

## ADSORBED RESIDUES FROM FORMIC ACID AND FORMATE ION GENERATED UNDER STEADY-STATE POTENTIOSTATIC CONDITIONS

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### INTRODUCTION

When a clean platinum electrode is exposed under open circuit conditions to formic acid or sodium formate solutions there is a rapid dehydrogenation reaction followed by a much slower interaction of adsorbed H atoms with formic acid or formate ions to give molecular hydrogen and free radicals (1, 2). The free radicals formed by this reaction and by the initial dehydrogenation reactions interact with the surface and each other to form residues which then hinder further dehydrogenation. Upon potentiostating the Pt electrode, one would expect that any atomic hydrogen formed by dehydrogenation would be readily oxidized. A previous steady-state potentiostatic study (3) on the anodic oxidation of formic acid and hydrogen in formic acid and formic acid + sulfuric acid mixtures showed that even though the initial rates of oxidation for formic acid and hydrogen in such solutions could be quite high, there is a gradual decrease in rates until at steady-state, the reaction rates would be considerably reduced. Evidently, the formation of free radicals also occurs under potentiostatic conditions and the resulting residue can affect the rates of oxidation of both formate species and hydrogen.

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The present investigation was for the purpose of determining the steady-state potential vs. coverage relationship of the organic residue on Pt in formic acid and formate ion solutions, both under helium and hydrogen saturated conditions. The amount of residue was determined by a high current density anodic galvanostatic pulse. Such charging curves show an increase in the number of  $\mu\text{coul}/\text{cm}^2$  required to form a monolayer of adsorbed oxygen atoms on the surface of the Pt electrode ( $\text{Pt-O}_{\text{ad}}$ ). This increase beyond the  $420 + 36 \mu\text{coul}/\text{cm}^2$  required to form a monolayer of  $\text{Pt-O}_{\text{ad}}$  on a clean Pt electrode plus double layer charging, respectively (4) was attributed to oxidation of the organic residue on the electrode. Such measurements only show the number of coulombs of charge required to oxidize adsorbed organic material plus water. Unreactable species on the surface may not be oxidized by the anodic galvanostatic pulse, but may be desorbed. Unreactable species which are chemisorbed may cause an increase in overvoltage for the formation of oxygen atoms. Because of the complexity of interpretation of the anodic charging curves and because qualitative identification of the organic residues or of the oxidized or desorbed products is an extremely difficult problem in itself, it is not possible, at the present time, to associate the amount of charge actually determined by this technique to specific reactants, reactions, or products. Therefore, in such a case the use of such terms as degree of surface coverage have little real meaning. Hence, in this study the number of electrons generated in the atomic oxygen adsorption region (from  $\sim 0.9$  to  $1.8$  v), after subtracting the monolayer contribution due to  $\text{Pt-O}_{\text{ad}}$  + double

layer, is expressed as  $q_{\text{org}}$  and solely represents the amount of charge used to remove the organic species adsorbed on the Pt surface at specific, steady-state anodic potentials.

## EXPERIMENTAL

The solutions investigated were: (a) 1 M HCOOH + 1 M H<sub>2</sub>SO<sub>4</sub> (pH  $\approx$  0), (b) 1 M HCOOH + 1 M HCOONa (pH = 3.5), and (c) 1 M HCOONa (pH = 7.9). The formic acid was reagent grade, the H<sub>2</sub>SO<sub>4</sub> was ultrapure (E. Merck, Darmstadt). Measurements were made in both helium- and hydrogen-saturated solutions (see ref. 2 for details of experimental techniques). The Pt working electrode potentials were controlled with a Wenking 61RS potentiostat, galvanostatic pulses (1-2 amp/cm<sup>2</sup>) were applied with either an Electro-Pulse 3450C or 3450D pulse generator and traces were photographed from a Tektronix 547 oscilloscope with a 1A1 plug-in. The circuitry used and the fast switching between potentiostatic and galvanostatic control were as previously described (5).

The time required to reach steady-state conditions, in most cases, required at least 14 hours. Fig. 1 gives two examples of the  $q_{\text{org}}$  relation with time. Curve (a) for the 0.1 M HCOOH + 1 M H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>-saturated solution is the only data obtained for this solution. Even though, in many cases, there was little change in  $q_{\text{org}}$  within the first 5 minutes, the steady-state values after a sufficient length of time showed considerably larger amounts of charge were required to remove the organic residue which slowly formed on the surface.

All potentials are referred to the reversible hydrogen electrode in the same solution (RHE). The temperature was  $25 \pm 1^\circ\text{C}$ .

