NRL Report 6627

On the Activity of Platinum Catalysts in Solution

Part 2 – Kinetics of the Pt-O Reaction with Hydrogen and of Pt-H Deposition Using a Double-Pulse Technique

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ABSTRACT

Surface coverages of oxygen and hydrogen were determined on electrodes of differing activities as a function of time and voltage in the potential decay curve following an anodic pulse. The electrolyte was 1M H_2SO_4 containing dissolved hydrogen. No important difference, other than rate, is found in the way Pt-O is removed from surfaces of differing activity; however, a significant difference is noted in the way hydrogen resorbs. The rate of Pt-O removal is of apparent first order in adsorbed oxygen when the initial fraction of the surface covered is about 1.0; it is zero order in adsorbed oxygen and amount reacted when the initial surface coverage is less than 0.8. It is zero order in hydrogen partial pressure in both cases. The rate of the decay reaction is probably not limited by mass transport of solution H_2 to the surface, by obstruction of active surface sites by sorbed product molecules, or by slow chemisorption of solution H_2 on the electrode prior to reaction with Pt-O.

PROBLEM STATUS

This is an interim report on one phase of the problem; work on this and other phases of the problem is continuing.

AUTHORIZATION

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ON THE ACTIVITY OF PLATINUM CATALYSTS IN SOLUTION

PART 2 - KINETICS OF THE Pt-O REACTION WITH HYDROGEN AND OF Pt-H DEPOSITION USING A DOUBLE-PULSE TECHNIQUE

INTRODUCTION

In Part 1 (1) and in a preceding paper (2) the reaction rate of oxygen, chemisorbed on smooth platinum, with hydrogen dissolved in 1M H_2SO_4 and in the Pt derma (the Pt-O/hydrogen reaction), was monitored by observing potential decay on open circuit after an anodic current pulse. The purpose in Part 1 was to examine how different thermal or chemical treatments affected the intrinsic catalytic activity of smooth platinum, using this reaction rate as a measure of activity. It was found that this intrinsic activity could be modified by several orders of magnitude. The purpose of this work was to determine if surfaces known to have different catalytic activities for the Pt-O/hydrogen reaction exhibited significant differences (other than rate) in the way oxygen was removed or hydrogen resorbed.

EXPERIMENTAL PROCEDURE

The apparatus and procedures were the same as in Part 1, except that two precisely spaced galvanostatic pulses were used.* A Hewlett-Packard 5214L Electronic Counter (clock rate 100 kc) provided two trigger pulses separated by a time known within 1 μsec. These pulses triggered a pulse generator (either an EH Model 132A or an Electropulse 3450D), sending two identical current pulses through the cell. The pulses were adjusted so that the first ended after a known amount, usually one monolayer, of chemisorbed oxygen atoms had been deposited on the electrode (Fig. 1). Current densities used were from 2.9 to 4.5 amp/cm^2.†

The anodic charging curves are conceptually divided into the usual regions, the "H ionization region" and the "O sorption region." In the subsequent decay the first region is called the "O removal region," and the second, the "H deposition region." These regions are diagrammed in Fig. 1a of Ref. 2, and they are apparent in Fig. 2 here. In the "O removal region," hydrogen is reacting with the oxygen chemisorbed on the electrode. After a known time into the decay t, called at different times either the "reaction time" or the "decay time," the second pulse was triggered to determine how much charge was required to bring Pt-O coverage up to one monolayer. With knowledge of the initial coverage and the value of this charge, the amount reacted could be computed. When the

*Unless otherwise specified, potentials are given versus the normal hydrogen electrode; all measures of precision are standard deviations of an individual measurement; and electrode areas are "true" (3) areas based on the assumption that q_{o+dl} = 456 μcoul/cm^2 when one monolayer of oxygen is deposited at a current density of 3 amp/cm^2. Precision of an individual area measurement was ±3.2%. q_0 is the charge required to deposit oxygen, q_{dl} is that needed to charge the double layer.

