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Oscillatory Behavior in the Electrochemical Oxidation of Formic Acid on Pt(100)

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The electrochemical oxidation of formic acid on Pt was studied in acidic supporting electrolyte using single-crystal electrodes. Very well-defined periodic (not chaotic) current oscillations on a stationary Pt(100) electrode were observed under both potentiodynamic and potentiostatic conditions. The oscillatory behavior is strongly dependent on the Pt surface structure and is seen on the (100) surface but not on the (111) surface. The periodicity, the amplitude, and the absolute magnitude of the current oscillations depends on at least three variables, electrode potential and potential history, formic acid concentration, and the anion of the supporting electrolyte. The pH of the electrolyte was not found to be an important variable, nor was mass transport, e.g. rotation or stirring. The behavior is extremely complex and difficult to analyze in terms of known electrode processes.

Introduction

The observation of periodic effects in (electro)chemically reacting systems was noted at the beginning of this century, but the real interest in oscillatory behavior has occurred in the past 10 years. Oscillations of either current or potential in electrochemical systems are well-known, particularly in the passivation of metals,[1-4] in the anodic oxidation of hydrogen,[5,6] and in reactions concerning the oxidation of small organic molecules.[7-12] In early work by Wojtowicz et al.[7] oscillatory kinetics during the electrochemical oxidation of formate and ethylene were studied at smooth, polycrystalline paladium and platinum electrodes. The oscillatory behavior has been related to mass transport effects and to the coverage of the electrode by electrochemically formed surface oxide species. Wojtowicz et al.[7] proposed that coverage by oxide would lead to the inhibition of the reaction, and the removal of surface oxide would occur via an autocatalytic step involving surface oxide and adsorbed formate radicals. Although various oxidation steps during formate oxidation were considered, the authors[7] did not discuss the role of strongly adsorbed organic intermediates in the course of the oxidation of formic acid. It is now widely accepted, however, that the oxidation of formate follows the dual path mechanism. One path includes a step in which inhibiting intermediates (CO, COH, HCO) are formed. Recently Shell et al.[9] proposed a modified model for the oscillatory behavior during the oxidation of formaldehyde and formate that includes the oxidative removal of strongly bound intermediates.

The early work with polycrystalline electrodes has been followed by the investigation of oscillatory behavior on single crystal electrodes. Raspel et al.[10] reported that sustained current oscillations in the oxidation of formic acid on Pt(100) were observed within the potential region where strongly adsorbed intermediates are oxidized by adsorbed OH. A local pH variation resulting in a sudden change in the surface coverage with OH during the oxidation was proposed to be responsible for sustained current oscillation to take place. A similar explanation was proposed for oscillations recorded on platinum single-crystal stepped surfaces, this time under potentiodynamic conditions.[11] In addition to a pH variation, Tripkovic et al.[11] proposed that the number of sites occupied by the bridge bonded CO would also play an important role in the oscillatory behavior during the formic acid oxidation.

The aim of this paper is not to propose any detailed mechanism for oscillations observed during the oxidation of formic acid but rather to report the dependence of oscillations upon electrode potential, the anion in the supporting electrolyte, and the formic acid concentration. We show that all three variables are factors in determining the shape and the frequency of oscillation on a Pt(100) surface and that the oscillatory behavior is much more complex than previously reported.

Experimental Section

The preparation and pretreatment of a Pt(100) single-crystal electrode was fully described in our earlier paper.[13] The electrochemical measurements were carried out in a conventional cell (see ref 14 for details). The counter electrode was a platinum wire separated from the working electrode compartment by a glass frit. The reference electrode (saturated calomel electrode (SCE)) was in separate compartment, isolated by a bridge with a closed stopcock. The surface area of single crystal was 0.572 cm^{-2}. Electrolyte solutions were prepared using concentrated $HClO_4$, H_2SO_4, and HCl (all ultragrade, J.T Baker). The water used was pyrolytically triply distilled water. The voltammograms were recorded with a scan rate of 10 mV/s.

Results

General Features of Current Oscillations. Potentiodynamic behavior of Pt(100) obtained in 1 mM $HClO_4$ with and without formic acid is shown in Figure 1. These curves are a representative example, illustrating the characteristic voltammetric features within the potential limits of hydrogen adsorption and oxide formation. Since the oxidation current of formic acid under anodic and cathodic potentiodynamic conditions overlap, voltammograms are shown "unfolded" in potential. In an acid solution containing formic acid, hydrogen adsorption is strongly inhibited, a result usually attributed[15,16] to the formation, in this potential region, of strongly adsorbed carbon monoxide, although other "CHO" fragments from formic acid dissociation are undoubtedly present as well.[17,18] For simplicity, we will refer to these species collectively, as "organic intermediates". The onset for the oxidative removal of organic intermediates, along with the faradaic oxidation of formic acid, coincides with the potential of "Pt oxide" formation (in a solution not containing formic acid), ca. 0.4 V, and the current slowly increases until about 0.48 V, where the first of five current oscillations begins. (We will use the term "Pt oxide" as a shorthand notation for the various oxygenated states of Pt and dissociation products of water collectively.) The appearance of oscillations on the anodic sweep with 25 mM formic acid is a new observation and was not reported in previous studies

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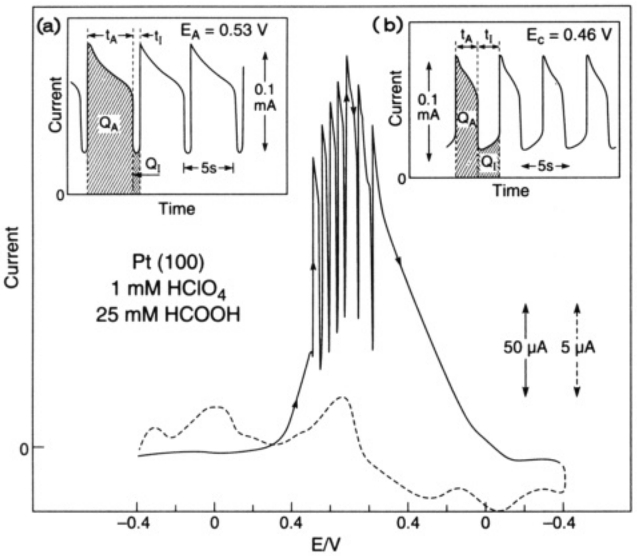


Figure 1. Potentiodynamic curves and potentiostatic transients (inserts) in 1 mM $HClO_4$ (- - -) and Pt(100) in 1 mM $HClO_4$ +25 mM HCOOH (—); 10 mV s^{-1}. Sweep reversed at 0.7 V. Insert (a) shows waveforms of potentiostatic transients with holding potential at 0.53 V after anodic sweep from –0.4 V. Insert (b) shows waveforms for sustained oscillations observed after sweeping anodically to 0.6 V and then cathodically to 0.46 V.

with Pt(100).[10,11] Upon reversal of the sweep at 0.7 V, the oscillations continue on the negative sweep to ca. 0.4 V, followed by a monotonic decay in current as the potential is decreased back to the starting potential. All the features of the voltammograms in Figure 1 are reproduced in subsequent scans, i.e., the features are relatively insensitive to the number of sweeps in the potential region shown.

