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Enhancement of the electrochemical oxidation of formic acid. Effects of anion adsorption and variation of rotation rate

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Abstract

Results are presented from a study on the electrochemical oxidation of formic acid. Perturbing a $\text{HCOOH} + \text{HClO}_4$ solution by causing a small amount of any one of several different anions to be present dramatically changes observed nonlinear behavior in an apparently unique manner. Quantitative changes are also observed. In current-control experiments, the presence of fluoroborate ions causes a substantial increase in the value of the applied current density for which low valued stationary potentials remain stable. In potential-control experiments, the current density substantially increases at relevant potential values. Although most properties possessed by the fluoroborate anion exist among the other anions studied, the presence of any one of these other ions in solution yields inferior current–potential characteristics. Results from current-control experiments show that changes in rotation rates have no effect on the observed behavior regardless of anion composition or whether the limiting state is stationary or oscillating. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Formic acid; Anion adsorption; Fuel cells; Oscillations; Rotating electrode

1. Introduction

The electrooxidation of formic acid at noble metals is an active research area because of applications in fuel cells and because it can be thought of as a basic model for processes involving more than one reaction pathway as well as adsorbed surface intermediates [1–4]. One purpose of this paper is to demonstrate that the behavior exhibited by the oxidation of a $\text{HCOOH} + \text{HClO}_4$ solution under constant-current conditions changes drastically when it is perturbed by the presence of a small amount of any one of several anions that are different from that in the supporting electrolyte.

Results from potential-control experiments provide quantitative relations between anion adsorption and the oxidation of small-oxygenated organic molecules [4–6]. In general, the current decreases with respect to the ‘adsorption strength,’ of the anions in the supporting electrolyte [5]. Consequently, a supporting electrolyte with anions that have relatively weak adsorption strengths is preferred in studying the oxidation of small organic molecules. For this reason, perchloric acid is usually the supporting electrolyte of choice for ambient laboratory conditions. Many quantitative results presented here are consistent with the results obtained under potential-control conditions. However, a second purpose of this paper is the presentation of results that demonstrate that perturbing the $\text{HCOOH} + \text{HClO}_4$ solution by mixing in a small amount of HBF_4 enhances reaction. In current-control experiments, more than a

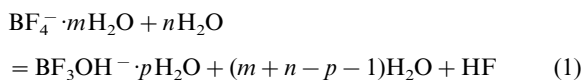
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60% increase occurs in the value of the applied current density for which low valued stationary potentials remain stable. An increase of more than 50% was obtained in the current density at relevant potential values in potential control experiments.

A third purpose of this paper is to present results on the effects of varying the electrode rotation rate on the oxidation of formic acid under current-control conditions. Changes in behavior in response to varying rotation rates would provide additional methods for distinguishing effects of different anions. However, the results clearly reveal that changes in the rate of transport of anions and reactants have a minimal influence on observed behaviors. Differences in the properties of 'adsorbed anions' and the influence these differences have on surface processes are the major causes of the observed qualitative changes that occur in response to small changes in the anion composition. The results also reveal that surface processes cause electrochemical instabilities [1,2,7–15] exhibited by formic acid oxidation in current-control experiments.

The anions used to perturb the $\text{HCOOH} + \text{HClO}_4$ solution were Cl^- , Br^- , SO_3CF_3^- , NO_3^- , HSO_4^- and BF_4^- . All anions are univalent. The two-halide anions are strongly adsorbed at the electrode surface: methanol oxidation is essentially blocked for $[\text{Cl}^-] \geq 2 \times 10^{-3} \text{ M}$ [16]. The anions, SO_3CF_3^- and BF_4^- , as well as the perchlorate ion, belong to a class known in inorganic chemistry as 'weakly coordinating anions' [17]. These anions are known to have weak interactions with metal complexes in solution chemistry. Consequently, weakly coordinating anions optimize the activity of catalytic sites of metal complexes. The three anions, SO_3CF_3^- , BF_4^- , and ClO_4^- , also have highly symmetric electronic distributions which minimizes their reactivity. Although most of the properties of BF_4^- are distributed among the other anions, it possesses one distinct characteristic. Despite its relative stability, BF_4^- is subject to hydrolysis [18]:



The equilibrium in Eq. (1) is established when an aqueous solution is made; it is not an electrochemical reaction.

2. Experimental

High purity water, obtained from a Millipore system and then cycled and stored in an Easypure Watersystem (Barnstead, Dubuque, IA), was used in preparing solutions, all cleaning procedures, and in all treatments of electrodes. Results are reported for an aqueous solution containing 0.10 M NaCOOH (Fisher Chemical, Fisher

Scientific) and 0.50 M HClO_4 [suprapur perchloric acid, EM Science (Merck), Gibbstown, NJ; redistilled perchloric acid, Optima grade, Fisher Chemical, Fisher Scientific, Fair Lawn, NJ; and redistilled perchloric acid, 99.999%, Aldrich Chemical Company, Milwaukee, WI; results reported here were obtained with each brand of HClO_4]. Results are also presented for solutions containing small amounts of another strong acid or a salt and, to maintain the theoretical pH, sometimes a slightly lower concentration of HClO_4 .

Experiments were conducted in a three-compartment cell. The main compartment was a three-neck, flask (Pine Instrument Co., Grove City, PA, part no. RRF696170) that contained approximately 250 ml of solution and was held at a temperature of $25.0 \pm 0.2^\circ\text{C}$. Another compartment, (Pine Instrument, AC01142), separated from the main compartment by a glass frit, contained the counter electrode, a platinum wire. The reference electrode was located in a third compartment that contained a solution with the same composition as that of the main compartment. Contact was made with the main compartment through a stopcock. The reference electrode was $\text{Ag}|\text{AgCl}|1.0 \text{ M}$ sodium sulfate (Fisher, cat. no. 13-620-216). All potential values are reported with respect to the reversible hydrogen electrode (RHE).