†At these current densities the IR drop in the solution is a large fraction of the total cell voltage. The IR drop was, at times, removed from the display by using a Tektronix Type 547 oscilloscope with a Type 1A1 dual trace preamplifier. The rectangular pulse at the generator output was applied to input 1 and appropriately attenuated; the cell voltage was applied to input 2, and the difference signal was displayed.

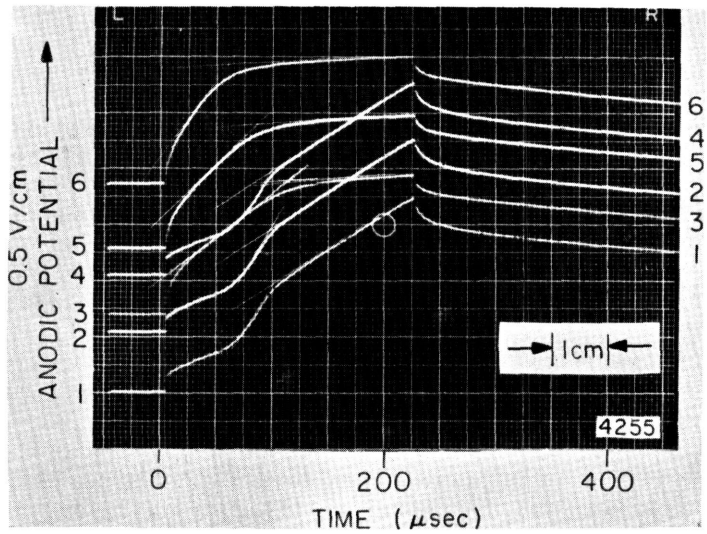

Fig. 1 - Double-pulse electrode polarization. First pulses (oxidation of H_{ad} followed by oxidation of H_2O to O_{ad}) are traces 1, 2, and 4; second pulses (oxidation of H_2O to O_{ad}) are traces 3, 5, and 6 taken after reaction ($Pt\text{-}O_{ad}$ + hydrogen) times of 10, 6, and 3 msec, respectively, on an electrode with a monolayer decay time of 21 msec.

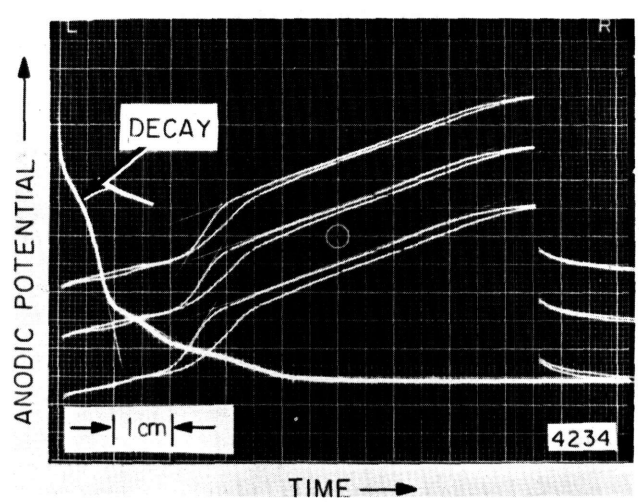

Fig. 2 - Double-pulse polarization of electrode on which some hydrogen had resorbed and typical full decay curve. Pulses are 20 μsec/cm and 0.5 v/cm; decays are 50 msec/cm and 0.2 v/cm. Reaction times between pulses were 200, 230, and 260 msec, reading from bottom to top on an electrode whose t_0 was 48 msec.

voltage decayed below 0.3 v, the second pulse gave both the charge required to form the oxygen region and the charge due to oxidation of adsorbed hydrogen.

