J. Phys. Chem. A **1998,** *102,* 7343−7352

Chaotic and Periodic Potential Oscillations in Formaldehyde Oxidation

Hiroshi Okamoto,* Naoki Tanaka, and Masayoshi Naito

Advanced Research Laboratory, Hitachi, Ltd., Hatoyama, Saitama 350-0395, Japan

Received: February 25, 1998; In Final Form: June 5, 1998

The appearance of chaos and windows of periodic oscillations in the galvanostatic oxidation of formaldehyde on platinum at 43 °C is studied using various applied currents and formaldehyde concentrations. Potential oscillation patterns change with time in such a way that, after a period-doubling cascade, a sequence of periodic oscillations interposed between chaotic states appears. The sequence of periodic oscillations occurs in two ways, that is, in descending and ascending orders of their periods. The descending-order sequence is observed at comparatively low formaldehyde concentrations (0.003−10 mol dm^{-3}), and the ascending one is observed at comparatively high concentrations (0.3−18 mol dm^{-3}). At formaldehyde concentrations between 0.3 and 10 mol dm^{-3}, the ascending-order sequence always appears at higher currents than the descending one. We plot bifurcation diagrams for these two order sequences where one axis is time, which is related to surface states. The next-minimum return map for chaotic oscillations shows a tendency to become more nonuniform with time, which tendency is confirmed by calculating the variance in local Lyapunov exponents. Current oscillation is related to the potential oscillation. Negative resistance hidden in an ordinary cyclic voltammogram is found when the potential sequence before oscillation occurs (an induction period) is simulated. The species responsible for the negative resistance is thought to be adsorbed water adjacent to adsorbed carbon monoxide.

Introduction

Chemical oscillations are intriguing phenomena, probably because we associate them with rhythms in ourselves, and for both practical and scientific reasons it is important that we know how and why they appear. This is because they are expected to be useful in producing power efficiently,[1] and because they are representative of phenomena shown in nonequilibrium open systems such as living bodies. The most famous chemical oscillation is the Belousov−Zhabotinsky reaction,[2,3] but electrochemical oscillations have a long history dating back to 1828.[4] And although there are various types of electrochemical oscillations,[5−7] we have been concerned with the potential oscillations in the galvanostatic electrochemical oxidation of formic acid and formaldehyde,[8−12] because this oxidation itself seems simple and has been studied extensively.

The periodic potential oscillation behavior in the oxidation of formic acid and formaldehyde has been studied by many researchers.[13−21] Various experimental techniques other than the electrochemical one have also been used, such as differential electrochemical mass spectroscopy (DEMS),[15] methods using an electrochemical quartz crystal microbalance (EQCM),[17,18,21] and probe beam deflection.[19] Single crystals have also been used to study the dependence of oscillation appearance on the crystal face direction,[22−26] although to our knowledge only current oscillations have been observed on single crystals. With regard to chaotic potential oscillations in the reaction, on the other hand, very few papers have been published,[10,12,27] since Schell et al. found these oscillations in 1989.[28] Although the chaotic behavior under a periodical constraint has also been found in the oxidation of methanol,[29−31] ethanol,[29,32] ethylene glycol,[33] and glycerol,[34] we focus here on the spontaneous chaotic oscillation in the oxidation of formaldehyde.

Electrochemical oscillations provide high-quality data because the data come from a reaction field itself (i.e., an electrode surface). And it is said[35,36] that chaotic behavior provides much more information than periodic behavior does, if it is properly analyzed. We previously found[12] that the appearance of oscillation in formaldehyde oxidation changed with time, and we thought this change was due to the change in surface adsorption states. In the present paper we report the results of a systematic measurement of the change in chaotic and periodic oscillations at a fixed temperature (43 °C).

To gain further insight into the oscillation mechanism, we also paid special attention to a negative resistance when we evaluated cyclic voltammograms. Although the negative resistance, which is thought to be critical to the oscillation, is hidden in the ordinary cyclic voltammograms, we were able to observe it without the aid of complex impedance analysis.[37]

Experimental Section

We measured current and potential with a conventional three-electrode cell at 43 °C. The reference electrode was a reversible hydrogen electrode (rhe), the counter electrode was a platinum wire, and the working electrode was a Pt net with a purity of 4 N (99.99%). Its true surface area was 2.6 cm^2. The working electrode was pretreated as follows: we heated it in a hydrogen flame for several seconds, immediately immersed it in an electrolytic solution, and then cleaned it by repeatedly applying a triangular potential sweep between 0.05 and 1.4 V at a rate of 0.1 V s^{-1}.

The supporting electrolytic solution was 0.5 mol dm^{-3} sulfuric acid prepared from Millipore “Milli Q” water and Cica-Merck “Ultrapur” sulfuric acid, and the formaldehyde solution was prepared by dissolving paraformaldehyde (Merck “extra pure”) in the supporting electrolytic solution at about 70 °C for several minutes. To deoxygenate the electrolytic solution, we bubbled nitrogen gas (Nippon Sanso, 6 N) through the solution before

S1089-5639(98)01292-4 CCC: $15.00

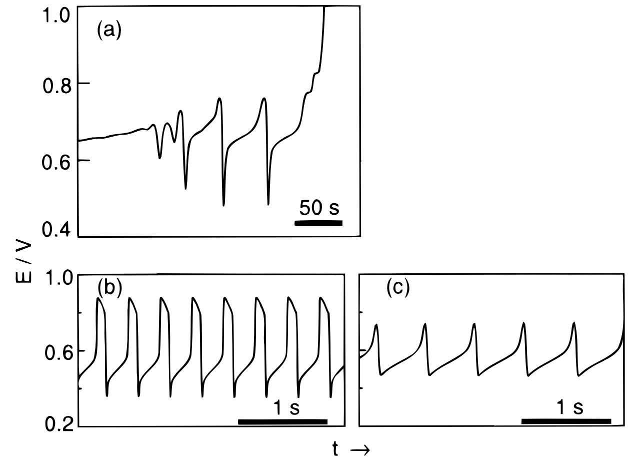

Figure 1. Periodic potential oscillation patterns in the oxidation of (a) 3 mmol dm^{-3} and (b) and (c) 0.1 mol dm^{-3} of formaldehyde. Here *E* is the electrode potential vs rhe. The applied currents are (a) 0.15 mA, (b) 10 mA, and (c) 3 mA.

the measurement, and to keep the solution deoxygenated, we flowed nitrogen over the solution during the measurement.

We used a Hokuto Denko potentiostat/galvanostat HB-105 and a Hokuto Denko function generator HA-501G. We acquired the time sequence of potential or current values with a Hewlett-Packard data acquisition/control unit (either 3852A or 75000) while simultaneously recording it with X−T and X−Y recorders. We sampled the data to 5.5 significant figures at a sampling interval of at least 3 ms. The number of sampled data values was usually 10 000 and the number of minimum peaks in the potential oscillation for a return map was between 200 and 500. Other experimental details have been described in previous papers.[8−10,12]

Experimental Results

Alternating Periodic and Chaotic Sequence in Descending Order. When we used a dilute formaldehyde solution (e.g., 3 mmol dm^{-3}), we could observe a galvanostatic potential oscillation like that in Figure 1a. The oscillation had a long oscillation period but a short life, a fact which made it impossible for us to determine if chaos was present or not, because we could not obtain sufficient data to determine if the pattern was chaotic. As shown in Figure 1b and c, when we used a more concentrated solution (0.1 mol dm^{-3}), we observed typical relaxational potential oscillations at high currents, such as 10 and 3 mA.

Upon decreasing the current we had to wait for some time before the oscillation started. As shown in Figure 2a, for example, at 1.2 mA, the induction period was about 20 min and a sinusoidal pattern appeared (a1). Then the amplitude became alternately large and small (a2), a phenomenon called period-doubling (the pattern is called a period-2 pattern). As time passed, the difference between the two amplitudes grew large, although the pattern remained period-2 (a3) until it turned into a period-1 pattern (a4), the original oscillation mode. That is, the period-2 pattern was observed as if it had broken into the period-1 pattern range. As shown in Figure 2b, when the current was low, 1.0 mA, we observed another period-doubling yielding a period-2^2 pattern as if it had broken into the period-2 pattern range.

When the current was further reduced, the potential oscillation showed chaotic and period-3 patterns as if they had broken into the period-2^2 pattern range. That is, after a period-doubling cascade, the oscillation showed chaos, a period-3 pattern, and another chaos, in that order, as shown in Figure 3(a1−c1). Because the period-3 pattern was observed in the middle of chaos, the pattern is called a window in chaos. The latter chaos was then followed by period-2^3 (d1), period-2^2, period-2, and period-1 patterns, that is, a reverse period-doubling cascade was observed. In this run, the current was 0.9 mA and the formaldehyde concentration was 1 mol dm^{-3}.

