NRL Report 6622

On the Activity of Platinum Catalysts in Solution

Part 1 - Effects of Thermal Treatment and Chemical Etching on the Pt-O/Hydrogen Specific Reaction Rate

THEODORE B. WARNER, SIGMUND SCHULDINER, AND BERNARD J. PIERSMA

Electrochemistry Branch
Chemistry Division

December 11, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

This document has been approved for public release and sale; its distribution is unlimited.

ABSTRACT

The effects of thermal treatment and chemical etching of platinum on the specific rate of the chemical reaction of chemisorbed oxygen with hydrogen were determined. The hydrogen was present in electrochemically clean 1M H_2SO_4 and in the derma of the metal. On successive thermal treatments of bright Pt beads, which were heated to the melting point and then slowly recrystallized under high temperatures, the specific rate varied randomly from trial to trial. Where heating was more uniform and the cooling rate slower, reaction of hydrogen with Pt-O was usually faster. Repeated aqua regia etching of a given Pt bead caused monotonic improvement until a rate between 0.014 and 0.021 amp/cm^2 was attained. Rates on Pt wire electrodes, which probably differed from the flame-formed Pt beads both in average crystallite size and number of defects (created by the drawing process and only partially removed by subsequent annealing), were highly variable but considerably lower than on beads. Surfaces whose activity for the Pt-O/hydrogen reaction differed manyfold showed no differences in anodic charging curves. Electrochemical rates of water oxidation at +0.617 v and +0.587 v (NHE) and reduction of hydrogen ions at +0.300 v also did not differ. It appears that many electrochemical reactions are insensitive to these differences in surface condition.

Because of its great sensitivity to catalyst pretreatments, the Pt-O/hydrogen reaction is identified as a "demanding reaction" especially useful for identifying and examining certain variables affecting contact catalysis in solution. Since impurity sorption is one such variable, the rate of this reaction is one of the most responsive cleanliness tests available.

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

NRL Problem C05-06,
Project SF 020-05-01-0809

Manuscript submitted July 28, 1967.

ON THE ACTIVITY OF PLATINUM CATALYSTS IN SOLUTION

Part 1 – Effects of Thermal Treatment and Chemical Etching on the Pt-O/Hydrogen Specific Reaction Rate

Theodore B. Warner, Sigmund Schuldiner, and Bernard J. Piersma*

Electrochemistry Branch
Chemistry Division

INTRODUCTION

Boudart, et al. (1), have pointed out that the rates of some catalyzed reactions are much more sensitive to subtle nonuniformities of solid surfaces than others. They suggested that it may be important to distinguish between these different types of reactions and proposed the terms demanding and facile reactions. They define a facile reaction as one for which the specific activity of the catalyst is practically independent of its mode of preparation. The selection and use of demanding reactions to monitor effects of changes in catalysts should offer considerable advantages in precision and discrimination.

It was previously found (2) that the rate of chemical reaction of oxygen, chemisorbed on a smooth platinum electrode, with hydrogen, present both in 1M H_2SO_4 solution and dissolved in the electrode, was very sensitive to changes in the composition of the surface. In particular, absorption of a monolayer of oxygen atoms in the top few atomic layers of the metal caused a change in the reaction mechanism and a sixfold reduction in rate; i.e., the Pt catalytic activity depended on the amount of dermasorbed oxygen, even when the amounts were much less than a monolayer. This reaction rate could be measured simply, quickly, and fairly precisely by observing the time required for potential decay after depositing known amounts of adsorbed and/or dermasorbed oxygen with an anodic current pulse. It appeared to be a demanding (1) reaction – well suited to study of other factors important in catalysis.

A study of catalysis must have as one prerequisite a way to eliminate effects due to impurity sorption. The responsiveness of the rate of the Pt-O/hydrogen reaction to surface variations made it more sensitive to trace impurities than any other rapid test we have had available; accordingly, the investigation was divided into two main sections. First, the effects of varying degrees of solution and metal cleanliness on rate were examined to determine under what conditions platinum could be considered sufficiently clean so that changes in catalytic behavior due to metallic factors were not obscured. The usefulness of this reaction rate as a cleanliness test was concurrently examined. Second, having established these criteria and while maintaining the necessary conditions, the effect on rate of changing the atomic arrangement and/or the surface condition of the metal was determined. This study was not designed to identify which types of surface conditions are the most active, although inferential evidence was obtained, but rather to demonstrate that subtle metal phase changes in a clean catalyst surface can have large effects on some reaction rates. The sensitivity of the studied reaction makes it a particularly useful experimental probe. Finally, the question was examined, will surface morphology changes that affect the catalytic activity for this chemical reaction necessarily cause changes in electrochemical reaction rates?

