Chaos During the Electrodissolution of Iron

Experiments were carried out on the electrodissolution of iron from a disk electrode rotating at 900 rpm in 1 M H_2SO_4. Current was measured as a function of applied potential. Potentiostatic current oscillations, all of which were chaotic, occurred over a range of applied potential. The characteristics of these chaotic oscillations were studied with the aid of state space plots and Poincaré sections, and with the calculation of ν, the correlation dimension; the latter quantity varied smoothly between 2.4 and 6.0 throughout the range of applied potential studied. The attractor for which $\nu = 2.4$ can be represented by a three-dimensional state space plot.

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Introduction

The aperiodic yet deterministic behavior termed chaos has been observed in a number of chemically reacting systems. In such experiments variables such as the species concentrations or temperature undergo irregular oscillations in time.

The isothermal continuous stirred reactor, most notably with the Belousov-Zhabotinskii reaction, has been studied in some detail. The observed chaos is of low order; the attractor can be embedded in three-dimensional state space, the next amplitude map is almost one-dimensional, and there is a single positive Liapunov exponent denoting a single direction of divergence of trajectories within the attractor (Hudson and Mankin, 1981; Roux et al., 1983). As yet there is no conclusive experimental evidence that higher order chaos requiring four dimensions for its attractor exists in well-stirred single-phase chemical reactors; however, mathematical studies show that higher chaos is possible in simple sets of four ordinary differential equations (Rossler, 1983) and in four-variable chemical reaction systems (Hudson and Rossler, 1984; Hudson et al., 1986).

Irregular oscillations have been observed during several studies of catalytic oxidation; these studies include those by Zuniga and Luss (1978), Plichta and Schmitz (1979), Keil and Wicke (1980), Rathousky et al. (1980, 1981), Rajagopalan et al. (1980), Rathousky and Hlavacek (1982), and Elhaderi and Tsotsis (1982). Oscillations, often irregular, have also been observed in anodic electrochemical reactions; nonsteady behavior of such electrochemical systems has been known for some time (Fechner, 1828; Kistiakowsky, 1909; Bonhoeffer et al., 1948; Wojtowicz, 1972). Many of these electrochemical studies involve the electrodissolution of metals. For example, oscillatory behavior has been observed by several investigators during the dissolution of iron in acid solution (Bartlett, 1945; Franck and Fitzhugh, 1961; Podesta et al., 1979; Russell, 1984; Beni and Hackwood, 1984; Orazem and Miller, 1986). Copper will also undergo current oscillations under potentiostatic conditions in acid medium (Kawczynski et al., 1984; Lee et al., 1985), as will cobalt (Franck and Meunier, 1953; Jaeger et al., 1985).

Much of the oscillatory behavior observed both during the heterogeneous chemical reactions and in the electrochemical reactions noted above has been chaotic rather than periodic in nature. In most cases no quantitative analysis was carried out on the data such as was done with the stirred-reactor results. Thus it was not known if the observed behavior was deterministic chaos as opposed to random noise; furthermore, if the behavior was chaos, there was no indication of the degree of complexity. Recently Grassberger and Procaccia (1983a,b) have developed a method of calculating the dimension of chaotic attractors. Examples of the use of such methods can be found in Babloyantz and Nicolis (1985), in Nicolis and Nicolis (1984), and in Mayer-Kress and Layne (1986). The methods have recently been applied to data from a chemical reaction by Razon et al. (1986), who analyzed the results of experiments on the oxidation of carbon monoxide on platinum. They calculated, *inter alia*, the dimension of the attractor, which indicated that the results require at least four variables for their description.

In this paper we consider the chaotic behavior of an electrochemical reaction, the electrodissolution of iron in sulfuric acid. Rotating disk electrode experiments were carried out as a function of a single parameter, the applied potential. In the nonsteady parameter region only chaotic behavior was observed. We characterize this behavior with the aid of state space plots, with Poincaré sections, and, most important, with the calculation of the dimension of the attractor. We also show how the behavior varies with change in the parameter.

