

Effects of Oxidizable Anion Adsorption on the Anodic Behavior of Platinum

SIGMUND SCHULDINER

*Electrochemistry Branch
Chemistry Division*

June 7, 1968



NAVAL RESEARCH LABORATORY
Washington, D.C.

ABSTRACT

The retardation of the hydrogen oxidation reaction, which commences at about 0.7 v (NHE) in sulfuric acid solution, can be modified by the presence of formate ions. Steady-state, potentiostatic measurements were made in formic acid solution and formic acid-sulfuric acid solution, both in the presence and absence of hydrogen.

The work showed that at potentials under 1.5 v passivity was due to adsorbed anions rather than adsorbed oxygen atoms, Pt oxides, or free radicals formed by the oxidation of water. Pure formic acid solutions were not passivated below 1.5 v; however, formate ions did retard hydrogen oxidation but not as strongly as sulfate ions. The oxidation of formic acid in solutions containing sulfuric acid was affected by adsorption of both sulfate and formate ions. The retardation of the net oxidation of hydrogen and formic acid in formic acid-sulfuric acid mixtures was less than that of hydrogen in sulfuric acid. In the presence of adsorbed oxygen, both formate and sulfate ions strongly retard the oxidation of added species. The effect of potential on reaction rate appears to depend on the particular organic species adsorbed and may reflect the potential of zero charge.

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 April 16, 1968.

EFFECTS OF OXIDIZABLE ANION ADSORPTION ON THE ANODIC BEHAVIOR OF PLATINUM

INTRODUCTION

Several recent papers (1-3) from NRL have indicated that under steady-state, potentiostatic conditions the retardation of the hydrogen oxidation reaction on a Pt anode, which commences at potentials about 0.7 v positive to the equilibrium hydrogen potential, is caused by anion adsorption. The possibility of this passivation being due to adsorbed oxygen atoms, oxides, or oxygen-containing free radicals was shown to be improbable because of the very rapid reaction of such oxygen species with hydrogen.

To further demonstrate the thesis that inert-anion adsorption can be the primary cause of retardation of the oxidation of reactable species at anodic potentials, experiments were designed to determine the effects of reactable (oxidizable) anions. Such oxidizable anions should compete with inert anions adsorbed at anodic potentials and may affect reaction rates. In addition, the total replacement of an inert anion with a readily oxidizable anion should eliminate or appreciably reduce passivation due to anion adsorption.

It was felt that an ideal oxidizable anion for this work would be formate ion, which is the simplest type of organic anion. It should be easily adsorbed at positive potentials and is fairly easily oxidized. Formate ions and formic acid could be dissociated on a Pt electrode, and neutral products, such as atomic hydrogen, carbon monoxide, and carbon dioxide, could be formed. However, if formate ion can adsorb on the anode surface (or highly polarizable formic acid, free radicals, or similar species), competition with inert anions are possible, and information concerning the effects of such adsorbed species* on the rate of anodic reactions would be available.

EXPERIMENTAL PROCEDURE

The experimental high-purity, gas-tight setup and conditions were the same as previously used (1,4). The solutions were 1M formic acid, and 0.1M and 1M formic acid in 1M sulfuric acid solution. Each solution was investigated under both helium and hydrogen saturated conditions (atmospheric pressure). The formic acid was reagent grade. An initial run through the potential range up to 2 v was made before data were recorded. The concentrations of formic acid given are the initial values; losses in concentration due to electrochemical reaction, decomposition, and vaporization during each experiment did occur. Titrations of acid content after termination of a run (some lasted for over a month) showed decreases in the order of 25 to 40% of formic acid. However, changes in the potentiostatic current-density-vs-voltage relations were not appreciable during a series of runs. In several cases, formic acid was added during a run to approximately approach the initial concentration. This made little difference.

It should be emphasized that this work was designed to determine the steady-state, potentiostatic behavior of formic acid oxidation and oxidation of hydrogen and formic acid mixtures with especial interest in the influence of the formic acid (or a derivative) on the

*No attempt was made in this work to determine the actual organic species which were adsorbed or oxidized, and the terms formic acid and formate ion are not used in a strict sense.

passive behavior of Pt in the potential region above 0.7 v (NHE). No attempt was made to correct for IR losses in the low-conductivity, pure formic acid solutions, to conduct a mechanistic or kinetic study which involved the various by-products of formic acid, or, indeed, to determine what the reaction steps or products were. The goal was to study the effects of formate-ion adsorption (or other oxidizable by-products)—in particular the effects of such species on the adsorption of an inert anion (sulfate ion) and on the reactivity of oxidizable species on a Pt anode.