The working electrode that was used to obtain the results reported was a rotating polycrystalline Pt disk (Pine Instrument, AFDD20Pt). The approximate real 'surface area' was 0.74 cm^2 . The working electrode was attached to a Pine Instrument AFASR Rotator. Unless otherwise stated the electrode was not rotated. When rotated, the rotation rate had a precision of $\pm 1.0\%$. Nitrogen flowed through each solution for one half-hour before the solution was used, and it flowed through the top of the solution, well above the level of the Pt disk, during all experiments.

The working electrode was polished with fine alumina mixed with water. The final particle size was $0.05 \mu\text{m}$. The electrode was washed and then usually placed in a cell containing a 0.50 M solution of HClO_4 . When transporting the electrode, the disk was either covered with a layer of water or with a layer of a formic acid solution. The head of the electrode was loosely fitted with a Teflon cap. The potential was cycled between 30 and 1580 mV at a rate of 100 mV s^{-1} until a limiting cyclic voltammogram corresponding to a clean polycrystalline Pt surface was obtained. The electrode was then transferred to a cell containing a formic acid solution. On occasions, the electrode was transferred directly to a formic acid solution. The different procedure did not change results.

Two types of current-control experiments were conducted. In one type the current density was changed in increments and the system was held at a given current density value for a set time. These procedures have the

advantage of a relatively short measurement time. Also, the responses of formic acid oxidation for different solutions can be compared under precisely the same conditions. To examine the precise nature of limiting behavior it was often necessary to change the current density as slowly as possible over an interval. For a fixed current density value, the system was allowed to relax until nonlinear behavior was stabilized. The system often has a long relaxation time [19,20], which leads to a long measurement time. To test whether the system was subject to changes after long times, the response to applying cyclic voltammetry of both the base solution and the formic acid solution was monitored. After the decay of transient cycles, the voltammograms [21] were maintained throughout the experiments, which were conducted for several hours. Experiments were repeated many times and they were conducted on two different systems.

Measurements were obtained using 2 Model RDE4, potentiostat/galvanostats (Pine Instrument). In one system, data was sent to both an x - y recorder and a Hewlett–Packard (HP), model-9237 computer through an HP, model-3852A, data-acquisition unit equipped

with a model-44702A, HP, 13-bit voltmeter. In the other system, data was sent to an IBM computer, Aptiva E76, through a Keithley DAS-1702HR-DA data acquisition board. Collection rates ranged between 20 and 2400 points per min.

3. Results

Results from current-control experiments conducted on the oxidation of a 0.10 M HCOOH + 0.50 M HClO₄ solution are considered first and then results are furnished from current-control experiments that used perturbed solutions, solutions in which small amounts of an anion different from that of the supporting electrolyte were present. After these results are provided, results are presented from potential-control experiments. Finally, effects of variation of rotation rates on formic acid oxidation in current-control experiments, for both the unperturbed and a perturbed solution, are presented.

3.1. The unperturbed solution

3.1.1. Limiting behavior

Oscillations are exhibited by the oxidation of the 0.10 M HCOOH + 0.50 M HClO₄ solution in current-control experiments. They can always be found if the applied current density is increased from zero in sufficiently small increments. To fully characterize sustained oscillations, it is often necessary to hold the system at fixed current density values for long periods of time. Unless the region where limiting oscillatory behavior first appears is approached with long intervals imposed between small current density changes, an overshoot occurs. If an overshoot occurs, potential oscillations at low current densities can still be found and characterized by backtracking. To confidently obtain a global picture of the sequential changes in oscillatory behavior as a function of increasing current density, it was necessary to examine different intervals of current density in separate experiments. The initial current density of an interval was chosen such that it and corresponding behavior overlapped with a preceding interval.

In experiments that examined potential oscillations at low current densities, it was always possible to find a short interval separating stationary behavior from oscillatory behavior. Repeating the procedure of applying a small increase and then decrease in current density moved the system back and forth between a stationary response and an oscillatory response that consisted of one large oscillation and several small oscillations within one period, a response like that in Fig. 1(a).

After stabilizing a low current density oscillatory state, increasing the applied current density caused the system to traverse a sequence of dynamical states in

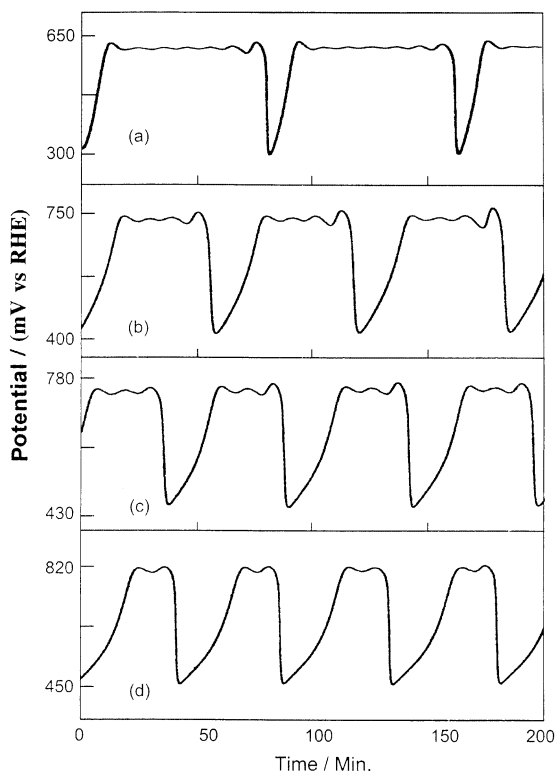


Fig. 1. Potential oscillations obtained after increasing the current density as slowly as possible. Potential (RHE) is plotted against time, [NaCOOH] = 0.10 M, [HClO₄] = 0.50 M. (a) $I = 6.67 \mu\text{A cm}^{-2}$. (b) $I = 19.3 \mu\text{A cm}^{-2}$. (c) $I = 20.0 \mu\text{A cm}^{-2}$. (d) $I = 20.7 \mu\text{A cm}^{-2}$.