Inserts in Figure 1 are representative of transients recorded at different potentials. To monitor current oscillations as a function of time, the potential was scanned in the positive direction from –0.4 V and then held in the current oscillation region at 0.53 V (insert (a)), or upon the sweep reversal at 0.7 V current oscillation were recorded at 0.46 V (insert (b)). The shape of current oscillations is typical for a so-called relaxation oscillation:[19] The system remains in either one or two quasi-stationary states (active t_A or inactive t_I) then followed by a sudden transition from one state to another. The total charge passed during a single oscillation is referred to as active Q_A or inactive Q_I as shown in Figure 1. The current oscillations under potentiostatic conditions are also obtained after a potential step from any initial potential where no current oscillations take place to a final potential where current oscillations are observed. Both experimental procedures displayed almost the same potentiostatic transients, and therefore this paper is mostly concerned with current oscillations recorded after scanning and holding the potential (see inserts in Figure 1); the results obtained with the potential step method are noted specifically.

Potentiodynamic Conditions. Voltammograms of Pt(100) in 1 mM $HClO_4$ containing various concentrations of formic acid are shown in Figures 2–4. Addition of formic acid to the supporting electrolyte resulted in two characteristic features: First, the incipient oxidation potential was shifted ca. 50 mV positively with increasing the formic acid concentration from 25 to 200 mM. This is in accord with the expectation that the surface coverage with OH decreases due to an increase in surface coverage with organic intermediates. The second characteristic is that in solutions containing more than 80 mM of formic acid, oscillations were suppressed on the positive sweep direction and appeared only on the negative sweep. The potentiodynamic curve for the oxidation of 50 mM of formic acid is different from the one obtained by Raspel et al.,[10] who did not observe any oscillations in the anodic sweep at this concentration. We attribute this difference possibly to the different levels of trace Cl impurities present in the $HClO_4$ in the two laboratories. The effect of Cl on the oxidation of formic acid will be discussed in a later section.

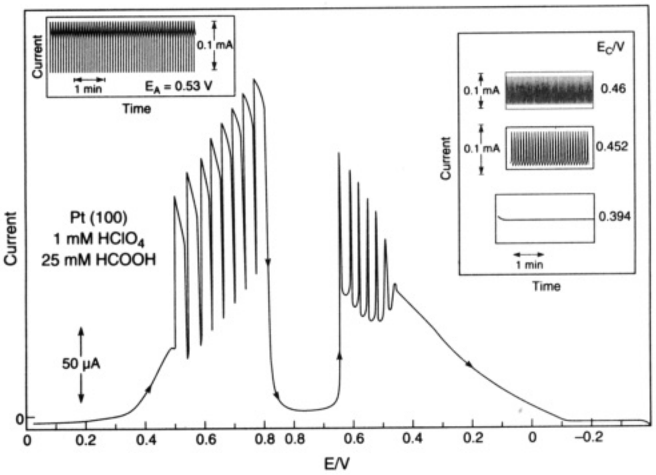


Figure 2. Potentiodynamic curves and potentiostatic transients (inserts) in 1 mM $HClO_4$ +25 mM HCOOH; 10 mV s^{-1}. Sweep reversed at 0.85 V. Notation for inserts as in Figure 1.

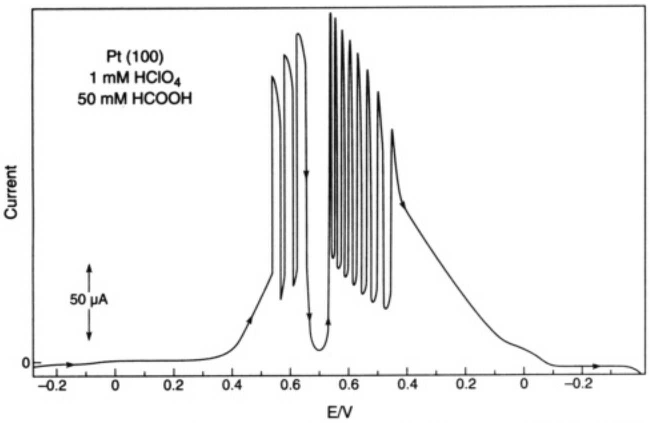


Figure 3. Potentiodynamic curve in 1 mM $HClO_4$ +50 mM HCOOH; 10 mV s^{-1}. Sweep reversed at 0.7 V.

