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Oxidation of Hydrogen on a Passive Platinum Electrode

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ABSTRACT

Under potentiostatic, steady-state conditions and at anodic potentials above 0.7 V (NHE), the rate of oxidation of molecular hydrogen decreases at a high-activity Pt electrode in 1M H_2SO_4. It is shown that this decrease is not owing to the formation of oxygen species on the electrode surface. It is believed that this passive behavior of Pt is due to anion adsorption — at least between 0.7 and 1.2 V. Depending on potential and previous potential sequence, passivity in this region is evidently sensitive to the amount of sulfate ion adsorbed, its heat of adsorption, and the presence of dermasorbed oxygen. At higher potentials both sorbed oxygen species and sulfate ion may be present and may contribute to the passivity. In the 0.7 to 1.2 V passive region, hydrogen oxidation is electrochemical. There is no significant chemical oxidation via an oxygen intermediate.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

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OXIDATION OF HYDROGEN ON A PASSIVE PLATINUM ELECTRODE

INTRODUCTION

A steady-state electrochemical investigation (1) in a high-purity closed system (2) showed very slow oxidation of water on Pt in a helium-saturated 1M H_2SO_4 solution in the potential region from 0.46 to 1.6 V (vs NHE). That work (1) established the solvent (water) reaction rates in this potential region. Since the oxidation of water occurs at such slow rates, it appears that on the addition of an easily oxidizable species to the system, the oxidation of this added species would predominate.

Several papers (3,4) by Wroblowa, Bockris, et al., demonstrated that even though the rate of hydrocarbon oxidation is increased as the potential is increased to about 0.9 V, the rate of oxidation decreases at higher potentials. They postulated that this decrease in reaction rate was caused by the formation of a Pt oxide which passivated the surface. Even though the work was done at 80°C, compared to the previously mentioned study (1) on water oxidation which was at 26°C, there is a question as to why an oxide should be formed in the presence of an oxidizable species in the potential region of interest.

The answer to this question is, of course, a matter of mechanisms. If water oxidation is rate-controlling, then in the presence of a species which is electrochemically inert but which is chemically oxidized rapidly by the oxidation product of water on Pt, the rate of water oxidation may be increased. However, in such a case the accumulation of the oxidation product of water would not occur and could not cause passivation of the surface. If the oxidizable species is electrochemically oxidized faster than water but retardation by a significant accumulation of an oxygen species from water may occur, then its rate will be controlling. However, it is difficult to conceive of an oxidation product of water on a Pt surface which would not be very easily reduced, so that chemical reaction of water oxidation products with added oxidizable species is very likely. In any case, if the current density is much greater at a given potential in the presence of an added oxidizable species, the very slow oxidation of water plus the high reactability of such oxygen species makes the passivation of the surface by an oxide or oxidation product of water hardly feasible.

Anodic passivation of a surface has been explained in another possible way by Frumkin (5). He believes that passivation could be caused by the saturation of the free valencies of the electrode surface by chemisorbed anions. Anodic passivation of Pt for the hydrogen reaction has been repeatedly observed by many investigators (6). Aikazyan and Fedorova (7) and Wicke and Weblus (8) attributed this passivation to either adsorption of anions or the appearance of surface oxides. Frumkin (6) claims that at high disk-electrode rotation rates the drop in the current maxima can occur at potentials of about 0.05 V, which is much too low for an oxide formation and he believes must be due to anion adsorption. Frumkin and coworkers believe that passivation by oxygen occurs at potentials of about 0.8 V.

Kazarinov and Balashova (9) showed that as the potential of platinized Pt became more positive, the concentration of adsorbed sulfate ion increased linearly until a potential of 0.8 V was reached. At higher potentials the sulfate-ion concentration decreased. They interpreted this decrease as due to the formation of an oxygen species on the surface

(their work was done in N_2-saturated solutions of H_2SO_4), which caused a partial displacement of sulfate ion. On smooth Pt they found that at potentials above 1.5 V there was a sharp increase in adsorbed sulfate ion, which they attributed to the incorporation of these anions in the oxides on the surface. Here again, one can ask the question: If an oxidizable species (other than water) is present, will it, under steady-state, potentiostatic conditions, interfere with the formation of oxygen species on the surface and influence the adsorption of the sulfate ion?