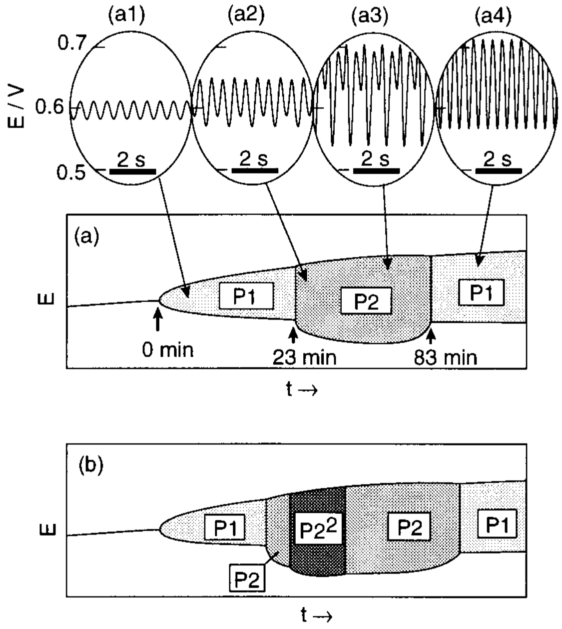

Figure 2. Typical appearance of periodic oscillation patterns at (a) 1. 2 mA and (b) 1.0 mA in the oxidation of 0.1 mol dm^{-3} formaldehyde: (a1, a4) period-1 patterns, (a2, a3) period-2 patterns. Symbols P1, P2, and P2^2, respectively, stand for period-1, period-2, and period-2^2 patterns.

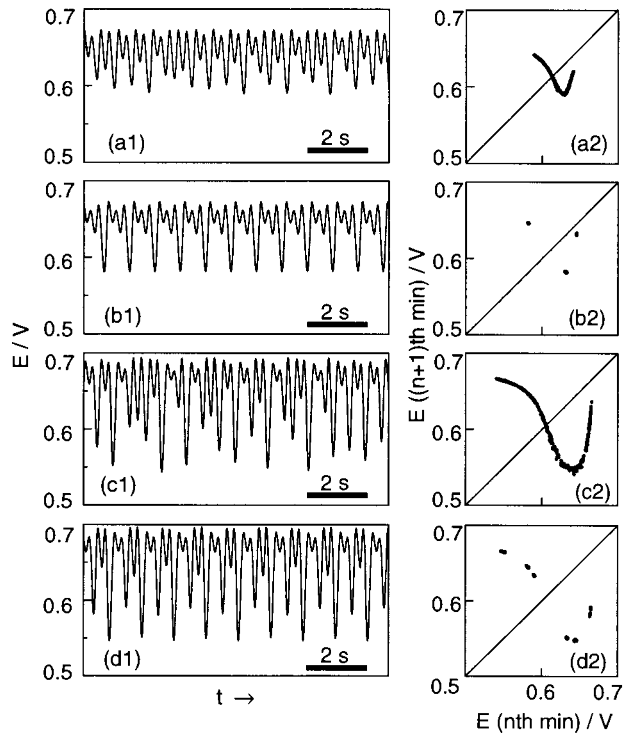

Figure 3. Temporal change in the oscillation patterns and their return maps during the oxidation of 1 mol dm^{-3} of formaldehyde at 0.9 mA: (a1) a chaotic pattern after a period-doubling cascade, (b1) a period-3 pattern, (c1) another chaotic pattern after the period-3 pattern, and (d1) a period-2^3 pattern. a2−d2 are the return maps corresponding to the adjacent oscillation patterns.

The oscillation pattern changed in this way even though the measurement conditions were constant. We can therefore assume that some surface states changed gradually, probably monotonically, during the experiment. We can say that the pattern change is not due to a slow diffusion velocity of formaldehyde compared to the velocity of surface reactions.[12]

As described in a previous paper,[12] the duration of each pattern ranged from a few minutes to several hours and depended on the history of the sample. And the current giving each pattern also varied with a large deviation, about 30% of the average current, from one set of experiments to another. The reproducibility of the oscillation pattern sequence itself was nonetheless good. Schell et al.[28] first reported good reproducibility in the oscillation pattern sequence and a large deviation in current producing bifurcations.

To extract information from the oscillation patterns, we plotted a return map, which is also called the Lorenz map or the one-dimensional Poincaré map. The abscissa in the map is one potential minimum and the ordinate is the next potential minimum. All the return maps corresponding to the oscillation patterns in Figure 3 are alongside the patterns. As expected, the periodic patterns, such as the period-3 and period-2^3 ones, gave discrete groups of dots. For the chaotic patterns, the shape of the return map changed with time from a fairly symmetrical valley to an unsymmetrical one. That is, it became more nonuniform. We will discuss this in the Discussion section.

Upon further decreasing the applied current, we could easily observe periodic oscillations with oscillation periods larger than three. As shown in Figure 4 (a1), when we applied 0.65 mA to the platinum electrode, after a period-doubling cascade, we observed chaotic large-amplitude oscillations among chaotic small-amplitude oscillations, a type of oscillation called mixed-mode oscillation.[38] The fraction of large-amplitude oscillations increased with time until a period-5 pattern was stabilized (b1, c1). Then the period-5 pattern became unstable and another chaotic pattern appeared (d1). We then observed a period-4 × 2 pattern (e1), a period-4 one, another chaotic one, and then a period 3×2^2 one (g). The period 3×2^2 pattern was followed by period-3 × 2 and period-3 patterns in that order (h, i). Incidentally, the highest measured periodicity was period-8, which was observed in a solution of 10 mol dm^{-3}, and small peaks were so small that they were difficult to recognize.

From such a pattern sequence we might conclude that period-*n* patterns ($n = 3, 4, 5, ...$) are interposed between chaotic patterns and appear in decreasing order of *n*. We call this sequence an alternating periodic and chaotic sequence in descending order.[12] We might further conclude that each periodic oscillation with *n* periods is preceded by periodic oscillations with $n \times 2^m$ periods, where $m = ..., 3, 2, 1$ in that order. That is, we have a reverse period-doubling cascade before each periodic oscillation. Both tentative conclusions, however, will be proved to not always be right. This will be shown later in this paper for the former conclusion and in the following paper for the latter conclusion.

Mixed-Mode Oscillation. Figure 4(a2, b2, d2) shows that the return maps for chaotic patterns present before the period-4 pattern scatter around the bottom of the map function. Schell et al. found[38] a similar scattering in the anodic dissolution of copper. Such scattering is caused by a mixture of large-amplitude and small-amplitude chaotic oscillations (i.e., mixed-mode oscillation). A one-dimensional return map, such as those shown here, therefore, cannot adequately represent such mixed-mode oscillation, and we probably need a two-dimensional or higher-dimensional map, which unfortunately cannot be represented on a two-dimensional plane.