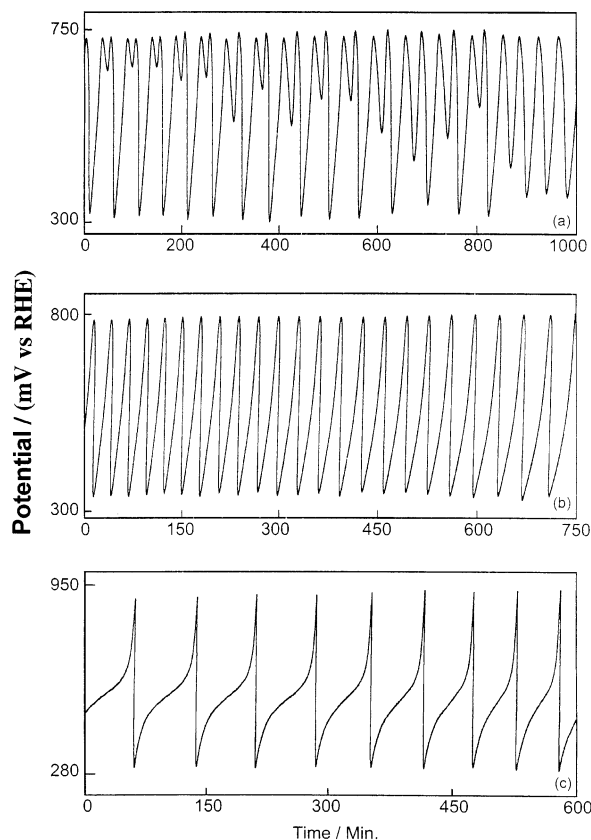


Fig. 2. Potential (RHE) is plotted against time, $[\text{NaCOOH}] = 0.10 \text{ M}$, $[\text{HClO}_4] = 0.50 \text{ M}$. (a) $I = 33.3 \mu\text{A cm}^{-2}$. Transients. (b) $I = 34.7 \mu\text{A cm}^{-2}$. (c) $I = 40.0 \mu\text{A cm}^{-2}$.

which the number of small oscillations per period decreased by one. Waveforms are displayed in Fig. 1(b)–(d) for oscillatory states possessing one large oscillation and 3, 2 and 1 small oscillations per period.

The time series in Fig. 2(a) corresponds to recorded transients. The beginning of the time series consists of oscillations like those in Fig. 1(d); a large amplitude oscillation is followed by a small amplitude oscillation, which is followed by a large one, and so on. The end of the time series is like the response in Fig. 2(b), which consists of one large amplitude oscillation per period. The transients in Fig. 2(a) are consistent with the idea that the state with one small and one large oscillation per period, Fig. 1(d), is linked to a state with only one large oscillation per period, Fig. 2(b), through a reverse period doubling bifurcation.

The potential response consisting of one large-amplitude oscillation per period, Fig. 2(b), remains stable for a large interval of current density. One noticeable change that occurs is that a shoulder smoothly forms in the oscillation with respect to increases in current density. A waveform in which the shoulder is well devel-

oped is shown in Fig. 2(c). Increasing the current density from a value where a response like that in Fig. 2(c) is observed eventually causes a transition from an oscillatory state to a high stationary potential. Many experiments were conducted and the stated nonlinear behaviors were reproduced several times. No other type of oscillatory behavior was seen.

3.1.2. Potential responses to a long sequence of current steps

Results from experiments in which the current density was held fixed for a specific time are presented in Fig. 3(a). Measured potential values are plotted as a function of applied current density. Using the $0.10 \text{ M HCOOH} + 0.50 \text{ M HClO}_4$ solution, the system was held under open-circuit conditions for 2 h. The current density was then changed in increments of $0.67 \mu\text{A cm}^{-2}$ every 15 min. Solid circles represent potential values recorded near the end of a time interval. At a current density value of approximately $53 \mu\text{A cm}^{-2}$, the potential began to oscillate. As stated in the discussion on limiting behavior, an overshoot of the oscillations occurs if long time intervals do not separate small current density changes. Because the system was held at a constant current density for a fixed time and it did not reach its limiting state, the transition to oscillatory behavior is first seen at a current density considerably larger than densities at which oscillations are seen in experiments that examine limiting behavior. This difference in the results from the two types of experiments applies for all solutions. Maxima and minima of potential oscillations are represented in Fig. 3(a) by, respectively, open circles and rectangles. As depicted in Fig. 3(a), oscillations were terminated by a transition to a very large stationary potential. The procedures can be widely varied. The stated procedures were implemented so that experiments on other solutions could precisely follow the same recipe. Results for other solutions (perturbed solutions) are also shown in Fig. 3 and will be subsequently discussed.

3.2. Effects of perturbing the $\text{HCOOH} + \text{HClO}_4$ solution by adding halide anions

3.2.1. Responses to a long sequence of current steps

The $\text{HCOOH} + \text{HClO}_4$ solution was perturbed by adding small amounts of HCl . Results from experiments that followed the same procedure used to obtain the results in Fig. 3(a), except the solution contained $1.0 \times 10^{-6} \text{ M}$, are shown in Fig. 3(b). The onset of oscillatory behavior and the transition to the high potential state occur at current density values lower than those in Fig. 3(a). Notice that the transition to the very high potential branch from the oscillatory region is not sharp. There are points plotted around 1200 mV and represent the first signal of a qualitative change.

The points were not observed using an HCl concentration of 5.0×10^{-7} M. In Fig. 3(c), potential values are plotted against applied current density for the case in which a solution containing 5.0×10^{-6} M HCl was used. In this case, the oscillations are terminated by a transition to a well-defined branch of potential states with values around 1200 mV. The potential remains around this latter value for a range of current densities until there is a transition to the very high stationary

potential values. The maxima and minima for oscillations in Fig. 3(c) appear somewhat randomly distributed due to transitions between different oscillatory behaviors possessing different amplitudes.

