but Au_2O is not a stable compound, and it decomposes to Au and Au_2O_3 [7]. Therefore the oxidized and reduced gold electrode potentials are fixed at the same value 0.6 V. This potential may be a mixed potential of various gold oxides.

Potential steps in the curves obtained with oxidized and reduced gold electrode in 1 N NaOH compared with equilibrium potentials in basic media have shown that electrode can be oxidized in basic media as well as in acidic media. The maximum potential of reduced gold electrode in 1 N NaOH solution (0.24 V) is close to the equilibrium potential of Au /AuO system [7].

If we consider the difference of the pH between acidic and basic solutions and potential drift of about 60 mV with each pH, the first potential steps obtained with oxidized gold electrode in 1 N NaOH + 0.125 M $K_2Cr_2O_7$ correspond to the steps seen around 1.6 V in acidic media.

b) Palladium:

The rest potential curves obtained with reduced and oxidized palladium electrode in the same oxidizing media as before are shown in Fig. 4. There is a potential step around 1.5 V in the curve obtained with oxidized palladium electrode in 1 N H_2SO_4. The curves obtained with reduced and oxidized palladium electrode in 1 N H_2SO_4+ 10^{-2}M $KMnO_4$ and in 1 N H_2SO_4+ 10^{-2}M Ce (IV) SO_4 fix around this potential step. The curves obtained with oxidized palladium electrode in 1 N H_2SO_4+ 0.125 M $K_2Cr_2O_7$, 1 N HNO_3+ 0.125 M $K_2Cr_2O_7$, 0.25 M CrO_3, 1 N HNO_3 also show this potential step. The potential of this step is very close to the equilibrium potential of Pd /PdO_2 and Pd /Pd $(OH)_4$ systems [8, 12]. However, potential is not stable at this value for a long time in 1 N HNO_3, 1 N H_2SO_4 and in acidic bichromate solutions, it is decreased to the 1.23 V in 1 N H_2SO_4+ 0.125 M $K_2Cr_2O_7$. This potential is very close to the equilibrium potential of PdO /PdO_2 or Pd_2O_3, (5 and 17 at table II).

The potential where oxidized and reduced palladium electrode became fixed in 1 N HNO_3 and the potential step around

0.850 V in 1 N H_2SO_4 are very close to the potential of Pd /PdO and Pd /Pd(OH)$_2$, (See table II and ref. 1, 8).

The potential of these steps also close to the reaction 8 at table II, only this reaction potential is depended to the oxygen gas pressure [12]. The same step is seen in the curve obtained with oxidized palladium electrode in 1 N H_2SO_4 in nitrogen atmosphere (Fig. 1) in the same duration of time. Therefore the relation of this step to the reaction 8 is hardly possible.

The curves obtained in 1 N NaOH and in 1 N NaOH + 0.125 M $K_2Cr_2O_7$ showed that palladium electrode can be oxidized in basic media as well as in acidic media. The potential where oxidized palladium electrode curve in 1 N NaOH get fixed is close to the potential of Pd /Pd$_2$O$_3$ (See 18 at table II and ref. 11). Reduced palladium electrode curves get fixed near the potential of Pd /Pd (OH)$_2$ (1 or 15 at table II). The potential of oxidized electrode curves in 1 N NaOH+0.125 M $K_2Cr_2O_7$ are decreased to 0.180 V in one day.

c) Platinum, rhodium and iridium:

The rest potential of platinum, iridium and rhodium electrodes in various oxidizing media have been investigated by us previously [2]. The rest potential values of these electrodes in different oxidizing media are given in table III and the curves obtained with these oxidized and reduced three electrodes in 1 N H_2SO_4+ 10^{-2}M $KMnO_4$ and in 1 N H_2SO_4+ 10^{-2}M H_2O_2 solutions are shown in figure 5.

The fixed potential values obtained in 1 N H_2SO_4+ 10^{-2} M $KMnO_4$ with oxidized and reduced electrodes correspond to the potential of Pt /PtO$_2$ for platinum electrode (ref. 1 page 380) and Ir /IrO$_2$ for the iridium electrode (ref. 1 page 375). The fixed potential value obtained in 1 N H_2SO_4+ 10^{-2}M H_2O_2 with oxidized and reduced electrodes correspond to the Ir /IrO equilibrium potential for iridium electrode, Rh /RhO for rhodium [16] and Pt /PtO for platinum electrodes [17].