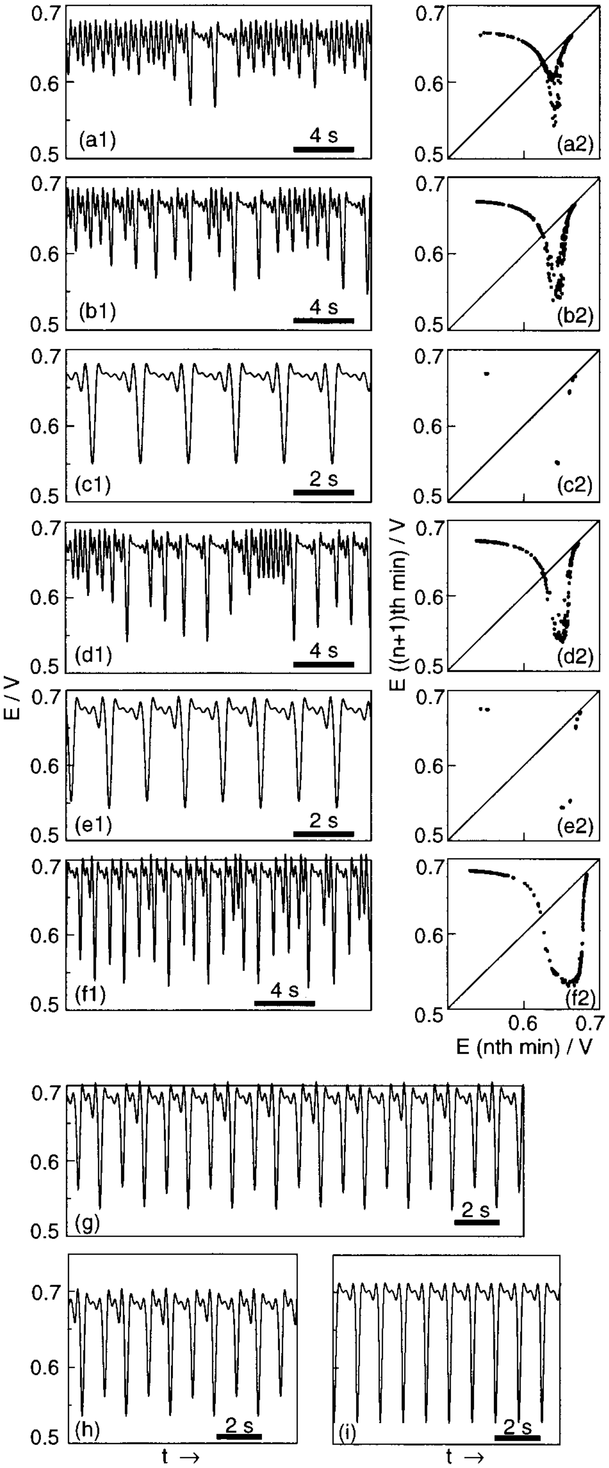

Figure 4. Temporal change in the oscillation patterns and their return maps during the oxidation of 1 mol dm^{-3} of formaldehyde at 0.65 mA: (a1) a chaotic pattern after a period-doubling cascade, (b1) a chaotic pattern just before a period-5 pattern, (c1) the period-5 pattern, (d1) a chaotic pattern between the period-5 and period-4 patterns, (e1) a period-4 × 2 pattern, (f1) a chaotic pattern between the period-4 and period-3 patterns, (g) a period-3×2^2 pattern, (h) a period-3 × 2 pattern, and (i) a period-3 pattern. a2−f2 are the return maps corresponding to the adjacent oscillation patterns.

To see if mixed-mode oscillation always appears before the period-4 pattern, we carried out an experiment at a further reduced current. We observed at 0.5 mA a chaotic pattern with small amplitudes after a period-doubling cascade, the map of

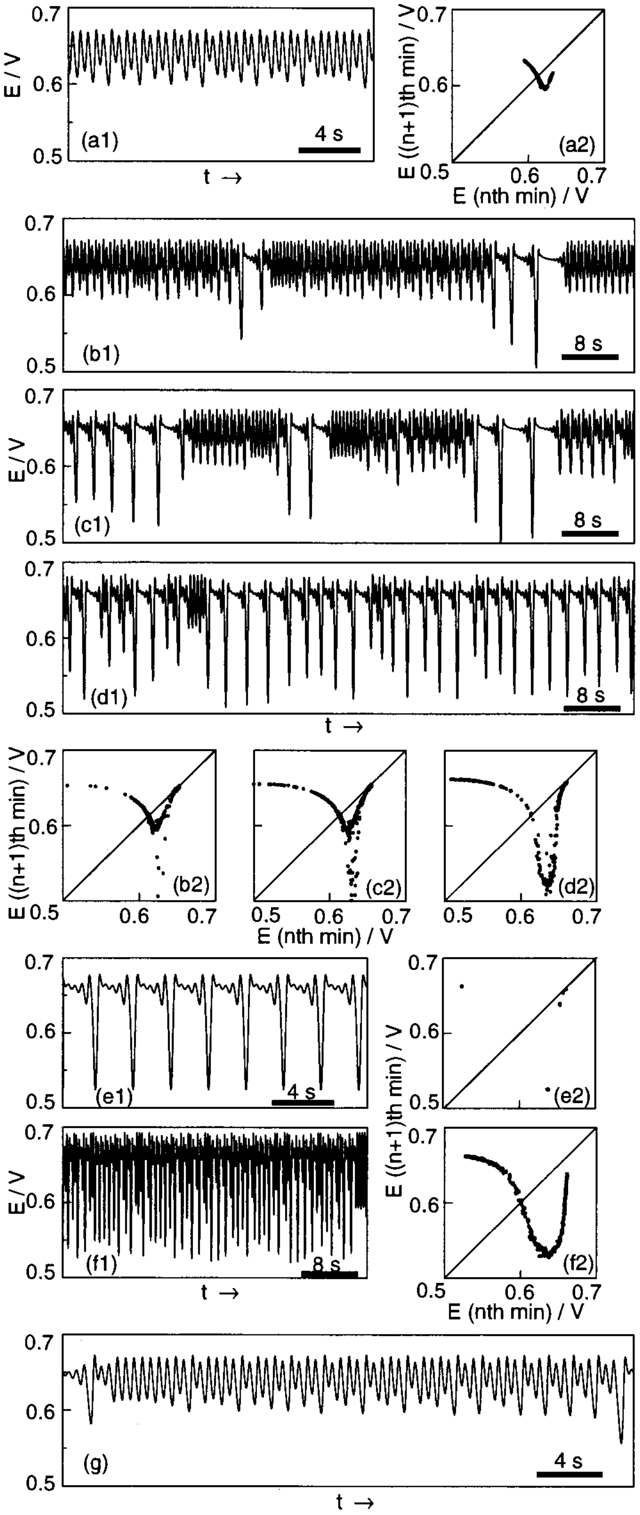

Figure 5. Mixed-mode oscillation patterns in the oxidation of 1 mol dm^{-3} of formaldehyde at 0.5 mA: (a1) a chaotic pattern after a period-doubling cascade, (b1−d1) mixed-mode oscillation patterns observed in that order after a1, (e1) a period-5 pattern, and (f1) a chaotic pattern between the period-5 and period-4 patterns. a2−f2 are the return maps corresponding to oscillation patterns a1−f1. g is an enlarged part of pattern b1.

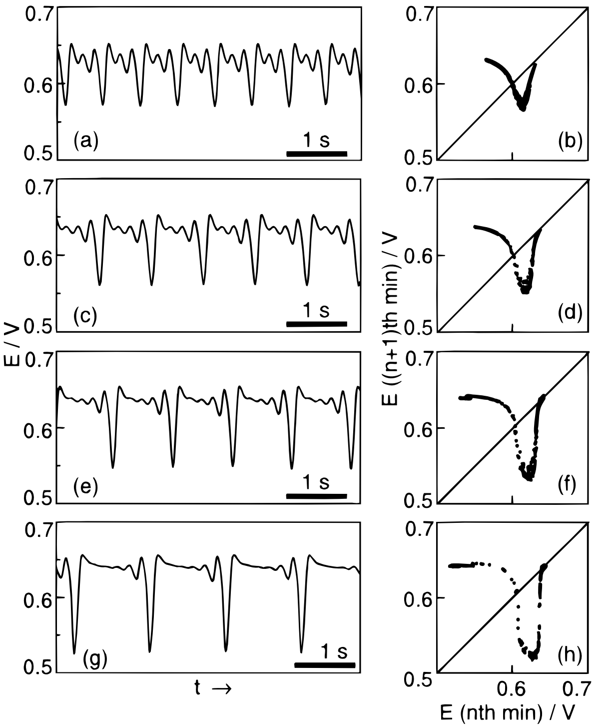

Figure 6. Temporal change in the oscillation patterns and their return maps during the oxidation of 1 mol dm^{-3} of formaldehyde at 1.6 mA: (a) a period-3 pattern, (c) a period-4 pattern, (e) a period-5 pattern, (g) a period-6 pattern, and (b, d, f, h) the return maps for the chaos observed after the periodic oscillations shown on the left side.

which pattern did not scatter, as shown in Figure 5(a1, a2). Then a very small fraction of chaotic oscillations with large amplitudes appeared among chaotic small-amplitude oscillations (b1, g). As in Figure 4, the fraction of large-amplitude oscillations increased with time (b1−d1). The return map began to show scattering when large-amplitude oscillation appeared, and the degree of scattering increased until a large new curve started to appear (b2−d2). Then a period-5 pattern appeared (e1) and was followed by a chaotic pattern (f1), which was not mixed-mode oscillation, and this provided the return map without scattering (f2).

This situation is different from that in Figure 4, in that here mixed-mode oscillation had already disappeared after the period-5 pattern while in Figure 4 it disappeared after the period-4 pattern. Mixed-mode oscillation always appeared after a chaotic pattern with small amplitudes following a period-doubling cascade, except when that chaotic pattern was followed by a period-3 pattern. Consequently, we can say that the presence of mixed-mode oscillation does not depend on the number of periods of nearby periodic oscillations, but it does depend on the amount of current applied.

Alternating Periodic and Chaotic Sequence in Ascending Order. When we used a solution containing 1 mol dm^{-3} formaldehyde, we usually observed chaos at low currents of at most 1.2 mA in an alternating periodic and chaotic sequence in descending order. We sometimes, however, observed chaotic oscillations at a high current, such as 1.6 mA. In this case, as shown in Figure 6, we also observed an alternating periodic and chaotic sequence, but the order of windows appearing was ascending, that is, reversed to that we had seen so far. That is, after a period-doubling cascade and chaos, the potential had period-3, chaotic, period-4, and chaotic patterns, and so on. Although it was difficult to recognize each peak in the small-oscillation part for a period-6 pattern, we could easily determine that the pattern was period-6 because the overall oscillation period increased in steps of one period of the small oscillation.