The two bright Pt-bead (99.99%) working electrodes used were about 0.5 cm² in true area (5), and the temperature was 25 ± 2°C. The gas flow into the cell was about 40 ml/min, until a steady-state current density was reached. The time necessary to attain this steady-state current density varied from a few minutes to more than a day, depending on both the set potential and the previous sequence of potentials. The gas-flow rate was then increased to well over 1000 ml/min, and the constant current density was recorded. Potentiostatic control was accomplished with a Pt-wire reference electrode for one series of runs and with a Pd-wire reference in a side arm for another series. The presence of a Pd wire made no apparent difference in the potentiostatic measurements. When hydrogen flowed, either a Pt/H₂ reference electrode or a miniature glass electrode was used to monitor the potential. The results were the same in either case. In the helium-saturated solution the potential-monitoring reference was always a miniature glass electrode. All potentials are referred to the normal hydrogen electrode (NHE) with the exception of the data in pure formic acid solutions, where the reference electrode is the hydrogen electrode, same solution (H.E.S.S.). To change the scale for these formic acid solutions to NHE would require a reduction of the H.E.S.S. values by about 0.1 v.

Cyclic current fluctuations usually ranging from about 10 to 20% were observed in the potential region between 0.3 and 1 v and on the decreasing-potential sequence from 1.3 to 0.9 v. The values shown in the figures are average values. The scatter of points was essentially the same as found for pure hydrogen (Fig. 1, Ref. 1). At least three increasing and decreasing potential sequences were determined, and wherever critical changes occurred, many additional checks were run. Figure 1 demonstrates the current-density-vs-time relation typically found when the potential was changed in regions where slow changes occurred.

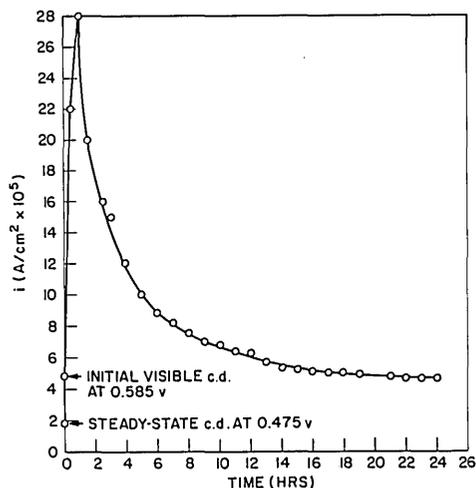


Fig. 1 - Typical current density-vs-time relation found when the potential is changed in a region where slow processes occurred. The potential was increased from 0.475 v to 0.585 v in .-0.1M formic acid and 1M sulfuric acid.

RESULTS AND DISCUSSION

Figures 2 and 3 show the potentiostatic current-density-vs-potential relations obtained in 1M formic acid in both helium-stirred and hydrogen-stirred solution. Figure 2 is for the increasing-potential sequence, whereas Fig. 3 is for the decreasing-potential sequence. The broken line in Figs. 2 to 7 is either the increasing or decreasing potential sequence for the oxidation of water in helium-saturated 1M sulfuric acid solution (4), and the dotted line in each figure is either the increasing or decreasing potential sequence for the oxidation of hydrogen (1) in 1M sulfuric acid solution.

The 1M formic acid curve in Fig. 2 shows that although the rate of oxidation of formic acid is much slower than hydrogen oxidation, there is no passivation of the Pt electrode to the formic acid oxidation below 1 v. Indeed, the rate of oxidation of formic acid increases with potential or remains constant in several potential regions until a potential of 1.6 v (H.E.S.S.) or about 1.5 v (NHE) is reached. From about 1.0 v to 1.8 v the rate of formic acid oxidation is about one order of magnitude faster than the rate of hydrogen oxidation in sulfuric acid solution.

