Effect of Electrode Surface Area on Chaotic Attractor Dimensions

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An experimental study of the dynamics of electrodissolution of iron in sulfuric acid is reported. The experiments were done under potentiostatic conditions with a rotating disk electrode as a function of two parameters, potential and electrode diameter. The dynamic behavior depends strongly on the latter parameter; with increasing electrode size we observe transitions from periodic oscillations to low-order chaos to higher-order chaos. The attractor dimension increases with increasing electrode size. In addition, for the large electrodes at more positive potentials, a secondary higher frequency oscillation also arises.

Introduction

Oscillatory behavior has been observed in several types of electrochemical reactions (Wojtowicz, 1972; Hudson and Bassett, 1990; Degn, 1968). The most commonly studied system has been electrodissolution of metals. Iron dissolution, particularly in acidic media, has been investigated by means of both experiments (Diem and Hudson, 1987; Russell and Newman, 1983, 1986a,b; Podesta et al., 1979; Li et al., 1990) and models (Franck and FitzHugh, 1961; Pearlstein and Johnson, 1990; Wang et al., 1990; Talbot et al., 1985). Copper electrodissolution has been studied in both phosphoric acids (Albahadily and Schell, 1988; Tsitsopoulos et al., 1987) and in acidic chloride solutions (Bassett and Hudson, 1988, 1989a,b, 1990), and nickel has also received some attention (Lev et al., 1988).

The emphasis of many investigations has been on the temporal dynamics. A typical experiment is done under potentiostatic or galvaniostatic conditions. In the former (more common) case, current is measured as a function of time. This current is a measure of the overall reaction rate on the electrode surface. In this manner, several types of interesting periodic and chaotic dynamic behavior have been found, such as period doubling to chaos (Albahadily and Schell, 1988), quasiperiodicity, Shil'nikov chaos, and period doubling of tori (Bassett and Hudson, 1989a, 1988, 1989b).

It is known, however, that the surface of the reacting electrode is not uniform. Examples of this have been reported in the fascinating studies of wave propagation of iron (Franck, 1951) and nickel (Lev et al., 1988). In fact, most reacting surfaces are probably nonuniform. Such nonuniformities have been noted, for example, in gas-solid catalytic reactions (Rotermund et al., 1989; Lobban and Luss, 1989; Schüth et al., 1990). In the case of metal electrodissolution, nonuniformities can be produced by pitting, general (yet rough) corrosion, film formation, and intrinsic nonuniform current distribution.

An important question is to what extent such nonuniformities can affect the overall reaction rate and thus also the overall dynamics of the electrochemical system. In what manner could coupling among reacting sites on a surface increase the complexity of the dynamics?

In this article we report the results of a series of experiments carried out on the electrodissolution of iron in sulfuric acid solution. A rotating disk electrode is used. The experiments are done potentiostatically, and the current is measured as a function of time. Two parameters are varied: the size of the electrode and the applied potential. The nature of the dynamics depends strongly on these two parameters, particularly the former; and as far as we know this is the first experimental study showing that dynamics of a surface reaction can depend on the area of the reacting surface, in our case the electrode size.

There are two purposes to this work. The first is a dynamic one, which gives an experimental example of a chemically reacting system in which the dimension or complexity of a chaotic attractor increases with a parameter over a range from periodic behavior to low-order chaos to higher-order chaos, that is to furnish an experimental example of the "chaotic hierarchy" (Rössler, 1983). The second purpose is physiochem-

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ical in nature, namely, to present experimental evidence that the dynamics of an electrochemical reaction can depend on the electrode size. Possible reasons for this effect are discussed.

Experiments

The experiments were carried out with a standard rotating disk apparatus. The rotation rate, which was held constant at 900 rpm for all experiments, was controlled with a Pine Instrument ASR2 rotator. The electrodes were made from iron rods (Johnson-Matthey, Puratronic, 99.9985%) embedded in a 2-cm-diameter Teflon cylinder, with the iron exposed at the end. The active electrode surface had a diameter in the range from 2.0 mm to 6.35 mm. The electrode surface was prepared by polishing sequentially with 180, 320 and 500 grit wet sandpaper, and 10 and 5 μm polishing paper, followed by cleaning with ethanol in an ultrasonic bath for 5 minutes. The cell was a 400-mL beaker with 25-mL side chambers. The counterelectrode was 0.1-mm-thick platinum foil of 25 × 50 mm cross-section, and the reference electrode was Hg/Hg_2SO_4; each of them was placed in one of the two side chambers. The cell contained 300 mL of 1.0-M H_2SO_4 held at 25°C with a water bath.

All the experiments were carried out potentiostatically by using a scanning potentiostat (Model 362, EG&G, Princeton Applied Research) and a universal programmer (Model 175, EG&G, PARC). The potential was stepped up from a slightly cathodic initial potential (-1.0 V Hg/Hg_2SO_4) to the set value. The resulting current was monitored through an oscilloscope (HP 141A). After the initial transient signal disappeared, the stationary oscillatory current signals were recorded by a computer through a data acquisition system. The data acquisition system consisted of a high-speed analog/digital I/O expansion board (Model DASH-16, Metra Byte) inserted into an AT&T 6312 WGS computer board with 50 = kHz maximum data acquisition rate.

Dimension Calculations

The emphasis of this article is on the increase in complexity of the dynamics of a reacting system with an increase in the reaction surface area. The main quantitative measure of this complexity is the calculation of attractor dimension.

Two methods of calculating attractor dimension were used. One is the "correlation integral" method (Grassberger and Procaccia, 1983a,b) which measures the spatial correlation between random points on the attractor. The method has been applied by several investigators to experimental data (Mayer-Kress, 1986; Razon et al., 1986; Diem and Hudson, 1987). The computation for this method is relatively simple and usually gives reasonable estimates for fairly uniform, low-order attractors with dimensions less than around three. This method, however, has limitations when applied to higher-dimensional, nonuniform attractors.

The other method is called the "nearest neighbor" method (N-N method), which calculates the distance between the reference point x and its kth nearest neighbor points on the attractor. The information dimension d can then be extracted from the calculation. This method was developed by Badii and Politi (1985), and an algorithm based on this method was written by Kostelich (1990). For a large enough data set, the nearest neighbor distance should scale as:

$$\left\langle \delta_k(n_j) \right\rangle \propto n_j^{-1/d} \qquad (1)$$

where d is the information dimension of the attractor. δ_k is the average distance between the reference points and their kth nearest neighbor points based on a sample of n_j other attractor points.