As shown in Figure 6, the return maps changed for chaotic oscillations in the same way as did those for the descending-order sequence. That is, with time they became more nonuniform. There was, however, no scattering around the bottom of

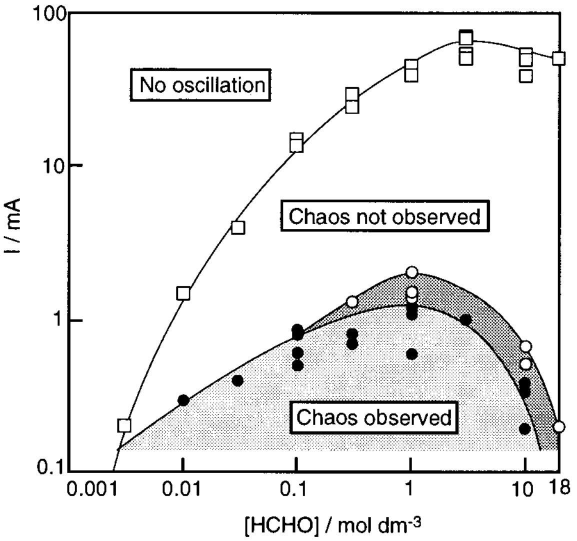

Figure 7. Chaos-yielding region in the plane of formaldehyde concentration and current at 43 °C. Open and closed circles are respectively the maximal currents for the occurrence of chaos in the ascending-order sequence and in the descending-order sequence. Open squares are the maximal currents for the occurrence of periodic oscillation. The dark and light gray zones, respectively, stand for regions of chaos in the ascending-order sequence and in the descending-order sequence. [HCHO] stands for a formaldehyde concentration.

the map function in the return map, probably because we did not observe mixed-mode oscillation in the ascending-order sequence.

We pretreated the platinum electrode and carried out experiments under exactly the same conditions, but we could not control the sequence order. We believe that a subtle difference in the initial surface states determines the sequence order.

We then investigated which of the two order sequences was likely to take place in a wide range of formaldehyde concentrations between 10^{-3} and approximately 18 mol dm^{-3}, the latter being saturated in a solution containing 0.5 mol dm^{-3} sulfuric acid at 43 °C. Figure 7 shows maximal currents for the occurrence of chaos in descending order (closed circles) and those in ascending order (open circles), together with maximal currents for the occurrence of periodic oscillations (open squares). We can see that the descending-order sequence was observed at comparatively low formaldehyde concentrations and the ascending-order sequence was observed at comparatively high concentrations. Both sequences were observed in a formaldehyde concentration range between 0.3 and 10 mol dm^{-3}, and the ascending-order sequence was always observed at higher currents than the descending-order sequence. Here we should note that we only observed one of these sequences in one set of experiments (in 1 day).

When the formaldehyde concentration was low, such as 10^{-3} mol dm^{-3}, we could not even observe oscillation. This is probably because in such a dilute solution the velocities of CO formation and water adsorption (see the Discussion section) are not fast enough to bring about instability. With increasing formaldehyde concentration, the maximal currents for the occurrence of periodic oscillation and chaos increase, reach maxima, and then decrease. For the occurrence of periodic oscillation, the tendency is very similar to that at 3 °C.[9] The formaldehyde concentration that gives a maximum of the maximal currents for chaos (both descending and ascending), 1 mol dm^{-3}, is different from the one that gives a maximum of the maximal current for periodic oscillation, 3 mol dm^{-3}. Here we should note that formaldehyde is virtually completely hydrated to methylene glycol, $CH_2(OH)_2$, because the hydrate-to-carbonyl ratio has been reported[39] to be 2280 at 25 °C, and it is difficult to think that the ratio decreases to about one at 43 °C. In a very concentrated solution such as 18 mol dm^{-3}, a formaldehyde oligomer might be present but we have no experimental information about this.

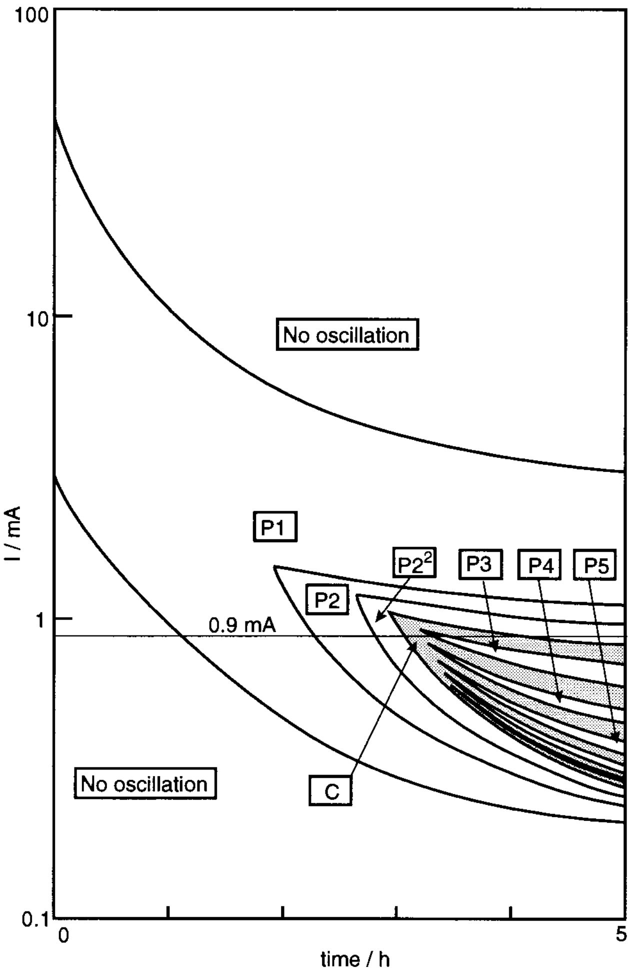

Figure 8. Bifurcation diagram for the descending-order sequence in the oxidation of 1 mol dm^{-3} formaldehyde at 43 °C. The horizontal axis, time, indicates some surface states. The vertical axis is the applied current *I*. The gray zone stands for a chaos region. Symbols P*n* stand for periodic patterns with *n* periods.

Bifurcation Diagram. On the basis of the experimental results, we roughly sketch a typical bifurcation diagram for the descending-order sequence in the oxidation of 1 mol dm^{-3} formaldehyde at 43 °C, as shown in Figure 8. The abscissa, time, indicates some surface adsorption states. We think that the surface adsorption states gradually become less active, because the potential tended to increase during the oscillation.

To sketch the diagram we took into consideration the following five facts. (1) At a high current we could not even observe periodic oscillation due to a slow diffusion velocity compared to the velocity of surface reactions. (2) The lower the current we applied, the longer the induction period became. (3) The alternating periodic and chaotic sequence in descending order appeared between the period-doubling cascade and the reverse period-doubling cascade. (4) The lower the current we applied, the longer the oscillation periods of periodic oscillation we observed. (5) The lower the current we applied, the longer we had to wait to observe an arbitrary definite periodic pattern. The resulting bifurcation diagram shows that in the chaotic region (gray zone) there are windows of periodic oscillations,

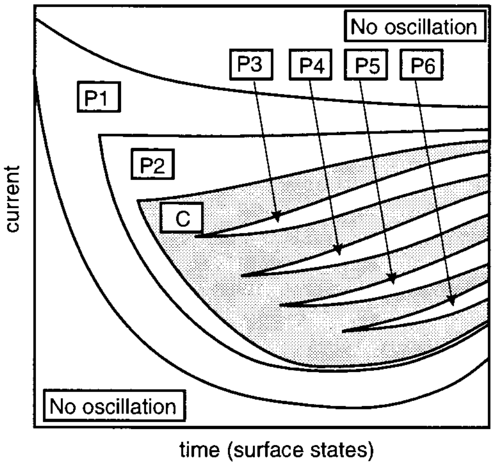

Figure 9. A sketch of bifurcation diagram for the ascending-order sequence. About symbols see legends in Figure 8.

the oscillation periods of which increase in the down direction, and that the boundary curves have negative slopes. Take 0.9 mA for example. We can see that after an induction period there are, in turn, a period-doubling cascade, chaos, a period-3 pattern, chaos again, and a reverse period-doubling cascade.