It was assumed that in the oxygen regions $q_O = q_{measured} - q_{dl}$, and in the hydrogen regions $q_H = q_{measured} - q_{dl}$. For the first pulse the significance of the various terms is well understood. For the second pulse the assumption made is that all of the charge designated q_O went to form Pt-O_{ad} via a net two-electron oxidation, and all of the charge designated q_H went to oxidize Pt-H to H^+. The validity of these assumptions will be supported later. The charge due to double-layer charging was subtracted from the various $q_{measured}$, using previously reported (3) double-layer capacitance vs potential data integrated over the potential region of interest.*

The "foot" of each charging curve in Fig. 1 (the horizontal trace to the left of time zero) gives the potential of the electrode prior to each pulse. The first of each pair of pulses started at the normal equilibrium hydrogen potential (0.000 v). The foot of the second pulse then defined the potential $E(t)$ in the decay from which the second pulse was taken.

Two bright platinum bead electrodes were used, one with a monolayer decay time t_0 of 47.8 ± 0.5 msec and one with t_0 of 21.3 ± 1.5 msec. The monolayer decay time is the time required for the reduction of a monolayer of chemisorbed oxygen with hydrogen. The electrode areas were about 0.1 cm^2. For convenience, the more active electrode (activity defined by the rate of the Pt-O/hydrogen reaction) with t_0 = 21 will be termed electrode *A* and the less active one, electrode *L*. It was important to confirm that each measurement of voltage and redeposited charge was made on an electrode whose t_0 was unchanged. This invariance was established by plotting measurements of potential vs reaction time t from a number of full decay curves taken before, during, and after the double pulse studies and then comparing these data with the voltage-vs-time information obtained from the foot of the second pulse. The t_0 for the electrodes used did not change during the course of the experiments.

RESULTS

Oxygen Removal Region: Pt-O + Hydrogen = Pt + H_2O

Voltage-vs-Time Relation — To facilitate comparison of results on electrodes with different intrinsic activities, the results for each electrode have been expressed in terms of relative decay times t/t_0, where t is the reaction time and t_0 is the monolayer decay time. Plots of electrode potential during the decay $E(t)$ vs t/t_0 (Fig. 3) for data obtained on electrodes with t_0 = 21 and 48 msec show no important difference nor are differences noted for the relation between voltage in the decay curve and fraction θ of surface covered with oxygen (Fig. 4). From repeated measurements on electrodes whose t_0 ranged from 17 to 180 msec, the potential at the end of the decay plateau, at $t = t_0$, was found to be 0.283 ± 0.004 v.

Oxygen Coverage vs Voltage and Time — Let a be the initial oxygen coverage of the electrode in μcoul/cm^2 deposited by the first pulse, and let $(a - x)$ be the coverage at any later time t. Let q_O be the amount of oxygen used in the second pulse to reform one monolayer of O_{ad}. We assume that $q_O + (a - x)$ = 420 μcoul/cm^2; i.e., the electrode is

*For the second pulse this treatment involved the assumption that q_{dl} (which includes a contribution from pseudocapacitance near 0.000 v) under the nonsteady-state conditions prevailing was not significantly different from that measured in Ref. 3. Consideration of the physical situation prevailing shows that this assumption is reasonable. Further, the q_{dl} terms are small compared to total q.