The above relationship held very well for the experimental data presented here. The information dimension d obtained from the slope of log $[\delta_k(n_j)]$ vs. log (n_j) is the function of nearest neighbor order (n.n. order) as well as the embedding dimension m. The determination of appropriate fitting parameters is an essential problem in calculating information dimension from experimental data. The criteria are somewhat subjective (Kostelich and Swinney, 1987). The information dimension d decreases monotonically as the n.n. order increases, but will eventually level off when the n.n. order is large enough. The information dimension d increases monotonically as the embedding dimension m increases, but the

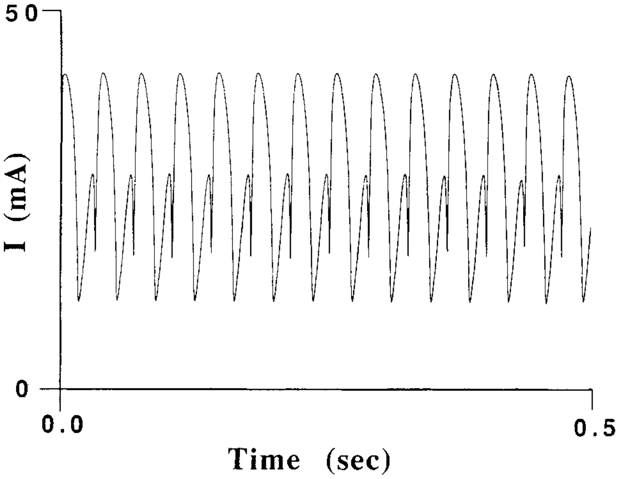

Figure 1a. Time series.

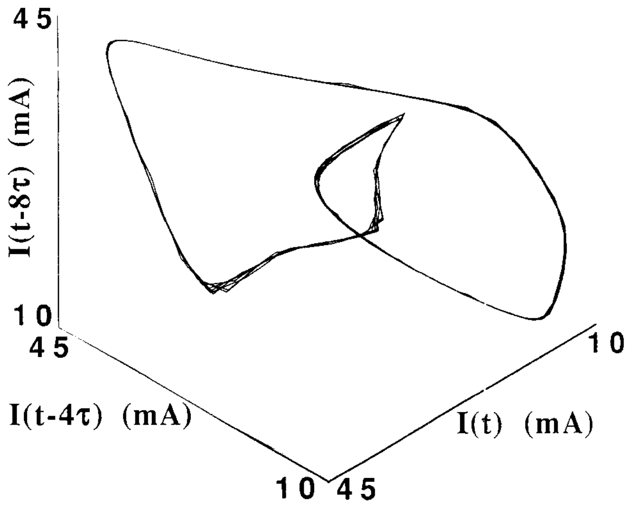

Figure 1b. Attractor ($\tau = 0.4$ ms).

Diameter = 2.0 mm, $E = -0.30$ V (vs. Hg/Hg_2SO_4, the same holds for the rest of the potentials shown).

increasing rate slows down for larger m. Since there is always some noise in experimental data, the distance from the reference points to their nearest neighbor has to be far enough away to reflect the true fractal structure of the attractor, yet has to be close enough to fall into the scaling region. We normally choose the value of d at n.n. order whose distance is around 2-4% of the whole attractor. The total number of data points N used for the calculation has to be large enough to approach the limit. We use 50,000 to 200,000 data points in the calculations depending on the sampling rate and complexity of the attractor. For small-size electrodes with relatively simple behavior, we use 50 k total data points in the calculation. For larger electrodes with more complicated behavior, we use 100 k total data points. For large electrodes at potentials where a high-frequency component appears, the sampling rate is much faster; therefore, we use 200 k total data points.

In general, the N-N method works better than the correlation integral method for high-dimensional, nonuniform attractors, with the trade-off of a much more complicated algorithm and a considerably longer CPU time. All the dimension presented in this work were calculated using the N-N method. We also calculated dimensions using the correlation integral method. The latter gave similar results as the former for uniform attractors, but was not satisfactory for the nonuniform cases. For example, the correlation integral method gave a dimension less than two for nonuniform, low-order chaotic attractors.

Results

As was noted above, the electrodissolution of iron in sulfuric acid has been studied by several investigators. Experiments are often done potentiostatically at a series of potentials, and the current is measured as a function of time. With increasing anodic potential, the current rises, begins to level off at the mass-transfer limited plateau, and then drops suddenly as passivation occurs. Two types of oscillations have been reported. One involves a large-amplitude oscillation between the active and passive transition conditions (Russell and Newman, 1983). The second is a smaller-amplitude and relatively faster oscillation on the mass-transfer-limited plateau (Russell and Newman, 1986a; Diem and Hudson, 1987). In this case, oscillations occur over a range of potential.

All the oscillations reported here are the latter type. The

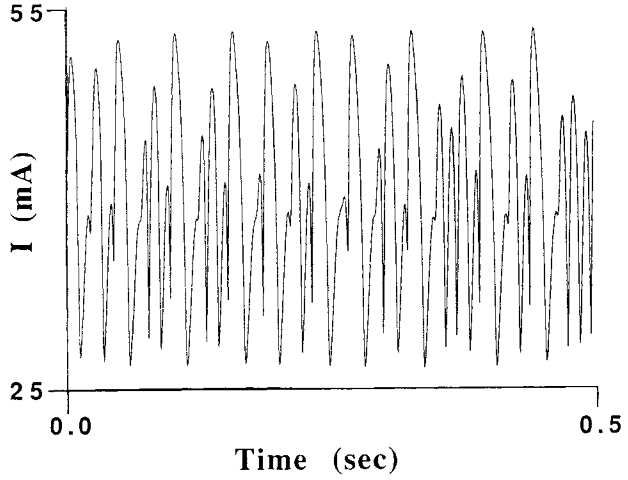

Figure 2a. Time series.

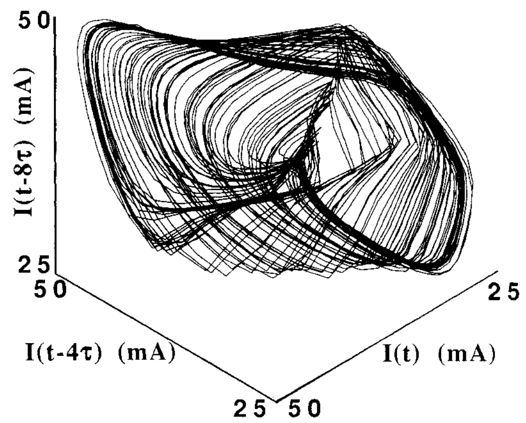

Figure 2b. Attractor ($\tau = 0.4$ ms).