With the sample which had the ascending-order sequence, we did not observe a return sequence like the ones in Figure 2 at any current. And when the current was very low, the oscillation appearing after a long induction period disappeared in several 10 min. Hence, as shown in Figure 9, to explain the ascending-order sequence the bifurcation diagram should be such that the slopes of almost all the boundaries are positive. Consequently, there must be another factor that influences the slopes of the boundary curves, which factor is believed to be initial surface states, as mentioned before. That is, the bifurcation diagrams shown in Figures 8 and 9 might be section planes of a three- or more-dimensional diagram.

Voltammograms and Current Oscillation. To gain further insight into the oscillation mechanism, we first measured ordinary cyclic voltammograms, CVs. As shown in Figure 10a, in a solution without formaldehyde, the CV did not have any current in the potential region for oscillation, 0.4−0.8 V. This means that in this potential region water does not give a surface OH radical through the following electrochemical reaction:

$$H_2O + * \rightarrow HO* + H^+ + e^- \qquad (1)$$

Here * stands for an adsorption site and HO* is an adsorbed OH radical. This fact does not always mean that water does not chemically adsorb, but on the contrary we think water adsorbs physically to chemically with increasing potential due to the enhancement of interaction with the adsorbed carbon monoxide,[9] as indicated in the Discussion section.

As shown in Figure 10b−d, the CVs obtained from solutions containing formaldehyde had one current peak in the anodic direction, peak II, and another in the cathodic direction, peak IV. This peak numbering is based on the reference.[9] Peak II split into two, and the one at the lower potential did not grow with an increase in the formaldehyde concentration, whereas the one at the higher potential did. Peak IV also split into two and behaved similarly. Peak II consisting of two peaks is widely thought to be formed through surface activation caused by the oxidation of an adsorbed CO and through surface deactivation caused by the adsorption of oxygen species such as OH and O. And Peak IV consisting of two peaks is formed through surface activation due to the reduction or desorption of the oxygen species and through surface deactivation due to the adsorption of CO formed in the reaction

$$HCHO + * \rightarrow OC* + 2H^+ + 2e^- \qquad (2)$$

Here we take into account the infrared spectroscopic result[40] that a nonhydrated form of formaldehyde is involved in the formation of the adsorbed CO.

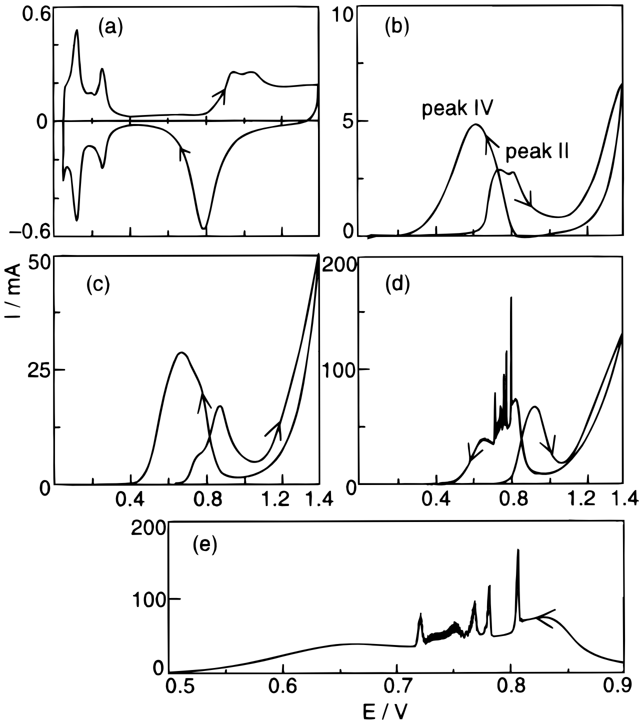

Figure 10. Cyclic voltammograms obtained at a sweep rate of 0.1 V s^{-1} from solutions with formaldehyde concentrations of (a) zero, (b) 0.01 mol dm^{-3}, (c) 0.1 mol dm^{-3}, and (d) 1 mol dm^{-3}. e is a horizontally enlarged version of d.

In a 1 mol dm^{-3} solution, the current in the cathodic sweep oscillated around peak IV, as shown in Figure 10d and e. The current oscillation immediately disappeared when we stopped the potential sweep at any potential during oscillation. Since Koper et al.[20,37] emphasized the importance of ohmic drop (IR drop) in the potentiostatic current oscillations, we connected a 5-Ω resistor in series with the working electrode and measured the CV again. The peak potential of peak II was then shifted by 315 mV, as shown in Figure 11(a1), which shift is very near the current I (peak II) $\times R = 62 \times 5 = 310$ (mV). Although no current oscillation occurred in the anodic sweep (a1), it did occur in the cathodic sweep and more stably than without external resistance (a2). Incidentally the slope of the linear part in Figure 11(a1) is approximately 7 Ω, which indicates the resistance of the solution is approximately 2 Ω.

When the external resistance was large, 20 Ω, current oscillation appeared in the first CV turn in both sweep directions (b1, b2). The number of oscillations, however, decreased with an increase in the number of CV turns (c1, c2). Here we note that the slope of maximal or minimal currents against the potential in Figure 11(b1, b2) is approximately 22 Ω, which indicates the resistance of the solution is approximately 2 Ω, in agreement with the previous value.

We also observed, for a finite duration, potentiostatic current oscillation whose period increased with time, as shown in Figure 12. This oscillation pattern is very similar to the galvanostatic

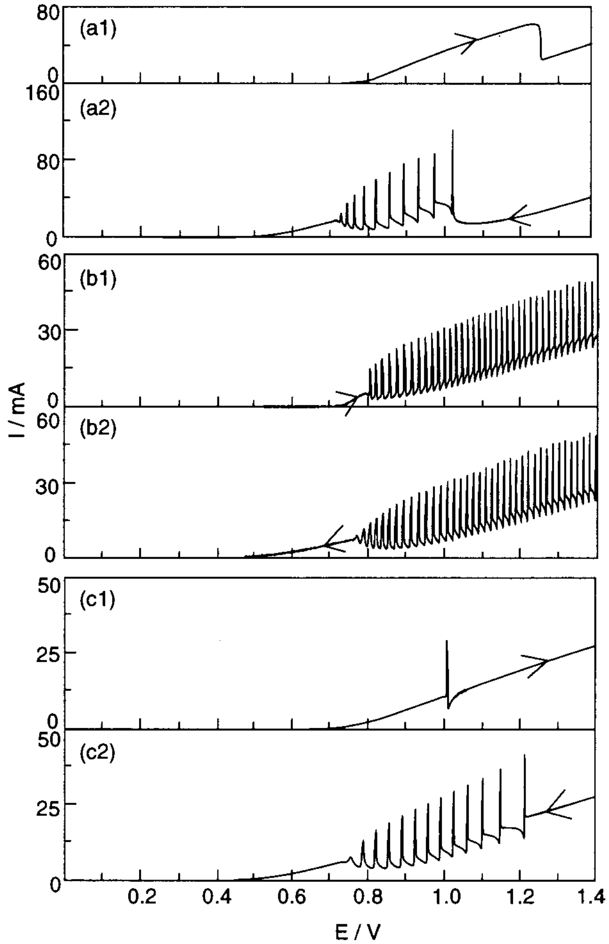

Figure 11. Cyclic voltammograms obtained from a solution of 1 mol dm^{-3} formaldehyde with an external resistance: (a1, a2) 5 Ω, 15th CV turn; (b1, b2) 20 Ω, first CV turn; (c1, c2) 20 Ω, 80th CV turn. a1, b1, and c1 are for the anodic (right direction) sweep; and a2, b2, and c2 are for the cathodic (left direction) sweep.

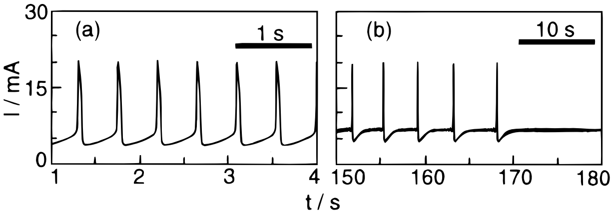

Figure 12. Potentiostatic current oscillation in the oxidation of 1 mol dm^{-3} formaldehyde at 0.86 V with 20 Ω external resistance.

potential oscillation pattern obtained at a high current like 10 or 3 mA (see Figure 1b and c). Because such a potential oscillation in a solution of 1 mol dm^{-3} formaldehyde also lasted only several minutes because of insufficient formaldehyde diffusion, we think this is also the reason for the finite duration of current oscillation. We also think it is the reason for the decrease in the number of current oscillations during CV measurement.