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Experiments

The experiments were carried out on a rotating disk electrode consisting of a 0.635 cm dia. iron rod (99.998% pure) embedded in a 2 cm dia. Teflon cylinder, with the iron exposed at the end. The iron was prepared by polishing its surface sequentially with 180, 320, 400, and 600 grit wet sandpaper and 10 and 5 μm polishing paper, followed by cleaning with ethanol in an ultrasonic bath for 5 min. The cell was a 400 mL beaker with 25 mL side chambers. The counter electrode was a 0.1 mm thick platinum foil of 25 × 50 mm cross section and the reference electrode was Hg/Hg_2SO_4; these were located in the side chambers.

The cell contained 300 mL of 1.0 M H_2SO_4 held at 25°C with a water bath. Nitrogen was bubbled through the solution during a run as well as 2 h beforehand to remove oxygen.

The potential was set using a Princeton Applied Research model 173 potentiostat/galvanostat and a PAR model 175 Universal Programmer. Digital data were taken with a Fluke 8520A voltmeter and a PDP 11/73 laboratory computer at 120 Hz.

To start a run the disk was lowered into the solution while set at a slightly cathodic potential (−1.0 V, Hg/Hg_2SO_4). The potential was then either swept through the range of interest or stepped to a potentiostatic value.

In this paper results will be reported as a function of a single parameter, the potential of the working electrode. All other parameters such as rotational rate of the disk (900 rpm), temperature (25°C), and solution concentration (1 M H_2SO_4) are held constant.

We also carried out a few experiments on a wire electrode. The wire was made of 99.998% pure iron 0.5 mm in diameter. The wires were shielded by Teflon so that a 10 mm length was exposed. The counter electrode was 0.5 mm dia. platinum wire. The experiments were carried out in a 150 mL beaker containing 60 mL of solution stirred with a stirring bar at 60 rpm.

Results

Rotating disk experiments: General behavior

A current vs. potential curve obtained at a sweep rate of 10 mV/s is presented in Figure 1. Oscillations occur on the mass transfer limited plateau prior to passivation, which occurs at about 0.3 V (Hg/Hg_2SO_4). It should be noted that there is no passivation during the oscillatory cycle. This is true for all the dynamic behavior obtained in this study using a disk at 900 rpm. This will be compared below to results obtained with a wire electrode and also to results obtained by others in which, during the course of an oscillation, passivation can occur where the current drops to an almost zero value.

Most of the experiments to be reported here were done at potentiostatic conditions after a step from −1.0 V. A typical result taken with an analog recorder is shown in Figure 2, which was obtained at a constant voltage of 0.1 V. The start of the run is indicated by the step jump in the measured current. After a transient decay of about 10 s duration the current undergoes oscillations whose mean and amplitude remain relatively constant over the course of the run (4 min). There must of course be some change in the oscillations with time since the iron disk is being oxidized; however, changes in the surface are apparently sufficiently slow so that the effect on the behavior of the system is small during a 4 min run. For some voltages the current is not oscillatory. In this case the current decays to an almost steady value after the initial transient; for example, at an applied potential of 0.0 V the current decays to 0.33 A in 15 s and to 0.32 A after 160 s.

A summary of the potentiostatic experiments is given in Figure 3 where the current I is shown as a function of the applied potential E. For $E \leq 0.4$ V the current is steady, whereas for $0.06 \leq E \leq 0.23$ V it is oscillatory. Above $E = 0.24$ V the electrode is passive. In the oscillatory region both the maxima and minima of the oscillations are shown (the upper and lower curves respectively); the absolute maxima and minima were taken for the entire oscillatory portion of a run after the initial transient had died out. These maxima and minima were obtained from the digital data. The transition from stable steady state to oscillatory behavior occurred over a small range in the applied potential near 0.05 V. All the observed nonsteady behavior over the range shown in Figure 3 was chaotic. We did not investigate the range of applied potential over fine enough increments to determine the nature of the bifurcations from steady behavior to chaos. In a subsequent paper we will report on bifurcations to chaos in the electrodissolution of copper. At higher potentials we note that there is an increase in the amplitude of the oscillations as the passive region is approached.