## RESULTS

Steady-state, potentiostatic polarization curves for formic acid and formic acid + sulfuric acid mixtures were published previously (3). Fig. 2 and 3 show the polarization behavior for 1 M HCOOH + 1 M HCOONa and 1 M HCOONa solutions. Both curves show hysteresis effects similar to those in other formic acid solutions (3). There are some important differences, however. In the 1 M HCOOH + 1 M HCOONa (He-saturated) solution (Fig. 2), on the decreasing potential arm, the current densities extend beyond the values found for the increasing potential arm at potentials of about 1.0 v. In the 1 M HCOONa solution (Fig. 3), there is a similar increase in current densities for decreasing potentials in  $\text{H}_2$ -saturated solution which extends from 1.0 to 0.1 v.

Fig. 2 shows a passivation effect for both He- and  $\text{H}_2$ -saturated 1 M HCOOH + 1 M HCOONa at about 1.4 v. This is well above the potential water can be oxidized to form  $\text{Pt-O}_{\text{ad}}$ . Fig. 2 further shows that in the presence of an oxidizable anion passivation does not occur at the relatively low potentials (vs. RHE) found in solutions containing inert anions (3, 6, 7). A slight passivation effect in He saturated 1 M HCOONa (Fig. 3) occurs at about 1.5 v but this also is well above the potential at which water can be oxidized

to form  $\text{Pt-O}_{\text{ad}}$ . In  $\text{H}_2$ -saturated 1 M  $\text{HCOONa}$  there is a slight decrease in oxidation rate at potentials positive to 1.0 v and a marked activation on the decreasing potential arm starting at about the same potential. However, these effects clearly show that the formation of oxygen species on Pt do not affect the retardation of the oxidation of formic acid or formate ion below 1.4 v. This verifies previous conclusions (3, 6, 7) that passivation effects in the presence of easily oxidized hydrogen or organic species is not due to the formation of oxygen species from water which retard the oxidation of  $\text{H}_2$  and/or formates.

Fig. 4, 5, and 6 show the effects of the steady-state, potentiostatic adsorbed residue found in formic acid and formate ion solutions. The  $q_{\text{org}}$  values in Fig. 4, 1 M  $\text{HCOOH} + 1 \text{ M H}_2\text{SO}_4$  in both He and  $\text{H}_2$ -saturated solution, start at about  $450 \mu\text{coul}/\text{cm}^2$  at open-circuit and go to maximums of about 525 to 575 at 0.5 v. If one would assume a monolayer coverage of the residue, then a little over two electrons per Pt site ( $210 \mu\text{coul}/\text{cm}^2 = 1 \text{ electron per Pt site}$ ) would be required to oxidize the residue. Contrasting these results with those of Breiter (8), Brummer and Makrides (9), Brummer (10), Minakshisandaram et al. (11), and Urbach and Smith (12), the amount of charge required to strip the adsorbed residue is more than twice the amount found by those investigators. It should be remembered, however, that we have measured the steady-state values, and as can be seen in Fig. 1, this can be about twice the values found for the coverages at the short adsorption times used in references (8-12). In addition, although the general shape of the curves in Fig. 4 are similar to those in (8-11), the details are quite different. For example, instead of the plateau found (8-11)

a linear increase in  $q_{\text{org}}$  with potential up to a maximum at about 0.5 v was found. The drop in  $q_{\text{org}}$  was also less abrupt. It is obvious that the residue formed under steady-state conditions is quite different from the one adsorbed on the surface after only short times. The adsorption results of Urbach and Smith (12) showed peaks at about 0.2 and 0.8 v and were different from the results of other workers (8-11) and to those shown here. However, Urbach and Smith determined coverage from radiometric measurements of tagged formic acid and were, in fact, determining the concentration of adsorbed tagged carbon rather than the concentration of adsorbed oxidizable species. It is possible also that the differences found by the various workers are due to the differences in the constantly changing composition of the surface species. This can be seen from Fig. 1, curve (a) where the initial 2.5 to 5 minute results gave  $q_{\text{org}}$  of 140 to 180  $\mu\text{coul}/\text{cm}^2$  or, on the basis of 210  $\mu\text{coul}/\text{cm}^2$  for fraction of surface coverage,  $\theta = 1$ , a  $\theta$  of about 0.7 to 0.9 is obtained.

The  $q_{\text{org}}$  found in 1 M HCOOH + 1 M HCOONa in He- and  $\text{H}_2$ -saturated solutions are shown in Fig. 5. In  $\text{H}_2$ -saturated solution the relationship between  $q_{\text{org}}$  and potential is similar to the sulfuric acid case (Fig. 4) except that the drop in  $q_{\text{org}}$  is less at potentials above 0.5 v. In He-saturated solution, however, the character of the residue must be quite different since the  $q_{\text{org}}$  runs considerably higher than in sulfuric acid solutions. In this case  $q_{\text{org}}$  runs as high as 775  $\mu\text{coul}/\text{cm}^2$  or about 3.7 electrons per Pt site. Such a high value of  $q_{\text{org}}$  appears to indicate that the organic residue which

is oxidized consists of complex molecules with oxidizable sites which extend several atomic distances away from the surface.

