Chaos in the Oxidation of Formaldehyde and/or Methanol

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The appearance of chaos is studied with a platinum electrode in acidic solutions of formaldehyde, methanol, and their mixtures at 43 °C under galvanostatic conditions. The oscillation mode changes with time, and chaos is found after the period-doubling bifurcation for formaldehyde alone, methanol alone, and their mixtures. Two types of alternating periodic and chaotic sequence are observed depending on the current value: descending and ascending orders respectively at currents lower and higher than approximately 0.5 mA cm^{-2} at 43 °C. The former is usually seen in the oxidation of formaldehyde and the mixtures of formaldehyde with a small molar fraction of methanol. The latter is ordinarily recognized for methanol and the mixtures of formaldehyde with a large fraction of methanol. Around 0.5 mA cm^{-2}, the oscillation pattern does not show the alternating sequence but rather a disordered periodic one. We identify aperiodic patterns as chaos by the presence of the period-doubling cascade and by the shape of the Lorenz map. We discuss the difference in the order of the alternating sequence in terms of the platinum surface state. Because oscillation occurs at even less than 0.6 V (rhe), we think adsorbed water is an important reactant with adsorbed carbon monoxide. We also think the nonuniformity of chaos shown in the Lorenz map prevails in a natural system and plays an essential role in the system.

Introduction

Chemical chaos and chemical oscillations have become well-known.[1−3] As deduced from a recent upward trend in the science of complexity, we believe that studying these nonlinear phenomena will become more important in the future. There are three reasons that the electrochemical nonlinear systems are especially suitable for study. First, high-quality data can be collected because they are obtained from a reaction field itself, i.e., an electrode surface. This is crucial for data analysis.[4−7] Second, it is easy to control an electrochemical reaction system because we can easily change current or potential. This is important because we often need to control a system when studying its characteristics by observing its response to an external stimulation.[8] And third, a characteristic curve, i.e., a voltammogram, is available, which connects current and potential with surface reactions as a whole. This is very useful when we consider an oscillation mechanism in terms of the characteristics of related molecules.[9−11]

There have been many studies on electrochemical nonlinear systems showing chaos. Among these studies the electrodissolution of metals has been being most intensively studied.[4,12−15] We, however, have been studying nonlinear behavior in the galvanostatic electrochemical oxidation of formic acid and formaldehyde,[7,8,11,16] which is one of surface electrocatalytic reactions. Although the periodic potential oscillation behavior in the reaction has been studied by many researchers,[5,6,9,17−24] very few papers on chaotic oscillations have been published.[5−7]

In the literature[5−7] relating to chaos, the electrolytic solution containing formaldehyde was made from commercial formalin (a formaldehyde solution). Commercial formalin usually contains methanol up to approximately 27 mol % vs formaldehyde, so it is possible that the observed chaos might be a phenomenon specific to a mixture of formaldehyde and methanol and would not be observed in a solution containing only formaldehyde. We have examined this possibility using paraformaldehyde, a polymer of formaldehyde. We report here the appearance of

chaos in a solution of formaldehyde alone, in mixtures of formaldehyde and methanol, and in a solution of methanol alone. During this study we found chaotic oscillations even in the oxidation of sole methanol. Although the chaotic behavior under a periodical constraint, i.e., under application of cyclic voltammetry, has been shown for methanol oxidation in interesting series of work by Schell et al.,[25−27] the chaotic behavior reported in the present paper is a spontaneous one.

Experimental Section

The experimental method in electrochemistry is a usual three-electrode one, with a reversible hydrogen electrode (rhe) as the reference electrode and a platinum wire as the counter electrode. The working electrode was a Pt net with a purity of 4 N (99.99%), and its true surface area was 2.6 cm^2. Before use, it was heated in a hydrogen flame for about 15 s, immersed in an electrolytic solution, and cleaned by repeatedly applying a triangular potential sweep between 0.05 and 1.4 V at a rate of 0.1 V s^{-1}.

The basic electrolytic solution was 0.5 mol dm^{-3} sulfuric acid, prepared from Millipore "Milli Q" water and Cica-Merck "Ultrapur" sulfuric acid. The formaldehyde solution was prepared by dissolving a calculated weight of paraformaldehyde (Merck "extra pure") into the basic electrolytic solution at around 70 °C for several minutes. For preparation of a solution containing methanol, a known amount of methanol (Merck "pro analysi") was added to the basic solution or the formaldehyde solution. For comparison, formalin (Kanto Chemical Co. "special grade") was occasionally used instead of paraformaldehyde.

Nitrogen gas (Nippon Sanso, 6 N) was used without further purification to deoxygenate the electrolytic solution by bubbling it through the solution before measurement and to keep the solution deoxygenated by passing the gas over the solution during measurement. The reaction temperature was fixed at 43 °C. The potentiostat and function generator used were the Hokuto Denko types HB-105 and HA-501G. The X−T recorder was a Hitachi type 561 and the X−Y recorder was a Riken

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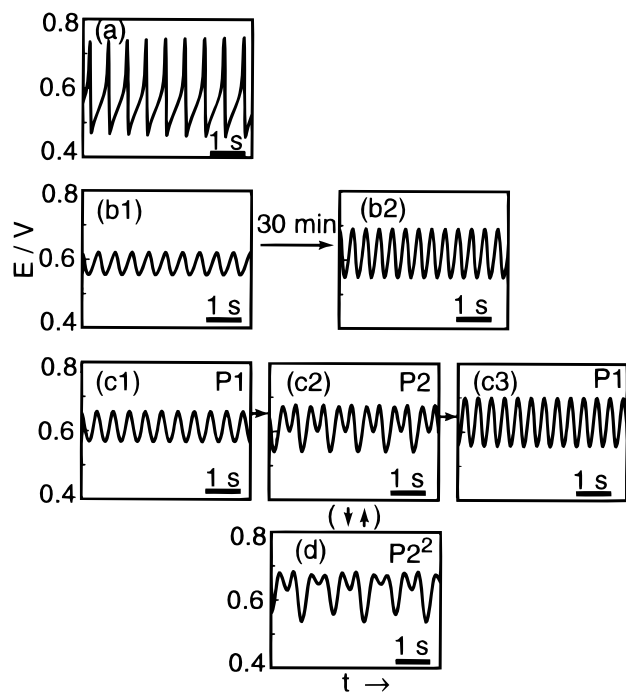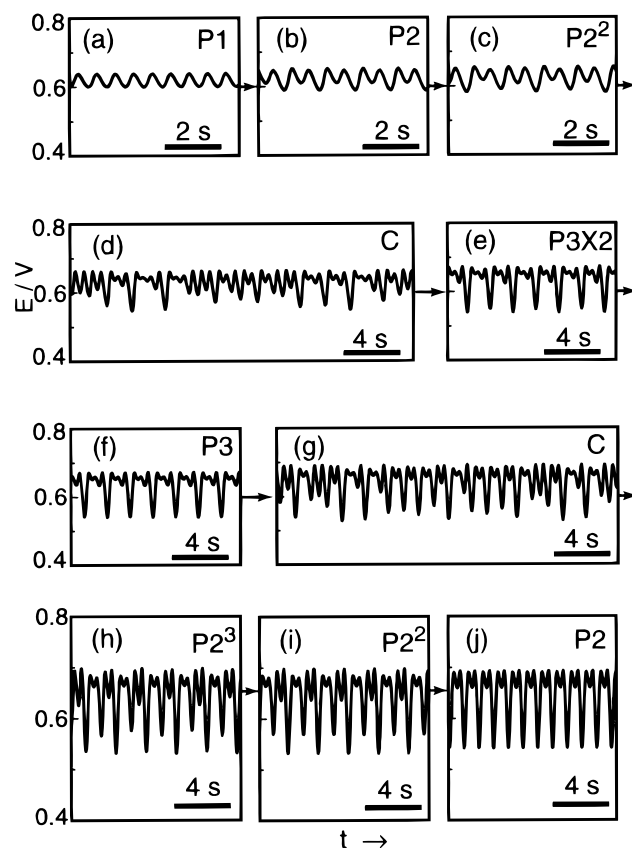