---

*National Academy of Sciences Postdoctoral Resident Research Associate at NRL. Present address: Eastern Baptist College, St. Davids, Pennsylvania.

APPARATUS AND GENERAL PROCEDURE

The gastight electrochemical system, He and H_2 purification trains, solutions, and general procedures were essentially the same as previously used (2,3). The cell contained a large platinum gauze counter electrode with a wetted geometric area of about 80 cm^2, a Pt wire reference electrode with a diameter of 0.064 cm extending about 3 cm into the solution, a miniature glass reference electrode, and two bright Pt-bead working electrodes with areas about 0.1 cm^2. The beads were formed by melting the end of a 99.99% pure Pt wire. One bead was mounted by sealing the wire into a Pyrex tube; the other was mounted in a Teflon tube and sealed with molten polyethylene. True electrode areas were determined from the amount of oxygen deposited in an anodic charging curve (3), and all areas given are true areas unless otherwise specified. The oscilloscope was a Tektronix Type 547 with Type 1A1 preamplifier; the electrolyte was 1M H_2SO_4 at 25 ±1°C, and all potentials are given versus the normal hydrogen electrode.

The cell was cleaned at various times using two different methods. The first method (4) used hot HNO_3, followed by numerous rinses with triply distilled water. In the second method the reference electrode and polyethylene-sealed bead were removed, and after cleaning with hot nitric acid, the cell and remaining electrodes were steamed for several days, while carrying the condensate out a side arm in a constant stream of purified H_2. Periodically, the cell was allowed to fill; on one such filling NaOH was added to make hot 1M NaOH; and the cell was soaked for 1 hour and then rinsed by further steaming. Finally, the condensate was again allowed to collect, and concentrated reagent grade H_2SO_4 was added to make up the electrolyte. In this cleaning technique the cell is isolated from the room atomsphere at all times except when adding the NaOH or H_2SO_4 or when replacing the electrodes. The laboratory air was continuously purified (5).

Solutions were cleaned by electrolysis with the Pt wire electrode as the cathode and all other electrodes as anodes under H_2 or He at 50 to 250 ma. The wire was susequently cleaned with HNO_2 and an H_2/O_2 flame, and any electrode removed was rinsed with concentrated HNO_3 and water before reinsertion.

Electrodes in the cell were cleaned by one or more of the following anodic treatments, listed in order of increasing severity and effectiveness: level 1, single anodic pulses just up to the O_2 evolution region, as in Fig. 1; level 2, multiple pulses as in level 1 with parital recovery of potential between pulses; level 3, dc anodization at 3 amp/cm^2; level 4, repeated (200/min) 7 amp/cm^2 pulses for periods of 1 to over 10 minutes.

Two classes of impurities could be distinguished by their influence on charging curves and by the difficulty of their removal from an electrode surface or from solution. Their exact natures are unknown; they will be defined as "readily oxidizable" or "difficultly" oxidizable" impurities. The first category could be removed from an electrode by level 1 or 2 anodization and could be removed from solution by extended electrolysis. The "difficultly oxidizable" impuriteis could be removed slowly, and sometimes only partially, with level 3 or 4 treatment, and they could not be removed from solution by electrolysis. They could be eliminated by celaning the cell and charging with fresh solution.

The strength of the bond between a foreign substance and a platinum lattice may vary continuously from weak physisorption to lattice incorporation. Impurities will be arbitrarily and operationally divided into those removable by the cell and cleaning techniques used and those not removable by these methods with the former being called "sorbed impurities" and the latter "lattice impurities." It should be understood that under this division a sufficiently tightly sorbed species could be classed as a lattice impurity and would be experimentally indistinguishable from one.