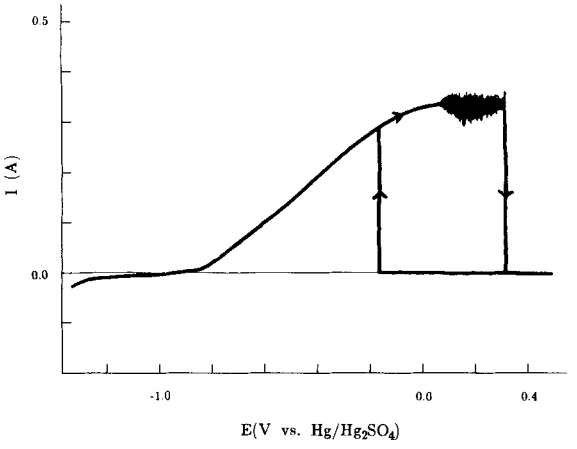

Figure 1. Current vs. potential for sweep rate of 10 mV/s.

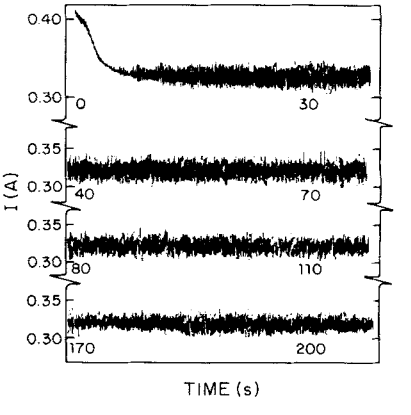

Figure 2. Current vs. time showing sustained oscillations.
0.1 V (Hg/Hg_2SO_4)

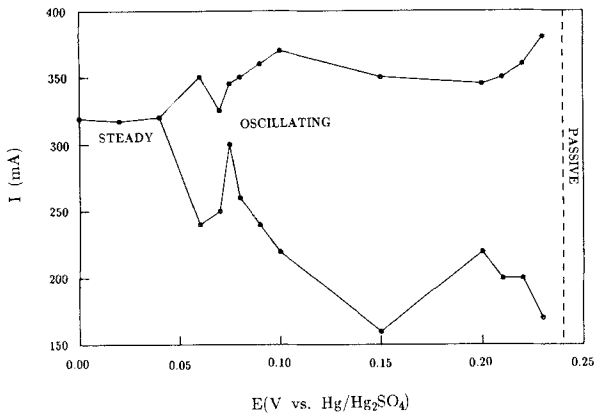

Figure 3. Potentiostatic experiments.
Upper and lower curves are absolute maxima and minima, respectively, of the oscillations

Characteristics of the time series

We shall now discuss the nature of the oscillatory behavior in more detail, considering only the behavior after the initial transients have died out.

Time series of the current at a constant potential $E = 0.07$ V are shown in Figure 4. The data points taken at 120 Hz are connected by straight lines. There are approximately four to five points per quasi period. Although this is sufficient to determine the general structure of the signal, there may be higher frequency components that we have missed. The three parts of the figure are segments of 1.0 s duration beginning at 10, 90, and 180 s into the run, respectively. Note again that there appears to be little change in the behavior of the system with time.

Time series at several applied voltages throughout the oscillatory region are shown in Figure 5. At a potential $E = 0.10$ V, Figure 5a, the oscillations are similar to those obtained at $E = 0.07$ V, Figure 4. As E is increased to 0.15 V, Figure 5b, the amplitude of the oscillations becomes greater. At $E = 0.20$ V,

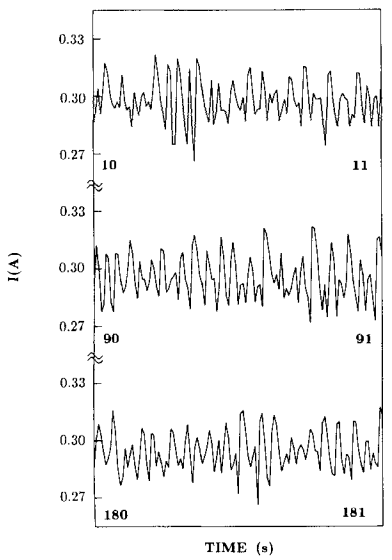

Figure 4. Time series of current under potentiostatic conditions.
$E = 0.07$V (Hg/Hg_2SO_4)