Figure 1. Periodic potential oscillation patterns in the oxidation of 0.1 mol dm^{-3} of formaldehyde alone. Here E is the electrode potential. The applied currents are (a) 3 mA; (b1), (b2) 1.5 mA; and (c1)−(c3), (d) 1.0 mA. Pattern (b2) was obtained 30 min after pattern (b1); (c2) the period-2 pattern; (d) the period-2^2 pattern; and the others the period-1 pattern.

Figure 2. Periodic and chaotic potential oscillation patterns in the oxidation of 0.1 mol dm^{-3} of formaldehyde alone at 0.6 mA: (a), (b), (c) the period-doubling cascade; (d), (g) aperiodic patterns; (e) the period-(3 times 2) pattern; (f) the period-3 pattern; and (h)−(j) the reverse period-doubling cascade.

Denshi model F-72F. The time sequence of potential data to 5.5 significant figures was acquired using a data acquisition/control unit (Hewlett-Packard type 3852A or type 75000), connected with GPIB to the controller (NEC type 9801 EX). Other experimental details were as described in previous papers.[7,10,11]

Experimental Results

Chaos in Formaldehyde. When a 3-mA current was applied to the platinum electrode in an acidic solution containing 0.1 mol dm^{-3} of formaldehyde at 43 °C, a relaxational oscillation pattern was observed as shown in Figure 1(a). This pattern is typical of the behavior in a nonlinear system. When the applied current was 1.5 mA, the observed oscillation pattern was sinusoidal as shown in Figure 1(b1). The pattern lasted 30 min or more and did not change the oscillation mode, though the amplitude grew large as shown in Figure 1(b2). With a further reduced current of 1 mA, after an induction period, the electrode potential showed a sinusoidal pattern, but this time its amplitude became alternately large and small as shown in Figure 1(c2). This phenomenon is called the period doubling and the pattern is called the period-2 pattern. Then the oscillation pattern returned to the original mode, a period-1 pattern. Sometimes the period-2 pattern underwent the second period-doubling bifurcation to give a period-2^2 pattern, as shown in Figure 1(d), which returned through the period-2 to the period-1 pattern. Thus we observe the period-2 (and -2^2) oscillation between the period-1 oscillations.

Since the oscillation pattern changed with time in this way, it can be assumed that the surface state gradually changed during the experiment. We can say that this is not due to a slow diffusion velocity of formaldehyde compared to the velocity of surface reactions. This is because a similar oscillation pattern change was also observed even in a solution as concentrated as 10 mol dm^{-3} of formaldehyde at a low current like 0.3 mA.

Although we have not been able to identify the reason for this change, we suppose some surface parameter changes monotonically, and the surface becomes less reactive, on the basis of the fact of a gradual potential increase throughout a run.

The time elapsed for each pattern depended on the history of the sample from a few minutes to an order of an hour, especially on the past current profile. The current giving the period-2 or the period-2^2 pattern also varied with a large deviation of approximately 30% of the average current from one set of experiments to another. This deviation is also probably due to the past history of the electrode. However, the reproducibility of the oscillation pattern sequence itself was quite good. As shown later, it was also good when a chaotic oscillation was observed. The good reproducibility of the oscillation pattern sequence but with a large deviation of the current producing bifurcations was first pointed by Schell et al.[5]

Upon decreasing the current to 0.6 mA, the potential oscillation pattern changed as shown in Figure 2. After an induction period, the potential began to oscillate sinusoidally, underwent period-doubling bifurcations twice, sometimes three times, and then gave an aperiodic pattern as shown in Figure 2(d). After approximately 20 min of the aperiodic pattern, the electrode potential showed a period-(3 times 2) oscillation, then a period-3, and then the second aperiodic oscillation as shown in Figure 2(e)−(g). This was followed by a period-2^3, a period-2^2, and then a period-2 patterns as shown in Figure 2(h)−(j). Finally the period-1 pattern followed.

The aperiodic patterns in Figure 2 are in chaotic states, since they emerged after a period-doubling cascade. We show another piece of evidence of chaos by plotting the Lorenz map, which
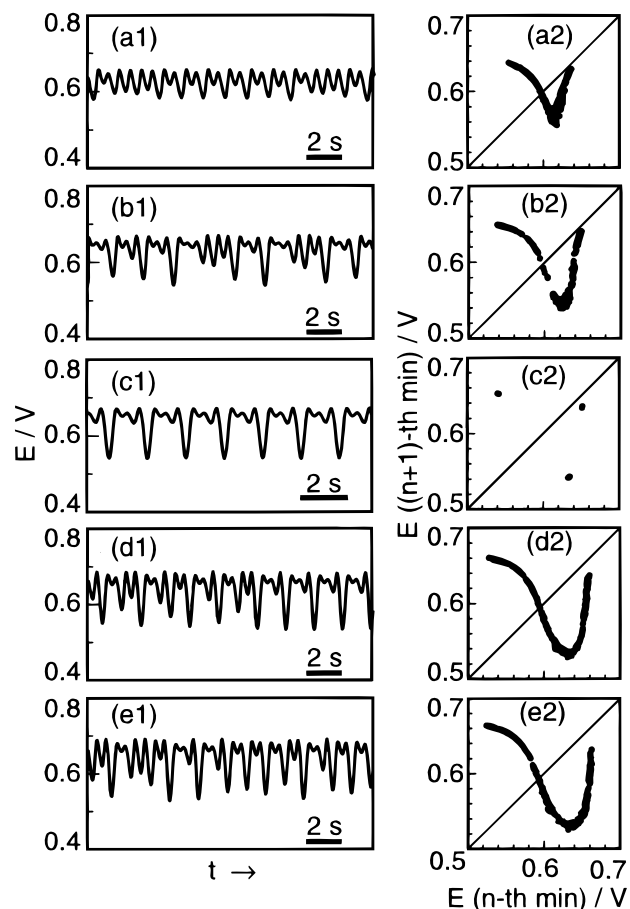
Figure 3. Chaotic and the period-3 oscillation patterns and their Lorenz plot in the oxidation of 0.1 mol dm^{-3} of formaldehyde alone at 0.6 mA: (a1) a chaotic pattern just after the period-doubling cascade; (b1) a chaotic pattern just before the period-3 pattern; (c1) the period-3 pattern; (d1) a chaotic pattern just after the period-3 pattern; and (e1) a chaotic pattern just before the reverse period-doubling cascade. (a2)–(e2) Lorenz maps corresponding to the oscillation patterns shown alongside.