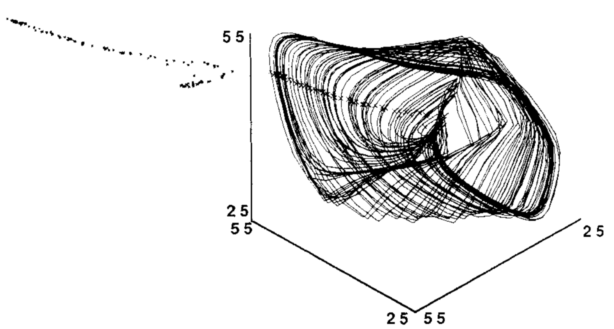

Figure 2c. Poincaré section using the plane defined by $3I(t) + 19I(t-4\tau) = 30I(t-8\tau) - 2{,}900$ (mA).

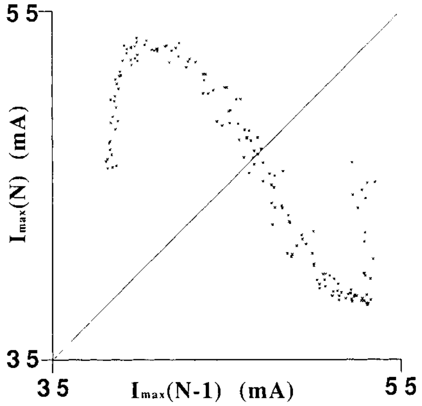

Figure 2*d*. Next maximum map.

Diameter = 2.4 mm, $E = -0.21$ V.

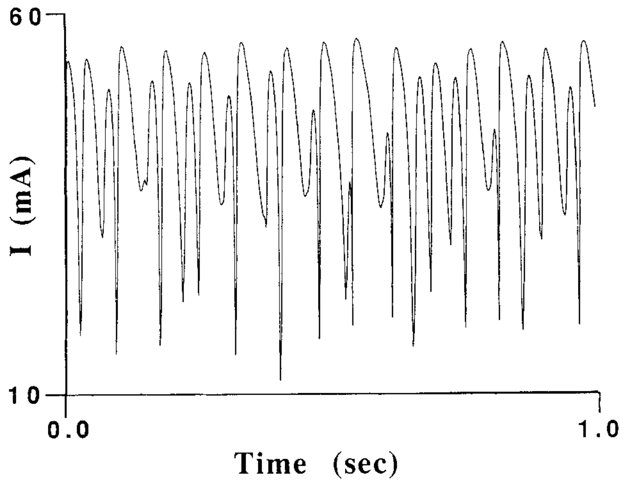

Figure 3a. Time series.

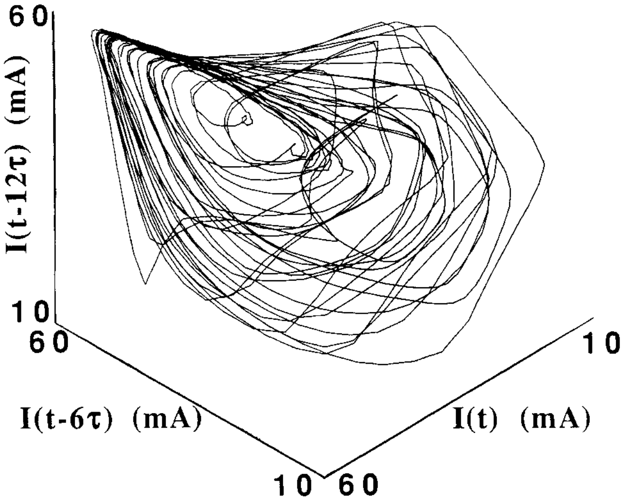

Figure 3b. Attractor ($\tau = 0.4$ ms).

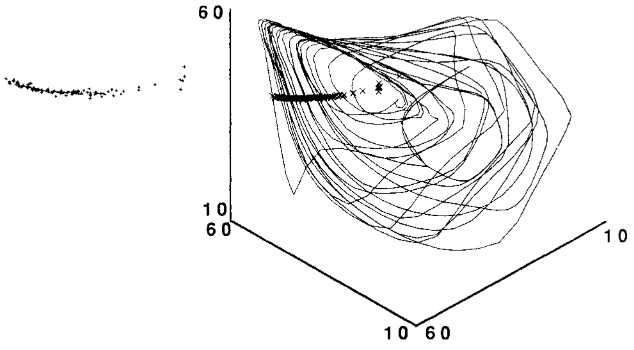

Figure 3c. Poincaré section taken at $I(t-12\tau)=40$ mA.

Diameter = 2.4 mm, $E=-0.30$ V.

current is measured under potentiostatic conditions as a function of potential. The experiments were carried out with several size electrodes. We start with the smallest electrode (diameter = 2.0 mm) and progress to the largest one (diameter = 6.35 mm). The disk rotation rate, the electrolyte concentration, and the temperature were held constant for all the experiments.

Behavior of the smallest electrode is shown in Figure 1. Both the time series and the attractor reconstructed by the time delay method are presented. As can be seen from both the time series and the reconstructed attractor, the behavior under these conditions is periodic. Figure 1 was made from an experiment carried out at potential $E = -0.30$ V (all potentials mentioned here are relative to a Hg/Hg_2SO_4 reference electrode). Oscillations occur over the range $-0.38 \text{ V} \leq E \leq -0.25$ V. Over part of the range, the oscillations are clearly periodic, as in Figure 1; for other potentials, particularly the lower ones, the oscillations are less regular and frequencies are somewhat lower. Nevertheless, the dominant feature of this smallest electrode is the occurrence of periodic oscillations.

Behavior obtained with a slightly bigger electrode (diameter = 2.4 mm) is shown in Figures 2 and 3. The time series and attractor obtained at a potential of $E = -0.21$ V can be seen in Figures 2a and 2b, respectively. The nearest neighbor dimension d for this attractor is 2.2. A Poincaré section and a next maximum map are presented in Figures 2c and 2d, respectively. For Poincaré sections, we show the location on the attractor where the cut was made as well as a slightly expanded version of the section itself. The shape of the attractor (locally sheetlike) and these of the Poincaré section (approximately one-dimensional) indicate that the behavior is the low-order chaos. This inference is also consistent with the value of the calculated dimension, which is slightly greater than 2.0. Additional information on the nature of low-order chaos is offered by Rössler (1983) and by Thompson and Stewart (1986). The lowest-order chaos arising either from experiments or from ordinary differential equations has an attractor that can be embedded in a three-dimensional state space. The attractor is locally two-dimensional. Because of folding, the third direction has a Cantor-set-type structure. When the dissipation is large, as it often is in chemical systems, the third direction can be compressed so that the attractor appears to be almost everywhere two-dimensional, as in Figure 2b. A cross-section of this attractor will then appear to be almost one-dimensional, as in Figure 2c.