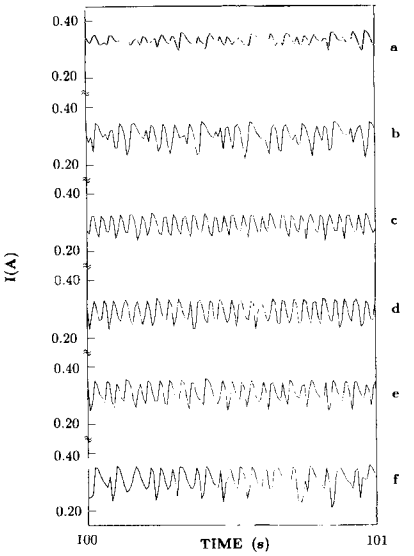

Figure 5. Time series of current at several applied voltages.
a. $E = 0.10$ V; d. $E = 0.21$ V;
b. $E = 0.15$ V; e. $E = 0.22$ V;
c. $E = 0.20$ V; f. $E = 0.23$ V

Figure 5c, the time series, although chaotic, appears to be somewhat more regular, and at $E = 0.21$ V, Figure 5d, we obtained the most regular oscillations seen under the conditions of these experiments. Although it is possible that periodic oscillations occur for potentials somewhat above 0.21 V, we only found chaotic behavior. At $E = 0.22$ V the oscillations are slightly less regular than at $E = 0.21$ V, and at $E = 0.23$ V the behavior is even more irregular. At $E = 0.24$ V the system becomes passive after a short transient.

The behavior seen in the above figures is reproducible; i.e., two experiments carried out at the same potential yield similar-looking time series with swings in current over the same range. The extent of the reproducibility of the results will be discussed again below when we consider the dimensionality of the attractor.

We occasionally observed anomalous behavior at the low end of the oscillating region ($E < 0.09$ V), namely, the amplitude of the oscillations underwent a sudden increase in amplitude with time. The behavior appeared to be unchanging both before and after the transition. These results are not shown and were not used in the analyses given below.

Dimension of the attractors

In order to characterize more fully the nature of the chaos observed in these experiments we calculated the dimensions of the attractors corresponding to the time series. We use the method developed by Grassberger and Procaccia (1983a,b).

Takens (1981) has shown that quantitative information on the behavior of a chaotic attractor can be obtained from a single variable. Our experiments yield a discrete series of measurements of the current at intervals between data points of 1/120 s. An attractor can be constructed in d-dimensional state space by employing the vector

$$\underline{I}_i = [I(t_i), I(t_i + \tau), I(t_i + 2\tau) \ldots I(t_i + (d-1)\tau)] \quad (1)$$

The quantity τ is the time delay, which in this paper will be taken to be the time between measurements or 1/120 s, and t_i is any time.

In the method of Grassberger and Procaccia one constructs the attractor using Eq. 1 in d-dimensional space where d is called the embedding dimension. The correlation integral

$$C(r) = \lim_{N\to\infty} \frac{1}{N^2} \sum_{i,j}^{N} \theta[r - |\underline{I}_i - \underline{I}j|] \qquad (2)$$

is then calculated where θ is the Heaviside step function, r is some distance, and $|\underline{I}_i - \underline{I}_j|$ is the distance between two points in d-dimensional space. The summation in Eq. 2 is equivalently over the number of pairs whose distance is less than r. It is proposed that

$$C(r) = Ar^{\nu} \qquad (3)$$

where A is some constant. The exponent ν is called the correlation dimension and is a lower bound on the Hausdorff dimension. Thus if ν can be determined, one has a lower bound on the dimension of the attractor and, equivalently, on the minimum number of first-order ordinary differential equations necessary to model the attractor.

It can be seen from Eq. 3 that the correlation dimension ν is the slope of a linear portion of a plot of $\log_2 C(r)$ vs. $\log_2 r$.