is a one-dimensional Poincaré map. In the map we plot the value of the potential minimum along the horizontal axis and the value of the next minimum along the vertical axis. Such maps together with the potential oscillation patterns are shown in Figure 3. Parts (a1) and (b1) of Figure 3 are the oscillation patterns between the period-doubling cascade and the period-3 pattern. The time sequence is in the following order: Figure 3(a1), Figure 2(d), and then Figure 3(b1). Parts (a2) and (b2) of Figure 3 are the Lorenz maps corresponding to the patterns of Figure 3(a1),(b1). They show the presence of a deterministic law in the system. Thus we can conclude that chaos occurs in a solution containing formaldehyde alone.

Parts (c1) and (c2) of Figure 3 are the period-3 pattern and its Lorenz map, the latter of which is made of three discrete groups of dots, which is the sign of periodicity. Parts (d1) and (e1) of Figure 3 are the patterns just after the period-3 pattern and just before the period-2^3 pattern. Here Figure 3(e1) is the same as Figure 2(g). Their Lorenz maps are similar to each other as shown in parts (d2) and (e2) of Figure 3. Thus, the Lorenz maps indicate that all the observed aperiodic patterns are in chaotic states. The shape of the Lorenz map changes with time from a comparatively sharp ravine to a broader valley. Since we cannot see such a distinct change in the chaotic oscillation patterns, it is convenient to plot the Lorenz map to study the chaotic states. We think that the change in the shape of the Lorenz map is related to some change in the surface state.
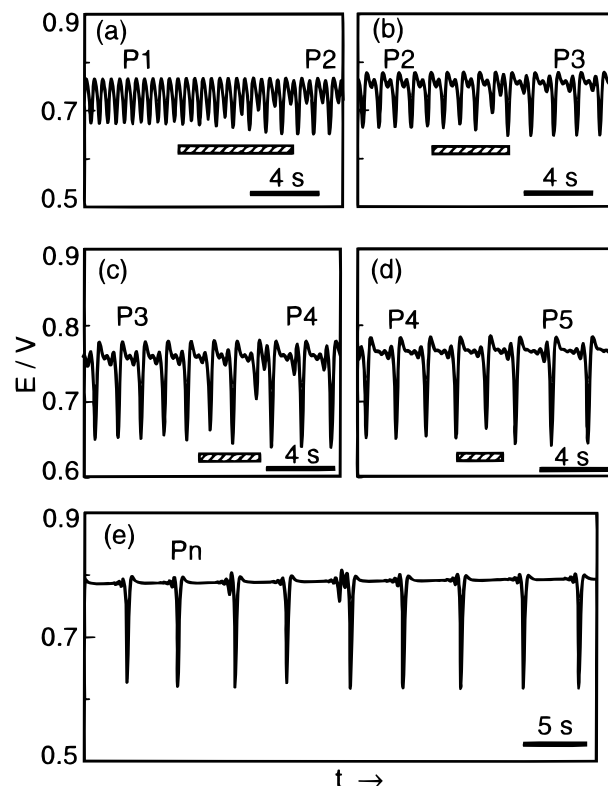

Figure 4. Periodic and chaotic oscillation patterns in the oxidation of 1 mol dm^{-3} of methanol alone at 5 mA. The hatched line shows a duration of pattern change: (a) a pattern shift from the period-1 to the period-2 oscillation; (b) a pattern shift from the period-2 to the period-3 oscillation; (c) a pattern shift from the period-3 to the period-4 oscillation; (d) a pattern shift from the period-4 to the period-5 oscillation; and (e) a disordered periodic pattern observed after (d).

Chaos in Methanol. We then studied the oscillation patterns in an acidic solution containing methanol alone. When a high current of 5 mA was applied to the platinum electrode in a solution containing 1 mol dm^{-3} of methanol, after an induction period of approximately 10 min, the period-1 oscillation was observed, which was followed by the period-2 pattern as shown in Figure 4(a). Although the time for the change from the period-1 to the period-2 pattern is similar to that observed for formaldehyde, that from the period-2 to the period-3 pattern is quite different from that for formaldehyde, as shown in Figure 4(b). That is, for methanol it took less than 4 s for the period-2 pattern to change into the period-3 pattern, whereas for formaldehyde this change took about 20 min as mentioned before.

Furthermore, the period-3 pattern was successively followed by period-4 and then period-5 patterns and so on, with aperiodic regimes as short as less than 4 s between each periodic oscillation as shown in Figure 4(c),(d). Although the duration of each aperiodic oscillation was too short for obtaining the Lorenz plot, we can say the aperiodic oscillation is in a chaotic state. This is because we observed the period-doubling cascade before these aperiodic oscillations.