The complexity of the potential vs.  $q_{\text{org}}$  relation shown in Fig. 6 makes analysis virtually impossible. There are some similarities between the peaks and valleys for the He- and  $\text{H}_2$ -saturated solutions, but the most obvious difference is the fact that in He-saturated solution the adsorption behavior is both more complex and  $q_{\text{org}}$  can rise to substantially higher peak values. The 0.95 v value of 925  $\mu\text{coul}/\text{cm}^2$  is equivalent to 4.4 electrons per Pt atom.

#### DISCUSSION

The most obvious effect of hydrogen in the solutions investigated is that the measured  $q_{\text{org}}$  is substantially lower at essentially all potentials. In  $\text{H}_2$ -saturated solutions, the open-circuit potentials were the equilibrium hydrogen potentials, even though the charging curves taken under steady-state conditions showed no visible hydrogen oxidation region. It appears that the trace amounts of hydrogen present on the electrode were sufficient to maintain the equilibrium hydrogen reaction at open-circuit (2). Some of the hydrogen from the  $\text{H}_2$  can associate with the surface and/or organic residue on the surface affecting the structure and composition of this residue. Previously reported work (13) has indicated that atomic hydrogen at potentials negative to 0.3 v can interact with  $\text{CO}_2$  which then prevents oxidation of this hydrogen at potentials below 0.9 v with a high amplitude galvanostatic pulse.

The interaction of hydrogen with formic acid and formate ion is much more complex, but it is apparent that the presence of hydrogen does affect the character of the steady-state organic residue.

Another factor which apparently also has a strong effect on the character of the organic residue is the pH. This can be especially seen for the He-saturated solutions shown in Fig. 4, 5, and 6 where the interfering effect of hydrogen is minimized. At potentials below 0.7 v,  $q_{\text{org}}$  decreases as the pH increases. This indicates that the structure of the adsorbed organic residue is in a higher oxidation state as the pH increases. This and the fact that the pH 7.9, 1 M HCOONa solution (Fig. 6) is more sensitive to potential indicates that in the more alkaline solution the adsorbed species may be more in the nature of adsorbed anions or simple dipoles rather than complex molecules. The lower pH adsorption is less dependent on potential and significant desorption does not occur below 0.5 v.

Further evidence for the pH effect on the structure can be seen from the He-saturated potentiostatic polarization curves shown in Fig. 2 and 3. The higher pH results (Fig. 3) show a limiting current density at  $2.5 \times 10^{-5}$  amp/cm<sup>2</sup> from 0.7 to about 1.2 v followed by a range of increasing oxidation rates with increasing potential. The hysteresis effect in the decreasing potential arm is relatively small. This and the data in Fig. 6 (which shows a strong coverage dependence on potential) indicates that the oxidation of formate ion itself is rate-determining and is not limited by the

amount or character of the organic residue on the surface. At potentials above 1.2 v, the surface is essentially free of the organic residue and the rate of oxidation gradually increases as the potential is increased to about 1.5 v. This implies that the oxidation mechanism of formate gradually changes at about 1.2 v. Perhaps, a mechanism involving a water oxidation intermediate has some effect on the reaction rate at potentials above 1.2 v.

In Fig. 3 there really is no pronounced passivation on the increasing potential arm for the He-saturated solution. It also is significant that in  $H_2$  saturated solution, the organic residue only slightly passivates the  $H_2$  oxidation component to the oxidation rate of the formate itself on the increasing potential arm above 1.0 v. In fact, there only is a little difference between the  $H_2$ - and He-saturated solutions from 0.7 to 1.6 v on the increasing potential arm. On the other hand, for the decreasing potential arm there is a significant activation effect which reaches a maximum at 0.7 v. The hysteresis at potentials below 1.0 v in  $H_2$ -saturated solution show increased activity for hydrogen oxidation. This and the decreasing potential increased activity shown in Fig. 2 are the first times such increases have been noted in the various formic acid, formate, sulfuric acid, and alkali solutions investigated here. Although these points were repeatedly checked and critical points kept potentiostated at a given value for three to four days, it is likely that very slow changes in reaction rate may still be occurring and that eventually a return to the values on the potential increasing curve would be obtained. It is difficult to see how this could be otherwise.