Such a plot is presented as Figure 6. The data used for the figure were taken at $E = 0.10$ V, the time trace of which can be seen in Figure 5a. 5,000 data points beginning 100 s into the run were used for the plot. $C(r)$ was calculated for embedding dimensions $4 \le d \le 10$ but to clarify only the curves for even d are shown. The straight lines were drawn over a range of r; this range was determined by maximizing the correlation coefficient

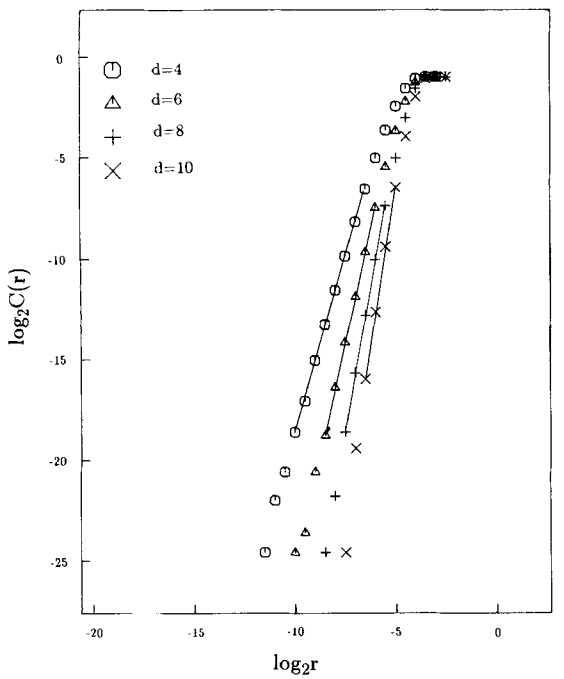

Figure 6. Correlation integral vs distance between points.
$E = 0.10$ V; $N = 5{,}000$

Table 1. Change of Slope with Increase in Embedding Dimension, N = 5,000, 100 s into Run

E, V	d	ν	ν	ν
0.06	4	3.4	3.7	—
0.06	5	4.0	4.6	—
0.06	6	4.5	4.1	—
0.06	7	4.3	3.9	—
0.06	8	4.8	4.4	—
0.06	9	4.7	4.6	—
0.07	4	3.8	—	—
0.07	5	4.1	—	—
0.07	6	5.4	—	—
0.07	7	5.6	—	—
0.07	8	5.7	—	—
0.07	9	5.9	—	—
0.075	4	3.6	—	—
0.075	5	4.1	—	—
0.075	6	5.0	—	—
0.075	7	5.4	—	—
0.075	8	5.3	—	—
0.075	9	5.7	—	—
0.08	4	3.3	3.5	3.1
0.08	5	3.6	3.9	3.5
0.08	6	4.1	4.2	4.2
0.08	7	4.4	4.9	4.6
0.08	8	5.0	5.3	—
0.08	9	5.4	5.6	5.3
0.09	4	3.5	—	—
0.09	5	4.2	—	—
0.09	6	4.6	—	—
0.09	7	5.0	—	—
0.09	8	5.8	—	—
0.09	9	5.8	—	—
0.10	4	3.6	3.5	—
0.10	5	4.1	4.0	—
0.10	6	4.6	4.6	—
0.10	7	4.8	5.0	—
0.10	8	5.2	5.6	—
0.10	9	5.8	6.0	—
0.10	10	6.0	—	—
0.15	4	2.3	—	—
0.15	5	2.7	—	—
0.15	6	3.1	—	—
0.15	7	3.5	—	—
0.15	8	3.9	—	—
0.15	9	4.2	—	—
0.20	4	1.6	—	—
0.20	5	1.8	1.8	—
0.20	6	2.0	1.9	—
0.20	7	2.3	2.1	—
0.20	8	2.4	2.4	—
0.20	9	2.7	2.6	—
0.21	4	1.6	—	—
0.21	5	1.8	—	—
0.21	6	1.9	—	—
0.21	7	2.1	—	—
0.21	8	2.2	—	—
0.21	9	2.4	—	—
0.22	4	1.9	—	—
0.22	5	2.2	—	—
0.22	6	2.3	—	—
0.22	7	2.6	—	—
0.22	8	2.8	—	—
0.22	9	2.9	—	—
0.23	4	1.9	—	—
0.23	5	2.2	—	—
0.23	6	2.5	—	—
0.23	7	2.8	—	—
0.23	8	3.0	—	—
0.23	9	3.4	—	—

of a least-squares fit using at least five points. The correlation coefficient was in all cases above 0.995.

