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Chaos and Spatiotemporal Pattern Formation in Electrochemical Reactions

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Abstract. Experiments on the dynamic behavior of some electrochemical reactions, with emphasis on metal dissolution, are discussed. Although patterns occur in the bistable, excitable, and periodic and chaotic oscillatory regions, we limit this presentation to the latter case. Emphasis is given to the importance of coupling of local reaction sites, in this case chaotic oscillators, in producing structure; in electrochemical systems long-range coupling often plays an important role. We discuss the use of arrays of electrodes in studying patterns and show examples of synchronization and clustering of chaotically reacting elements.

1. Introduction

Electrochemical systems exhibit a wide variety of types of dynamical behavior including bistability, periodicity, quasiperiodicity, and chaos (WOJTOWICZ, 1972; HUDSON and BASSETT, 1991; HUDSON, 1993; HUDSON and TSOTSIS, 1994; KOPER, 1996, 1998; KRISCHER, 1998; HUDSON, 1999). In the past few years spatiotemporal behavior has received considerable interest (KOPER, 1996). Spatiotemporal structures have been observed during electrodissolution processes (LEV, 1988a; HUDSON *et al*., 1994; SAYER and HUDSON, 1995; OTTERSTEDT *et al*., 1994), electrocatalytic reactions (FLÄTGEN and KRISCHER, 1995; CHRISTOPH *et al*., 1999a), and deposition processes (KRASTEV and KOPER, 1995).

Spatiotemporal patterns arise through the interaction of nonlinear reaction and coupling among reacting sites. The effect of different types of coupling has been studied numerically (MAZOUZ *et al*., 1997a; CHRISTOPH *et al*., 1999b; MAZOUZ *et al*., 1997b) and in experiments (CHRISTOPH *et al*., 1999a, 1999b; OTTERSTEDT, 1996; GRAUEL *et al*., 1998). In electrochemical systems the migration through the electric field in the electrolyte represents a strong long-range coupling between the reacting sites (FRANCK and MEUNIER, 1953). The role of different types of coupling has been explored by several investigators using small numbers, often two, of interacting electrodes (WANG and HUDSON, 1992; BELL *et al*., 1992; MUKOUYAMA *et al*., 1996; NAKABAYASHI *et al*., 1996; MATSUDA *et al*., 1997).

In this paper we stress one type of pattern formation, viz., the spatiotemporal structure that occurs under conditions in which chaotic dynamics are observed. We limit the

discussion to metal electrodissolution. Additional information on pattern formation (WOJTOWICZ, 1972; HUDSON and TSOTSIS, 1994; KOPER, 1996, 1998; KRISCHER, 1998; HUDSON, 1999) and chaotic behavior (SCOTT, 1991; HUDSON, 1989) in electrochemical systems can be found in several review papers and books. We start by describing some of the chaotic dynamics that have been observed on single, small electrodes. The dependence of the complexity of the chaotic signals on the size of an electrode (or number of electrodes in an array) is then discussed. Patterns seen on a simple electrode array configuration, a ring, are described. Finally we show how global coupling can lead to synchronization and clustering in arrays of electrodes.

This short paper is not meant to be a general review of the literature. Instead, we simply take examples of the behavior from our own publications; it should be noted, however, that related contributions from others can be found in the references. Our goal here is a modest one—to give the reader an idea of chaotic dynamics in electrochemical systems by focusing on examples on the electrodissolution of metals.

2. Chaos on Single Electrodes

Copper electrodissolution in NaCl and H_2SO_4 shows a rich variety of interesting behavior including period doubling to simple chaos, type II intermittency, windows of period three oscillations with chaotic regions (BASSETT and HUDSON, 1987), Shil'nikov chaos (BASSETT and HUDSON, 1988), quasiperiodicity, chaos on a broken torus (BASSETT and HUDSON, 1989a), and period doubling of tori (BASSETT and HUDSON, 1989b). Iron electrodissolution has also been shown to exhibit intermittent turbulence, period doubling and other periodic and aperiodic oscillations in the active/passive transition region (BENI and HACKWOOD, 1984). Galvanostatic nickel dissolution exhibits bifurcations to chaos via quasiperiodicity and via period doubling (LEV *et al.*, 1988b).