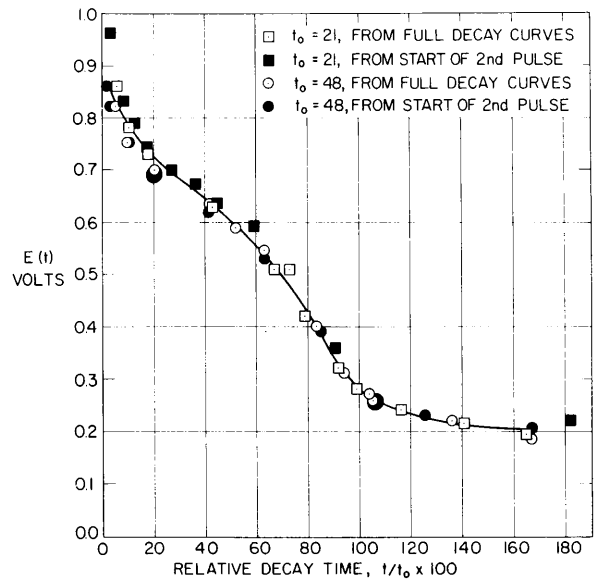

Fig. 3 - The basic decay curve: potential vs relative decay time

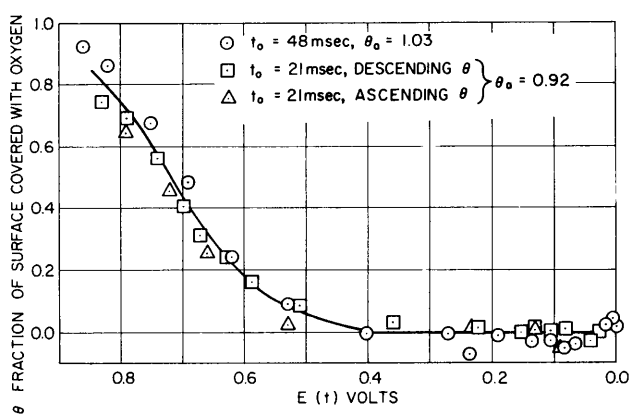

Fig. 4 - Fraction of surface covered with O_{ad} vs potential during decay. The initial coverages are denoted θ_a.

once again polarized up to the O_2 evolution region when its total oxygen coverage is brought back to one monolayer. The fraction θ of the surface covered with oxygen is

$$\theta = \frac{420 - q_o}{420} . \tag{1}$$

It is necessary to keep the following distinct: a the initial concentration in μcoul/cm^2 of oxygen on the surface; θ_a, this initial concentration expressed as the fraction of Pt surface sites covered with O_{ad} ($\theta_a = a/420$ μcoul/cm^2); and θ the fraction of the surface covered with oxygen at time t after some of the oxygen initially deposited has reacted with hydrogen.

The results in Figs. 5 and 6 show that the relationships between θ and t/t_0 for the cases where $\theta_a \approx 1$ and for $0.32 \leq \theta_a \leq 0.77$ are quite different. For $0.32 \leq \theta_a \leq 0.77$ Fig. 6a shows that the rate of oxygen removal is zero order in the initial concentration a and in the amount reacted x. The slopes are independent of a and average 700 μcoul/cm^2. Converting into units of θ, the rate of oxygen removal is

$$\theta = \theta_a - 1.67 \frac{t}{t_0} . \tag{2a}$$

However, for $0.92 \leq \theta_a \leq 1.03$ the rate of oxygen removal is given by a first-order relation,

$$\theta = \exp\left(-k \frac{t}{t_0}\right) , \tag{2b}$$

over the range $1 \leq \theta \leq 0.15$, where k is the first-order rate constant of about 3.2. The curves, plotted separately, show logarithmic relations; the slopes are not considered to be significantly different. (The slopes are strongly dependent on the average values used for t_0 and $q_{o,monolayer}$, as well as the extent to which some hydrogen may or may not be oxidized in the oxygen region.)

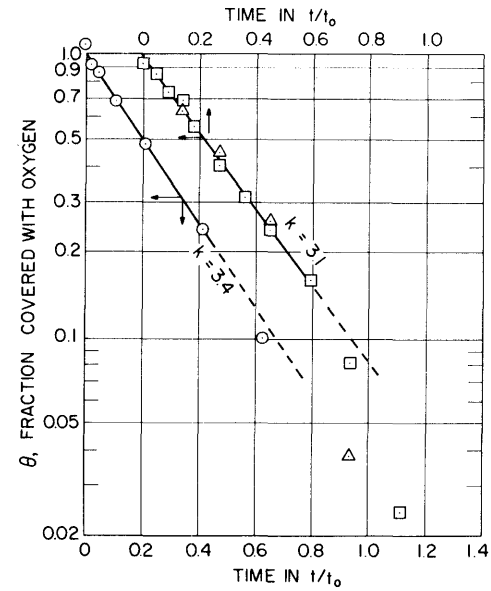

Fig. 5 - Rate of removal of oxygen for case where fraction of surface initially covered is near unity