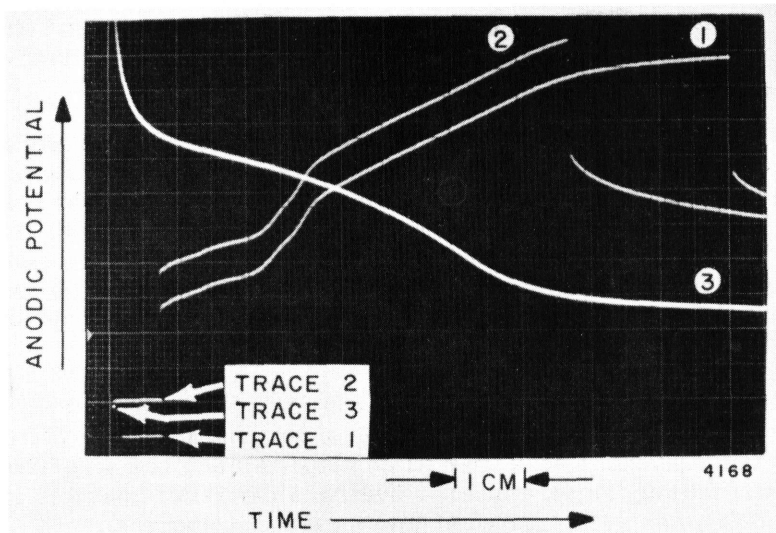

Fig. 1 — Traces 1 and 2; clean electrode charging curves at 2.3 amp/cm^2, 25° C, time = 50 μsec/cm, voltage = 0.5 v/cm. Trace 1 shows a full charging curve up to and into the O_2 evolution region, used to determine how much charge was required to deposit a monolayer of Pt-O. Trace 2 represents the pulse, adjusted in length such that just one monolayer of Pt-O was deposited, whose decay time was subsequently measured. Trace 3 is the subsequent decay curve; time = 5 msec/cm, voltage = 0.2 v/cm. Decay time ≈ 30 msec. The starting point of each trace is 0.000 v. The end point of trace 2 is 1.68 v, just below the 1.76 v normally associated with the beginning of the O_2 evolution region (3).

MEASUREMENT OF DECAY TIMES

The Pt electrode was exposed to a one-atmosphere hydrogen-saturated electrolyte until an equilibrium H^+/H_2 potential was reached. The electrode was then anodized with a single constant-current pulse, such that just one monolayer of atomic oxygen was deposited. Current densities of 2.5 to 7.0 amp/cm^2 were used to avoid dermasorption of oxygen in the metal lattice. Also, because of these high current densities and since the pulses were terminated before the O_2 evolution region was reached, an insignificant amount of O_2 was formed. At pulse cutoff the electrode potential became less positive as Pt-O was reduced by reaction with hydrogen. The time required for the potential to drop to a plateau at about 0.3 v is defined as the decay time. At 0.3 v the electrode is virtually free of O_{ad}, and significant H sorption commences. Figure 1 shows a typical display (for details see Ref. 2). In Ref. 2 varying amounts of oxygen q_O were deposited on the electrode, and the observed decay times t_{decay} were converted to reaction rates i_r, where

$$i_r \text{ (amp/cm}^2) = \frac{q_O \text{ (coul/cm}^2)}{t_{decay} \text{ (sec)}} . \qquad (1)$$

In this study the t_{decay} which resulted during removal of one monolayer of oxygen (420 μcoul/cm^2), deposited on the electrode in the manner described above, was defined as t_0, and reaction rates are frequently discussed in terms of the corresponding t_0. This procedure eliminates need for a priori knowledge of electrode area; it measures a quantity related to specific reaction rate, automatically adjusted for surface area changes. In

these terms the i_r previously found for a clean system of 0.014 amp/cm^2 (from Fig. 4a of Ref. 2; blank correction requires that ordinate values of Figs. 4 and 5 be divided by 2) is equivalent to a monolayer decay time t_0 of 30 msec.

During pulse cutoff and potential decay, the impedance between the working electrode and any other cell component must be high enough so that an insignificant current flow results. This condition is achieved by using a 10-megohm probe (for the circuit see Fig.3, Ref. 3) and adding blocking diodes to the pulse generator output to impede back flow of current after the pulse terminates (as in Fig. 2, Ref. 6). Long decay times of over 100 msec, that later decrease with additional purification, are excellent evidence for the absence of significant current leakage. Absence of long t_0 in less active systems would indicate undetected leakage paths.

Previous results (2) showed that decay times in clean solutions are not a function of hydrogen stirring rates from 0 to 560 ml/min nor of current density in the range used. The t_0 values are independent of soak time (time elapsed since last polarizing pulse) from 1 min to many days; neither temperature nor hydrogen partial pressure is important (although longer soak times are required at lower partial pressures).

CLEANLINESS CRITERIA

For the purposes of this report an electrode or a solution has been called clean if the following criteria were met. These criteria were monitored during the course of the experiments and were also used to estimate relative amounts and types of contaminants, when present.

1. Hydrogen electrode potentials – For a clean system at P_{H_2} = 1 atm, the potentials of the four smooth platinum electrodes differed by no more than 0.1 mv.

2. Current - voltage relations – Recent measurements (7) in a He-saturated solution in a separate "improved gastight system" showed that the rate of electrode recontamination with oxidizable or reducible species was no more than one millionth of the surface area per second – roughly equivalent to contamination rates in a 10^{-12} torr vacuum system. Further, there was no indication of the presence of any nonoxidizable electrode poisons. Certain of the present experiments were carried out in this improved gastight system immediately after termination of the previous work (7).