The behavior again somewhat depends on potential. For this size, electrode (diameter = 2.4 mm) oscillations occur over the range $-0.35 \text{ V} \leq E \leq -0.12$ V. For more positive values of the potential, the behavior resembles a low-order chaos with a rather uniform attractor, as in Figure 2. For more negative potentials, the time series and attractor resemble those shown in Figure 3. The attractor is somewhat less regular. Nevertheless, the behavior still appears to be a low-order chaos. The nearest neighbor dimension is still only somewhat above two: $d = 2.4$. In addition, a Poincaré section (Figure 3c) made from a cut with increasing value of the current (through the left side of the attractor) still has an almost one-dimensional shape. (The section made with decreasing value is more complex). Thus, the behavior of Figure 3 appears to be a low-order chaos with somewhat less contraction than that exhibited by the attractor of Figure 2. Although the shape of the time series and attractors do depend somewhat on potential, the calculated dimension is not a strong function of potential; this is true for all sizes of electrodes.

The time series and attractor for the next bigger electrode (diameter = 3.0 mm) are shown in Figure 4. The behavior is

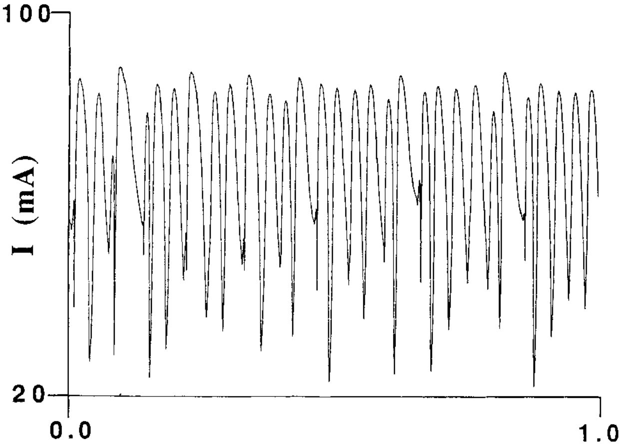

Figure 4a. Time series.

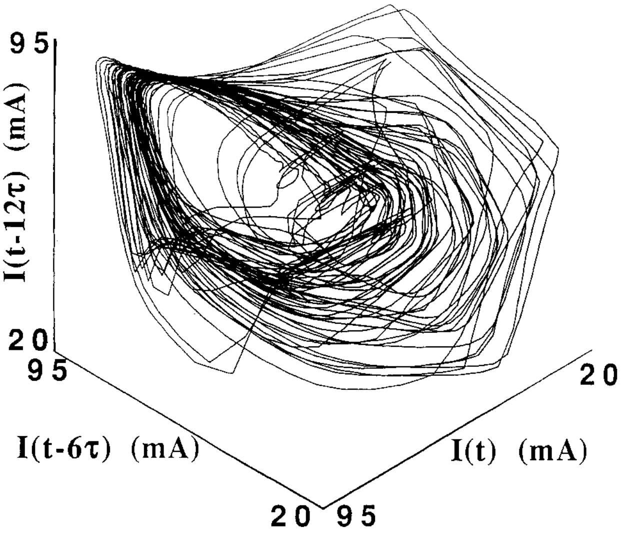

Figure 4b. Attractor ($\tau = 0.4$ ms).

Diameter = 3.0 mm, $E = -0.20$ V.

slightly more complex than that of Figure 3. The attractor is somewhat more tangled and less uniform, and the dimension, 2.6, is slightly higher.

Results for the next bigger electrode, diameter = 4.0 mm, are shown in Figures 5 and 6. For all the large electrodes used, which have a diameter of 4.0 mm and greater, two types of behavior were observed: one occurring at lower potentials and the other at higher potentials.

A time series and attractor representative of the behavior at lower potential are shown in Figure 5. There appears to be a straightforward increase in complexity over that seen in the earlier figures. The attractor is even more tangled and nonuniform. More importantly, from a quantitative standpoint, there is an increase in dimension. Now the dimension d is around 3.2.

For more positive potential, a higher-frequency component of the oscillations appears. A time series is shown in Figure 6a, and a shorter segment on an expanded time scale is presented in Figure 6b. Figure 6b shows that the higher-frequency components are not noise (as they appear to be in Figure 6a), but rather a regular higher-frequency signal that can only be seen at a fast enough sampling rate. We recorded data at a rate of 20,000 Hz for such signals. A higher-frequency signal has been seen previously by Russell and Newman (1986a). They referred to this component of the signal as noise, but did point out that it could be produced by a rapid transition between two states, active and passive. It is apparent now that the high-frequency component in Figure 6b is a reproducible part of the dynamics of the electrochemical system.

Attractors are shown in Figures 6c and 6d. The choice of time delay for the reconstruction is made depending on whether one wishes to capture the nature of the higher-frequency signal or that of the overall slower motion. In the former case, a short time delay is used as is shown in Figure 6c. The higher-

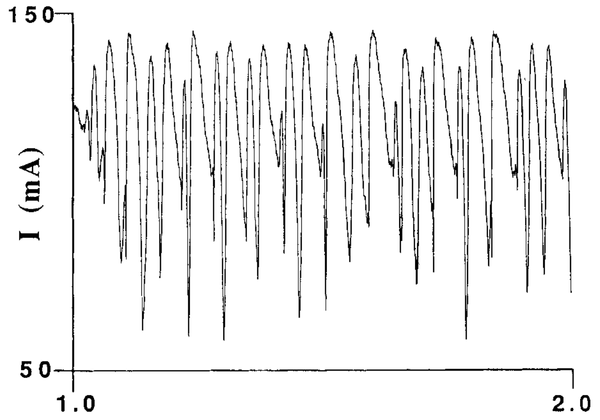

Figure 5a. Time series.

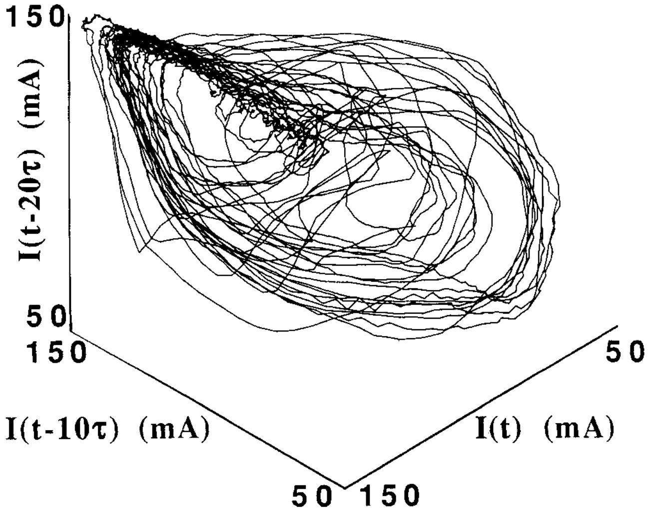

Figure 5b. Attractor ($\tau = 0.2$ ms).