The embedding dimension d must be chosen large enough so that there is no further increase in the correlation dimension ν with increasing d. For the data in Figure 6 the correlation dimension ν was 5.2, 5.8, and 6.0 for embedding dimensions of 8, 9, and 10, respectively; this shows reasonable convergence. The value of $\nu = 6.0$ is the highest obtained in this study.

The calculated correlation dimension ν is shown as a function of embedding dimension d for several applied voltages in Table 1. All calculations were done with 5,000 data points beginning 100 s into the run. In some cases two or three independent runs were analyzed, as indicated by the presence of two or three columns in the table.

The convergence toward a constant value of ν with increasing d is usually quite good, but in some cases, most notably for $E = 0.15$ V and $E = 0.23$ V, it is less satisfactory.

There is excellent agreement among the columns at a given applied voltage, indicating good reproducibility among runs. Furthermore, it should be noted that in the range $0.07 \leq E \leq 0.10$ V, for which data are available for several values of potential, the variation in correlation dimension is small. In fact it can be seen from Figure 7 that the correlation dimension varies smoothly with changes in potential over the entire range.

Some of the calculations in Table 1 were repeated using 10,000 points (83.3 s) in place of 5,000 (41.7 s). This changed the calculated dimension by no more than 0.1.

The calculated correlation dimensions thus are known to within about 0.2, based on the determination of the slope and variations with embedding dimension. Mayer-Kress and Layne (1986) discuss other possible errors in the Grassberger-Procaccia method.

It appears that the attractors have dimensions between 2.4 and 6.0, depending on the voltage. The calculated correlation dimension ν is largest for low values of voltage, i.e., $E \leq 0.10$ V. Lower values for ν are obtained for larger E, particularly $0.20 \leq E \leq 0.22$ V, for which ν is less than three. The correlation dimension is a lower bound on the Hausdorff dimension. If the latter is less than three the chaotic attractor should be embeddable in three-dimensional state space. A three-dimensional state space

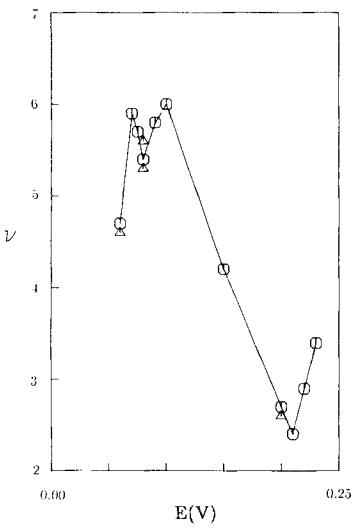

Figure 7. Correlation dimension vs. potential.

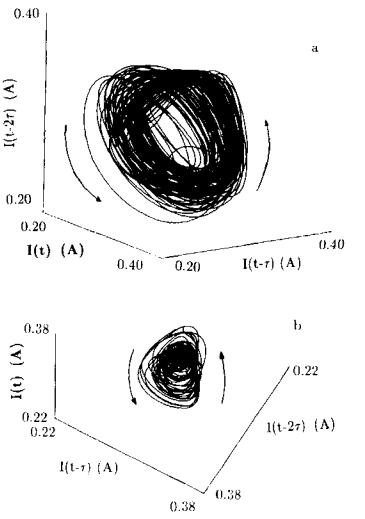

Figure 8. Three-dimensional state space plots using splined points.

a. $E = 0.21$ V ($\nu \simeq 2.4$; 4,000 points)
b. $E = 0.08$ V ($\nu \simeq 5.4$; 2,000 points)
Direction of flow is indicated

plot is given in Figure 8a for $E = 0.21$ V, for which $\nu = 2.4$ (the lowest found). A cubic spline was used to interpolate between measured points. The attractor appears to be fairly simple. However, it is not possible to say for certain that it can be represented in three-dimensional state space since we have no firm evidence that the trajectory does not cross itself. (If it did cross, at least one more dimension would be required.) For contrast a state space plot is given in Figure 8b for $E = 0.08$ V, for which $\nu = 5.4$; this attractor is considerably more complicated than that shown in Figure 8a and, based on both its appearance and correlation dimension, cannot be embedded in three dimensions.