An example of a chaotic attractor obtained from a time series during an electrochemical reaction is shown in Fig. 1. The experiment was done with a single nickel electrode in 4.5 M sulfuric acid. The working electrode consisted of the end of a wire of diameter 1 mm embedded in epoxy. The potential was held constant at 1.355 V (versus $Hg/HgSO_4$) and the current measured at a data acquisition rate of 200 Hz. Additional details can be found in (KISS *et al.*, 2000).

The result shown is typical for chaotic attractors for which the dimension (information, correlation, etc.) has a value slightly over two. Such behavior can be modeled with sets of three ordinary differential equations (RÖSSLER, 1976; SCOTT, 1991). Other metal dissolution systems have also exhibited this chaotic behavior. Copper in both acid chloride media and phosphoric acid electrolytes undergoes low-order chaotic behavior (BASSET and HUDSON, 1987; ALBAHADILY and SCHELL, 1988). Iron in sulfuric acid also oscillates chaotically but the behavior is somewhat more complicated (WANG and HUDSON, 1991).

3. Increase in Complexity with Increasing Size

The surface of a reacting electrode is generally not uniform. It has been observed with the iron/sulfuric acid system that the complexity of the chaotic signals (the dimension of the attractor) increases as the size of the working electrode increases (WANG and HUDSON,

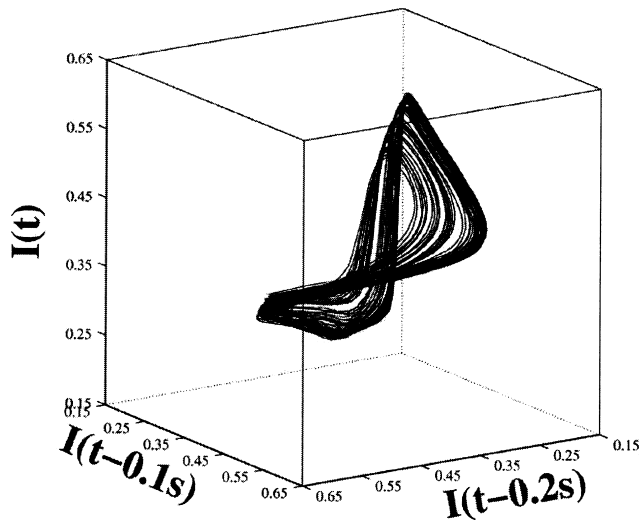


Fig. 1. Attractor constructed with the time series of a single nickel electrode (1 mm diameter) undergoing electrodissolution at 1.355 V (versus $Hg/HgSO_4$) with in 4.5 M sulfuric acid at 11°C. An external resistance of 906 ohm is used.

1991). The authors used a series of electrodes (employing a rotating disk electrode system) and showed that as the area of the electrode was increased that the behavior changed from periodic to chaotic and that further increase produced an increase in the dimensionality of the chaotic attractors.

Related experiments were later carried out with arrays of electrodes (FEI *et al.*, 1996). Rather than increasing the size of a single electrode, the number of identical electrodes in an array was increased. Sets of electrodes of diameter 0.5 mm were used and the number of electrodes is increased in steps from 1 to 61.

Results from the two types of experiments are shown in Fig. 2. The information dimension of the current signal from both the series of single electrodes and from the total current (the sum) from the arrays is presented. The total area of an array corresponds to the value given on the abscissa of the figure. Note that in both experiments that the dimension of the signal increases with the size of the reacting surface. Furthermore, it should be noted that the calculated dimension for an array and for a single electrode of the same size is approximately the same. In general, the dynamics and the spatiotemporal patterns on an array mimic those of a single electrode (FEI *et al.*, 1996) at a spatial scale of the order of the size of the entire system; of course, at a smaller scale, that of the individual electrodes of the array, the two cases differ.

4. Example of Spatiotemporal Patterns: Ring of Iron Electrodes

Experiments were carried out with the iron/sulfuric acid system using an array of electrodes in a ring configuration (FEI *et al.*, 1999). The array consists of two concentric