Diameter = 4.0 mm, $E = -0.10$ V.

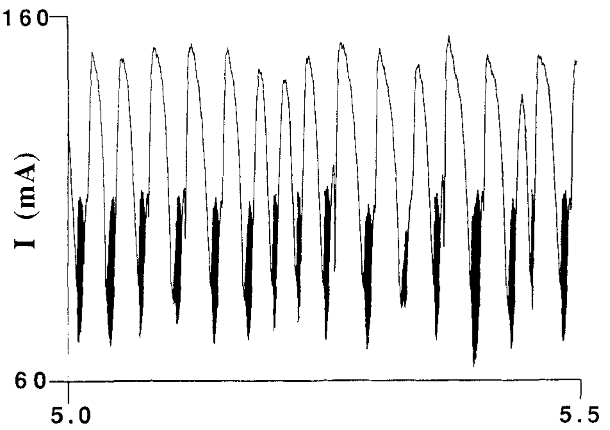

Figure 6a. Time series.

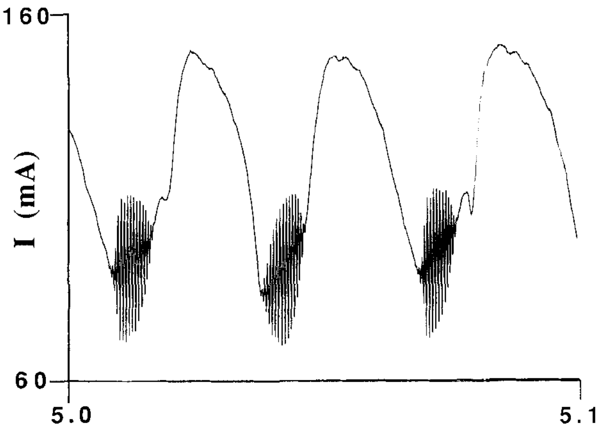

Figure 6b. Expanded time series.

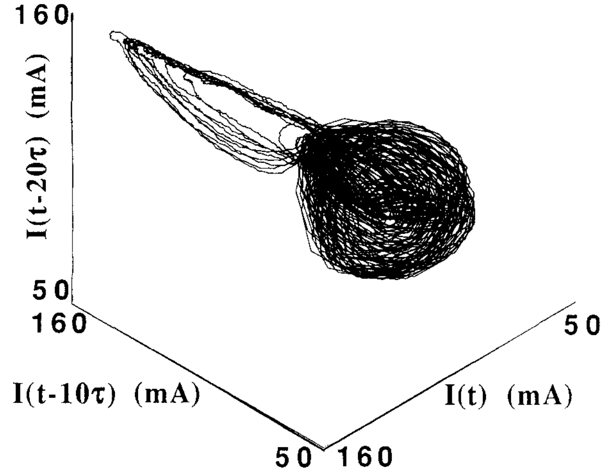

Figure 6c. Attractor (delay = 10τ, $\tau = 0.05$ ms).

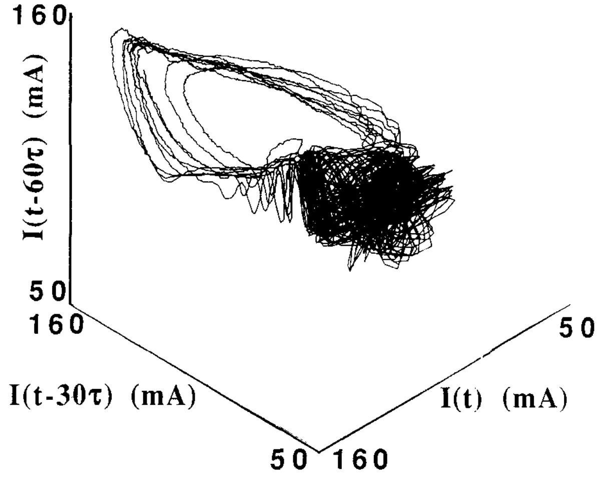

Figure 6d. Attractor (delay = 30τ, $\tau = 0.05$ ms).

Diameter = 4.0 mm, E = 0.02 V.

frequency component is represented nicely as is seen in the ball on the lower right portion of the attractor; and the slower portion of the time series is then compressed and forced to lie near the diagonal as seen in the upper left portion of the figure. If a large time delay is chosen so that the nature of the slower motion component is captured, the higher-frequency component appears to be noise; the well-shaped ball is lost. In calculating the dimension using the nearest-neighbor method, a similar trade-off must be made. Using the short time delay (as in Figure 6c), the overall dynamics of the attractor are so compressed that one calculates a dimension that is determined by the higher-frequency ball and a compressed overall attractor. Its value is around 2.7. While the large time delay is used, a value more representative of the overall attractor is obtained: $d = 3.5$.

As the electrode size was increased further, similar, but more pronounced, behavior was observed. There is again behavior at more negative potentials, which does not have a strong higher-frequency component; in addition, there is behavior at more positive potentials, which does not have this component.

Results for the next bigger electrode (diameter = 5.0 mm) are shown in Figures 7 and 8. For the lower potentials (Figure 7), the calculated dimension is around 3.3. Note in Figure 8 (representative of more positive potential) that the higher-frequency component has a larger amplitude and is somewhat less regular than that seen for the electrode of 4.0 mm in diameter (Figure 6). We again present two representations of the attractor emphasizing the higher-frequency component (Figure 8c) and the lower-frequency component (Figure 8d), respectively.

This trend continues in the next bigger electrode investigated (diameter = 5.9 mm), for which detailed results are not shown.

We also present results for the biggest electrode (diameter = 6.35 mm) investigated. Representative behavior at lower potential is shown in Figure 9. The dimension of the attractor continues to increase with increasing electrode surface area. For this attractor, a dimension as high as 5.0 was found.

The behavior at higher potential is represented in Figure 10. Again, there is a large-amplitude, higher-frequency component that can be seen in the time series of Figure 10a, particularly

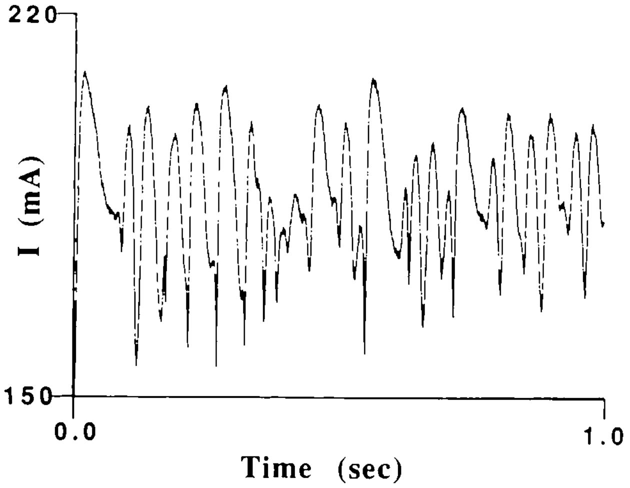

Figure 7a. Time series.