Hence we conclude that the methanol oxidation provides the alternating periodic and chaotic sequence in an ascending order. This order is opposite to that for formaldehyde alone. For formaldehyde the period-doubling bifurcation was followed by period-3 (including a period-(3 times 2)) and period-2 (including periods-2^3 and -2^2) patterns with chaos between each periodic mode. That is, the formaldehyde oxidation gives the alternating sequence in a descending order. The formaldehyde oxidation is now being studied in detail regarding the bifurcation sequence.
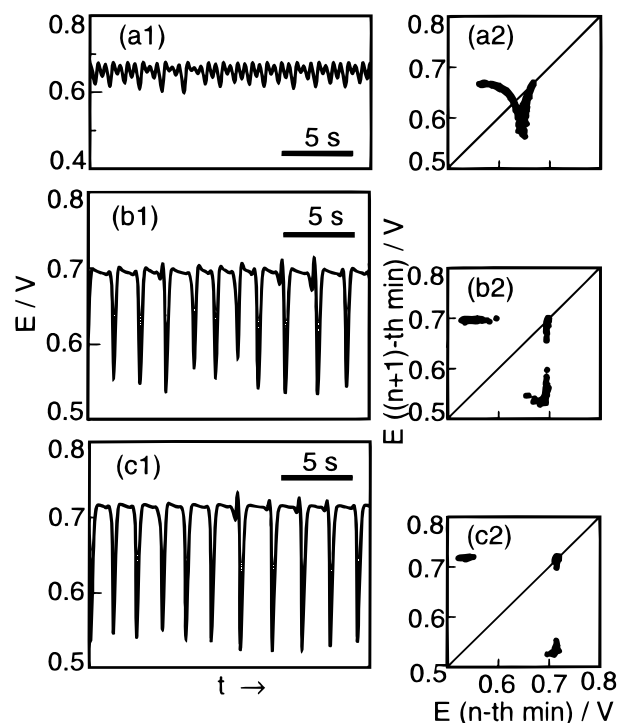
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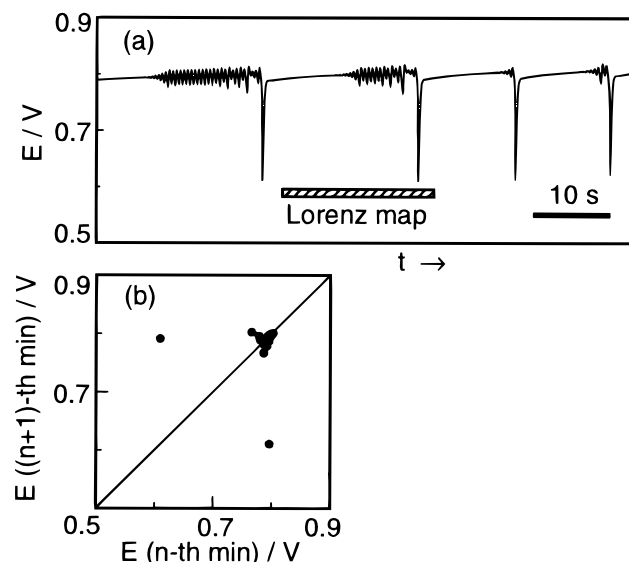
Figure 5. Intermittent oscillation patterns in the oxidation of 1 mol dm^{-3} of methanol alone at 4.5 mA: (a) an intermittent pattern and (b) the Lorenz map for the interval marked in (a).

The period-5 pattern was succeeded by slightly disordered periodic patterns as shown in Figure 4(e). We cannot discriminate between one periodic oscillation and the next. When the current was decreased to 4.5 mA, we observed an intermittent pattern as shown in Figure 5(a). The Lorenz map for the interval indicated in Figure 5(a) is shown in Figure 5(b). Although the number of iterates is few, we can detect a regularity. At a current higher than 6 mA, on the other hand, we observed only a period-1 pattern. Therefore, we could not observe the alternating sequence in a descending order in the oxidation of methanol alone.

Chaos in Mixtures of Formaldehyde and Methanol. When a 0.1 mol dm^{-3} formaldehyde solution was mixed with 0.027 mol dm^{-3} of methanol, corresponding to the composition of formalin, we could not find any difference between the oscillation behavior in the oxidation of the mixture and that in formaldehyde alone. With a mixture of 0.1 mol dm^{-3} formaldehyde and 0.1 mol dm^{-3} methanol, we could detect a slight difference in the current providing chaos, i.e., approximately 1 mA compared with 0.8 mA for sole formaldehyde. The alternating sequence was in a descending order.

With a solution of 0.1 mol dm^{-3} formaldehyde and 0.3 mol dm^{-3} methanol, we found a clear difference. The chaotic pattern appeared at the comparatively high current of 1.2 mA as shown in Figure 6(a1). The oscillation pattern was like the one for formaldehyde alone that is shown in Figure 3(a1). It is in a chaotic state because it was observed via the period-doubling cascade and the Lorenz map exhibits the presence of a deterministic law as shown in Figure 6(a2).

The chaotic oscillation pattern changed to another disordered pattern after about 15 min as shown in Figure 6(b1). This pattern is quite different from that corresponding to formaldehyde (Figure 3(b1)). We can determine from the Lorenz map shown in Figure 6(b2) that this oscillation pattern is still chaotic. This oscillation mode did not change much for about 20 min as shown in Figure 6(c1). During this period we could not find a clear period-3 pattern like that observed for formaldehyde alone. The pattern shown in Figure 6(c1) is not like the corresponding one for formaldehyde alone depicted in Figure 3(e1). The Lorenz map is an intermediate one between chaotic and periodic oscillations as shown in Figure 6(c2). Thus we can say that a mixture of formaldehyde with an intermediate


Figure 6. Chaotic potential oscillation patterns and their Lorenz maps in the oxidation of a mixture of 0.1 mol dm^{-3} formaldehyde and 0.3 mol dm^{-3} methanol at 1.2 mA: (a1) a chaotic pattern just after the period-doubling cascade; (b1) a chaotic pattern 15 min after (a1); (c1) a disordered periodic pattern 20 min after (b1); and (a2)−(c2) the Lorenz maps each corresponding to the left side oscillation pattern.
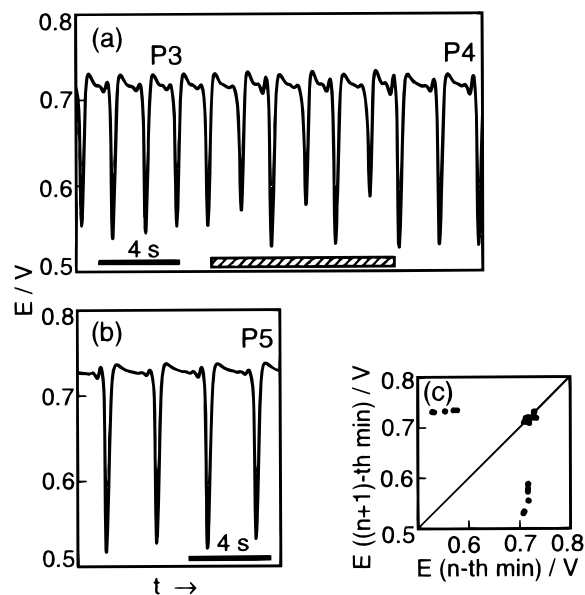
Figure 7. Periodic and chaotic oscillation patterns in the oxidation of a mixture of 0.1 mol dm^{-3} formaldehyde and 1 mol dm^{-3} methanol at 3 mA. The hatched line shows the duration of a pattern change: (a) a pattern shift from the period-3 to the period-4 oscillation; (b) the period-5 pattern; and (c) the Lorenz map for the aperiodic regime shown by the hatched line in (a).

molar fraction of methanol like the one shown here does not show the alternating periodic and chaotic sequence.