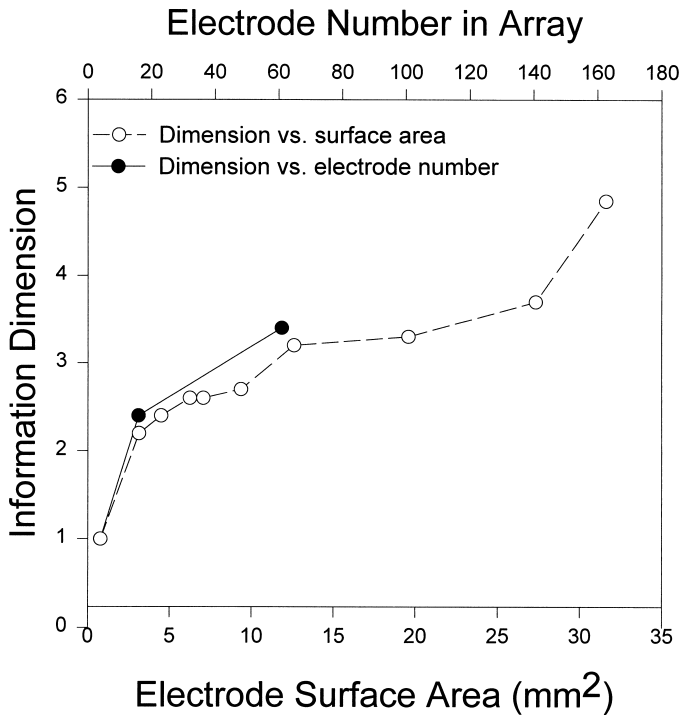


Fig. 2. Information dimension versus electrode surface area or number of electrodes in the array. The iron electrodes are undergoing potentiostatic electrodissolution in sulfuric acid. Taken from WANG and HUDSON, 1991 and FEI and HUDSON, 1998.

rings of 29 electrodes each where each individual electrode is the end of an iron wire of diameter 0.5 mm. The total current from all 58 electrodes as a function of time is shown in Figs. 3a and 3b for periodic and chaotic conditions respectively. The currents on the individual electrodes of the inner ring are shown in the figure as space/time plots. The gray scale is calibrated such that light corresponds to high current and dark to low current. Note that in both the periodic and chaotic cases the system is not homogeneous but rather spatiotemporal patterns form on the array. Other patterns on the ring can be seen in FEI *et al.* (1999).

Several investigators have used a ring-geometry in studying spatiotemporal patterns during chemical reactions. In the electrochemical field, rings have been shown to undergo a spatiotemporal period doubling (SAYER and HUDSON, 1995), exhibit rotating and modulating waves (OTTERSTEDT *et al.*, 1996). Negative coupling has been studied on these rings and has been shown to cause pattern formation (CHRISTOPH *et al.*, 1999b) and allow for remote triggering of waves (CHRISTOPH *et al.*, 1999a). In addition, studies have been carried out with gas-solid reactions on a ring. Patterns such as rotating pulses, back-and-forth swinging pulses, and alternating hot spot formation at two locations have been reported (YAMAMOTO *et al.*, 1995; LANE and LUSS, 1993; LIAUW *et al.*, 1997).

