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Control of chaos in an electrochemical cell

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We report control of chemical chaos observed during the electrodissolution of a rotating copper disk in a sodium acetate–acetic acid buffer. An adaptation of a simple recursive proportional-feedback control strategy, generally applicable to systems well described by one-dimensional maps, was used to stabilize the chaotic response of the system on an unstable period-1 orbit. The successive minima in the measured anodic current generated a return map that was used to characterize the dynamics and the control algorithm prescribed small changes in the anodic potential to affect the control.

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Chaotic oscillations of nonlinear deterministic systems are ubiquitous and many unstable periodic orbits are distributed throughout the chaotic attractor of such systems. The possibility of deliberately selecting and stabilizing a particular periodic orbit, by methods based on work by Ott, Grebogi, and Yorke (OGY) [1], and the flexibility of using the chaotic attractor as a path from one controlled periodic orbit to another have been demonstrated in many numerical simulations [1–5] and in several real systems [6–9]. While many control applications focus on stabilizing a fixed steady state, these new flexible control strategies for stabilizing periodic orbits are worthy of consideration for practical application. A spectacular illustration of the possibilities is the very recent report [9] of stabilizing chaotic arrhythmias of a rabbit heart, in real time, using methods based on the general OGY algorithm.

We report here the stabilizing of an unstable periodic orbit in an electrochemical system exhibiting chaos. As suggested by Petrov, Peng, and Showalter [4], the control of chemical chaos is of particular interest not only because there may be practical applications to chemical systems themselves but also because of the possible implications for the dynamics of biological systems. The primary control strategy used in this work was a version of the recursive proportional-feedback (RPF) algorithm developed recently by Rollins, Parmananda, and Sherard [5]. The algorithm is simple to apply and is generally applicable to highly dissipative systems that are well described by measurements of a one-dimensional return map of a single variable. The RPF algorithm is based on the OGY method as modified by Dressler and Nitsche [3].

The experimental system consisted of a three-electrode electrochemical cell that was used to study the electrodissolution of copper [10,11]. The anode was a rotating copper disk (5 mm diameter) shrouded in a rod of Teflon. The supporting electrolyte solution was a mixture of 60 parts glacial acetic acid to 35 parts $2M$ sodium acetate. The potential of the anode was measured relative to a saturated Calomel reference electrode and the cathode was a 2.5-cm^2 platinum foil disk. The emf of the circuit was continuously adjusted by a potentiostat to maintain the desired set value of the anodic potential (the potential between the anode and the reference electrode). We used the anodic potential as our control parameter and collected the time-series data of the anodic current (the current between the anode and the cathode). A schematic of the experimental setup is presented in Fig. 1 and more details are provided in Refs. [10,11]. The set point for the anodic potential could be adjusted by computer interface with the smallest increment being 0.1 mV.

For the range of parameter values of interest in this work, the electrochemical system exhibits a sequence of mixed-mode oscillations separated by bands of chaotic behavior as a function of anodic potential. Mixed-mode oscillations are defined as a series of large- and small-amplitude oscillations with a range of intermediate amplitudes unrealized [12]. The region chosen for attempting control was the chaotic intermediate region between a period-1 (1^0) state (large amplitude oscillation only)

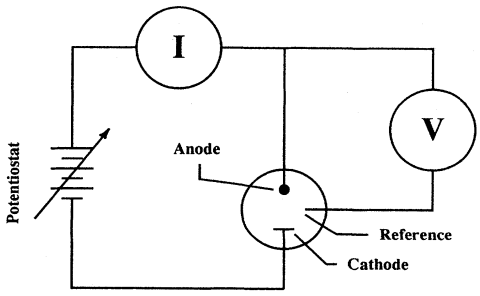

FIG. 1. Schematic representation of the three-electrode electrochemical cell used for controlling chemical chaos. V is the anodic potential and I is the anodic current. The potentiostat adjusts the emf to hold V at the desired set value.

and a period-2 (1^1) state (alternating one large- and one small-amplitude oscillation). The time period for large-amplitude oscillations was about 2.0–4.0 sec with the current ranging between 2 and 6 mA. For a fixed rotation rate (~2000 rpm), the chaotic behavior was observed over a range in anodic potential of about 8–12 mV centered at about 720 mV, bounded below by 1^1 and above by 1^0 behavior. When implementing control, the anodic potential was set near the middle of this range. Since changes in the anodic potential during control were usually less than 0.5 mV, it was ensured that the system was not simply shifted to the period-1 regime.

Two different proportional-feedback control strategies were tried. A simple proportional-feedback strategy for systems described by one-dimensional return maps [2, 4] was found not to work unless the proportionality constant was adjusted far away from its expected value. We were much more successful when a recursive proportional-feedback control strategy [5] was used. We denote the nth minima in anodic current as I_n. According to the RPF algorithm, control is established by adding an increment to the anodic potential during the nth cycle given by

$$\delta V_n = K(I_n - I_F) + R\delta V_{n-1}, \tag{1}$$

where I_F is the unstable fixed point of the target orbit for the return map obtained for a time series taken at $V = V_0$. The constants K and R are determined from measurements of return maps, as explained below.