Contrasting the behavior in 1 M HCOONa with that in 1 M HCOOH + 1 M HCOONa (Fig. 2) important differences are noticeable. In the first place, Fig. 2 shows little difference in the behavior in He- and H<sub>2</sub>-saturated solutions except in the potential range from open circuit to about 0.9 v. At lower potentials the current densities are higher in the presence of H<sub>2</sub>. The increased reaction rates for both the data shown in Fig. 2 and 3 are due to the contribution of H<sub>2</sub> oxidation which is faster in this potential range than is the oxidation of formate species. The fact that the net oxidation rate in Fig. 2 reaches a peak of about  $7 \times 10^{-3}$  amp/cm<sup>2</sup> at about 1.4 v is of interest because this rate of oxidation is 3.5 times faster than the maximum rate of oxidation of hydrogen in sulfuric acid solution (6). The pronounced passivation which occurs at higher potentials can be explained by adsorbed oxygen atoms generated by the oxidation of water. The marked hysteresis for the decreasing potential arm indicates the strong effect of adsorbed oxygen atoms on the reaction rates.

## CONCLUSIONS

A limitation to the use of organic fuels for low temperature fuel cell applications is the formation of organic residues primarily from the free radicals which are generated at the surface. To better understand these residues it is necessary to study their formation, to characterize their electrochemical behavior, and to determine their chemical composition. Transient electrochemical studies which primarily avoid the effects of these

residues and which deal only with the reactions of the original species in solution on a clean electrode must be carried out on rigorously controlled surfaces characterized in a meaningful way. The rates of the various processes occurring on a clean surface may be controlled and separated in certain instances. However, the character of the surface is constantly changing and of real import from both a fundamental and practical viewpoint is the steady-state behavior.

The work reported here shows that at low polarization potentials the rates of fuel oxidation are strongly retarded by the organic residues formed on the surface. This most likely occurs by removing sites at which dehydrogenation of the organic material can take place (2). Dehydrogenation appears to be the desired process which can produce easily oxidizable H atoms which are the effective fuel at low polarization. It appears that oxidation of carbon itself can readily occur at higher potentials, but this reaction would be of no obvious value for fuel cell operation. Dissociation of organic fuels to atomic hydrogen also implies that full low temperature oxidation of the fuel to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  would not be practicable in many cases, and that a large part of the chemical energy of the fuel could not be utilized in the generation of electricity.

Some degree of control of the organic residue results from the presence of molecular hydrogen and by changing the pH. Both increased pH and hydrogen lower the number of coulombs of charge required to oxidize the organic residue and allow higher anodic current densities at low polarization potentials.

Activation of a Pt electrode by anodic charging appears to have long-time effects on increasing the rate of fuel oxidation. This effect is most pronounced in  $H_2$ -saturated 1 M HCOONa.