The mixture of formic acid and hydrogen, as illustrated in Fig. 2, shows a great increase in the rate of oxidation at potentials below 1.0 v. This shows that the primary reaction in this region is the oxidation of hydrogen. The formic acid under these potential conditions retards the hydrogen oxidation reaction. There is a retardation of the oxidation

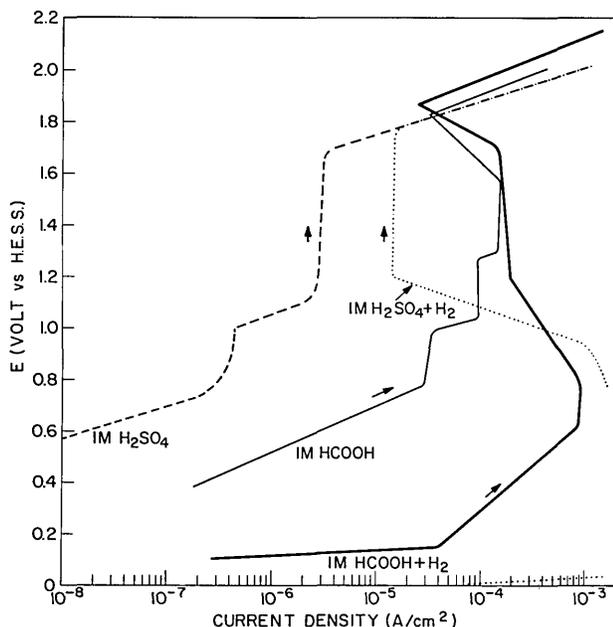


Fig. 2 - Potentiostatic anodic current density-vs-potential relation on a bright Pt electrode for the increasing-potential sequence. The solid lines represent 1M formic acid in helium-saturated and hydrogen-saturated solutions (1 atm). The broken line represents 1M sulfuric acid in a helium-saturated solution. The dotted line represents 1M sulfuric acid in a hydrogen-saturated solution. H.E.S.S. is the hydrogen electrode, same solution.

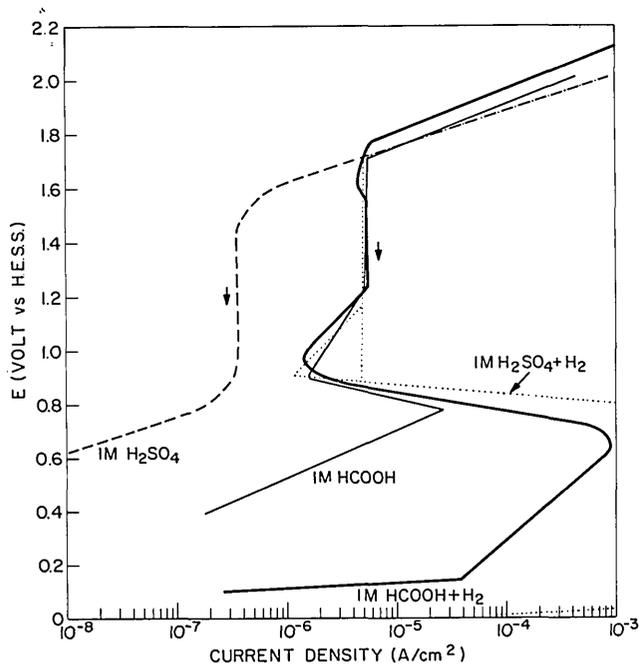


Fig. 3 - Potentiostatic anodic current density-vs-potential relation on a bright Pt electrode for the decreasing-potential sequence. The solid lines represent 1M formic acid in helium-saturated and hydrogen-saturated solutions (1 atm). See the caption for Fig. 2 for the meaning of the solid, broken, and dotted lines. H.E.S.S. is the hydrogen electrode, same solution.

reaction at about 0.8 to 1.2 v, but it is not as sharp as for pure hydrogen in sulfuric acid solution. At potentials more noble than 1.2 v, the rate of oxidation of the formic acid-hydrogen mixture is essentially the same as for formic acid alone.

The data in Fig. 2 clearly show that passivation of Pt for formic acid oxidation does not occur below 1.6 v. Hence, the formation of either oxides or adsorbed oxygen atoms which passivate the electrode is not possible. In the case of the formic acid-hydrogen mixture, formate ion most likely is being adsorbed, which in fact retards the hydrogen oxidation reaction, even though the formate ion itself can be oxidized but at a much slower rate. Determinations of the overall rate of oxidation of a monolayer of Pt-O_{ad} with formic acid gave reaction rates of about 5×10^{-4} amp/cm². Thus, the rate of reaction of adsorbed oxygen atoms with formic acid is well over two to three orders of magnitude faster than the oxidation of water in the potential range from 0.7 to 1.6 v. Hence, significant amounts of oxygen cannot remain on the surface below 1.6 v.