Because current oscillation occurred at high potentials, it may be thought that the mechanism for current oscillation involves some oxygen species[25] or oxide film[20] and is different from the mechanism for potential oscillation. We can, however, show by taking ohmic drop into consideration[25] that this is not the case. Take the current oscillation shown in Figure 12a for example. The ohmic drop at the highest current (approximately 20 mA) is 0.44 V (= 0.02 (A) × 22 (Ω)), and that at the lowest current (approximately 4 mA) is 0.09 V. Because the applied potential is 0.86 V, the real potential difference between the electrode surface and the nearby bulk solution (i.e., across the double layer is calculated to be between 0.42 and 0.77 V, where the potential oscillation occurs. Here we should note that the ohmic drop is negligible during the potential oscillation, because the applied current is of the order of 1 mA and the resistance of the bulk solution is approximately 2 Ω.

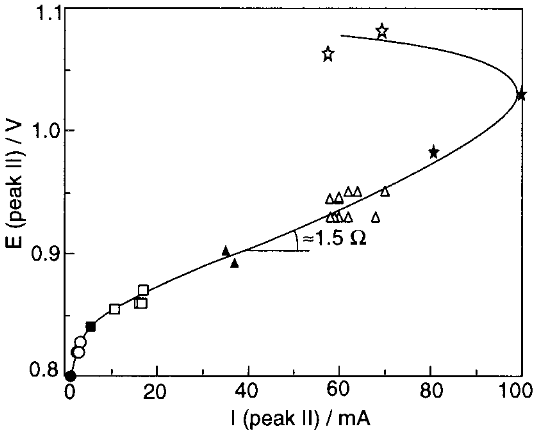

Figure 13. Relation between the current and potential of peak II at various formaldehyde concentrations: (closed circles) 0.003 mol dm^{-3}, (open circles) 0.01 mol dm^{-3}, (closed square) 0.03 mol dm^{-3}, (open squares) 0.1 mol dm^{-3}, (closed triangles) 0.3 mol dm^{-3}, (open triangles) 1 mol dm^{-3}, (closed stars) 3 mol dm^{-3}, (open stars) 10 mol dm^{-3}.

Figure 10 shows that both the current and the potential of peak II increase with increasing formaldehyde concentration. Because neither formaldehyde nor its hydrate is an electrolyte, it influences the resistance of the solution very little as long as its concentration is not so high. Although the solution resistance is almost constant, the IR drop may push the peak potential up because of the increase in the peak current with increasing formaldehyde concentration. We then plotted, for various formaldehyde concentrations, the peak potential against the peak current. Figure 13 shows that in a concentration range between 0.1 and 1 mol dm^{-3} the slope is approximately 1.5 Ω. This value agrees well with the solution resistance indicated previously and is of the order of resistance calculated when using 2 Ω cm specific resistance, obtained from the real part of impedance at 5 kHz obtained at 43 °C in a solution without formaldehyde. Consequently, the increase in peak potential is probably due to the IR drop in the formaldehyde concentration range between 0.1 and 1 mol dm^{-3}.

Observation of Negative Resistance. In studying the mechanism of potential oscillation we have been paying particular attention to the role of negative resistance.[8,9,11] Koper[37,41] also stressed the importance of negative impedance in general electrochemical oscillations. As shown in Figure 10b−d, in the oscillation potential region, 0.4−0.8 V, the CV did not have a negative resistance in the anodic sweep. Because negative resistance is necessary for the occurrence of oscillation, it must be present but hidden.[37,41] The CV itself, however, can have different appearances, depending on sweep velocity and sweep potential range. Consequently if the sweep rate is increased, we may be able to observe negative resistance around 0.6 V, because the low current there is due to the adsorbed CO formed at lower potentials, such as 0.05−0.55 V. We could not, however, observe negative resistance at 43 °C, though we could at 3 °C.[9]

In the present work we therefore tried to duplicate the situation in the induction period and at the beginning of oscillation by producing the potential sequence. This is because

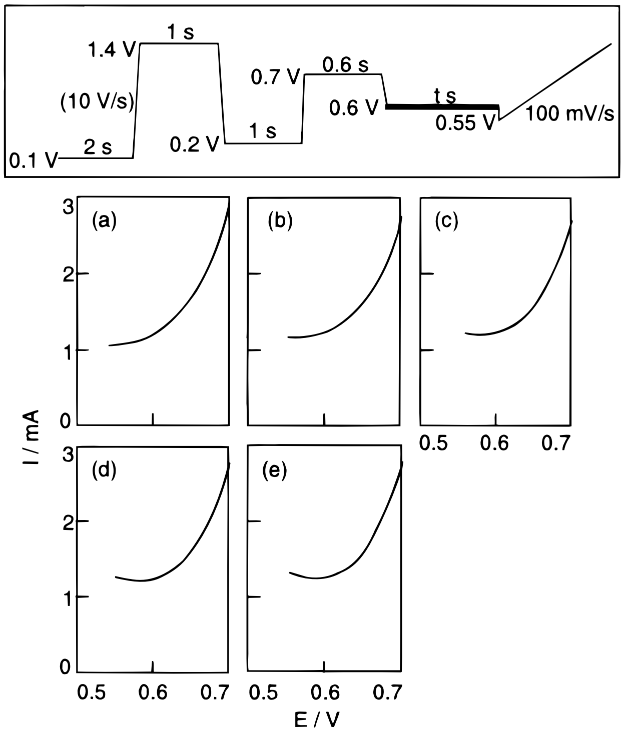

Figure 14. Voltammograms starting at 0.55 V in the anodic direction obtained from a solution of 1 mol dm^{-3} formaldehyde after keeping the potential at 0.6 V for t = (a) 10 s, (b) 20 s, (c) 30 s, (d) 50 s, and (e) 100 s. The top panel is a potential profile.

we wanted to know the relation between the change from the induction period to oscillation and the resistance change from positive to negative. Referring to preliminary experimental results, we controlled the potential as shown in the top panel of Figure 14 and measured the CV (same panel). That is, we first applied 0.1 V for 2 s and 1.4 V for 1 s in order to oxidize and eliminate organic adsorbates, then set the potential at 0.2 V for 1 s in order to adsorb CO, and then changed the potential to 0.7 V in order to remove a little of the adsorbed CO. (We introduced that last step because when we applied a current to observe oscillation, the potential almost always overshot to about 0.7 V.) Then we set the potential at 0.6 V for time t (seconds) to mimic the induction period, and finally we measured the CV from 0.55 V in the anodic direction. Although transient current was observed when the potential changed fast, we could neglect it because the duration of the transient was less than 0.1 s.

As a result, as shown in Figure 14, with an increase in t the CV had a negative resistance near 0.6 V, where potential oscillation began (Figure 2(a1)). That is, the slope was positive near 0.6 V at $t = 10$ s (Figure 14a), where it became almost zero at $t = 30$ s (c), when the potential became unstable at a constant current and was thought to begin to have oscillation with a small amplitude. And the current there, 1.2 mA, was also reasonable for the beginning of small-amplitude oscillations, though the induction period was a little longer (about 20 min). For t longer than 30 s, the slope became negative (d, e). Thus we could observe hidden negative impedance. Here we should note that the CV of course does not have a stationary state but instead reflects a dynamical surface state. We have to have this in mind when studying chemical dynamics. Incidentally, the information from the CV in the cathodic direction has nothing to do with the mechanism of potential oscillation, because the oscillation potential never goes beyond the peak potential of peak II. This means that no poisonous oxygen species nor oxide film is involved in the oscillation.

Discussion

The potential oscillation pattern at a constant applied current changed with time showing an alternating periodic and chaotic sequence in descending or ascending order after a period-doubling cascade. If we take time t as a parameter relating to some surface states, we can sketch a bifurcation diagram such as that shown in Figure 8 and Figure 9. To see if t is an appropriate bifurcation parameter, we compare t with A, a parameter in the logistic difference equation: $x_{n+1} = Ax_n(1 - x_n)$. We do this because the reaction system shows a period-doubling bifurcation and has a continuous and continuously differentiable map with a single extremum, and the most representative model system with these characteristics is the logistic system.

We define $\delta_A(m)$ as $\{A(m + 1) - A(m)\}/\{A(m + 2) - A(m + 1)\}$, where $m = 0, 1, 2, ...$ and $A(m)$ stands for the A at which oscillation begins to show a period-2^m pattern in the logistic difference equation. The value of $\delta_A(0)$, 4.45, is already very near the Feigenbaum constant,[42] $\delta_A(\infty) = 4.669...$, which is universal for the map defined above. Consequently, we expect $\delta_t(0) \cong \delta_t(\infty) = \delta_A(\infty)$ if t is a proper bifurcation parameter, where $\delta_t(m) = \{t(m + 1) - t(m)\}/\{t(m + 2) - t(m + 1)\}$ and $t(m)$ stands for the t at which the oscillation in the reaction begins to show a period-2^m pattern. The measured $\delta_t(0)$ values, however, scattered from 1.5 to 8, and we therefore could not determine whether t was proportional to A and thus an appropriate bifurcation parameter. This result may suggest that t actually subsumes two or more parameters, and this suggestion will be discussed below.