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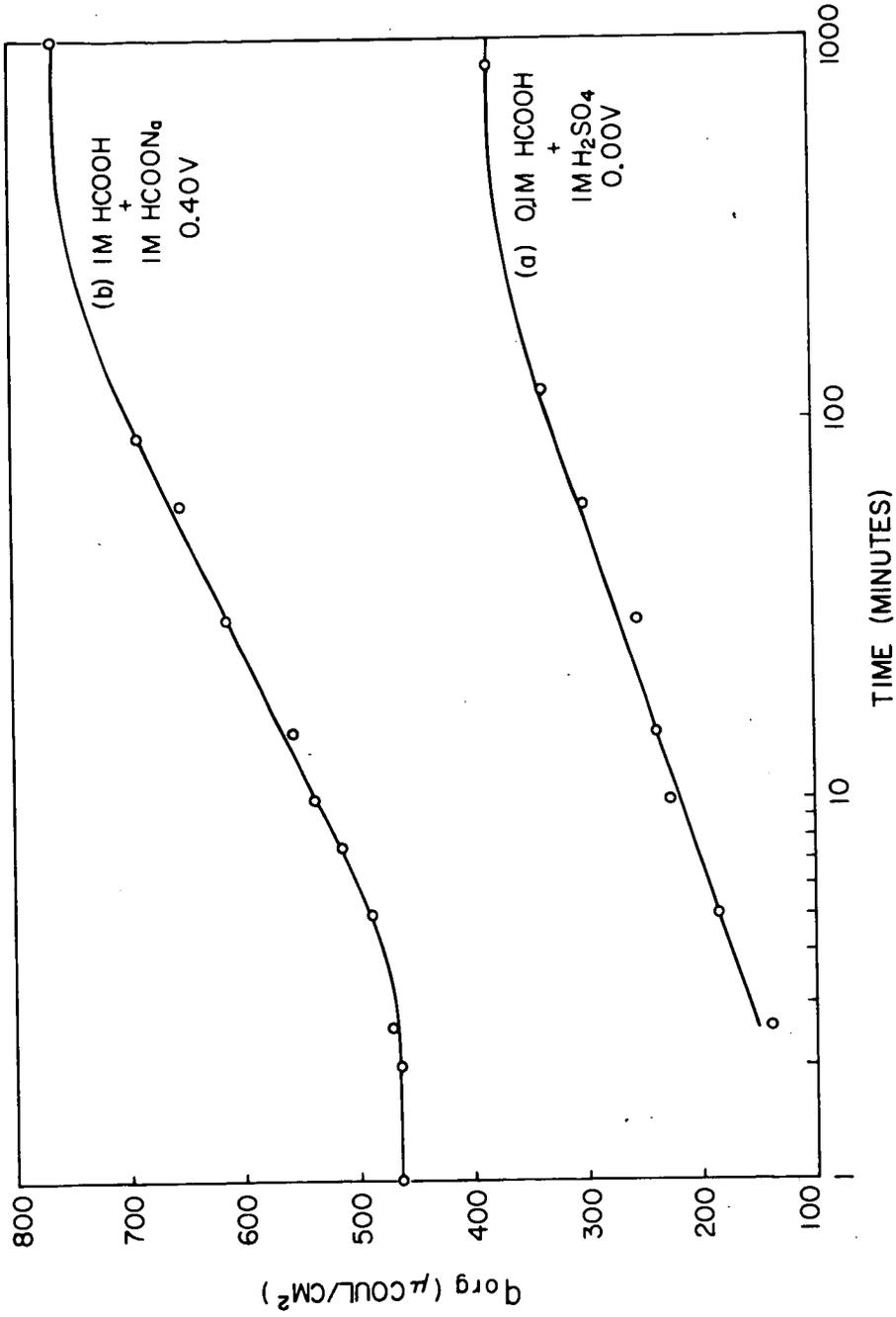
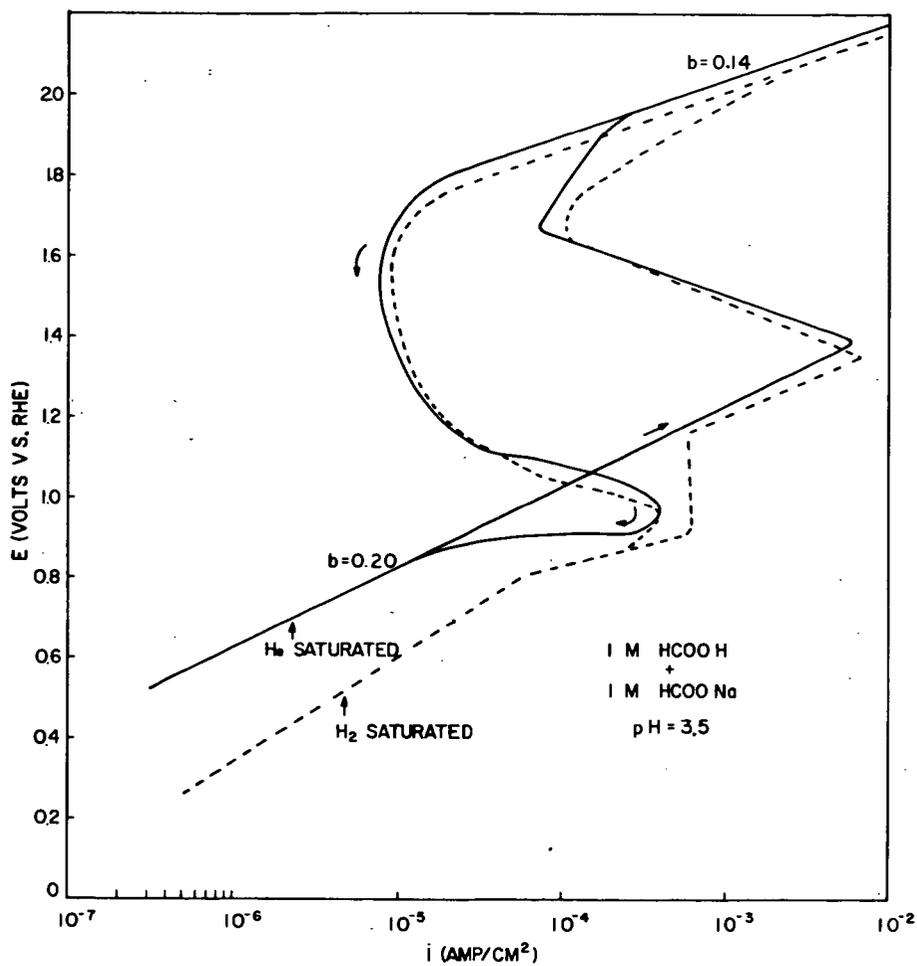


Fig. 1. Typical build-up of organic residue with time.