The precontrol procedure used to determine K and R consisted of two steps. First the system was fixed at a certain rotation rate and anodic potential (V_0) to obtain the desired chaotic behavior, and the return map I_n versus I_{n-1} was measured. Then, using the points near the line of identity ($I_{n-1} = I_n$) the fixed point I_F and the slope μ of the return map at the fixed point were determined using a linear least-squares fit. The second step consisted of measurements that described the response of the system to *changes* in anodic potential. A sequence of anodic current minima, I_n, was measured while repeatedly alternating the anodic potential up to $V_0 + \Delta V$ for one cycle and then back to V_0 for the next cycle (ΔV was typically 0.3 mV). Alternate pairs (I_{n-1}, I_n) taken from this measured sequence lay on two maps. From these two maps, the fixed points I_F^u and I_F^b of the up and back maps were determined, and were then used to calculate constants g_u and g_b defined by

$$g_u = \frac{I_F^u - I_F}{\Delta V} = \frac{\Delta I_F^u}{\Delta V}, \tag{2}$$

$$g_b = \frac{I_F^b - I_F}{\Delta V} = \frac{\Delta I_F^b}{\Delta V}. \tag{3}$$

Finally, using g_u and g_b and slope μ from the first part, the control constants K and R were calculated from the relations derived in Ref. [5],

$$K = \frac{\mu^2}{(\mu - 1)(\mu g_u + g_b)}, \tag{4}$$

$$R = \frac{-\mu g_b}{(\mu g_u + g_b)}. \tag{5}$$

Typically these control constants K and R could be determined within 10 min (corresponding to approximately 200 cycles of the experimental return map) from the start of data acquisition. With these control constants available, the control algorithm could be initiated.

When the control algorithm was activated, the anodic potential V was changed according to the RPF algorithm of Eq. (1) whenever a minimum of the anodic current I_n came within 0.2 mA of the measured fixed point I_F. During successful control, the anodic current executed a period-1 oscillation with minima typically remaining within 0.025 mA of the unstable fixed point I_F. When the control was shut off the system moved away from the fixed point along the return map reverting to chaotic behavior within a few cycles.

Figure 2 shows the anodic current minima plotted versus time for a time interval when the control is turned on and off and then back on again. The control signal is also shown to illustrate the small corrections needed to keep the system stabilized. We note that the corrections in the control signal are less than 0.05% of the applied anodic potential. Figure 3 shows the return map for the uncontrolled chaotic system together with the controlled period-1 orbit obtained while the control was activated. Figure 3 also shows that the full return map is not visited by the system but rather the points tend to fall in chaotic bands. This was a property typical of the return maps we measured in this chaotic regime. Figure 4(a) shows the uncontrolled chaotic attractor projected onto a plane in phase space reconstructed by the method of time delays using time-series measurements of the anodic current [13]. Figure 4(b) shows the reconstructed trajectory while control is on.

As a result of the banded nature of the chaos it was sometimes difficult to obtain the value for I_F^b and thus g_b during the oscillatory part of the precontrol procedure. It then became necessary to use an estimate for the value of g_b in the calculation of K and R. From the experience gained in previous trials, it was found that ΔI_F^b was a

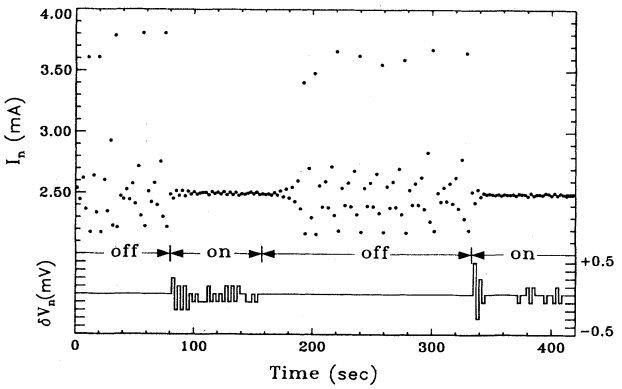

FIG. 2. The minima in anodic current plotted continuously over a time period during which the control algorithm is switched on and off and then back on again. The perturbations added to the anodic potential to maintain control are shown in the bottom graph. The rotation rate is 2000 rpm, the anodic potential with control off is $V_0 = 0.720$ V, and the proportionality constants used for the RPF control algorithm are $K = -5.90$ mV/mA and $R = -0.196$.