Experiments were conducted using solutions with small amounts of Br^- present. One motivation was to examine whether qualitative changes in dynamical behavior induced by the addition of a given anion can be distinguished from those induced by the addition of a

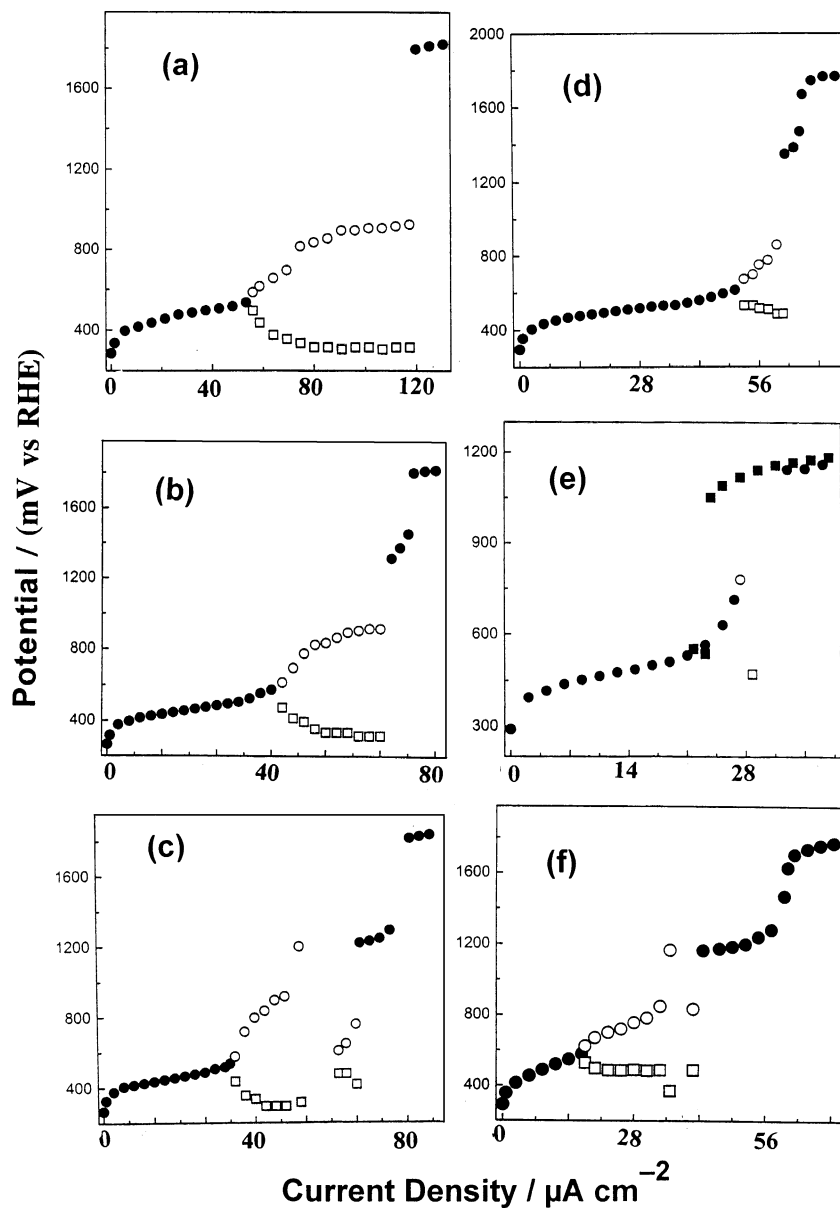


Fig. 3. Measured potential values (RHE) plotted against the applied current density. Solid circles and rectangles represent potentials that appear stationary. Open circles and rectangles represent maxima and minima of oscillations, respectively. $[\text{NaCOOH}] = 0.10$ M. $[\text{HClO}_4] = 0.50$ M. (a) Unperturbed solution. (b) $[\text{HCl}] = 1.0 \times 10^{-6}$ M. (c) $[\text{HCl}] = 5.0 \times 10^{-6}$ M. (d) $[\text{HBr}] = 1.0 \times 10^{-8}$ M. (e) $[\text{HBr}] = 1.0 \times 10^{-7}$ M. (f) $[\text{SO}_3\text{CF}_3\text{Na}] = 0.010$ M.

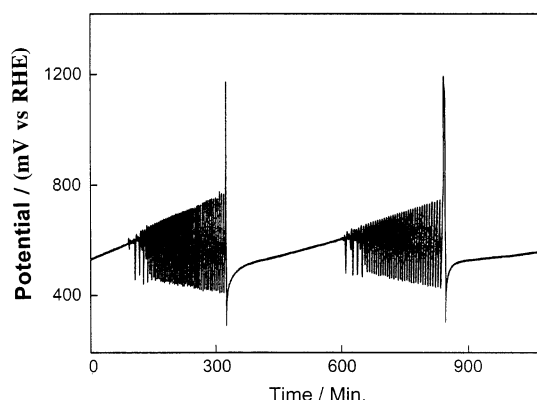


Fig. 4. Potential oscillations obtained using a perturbed solution. $[\text{NaCOOH}] = 0.10 \text{ M}$, $[\text{HClO}_4] = 0.50 \text{ M}$, $[\text{HCl}] = 5.0 \times 10^{-6} \text{ M}$, $I = 30.7 \mu\text{A cm}^{-2}$.

different anion, but one with some similar properties. Behaviors qualitatively different from those exhibited by the unperturbed solution occur in a solution containing a concentration of HBr that is lower than the concentration of HCl where qualitative differences were first noted. The result is not surprising since Br^- is adsorbed to a greater extent than is Cl^- [12]. Qualitative changes in exhibited behavior occur using a solution with $[\text{HBr}] = 1.0 \times 10^{-8} \text{ M}$. Results for this concentration are shown in Fig. 3(d). The anion Br^- quenches oscillations. Results from an experiment in which the addition of HBr quenched almost all oscillations ($[\text{HBr}] = 1.0 \times 10^{-7} \text{ M}$) are shown in Fig. 3(e). After the jump to a potential value slightly less than 1200 mV, additional increases in current densities eventually cause a jump to very high potential states. However, if the current density is reversed in value before the latter jump occurs, solid rectangles in Fig. 3(e), it is seen that relatively high valued stable potentials (1050–1200 mV) are obtained under the same conditions that lower potential states exist. The results imply that, in the potential range under consideration, the system is bistable. The range of the bistable region increases with the Br^- concentration.

