Resonant Control of Electrochemical Oscillations

P. Parmananda,* M. Rivera, and R. Madrigal

Facultad de Ciencias, UAEM, Av. Universidad 1001, Col. Chamilpa, Cuernavaca, Morelos, México

I. Z. Kiss and V. Gáspár

Institute of Physical Chemistry, University of Debrecen, H-4010 Debrecen, P.O. Box 7, Hungary

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We report experimental control of complex (periodic and chaotic) oscillatory dynamics in an electrochemical system by applying a nonfeedback control method. By choosing an appropriate frequency for the periodic modulation of an accessible control parameter (e.g., circuit potential) not only are the chaotic dynamics converted to regular periodic behavior (controlling chaos) but also the character of the oscillatory dynamics is altered (for example, $1^1 \rightarrow 1^0$). This is different from previously reported experiments involving simple entrainment of oscillatory dynamics, since in our experiments the frequency of sinusoidal modulation is chosen such that the existing unstable dynamics are targeted and subsequently stabilized. Consequently, the maximum amplitude of the control signal is less than ±5% of its base value. Since resonant control strategy can be easily implemented without a complicated precontrol procedure it seems relevant for applications to real systems.

I. Introduction

Due to advances in the field of nonlinear dynamics, interest in electrochemical oscillations has been renewed during the past decade. Nonlinear phenomena typical of deterministic systems such as multistability, simple, and mixed-mode oscillations, period-doubling bifurcations and chaos have all been observed in electrochemical processes. These include both anodic and cathodic reactions under potentiostatic or galvanostatic conditions.[1]

Despite the prevalence of chaos in electrochemical processes most of the experiments, even today, are designed to avoid parameter regimes where the system may exhibit such unpredictable behavior. However, with the advent of several different algorithms for controlling chaos it has been realized that operating a dynamical system in a chaotic regime may even be advantageous: controlling chaos allows one to target any of the unstable periodic orbits (or steady states) embedded in a chaotic attractor.

The idea of controlling chaos by a *feedback technique* was introduced by Ott, Grebogi, and Yorke (OGY).[2] In this control method, small perturbations are applied to a control parameter. The motion of the system in the phase space of the dynamical variables is monitored on a Poincaré section of the chaotic attractor. When the trajectory crosses this section, the size of perturbation is calculated according to the OGY-formula, and the required feedback is applied for the next cycle. In practice, there is always a small error in targeting, therefore the procedure is repeated over and over again at every cycle. As a result of these feedback perturbations, the system is stabilized on one of the originally unstable periodic orbits embedded in the chaotic attractor. The OGY-algorithm and its variations[3−5] have been successfully applied to convert chaotic behavior to simple periodic responses in various experimental systems.[6−11]

Interestingly, before the OGY method Hübler and Lüscher[12] and Lima and Pettini[13] independently proposed a *nonfeedback technique* of stabilizing a chaotic system toward a desired periodic state. In this perturbative method, which we shall call *resonant control strategy* (RCS)[12,14] the periodicity of the perturbations is fixed by the frequency of the modulated control signal. The effects of such parametric perturbations was first studied experimentally by Azevedo and Rezende[15] with a system of spin waves excited by microwaves. In their pioneering experiments, they demonstrated that a synchronization mechanism between a chaotic attractor and a periodic perturbation could be considered as a reliable control method.

Since RCS can be easily implemented without a complicated precontrol procedure, it is an experimentally less demanding method than OGY. Still, there have been few applications reported only. One reason for this could be that the RCS technique requires a suitable scan over a large frequency band in order to identify the forcing frequencies leading to a global periodic behavior of the system. Recently, the RCS technique has been applied for controlling unstable periodic orbits orbits in a single mode CO_2 laser[16,17] and the Belousov−Zhabotinsky (BZ) reaction in a well-stirred open reactor.[18] In the BZ experiments, the superimposed perturbation was the sinusoidally modulated electric current (AC) acting on a platinum working electrode.

So far the RCS technique has not been tested on chaotic electrochemical systems. It is quite puzzling, since the experimental procedure is much the same as that used for impedance measurements.[19] Impedance spectroscopy has been widely applied to explore the kinetics of electrochemical reactions and to study the stability of steady states of electrochemical cells.[20,21] Generally, the circuit potential of a stable cell (showing steady-state behavior) is perturbed with sinusoidal signals of small amplitude, while the amplitude and phase of the response current is measured. The effect of sinusoidal potential perturbation on the active-passive transition has been studied by Sazou et al.[22,23] Also, the entrainment of simple oscillatory dynamics by periodic forcing has already been observed.[24,25] However, the effect of

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small sinusoidal potential perturbations on electrochemical systems with inherent chaotic dynamics has not been studied so far.