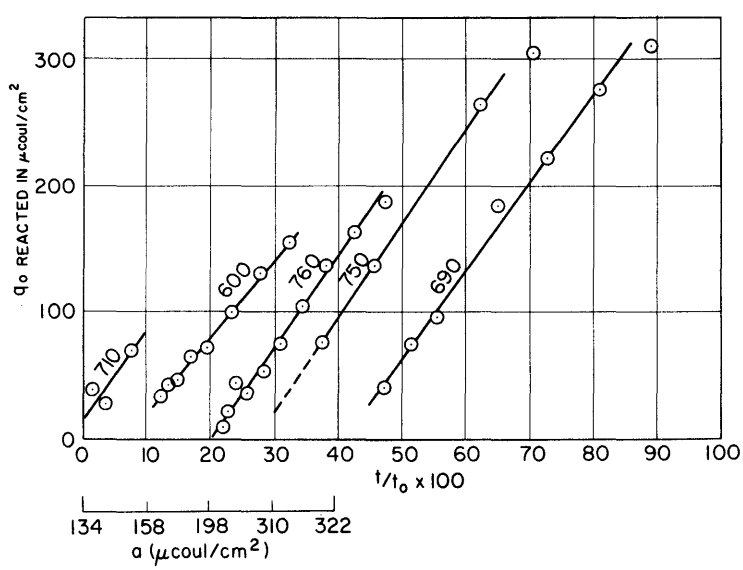

Fig. 6a - Rate of removal of oxygen for case where fraction of surface covered initially is < 0.8. The initial coverage a for each curve is indicated on the abscissa below $t/t_0 \times 100$ values. The origin of each succeeding curve is displaced 10 time units to the right of the preceding curve.

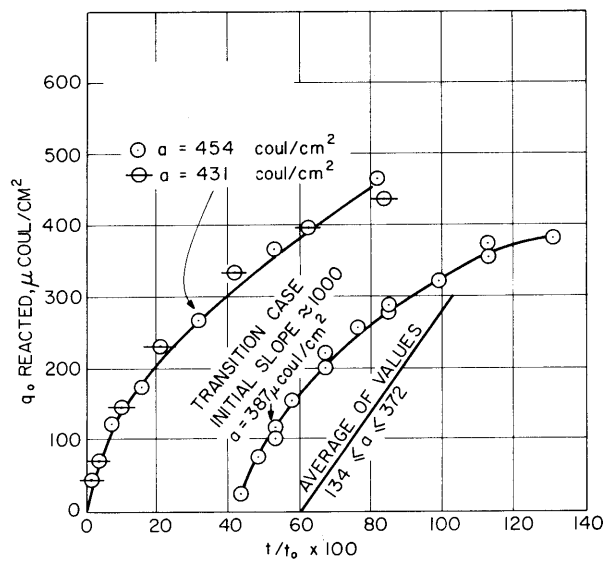

Fig. 6b - Comparison of cases where $\theta_a \approx 1$ with ones where $\theta_a < 0.8$; initial slope $\approx$ 1800 where $\theta_a \approx 1$ (i.e., $a \approx 420$ μcoul/cm^2)

Hydrogen Redeposition Region: Pt + Hydrogen = Pt-H

For the hydrogen redeposition region the measured quantities were q_{H+dl}, q_{O+dl}, $E(t)$, and t, which is time since the end of the first pulse. The time available for hydrogen sorption was taken as $(t - t_0)$. Since charging curves at times up to $t = t_0$ gave little or no indication of any sorbed hydrogen, it was assumed that all hydrogen reaching the electrode up to this time was consumed in reaction with Pt-O, which was known to be present up to $t = t_0$. The validity of this assumption is examined in the Discussion section. After correction for double layer charging, the data resulting for q_H vs $E(t)$, q_O vs $E(t)$, and $E(t)$ vs $(t - t_0)$ are shown in Figs. 7 and 8.