To try to answer the question of water oxidation in the presence of other oxidizable species and to try to gain some further insight into the passivation of Pt, it was decided to study further the oxidation of hydrogen in the passive Pt region. Hydrogen was selected because it is easily oxidized on active Pt, and its maximum rate of oxidation of 2×10^{-3} A/cm^2 (true-area basis) in H_2SO_4 is from two to seven orders of magnitude greater than water oxidation (1) in the same potential region. Use of the high-purity closed system (1,2) developed at NRL would permit long-time steady-state measurements where relatively slow sorption phenomena could affect electrode behavior. This system also allowed a determination of the hysteresis, when high potentials are decreased, noted by Frumkin and Aikazyan (10).

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental setup and conditions were the same as described in Ref. 1, except that a constant flow of hydrogen, purified by flowing through heated Pd-Ag tubes and saturated with pure water, replaced helium. It was found that an N_2 atmosphere in the environment box was unnecessary, and part of the data was taken with the front panel removed. The hydrogen flow into the cell remained at about 40 ml/min until a constant current was reached under potentiostatic control. The time required ranged from a quarter of an hour to many hours, depending both on the set potential and the previous sequence of potentials. The hydrogen flow rate was then increased to well over 1000 ml/min, and the constant current recorded. Potentiostatic control was by a Pt/H_2 wire electrode in the cell. The sulfuric acid solution was one molar, the temperature was 25 ±2°C, and the true (11) area of the three Pt-bead working electrodes used was each close to 0.2 cm^2.

The experimental results, which are steady-state values, are shown in Fig. 1. Figure 1 is for the case of very rapid stirring with hydrogen and gives potentiostatic current density vs potential relations under conditions where diffusion effects in solution are minimized. For the slopes shown, $b = \Delta E/\Delta \log i$. The b = -0.025 and 0.025 values shown are the well-known Tafel slopes (12) in the cathodic and anodic polarization regions, respectively. At anodic potentials above 40 mV, a limiting current density of 2×10^{-3} A/cm^2 is observed up to a potential of about 0.7 V. At potentials above this value, the current density decreases, at first slowly up to 1.0 V, then rapidly along the slope designated as b = -0.11 down to a second limiting current density of about 1.5×10^{-5} A/cm^2. At potentials above 1.6 V (the b = 0.13 slope) the normal oxygen evolution reaction is observed. The diamond-shaped symbols show that potential reversal within a given region gave the same current densities.

After the oxygen evolution region was reached, a subsequent decrease in potentials gave the hysteresis shown. The time required to obtain steady-state for each point in this region ranged from a few hours to a day. The scatter of points, and especially the two paths shown in the potential range from 1.16 to 0.88 V, appeared to be real. Using the same electrode a consistent set of points on either path was followed for a particular run. The path shown by the solid line, however, was favored over the dotted line. The broken line shown in Fig. 1 comes from Fig. 1 of Ref. 1 and represents the potential vs current density relation found in a pure helium-saturated solution.

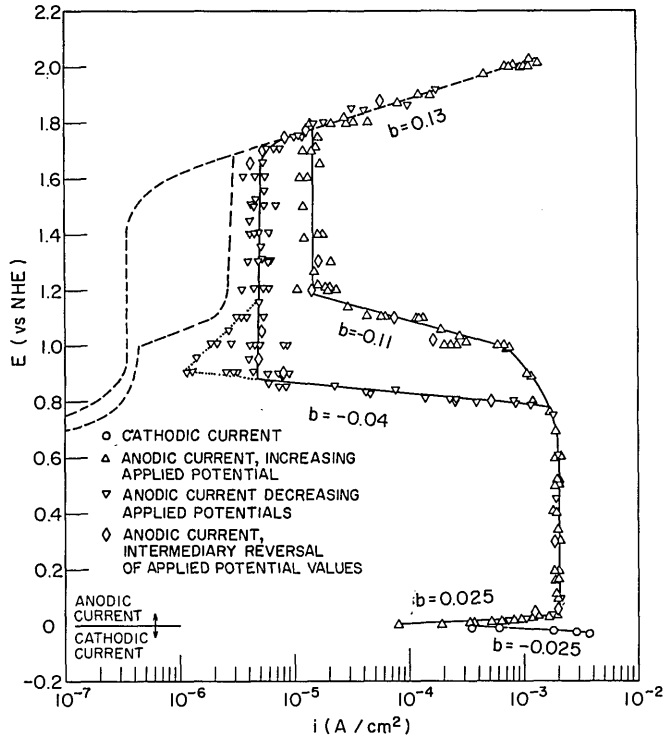

Fig. 1 – Steady-state, potentiostatic current density vs potential relationship on Pt in hydrogen-saturated 1M H_2SO_4; H_2 flow rate >1000 ml/min; the broken line gives the current density vs potential relationship in helium-saturated solution where the hysteresis line to the right is for increasing applied potentials, and the hysteresis line to the left is for decreasing applied potentials. The meaning of the dotted line is explained in the text.