The data for the decreasing-potential sequence, Fig. 3, clearly show that from 1.7 to 0.9 v, the behavior of formic acid, formic acid plus hydrogen, and hydrogen in sulfuric acid solution is virtually identical. Evidently, the formation of dermasorbed oxygen decreases the catalytic activity of the Pt so much that the rate of oxidation of formic acid is identical to that of hydrogen in the presence of sulfate ions. However, the rate of water oxidation under similar potential conditions is still significantly slower. It should be mentioned that the presence of dermasorbed oxygen also considerably reduces the reaction rate of adsorbed oxygen with oxidizable species such as hydrogen (6). However, it is doubtful that

adsorbed oxygen is an important factor under these conditions. This is because the reduced reaction rate between adsorbed oxygen and hydrogen or formic acid would still be well above the rate of water oxidation.

Potentiostatic polarization curves (increasing-potential sequence) for a formic acid-sulfuric acid mixture at two nominal concentrations of formic acid (0.1 and 1M) are shown in Fig. 4. Here again, even though at lower potentials, the rate of oxidation of formic acid is considerably slower than that of hydrogen; no passivation occurs at 0.7 v. Passivity is evident at about 1.6 v only. Furthermore, in the potential range between 1.2 and 1.6 v, the rate of oxidation of formic acid is greater than that of hydrogen. At potentials above 1.7 v, where the principal reaction is the oxidation of water to oxygen, formate ions slightly increase the net oxidation current.

For the potential-decreasing sequence shown in Fig. 5, in the potential range from 1.7 to 0.9 v, the rate of the oxidation of formic acid mixed with sulfuric acid is well below that of either formic acid, formic acid plus hydrogen, or hydrogen in sulfuric acid solution (Fig. 3). This shows that sulfate-ion adsorption on the Pt electrode containing dermasorbed oxygen retards the formic acid oxidation considerably more than the hydrogen oxidation. Thus, under similar conditions of sulfate ion plus dermasorbed oxygen, hydrogen is more readily oxidized than is formic acid. This indicates that even though formate ions may be present, the bulk of the coverage of the electrode is with sulfate ions and that under similar surface conditions and at high positive potentials the electrostatic attraction of formate ions does not have as great a bearing on the rate of oxidation as does the presence of a neutral but more easily oxidizable species such as hydrogen. This is in contrast with the case of

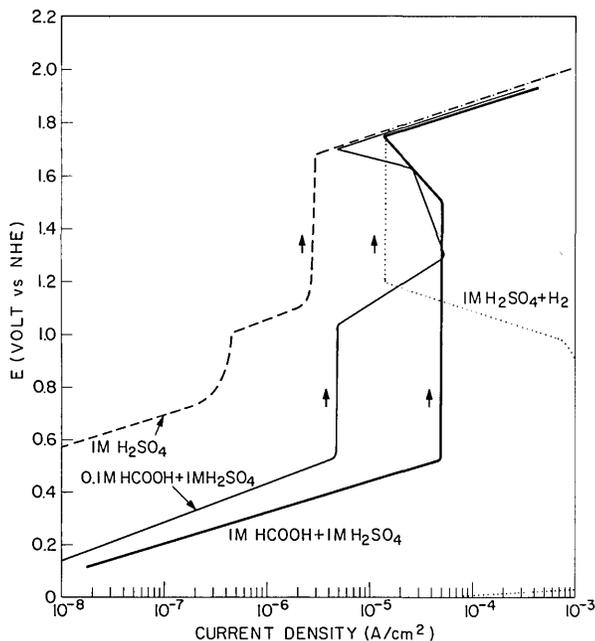


Fig. 4 - Potentiostatic anodic current density-vs-potential relation on a bright Pt electrode for increasing-potential sequence. The solid lines represent 0.1 and 1M formic acid in 1M sulfuric acid in a helium-saturated solution. See the title for Fig. 2 for the meaning of the broken and dotted lines.