3. Anodic charging curves – Figure 1 represents curves typical of a clean system (8). They show detail in the hydrogen region, a small plateau in the double-layer region, and a linear oxygen region. To test system cleanliness with charging curves, it is first left under flowing hydrogen at open circuit for extended periods (usually 16 or 64 hours, sometimes longer). Polarization resulting from the very first pulse applied is photographed. After several intermediate charging curves to clean the surface, followed by a soak time of no less than 4 min, an additional pulse is photographed without changing trace position. If the two superimposed traces are essentially the same and if they meet the above criteria concerning shape, the system is judged clean. If the pulses do not coincide, the differences in pulse shapes, when correlated with soak time, can give information on the type and amounts of contaminants present.

4. Decay time – In the course of this work it was found that a low decay time, together with a linear O_{ad} formation region, is a dependable measure of cleanliness of an electrode and its associated electrolyte. Whenever possible, one electrode with a t_0 below 30 msec was obtained and used as a probe for solution condition, while the other electrode was treated in various ways. So long as the solution probe electrode retained its short and unchanging t_0, the solution was considered clean and unchanging.

RESULTS

Impurities and Decay Times

Removal of Impurities – Decay times are directly related to solution and/or platinum cleanliness. Given an imperfectly cleaned solution, as shown by charging curve tests, newly prepared Pt electrodes generally showed relatively high t_0 values of over 100 msec. This initial value depended on a number of variables. Repeated solution and electrode cleaning caused a steady reduction of t_0 to some limiting value, which will be called the base value of t_0. When this base value was reached, further cleaning of solution and electrode had no effect on t_0, and unchanged values of t_0 could then be observed for many weeks. When a base value was attained, other tests indicated a clean solution. Base values attained on different electrodes differed considerably, ranging from 25 to over 100 msec.

Factors Other Than Cleanliness – Factors other than solution or platinum cleanliness influence decay times. Two Pt electrodes, nominally the same and in the same solution at the same time, usually showed different initial values of t_0, differing on occasion by almost two orders of magnitude. Extended cleaning generally yielded base values of t_0 that also differed, a typical pair being 32.7 ± 3.2 and 100 ± 15 msec (all errors given for t_0 are standard deviations). Previous work* indicated that a t_0 value of 29.6 ± 3.0 msec could be attained in clean solution, so that Pt with a significantly higher t_0 was assumed to be capable of increased catalytic activity. Of the pair of electrodes mentioned above, the one with an invariant t_0 value of 33 msec indicated that the solution was clean and unchanging. The other was unaffected by any of the above cleaning techniques up to, and including, level 4 anodization while simultaneously boiling the solution. Other tests gave no evidence of impurity present. It was concluded that some factor other than solution cleanliness or undesired sorbed species also influenced t_0. In a series of experiments the higher base value t_0 of a given pair was independent of type of electrode mounting (glass or Teflon-polyethylene), eliminating that variable. The two-electrode studies described above also showed that given a clean solution, as indicated by the solution probe electrode, a newly prepared Pt electrode could be inserted into the cell without detectable solution contamination. This result was a necessary precondition to experiments described below. Such a newly inserted electrode would sometimes have sorbed impurity on it, as indicated by high initial t_0, that could be removed by the cleaning techniques used. The resulting base value t_0 varied over wide limits.

Introduction of Impurities – Decay time on "active" platinum in a clean solution increases upon introduction of impurities to the solution. Active Pt is defined here as Pt with a value of t_0 less than 35 msec in clean solution. The amount of impurity required to cause a detectable change in t_0 is related to the base value of t_0 originally shown; i.e., the lower the base value t_0, the more sensitive it is to traces of impurities. Clean solution containing two "active" electrodes were observed over long periods under conditions, such as frequent opening of the cell for short periods to insert or remove one electrode, where gradual solution recontamination from impurities in the room atmosphere was expected to occur. The presence or absence of impurity was estimated from charging curves, the relative amounts of impurity from amount accumulated in a given soak time. Simultaneously, the base values of t_0 were monitored, as well as the amount and level of electrode cleaning required to reattain the base value after long times on open circuit.

In solutions believed to be very clean the decay time from the very first charging curve applied after 12 days soak time was the same as the base value. With continued use, however, the "first decay time" after a given soak time became higher and higher, and successively more severe electrode cleaning was required to bring t_0 back to the base value. Finally, the original base value became unattainable, and "apparent base values" were observed that rose as more impurity collected in solution. These "apparent

*Data taken from that used in Ref. 2, Fig. 4a and i_r values converted to corresponding t_0.

base values" were unaffected by electrode cleaning up to level 4 or by extended pre-electrolysis of solution. Under these conditions, both the solution probe electrode and the working electrodes would show similar rises in apparent base value t_0; that is, they both appeared to be controlled by some external factor and took essentially the same value as they slowly rose together.