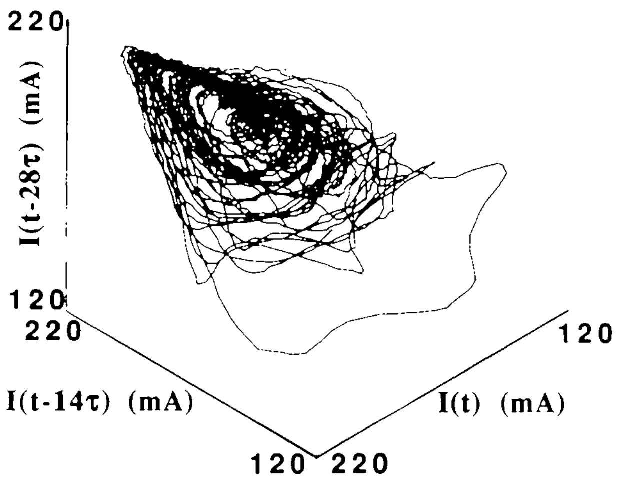

Figure 7b. Attractor ($\tau = 0.2$ ms).

Diameter = 5.0 mm, $E = -0.01$ V.

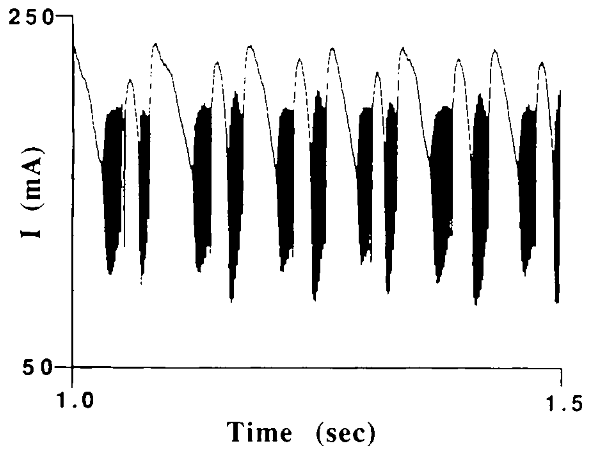

Figure 8a. Time series.

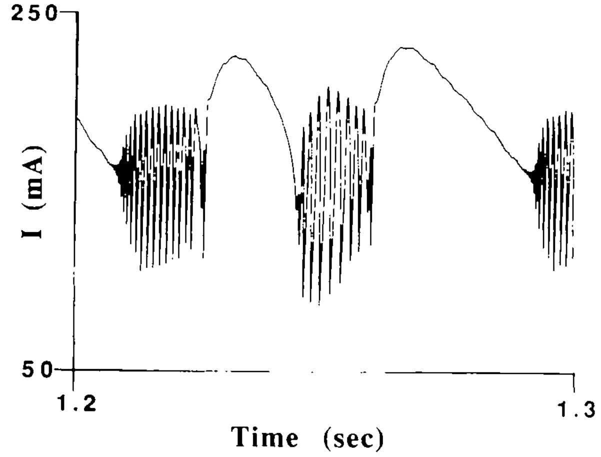

Figure 8b. Expanded time series.

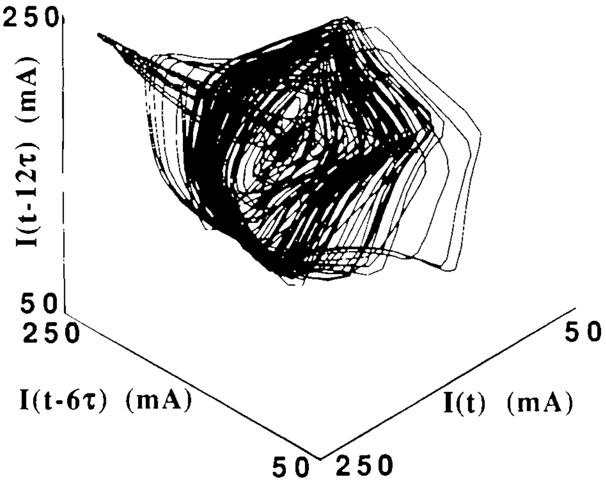

Figure 8c. Attractor (delay $= 6\tau$, $\tau = 0.05$ ms).

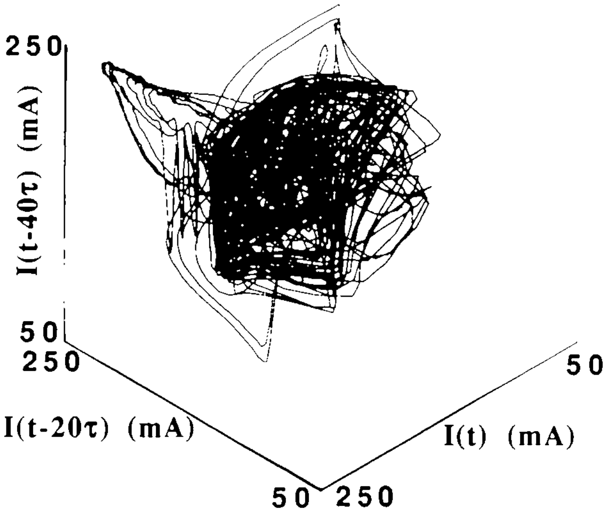

Figure 8d. Attractor (delay $= 20\tau$, $\tau = 0.05$ ms).

Diameter = 5.0 mm, $E = 0.16$ V.

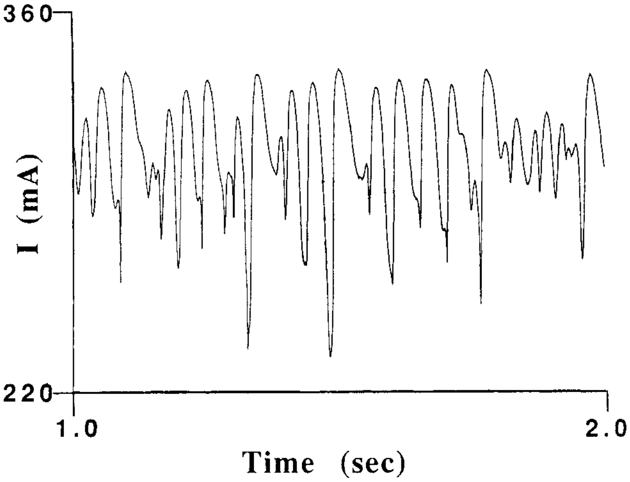

Figure 9a. Time series.