In the case of a methanol-rich mixture of 0.1 mol dm^{-3} formaldehyde and 1 mol dm^{-3} methanol, the chaotic pattern was shown at the high current of 3 mA and the oscillation mode change became like that of methanol alone as shown in Figure 7. Namely, period-3, -4, and -5 patterns were seen in this order though not so highly periodic. The elapsed time from the
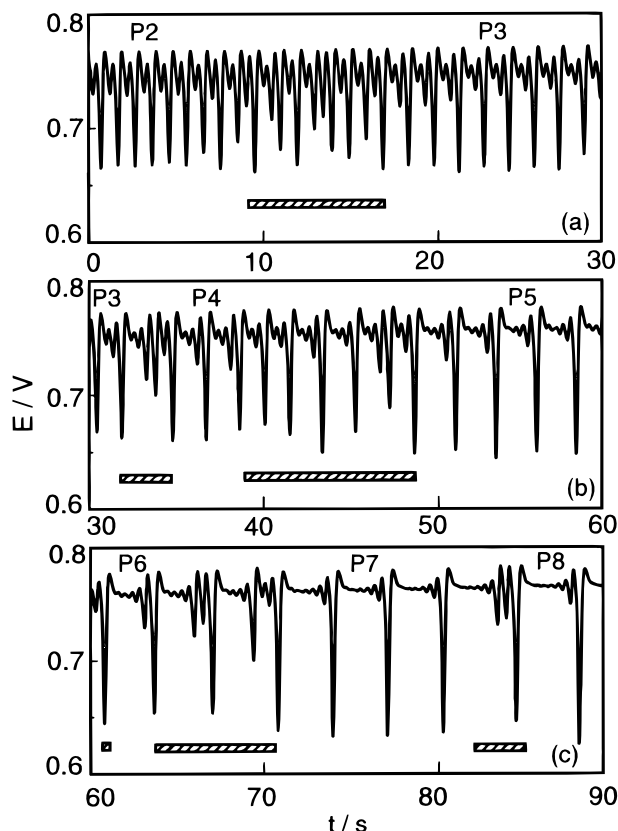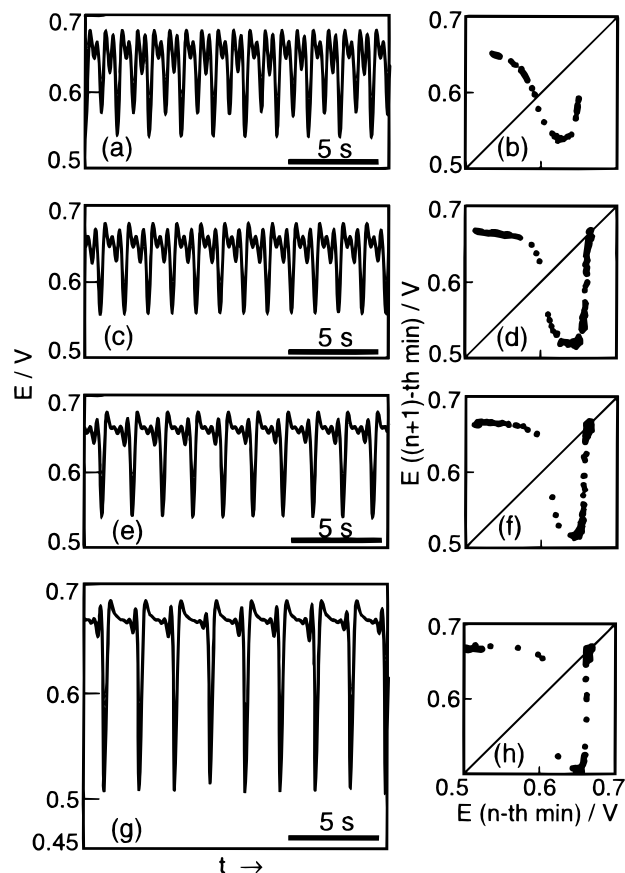
Figure 8. Periodic and chaotic oscillation patterns in the oxidation of a mixture of 0.01 mol dm^{-3} formaldehyde and 1 mol dm^{-3} methanol at 4 mA. Hatched lines show the duration of pattern changes.


Figure 9. Periodic oscillation patterns and Lorenz maps for the following chaos in the oxidation of a mixture of 1 mol dm^{-3} formaldehyde and 3 mol dm^{-3} methanol at 1.6 mA: (a) the period-2^2 pattern; (c) the period-3 pattern; (e) the period-4 pattern; (g) the period-5 pattern; and (b), (d), (f), (h) the Lorenz maps each for the chaos shown after the corresponding left side periodic oscillation.

period-3 to period-4 mode, however, was longer than that for methanol alone, and hence we could obtain the Lorenz map which exhibited chaos, as shown in Figure 7(c). At a lower current of 2 mA we could not obtain the oscillation itself but obtained a monotonical potential increase. Thus we could observe the alternating periodic and chaotic sequence in an ascending order in the methanol-rich mixture.

We studied the oscillation behavior in a very methanol-rich mixture of 0.01 mol dm^{-3} formaldehyde and 1 mol dm^{-3} methanol to make sure that the appearance of oscillation waves becomes more like that for methanol alone. We could apparently observe the alternating periodic and chaotic sequence in an ascending order at 4 mA as shown in Figure 8. Namely, we can clearly recognize the period-3, -4, -5, -6, and -7 waveforms in this order with chaos between each one and the next. The period-7 pattern was succeeded by slightly disordered periodic patterns with less clear small oscillations as shown in Figure 8. The period passing from one periodic oscillation to another is a little longer than that for methanol alone. This is thought to be due to the presence of formaldehyde. At a lower current of 3 mA we could only obtain a monotonical potential increase with one-stroke oscillation at around 0.85 V.

Upon increasing the concentration of formaldehyde from 0.1 to 1 mol dm^{-3} with a fixed molar fraction of methanol, 0.75, we found the alternating periodic and chaotic sequence in an ascending order as shown in Figure 9. Each of the oscillation patterns, the period-2^2, -3, -4, and -5 patterns shown in Figure 9(a), (c), (e),(g), was followed by a comparatively long (approximately 50 s) chaotic oscillation, which gave one of the Lorenz maps shown in Figure 9(b),(d),(f),(h). The sequence, however, was not observed in the diluted mixture of 0.1 mol dm^{-3} formaldehyde with the same methanol molar fraction, 0.75 (Figure 6). Hence we can say that the presence of the alternating

pattern sequence depends not only on the molar fraction of methanol but also on the concentration of formaldehyde.

In the solution containing 1 mol dm^{-3} formaldehyde or in the solution mixture of 1 mol dm^{-3} formaldehyde and 1 mol dm^{-3} methanol, we observed the alternating sequence in a descending order. We compare the latter result with those shown in Figures 7 and 8, where the solution mixture contained the same concentration of methanol, 1 mol dm^{-3}, and lower concentrations of formaldehyde, and the alternating sequence was in an ascending order. Therefore, we can say that the order of the alternating pattern sequence depends on the concentration of formaldehyde, although we already found that the order depended on the concentration of methanol. Hence we think the presence of the alternating sequence and its order depend on a parameter other than the molar fraction or concentration of methanol or formaldehyde. This will be shown later in this section and discussed in the next section.