Rising apparent base values were connected with "difficultly oxidizable" impurities described more fully below. The point in this sequence at which such an impurity could be observed on the electrode using the charging curve test was highly variable, but, in general, "first decay times" observed after a few minutes soak that were higher than the base value would signal the presence of a "difficultly oxidizable" impurity under conditions where a charging curve after 8 to 24 hours frequently would not. On the other hand, when the impurity level in the solution was high enough to cause apparent base values to rise, its presence could be confirmed via charging curves after 8-hour soak periods.

This "difficultly oxidizable" impurity had a number of interesting properties. It was classed as "difficultly oxidizable" because it could not be removed from solution by extended electrolysis, and because when present in sufficient concentrations, it could not be removed from the electrode by anodization, as indicated by charging curves and by the rising apparent base values. Yet after long standing in H_2-saturated solutions, charging curves showed a species on the electrode surface that was oxidized at about 1 v. After this "readily oxidizable" species was removed, the electrode still had impaired catalytic activity, yet charging curves gave no indication of any remaining impurity. It was tentatively concluded that this condition was caused by some nonvolatile, oxidized form of an impurity that could interact only slowly with H_2 to give an oxidizable product on the electrode surface, yet was itself not removed with anodic treatment. Note the interesting similarities between this substance and CO_2, which, when present in solutions containing H_2, also causes anodic charging curves to show something being oxidized at around 1 v (9).

The importance of these observations is that "difficultly oxidizable" impurities might accumulate in any real system under prolonged use. Even if the amount of surface covered with these impurities were too small to influence charging curves, demanding reactions, such as the Pt-O/hydrogen reaction, could be affected. Hence, to study such demanding reactions the usual kinds of anodic cleaning may not suffice.

The above results indicated that the increasing values of t_0 were due to impurity sorption. However, it was also possible that some other process, such as a slow change in the catalyst lattice, could be affecting the base t_0. If the increase in t_0 had been due to sorption of some impurity very resistant to removal by anodic polarization, recleaning the solution and cell should cause the original value of t_0 to be regained. These treatments would not affect a changed catalyst structure, however. Experimentally, the original base value could be regained by recleaning the cell, recharging with fresh solution, and again cleaning the solution and the electrodes in situ. In a typical case the initial base value was 23 msec, the highest apparent base value was 55 msec, and the regained base value after recleaning was 25 msec. It might be argued that the solution electrolysis following recleaning of the cell would once again modify the base lattice to make it "active" again; however, the results described subsequently (in the section "Thermal Annealing") show that anodization of a surface is not a necessary prerequisite for an active surface, and, further, that anodization of an inactive but clean surface will not affect its activity in the least.

High Decay Times in Clean Solutions – If under the treatments described the only variable causing changes in t_0 was sorbed impurity, and if a system were sufficiently clean initially, then the initial value t_0 should be the same as the base value. It was desirable to obtain evidence in a system whose cleanliness was measured by an independent method. The "improved gastight system" (7) was such a system. The initial value of t_0 was 270 msec; it was unaffected by increasingly severe anodic treatment up to level 4 while simultaneously boiling the solution.

Variables Intrinsic to Platinum

Different Pt electrodes, nominally the same, showed widely differing values of t_0, even when clean and in clean solutions. The variables that could affect the catalytic activity for the Pt-O/hydrogen reaction fivefold or tenfold appeared to be fixed in the platinum when the electrodes were frozen. The following experiments were primarily designed to show that this effect occurred. The Pt surfaces were rearranged by remelting and by different heat treatments, and the effect on decay time was observed. Surfaces were also etched with aqua regia. In the following work, unless otherwise specified, solutions were clean as indicated by an active solution probe electrode with unvarying decay time, usually less than 25 msec. Cleanliness also was checked against the other criteria mentioned. Effects due to impurities introduced into the cell on a newly inserted electrode were eliminated, and all t_0 values under these conditions are necessarily base values.