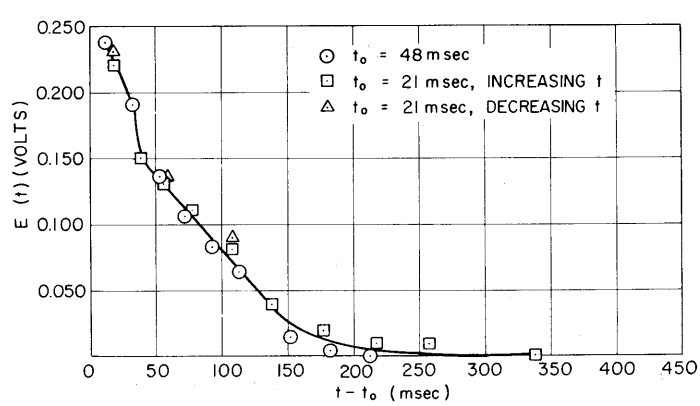

Fig. 7 - Decay potential vs time allowed for hydrogen resorption

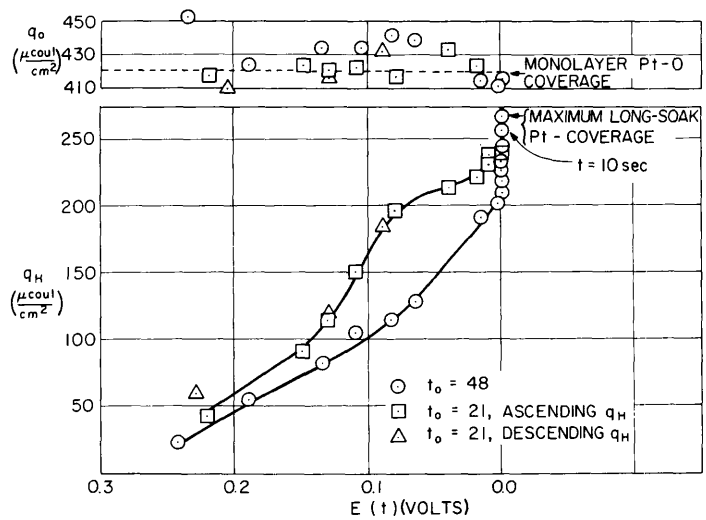

Fig. 8 - Amounts of hydrogen found in the hydrogen region and oxygen found in the oxygen region vs potential attained in decay curve

DISCUSSION

Hydrogen Redeposition Region

The factors that affect rate of potential decay in the Pt-O removal region exert no influence on the rate of potential change in the hydrogen resorption region. However, the amount of hydrogen found sorbed on the electrode after decay to a given potential does vary with the intrinsic activity of the electrode. The more active electrode *A* shows faster hydrogen reappearance in the hydrogen ionization region and no excess charge in the oxygen region, whereas electrode *L* shows less q_H in a given time, while the q_O measured simultaneously is anomalously high. It appears that the overall rate of the hydrogen resorption is not greatly different in the two cases, but on *L* considerably more time is required for hydrogen to be sorbed in a form detected below 0.8 v in a charging curve. Therefore, on *L* some hydrogen, not yet sorbed in the usual ways, is oxidized in the O sorption region, adding to the charge measured there. The slow process impeding hydrogen sorption could be either diffusion to a suitable chemisorption site, sorption of H into the derma, or the act of strong chemisorption itself. An alternate possibility is that it is not the sorption of the hydrogen that governs the potential at which it oxidized but the kinetics of its subsequent oxidation. Then, tiny amounts of unremoved oxygen in the Pt could act as a catalytic poison, impeding the oxidation of hydrogen sorbed near it. It is reasonable that the *L* electrode would hold oxygen more firmly in the H resorption region just as it did in the O removal region. The fact that oxygen coverage measured on *L* returns to the normal one monolayer at long times assures that no error in electrode area distorts these data.