In this paper, we apply the RCS technique for taming the aperiodic current oscillations observed during the anodic dissolution (corrosion) of copper in an acidic medium. This is clearly different from the previously reported experiments,[22−25] since in our experiments the frequency of sinusoidal modulation is chosen such that the existing unstable dynamics are targeted and subsequently stabilized.

This article is organized as follows. First a brief description of RCS is presented, then the results from the application to an experimental electrochemical system are presented along with a discussion. Our experiments include (a) control of chaotic behavior via conversion to periodic states and (b) changing the character of complex, mixed-mode periodic behavior without shifting the system to a new regime of system parameters.

II. Resonant Control Strategy

We consider a dynamical system which is described by a general set of differential equations:

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}(t),\mathbf{p}) \tag{1}$$

where $\mathbf{x} = (x_1, x_2, x_3, ..., x_n)$ are the system variables and $\mathbf{p} = (p_1, p_2, p_3, ..., p_m)$ are the bifurcation (control) parameters. Depending on the values of these parameters, a given system may exhibit a wealth of dynamical responses such as steady state(s), periodic or chaotic oscillations, etc. A discontinuous transition between these states is called bifurcation, and the map showing the location of different dynamical states in the parameter space is the bifurcation diagram of the system. Our goal is to control the chaotic behavior without changing the position of the system in the bifurcation diagram.

Considering that in our electrochemical experiments there exist an easily measurable system variable x_1 (e.g., the anodic current) and an easily accessible control parameter p_1 (e.g., the anodic potential), the bifurcation diagram of the system is readily available. To control chaos, the bifurcation (control) parameter is continuously perturbed such that

$$p_1(t) = p_1(0) + \gamma \sin(2\pi\upsilon t) \tag{2}$$

where $p_1(0)$ is the initial value of the parameter in the unperturbed system. The term $\gamma\sin(2\pi\upsilon t)$ is a sinusoidal modulation of the control parameter, where γ and υ are the amplitude and frequency of perturbations. The optimal value of υ can be determined from the Fourier spectra of time-series current data measured in the unperturbed system.

It is important to point out that, despite of the continuous and time-dependent perturbations, the system never moves out of the chaotic range of the bifurcation diagram. This is reflected by the fact that the time average of $p_1(t)$ over a full cycle is equal to $p_1(0)$ because of the sinusoidal character of perturbations. As the results in the following section indicate, after switching "off" the control, the system always reverts back to executing the initial unperturbed behavior.

III. Experimental Results

The experimental system was an EG&G Princeton Applied Research Model K60066 three-electrode electrochemical cell set up to study the potentiostatic electrodissolution of copper in acetate buffer[26] under ambient temperature (295−300 K) and with no external resistor in the circuit.[27] The anode is a rotating copper disk (5 mm diameter) shrouded by Teflon. The electrolyte is an acetate buffer: a mixture of 70 cm^3 glacial acetic acid and 30 cm^3 of 2 mol dm^{-3} sodium acetate. The anodic potential is measured relative to a saturated calomel reference electrode (SCE), while the cathode is a platinum foil disk (2.5 cm^2 area). Under potentiostatic conditions, the circuit potential is continuously adjusted by a potentiostat (EG&G Princeton Applied Research Model 362) to maintain a desired set value of the anodic potential V, and the anodic current I is measured between the anode and cathode. Time series current data are collected and stored in a computer by sampling the anodic current with a data-acquisition card (sampling frequency is 25 Hz). In all reported experiments the anodic potential was held constant at $V(0) = 0.720$ V. The rotation rate has been varied to move the unperturbed system to different locations in the bifurcation diagram, that is to arrive at the desired dynamical behavior, which then will be controlled by the continuous perturbations.