Thermal Annealing – Platinum beads were melted and recrystallized repeatedly, with determination of t_0 between subsequent treatments. They had highly variable decay times on successive trials. Figure 2* shows the typical appearance of a well-annealed Pt bead before mounting. It is nominally spherical with a number of well-developed flat regions that may have crystallographic significance. Not only are the developed flats regularly arrayed, but emerging flat regions are also part of the pattern. For example, the emerging regions at 2 and 8 o'clock in the 45-degree view are spaced between the large flats at 11 and 5 o'clock. A similar emerging region can be seen in the 225-degree view. Under proper conditions, an entire bead could be held molten for as long as desired in a relatively large flame, whose temperature was adjusted by changing the H_2/O_2 ratio. By reducing the temperature gradually the bead could also be kept indefinitely just below the crystallization temperature and then slowly cooled from there. Beads so formed had variable t_0 values ranging from 20 to over 100 msec. They were highly reflective and, in general, would have no visible (10X optical) surface irregularities other than the flats. Beads made with smaller flames or cooled rapidly from a molten condition frequently showed fissures due to contraction on cooling, and flats were neither so numerous nor well formed. Their t_0 values also varied with repeated reforming of the same bead. They were frequently much higher, a typical series being 550, 200, 600, and 650 msec.

Typically, on inserting a newly formed bead, it was repeatedly anodized to oxygen evolution (in such a way as to introduce dermasorbed O) to remove surface impurities. Usually this procedure caused the value of t_0 to fall lower than the initial value. It was possible that the repeated introduction of oxygen into the lattice followed by its removal with hydrogen was alternately expanding and contracting the Pt surface layers and that this process was essential in changing t_0. However, on several occasions the initial t_0, before any anodic polarization other than the single charging curve, was less than 30 msec and was also the base value; i.e., heavy anodic polarization in clean solutions is not a prerequisite for low t_0. Furthermore, heavy anodization of an originally clean electrode does not affect t_0 even when it is as high as 270 msec (c.f. Section "High Decay Times in Clean Solutions"). Anodization is presumed to reduce t_0 primarily by removing sorbed species.

Chemical Etching – Decay time on a given Pt bead decreased monotonically with time etched in hot aqua regia until a t_0 value was reached which matched the solution probe electrode (between 20 and 30 msec). Further etching caused no change in t_0, and it would then remain unchanged as long as the solution remained clean. Since t_0 remained unchanged over long periods, it was concluded that contamination by Cl_2 or Cl^- had been avoided. Microscopic examination showed that etching occurred first in the regions between flats and more and more area was attacked as etching continued, but the centers of many of the flats remained bright even after 15 min etching. Since attack is expected at

*Photographs were obtained by surrounding the bright, reflective bead with a white right-circular cylinder marked with a black grid of parallel lines. Illumination was projected downward through a translucent planar surface, also marked with a rectangular grid, that appears as a bright circle in the photographs.

the most highly strained areas first these observations supported the hypothesis that the flats might be crystallographically significant.

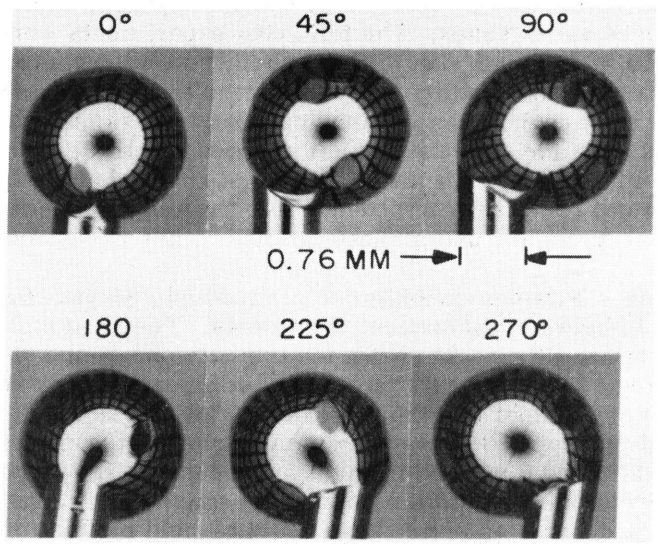

Fig. 2 – Views of a flame-formed platinum bead at various approximate amounts of clockwise rotation. Magnification ≈12X. Photos by A.C. Simon.

Platinum Wires versus Platinum Beads – If the structural form of the underlying crystal lattice is significant, rates on wires should be different from rates on beads, because the drawing process introduces large numbers of defects and possibly also surface impurities that can only be partially removed by annealing. Furthermore, a wire is unquestionably composed of many small crystallites. Wire electrode t_0 values under extended aqua regia treatment could not be brought down to active bead values; the lowest wire decay time achieved was 120 msec.

Electrochemical Rates on Different Pt Electrodes – Previous measurements of hydrogen overvoltage, anodic charging curves, etc., in this Laboratory have not shown any detectable variation when measured on different electrodes, yet the foregoing indicates that substantial differences in catalytic activity for the chemical Pt-O/hydrogen reaction are the general rule. This result suggested that these electrochemical reactions may be facile reactions, i.e., independent of Pt pretreatment.