A Poincaré section of Figure 8a is given in Figure 9. The figure is made by determining the intersection of the attractor with

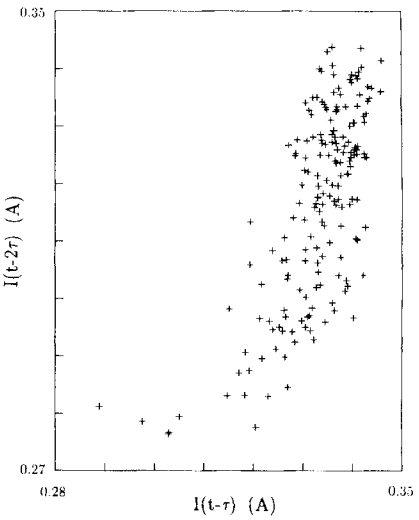

Figure 9. Poincaré section of Figure 8a.

Plane through (0.2, 0.2, 0.2), (0.2, 0.4, 0.2), (0.41, 0.2, 0.4); points taken for decreasing values of $I(t)$
Abscissa is $I(t - \tau)$, ordinate is the projection onto the $I(t - 2\tau)$ axis

the plane defined by the three points (0.2, 0.2, 0.2), (0.2, 0.4, 0.2), and (0.41, 0.2, 0.4). Only intersections with the plane for which $I(t)$ is decreasing are shown.

Both the shape of the Poincaré section and the value of $\nu = 2.4$ are consistent with the notions that the attractor is three-dimensional and that the rate of convergence of trajectories toward the attractor is not overly strong. Consider the Liapunov exponents for this attractor. For a three-dimensional chaotic attractor $\lambda_1 > 0$, $\lambda_2 = 0$, and $\lambda_3 < 0$; furthermore, since the system is dissipative, $\Sigma_i \lambda_i < 0$, i.e., $|\lambda_3| > \lambda_1$. The Kaplan-Yorke (1978), or Liapunov, dimension is defined as

$$D_L = j + \frac{\sum_{i=1}^{j} \lambda_i}{|\lambda_{j+1}|} \tag{4}$$

where j is the largest number for which $\Sigma_{i=1}^{j} \lambda_i > 0$. In the three-dimensional case $j = 2$ and the equation becomes

$$D_L = 2 + \frac{\lambda_1}{|\lambda_3|} \tag{5}$$

For a discussion of the Kaplan-Yorke and other dimensions see Farmer et al. (1983). Grassberger and Procaccia (1983b) show that $\nu \leq D_L$, so therefore when $\nu = 2.4$ there follows from Eq. 5:

$$\frac{\lambda_1}{|\lambda_3|} \geq 0.4 \tag{6}$$

The exponent governing the rate of exponential divergence on the attractor (λ_1) is thus about 40% of that governing the rate of convergence in a transverse direction. This implies a rather weak contraction toward the attractor and could account for the scattering of points in Figure 9. This might be contrasted, for example, with the well-known Lorenz attractor (Lorenz, 1963), a three-variable differential equation model, which has a correlation dimension of 2.05 for given parameters (Grassberger and Procaccia, 1983b).

Other experiments

We carried out a few disk experiments at lower acid concentrations, using mixtures of H_2SO_4 and K_2SO_4 so that the sum of the concentrations was 1.0 M. The range of potentials over which the oscillations occured was smaller than those shown in Figures 1 and 3. The oscillations, however, were qualitatively similar to those shown in Figures 4 and 5.

The behavior observed in the wire experiments differed from that obtained with the rotating disk. Representative time series taken with a wire are shown in Figure 10. It can be seen in Figure 10a that passivation can occur during the course of an oscillatory cycle where the current is almost zero for a finite time; by contrast, Figure 10b, the time spent at a low current density can be very short under other conditions. Thus there are two differences between these results and those obtained with the rotating disk seen in Figures 4 and 5. The oscillations with the wire are much slower and have minima at a very low current density. We show these results not only because they differ from those obtained with the disk but also because they are similar to those obtained by others under other conditions. Podesta et al. (1980)