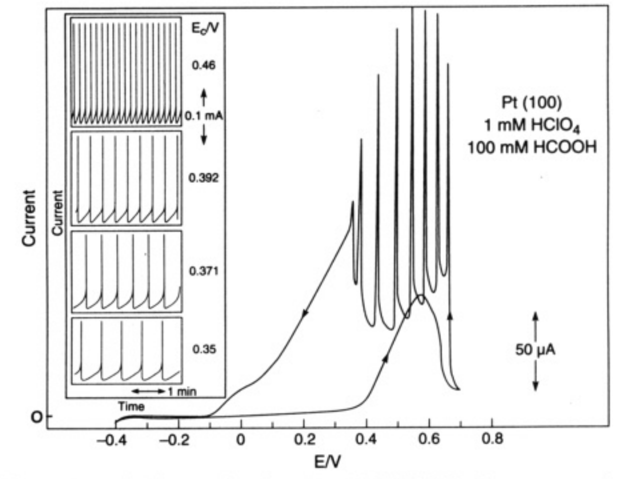


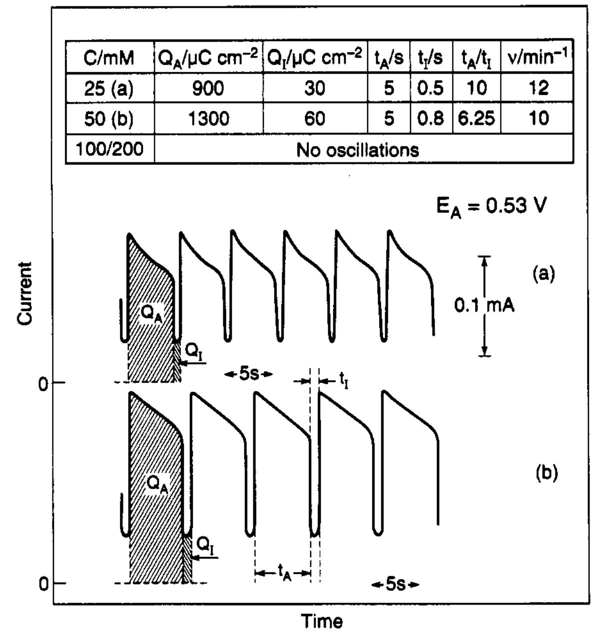
Figure 4. As in Figure 2 but for 100 mM HCOOH. Sweep reversed at 0.7 V.

The role of the relative surface coverage by adsorbed organic intermediates and "Pt oxide" in sustaining current oscillations can be seen in the dependence of oscillations on formic acid concentration and on potential, as shown in Figures 2–4. In the solution with 25 mM formic acid, the current spikes are regularly developed from 0.48 to 0.85 V; above 0.85 V the current falls dramatically to a low value, i.e., the electrode becomes deactivated.

From the voltammetry without formic acid present, the drop in activity above 0.85 V could be attributed to the relatively high coverage of "Pt oxide" above this potential. With the increase in formic acid concentration to 50 mM the potential where deactivation occurs shifted to 0.7 V, and with an increase to 100 mM it has shifted to near 0.6 V. Also the absolute value of the activity in the inactive state is inversely proportional to the formic acid concentration. Thus, in this case the deactivation appears to be caused by a high coverage by adsorbed organic intermediates.

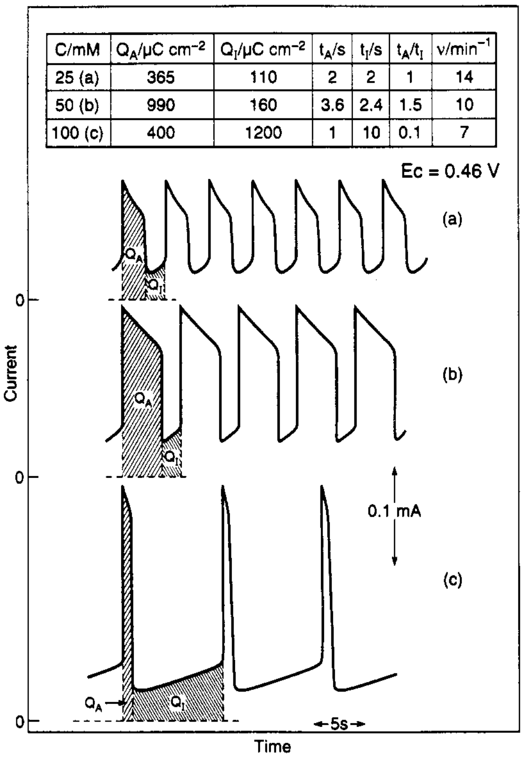
Figure 2 clearly shows that upon the sweep reversal at the deactivation potential, the electrode remained inactive down to 0.65 V, at which point the current increased rapidly, producing the first of seven current spikes. The onset of the first current spike appears to coincide with the beginning of "Pt oxide" reduction (Figure 1) and the regeneration of bare platinum sites. Figure 3 shows that in the reverse sweep the transition from inactive to active state in 50 mM of formic acid occurs at 0.68 V or at almost the same potential as in 25 mM formic acid. Similar behavior is also obtained in the solution containing 100 and 200 mM of formic acid, as shown in Figure 4, but the potential for the onset of the oscillations is shifted cathodically to 0.6 and 0.635 V, respectively. These shifts are indicative of an increasing coverage by organic intermediates with increasing formic acid concentration, a not unexpected result. This indicates that if the electrode is deactivated by excessive organic intermediate formation on the anodic sweep, current oscillations appear on the reverse sweep, even in the solution with 100 and 200 mM of formic acid where there are no oscillations on the anodic sweep.

Potentiostatic Conditions. *Effect of Formic Acid Concentration.* The cyclic voltammetry in Figures 2–4 suggest that *sustained* current oscillations might be developed during the oxidation of formic acid. We sought to confirm the true oscillatory behavior by holding the potential within the potential region where current oscillations were predicted by the potentiodynamic experiment. In these experiments, the potential was scanned positively from –0.4 V, and then the potential was held at E_A on the anodic or at E_C on cathodic sweep. The results of these experiments are shown as inserts in Figures 1, 2, and 4. Current oscillations obtained during the oxidation of 25 mM formic acid, shown as insert (a) in Figure 2, were regularly developed for more than 45 min, after which the experiment was stopped. Similar current transients were recorded from the solution containing 50 mM formic acid. In the solutions with 100 and 200 mM formic acid, however, potentiostatic transients displayed monotonic current decays with no sign of oscillatory behavior at E_A = 0.53 V. To establish the detailed shape of a single oscillation and the dependence of shape on other variables, oscillations for two different concentrations of formic acid were recorded with an expanded time scale, as shown in Figure 5. It is obvious that the amplitude, the relative period of time the system remains in either one of the two quasi-stationary states, and the active state (t_A) and the inactive state (t_I), as well as their corresponding coulombic charge (Q_A and Q_I) passed while in each state increase with the increase in formic acid concentration from 25 to 50 mM. On the other hand, the frequency of oscillations decreases with increasing formic acid concentration. The magnitude of the charge values of Q_A indicate that in the active state of the electrode (during t_A) faradaic reactions must occur concurrently with the oxidation of surface species. For example, oxidative removal of a monolayer of adsorbed CO requires 420 μC/cm^2, which is only one-half to one-third of the total charge in the active state.