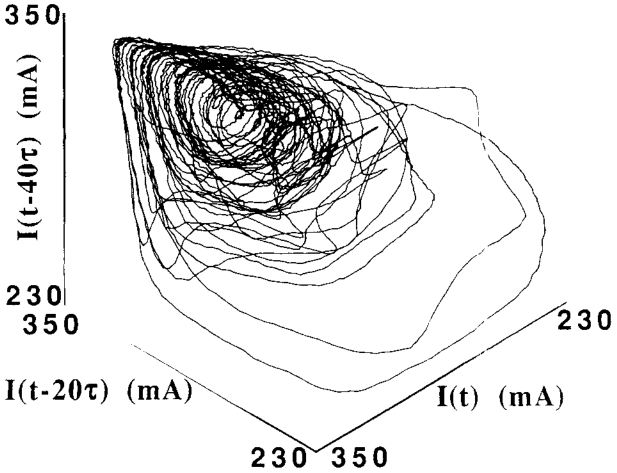

Figure 9b. Attractor ($\tau = 0.2$ ms).

Diameter = 6.35 mm, $E = 0.14$ V.

with the expanded time series of Figure 10b. The attractor made with time delays representative of the high-frequency component and the overall behavior are shown in Figures 10c and 10d, respectively.

Concluding Remarks

There are two related aspects to the results of this study. The first deals with the dynamics of chemically reacting systems. An experimental example of a progression of increasing attractor dimension (or complexity) with change in some parameter has been presented.

There are now several experimental examples of chaos in the literature on chemical reactions. These consist mainly of two types of dynamics. The first is very low-order behavior such as periodic oscillations and low-order chaos (dimension somewhat above 2.0) and transitions among them. Examples are the early studies on stirred tank reactors (Hudson et al., 1979; Roux et al., 1981) and more recent studies in electrochemistry (Hudson and Bassett, 1991). This low-order behavior is fairly well understood from a dynamic point of view. In addition, there are examples of apparent higher-order chaos in reacting systems in the literature (Razon et al., 1986). In the latter case, the dynamics are somewhat more difficult to quantify, although dimensions have been calculated. This work furnishes an example of a reacting system in which with change in a parameter, transitions can be seen not only from periodic behavior to low-order chaos, but also from low-order chaos into the higher-order chaos regime. The more complex behavior comes from the simpler (with change in a parameter) and thus additional evidence available that the observed behavior is in fact high-order deterministic chaos rather than noise, for example.

The increase in complexity can, of course, be seen qualitatively from inspection of the time series and the attractors. Moreover, it can be seen quantitatively from the increase in the calculated information dimension. This dimension is tabulated as a function of electrode diameter in Table 1. These values for the dimension are given, which are representative of

Table 1. Calculated Dimension As a Function of Electrode Diameter

Electrode Diameter (mm)	Surface Area (mm^2)	Potential (V) vs. Hg/Hg_2SO_4	Time Delay (ms)	Estimated Dimension	Sampling Rate (Hz)	Total No. of Data Points
2.4	4.52	−0.30	2.4	2.4	2,500	50,000
		−0.21	1.6	2.2	2,500	50,000
3.0	7.07	−0.20	2.6	2.6	2,500	50,000
		−0.11	2.4	2.8	2,500	50,000
4.0	12.57	−0.10	2.0	3.2	5,000	100,000
		+0.02	0.5	2.6	20,000	200,000
			1.5	3.5		
5.0	19.63	−0.01	2.8	3.3	5,000	100,000
		+0.16	0.3	2.8	20,000	200,000
			1.0	3.5		
5.9	27.34	+0.12	2.8	3.7	5,000	100,000
		+0.24	0.5	3.3	20,000	200,000
			1.0	3.7		
6.35	31.67	+0.14	4.0	5.0	5,000	100,000
		+0.33	1.0	4.0	20,000	200,000
			2.0	4.4		