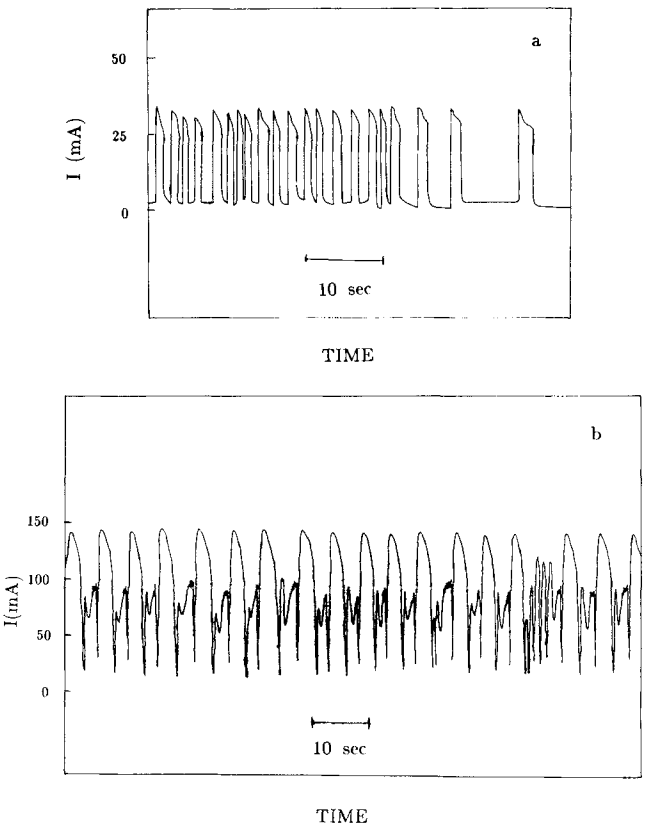

Figure 10. Oscillations on a wire electrode.
a. $E = -0.1$ V (Hg/Hg_2SO_4), 0.4 M H_2SO_4/0.6 M K_2SO_4
b. $E = -0.22$ V (Hg/Hg_2SO_4), 0.6 M H_2SO_4/0.4 M K_2SO_4

observed similar (but apparently periodic) oscillations on a disk rotating up to 450 rpm. Russell (1984) has developed a model which shows this type of behavior, namely, a spike in current followed by a finite time during which the electrode is essentially passivated. Both the experimental results and the model of Franck and Fitzhugh (1961) showed a similar passivation during the oscillatory cycle. All these results indicate that the rate of mass transfer to the disk has a great influence on the qualitative and quantitative behavior of the oscillations as well as the physical processes on the electrode which cause them.

Concluding Remarks

The rotating disk experiments with iron yielded oscillatory behavior which appeared to remain stable over a period of time sufficiently long that the data could be used to calculate a dimension. We found good agreement for the correlation dimension obtained from different experiments run under the same conditions. Furthermore, both the amplitude of the oscillations and the correlation dimension varied smoothly with changes in the applied voltage.

A correlation dimension as low as 2.4 was obtained; this result and the corresponding state space plot imply that the attractor, for at least one set of conditions, can be represented in three-dimensional state space. It is noteworthy that the dynamics of such a complicated system could be so simple.

The correlation dimension was calculated to be between 2.4 and 6.0, depending on the applied potential. This correlation dimension is a lower bound to the state space dimension, but this

latter quantity is not known exactly. It may be the case that the method used to calculate the correlation dimension misses slow variations in the time signal (Hudson et al., 1986); if this is true then the actual (Hausdorff) dimension of the attractor could be substantially greater than the computed correlation dimension.

In any case it appears that at least seven first-order ordinary differential equations would be necessary to model the dynamics of the dissolution of iron under some conditions. This is perhaps not surprising since the system has inherently spatial variations (such as concentration variations through a surface film or a radial dependence of dissolution rate) and thus partial differential equations (an infinite-order system) would be required for its complete description.

Acknowledgment

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Notation

$C(r)$ = correlation integral
d = embedding dimension
D_L = Kaplan-Yorke dimension, Eq. 4
E = voltage relative to Hg/Hg_2SO_4, V
I = current, A
N = number of data points
r = distance in d-dimensional space, A
t = time, s

Greek letters

ν = correlation dimension
τ = time delay, s
θ = Heaviside step function
λ = Liapunov characteristic exponent

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