**Fig. 2. Steady-state potentiostatic current density vs. potential relation in 1 M HCOOH + 1 M HCOONa.**

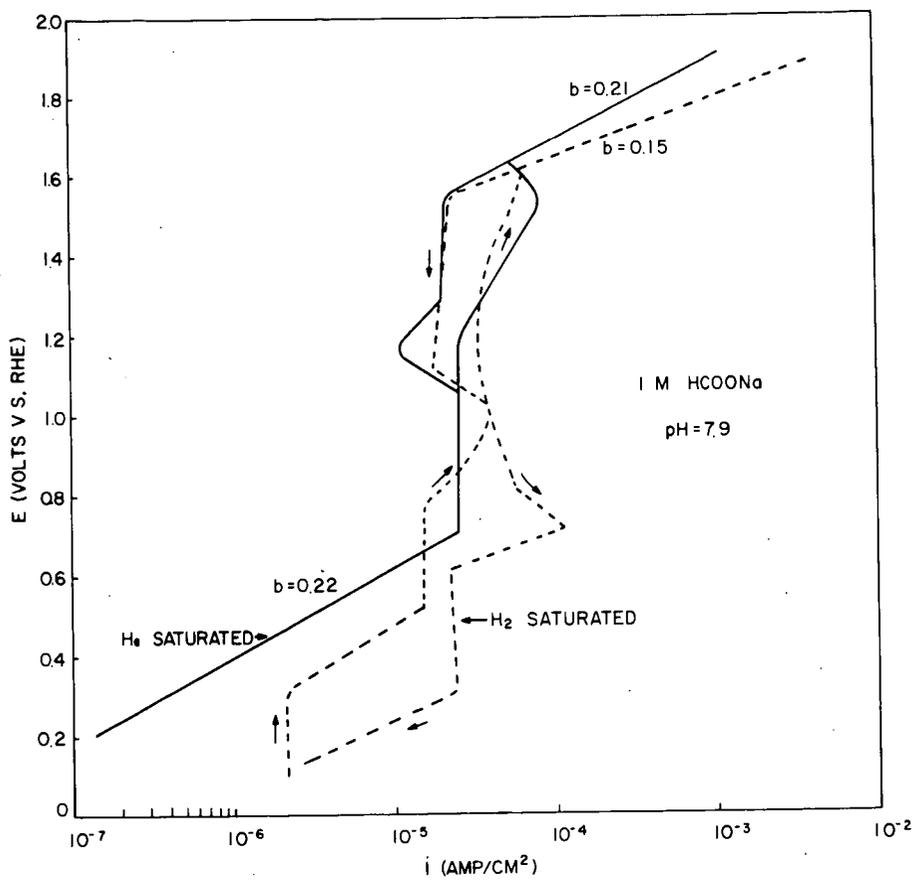


Fig. 3. Steady-state potentiostatic current density vs. potential relation in 1 M HCOONa.