3.2.2. Limiting behavior

For perturbed solutions, limiting behaviors were found that were drastically different from that exhibited using the $\text{HCOOH} + \text{HClO}_4$ solution, but only for concentrations of the added salt or acid that was above a critical value. No limiting oscillatory states are observed using a solution containing $1.0 \times 10^{-6} \text{ M}$ HCl that are different from those in Figs. 1 and 2. However, the patterns in Fig. 1(a)–(c) could only be seen in transients. The response in Fig. 1(d) was the only response in Fig. 1 that could be stabilized. The break-up and subsequent disappearance of the states in Fig. 1

occurred for all perturbed solutions upon increasing the perturbing anion concentration. The state with one large and one small oscillation in a period, Fig. 1(d), was always the last one detected. Depending on the specific perturbed solution, the set of states disappeared at a concentration greater or less than the concentration at which completely different behavior was observed.

When $[\text{HCl}]$ was increased to $5.0 \times 10^{-6} \text{ M}$, oscillations were seen that were drastically different from any observed using the $\text{HCOOH} + \text{HClO}_4$ solution. An example is presented in Fig. 4. The time series is very different from any of those in Figs. 1 and 2. Responses with the same general features as the one in Fig. 4 were found in a large range of current densities.

The major effect that HBr has on limiting oscillatory behavior is to replace complex oscillations, like those in Fig. 1, with simple oscillations. When a solution was used with $[\text{HBr}] = 1.0 \times 10^{-7} \text{ M}$, only responses with one oscillation per period were observed.

3.3. SO_3CF_3^-

In Fig. 3(f), results are shown from experiments that followed the same procedure used to obtain the results in Fig. 3(a), except that the solution contained 0.01 M $\text{SO}_3\text{CF}_3\text{Na}$. Behaviors exhibited by the oxidation of formic acid using this solution were qualitatively different from that exhibited using the unperturbed solution. A distinct branch of stationary potentials exists around 1200 mV for a substantial range of current densities in Fig. 3(f). The oscillatory region, which precedes the latter branch of points, contains amplitudes up to 1200 mV, which are substantially greater than those for the unperturbed solution, Fig. 3(a).

In experiments in which limiting behavior was examined, oscillatory states were found (for $[\text{SO}_3\text{CF}_3\text{Na}] \geq 0.005 \text{ M}$) that are not seen using the unperturbed solution or any other perturbed solution. A sequence of oscillatory states observed using a solution containing $\text{SO}_3\text{CF}_3\text{Na}$ is shown in Fig. 5. Each state in the sequence is at a higher current density. It is clear that the oscillatory states are of a different nature than those obtained using the $\text{HCOOH} + \text{HClO}_4$ solution, Figs. 1 and 2.

Compared to the halides, relatively large concentrations of $\text{SO}_3\text{CF}_3\text{Na}$ were required to observe behavior different from that of the unperturbed solution. This result might be attributed to the fact that SO_3CF_3^- is a weakly coordinating anion in solution chemistry [17]. However, even larger quantities of NO_3^- or HSO_4^- (SO_4^{2-}), $> 0.10 \text{ M}$, are required before limiting behavior is observed that is qualitatively different from that obtained using the unperturbed solution. The anions also produce less of a quantitative effect. Using procedures used to obtain the results in Fig. 3, and a solution

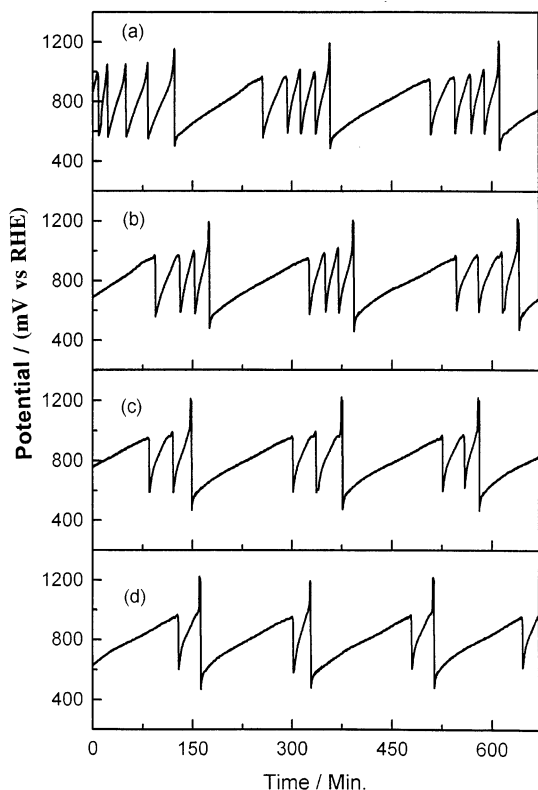


Fig. 5. A sequence of oscillatory states obtained using a perturbed solution. $[\text{NaCOOH}] = 0.10 \text{ M}$, $[\text{HClO}_4] = 0.50 \text{ M}$, $[\text{SO}_3\text{CF}_3\text{Na}] = 0.005 \text{ M}$. (a) $I = 18.7 \mu\text{A cm}^{-2}$. (b) $I = 19.3 \mu\text{A cm}^{-2}$. (c) $I = 20.0 \mu\text{A cm}^{-2}$. (d) $I = 20.7 \mu\text{A cm}^{-2}$.

containing either 0.01 M NaNO_3 or $0.01 \text{ M H}_2\text{SO}_4$, revealed critical values where low potential stationary states become unstable that are below the critical

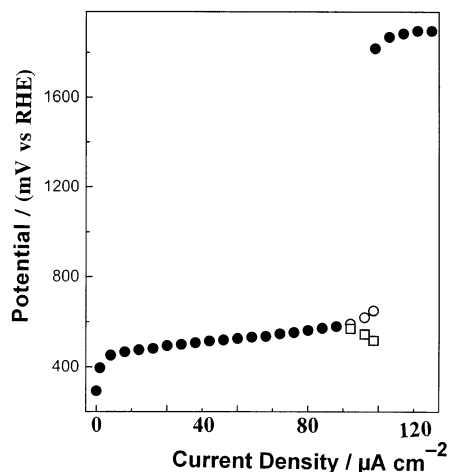


Fig. 6. Same as Fig. 3 but for the solution $[\text{NaCOOH}] = 0.10 \text{ M}$, $[\text{HClO}_4] = 0.49 \text{ M}$, $[\text{HBF}_4] = 0.01 \text{ M}$.

value in Fig. 3(a) by amounts less than 5% of that value.