C/mM	Q_A/μC cm^{-2}	Q_I/μC cm^{-2}	t_A/s	t_I/s	t_A/t_I	v/min^{-1}
25 (a)	900	30	5	0.5	10	12
50 (b)	1300	60	5	0.8	6.25	10
100/200	No oscillations					

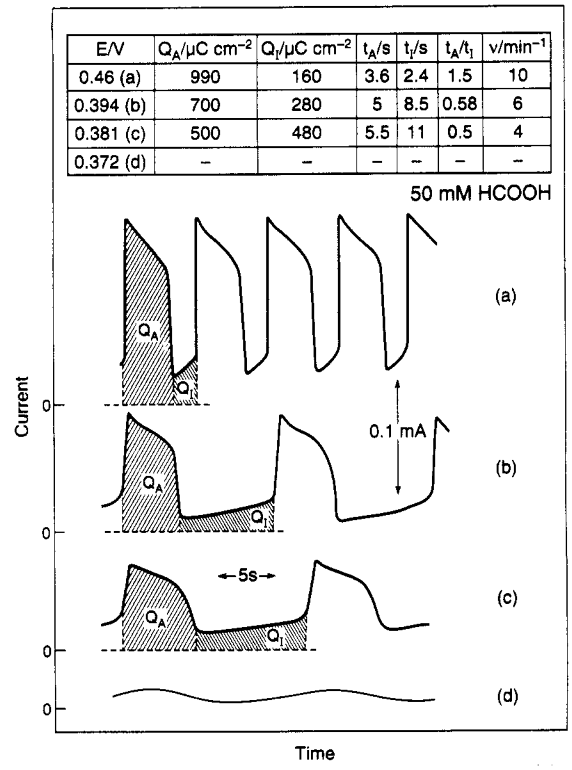
Figure 5. Summary of waveforms of potentiostatic transient at E_A = 0.53 V as a function of HCOOH concentration.



C/mM	Q_A/μC cm^{-2}	Q_I/μC cm^{-2}	t_A/s	t_I/s	t_A/t_I	v/min^{-1}
25 (a)	365	110	2	2	1	14
50 (b)	990	160	3.6	2.4	1.5	10
100 (c)	400	1200	1	10	0.1	7

Figure 6. Summary of waveforms of potentiostatic transients at E_c = 0.46 V as a function of HCOOH concentration.

The sensitivity of the current transients to the electrode potential is revealed in Figure 6, where the potential was scanned from –0.4 V in the positive direction, then reversed at 0.7 V, and finally held at 0.46 V. Here, in contrast to the previously described experiment (Figure 5), current oscillations could be observed even at 100 mM concentration of formic acid. There are several characteristics of the current transients recorded at 0.46 V that depen on formic acid concentration. Figure 6 shows that an increase of the formic acid concentration from 25 to 100 mM leads to an increasing current amplitude but at a concentration of 200 mM the current amplitude decays to zero. The deactivation at high formic acid concentration is probably associated with the accumulation of surface intermediates above a critical coverage. The time in which the system stays in one of two quasi-stationary states t_A and t_I is also dependent on formic acid concentration; the period of oscillations decreases with an increase of formic acid concentration. It is interesting to note that at 0.46 V the charge Q_A and the time t_A show maxima at a formic acid concentration of 50 mM and that only for this concentration did Q_A exceed the charge for oxidative removal of a monolayer of adsorbed CO.



E/V	Q_A/μC cm^{-2}	Q_I/μC cm^{-2}	t_A/s	t_I/s	t_A/t_I	v/min^{-1}
0.46 (a)	990	160	3.6	2.4	1.5	10
0.394 (b)	700	280	5	8.5	0.58	6
0.381 (c)	500	480	5.5	11	0.5	4
0.372 (d)	–	–	–	–	–	–

Figure 7. Summary of waveforms of potentiostatic transients in 1 mM $HClO_4$ +50 mM HCOOH for different values of E_A.

Effect of Potential. We described above the effect of different amounts of formic acid on oscillatory behavior at constant potential. If we assume that at a given potential the surface coverage by "Pt oxide" is independent of the bulk concentration of formic acid (the rate of OH adsorption is much faster than the rate of formic acid adsorption) we would expect that during a transition from one steady state to another (at constant potential) the "oxide" coverage remains constant. To establish the role of adsorbed "oxide" on current oscillations, current transients were monitored at varying potentials while keeping the concentration of formic acid constant, as shown in Figure 7. Coulometry indicates that in formic acid free solution, Figure 1, the surface coverage by "oxide" decreases from 0.25 ML (as true OH) at 0.46 V to 0.05 ML at 0.37 V (ML = monolayer). This change in "oxide" coverage appears to have a predominant influence on the shape of current oscillations, if we assume that in the same potential region the change in the surface coverage by formic acid with potential is negligible. Unfortunately, the true adsorption isotherm is not available for formic acid on Pt(100). However, if we assume for Pt(100) the bell-like shape of the adsorption isotherm proposed for polycrystalline platinum[20] with the maximum in the double-layer potential region, then, referring to the voltammogram in Figure 1, the maximum surface coverage with formic acid and, therefore, the maximum amplitude should be obtained around 0.36 V. Figure 7 shows that holding the potential negatively of 0.46 V decreases the current amplitude, and current oscillations vanish at 0.37 V, consistent with the hypotheses made above.

Induction Periods. The sweep-and-hold experiments described above do not provide information about possible induction periods for the oscillations. To observe induction period behavior, we performed potential step experiments, examples of which are shown in Figure 8. These examples characterize a general pattern of induction period, with shorter (10–20 s) induction periods observed with anodic potential steps from a inactive state at low potential, and longer induction periods (100–200 s) for cathodic steps from the deactivated state at high potential. In both cases, the potential was stepped into a region where sustained oscillations were observed previously in sweep-and-hold experiments.

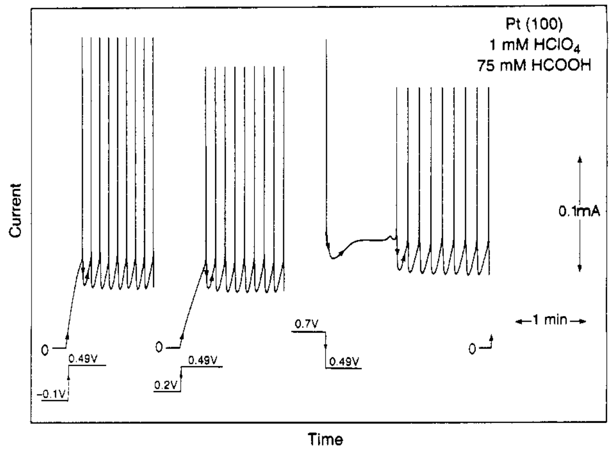


Figure 8. Potentiostatic transients that develop following different potential steps.