We observed an alternating periodic and chaotic sequence in descending order after a period-doubling cascade at comparatively low formaldehyde concentrations. The sequence order for periodic oscillations is not consistent with the U (Universal)-sequence.[43] That is, a periodicity that changes such as 1, 2, 2^2, ..., 4 × 2, 4, ..., 3 × 2, 3, ..., 2^2, 2, 1 does not fit the U-sequence. This is probably because to produce the U-sequence the map function with the characteristics defined above should have a form,[43] $x_{n+1} = Af(x_n)$, with a single parameter A, like the logistic equation.

For the reaction, on the other hand, the map function changed with time in two ways as shown in Figures 3, 5, and 6, that is, its size grew and its shape became more nonuniform. There seem to be two parameters corresponding to these changes, the first of which corresponds to A. Thus, as suggested above, the parameter t may indeed subsume at least two parameters. Incidentally, the relation between the map function and the oscillation period of periodic oscillations is similar to that shown by Pikovsky[44] for the Belousov−Zhabotinsky reaction, in the sense that the right-side slope in the return map goes far from the diagonal line when the oscillation period in the descending-order sequence decreases.

The period-doubling cascade and the sequence in reverse order, ascending order, however, are consistent with the U-sequence. Because, as shown in Figure 6, the map function for the sequence in this order changed with time in the same ways as those just described, there seem to be at least two parameters. Hence, we think that the consistency with the U-sequence is accidental.

As described several times, the return map for chaos became more nonuniform for both the order sequences. We calculate the degree of nonuniformity of the map using the variance in local Lyapunov exponents. We first divide the range of x-axis value into, say, six equal intervals as shown in Figure 15a. We then divide each interval into five sections, and we average the

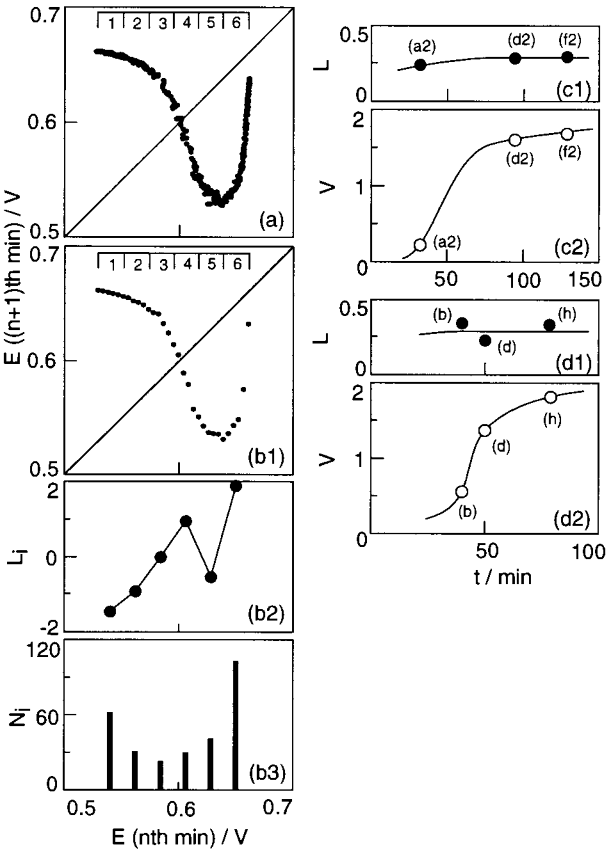

Figure 15. Local Lyapunov exponents and their variance: (a) a return map, same as f2 in Figure 5; (b1) a plot of an averaged E ((n+1)th min) versus a discrete E (nth min) that divides a whole range of E (nth min) values into 30 sections; (b2) local Lyapunov exponents, L_i, for an interval, 1/6 of a whole range of E (nth min) values; (b3) data population, N_i, for the same interval; (c1, c2) temporal changes in the global Lyapunov exponents L and in the variances V of the local Lyapunov exponents for the descending-order sequence (symbols in the figures corresponding to the ones in Figure 5); and (d1, d2) temporal changes in L and V for the ascending-order sequence (symbols in the figures corresponding to the ones in Figure 6).

y-axis values in the vicinity of each of the section boundaries, obtaining an averaged map (b1). We then calculate the local Lyapunov exponent using the averaged map for each interval, L_i, by averaging, over the five sections of each interval, the quantity obtained by multiplying the logarithm of the slope in one section by the data population in the same section. The L_i and the data population for each interval, N_i, are shown in Figure 15(b2, b3). We then calculate the global Lyapunov exponent, L, by averaging L_i using N_i over the six intervals. And last we obtain the variance, V, in the local Lyapunov exponents.

L and V for the descending-order sequence are shown in Figure 15(c1, c2). We see that L changes little with time but that V increases monotonically. This tendency was also found in two other runs. For the sequence in reverse order we obtain a similar tendency (d1, d2). Thus we have confirmed for both the order sequences that the nonuniformity increases monotonically with time. In terms of information theory, as mentioned in a previous paper,[12] the nonuniformity of chaos is related to a noise-induced order,[45] to the spreading of localized information over a whole system,[46] and to the copying of input information.[47] In terms of chemical reaction, however, the meaning of nonuniformity is still obscure.

With regard to the oscillation mechanism, we should bear in mind that the observed current in the voltammogram and the applied current during oscillation are mainly due to what is called a direct reaction path via unknown reactive species. The reactant in this path is thought[20] to be methylene glycol, the hydrated form of formaldehyde. Because this reaction is thought to occur on a Pt adsorption site at any potential, another path to determine the number of adsorption sites is necessary for the occurrence of oscillation. Capon and Parsons[48] first suggested such a dual-path mechanism for formic acid oxidation, and we will discuss the latter reaction path in relation to negative resistance.

The main oscillation potential region was between 0.5 and 0.7 V, where water does not react electrochemically by itself, as shown in Figure 10a. Reaction 1 therefore does not play an important role in oscillation. We could observe negative resistance at approximately 0.6 V and at 1.2 mA, at which potential and current oscillation began to appear as shown in Figure 2(a1). Consequently, it is important to identify the species responsible for the negative resistance. The species inactivate the surface with increasing potential, namely, it is one determiner of the number of adsorption sites near 0.6 V. Candidate species are a sulfate anion, a bisulfate anion, an adsorbed CO radical, and an adsorbed water molecule. Here we regard the adsorbed CO radical as a representative of some carbon-containing adsorbed species such as COH, because the classification of the species is not very helpful at this stage for an understanding of the oscillation mechanism.

Because we could observe similar oscillations in a perchloric acid solution containing formaldehyde, the sulfate or bisulfate anion is not the responsible species. Of course the anions may have influenced oscillation patterns, but we could not clearly determine the difference because our measurement had a large deviation of approximately 30%, as mentioned in the previous section. The velocity for the formation of CO from formic acid is reported to be the greatest at 0.2 V,[8] and we observed a similar tendency for the velocity of CO formation from formaldehyde. Infrared techniques[49] also indicated that the maximal velocity for the formation of a linearly adsorbed CO from formaldehyde was attained near 0.1 V. Consequently, it is difficult to imagine that during oscillation CO formation causes the potential to increase at an increasing speed at about 0.6 V as shown in Figure 1c. Thus we think the most probable candidate is adsorbed water.[9]

In the electric-double-layer potential region, 0.4−0.8 V, water adsorbs on a Pt surface as a water molecule. This does not always mean that water physically adsorbs. At a potential as low as 0.5 V the adsorbed CO interacts with the adsorbed water very slightly, while at a potential as high as 0.8 V the interaction between the two adsorbed species is so strong that they readily react to produce CO_2 through the following reaction:

$$\mathrm{CO^* + H_2O^* \rightarrow CO_2 + 2^* + 2H^+ + 2e^-} \qquad (3)$$

We therefore think that at an intermediate potential the strength of the interaction between the two adsorbed species is somewhere between almost zero and strong enough to make a chemical bond. The interaction results in the adsorbed water having two contrasting characteristics: poisonous and reactive. The adsorbed water is poisonous because it stays on the surface and blocks the adsorption site for a while according to the strength of interaction. In this sense, water adsorbs chemically rather than physically at least in the presence of adsorbed CO because of interaction. Because the interaction strength increases with increasing potential, the severity of the poisonous characteristic also increases with increasing potential. This explains the negative resistance in the voltammogram.