3.4. The fluoborate anion

Experiments were conducted using a solution containing HCOOH , HClO_4 and a small amount of HBF_4 . The presence of BF_4^- causes the replacement of complex oscillations with simple oscillations and it decreases the length of the interval of current densities in which oscillations occur. Some of the stated behavior can be deduced from Fig. 6 where results are presented from an experiment using a solution that contained 0.01 M HBF_4 and that followed the same procedure used to obtain the results in Fig. 3. At this concentration of HBF_4 , there is only a short range of current densities in which the oxidation of formic acid exhibits oscillations. Fig. 6 reveals a quantitative result for BF_4^- distinctly different from that obtained for each of the other anions. The current density in Fig. 6 where low potential stationary states first become unstable (ca. $95 \mu\text{A cm}^{-2}$) is more than 60% larger than the corresponding critical value for the $\text{HCOOH} + \text{HClO}_4$ solution, Fig. 3(a). This critical value decreased when any one of the other perturbed solutions were used. The result indicates that addition of HBF_4 improves the steady-state efficiency of the reaction process: The reaction maintains a low constant potential for a larger applied current density.

3.5. Potential-control experiments

Cyclic voltammetry was applied to the $\text{HCOOH} + \text{HClO}_4$ solution and all perturbed solutions. Current–potential curves (I/E curves) for the solution containing BF_4^- (solid curve) and the unperturbed solution (dashed curve) are shown in Fig. 7(a). The I/E curve for the unperturbed solution is also shown in Fig. 7(b) but on a different scale. The I/E curve for the unperturbed solution has the largest peak, but it is located at a potential (ca. 800 mV). Two peaks occur in the I/E curve for the solution containing BF_4^- . The low potential peak current has a value more than $3/2$ times the value of the unperturbed solution. A shoulder occurs in the I/E curve for the unperturbed solution in the same potential range. All the other perturbed solutions, perturbed by using another anion, have current densities less than or equal to those in Fig. 3(b) at corresponding potentials.

Finally, experiments were conducted on a solution perturbed by adding HF . The results reveal HF is not the source of enhancement that was achieved by perturbing the $\text{HCOOH} + \text{HClO}_4$ solution by mixing in HBF_4 ; see Eq. (1).

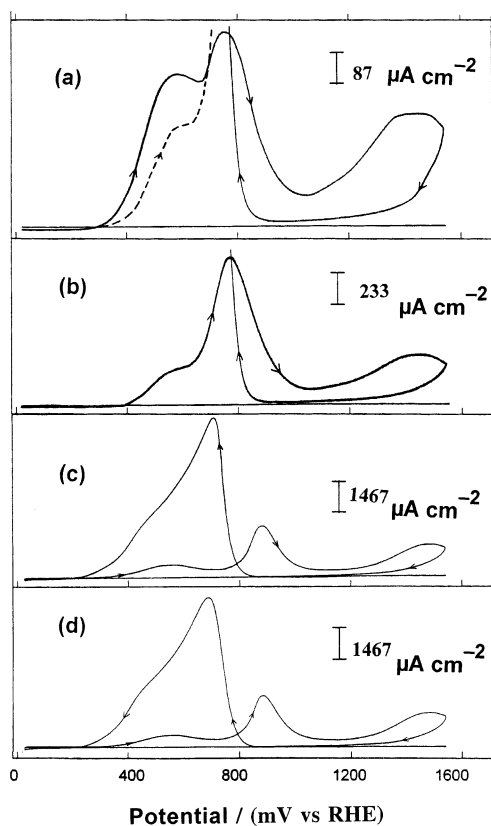


Fig. 7. Cyclic voltammograms. Current density is plotted against potential. 0.10 M HCOONa . (a) Scan rate = 1.0 mV s^{-1} . Solid curve: $[\text{HClO}_4] = 0.49 \text{ M}$, $[\text{HBF}_4] = 0.01 \text{ M}$. Dashed curve: $[\text{HClO}_4] = 0.50 \text{ M}$, $[\text{HBF}_4] = 0.00 \text{ M}$. (b) Dashed curve in (a) and its continuation but on a different scale. (c) Scan rate = 100 mV s^{-1} . $[\text{HClO}_4] = 0.50 \text{ M}$, $[\text{HBF}_4] = 0.00 \text{ M}$. (d) same as (c) except $[\text{HClO}_4] = 0.49 \text{ M}$, $[\text{HBF}_4] = 0.01 \text{ M}$.

3.6. Effects of varying rotation rates

Changes in both stationary and oscillatory behaviors were studied as a function of rotation rate using the $\text{HCOOH} + \text{HClO}_4$ solution and a perturbed solution ($1.5 \times 10^{-6} \text{ M HCl}$). Under the conditions studied here, instabilities do not occur in potential-control experiments, and so effects of changing the rotation rate were only studied in detail in current-control experiments.

The rotation rate was set at 1000 rpm and the current density was increased from zero following the same procedures for which the results in Fig. 3 were obtained. After reaching a given stationary or oscillatory state, the rotation rate was increased to 3000 rpm. The rotation rate was then decreased so that it passed through the values plotted in Fig. 8. The rotation rate was held at each value for about 40 min. The solid

rectangles in Fig. 8 represent stationary potential values and the solid circles represent the peak values of sustained periodic oscillations. It can be seen that varying the rotation rates has little effect on the oxidation of formic acid for both the perturbed, Fig. 8(a), and the unperturbed solution, Fig. 8(b). The result holds for both stationary and oscillatory behavior.

Sometimes quantitative effects were seen on increasing the rotation rate by large amounts. For example, increasing the rotation rate by 2000 rpm could increase steady states or peaks of oscillations up to 50 mV. However, these effects occurred during the decay of transients, which can be very slow. If the stated experiment is conducted with the initial rotation rate set to 3000 rpm, then after reaching any of the current densities used in Fig. 8, continuous variation of the rotation rate, including large jumps, has no effect.