Rates of oxidation and reduction of water were measured in an "improved gastight system" (7) with a t_0 = 270-msec electrode. Brief aqua regia treatment reduced t_0 to 50 msec, and three representative points were redetermined. Data are shown in Table 1; the currents were measured under He stirring rates of 350 ml/min, and the currents given for the t_0 = 270-msec electrode are mean values taken from Fig. 1 of Ref. 7. Current uncertainty at a given potential is about ±30%. Etching the Pt bead did not affect these rates within experimental error, although it increased the rate of the Pt-O/hydrogen chemical reaction involved in the decay fivefold.

Table 1
Reaction Rates on Different Electrodes

Potential vs NHE (v)	Current (amp/cm^2)	
	$t_0 = 50$ msec	$t_0 = 270$ msec
+0.617	$+2.0 \times 10^{-8}$	$+2.0 \times 10^{-8}$
+0.587	$+1.2 \times 10^{-8}$	$+1.2 \times 10^{-8}$
+0.300	-4.5×10^{-8}	-6.0×10^{-8}

DISCUSSION

The results show that each Pt electrode as formed had some intrinsic activity for the chemical reaction

$$\text{Pt-O}_{ad} + \text{hydrogen} = \text{Pt} + \text{H}_2\text{O}. \tag{2}$$

Hydrogen is available from solution as H_2 and from the Pt metal as dermasorbed H. The intrinsic activity, that is, the catalytic activity of the clean metal, varied widely depending on how the metal was orginally crystallized, worked after being crystallized, or etched. These treatments should affect the state of the surface, possibly by changing the type and number of grain boundaries exposed at the surface, by changing the number and distribution of crystal defects at or near the surface, or by changing the number and distribution of impurity atoms in the lattice and exposed at the surface. Carbon is one such impurity persistently present in trace amounts in platinum, and the platinum atoms surrounding such an impurity are expected to be quite different energetically. Previous work (2) indicated that oxygen present as an impurity in the lattice would change activity. The relative importance of each of these factors cannot be established on the basis of these experiments.

Since the detailed mechanisms of the chemical Pt-O/hydrogen reaction and the electrochemical reactions investigated are not known, it is not possible to establish why the former should be so sensitive to surface changes while the latter are unaffected. However, it may be suggested that one way these reactions differ is in the extent that surface diffusion of reactant is rate limiting. Notwithstanding the many differences between gas and solution phases, diffusion over the surface of a metal is expected to be very sensitive to structural differences. For example, working in the gas phase Ehrlich and Hudda (10) observed that surface diffusion of tungsten adatoms on tungsten occurred at different rates on different single crystal planes, that migrating atoms were reflected at boundaries of certain planes, and that in some planes motion along atomic rows was favored over diffusion across lattice steps. The thermal and chemical treatment used could act in a way to remove barriers to rapid surface diffusion. It was previously concluded (1) that the probable rate-determining process in the decay reaction was diffusion of either O_{ad} or H_{ad} over the surface to an active site.

It is not appropriate to speak in general about "active" or "inactive" electrodes, because one may be more active than the other for a demanding reaction, but both may be equivalent and as active as possible for a facile reaction. If the reaction that defines the "activity" is explicitly given, then such ambiguity is avoided. This necessary distinction obviously also applies to such terms as "electrode activation." One aspect of this investigation should be stressed. Anodic pretreatment of clean electrodes, for extended periods at up to 7 amp/cm^2, changes neither the surface area nor the Pt "activity" for the

Pt-O_{ad}/H_2 reaction. If, however, Pt electrodes have impurities sorbed on them, anodization can improve such activity. Platinum electrodes, equal in activity to the best obtained, could be achieved with no initial anodic treatment. Such "active" surfaces stay active and unchanged indefinitely on open circuit – as long as they remain clean.

The combination of a charging curve and its subsequent decay curve gives extensive information concerning solution and electrode cleanliness. Charging curves are extremely sensitive to chemisorbed oxidizable substances (9), whereas this work shows that they may fail to signal the presence of traces of "difficultly oxidizable" impurities. On the other hand, decay curves may not be influenced by trace amounts of easily oxidized species, which would tend to be removed by the preceding charging curve, but they are dependably influenced by "difficultly oxidizable" species present in quantities too small to be detected by any other technique. Experience indicates that these "difficultly oxidizable" impurities are more prevalent than heretofore expected, and while they require demanding reactions to detect their presence in trace amounts, they can seriously affect catalysis. Experience also suggests, however, that the electrochemical reactions previously studied in this Laboratory are relatively facile and unaffected by Pt surface structure.