DISCUSSION

A comparison of Fig. 1 with the data shown by Frumkin and Aikazyan (6,10) for hydrogen ionization on a smooth Pt disk electrode in 1M H_2SO_4 at a rotation speed of 20,000 rpm shows some important differences. Figure 1 shows a maximum current density from 0.04 to 0.7 V of 2 mA/cm^2 (since this current density is on a true-area basis, it is equivalent to about 4 mA on a geometric-area basis). This limiting current density is essentially the same as the Frumkin and Aikazyan value of 3.8 mA/cm^2 (geometric-area basis). In the Frumkin and Aikazyan case, however, the current density maximum is at 0.05 V and there is a continuous dropping off of current density with increasing potential up to 1.2 V. Figure 1 shows a constant current density of 2 mA/cm^2 up to 0.7 V (for both the increasing and decreasing sequence of potentials), followed by a slow decrease, and then a linear log decrease in current density up to 1.2 V.

The essentially equivalent maximum current densities found by Frumkin and Aikazyan and this work show that the Pt electrodes were of equal activity. The important difference is that Frumkin and Aikazyan anodically and cathodically pre-electrolyzed their electrode just before taking measurements, which were than taken in a matter of minutes at each

potential setting. With the high-purity system, long-time steady-state measurements were possible because poisoning of the electrode did not occur (as, for example, evidenced by the constancy of the maximum current density for long periods of time). Whether the Frumkin and Aikazyan decrease in current density (from 0.05 to 0.7 V) was due to impurity adsorption or a lack of true steady-state conditions at the electrode is uncertain.

Considering Pt passivation above 0.7 V, the possibility of a stable oxygen species remaining on the surface is remote. In the first place, the oxidation of water, which appears to be limited by slow discharge (1), occurs at rates from about five to one order of magnitude slower. In addition, Schuldiner and Warner (13,14) have shown that oxygen chemisorbed on Pt reacts rapidly with molecular hydrogen. Warner and Schuldiner (15) have shown also that the reaction rate is potential independent and zero order in both hydrogen and chemisorbed oxygen when the initial fractional coverage with chemisorbed oxygen is less than 0.8. Reaction rates of chemisorbed oxygen with hydrogen in this particular system for the three different working electrodes used were 0.4, 1.2, and 8 mA/cm^2. All three electrodes gave virtually the same potential vs current density results.

The chemical rate of reaction of any oxygen which may be formed on the surface with hydrogen would, with a few exceptions, always be faster than the rate of anodic hydrogen oxidation. Hence, there is little possibility that chemisorbed oxygen or an oxygen species exists on the surface, at least up to a potential of 1.2 V. This analysis does not, of course, prove that an oxygen species may not be formed which rapidly oxidizes the hydrogen and that the rate-controlling process depends either on the rate of formation of this oxygen species or its reaction rate with hydrogen. However, it is very unlikely that the anodic hydrogen reaction under these conditions would be slower than the oxidation of water. (It will subsequently be shown that in this region a chemical oxidation of hydrogen with an oxygen intermediate does not occur.) These results show that the oxidation of Pt or the formation and adsorption of oxygen species are not the cause of the Pt passivation and retardation of the anodic hydrogen oxidation reaction at least up to 1.2 V.