We think it interesting that the Lorenz maps shown in Figure 9 become sharper with time, whereas those in Figure 3 become broader as mentioned earlier. This finding may relate to the ascending or descending order of the alternating periodic and chaotic sequence, although it needs more study relating the change in the surface state.

We summarize the effect of methanol addition to the formaldehyde solution in Figure 10. In the figure, for a relative comparison we show boundaries: the maximum current i_o for the occurrence of oscillation (open circles) and the maximum current i_c for the appearance of chaos (closed circles). The current vs concentration graphs for formaldehyde concentrations

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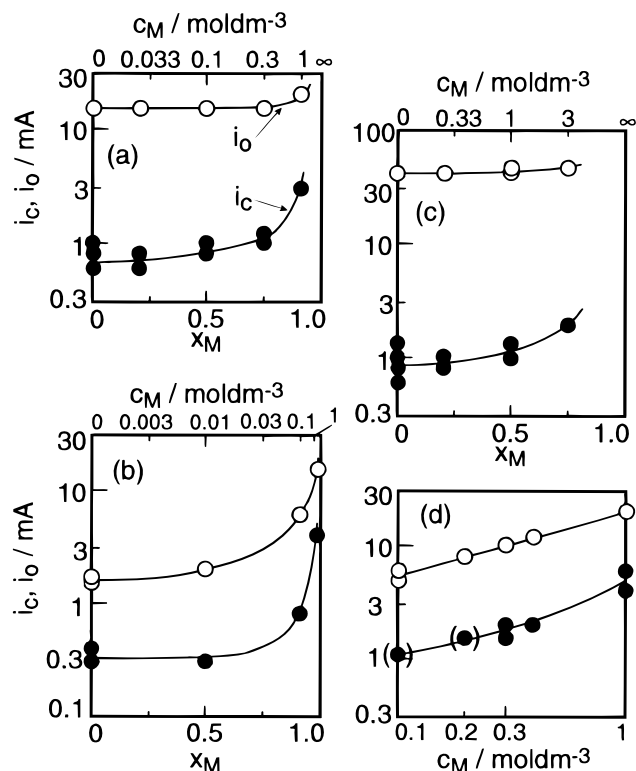
Figure 10. The effect of methanol addition to the formaldehyde solution. The formaldehyde concentrations are (a) 0.1, (b) 0.01, and (c) 1 mol dm^{-3}. (d) is for methanol alone. Here x_M is the molar fraction for methanol; c_M in (a)−(c) is the methanol concentration corresponding to x_M; c_M in (d) is the methanol concentration (log scale); open circles are the maximum current, i_o, for the occurrence of oscillation (log scale); closed circles are the maximum current, i_c, for the occurrence of chaos (log scale); and closed circles in parentheses are the maximum current showing the period-2 pattern.

of 0.1, 0.01, and 1 mol dm^{-3} are respectively shown in parts (a), (b), and (c) of Figure 10. The duration of oscillation at i_o was often 1 or 2 s. Each of the rightmost closed circles in the figures gave the alternating periodic and chaotic sequence in an ascending order. The others showed the sequence in a descending order except one closed circle at a methanol molar fraction, x_M, of 0.75 in Figure 10(a), which gave a disordered periodic pattern as described before. The current is greater than 1.6 mA when the order is ascending, and this fact will be discussed in the next section.

For reference we plot i_o and i_c for methanol alone in Figure 10(d). The closed circles in parentheses show the maximum current for the occurrence of the period-2 pattern. This is because in the methanol only solutions with methanol concentration less than 0.3 mol dm^{-3} we observed at most the period-2 pattern.

Although the scattering of i_c is large, we can see that in each case i_c and i_o hardly change in the region of x_M less than 0.5, whereas i_c increases greatly when x_M is larger than 0.5. Hence we can say that the oscillation behavior for formalin is almost the same as that for formaldehyde alone. Other features in Figure 10 indicate that the difference between i_o and i_c in the figures, i.e., the ratio of i_o to i_c because of the logarithmic scale, increases with an increase in the concentration of formaldehyde. Moreover, i_o for methanol alone is smaller than that for formaldehyde alone, whereas the i_c for methanol alone is larger than that for formaldehyde alone.

To explore differences among the surface adsorption states for formaldehyde, methanol, and their mixtures, we studied the cyclic voltammogram, CV. The CV for 0.1 mol dm^{-3} of
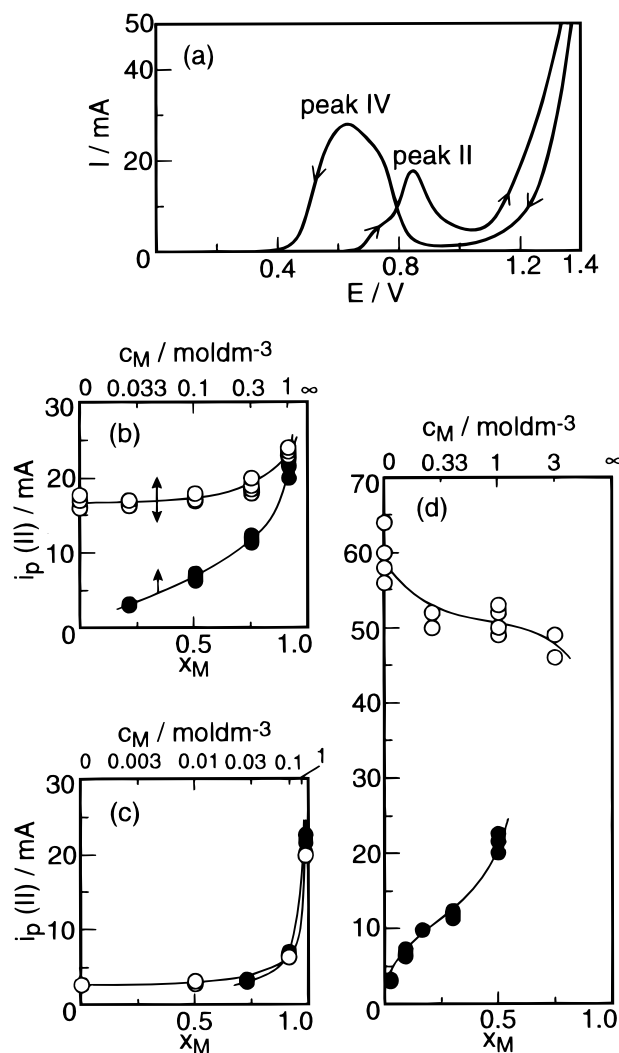
Figure 11. The cyclic voltammogram for formaldehyde and the peak II current for formaldehyde, methanol, and their mixtures. (a) is the cyclic voltammogram for 0.1 mol dm^{-3} of formaldehyde. The formaldehyde concentration is (b) 0.1, (c) 0.01, and (d) 1 mol dm^{-3}. Here I is the current; i_p (II) is the peak current for peak II; x_M and c_M, see Figure 10; open circles are i_p (II) for the mixtures, the abscissa scale being x_M and c_M; and closed circles are i_p (II) for methanol alone, the abscissa scale being only c_M.

formaldehyde is shown in Figure 11(a). It was measured by sweeping the potential between 0.05 and 1.4 V at a sweep rate 0.1 Vs^{-1}. We observed two current peaks, peaks II and IV, in the shown potential region. The other two current peaks, I and III,[11] were not observed under such experimental conditions.