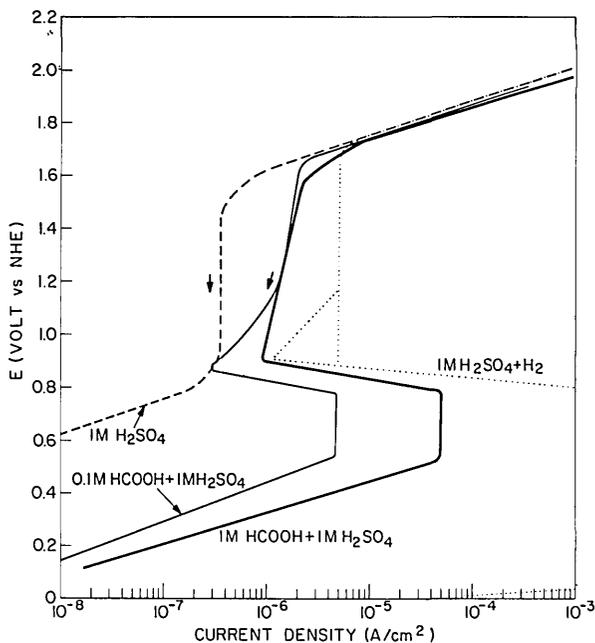


Fig. 5 - Potentiostatic anodic current density-vs-potential relation on a bright Pt electrode for decreasing-potential sequence. The solid lines represent 0.1 and 1M formic acid in 1M sulfuric acid in a helium-saturated solution. See the title for Fig. 2 for the meaning of the broken and dotted lines.

the increasing-potential sequence (Fig. 4), where formate ions do effectively compete with sulfate ions. The difference is most likely due to the reduction in catalytic activity owing to dermasorbed oxygen. The dermasorbed oxygen affects the rate of formic acid oxidation much more than that of hydrogen.

The data shown in Figs. 6 and 7 show the potentiostatic behavior in formic acid plus sulfuric acid in the presence of hydrogen for the increasing and decreasing potential sequence, respectively. Figure 6 shows that in the active low-potential range, high concentrations (1M) of formic acid in the presence of sulfate ion retard the hydrogen oxidation rate considerably more than in the absence of sulfuric acid (Fig. 2). At low concentrations of formic acid (0.1M), however, oxidation of hydrogen is affected only moderately.

In the potential range from 0.7 to 1.6 v, passivation does occur as in the case of pure hydrogen; however, the presence of formic acid has a moderating effect and significantly increases the rate of the net oxidation reaction. This is believed to be due to the competitive adsorption of formate ions which can be oxidized and can contribute to the net anodic current. Figure 7 again shows that the presence of formic acid considerably retards the hydrogen oxidation reaction when dermasorbed oxygen is present. In the low current-density regions shown in both Figs. 5 and 7, water oxidation may contribute significantly to the net current density.

Investigations of formic acid oxidation (7,8) offer only a limited amount of information on the steady-state, potentiostatic oxidation of formic acid at potentials positive to 0.9 v. Gilroy and Conway (9) refer to data from Conway's laboratory which indicate a passivation of formate-ion oxidation in aqueous solution at about 1 v. They attribute this passivation

Fig. 6 - Potentiostatic anodic current density-vs-potential relation on a bright Pt electrode for increasing-potential sequence. The solid lines represent 0.1 and 1M formic acid in 1M sulfuric acid in a hydrogen-saturated solution. See the title for Fig. 2 for the meaning of the broken and dotted lines.

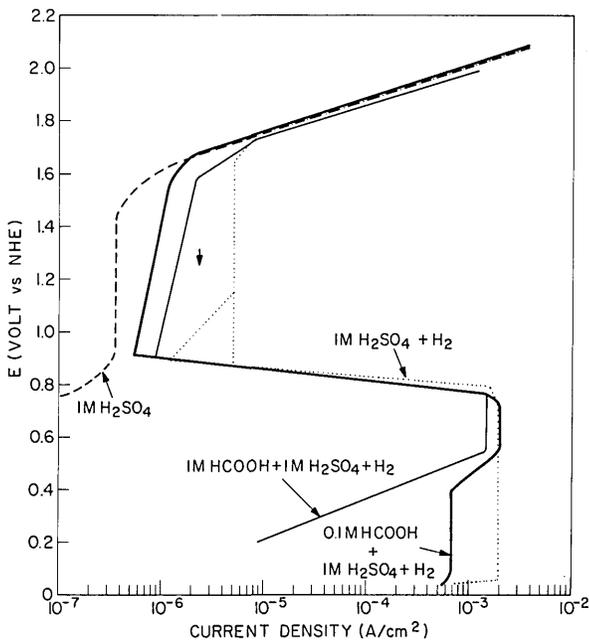
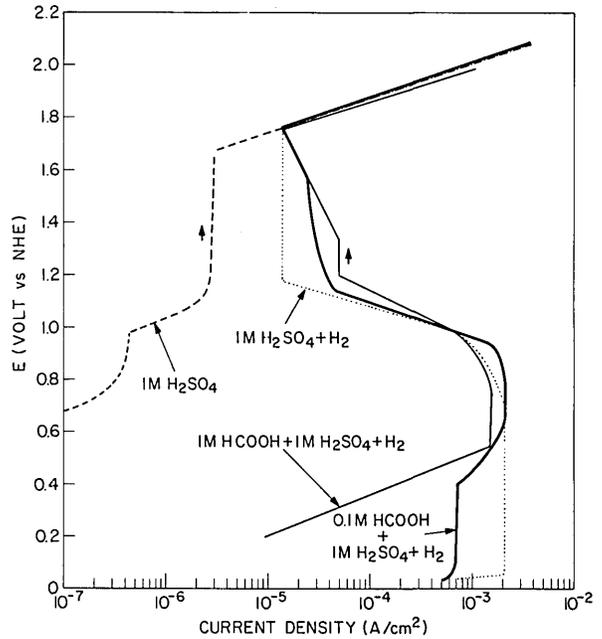