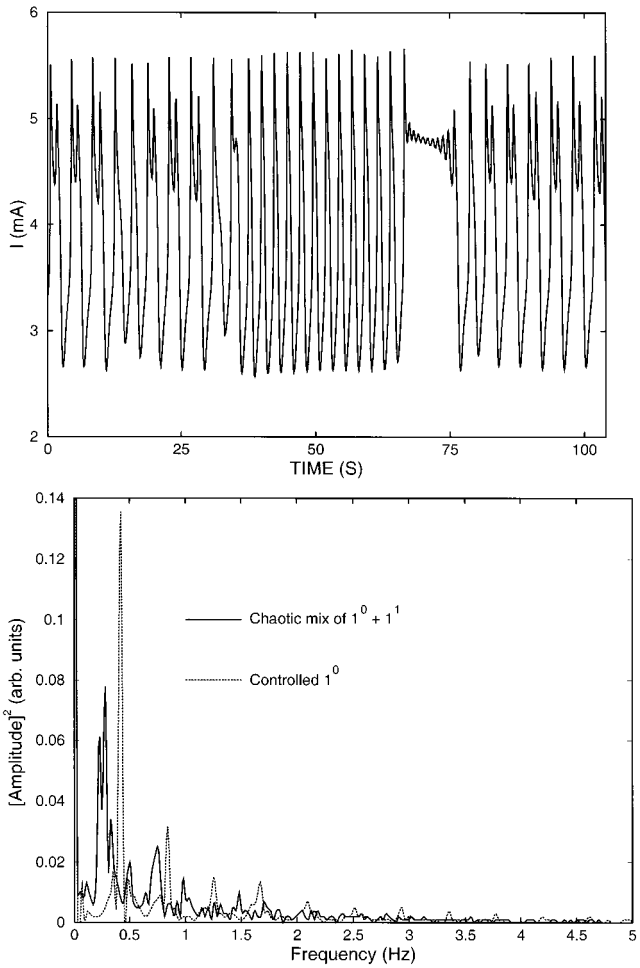

Figure 1. (a) Control of 1^0 periodic orbit in the copper/acetic acid electrochemical system exhibiting ($1^0 + 1^1$) type mixed-mode (chaotic oscillations). The rotation rate is 1700 rpm, while the anodic potential $V(0)$ is 0.720 V. The anodic current is plotted over a period during which control is switched off, on, and off again. The control parameters are $\gamma = 20$ mV and $\upsilon = 0.36$ Hz. (b) Fourier-spectra from the timeseries corresponding to the chaotic timeseries (solid) and the controlled 1^0 orbit (dashed).

At 1700 rpm (rotation rate of the anode: rotating copper disk), the uncontrolled electrochemical system exhibits chaotic current oscillations (Figure 1). The observed dynamics is a chaotic mix of the adjacent periodic windows, 1^0 and 1^1 in the bifurcation diagram.[26] To characterize the dynamics of a periodic window we apply the standard L^S notation, where L indicates the number of large amplitude oscillations followed by S number of small

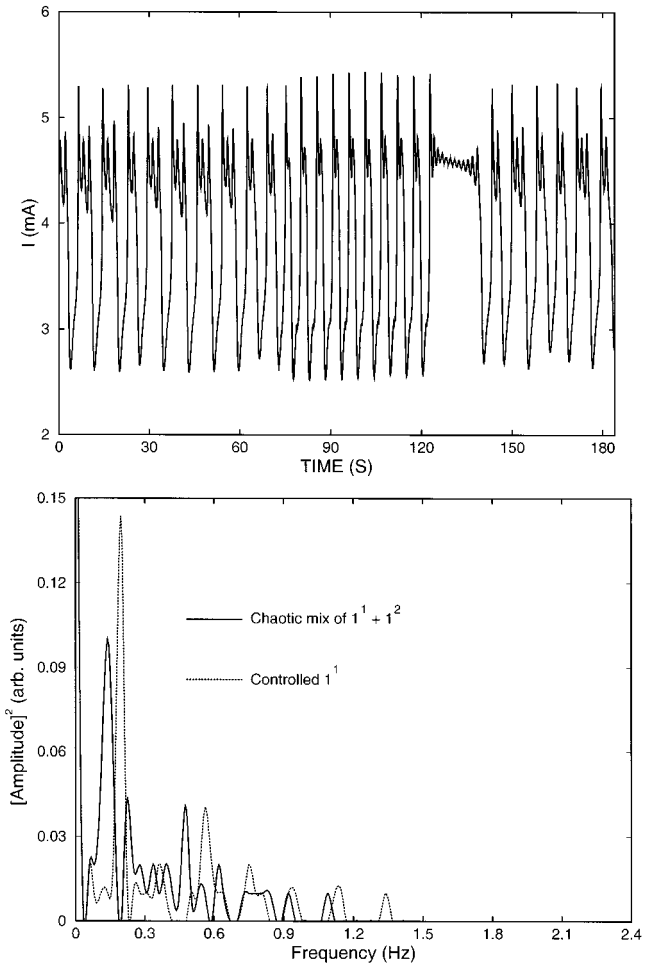

Figure 2. (a) Control of 1^1 type periodic orbit in the electrochemical system exhibiting ($1^1 + 1^2$) type mixed-mode (chaotic oscillations). The rotation rate is 2400 rpm, while the anodic potential $V(0)$ is 0.720 V. The anodic current is plotted over a period during which control is switched off, on, and off again. The control parameters are $\gamma = 16$ mV and $\upsilon = 0.14$ Hz. (b) Fourier-spectra for the timeseries corresponding to the chaotic timeseries (solid) and the controlled 1^1 orbit.