The cathodic induction period shown in Figure 8 is the most interesting behavior we observed. The induction time is longer (by orders of magnitude) than the diffusion times for either molecular or ionic species present in solution at 1–100 mM concentration, so that mass transport of any species other than impurities cannot be a factor in the induction period. Referring to Figure 1, the cathodic potential step in Figure 8 is from a potential where the coverage by "Pt oxide" is high (and the surface is in a deactivated state) to a potential where oxide reduction occurs. Reduction of oxide appears to produce a momentary active state, i.e., a single oscillation, followed by a long (ca. 1 min) induction period in the active state before sustained oscillations begin. On the other hand, anodic potential steps from near 0 V have much smaller induction periods, e.g., the step from –0.1 V has an induction period approximately equal to t_I.

Effect of Adsorbing Anions. To develop a better understanding of the nature of oscillations, the influence of chloride and sulfuric acid anions was investigated. A complete discussion of the effect of the anions on the oxidation of formic acid on platinum single-crystal surfaces will be presented elsewhere. Here we are focusing on the effect of Cl^- and (bi)sulfate anions on the shape of cyclic voltammetric curves in the potential region within which current oscillations were recorded.

The role of (bi)sulfate anions is easily observed by simply comparing the potentiodynamic curves for formic acid (25 mM) oxidation in perchloric acid without (Figure 3) and with sulfuric acid anions (Figures 9 and 10). No changes were observed for sulfate concentrations up to approximately 1×10^{-4} M, whereas increasing the (bi)sulfate concentration to 5×10^{-4} M resulted in a shifted onset potential for formic acid oxidation. In addition, the number of sharp current spikes in the positive sweep decreases with increasing (bi)sulfate concentration and in the 5×10^{-3} M solution the oscillatory behavior disappears, Figure 10a. Upon the sweep reversal at 0.7 V, oscillations still occur in the negative sweep, even for 5×10^{-3} M concentrations of sulfuric acid anions, shown in Figures 9 and 10. Similar potentiodynamic behavior was also observed in 5×10^{-2} M H_2SO_4 containing 50 mM formic acid. The Q_A, Q_I, t_A, and t_I of the oscillations appeared to depend on the relative concentrations of (bi)sulfate anions and formic acid (summarized in Figure 11), indicating that oscillations are controlled in part by the potential dependence of (bi)sulfate adsorption. The amplitude and the period of oscillations greatly increase with increasing sulfuric acid concentration. It is interesting that with increasing the concentration of (bi)sulfate anions both Q_A and t_A decrease, which is opposite of the effect of formic acid concentration, (Figure 5). This behavior suggests there is competitive adsorption between sulfuric acid anions and formic acid molecules for the bare (oxide-free) Pt surface. Although the presence of sulfuric acid anions on the surface may reduce the coverage by self-poisoning intermediates, the period

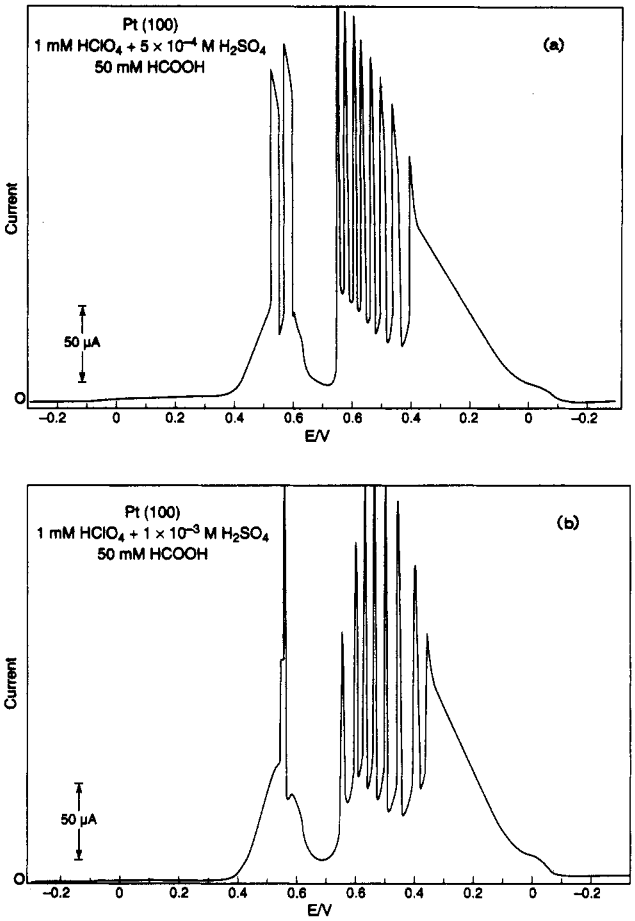


Figure 9. Potentiodynamic curves for 1 mM $HClO_4$ +50 mM HCOOH with the addition of H_2SO_4; 10 mV s^{-1}. Sweep reversed at 0.7 V.