The cause of passivation is much more likely the anion adsorption explanation as given by Frumkin (5), that is, the adsorption of sulfate ion as was demonstrated by Kazarinov and Balashova (9). In the Kazarinov and Balashova paper a dropping off of the amount of sulfate ion adsorbed above 0.8 V was observed. However, this work was done in a N_2-saturated solution, where formation and adsorption of an oxygen species and the partial replacement of sulfate are possible. In a hydrogen-saturated solution, a residue of oxygen would not remain on the surface, so that as the potential increased beyond 0.8 V, an increase in the amount of sulfate would be expected. And, in fact, as was shown by Kazarinov and Balashova, at higher potentials the coverage with sulfate ion can increase even in the presence of oxygen. With the elimination of a chemisorbed oxygen species, or Pt oxide, the bonding and coverage of the surface with sulfate ion should increase and is a reasonable explanation of the increased passivity shown in Fig. 1. The limiting current density from 1.2 to approximately 1.8 V can be due to a saturation of the surface with sulfate ion.

It should be noted that the b = -0.11 and -0.04 slopes in Fig. 1 are not Tafel slopes. The fact that the rate of hydrogen oxidation decreases with increasing potential demonstrates that the rates are not controlled by the exponential overvoltage term in the kinetic equation. The controlling term is obviously in the free energy of activation for the oxidation of hydrogen. As the potential increases, the free energy of activation can increase because of the increased coverage with sulfate ion and because of the increase in bonding of the sulfate ion with the surface.

It may be surprising that in the oxygen-generating region (b = 0.13) the presence of hydrogen has no apparent effect on the rate of oxidation of water. There is no "so-called"

depolarization effect. This must be because the combined sulfate and oxygen sorption in this region is so extensive that significant anodic oxidation of hydrogen is virtually completely blocked. The data also show that the oxidation of water is primarily under charge-transfer control. Otherwise, the chemical reaction of hydrogen with oxygen on the surface could influence the rate. In this region current densities were independent of stirring rate, which also indicates virtually complete kinetic control.

The effects of dermasorbed oxygen (16) can be seen in the Fig. 1 data. Once the potential exceeds 1.8 V, extensive dermasorption occurs and hysteresis results. In the potential range from 1.7 to 1.2 V, the rate of hydrogen oxidation is reduced by about one-half. From about 1.16 to 0.88 V either the solid or dotted line was followed. Evidently, the amount or distribution of dermasorbed oxygen may vary from run to run and may markedly influence the passivity behavior of the electrode. This influence of dermasorbed oxygen is evinced also by the scatter of points, which were, however, consistent for a particular run, in the entire region from 1.7 to 0.88 V.

Something remarkable occurs in the b = -0.04 region. At current-density values greater than 1.5×10^{-5} A/cm^2, the potential required for the oxidation of hydrogen at a given current density can be as much as 0.3 V less than in the b = -0.11 region. In the b = -0.04 region most of the dermasorbed oxygen would be removed, but a trace must remain because one can go up and down in potential in this region and remain on the b = -0.04 line. Once the intersection at about 0.8 V is reached, increasing potentials will follow the path leading to the b = -0.11 slope. This eliminates the possibility of an impurity in the region of decreasing potential. However, at the same potentials on the increasing potential arm of the curve, the current densities are considerably higher. The lower current densities in the b = -0.11 region are evidently due to increased sulfate ion adsorption. Hence, in the b = -0.04 region the presence of dermasorbed oxygen plus the lower sulfate ion adsorption reduces the activation energy (potential) required to oxidize hydrogen at a given rate. However, at a given amount of sulfate ion adsorption the rate of hydrogen oxidation would always be lower in the presence of dermasorbed oxygen.

Another interesting consequence of this region is that the previous work (1) in helium-saturated solution showed that in the presence of dermasorbed oxygen a given rate of oxidation of water to an oxygen species (which was not retarded by increased sulfate ion adsorption) always occurred at a higher potential. If the oxidation of hydrogen took place via an intermediate oxygen species, then in the presence of dermasorbed oxygen a given rate of hydrogen oxidation should never occur at a lower potential. Since in the b = -0.04 region oxidation of hydrogen at a given rate can occur at a lower potential than in the b = -0.11 region (which is free of dermasorbed oxygen (1)), the oxidation cannot be through an oxygen intermediate but must involve a direct electrochemical oxidation of hydrogen. Another conclusion is that pulsing or other electrochemical activation procedures of electrodes may do more than just clean the surface.

The catalytic properties of Pt are strongly affected by adsorbed sulfate ions and by dermasorbed oxygen. The relationships are very complex, but it appears that a narrowing down of possibilities is resulting. Since information is available concerning very slow solvent oxidation and relatively fast oxidation of the ideal fuel, hydrogen, similar studies made with organic fuels of intermediate oxidizability should be revealing.

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