The adsorbed water also becomes more reactive as the potential increases because of the enhancement of the interaction strength. Because an interaction strong enough to make a chemical bond must be stronger than the mere interaction between the two adsorbed species, at a low potential the poisonous characteristic predominates and at a high potential the reactive characteristic predominates. We should note here that the adsorbed water has both characteristics at any potential in the oscillation potential range, and the potential at which either characteristic is predominant depends on the individual reaction conditions. For example, Figure 2(a1) shows potential oscillation between 0.58 and 0.62 V, and these low potentials mean that the reactive characteristic is greater than the poisonous one even at a potential as low as 0.62 V. The reaction between water and carbon monoxide is known as the water-gas shift reaction, and reaction 3 means that we can control the rate of this reaction by adjusting the potential. Reaction 3 on a platinum electrode was first proposed by Gilman[50] and has been reported to be theoretically possible by Shiller and Anderson.[51] Thus we think the adsorbed water is the species responsible for the negative resistance and for the occurrence of oscillation.

Summary

We showed how chaos and windows of periodic oscillations appeared in the galvanostatic oxidation of formaldehyde on Pt at 43 °C under various conditions of applied currents and formaldehyde concentrations. At comparatively low formaldehyde concentrations (0.003−10 mol dm^{-3}), we observed after a period-doubling cascade an alternating periodic and chaotic sequence in descending order, that is, the periodic oscillations interposed between chaotic states appeared in decreasing order of their oscillation period. At comparatively high concentrations (0.3−18 mol dm^{-3}), on the other hand, we observed the sequence in reverse order. We explained that these two order sequences resulted from a difference in the sign of the slopes of curves in the bifurcation diagram where the applied current was plotted as the ordinate and the time as the abscissa. Here we regarded time as a parameter relating to surface states. The period-doubling cascade and descending-order sequence were not consistent with the-U sequence, probably because the parameter time for the reaction subsumes two or more parameters, while the map for the U-sequence has a single parameter.

We observed a temporal change in return maps, which became more nonuniform regardless of the sequence order. We confirmed this change by calculating the variance in local Lyapunov exponents and by showing that it increased monotonically. For mixed-mode oscillation, which is a mixture of chaotic patterns with large and small amplitudes, the one-dimensional return map did not provide a curve but it was partly scattered. The map should have more than one dimension.

By taking ohmic drop into consideration, we related to the potential oscillation a current oscillation observed during the measurement of a cyclic voltammogram (CV) or at a constant applied current, in such way that the mechanism for current oscillation was the same as that for potential oscillation. Although an ordinary CV did not show a negative resistance, which is necessary for the occurrence of oscillation, we could observe negative resistance by simulating the potential sequence before the occurrence of oscillation (induction period). We think the species responsible for the negative resistance is adsorbed water adjacent to adsorbed carbon monoxide.

References and Notes

(1) Hjelmfelt, A.; Schreiber, I.; Ross, J. *J. Phys. Chem*. **1991**, *95*, 6048.

(2) Belousov, B. P. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; John Wiley & Sons: New York, 1985; p 605.

(3) Zhabotinskii, A. M. *Biofizika* **1964**, *9*, 306.

(4) Fechner, A. Th. *Schweiggers J. Chem. Phys*, **1828**, *53*, 141.

(5) Bassett, M. R.; Hudson, J. L. *Chem. Eng. Commun*. **1987**, *60*, 145.

(6) Hudson, J. L.; Tsotsis, T. T. *Chem. Eng. Sci.* **1994**, *49*, 1493.

(7) Sazou, D. *Electrochim. Acta*. **1997**, *42*, 627.

(8) Okamoto, H. *Electrochim. Acta* **1992**, *37*, 37.

(9) Okamoto, H.; Tanaka, N. *Electrochim. Acta* **1993**, *38*, 503.

(10) Okamoto, H.; Tanaka, N.; Naito, M. *Electrochim. Acta* **1994**, *39*, 2471.

(11) Okamoto, H.; Tanaka, N.; Naito, M. *Chem. Phys. Lett.* **1996**, *248*, 289.

(12) Okamoto, H.; Tanaka, N.; Naito, M. *J. Phys. Chem*. **1997**, *101*, 8480.

(13) Wojtowicz, J.; Marincic, N.; Conway, B. E. *J. Chem. Phys*. **1968**, *48*, 4333.

(14) Horányi, G.; Inzelt, G.; Szetey, E. *Acta Chim. Acad. Sci. Hung.* **1978**, *97*, 299.

(15) Anastasijevic, N. A.; Baltruschat, H.; Heitbaum, J. *J. Electroanal. Chem.* **1989**, *272*, 89.

(16) Albahadily, F. N.; Schell, M., J. *J. Electroanal. Chem.* **1991**, *308*, 151.

(17) Inzelt, G.; Kertész, V. *Electrochim. Acta* **1993**, *38*, 2385.

(18) Inzelt, G.; Kertész, V. *Electrochim. Acta* **1995**, *40*, 221.

(19) Kertész, V.; Inzelt, G.; Barbero, C.; Kötz, R.; Haas, O. *J. Electroanal. Chem*. **1995**, *392*, 91.

(20) Koper, M. T. M.; Hachkar, M.; Beden, B. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3975.

(21) Inzelt, G.; Kertész, V. *Electrochim. Acta* **1997**, *42*, 229.

(22) Raspel, F.; Nicholis, R. J.; Kolb, D. M. *J. Electroanal. Chem*. **1990**, *286*, 279.

(23) Markovic, N.; Ross, P. N. *J. Phys. Chem*. **1993**, *97*, 9771.

(24) Raspel, F.; Eiswirth, M. *J. Phys. Chem*. **1994**, *98*, 7613.

(25) Strasser, P.; Lübke, M.; Raspel, F.; Eiswirth, M.; Ertl, G. *J. Chem. Phys*. **1997**, *107*, 979.

(26) Strasser, P.; Eiswirth, M.; Ertl, G. *J. Chem. Phys*. **1997**, *107*, 991.

(27) Xu, Y.; Schell, M. *J. Phys. Chem.* **1990**, *94*, 7137.

(28) Schell, M.; Albahadily, F. N.; Safar, J.; Xu, Y. *J. Phys. Chem.* **1989**, *93*, 4806.

(29) Schell, M.; Cai, X. *Electrochim. Acta* **1993**, *38*, 519.

(30) Xu, Y.; Amini, A.; Schell, M. *J. Phys. Chem*. **1994**, *98*, 12759.

(31) Schell, M.; Xu, Y.; Amini, A. *J. Phys. Chem*. **1994**, *98*, 12768.

(32) Xu, Y.; Amini, A.; Schell, M. *J. Electroanal. Chem*. **1995**, *398*, 95.

(33) Xu, Y.; Zdraveski, Z.; Schell, M. *Chem. Phys. Lett*. **1995**, *247*, 589.

(34) Schell, M.; Xu, Y.; Zdraveski, Z. *J. Phys. Chem*. **1996**, *100*, 18962.

(35) Scott, S. K. *Chemical Chaos*; Clarendon Press: Oxford, 1991.

(36) Gray, P.; Scott, S. K. *Chemical Oscillations and Instabilities*; Clarendon Press: Oxford, 1990.

(37) Koper, M. T. M. In *Advances in Chemical Physics XCII*; Prigogine, I., Rice, A., Eds.; John Wiley & Sons: New York, 1996; p 161.

(38) Schell, M.; Albahadily, F. N. *J. Chem. Phys*. **1989**, *90*, 822.

(39) Guthrie, J. P. *Can. J. Chem*. **1975**, *53*, 898.

(40) Olivi, P.; Bulhoes, L. O. S.; Léger, J.-M.; Hahn, F.; Beden, B.; Lamy, C. *J. Electroanal. Chem*. **1994**, *370*, 241.

(41) Koper, M. T. M.; Sluyters, J. H. *J. Electroanal. Chem*. **1994**, *371*, 149.

(42) Feigenbaum, M. J. *J. Stat. Phys*. **1978**, *19*, 25.

(43) Metropolis, N.; Stein, M. L.; Stein, P. R. *J. Comb. Theory A* **1973**, *15*, 25.

(44) Pikovsky, A. S. *Phys. Lett.* **1981**, *85A*, 13.

(45) Matsumoto, K.; Tsuda, I. *J. Stat. Phys.* **1983**, *31*, 87.

(46) Matsumoto, K.; Tsuda, I. *Physica* **1987**, *26D*, 347.

(47) Tsuda, I.; Shimizu, H. In *Complex Systems-Operational Approaches*; Haken, H., Ed.; Springer: Berlin, 1985; p 240.

(48) Capon, A.; Parsons, R. *J. Electroanal. Chem*. **1973**, *44*, 239.

(49) Kitamura, F.; Takahashi, M.; Ito, M. *Chem. Phys. Lett*. **1986**, *123*, 273.

(50) Gilman, S. *J. Phys. Chem*. **1964**, *68*, 70.

(51) Shiller, P.; Anderson, A. B. *J. Electroanal. Chem*. **1992**, *339*, 201.