Since the oscillation potential range is lower than or equal to the approximate potential of peak II, the maximum current, i_o, for the occurrence of oscillation is thought to be related to the peak current, i_p (II), for peak II. We expect a positive correlation between i_o and i_p (II), which was actually observed for 0.1 and 0.01 mol dm^{-3} of formaldehyde as shown in Figure 10(a),(b) and in Figure 11(b),(c) with open circles. For 1 mol dm^{-3} of formaldehyde, however, this correlation was negative as shown in Figures 10(c) and 11(d). This is probably because i_p (II) is characterized by the surface state at a constantly changing potential, whereas i_o is characterized by that during a more complicated potential change like a potential oscillation. And the difference between the two surface states increases with an increase in the concentration of formaldehyde.

For comparison we also plot i_p (II) for methanol alone in Figure 11(b)−(d) with closed circles. We see that i_p (II) values

for the mixtures and for methanol alone approach each other when the concentration of methanol increases, which is reasonable.

Discussion

We discuss three issues here: the oscillation mechanism, the alternating periodic and chaotic sequence, and the Lorenz map.

In most papers[6,18,19,28,29] the oscillation is considered to occur due to the accumulation and consumption of a poisonous adsorbate. The direct experimental evidence for the surface mass oscillations were shown for formic acid oxidations by Inzelt et al. using the electrochemical quartz crystal microbalance (EQCM)[23,24,30] and the probe beam deflection.[31] Infrared spectroscopy[32,33] revealed that the poisonous adsorbate is almost certainly carbon monoxide adsorbed on platinum. We agree with this overall reaction mechanism skeleton, but we think that the poisonous species is mainly consumed by a reaction with an adsorbed water molecule rather than with the adsorbed OH radical or oxide as often reported. This is because the oscillation can occur in the potential range less than 0.62 V vs rhe as shown in Figure 1 or sometimes even less than 0.6 V. These potentials are in the electric double-layer region and water is not dissociatively adsorbed on Pt.

Although it is possible that the adsorbed OH radical also reacts with the poisonous adsorbate when the highest oscillation potential is around 0.8 V, we still think that the surface poison reacts mainly with the adsorbed water. The reaction between water and carbon monoxide is not uncommon but is known as the water-gas shift reaction[34] in the research field of catalysis. What is more, such a reaction on a platinum electrode has been proposed by Gilman,[35] and calculations reported by Schiller et al.[36] indicate that such an electrochemical reaction on platinum is possible.

The alternating periodic and chaotic sequence in the oxidation of formaldehyde has already been reported by Schell et al.[5,6] In their sequence the periodic oscillations appear in an ascending order, i.e., in the order of period-3, -4, and -5 patterns and so on, with decreasing current. Since a period-doubling bifurcation occurs with decreasing current in their experiment, the order is interpreted to be ascending with time under our experimental conditions, i.e., static conditions. This order is the reverse of that we observed in the oxidation of formaldehyde. Although their solution was made from formalin and contained 0.4 mol dm^{-3} of formaldehyde, such a mixture is expected from our results to show a descending order.

Although we cannot identify the reason for not showing a descending order in their experiments, different experimental conditions might be the main reason. Their experiments were conducted with a rotating electrode at 50.0 °C, a temperature higher than the 43.0 °C in our experiment. The experimental conditions might also be related to the difference in the current producing chaos, 12.5−29 μA cm^{-2} in their experiment while 100−500 μA cm^{-2} in ours (true surface area: 2.6 cm^2), although the absolute current had a large deviation of about 30% as mentioned before.

We also observed the alternating sequence in an ascending order for methanol and the mixtures of formaldehyde with a large fraction of methanol. This might be thought to be related to poisonous adsorbates other than CO such as COH, which has often been claimed to be present.[37] Wilhelm et al.,[37] however, showed that the main reaction adsorbate is CO in a concentrated solution of methanol like 0.5 mol dm^{-3} and that it is COH in a dilute solution like 10^{-2} mol dm^{-3}. Since ascending order was found in a solution containing methanol more concentrated than 0.3 mol dm^{-3}, we can regard the

poisonous intermediate as CO in a first approximation in the region where the ascending order is observed. That is, we think that the main poisonous adsorbate is the adsorbed carbon monoxide both in the solution of formaldehyde and in the mixtures of formaldehyde with a large fraction of methanol.

We do not think that the order of the sequence is determined by the concentration or molar fraction of methanol. Rather, it seems to depend on the applied current value due to two reasons. One reason is that the ascending order was observed at a current larger than 1.6 mA as shown in Figure 10(a)−(c), where the current was independent of the concentration or molar fraction of methanol or formaldehyde. The other reason is that for some reason we barely observed an ascending order of the sequence with a solution of 1 mol dm^{-3} of formaldehyde alone at a high current of 1.3 mA, although this phenomenon was a rare case and did not usually occur.

Figure 10 also shows that the sequence in a descending order was observed at a current lower than 1.3 mA and that a disordered periodic pattern was observed at 1.2 mA. Thus we can conclude that the ascending and descending orders of the sequence are respectively obtained at currents higher and lower than approximately 1.3 mA, and that a disordered periodic pattern is obtained around 1.3 mA with a deviation of approximately 30%. Since the current producing chaos increased with an increase in the methanol molar fraction as described in the previous section, it only appeared as if the order of the sequence would be related to a methanol molar fraction. Incidentally, the average or the highest oscillation potential does not seem to be related to the order of the sequence, because both of the orders were observed in a similar oscillation potential region less than 0.7 V as shown in Figures 2 and 9.

The ascending order is considered to mean a gradual surface inactivation because the portion of the high-potential regime increases, while the descending order is thought to mean the reverse. Namely, the surface gradually becomes inactive or active according to the current higher or lower than approximately 1.3 mA. We suppose this is due to a tentative adsorption, i.e., metastable state of adsorption for a product of carbon dioxide, which hinders adsorption of reactants. There is another factor inactivating the platinum surface state, and it is independent of the applied current value. This comes from the fact that the average or the highest oscillation potential always increased with time. This might be due to some surface reconstruction.[38]

The alternating periodic and chaotic sequence has also been observed in other chemical reaction systems such as the Belousov−Zhabotinsky reaction[42−45] and the oxidations of methanol,[25−27] ethanol,[25,39] ethylene glycol,[40] and glycerol[41] during application of cyclic voltammetry. The B−Z reaction system is an autonomous system like the one in the present paper, whereas the latter reaction systems are periodically forced nonlinear systems. The chaotic pattern for the B−Z reaction has a mixed characteristic between the adjacent periodic oscillation modes. This was also found in the oxidation of formaldehyde by Schell et al.,[5,6] but was not found in the present system as shown in Figures 2, 3, and 8. If the periodic regimes are regarded as the windows in chaos, we think the nonmixed chaotic patterns reasonable. We are now investigating the details of chaos in the solution of formaldehyde alone.