DISCUSSION

When the potential values of figures 1–4 and table I and II in the previous work [2] and figures 1–5 and table I to III in the present study is compared, one can deduce that one of the potential steps corresponds to MeO in 1 N HNO_3, 1 N H_2SO_4 and in 1 N $H_2SO_4 + 10^{-2}M$ H_2O_2. The potential values correspond to the Me/Me_2O can also be observed in 1 N H_2SO_4 solution as Au_2O. The potential of Me/Me O_2 system can be reached in the solution of 1 N $H_2SO_4 + 10^{-2}M$ Ce (IV) SO_4, (Table III). This potential step can also be seen in the other oxidizing media for gold and palladium electrodes as it is shown above in H_2SO_4 and HNO_3.

The potential steps obtained in the different chromates solutions with these electrodes correspond to the oxides of Me_2O_3 or MeO/Me O_2 as is shown above for the gold and the palladium electrodes. According to the Llopis [18] the potential of RhO/RhO_2 system is 1. 30 V. This value is very close to the rest potential found in different chromates solutions with the rhodium electrode by us [2], (See Table III).

Although there are not enough potential values for the systems of Pt_2O_3 or PtO/PtO_2 and Ir_2O_3 and IrO/IrO_2, for comparing the results, the potential step obtained in different bichromate solutions with the oxidized and reduced platinum electrode (around 1. 25 V) can be attributed similarly to Pt_2O_3 or PtO/PtO_2. This step is also seen on the oxidation current/potential curves obtained by Böld and Breiter [19] in 2.3 M H_2SO_4 solutions and by Brieter [20] in 1 N $HClO_4$. Similarly there is a potential step on the oxidation and reduction current/potential curves obtained by Brieter [20], Böld and Breiter [21], and by us [22] with the iridium electrode in different oxidizing media, (about 1.29 V). The corresponding step is seen on the oxidation current/potential curves obtained by Böld and Breiter [21], Breiter [20], Will and Knorr [3] and by us [22] with the rhodium electrodes in different media. We are going on to find out the identity of these potentials with Me_2O_3 of platinum, iridium and rhodium.

The potential steps seen on the potential/time curves obtained in various oxidizing media do not depend on the oxidant in various media. Therefore these potential steps are related to the oxides of the corresponding metals rather than the reduction product of different oxidants. The rest potentials of these noble metals in the solutions mentioned above are very close to the equilibrium potentials of the same metals in the oxidized form, (See table II in the previous work and table I to III in the present work). When these 5 noble metals are not oxidized in the solutions mentioned above, the rest potential measured with the reduced electrodes must be about the same value within the experimental errors. As it will be seen in the last three column of table III, the average deviations of the rest potentials of these five electrodes would be bigger than the experimental errors.

CONCLUSION

In this work, it is shown that iridium, rhodium, platinum, gold and palladium electrodes that come first in the order of thermodynamic nobility are oxidized in various oxidizing media. Using the same electrolyte, the rest potentials for these five metals were found to have different potential values. The rest potential of the oxidized and reduced electrodes reached the same value. The rest potentials obtained in various oxidizing media are cumulated in the definite potential regions. This can be explained by the fact that the definite oxides are formed on the surface of electrodes in accordance with the oxidizing power of the solutions. The rest potentials of these metals in the oxidizing solutions mentioned above were very close to the equilibrium potentials of the same metals in the oxidized state. The time required for such a metals to reach the equilibrium potential was, shortest for the iridium next for rhodium, platinum, palladium and gold.

When these electrodes were used to determine the redox potential of a system, great care must be taken into account for the pretreatment of these electrodes especially for gold and palladium electrodes. The surface of the electrodes must be free from the oxide cover as it is shown in the experimental part of the present work and in the previous work [1].

	Reactions	Potentials (V)
Latimer [9]	1. $Au(OH)_3 + 3H^+ = Au + 3H_2O$	$E° = 1.45$
	2. $2 Au + 3 H_2O = Au_2O_3 + 6 H^+ + 6 e$	$E° = 1.457 — 0.00591$ pH
	3. $Au_2O_3 + H_2O = 2 AuO_2 + 2 H^+ + 2 e$	$E° = 2.630 — 0.0591$ pH
Pourbaix [1]	4. $Au + 3 H_2O = H_3 AuO_3 + 3 H^+ + 3 e$	$E° = 1.565 — 0.0591$ pH $+ 0.197 \log (H_3 AuO_3)$
	5. $H_3 AuO_3 = AuO_2 + H_2O + H^+ + e$	$E° = 2.305 — 0.0591$ pH$—0.0591 \log (H_3 AuO_3)$
	6. $H_2 AuO_3^- = AuO_2 + H_2O + e$	$E° = 1.611 — 0.0591 \log (H_2 AuO_3—)$
	7. $Au — O + 2 H+ + 2 e = Au + H_2O$	$E° = 0.980 \mp 0.020$
Hoare [6]	8. $Au_2O_3 + 6 H^+ + 6 e = 2 Au + 3 H_2O$	$E° = 1.350 \mp 0.010$