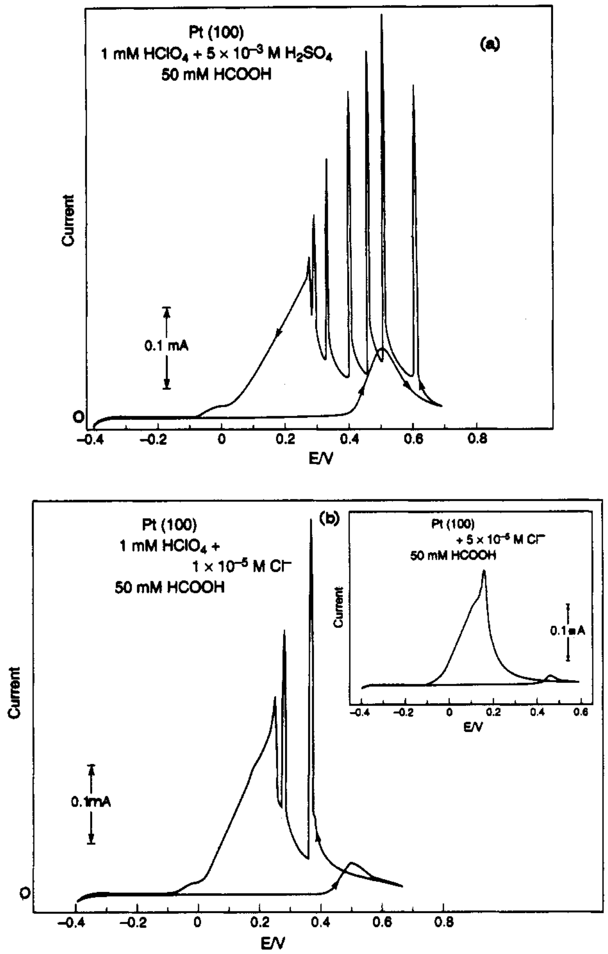
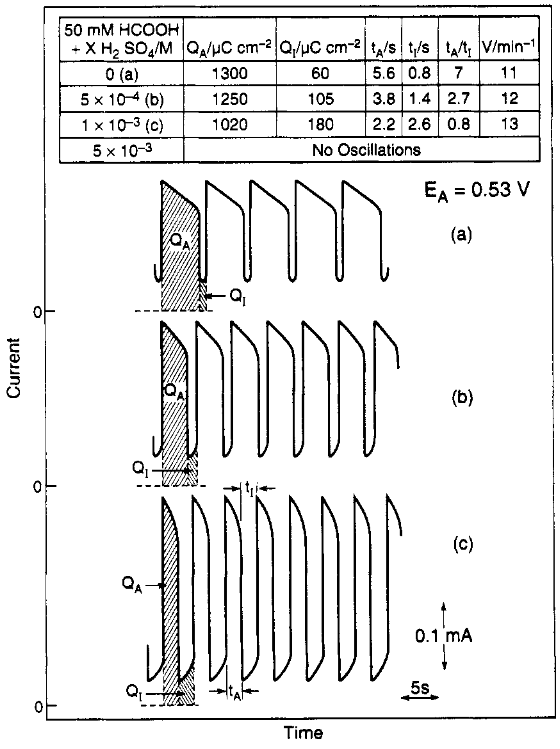


Figure 10. Potentiodynamic curves in 1 mM $HClO_4$ +50 mM HCOOH with the addition of (a) H_2SO_4 and (b) HCl; 10 mV s^{-1}.



50 mM HCOOH + X H_2SO_4/M	Q_A/µC cm^{-2}	Q_I/µC cm^{-2}	t_A/s	t_I/s	t_A/t_I	V/min^{-1}
0 (a)	1300	60	5.6	0.8	7	11
5 × 10^{-4} (b)	1250	105	3.8	1.4	2.7	12
1 × 10^{-3} (c)	1020	180	2.2	2.6	0.8	13
5 × 10^{-3}	No Oscillations					

Figure 11. Summary of waveforms of potentiostatic transients in 1 mM $HClO_4$ +50 mM HCOOH with addition of H_2SO_4 to different concentrations.

of time in which the system remains in an inactive quasi stationary state, t_I, and corresponding charge, Q_I, increases with an increasing concentration of anions, implying that anion adsorption plays a role in the deactivation cycle of the oscillation.

The effects of chloride on formic acid oxidation were qualitatively similar, but 3 orders of magnitude lower concentrations sufficed to produce changes as observed in the case of (bi)sulfate anions. The shape of voltammograms in Figure 10b indicates that in the presence of 1 × 10^{-5} and 5 × 10^{-5} M Cl^- (insert Figure 10b) the oxidation of formic acid is strongly inhibited. In the presence of 1 × 10^{-5} M of HCl oscillatory-like behavior is developed only in the positive sweep direction. In the solution containing 5 × 10^{-5} M Cl^- the characteristic current spikes disappeared completely; the voltammogram is almost the same as the ones published in the literature for the oxidation at a comparable formic acid concentration but in 0.1 M $HClO_4$,[11,16] which did not have any Cl^- added intentionally. Thus, our results indicate that the shape of the formic acid oxidation wave and the presence or absence of oscillations on Pt(100) in previous work may have been determined by the levels of Cl^- present in perchloric acid as an impurity.

Other Variables. Other variables besides the four discussed above (formic acid concentration, electrode potential and potential history, and the anion in the supporting electrolyte) were examined in lesser detail, in part because they were the focus of previous work by Raspel et al. and because some were found not to be a factor in oscillatory behavior. As reported by Raspel et al., we found that surface structure is an important variable, we could not produce oscillatory behavior on a Pt(111) crystal even at other conditions of formic acid concentration and solution pH. However, contrary to their findings, we did not find that pH is an important variable, as similar oscillatory behavior was observed with solutions having both higher (pH = 4) and lower pH (pH = 2) than the results shown in Figures 1–4, nor did we find that stirring is an important variable, i.e, mass transport of the majority species is not controlling the oscillations. All the important variables in the oscillatory behavior point to surface chemistry as the controlling phenomenon.

Discussion

The experimental results we have reported in the previous sections demonstrate clearly that current oscillations in the oxidation of formic acid are a complex process strongly affected by a number of variables: the bulk concentration of formic acid, the surface structure of the Pt electrode, the potential history and the bulk concentration of (bi)sulfate and chloride anions in the supporting electrolyte. Thus, the current oscillations in this reaction are certainly more complex than was thought earlier, particularly in regards to the number of variables contributing to the periodic behavior. The absence of a stirring or pH dependence in the oscillatory behavior points to a surface process or combination of surface processes as the principal phenomena causing current oscillations. We will not attempt to present a "model" for the oscillations, nor do we claim to understand the processes in a detailed way. Rather, what we present here is a discussion of possible surface processes that might be involved, and how these might be coupled to produce most of the observed behavior.