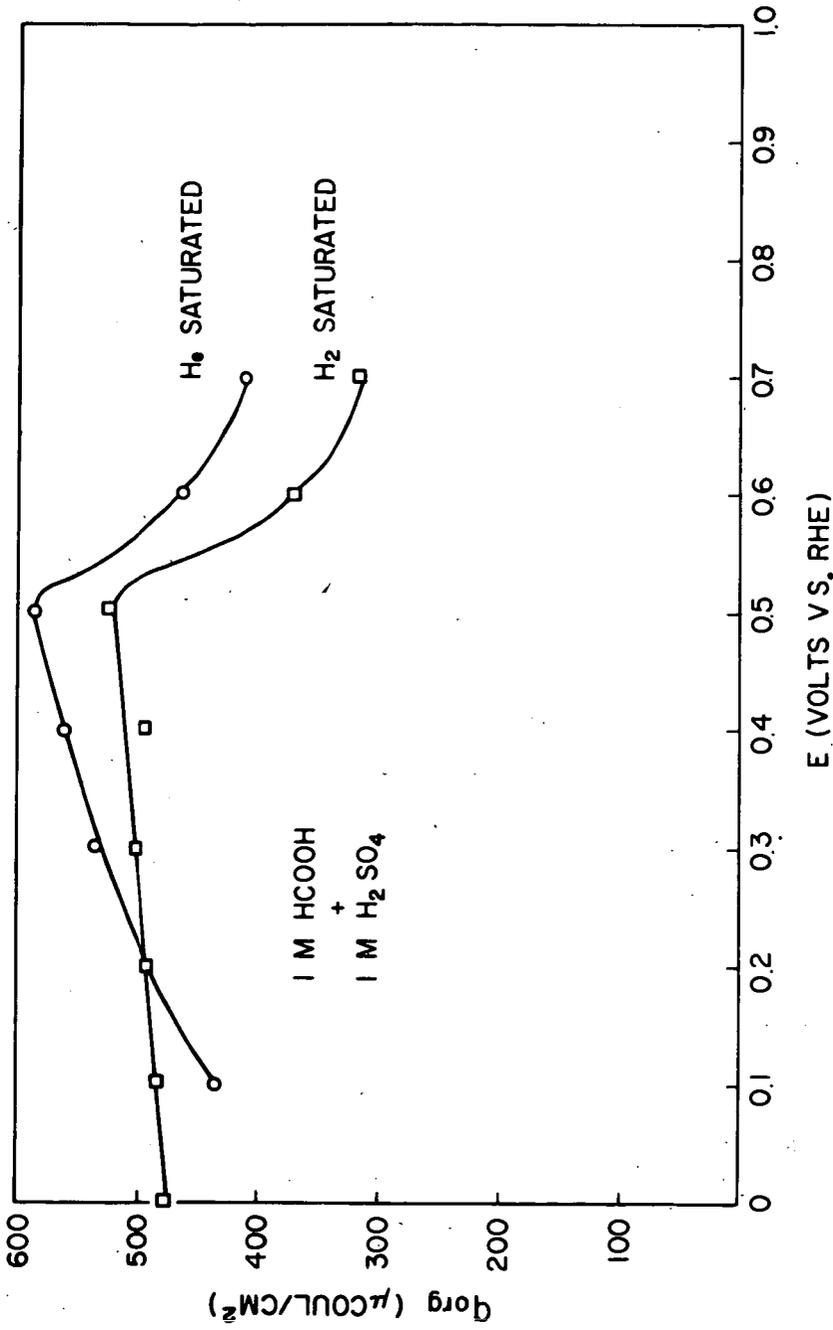


Fig. 4. Steady-state dependence of amount of charge,  $q_{org}$ , required to oxidize organic residue at set potentials; 1 M HCOOH + 1 M H<sub>2</sub>SO<sub>4</sub>.