A very long time, much greater than 10 sec, is required to cover the electrode with full steady-state H coverage, although the equivalent of one monolayer (210 μcoul/cm^2) is sorbed in about 0.2 sec on each electrode. This fact is fully consistent with the view repeatedly expressed by this Laboratory that hydrogen sorbed on the surface is present in various forms, namely, weakly and strongly bonded H and dermasorbed hydrogen (hydrogen present in the Pt atomic layers just below the surface layer). It is probable that resorption of hydrogen into the derma is the slow process governing uptake of the last portion of the hydrogen sorbed.

The difference between A and L which affects the rate of Pt-O_{ad} reaction with hydrogen also affects the manner in which hydrogen resorbs on the electrode. It does not, however, affect the $E(t)$-vs-time relation or the overall rate of sorption materially.

Oxygen Removal Region

Oxygen Coverage Versus Potential — It is apparent from Figs. 3 and 4 that the intrinsic difference between the reaction rates on the two electrodes is removed by normalization, giving voltage-vs-time and oxygen coverage-vs-time behaviors that are essentially the same. The data for $0.3 \text{ v} > E(t) > 0.0 \text{ v}$ (Fig. 4), in which the oxygen coverage of L appears to drop below zero, results from the anomalously high "oxygen" coverages found in the second pulse at certain times (c.f. Fig. 8 and discussion in preceding section). It appears that true zero Pt-O coverage may be more closely related to the point of inflection in the decay curve at 0.35 v and $t/t_0 = 0.90$. Conclusions previously drawn, based on comparisons of decay times, would not be influenced materially by a 10% change in the decay time used.

Rate of Oxygen Removal — The rate of oxygen removal was previously shown (2) to be zero order in hydrogen partial pressure and stirring rate. Hence, mass transport of solution H_2 to the surface is not rate-limiting. There is no indication that bare surface must be available for H_2 to chemisorb prior to reaction with Pt-O, for the integrated removal rate of oxygen was the same for initial coverages ranging from less than a monolayer to two monolayers (2). In this study the kinetics of the removal were essentially the same for initial coverages of 0.92 and 1.03 monolayers.

The changes observed, both in reaction order and rate when initial Pt-O concentration was less than 0.8 monolayer, indicate that the mechanism of the oxygen removal reaction changes. For this reason the cases where the initial coverage θ_a is less than 0.8 and where it is about 1.0 are discussed separately.

Case Where $\theta_a < 0.8$ — The rate of oxygen removal is independent of θ_a and x. This behavior is to be expected if the surface contains sites with widely differing activities, and if the overall rate of the reaction υ_R is determined by the rapid rate υ_R^* at relatively few "active sites" that comprise fraction ℓ of the surface and that are supplied (rate of surface diffusion υ_D) as rapidly as necessary from the reservoir of oxygen atoms sorbed on the rest of the surface. Recognizing that, in fact, there is probably a whole spectrum of sites of differing activity on the surface, we may for simplicity consider the surface to have two kinds of sites, active and inactive (or less active), of fractions ℓ and m with the fraction of ℓ and m covered with oxygen being θ_ℓ and θ_m. If ℓ is quite small, say less than 0.05 and if $\upsilon_D \gg \upsilon_R^*$, then as long as Pt-O is still present on inactive sites, ℓ remains fully covered until θ_m becomes very low. Hence, the rate of the reaction of the species on ℓ, which is the only area catalytically significant, will be zero order in reactant. This model would make reasonable the very wide variations in υ_R that have been observed as a result of thermally annealing or chemically etching the surfaces (1), because if ℓ is sufficiently small, then addition or subtraction of relatively few active sites can change ℓ substantially.