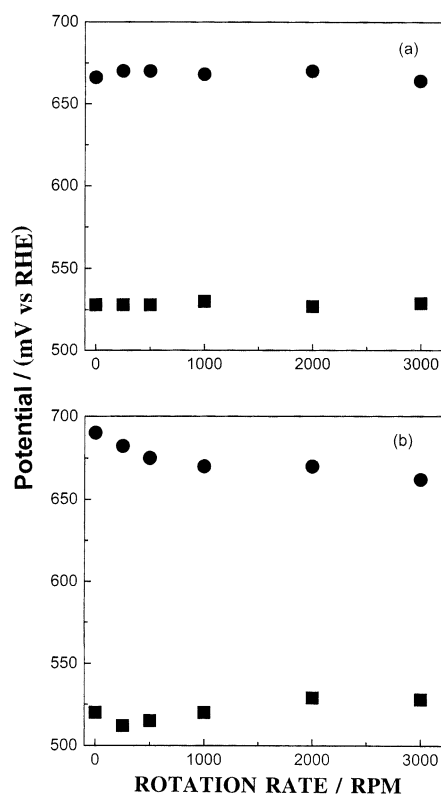


Fig. 8. Potential plotted as a function of rotation rate. 0.10 M HCOONa , 0.50 M HClO_4 . (a) $5.0 \times 10^{-6} \text{ M HCl}$. Solid rectangles are steady state values; $I = 22.0 \mu\text{A cm}^{-2}$. Solid circles represent the peaks of oscillations; $I = 36.7 \mu\text{A cm}^{-2}$. (b) Same as (a) but without HCl. Steady state values (rectangles) were recorded at $I = 22.0 \mu\text{A cm}^{-2}$. Oscillations were recorded at $I = 47.3 \mu\text{A cm}^{-2}$.

4. Discussion

The results presented here reveal that small differences in anion composition cause quantitative differences and also dramatic qualitative differences in the dynamical behavior exhibited by formic acid oxidation in current-control experiments. Changes in rotation rates have no effect on limiting behavior in current-control experiments. The latter result holds for different anion compositions and for both stationary and oscillatory responses. The results on rotation rates imply that transport has no relation with the changes caused by the presence of different anions and no relation with the occurrence of instabilities. The changes in behavior induced by small changes in anion composition must only involve properties of 'adsorbed anions' and surface processes they affect. The occurrence of instabilities is determined by the specific nature of the potential dependent surface reactions. The latter conclusion was previously reached by Wojtowicz et al. [22].

Qualitative changes induced by the presence of a small amount of an anion appear to be unique to that anion. Probably, further investigations will show that other anions at least approximately duplicate the behavior reported here. However, although it may be overly optimistic, the results indicate that the procedures employed might serve as a basis for developing techniques for the detection of specific anions. Greater potential for the application will be indicated if results like those presented here are obtained when small amounts of a mixture of anions are added to a $\text{HCOOH} + \text{HClO}_4$ solution and, if the changes in dynamical behavior are related to the composition of the mixture.

The quantitative changes that occurred when the $\text{HCOOH} + \text{HClO}_4$ solution was perturbed by the presence of a small amount of BF_4^- may be important practical results. The presence of BF_4^- enhances formic acid oxidation. In current-control experiments, the applied current density at which low valued stationary states remain stable increases substantially. In potential-control experiments, the current density undergoes a large increase at relevant potential values.

Although the presentation of the stated new findings is the main focus of this paper, we use the data presented here and results published elsewhere [23–35] to formulate a possible explanation for the differences in the behavior exhibited by the oxidation of formic acid in the presence of small amounts of different anions. As with most explanations of new results, it contains points that possess some degree of speculation that will require further testing. First, the mechanism for the oxidation of formic acid is outlined. Formic acid oxidation follows at least two reaction paths, the direct and indirect routes [4,36]. In the direct route all reactions are rapid at vacant surface sites even at low potentials.

Surface bonded CO forms in the indirect route. At low potentials CO blocks reactions of the direct route. Rapid removal of CO only begins at relatively high potentials.

Since the anion induced differences in behavior exhibited by formic acid oxidation include drastic ones and one in which the oxidation process was enhanced, the explanation for the differences must go beyond the idea that anions only block surface sites. The results from the experiments in which rotation rates were varied eliminate all explanations except those involving differences in processes that take place on the electrode surface. The general results from using different anions imply that anions either take part in these processes or directly influence them.

It may seem plausible that electronic distributions of surface anions or discharged anions could affect the rearrangement and transfer of electrons during reactions at neighboring sites. Only the rates of reactions would be changed. Because the rates of the direct and indirect routes are greatly different, it is difficult to see how these changes could vary sufficiently among anions, as well as discharged species, to cause the observed qualitative differences. Furthermore, the results of studying the effects of other adsorbed species on the oxidation of oxygenated organics [23–29] reveal that these effects are caused for other reasons and not by the influence of electron distributions.

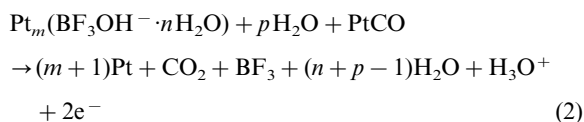
It is useful to review the ways other types of adsorbed species affect the oxidation of organics and examine whether any effects might be in common with those that accompany the adsorption of anions. Excluding special details such as steric properties, there are two general ways that adatoms affect reaction. One way adatoms, such as sulfur, affect the oxidation of formic acid is by controlling the number of neighboring vacant sites available for reaction [23,24]. Distinct neighborhoods of vacant sites, separated by adatoms, form on the electrode surface. If the majority of these neighborhoods have enough vacant sites to accommodate the reactions of the direct route but not for the formation of surface CO, then formic acid oxidation is enhanced. This mechanism does not appear to play a role here as revealed by results obtained with BF_4^- present in solution. The stated adatom effect does not depend on the radius of the adatom and so it would be expected that an anion belonging to the class of weakly coordinating anions and that possessed a symmetric electron distribution would also enhance the oxidation of formic acid. Furthermore, the stated adatom effect was observed to increase current densities throughout forward potential scans that went well into the oxygen region [24]. The current–potential curve in Fig. 7(a) shows that formic acid oxidation is enhanced only at relatively low potentials.