		0.1 N H_2SO_4	0.1 N $Na_2 CO_3$
	9. Au / Au_2O	0.36	− 0.24
El Wakkad and	10. Au / Au – O	0.98	(0.38)
El Din [7]	11. Au / Au_2O_3	1.30	0.70

		1 N H_2SO_4	0.1 N Na_2CO_3
	12. Au_2O / Au	0.42	− 0.24
Lee, Adams	13. AuO / Au	1.04	0.38
and Bricker [8]	14. Au_2O_3 / Au	1.36	0.70

TABLE II. Potential of some palladium oxides systems (V)

	Reactions		Potentials
	1. $Pd(OH)_2 + 2e = Pd + 2 OH^-$		$E^\circ = 0.07$
Latimer [9]	2. $Pd(OH)_4 + 2e = Pd(OH)_2 + 2 OH^-$		$E^\circ = 0.73$
	3. $PdO_3 + H_2O + 2e = PdO_2 + 2 OH^-$		$E^\circ = 1.2$
	4. $Pd + H_2O = PdO + 2 H^+ + 2e$	a)	$E^\circ = 0.897 - 0.0591$ pH b) $E_o = 0.917 - 0.0591$ pH
Pourbaix [1]	5. $PdO + H_2O = PdO_2 + 2 H^+ + 2e$	a)	$E^\circ = 1.283 - 0.0591$ pH b) $E_o = 1.263 - 0.0591$ pH
	6. $PdO_2 + H_2O = PdO_3 + 2 H^+ + 2e$		$E^\circ = 2.03 - 0.0591$ pH
	7. $PdO + 2 H^+ + 2e = Pd + H_2O$		$E^\circ = 0.790 \mp 0.010$
Hoare [12]	8. $O_2 + Pd^{++} + 2e = PdO_2$		$E^\circ = 0.85$
	9. $PdO_2 + 4 H^+ + 4e = Pd + 2 H_2O$		$E^\circ = 1.470 \mp 0.010$

	Reactions	0.1 N H_2SO_4	0.1 N NaOH
	10. Pd / Pd $(OH)_2$	0.85	0.16
El Wakkad and	11. Pd $(OH)_2$ / Pd $(OH)_4$	1.49	0.77
El Din [7]	12. $Pd + 2 OH^- = Pd(OH)_2 + 2e$	$E^\circ_B = 0.10$	
Lee, Adams	13. Pd $(OH)_4$ / Pd	1.55	
and Bricker [8]	14. Pd $(OH)_2$ / Pd	0.91	

	Reactions	1 N H_2SO_4	1 N NaOH
	15. $Pd + PdO . H_2O$	0.85	0.1
	16. $Pd + PdO_2 . \times H_2O$	1.29	0.48
Hickling	17. $Pt + PdO . H_2O + PdO_2 . + H_2O$	1.23	0.44
and Vrjosek [11]	18. $Pd + Pd_2O_3 . \times H_2O$	—	0.44

T A B L E III: The rest potentials and potential steps on the potential-time curves of oxidized and reduced gold, palladium, platinum, rhodium and iridium electrodes in various media