For several reasons it is improbable that active sites are obstructed by product molecules as the reaction proceeds. First, the product will either be H_2O, the same as the solvent, or if it is an intermediate, it is likely unstable with a short lifetime. Second, if active sites were obscured, then reaction rate would decrease with amount reacted, contrary to the data in Fig. 6. Finally, when all of the O_{ad} was reduced, the second charging curve in the O sorption region showed $q_O = 420$ μcoul/cm^2, the amount required for adsorption of one monolayer of O_{ad}. If during decay a significant amount of O_{ad} were reduced to a product that required only one electron per O_{ad} atom reformed, then recharging to full O_{ad} coverage would require less than 420 μcoul/cm^2.

Case Where $\theta_a \approx 1.0$ — The rate of oxygen removal was found to be first order in oxygen coverage. The reason for this difference in reaction order and the increase in initial rate at $a \approx 1.0$ is obscure. It is not the same sort of apparent reaction order change frequently noted in catalytic reactions, where as concentration of the reactant on the active surface increases, the reaction order decreases from unity to zero. Here, in the $\theta_a < 0.8$ case the active surface is thought to be fully covered at the lowest initial concentrations used, yet in the $\theta_a \approx 1$ case the additional adsorbed oxygen somehow causes a change in the reaction order.

Tucker (4) has reported that when oxygen at 2×10^{-6} torr interacts with Pt at 400°C, the results may be interpreted in terms of surface Pt atoms being displaced from their normal positions. If the high activity of the oxygen generated electrochemically in this work is a sufficiently large driving force, then perhaps a related rearrangement occurs here. In such a case the electrode surface at high oxygen coverages would be quite different from that at lower coverages, and a different mechanism would be reasonable. It is also conceivable that at very high coverages additional sites on the surface become catalytically important; hence, the initial rate becomes larger. However, it is then not clear why, when coverage has declined to 0.8, the other sites do not control the course of the reaction. In such a case a zero-order reaction rate should be observed for the removal of the remaining oxygen.

CONCLUSIONS

1. This work verifies that in H_2-saturated solution the time required for potential decay to about 0.300 v, after a preceding anodic pulse, is also the time required for removal of the chemisorbed oxygen deposited by that pulse.

2. The rate of removal of O_{ad} is of apparent first order in adsorbed oxygen when the initial fraction of surface covered is about 1.0; it is zero order in adsorbed oxygen and in amount reacted when the initial fraction of surface covered is < 0.8. It is zero order in hydrogen partial pressure in both cases.

3. Several alternative rate-determining steps in the decay reaction were considered, one being the rate of surface diffusion of O_{ad} or H_{ad} to the active sites, another being the actual rate of reaction at these active sites. The latter is favored as somewhat more probable, for it appears that active sites are involved rather than the whole surface, at least for $\theta_a < 0.8$. Steps probably excluded as rate-limiting are: (a) mass transport of solution H_2 to the surface, (b) obstruction of active surface sites by adherent product molecules, and (c) chemisorption of solution H_2 on electrode prior to reaction with Pt-O.

4. For electrodes of differing activities a significant difference is found in the way hydrogen resorbs on recently stripped electrodes — no difference other than rate is found in the way the Pt-O is removed.

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13. ABSTRACT

Surface coverages of oxygen and hydrogen were determined on electrodes of differing activities as a function of time and voltage in the potential decay curve following an anodic pulse. The electrolyte was 1M H_2SO_4 containing dissolved hydrogen. No important difference, other than rate, is found in the way Pt-O is removed from surfaces of differing activity; however, a significant difference is noted in the way hydrogen resorbs. The rate of Pt-O removal is of apparent first order in adsorbed oxygen when the initial fraction of the surface covered is about 1.0; it is zero order in adsorbed oxygen and amount reacted when the initial surface coverage is less than 0.8. It is zero order in hydrogen partial pressure in both cases. The rate of the decay reaction is probably not limited by mass transport of solution H_2 to the surface, by obstruction of active surface sites by sorbed product molecules, or by slow chemisorption of solution H_2 on the electrode prior to reaction with Pt-O.

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Catalysis, heterogeneous						
Hydrogen-oxygen reaction						
Electrode reactions						