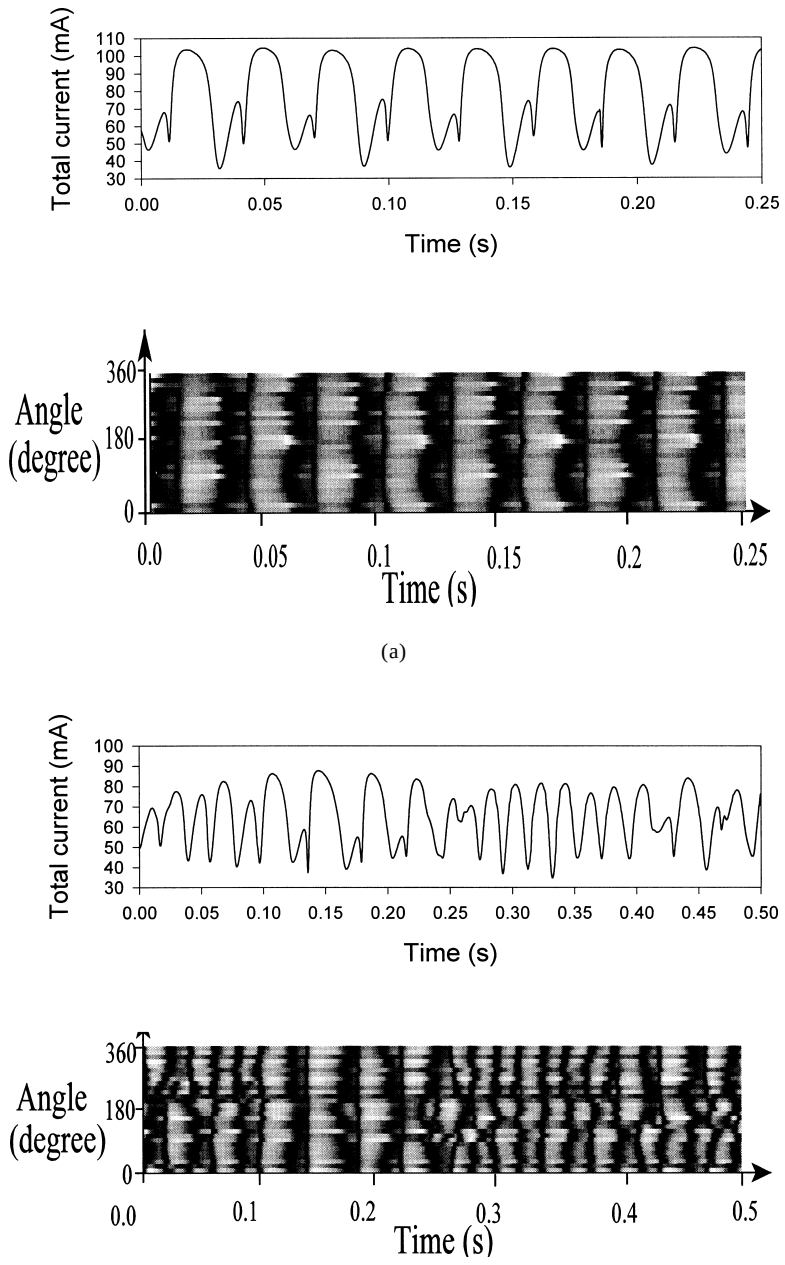


Fig. 3. Total current time series and space/time of current densities on a ring array of 29 iron electrodes during electrodissolution in an impinging jet cell. Black represents low current and white high current. Jet speed = 18 cm/s, 1 M H_2SO_4 (a) Cross-directional wave, E = –250 mV versus Hg/Hg_2SO_4 (b) Chaos, E = –300 mV versus Hg/Hg_2SO_4. Taken from FEI *et al.*, 1999.

5. Synchronization and Clustering of Globally Coupled Chaotic Electrochemical Oscillators

We now turn to studies of the effect of global coupling on the dynamics of interacting chaotic chemical oscillators.

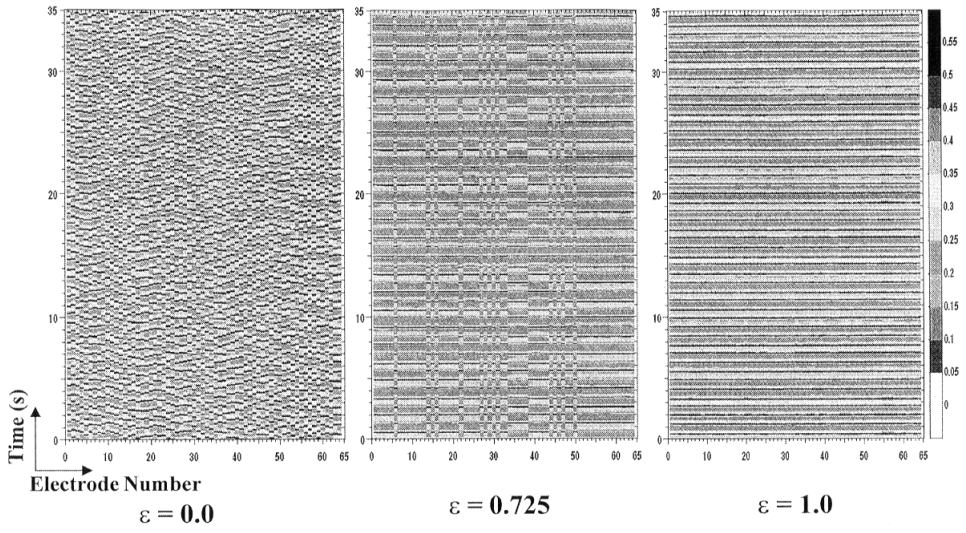
Global coupling is of major importance in many physical (KANEKO, 1990) and chemical systems (VESSER, 1993). The global nature of coupling serves as a constraint that can produce patterns. Many elegant simulation studies on global coupling of chaotic elements using maps (KANEKO, 1991) and differential equations (ZANETTE and MIKHAILOV, 1998) have been made. Fewer experimental studies have been made. An external resistance connected to the working electrode can be used to add a global coupling to an electrochemical system (OTTERSTEDT *et al.*, 1999; MAZOUZ *et al.*, 1998). However, the addition of the external resistance will generally also change other conditions such as the driving potential for the reaction. We have developed an experimental setup in which the effect of global coupling can be studied on an array of electrodes without changing other conditions (KISS *et al.*, 1999; WANG *et al.*, 2000). Altering of the degree of global coupling (and holding all other parameters constant) is done through the use of external resistors; the total external resistance is held constant while the fraction dedicated to individual currents, as opposed to the total current, is varied. In those studies we investigated arrays of two to eight (KISS *et al.*, 2000) and of 64 globally coupled chaotic (WANG *et al.*, 2000) and periodic (KISS *et al.*, 1999) oscillators.