Reaction Pathway and Adsorbed Species. A consensus now appears to exist that the oxidation of formic acid on platinum proceeds via the dual path mechanism, as was proposed by Capon and Parsons.[21] Ignoring details, we might envisage the following simplified mechanism: the initial adsorption of formic acid is followed by formation of COOH species:

$$HCOOH \rightarrow \mathcal{C}OOH + H^+ + e^- \qquad (1)$$

Adsorbed formate is either oxidized to CO_2:

$$\mathcal{C}OOH \rightarrow CO_2 + H^+ + e^- \qquad (2)$$

or undergoes further surface reaction to form strongly adsorbed intermediates, such as $\mathcal{C}O$:

$$\mathcal{C}OOH \rightarrow \mathcal{C}O + \mathcal{O}H \qquad (3a)$$

$$2\mathcal{C}OOH \rightarrow \mathcal{C}O + CO_2 + H_2O \qquad (3b)$$

There has long been a controversy over the nature of poisoning species (i.e., strongly adsorbed intermediates) which form during the electrochemical oxidation of formic acid on platinum. It has been suggested that the blocking species are either $\mathcal{C}O$[16] or intermediates containing both hydrogen and oxygen bonds, e.g., $\mathcal{C}OH$[17] and $H\mathcal{C}O$.[18] To simplify the discussion in the present work, $\mathcal{C}O$ will be considered as the only strongly bound intermediate. Electrooxidative removal of adsorbed CO is presumed to occur through a surface reaction with adsorbed hydroxyl species derived from the dissociation of water:

$$H_2O \rightarrow \mathcal{O}H + H^+ + e^- \qquad (4)$$

$$\mathcal{O}H + \mathcal{C}O \rightarrow CO_2 + H^+ + e^- \qquad (5)$$

For high surface converage with $\mathcal{C}O$, reaction 5 on Pt(100) is autocatalytic,[22] i.e., the rate increases as the reaction proceeds. For electrochemical reactions, antocatalytic behavior is manifested by current peaks in voltammetry that are extremely sharp, e.g., <15 mV in fwhm, and CO oxidation on Pt(100) is a classic example of this behavior. Water dissociation on Pt leading to the formation of adsorbed hydroxyl and other oxygenated species is an extremely complicated reaction and is still only qualitatively understood in spite of extensive research. The current state of understanding is discussed in a recent review,[23] and for the purposes of our discussion here, we will paraphrase portions of this review that relate to the surface processes of interest here.

In dilute perchloric acid solution, the dissociation of water begins at ca. 0.4 V (vs our reference electrode), corresponding to the anodic current wave which appears at this potential in Figure 1, and the dissociation produces adsorbed oxygenated species whose molecular configuration changes as a function of potential. The exact molecular configuration at different potentials is still a matter of debate, but we prefer the Conway interpretation,[23] which is consistent with other work from this laboratory specifically on Pt(100).[24] The species which forms at the lowest potential is also the most facile, i.e., the adsorption is quasi-reversible, of the oxygenated species and thus is probably the one involved in surface reactions with organic fragments, like $\mathcal{C}O$. The molecular identity of this species is most probably $\mathcal{O}H$. As the coverage by $\mathcal{O}H$ increases with potential there is a change in the chemistry of the $\mathcal{O}H$, probably due both to intermolecular interaction at high coverage and to place exchange, the latter causing a rearrangement of Pt surface atoms, and the creation of a true "oxide" state of Pt, which one can define as a change in the formal valence of Pt surface atoms to at least +1 or +2. It is our view that only the quasi-reversible $\mathcal{O}H$ species are active in organic reactions, and at higher coverages (and potentials) the Pt surface becomes covered with inactive ("spectator") oxygenated species that most probably is the oxide state of Pt. Thus, water dissociation produces both reactive and unreactive surface species, just as formic acid dissociation does, and we suggest that oscillatory behavior is the consequence of oscillating between two surface states having different combinations of these species.

A further complication to interpreting the oscillations in terms of known surface processes is the possibility that the processes are probably strongly coupled, and that studying one in isolation of the other(s) is not meaningful. The most immediate example of this is the formation of various oxygenated species from the dissociation of water (eq 4). In the foregoing we have cited conclusions from detailed studies of this process in highly purified electrolyte, but it is not necessarily the case that the details of the process proceed in the same way, or in the same potential region, when organic molecules like formic acid or its dissociation products are present.

Local Change of pH. In the paper by Raspel et al.[10] it was proposed that the local change of pH, which occurs due to a synchronized change in the proton concentration in the vicinity of the electrode, can control the formation of $\mathcal{O}H$ (eq 4), which in turn controls formation and removal of poisoning species (reactions 1, 2, and 5). The extinction of the oscillations by stirring was an important observation supporting the pH hypothesis, i.e., more rapid diffusion of protons to the surface prevents oscillation in pH at the electrode surface, as was the effect of changing the acid concentration. According to these authors only two conditions are necessary to produce current oscillations during the oxidation of formic acid: (a) a Pt single crystal with the (100) orientation and (b) a solution pH of >2.[10] Our results, however, show that these conditions are neither necessary nor sufficient conditions to produce oscillations. We observed even sustained oscillations at pH = 1, and no stirring dependence in the absence added species like HCl or H_2SO_4. We would attribute the stirring effect of Raspel et al.[10] to a chloride impurity in their perchloric acid. The voltammetry of a Pt(100) surface in 1 mM $HClO_4$ (pH > 2) shows clearly that under potentiodynamic conditions in the presence of a small concentration of Cl^- (5×10^{-5} M, insert in Figure 10b) oscillations are not developed. At lower levels of added Cl^-, e.g., 5×10^{-6} M, oscillations were observed in stagnant solution but were extinguished upon stirring. Therefore, we have concluded that fluctuations in local pH are not a primary factor in producing current oscillations.

Pt(100) Reconstruction. The observation that the oscillations do not occur at all on the (111) surface immediately sugests that the reconstruction of the Pt(100) surface may play an important role here as it does in oscillations in the rate of gas-phase oxidation of CO. The latter has been studied in great detail and is now understood.[25,26] Briefly summarizing the mechanism for the purposes of our discussion here, the origin of the gas-phase oscillation lies in two highly structure dependent surface processes. The rate of dissociative chemisorption of oxygen on Pt(100) differs by orders of magnitude between the two structures, being much lower on the reconstructed surface; CO chemisorption to a coverage above ca. 0.2 ML lifts the reconstruction, while nearly a monolayer of oxygen is needed to lift the reconstruction. At a certain set of conditions of temperature, pressure and CO/O_2 ratio, the system oscillates between the active state, having an unreconstructed surface with a high coverage of dissociated oxygen, and an inactive state, having a reconstructed surface with some chemisorbed CO and no surface oxygen. The system is driven between the two states by the oscillating coverage of *C*O, which accumulates on the surface in the inactive state and is "cleansed" from the surface in the active state. Equivalent processes in solution during formic acid electrooxidation seem possible if Pt(100) is reconstructed in electrolyte in the potential region where the oscillations occur. It is now well-established that there are regions of electrode potential where the Au(100) surface is reconstructed in both acidic and basic solution.[28,29] The reconstructions on Au(100) and Pt(100) are very similar in structure,[30] and the differences in total surface energy between the reconstructed and unreconstructed surfaces is very similar in both metals. It is reasonable to suppose that the Pt(100) may be reconstructed in the same potential region as for the Au(100), and perhaps even at somewhat more positive potentials, since the work function of Pt(100) is slightly higher than that of Au(100). If that supposition were correct, then in 10 mM $HClO_4$, in the absence of formic acid or any other species in the electrolyte, the reconstruction would be stable up to at least 0.8 V (nhe),[31] or ca. 0.6 V vs the reference electrode used here, which is in the potential region of the oscillations. Thus, an oscillation driven by surface transformations similar to those which occur in the gas-phase oxidation of CO seem possible, but so little is actually known about such transformations on Pt(100) in electrolyte that it would be pure speculation to attempt to formulate a "model" based on these transformations at this point in time. Also, based on the dynamics of the reconstruction for Au(100) in electrolyte,[28,29] it would seem that these structural changes are too slow to account for the sharp changes in activity observed.