Media	GOLD		PALLADIUM		PLATINUM		RHODIUM		IRIDIUM		Average of the rest potentials (V)	Max. deviations from the average of rest potentials (V)	Max. errors in the experiments (V)
	ox. (V)	red. (V)	ox. (V)	red. (V)	ox. (V)	red. (V)	ox. (V)	red. (V)	ox. (V)	red. (V)			
10^{-2}M Ce (IV) SO$_4$+ 1 N H$_2$SO$_4$	1.262∓0.002 1.528∓0.008	1.557∓0.015	1.550∓0.000	1.540∓0.000	1.573	1.585	——	1.560	——	1.532	1.546	+0.039 −0.021	∓0.015
10^{-2}M KMnO$_4$+ 1 N H$_2$SO$_4$	1.393∓0.028 1.535∓0.008	1.522∓0.003	1.520∓0.000	1.515∓0.010	1.496∓0.020	1.489∓0.014	1.477∓0.004	1.481∓0.003	1.452∓0.001	1.458∓0.000	1.496	+0.039 −0.044	∓0.014
0.125 M K$_2$Cr$_2$O$_7$+ 1 N H$_2$SO$_4$	1.600∓0.010 1.273∓0.025	1.242∓0.012	1.470∓0.006 1.285∓0.023	1.230∓0.027	1.245∓0.003	1.232∓0.004	1.269∓0.003	1.268∓0.008	1.294∓0.004	1.292∓0.000	1.256	+0.038 −0.036	∓0.027
0.125 M K$_2$Cr$_2$O$_7$+ 1 N HNO$_3$	1.305∓0.005	1.290∓0.000	1.480∓0.000 1.193∓0.018	1.150∓0.000	——	1.255	1.275	1.279	——	1.292	1.251	+0.054 −0.101	∓0.018
0.250 M CrO$_3$	1.500∓0.002 1.265∓0.001	1.24	1.427∓0.010 1.146∓0.035	1.187∓0.028	1.17	1.150	1.2	1.2	1.245	1.240	1.204	+0.061 −0.058	∓0.035
1 N HNO$_3$	1.575∓0.018 1.235∓0.010 1.265∓0.000 0.990∓0.001	1.081∓0.002	1.479∓0.008 0.895∓0.023	0.897∓0.014	1.078∓0.003	1.071∓0.003	1.069∓0.000	1.069	1.062	1.066	1.028	−0.038 +0.053	∓0.023
1 N H$_2$SO$_4$	1.585∓0.015 1.224∓0.008 1.270∓0.009 0.580∓0.018	0.543∓0.002	1.480∓0.000 0.850∓0.000 0.710∓0.002	——	0.910∓0.010	0.932∓0.002 0.881∓0.001	0.776∓0.015	0.795∓0.001 0.786∓0.001	0.791∓0.013	0.832∓0.018 0.808∓0.008	0.754	−0.211 +0.154	∓0.020
1 N H$_2$SO$_4$+ 10^{-2}M H$_2$O$_2$	1.060∓0.008 0.813∓0.022	0.855∓0.007 0.825∓0.005	0.782∓0.007	0.792∓0.000	0.820∓0.004	0.832∓0.003	0.831∓0.001	0.821∓0.001	0.860∓0.004	0.881∓0.005	0.826	+0.051 −0.046	∓0.022
1 N NaOH	0.407∓0.004	0.120∓0.017	0.613∓0.024 0.557∓0.007 0.441∓0.006	0.186∓0.002	0.178	0.157	0.144	0.142	0.152	0.143	0.207	+0.233 −0.087	∓0.017
1 N NaOH + 0.125 M K$_2$Cr$_2$O$_7$	0.967∓0.044 0.431∓0.019	0.202∓0.000 0.117∓0.019	0.365∓0.005 0.186∓0.004	0.455∓0.005 0.154∓0.014	——	0.152	0.110	0.112	0.123	0.127	0.168	−0.058 +0.238	∓0.019

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ÖZET

Oksitli ve redüklenmiş altın ve palladyum elektrotlar 1 N H_2SO_4, 1 N HNO_3, 1 N H_2SO_4 + 0,125 M $K_2Cr_2O_7$, 1 N HNO_3 + 0,125 M $K_2Cr_2O_7$, 1 N H_2SO_4 + 10^{-2}M H_2O_2, 1 N H_2SO_4 + 10^{-2}M Ce (IV) SO_4, 1 N H_2SO_4 + 10^{-2}M $KMnO_4$, 0,250 M CrO_3, 1 N NaOH + 0,125 M $K_2Cr_2O_7$ içine daldırılarak potansiyelleri doygun kalomel elektroda karşı izlenmiştir. Oksitli ve redüklenmiş elektrotların potansiyelleri bir süre sonra aynı değeri almaktadır. Elektrotlar iki türlü ön işleme tâbi tutulmuştur.

1. 5 dakika 10 mA de anodik olarak oksitlenen elekrotlar potansiyostat kullanarak, anodik polarizasyonla meydana getirilen oksit tabakasının giderilebildiği ve fakat hidrojen adsorpsiyonunun başlamadığı bir potansiyelde, redüklenmişlerdir, (redüklenmiş elektrot).

2. Yukarıdaki yolla redüklenen elektrotlar tekrar 5 dakika 10 mA de anodik olarak oksitlenmişlerdir, (oksitli elektrot).

Oksitli ve redüklenmiş altın, palladyum, platin, rodyum ve iridyum elektrotlarla elde edilen potansiyel zaman eğrilerinde görülen basamaklar, bu metallerin literatürde verilen oksitlerinin normal potansiyellerine tekabül etmektedir. Aynı bir yükseltgen ortamda bu elektrotlar için elde edilen sükûnet potansiyellerinin birbirinden farkı olduğu tesbit edilmiştir.