Fig. 7 - Potentiostatic anodic current density-vs-potential relation on a bright Pt electrode for decreasing-potential sequence. The solid lines represent 0.1 and 1M formic acid in 1M sulfuric acid in a hydrogen-saturated solution. See the title for Fig. 2 for the meaning of the broken and dotted lines.

to the presence of a passivating "oxide." For pure formic acid-potassium formate solutions, Conway, et al. (10), indicated passivation by the formation of intermediates. The results reported here (Fig. 2) indicate no passivation in aqueous formic acid solution up to 1.6 v. The data obtained in this investigation verify previous findings (1-3) that passivation in the vicinity of 0.7 v is due to sulfate-ion adsorption rather than the formation of adsorbed oxygen, an oxide, or other oxidation products of water. Water oxidation is too slow below 1.6 v, and the oxidation products of water on a Pt surface react so rapidly with oxidizable species in solution that the possibility of the buildup of a passive layer by such oxygen species is most unlikely. Only at high noble potentials is the combined effects of anion adsorption and sorbed oxygen adequate to effectively retard the oxidation of hydrogen and formic acid. At sufficiently noble potentials, the rate of water oxidation exceeds the rate of hydrogen and/or formic acid oxidation.

The data can therefore be reasonably explained by attributing passivity to anion adsorption. As shown in Fig. 2, formate ion can cause passivation of the hydrogen oxidation reaction, but the retardation of the reaction rate is much less than for inert sulfate ions. Since formic acid is more difficult to oxidize than hydrogen, it would tend to increase the retardation if oxygen passivated the Pt electrode, but the reverse is obtained.

One may argue that some formate ion attracted to the positive surface in the passive region may cause a partial breakdown of a passive oxygen layer and, thereby, increase the rate of oxidation. However, this is not borne out by the behavior observed in the decreasing-potential sequence curves (Figs. 3, 5, and 7). Figure 3 shows that in the presence of dermasorbed oxygen the formate ion retards the rate of hydrogen oxidation just as much as does sulfate ion. The data in Figs. 5 and 7 show that in the presence of dermasorbed oxygen and both sulfate and formate ions, the rate of oxidation of hydrogen is less than in the presence of only sulfate or formate ion (Fig. 3). Figure 2 clearly shows that even though formate ion does not passivate its own oxidation below 1.6 v, it passivates hydrogen oxidation at 0.8 v. In addition, a breakdown in passivity due to formate-ion adsorption assumes a complete oxygen coverage of the Pt surface at potentials in the vicinity of 0.7 v. Data previously given (2) show that such a complete oxygen film is not obtained. The 1M formic acid-1M sulfuric acid curve in Fig. 4 shows that a limiting current density is reached at 0.5 v, and passivation does not occur until 1.5 v. Contrasting this with the results for 1M formic acid shown in Fig. 2, the initial limiting current density occurs at 0.8 v. These results show that sulfate ions do play an important role in the oxidation of formic acid.