CONCLUSIONS

The specific rate of the chemical reaction of oxygen, chemisorbed on platinum with hydrogen, is particularly sensitive to metallic pretreatment. Under clean conditions, certain thermal, chemical (etching), and physical treatments can modify this rate manyfold, while several electrochemical reaction rates monitored concurrently are unchanged.

This "demanding reaction" is proposed as especially useful for identifying and examining certain variables affecting catalysis. Because impurity sorption is one such variable, the rate of this reaction is one of the most responsive cleanliness tests available. It is quickly and easily applied and is a convenient way to monitor solution purity.

Anodization of a platinum surface is not a necessary prerequisite for maximizing its catalytic activity for either the Pt-O/hydrogen reaction or the electrochemical reactions investigated. Under clean conditions, anodization of Pt that has low activity for this reaction does not affect its activity in the least. When sorbed impurities are present, anodic treatment can improve "activity" by removing these sorbed species, but such anodization cannot do more than bring activity up to that intrinsic to the clean metal itself.

ACKNOWLEDGMENTS

We thank Mr. A.C. Simon for devising the technique and obtaining the photographs shown in Fig. 2, Mrs. J.B. Burbank, and Dr. R.L. Jones for fruitful discussions concerning crystallography.

REFERENCES

1. Boudart, M., Aldag, A., Benson, J.E., Dougharty, N.A., and Harkins, C.G., J. Catalysis 6:92 (1966)

2. Schuldiner, S., and Warner, T.B., J. Electrochem. Soc. 112:212 (1965)

3. Schuldiner, S., and Roe, R.M., J. Electrochem. Soc. 110:332 (1963)

4. Schuldiner, S., Piersma, B.J., and Warner, T.B., J. Electrochem. Soc. 113:573 (1966)

5. Warner, T.B., and Schuldiner, S., J. Electrochem. Soc. 112:853 (1965)

6. Schuldiner, S., and Presbrey, C.H., Jr., J. Electrochem. Soc. 111:457 (1964)

7. Schuldiner, S., Warner, T.B., and Piersma, B.J., J. Electrochem. Soc. 114:343 (1967)

8. Schuldiner, S., and Warner, T.B., J. Phys. Chem. 68:1223 (1964)

9. Piersma, B.J., Schuldiner, S., and Warner, T.B., J. Electrochem. Soc. 113:1319 (1966)

10. Ehrlich, G., and Hudda, F.G., J. Chem. Phys. 44:1039 (1966)

This page intentionally left blank.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D. C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

On the Activity of Platinum Catalysts in Solution. Part 1 – Effects of Thermal Treatment and Chemical Etching on the Pt-O/Hydrogen Specific Reaction Rate

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

This is an interim report on one phase of the problem

5. AUTHOR(S) *(First name, middle initial, last name)*

T. B. Warner, S. Schuldiner, B. J. Piersma

6. REPORT DATE December 11, 1967	7a. TOTAL NO. OF PAGES 15	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. NRL Problem C05-06 b. PROJECT NO. SF 020-05-01-0809 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6622 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribtuion is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Ship Systems Command) Washington, D. C. 20360

13. ABSTRACT

The effects of thermal treatment and chemical etching of platinum on the specific rate of the chemical reaction of chemisorbed oxygen with hydrogen were determined. The hydrogen was present in electrochemically clean 1M H_2SO_4 and in the derma of the metal. On successive thermal treatments of bright Pt beads, which were heated to the melting point and then slowly recrystallized under high temperatures, the specific rate varied randomly from trial to trial. Where heating was more uniform and the cooling rate slower, reaction of hydrogen with Pt-O was usually faster. Repeated aqua regia etching of a given Pt bead caused monotonic improvement until a rate between 0.014 and 0.021 amp/cm^2 was attained. Rates on Pt wire electrodes, which probably differed from the flame-formed Pt beads both in average crystallite size and number of defects (created by the drawing process and only partially removed by subsequent annealing), were highly variable but considerably lower than on beads. Surfaces whose activity for the Pt-O/hydrogen reaction differed manyfold showed no differences in anodic charging curves. Electrochemical rates of water oxidation at +0.617 v and +0.587 v (NHE) and reduction of hydrogen ions at +0.300 v also did not differ. It appears that many electrochemical reactions are insensitive to these differences in surface condition.

– Continues

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Dermasorbed oxygen						
Chemisorbed oxygen						
Platinum						
Hydrogen						
Catalysis heterogeneous						
Hydrogen-oxygen reaction						
Electrode reactions						

Because of its great sensitivity to catalyst pretreatments, the Pt-O/hydrogen reaction is identified as a "demanding reaction" especially useful for identifying and examining certain variables affecting contact catalysis in solution. Since impurity sorption is one such variable, the rate of this reaction is one of the most responsive cleanliness tests available.