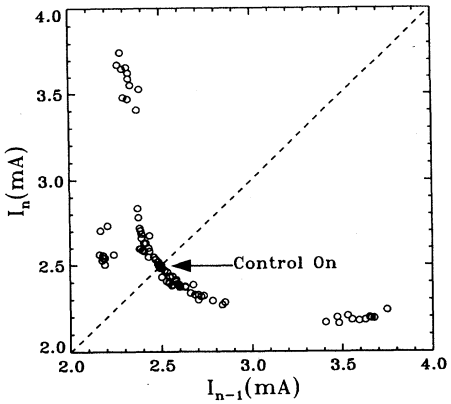

FIG. 3. The return map (open circles) obtained using minima in the chaotic time series of anodic current shown in Fig. 2. The superimposed filled circles are the minima in anodic current while the control algorithm was implemented.

small negative number around -0.005 mA. The typical value for ΔI_F^u was found to be about -0.02 ± 0.006 mA. There were also large uncertainties in the calculation of the slope of the return map at the fixed point and the initial attempt at control was not always successful. However, in such cases we were able to repeat the precontrol procedure and obtain values for K and R that would successfully control the desired period-1 oscillation. We were also successful in obtaining control when the precontrol procedure failed, by varying the parameter g_b, while attempting control until successful stabilization occurred.

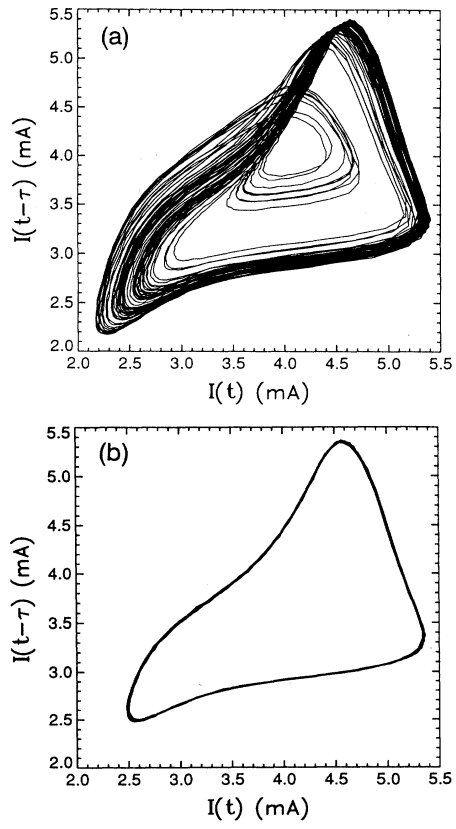

FIG. 4. (a) The reconstructed chaotic attractor in the embedding phase space from the time series of Fig. 2 using a delay time of 120 msec. (b) shows the trajectory while the control is being implemented.

We also attempted to use the simple nonrecursive proportional-feedback control algorithm as proposed by Peng and co-workers [2, 4]. The change in anodic potential required to establish control using this method is given by $\delta V_n = K'(I_n - I_F)$, where $K' = \mu/((\mu - 1)g)$, μ is the slope of the return map at the fixed point $I_{n-1} = I_n = I_F$, $g = \Delta I_F/\Delta V$, and ΔI_F is the shift in the fixed point when the control voltage is incremented from V_0 to $V_0 + \Delta V$ and held constant. For $\Delta V = 1$ mV (which was more than three times the ΔV used in the oscillations of the RPF precontrol procedure) there was no measurable change in the fixed point for the period-1 orbit; therefore $g \approx 0$. This made a meaningful determination of K' experimentally impossible. We were able to establish control using the simple algorithm, but the value of K' required was much smaller than expected from the μ and g measurements. For this reason, we used the RPF algorithm as described above.

A sum rule $g_u + g_b = g$ [Eq. (7) of Ref. [5]] connects the RPF with the simple proportional-feedback control technique. In our case, for the sum rule to hold, g_u and g_b would have to be of approximately equal magnitude but of opposite signs. This is contrary to our experimental observations where typical values for g_u and g_b were -70 ± 20 (mA/V) and -15 ± 20 (mA/V), respectively. In fact, whenever the values of g_u and g_b were chosen such that sum rule was satisfied, the control was unsuccessful. This discrepancy remains unresolved. Our measurements showed that the system responds differently to repeated changes (oscillation) of the anodic potential than it does to a static change. Since repeated changes are necessary when the control is applied, it is important to know how the system reponds to dynamic changes in the control parameter when developing a control strategy. The procedure used in implementing the RPF algorithm takes this into account.

In summary, we have stabilized a period-1 orbit from chaotic oscillations in the anodic current during the dissolution of a copper anode in an electrochemical cell. A recursive proportional-feedback algorithm was most effective. A nonrecursive algorithm would also work, at least in some cases, but the proportionality constant required was not the expected value. We plan to investigate the application of these control algorithms to other electrochemical systems known to exhibit chaos. Experiments to achieve control on higher periods and to stabilize the system on a fixed steady state are also underway.

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