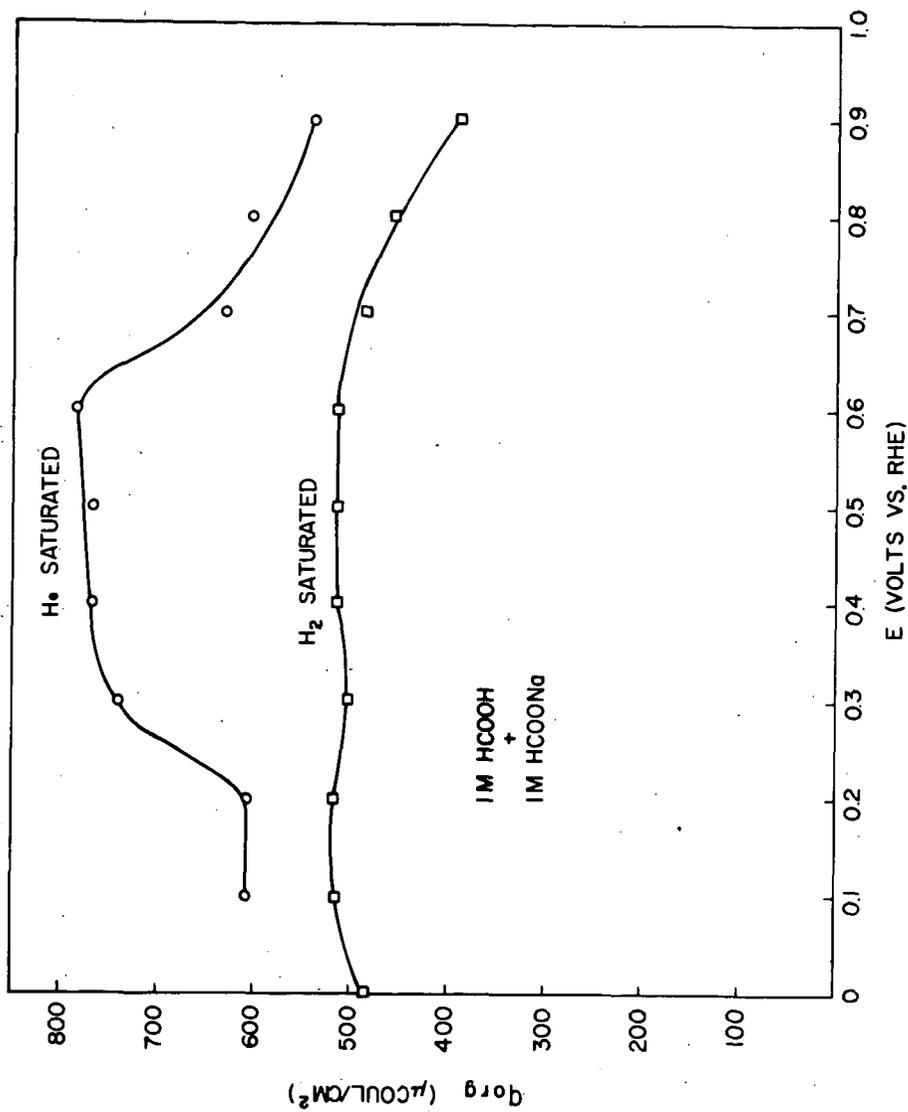


Fig. 5. Steady-state dependence of amount of charge,  $q_{org}$ , required to oxidize organic residue at set potentials; 1 M HCOOH + 1 M HCOONa.

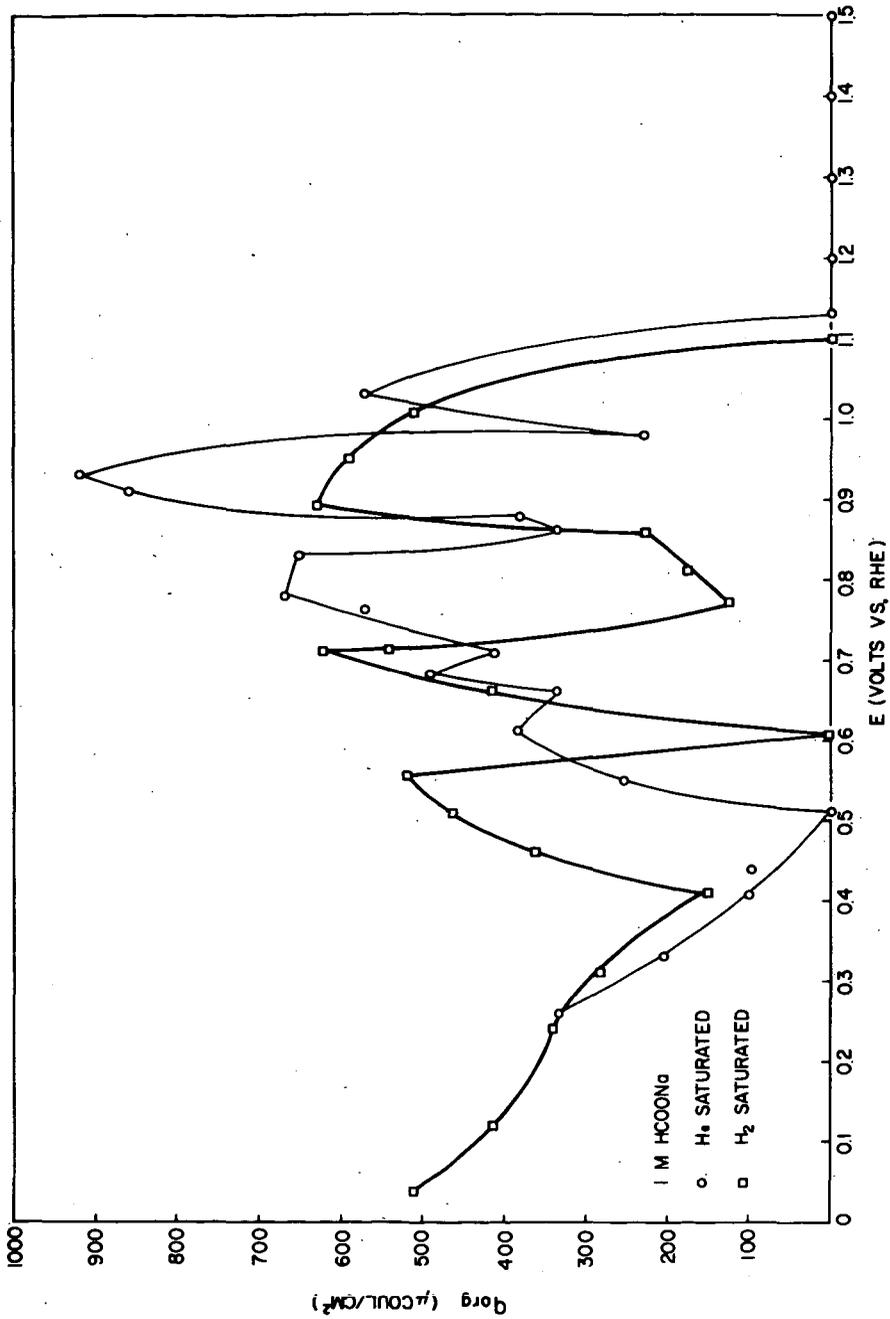


Fig. 6. Steady-state dependence of amount of charge,  $q_{ox}$ , required to oxidize organic residue at set potentials; 1 M HCOONa.