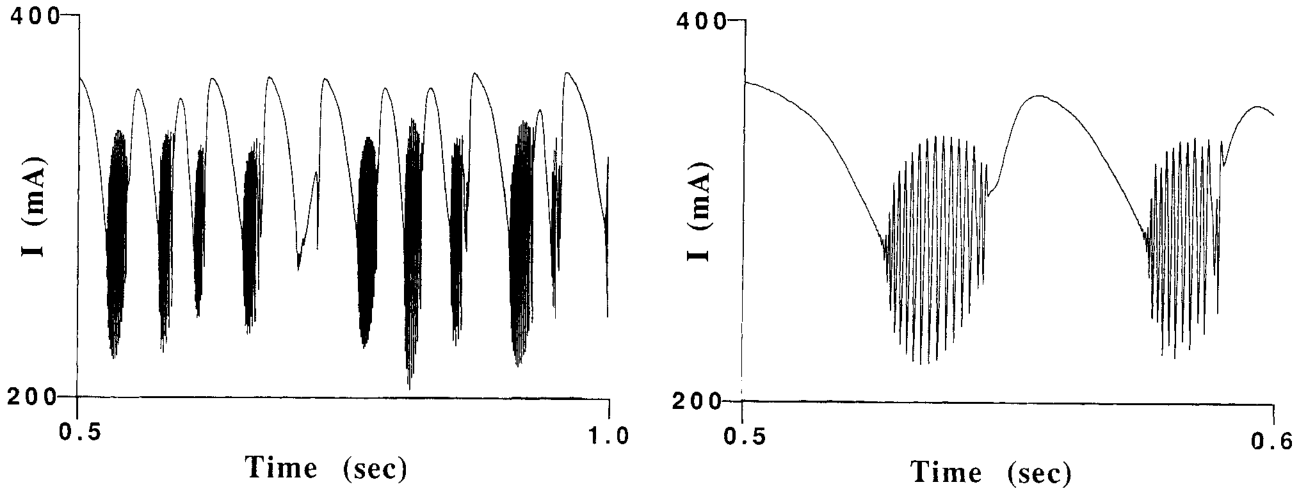

Figure 10a. Time series. **Figure 10b. Expanded time series.**

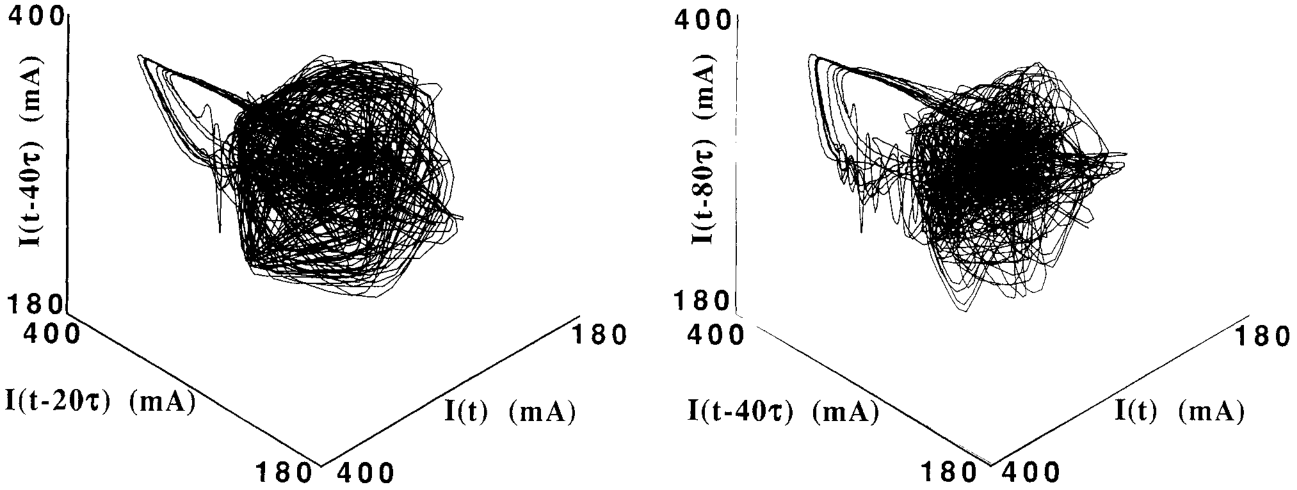

Figure 10c. Attractor (delay = 20τ, τ = 0.05 ms). **Figure 10d. Attractor (delay = 40τ, τ = 0.05 ms).**

Diameter = 6.35 mm, E = 0.33 V.

the low potential range and the high potential range for all size of electrodes. In addition, for large electrodes at the high potential, we also give the dimension value with short and long time delays, respectively. These dimensions are plotted as a function of electrode surface area in Fig. 11. We show two curves. One is the dimension at the lower end of the potential range. The second is the dimension representative of higher potentials; in the latter case, the long delay time was used in calculating the dimension for the larger electrodes. Both curves show the same trend. The increase in dimension with increasing surface area is clear. It should be noted that the calculation of dimension is not exact and that dimension values vary slightly with parameters used (Kostelich and Swinney, 1987). Nevertheless, the evidence presented above appears to be sufficiently strong to justify a claim that we are seeing transitions from periodic oscillations to low-order chaos and then to higher-order chaos, that is, an example of the "chaotic hierarchy" (Rössler, 1983; Killory et al., 1987).

The second aspect of the work is physio-chemical. It is clear, at least under the conditions of these experiments, that there is a significant change in the dynamics of a heterogeneous chemical reaction with increase in reaction surface area. As far as we know, this is the first systematically obtained experimental evidence of this phenomenon.

The reason for the dependence on surface area is not definitively understood. The current is, of course, a measure of the overall rate of reaction. There are likely variations across the surface of the electrode.

One type of nonuniformity that may play some role is the radial current distribution which is always present to some extent on a rotating disk surface; and this distribution is present even when the current is steady and will change as the electrode size is altered. The radial current distribution has been described in detail by Newman (1973). However, we are working with fairly concentrated solutions (1M H_2SO_4) near the mass-transfer-limited plateau. It is likely that under these conditions the underlying current distribution is nearly uniform. It should be noted that the surface is not perfectly smooth, and the

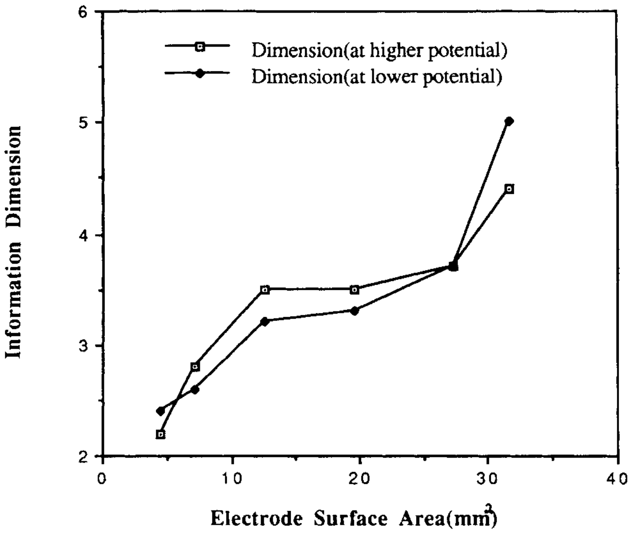

Figure 11. Dimension vs. surface area.

□, first dimension values in Table 1 for each size of the electrode; ◆, last dimension values in Table 1 for each size of the electrode

actual area is thus greater than that calculated from the known diameter.

A second possible cause of the dependence on surface area is more local in nature. During the iron electrodissolution, a film is produced on the surface. Franck (1951) has described local currents that can arise as the film grows and decays. Such surface heterogeneities, including coupling among reacting sites via migration and transport, may contribute to the effects discussed here. Through an increase in electrode size, both the number of active sites and the distances among them would be changed. If an increase in the number of interacting reacting sites does contribute to the increase in complexity, then the results would have implication for other types of surface reactions such as gas-solid catalytic reactions. Perhaps the observations are related to the coupled catalytic sites in gas-solid reactions which have been described in the literature. For example, Ertl and coworkers have investigated waves on the surface of single crystal platinum during the oxidation of carbon monoxide (Rotermund et al., 1989). Brown et al. have investigated steady-state thermal communication between two particles of supported catalyst during hydrogen oxidation (1985). Onken and Wolf have studied coupling of chemical oscillators via heat conduction (1988). Onken and Wicke observed mutual interaction of reaction rate oscillations on catalyst pellets (1989), and Jaeger et al. studied thermal coupling among three areas of a supported catalyst (1986). Schüth et al. have developed a model of thermal coupling among ten randomly-placed oscillators on a 10 × 10 matrix (1991). Tsai et al. (1988) and Ehasi et al. (1990) have studied coupling through the gas phase during CO oxidation. In a similar fashion, communication among sites on the surface of the electrode may contribute to these effects where the increase in the surface area increases complexity.

To explain the physico-chemical sources of the observations more fully, additional surface measurements will have to be made. Studies under way by several research groups should cast light on the relationships between changing surface patterns and the overall dynamics of heterogeneous reacting systems.

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