Oscillating Surface Coverages. An alternative to the surface transformation hypothesis above is to consider that the oscillation is still between two different states having very different distributions of surface coverage by active and inactive intermediates but that some other process initiates the change between the two states. The relation between the charge passed in the active (Q_A) and inactive (Q_I) states and the variables of potential and formic acid concentration give an indication of what those processes might be.

As shown by the charges tabulated in Figures 5–7, in most cases the charge passed in the active state is much more than the charge to oxidize a monolayer of *C*O or any other fragment from formic acid dissociation, meaning that in the active state there are several "turnovers"[32] of surface species and the consumption of formic acid from bulk solution in these periods. The detailed shape of the current–time curve in these active periods indicates that the reaction turns on suddenly, slowly decays from the most active state, and then suddenly is deactivated. In most cases, the system is in the inactive state about as long as it is in the active state, but with some instances where the active state is as much as 10 times longer. These observations suggest to us that the surface coverages are constantly changing, i.e., truly periodic, but the surface reactions have a highly nonlinear dependence on the coverages and/or the rate-determining reaction may switch depending on the coverages. In this "model" the active and inactive states are not quasi-steady states but are phases of the periodic oscillation in coverage when the reaction has a nearly zero-order dependence on the coverage of one or more species. Albahadily and Schell[9b] derived a mathematical model for essentially the same physical processes discussed above and applied it to explain potential oscillations under galvanostatic conditions of formic acid oxidation on polycrystalline Pt. We have not tried to write a system of kinetic rate expressions and produce a mathematical model that can be exercised to see if it fits the observed behavior. We feel that such an endeavor is premature at this stage and that the mathematical model is likely to have so many adjustable parameters that it would not provide any physical insight about the surface processes producing the observed behavior.

The oscillations at 100 mM formic acid, Figures 4 and 5c, appear to have both a qualitatively and quantitatively different character than the others. In this case, the charge during the active state is close to that for oxidation of a monolayer of *C*O, and the system is in the inactive state 10 times longer than in the active state. The most readily available explanation for this particular behavior is a relatively simple two-cycle model, where autocatalytic oxidation of adsorbed *C*O occurs in the active state, followed by adsorption of formic acid and reformation of adsorbed *C*O in the inactive state. In this case, consumption of formic acid from the bulk occurs in the inactive state, the exact opposite of what we propose occurs in the other types of oscillations. However, it is difficult to explain why the autocatalytic oxidation of adsorbed CO suddenly begins while the system is being held at constant potential. We can only speculate that during formic acid adsorption, there is a slow change in the coverage *and reactivity* of the oxygenated species on the surface. Since some *O*H species can be generated chemically during formic acid adsorption (reaction 3a), in addition to the electrochemical formation of *O*H (reaction 4) that is relatively fast compared to t_I,[23] possibly there is an accumulation of *O*H species during t_I that act as spectators up to some coverage (either total coverage by all species or some combination of all species present) where there is a surface phase transition that results in a reactive state of *O*H. Such a surface chemistry implies very large configurational entropies (and thus anomalous preexponential terms in the rate constant) are involved in these surface reactions, which is, in fact, a characteristic of many oscillating catalytic reactions.[19]

If the (100) reconstruction, which is unique to that face of Pt and not to (111) or (110), is not a factor in the oscillation, why then are there no oscillations on other surface structures of Pt. This question cannot be dealt with easily, nor without a great deal of speculation, given the state of knowledge of the details of the reaction. In terms of the kinds of processes just discussed, we can suggest a role that surface structure might play via the structural dependence of these processes. The crystallographic effect might be understood in terms of differences in the mobility, reactivity, and coverage of the adsorbed intermediates on the different crystals faces of Pt. Unfortunately, we do not know that much about these intermediate states at this level (molecular) of detail. Very little is known about variations with crystal face in *O*H and related oxygenated species at the molecular level. Some details are known about *C*O. Recent in situ infrared spectroscopy data[15] does show significant differences in the details of the bonding of *C*O on the different crystal faces of Pt. On Pt(100), IR bands for linearly bonded (CO_l) and bridge-bonded (CO_b) carbon monoxide have comparable intensity, while on (110) the band for CO_2 is much more intense, and on (111) the band for CO_b is more intense. The steady-state activity of the (111) surface formic acid surface (at all potentials) is much higher than that of the (110) surface. In fact, at a given electrode potential and formic acid concentration, the activity of the (100) surface in the active state is comparable to the activity of the (111) surface, and in the inactive state is comparable to the activity of the (110) surface. On the basis of just this observation, it would appear that bridge-bonded *CO* is the more reactive species, and that linearly bonded *CO* is more the spectator (and site-blocking) molecule. On Pt(100) in UHV, the relative ratio of CO_l to CO_b is a strong function of coverage, and a comparable change occurs in solution as a function of coverage and potential.[33] Interconversion between these two states with changing total coverage on the (100) surface could be a factor in the oscillations.

Conclusions

We have shown that formic acid oxidation develops well-defined periodic (not chaotic) current oscillations on a stationary Pt(100) electrode under both potentiodynamic and potentiostatic conditions. The oscillatory behavior is unique to the (100) crystal plane of Pt and is not seen on the other two low-index faces. The periodicity, the amplitude, and the absolute magnitude the current oscillations depends on at least three variables, electrode potential and potential history, formic acid concentration, and the anion of the supporting electrolyte. The pH of the electrolyte was not found to be an important variable, nor was mass transport, e.g., rotation or stirring. The behavior is extremely complex and difficult to analyze in terms of known electrode processes.

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