Some results obtained with an array of 64 nickel electrodes, each of diameter 0.5 mm, are shown in Fig. 4. The electrolyte is 4.5 M sulfuric acid and a total external resistance of 906 Ohms is used. The external resistances are in parallel and series and the fraction is each can be varied so the strength of the global coupling can be varied. A parameter (ε) is defined such that $\varepsilon = 0$ for no added global coupling and $\varepsilon = 1.0$ for maximum coupling.

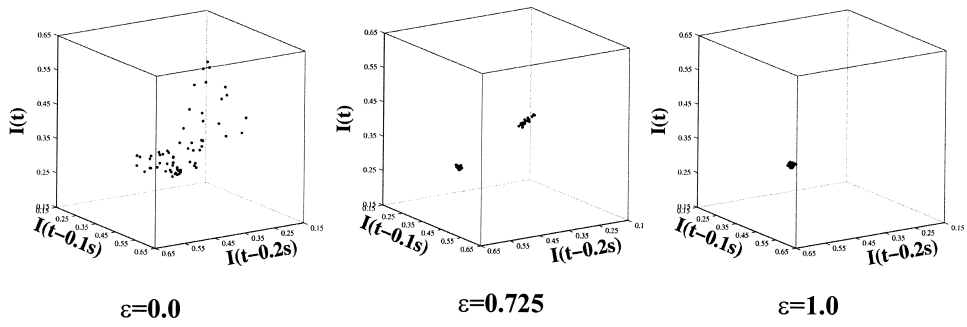
Space-time plots for the 64 electrodes are shown in Figs. 4a, 4b, and 4c for three values of the coupling parameter. Note that for $\varepsilon = 0$ (Fig. 4a) the coupling among the elements is weak. For $\varepsilon = 1.0$ (Fig. 4c) the chaotic oscillators are synchronized. At an intermediate value of the global coupling parameter ($\varepsilon = 0.725$, Fig. 4b) clusters of chaotic elements appear. The behavior is shown in Figs. 4d, 4e, and 4f in the form of snapshots. These plots are made in the same manner as the standard attractor such as that shown in Fig. 1 except that only one instant of time is shown here and all 64 elements are represented. As a function of time (such as on a video) one sees the 64 points moving about on the surface of the chaotic attractor. In Fig. 4d for no added global coupling the points are distributed about on the attractor. For maximum coupling (Fig. 4f) the elements behave almost as a single entity although there is some amount of noise and also differences since the electrodes are not exactly identical. At the intermediate coupling value (Fig. 4e) the two clusters are seen. Points in one cluster remain in that cluster. The two clusters move about the attractor, sometimes approaching very close to one another but then always separating again. Disturbances can be made to the system to cause elements to move from one cluster to the other. Additional information can be found in (WANG *et al.*, 2000).

6. Concluding Remarks

In this short paper we have tried to give the reader some idea of some of our studies on spatiotemporal patterns under chaotic conditions in electrochemical systems. Obviously



(a)



(b)

Fig. 4. An array of 64 nickel electrodes undergoing electrodissolution at the same conditions as in Fig. 1 with an equivalent external resistance of 906 ohm at different global coupling strengths. (a) Space/time plot of the local currents; dark corresponds to high current, light to low current, (b) Snapshots in state space of each of the elements obtained from the current and two time delays. Position represents the state of the element. Taken from WANG *et al.*, 2000.

this is not a complete review of the field. Additional information can be found in the references cited in this paper. Furthermore, the dynamic behavior of electrochemical reactions has been studied recently by several investigators. Many of these investigators, including Nakato, Krischer, Eiswirth, and Strasser, are present at this symposium and are presenting their work in this volume. Other research groups of course consider spatiotemporal patterns in liquid phase reactions and in gas-solid systems.

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