We consider the Lorenz map. If we can obtain a one-dimensional map, the Lorenz map is very convenient. The method using the Poincaré section is complicated, but the resultant map is nevertheless very similar to the Lorenz map. Namely,[7] first we determine the delay time, τ, using the autocorrelation function or take it as approximately 30% of the

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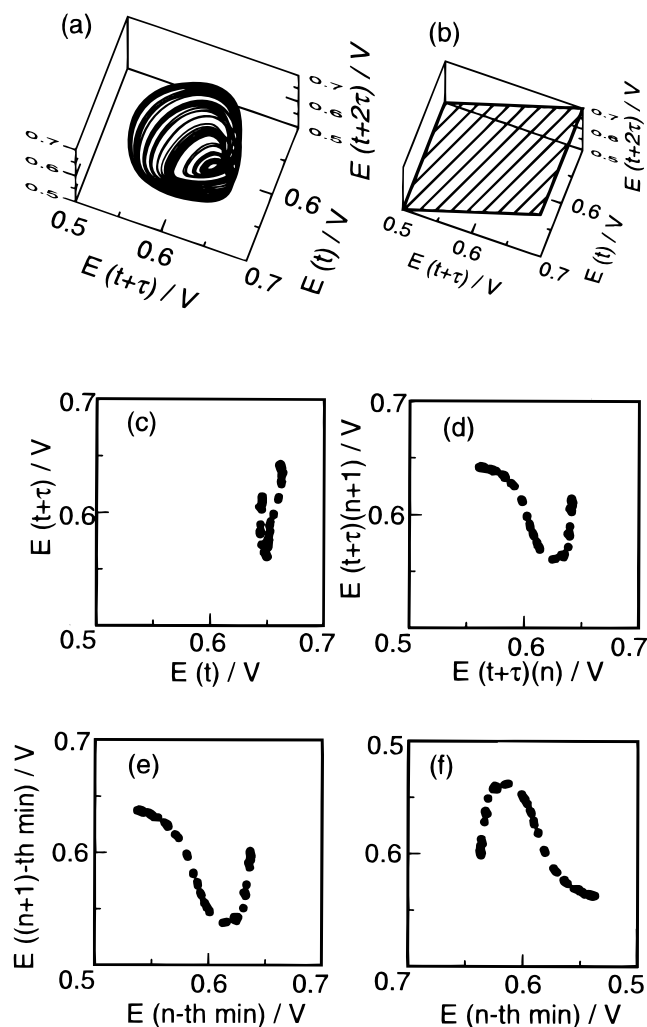
Figure 12. The Lorenz map and the one-dimensional map obtained using the Poincaré section: (a) an attractor orbit, τ being a delay time; (b) the Poincaré section ($E(t+\tau) = E(t+2\tau)$); (c) a plot of the points piercing through the section by the orbit from under; (d) one-dimensional map using the Poincaré section; (e) the Lorenz map; and (f) the Lorenz map with the abscissa right-side left and the ordinate upside down.

basic period of the period-1 oscillation. Then we construct an attractor orbit in the three-dimensional space as shown in Figure 12(a). Next we determine the Poincaré section, for example $E(t+\tau) = E(t+2\tau)$ as shown in Figure 12(b), where $E(t)$ is the electrode potential at time t. The points piercing through the section by the orbit from under are shown in Figure 12(c). Last, we plot the $E(t+\tau)$ coordinates of the nth and $(n+1)$th piercing points as abscissa and ordinate as shown in Figure 12(d). Despite such a complex procedure, the resultant map is very similar to the Lorenz map, the next minimum map, as shown in parts (d) and (e) of Figure 12.

If we reverse the coordinates top to bottom and right to left in the Lorenz map, we obtain the map shown in Figure 12(f). The two maps, Figure 12(e),(f), are of course the same. Since the map function shows the dynamics of the system, the dynamics in the electrooxidation of formaldehyde or methanol has characteristics that show one unsymmetrical peak. Such characteristics are found not only in the electrochemical reaction shown here and in ref 5 but also in the Belousov−Zhabotinsky reaction[45] and in the enzymatic reaction.[46] What is also interesting is that such characteristics are provided even in the spontaneous neuronal spikes of a kind of mollusk, onchidium,[47] and in the neuronal responses of the rat hippocampus C3 under

periodic stimulation.[48] We feel that there may be some universal principle in the natural system.

Although such characteristics seem to be very common and trivial, they seem to have a great nature due to the nonuniformity of chaos exhibited as an unsymmetrical peak in the Lorenz map. Matsumoto and Tsuda showed a noise-induced order in the presence of nonuniformity of chaos.[49] They also showed[50] that initially localized information spreads over a whole system as time passes. Tsuda and Shimizu reported[51] that the input information can be copied and maintained by the system due to the nonuniformity of chaos. In this sense we feel it is very interesting that the one-dimensional map in the natural system shows nonuniform chaos.

Summary

We have shown the appearance of chaos in the galvanostatic oxidation at 43 °C with a platinum electrode of formaldehyde, methanol, and their mixtures. The oscillation pattern changes as time passes, and this change is probably due to a change in the surface state. Two types of alternating periodic and chaotic sequence are observed depending on the current value: descending and ascending orders respectively at currents lower and higher than approximately 0.5 mA cm^{-2} at 43 °C. The descending order is usually seen in the oxidation of formaldehyde and the mixtures of formaldehyde with a small molar fraction of methanol. The ascending order is ordinarily recognized for methanol and the mixtures of formaldehyde with a large fraction of methanol. Around 0.5 mA cm^{-2} the oscillation pattern does not show the alternating sequence but shows a disordered periodic one.

The maximum current for the occurrence of oscillation is related to the peak current of peak II in the voltammogram. Because oscillation occurs at even less than 0.6 V, we think that the adsorbed water is an important reactant with the adsorbed carbon monoxide.

Chaos is identified by the presence of period-doubling cascade and by the shape of the Lorenz map. For the alternating sequence in a descending order the map becomes broader with time, while for the sequence in an ascending order it becomes sharper. The duration for chaos has a tendency to become short when the mixture contains a large amount of methanol. The chaotic pattern does not show a mixed characteristic between the adjacent periodic modes. We have shown that if we can obtain a one-dimensional map, the Lorenz map is more convenient than the map obtained using the Poincaré section. We think the nonuniformity of chaos shown in the Lorenz map prevails in a natural system and plays an essential role in the system.

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