Adatoms also influence the oxidation of organics by affecting the reaction with surface bonded CO (Of course, some adatoms cause a combination of both mechanisms stated here.). Oxygen containing species must react with PtCO to produce CO₂. At low potentials the reactant is most likely water, but this reaction is slow. Surface CO is removed rapidly only at relatively high potentials where it reacts with either an activated or chemically transformed (surface bonded OH) form of surface water [7,8,34,36–39]. Adatoms like Ru, Sn, and Ge provide the activated oxygen containing species that reacts with surface CO at potentials lower than metals like Pt [25–29]. Since the potential at which surface CO is removed at a significant rate is lowered, the oxidation process is enhanced. This effect also motivates investigations that examine Pt alloys as catalytic material [25,40–42]. Although in general there is no enhancement, the adsorption of anions shares at least one feature with the latter adatom mechanism. Just like the adatoms, adsorbed anions have strong interactions with water molecules. Unless hydrated anions suddenly lose all water molecules in the adsorption process, adsorbed anions initially interact with water molecules through ion–dipole and dipole–dipole interactions [30,31]. These water molecules and the more highly activated components that form in the surface anion complex at higher potentials [30,31] react with surface CO. The reaction of components of a surface anion complex explains the drastic differences in behavior exhibited by the oxidation of formic acid. The reactivity of the components depends on the properties of the anion surface complex. These properties include surface hydration number, strength and type of interactions between oxygen containing components and other atoms in the complex, the potential dependence of the form of the components, the potential dependence of anion discharge, and the geometry of the anion complex. Since these properties vary among anions, exhibited dynamical behavior varies with anion composition. Experimental evidence supports the existence of surface anion complexes with oxygen containing components [32].

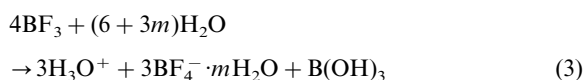
Because the explanation presented here does not depend on the potential at which surface OH forms, it is consistent with results that challenge the contemporary theory in which surface bonded OH reacts with surface CO [8,37]. Anion adsorption influences the potential dependence of methanol oxidation [33], and reactions removing surface CO during methanol oxidation are not related to the potential where surface OH first forms [34]. As a cautionary note, when methanol oxidation is referred to, it is only the reaction of surface CO that is being considered. Although similarities exist, there are major differences between the electrooxidation of methanol and formic acid

Although assumptions are required for a complete connection, the enhancement of formic acid oxidation in the presence of BF₄[−] is consistent with the explanation of anion induced differences in behavior. The first peak in the *I/E* curve for the solution containing BF₄[−] is consistent with the idea that it is an extension of the shoulder in the *I/E* curve for the HCOOH + HClO₄ solution; See Fig. 7(a) and (b). At these potentials an increase in the overall rate of the direct route is compatible with the result. Because reactions of the direct route are rapid at vacant sites an increase in the overall rate implies less CO blocks surface sites. A decrease in blockage by CO could be caused by a decrease in the rate of surface CO formation. If this was the primary cause of decreased blocked sites, the differences between the *I/E* curves for the perturbed and unperturbed solutions in Fig. 7(a) would increase with respect to increases in scan rate. The results in Fig. 7(c) and (d) reveal that differences between the *I/E* curves decrease with respect to increases in scan rate. An increase in the rate of removal of surface CO at low potentials is consistent with the results.

At low potentials, ion–dipole interactions are expected to be the strongest interaction between most adsorbed anions and water components. These components have a small reactivity with CO. Most of the anions studied in this paper did not enhance formic acid oxidation. If surface anion complexes with the more reactive OH components existed at low potentials, the rate of removal of CO and the overall rate of the direct route would increase. The main difference between the anion BF₄[−], which enhanced formic acid oxidation, and the other anion studied, is that an equilibrium exists between it and the anion BF₃OH[−], Eq. (1). Assuming that the group OH is highly reactive with surface CO, it is feasible that adsorption of hydrated BF₃OH[−] either directly or indirectly provides an efficient reaction path for removal of surface CO at lower potentials. An overall reaction involving surface CO and adsorbed BF₃OH[−] is written as follows:



Although BF₃ is a strong Lewis acid, it rapidly interacts with water and regenerates some BF₄[−] [18]:



5. Summary

Definitive deductions that follow from the results of the study presented in this paper are the following.

Variation of rotation rates does not affect the limiting dynamical behavior exhibited by the oxidation of formic acid under current-control conditions. Perturbing a $\text{HCOOH} + \text{HClO}_4$ solution by adding a small amount of an anion, different from ClO_4^- , can cause drastic changes in the behavior exhibited by the oxidation of formic acid. When HBF_4 is added so that it has a concentration of about 2% of the concentration of HClO_4 , formic acid oxidation is enhanced: In potential-control experiments, current densities increase more than 50% at relevant potentials. In current-control experiments, the value of the applied current densities at which low valued potential stationary states remain stable increases by more than 60%.

It is concluded that surface reactions have a strong influence and transport has little influence on the overall potential dependent process rate. The specific nature of the surface reactions leads to observed instabilities in formic acid oxidation under current-control conditions [22]. The properties of the individual type of anion and the surface processes they influence cause the quantitative and dramatic qualitative changes when the anion composition is changed a small amount.

It was hypothesized that surface anion complexes with oxygen containing components form on the electrode surface. These complexes react with surface CO. Anion complexes with more reactive OH components usually exist only at high potentials. Their existence at lower potentials causes a more rapid removal of CO at these potentials. Consequently, the overall rate of the direct route increases and I/E characteristics improve. The presence of BF_4^- indirectly causes adsorption of an anion complex at low potentials, hydrated BF_3OH^- , which possesses a more reactive OH component. Some of the ideas introduced here can be tested by applying surface infrared spectroscopy [42–48] but, it must be coupled with much slower potential scans than usual (see Fig. 7). The concentration of surface CO at relatively low potentials is expected to decrease in solutions mixed with HBF_4 . Another important test is to examine how the oxidation of simple organic molecules is affected by other inorganic anions that possess OH groups. The anions must be stable in acid solution.

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