One may speculate on the potential of zero charge (p.z.c.) and the region in which adsorption of formic acid species are at a minimum. This effect is best seen in Fig. 6 in the 0.1M formic acid-1M sulfuric acid-hydrogen curve. These data show a current-density maximum between 0.6 and 0.8 v. Below 0.6 v the rate of hydrogen oxidation is moderately retarded by formic acid, but in the potential range from 0.6 to 0.8 v a current density of 2×10^{-3} amp/cm² is reached. This is exactly the maximum current density found for pure hydrogen oxidation in high-purity sulfuric acid solution (1). This may indicate that the p.z.c. is in the vicinity of 0.6 to 0.8 v, because at the p.z.c. the adsorption of a highly polarizable species, such as formic acid or of formate ion, should be at a minimum. The maximum current density of 2×10^{-3} amp/cm² does not decrease until a potential of 0.8 v. Contrast this to the 1M sulfuric acid-hydrogen curve which starts decreasing at 0.7 v. This also shows that formate ion does compete with sulfate ion in the passivation of the Pt surface.

CONCLUSIONS

This work verifies that at potentials negative to 1.5 v, passivation of a Pt electrode to the oxidation of hydrogen is not due to the adsorption of species from the oxidation of water or to the formation of Pt oxides. Passivity is caused by anion adsorption.

If the oxidizable material exists as an adsorbable anion which can oxidize faster than water, then no passivation will occur. If a species is present which is more rapidly oxidized than the adsorbable anion, then the oxidation of that species will be retarded when the potential is noble enough to significantly adsorb such anions.

In the presence of dermasorbed oxygen, passivation in a combination of sulfuric and formic acids is much more pronounced than in the presence of either acid alone. The oxidation reaction rates may give a clue as to the p.z.c. in the presence of an organic species which is both easily polarized and ionized.

REFERENCES

1. Schuldiner, S., J. Electrochem. Soc. 115:362 (1968)
2. Schuldiner, S., J. Electrochem. Soc., submitted for publication
3. Schuldiner, S., and Shepherd, C.M., J. Electrochem. Soc., submitted for publication
4. Schuldiner, S., Warner, T.B., and Piersma, B.J., J. Electrochem. Soc. 114:343 (1967)
5. Schuldiner, S., J. Electrochem. Soc. 107:452 (1960)
6. Schuldiner, S., and Warner, T.B., J. Electrochem. Soc. 112:212 (1965)
7. Conway, B.E., pp. 430-437 in "Progress in Reaction Kinetics," Vol. 4, G. Porter, editor, Oxford:Pergamon, 1967
8. Piersma, B.J., and Gileadi, E., pp. 102-114 in "Modern Aspects of Electrochemistry," J. O'M. Bockris, editor, New York:Plenum, 1966
9. Gilroy, D., and Conway, B.E., J. Phys. Chem. 69:1259 (1965)
10. Conway, B.E., Gileadi, E., and Dzieciuch, M., Electrochim. Acta 8:143 (1963)

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 EFFECTS OF OXIDIZABLE ANION ADSORPTION ON THE ANODIC BEHAVIOR OF PLATINUM			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim report; work is continuing.			
5. AUTHOR(S) (First name, middle initial, last name) S. Schuldiner			
6. REPORT DATE June 7, 1968		7a. TOTAL NO. OF PAGES 13	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. NRL Problem C05-06		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6737	
b. PROJECT NO. SF 020-05-01-0809		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Ship Systems Command), Washington, D.C. 20390	
13. ABSTRACT The retardation of the hydrogen oxidation reaction, which commences at about 0.7 v (NHE) in sulfuric acid solution, can be modified by the presence of formate ions. Steady-state, potentiostatic measurements were made in formic acid solution and formic acid-sulfuric acid solution, both in the presence and absence of hydrogen. The work showed that at potentials under 1.5 v passivity was due to adsorbed anions rather than adsorbed oxygen atoms, Pt oxides, or free radicals formed by the oxidation of water. Pure formic acid solutions were not passivated below 1.5 v; however, formate ions did retard hydrogen oxidation but not as strongly as sulfate ions. The oxidation of formic acid in solutions containing sulfuric acid was affected by adsorption of both sulfate and formate ions. The retardation of the net oxidation of hydrogen and formic acid in formic acid-sulfuric acid mixtures was less than that of hydrogen in sulfuric acid. In the presence of dermasorbed oxygen, both formate and sulfate ions strongly retard the oxidation of added species. The effect of potential on reaction rate appears to depend on the particular organic species adsorbed and may reflect the potential of zero charge.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fuel cells Corrosion Passivity Primary cells Adsorption Platinum anode Hydrogen Hydrogen overvoltage						