amplitude oscillations. The chaotic nature of the mixed orbit ($1^0 + 1^1$) has been justified by determining the largest Lyapunov-exponent of the attractor, which was found to be 0.21 bits/s, a positive value. Figure 1b shows the Fourier spectra for the time series in Figure 1a. From inspection, the highest peak in the Fourier-spectrum of the unperturbed system is $\upsilon = 0.28$ Hz. It has been found, however, that control of 1^0 oscillations is possible only with a slightly larger frequency of 0.36 Hz. Note that at this frequency there also exists a peak in the Fourier spectrum of the uncontrolled system. It can be seen, however, from the short timeseries we analyzed (Figure 1a) that the 1^0 behavior occurs less frequently, and, therefore, it is not the highest peak in the spectrum. The sinusoidal control is turned on at $t = 30$ s by continuously perturbing the anodic potential $V(t)$ according to the following control formula:

$$V(t) = V(0) + \gamma \sin(2\pi\upsilon t) \qquad (3)$$

The applied values of γ and υ are given in the figure caption. The value of γ has been chosen such that the maximum perturbation is less than 3% of the base value $V(0)$. This rule applies to all reported experiments. As a result of the superimposed periodic signal, the chaotic oscillations are transformed to 1^0 type oscillations (Figure 1a). When control is turned off at $t = 70$ s, the system moves away from the simple periodic

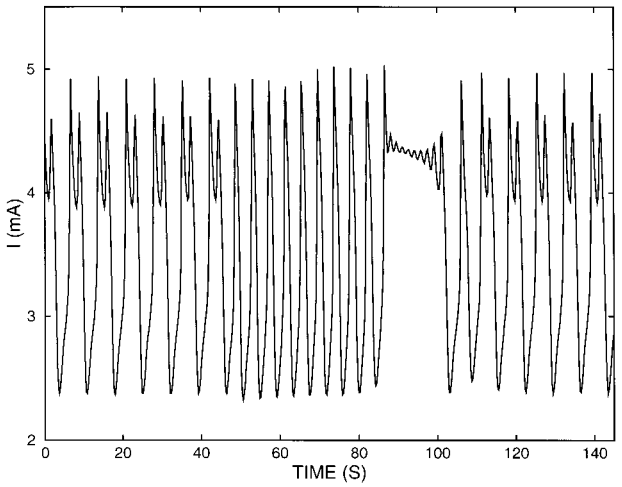

Figure 3. Stabilization of 1^0 type periodic orbit in the electrochemical system exhibiting (1^1) type mixed-mode oscillations. The rotation rate is 2000 rpm, while the anodic potential $V(0)$ is 0.720 V. The anodic current is plotted over a period during which control is switched off, on, and off again. The control parameters are $\gamma = 15$ mV and $\upsilon = 0.28$ Hz (obtained from the spectra of Figure 1b).

dynamics, and after a short transient period (approximately 25 s) the system reverts to executing the original mixed-mode chaotic oscillations. Note that the frequency of the controlled orbit (0.4 Hz) is very close to the frequency applied for perturbations (0.36 Hz), which indicates that, indeed, the control is achieved by true resonance.

At a higher rotation rate (2400 rpm) the unperturbed electrochemical system exhibits a chaotic mix of $1^1 + 1^2$ type current oscillations. The largest Lyapunov exponent for this chaotic attractor has been found to be a bit higher value, 0.26 bits/s. Figure 2b shows the Fourier spectra for the time series in Figure 2a. From inspection, the highest peak in the Fourier transform is determined to be $\upsilon = 0.14$ Hz. We have chosen this frequency for the resonant control according to eq. 3. The fact that the frequency of the controlled orbit (0.2 Hz) is a bit higher than that of the perturbations indicates that RCS is a very robust method. It can work even if the control frequency does not exactly match the frequency of the desired orbit. During control (between 70 and 125 s), the chaotic oscillations are converted to 1^1 oscillations (Figure 2a). When control is turned "off", the system moves away from the 1^1 response and reverts back to executing chaotic oscillations again.

Using frequencies obtained from the Fourier-spectra shown in Figures 1b and 2b the periodicity of some regular oscillatory dynamics (occurring at rotation rates given in Figures 3 and 4) could also be changed. Figure 3 shows, for example, how the simple 1^1 type oscillations can be converted to a 1^0 type response by sinusoidal perturbations according to eq 3. Again, when control is turned off the system moves away from the 1^0 orbit and reverts to executing 1^1 type oscillations again. Figure 4 shows the transformation of the unperturbed 1^2 dynamics to a 1^1 type oscillations by appropriate sinusoidal perturbations.

The experimental system shows mixed mode oscillations.[26] A typical experimental bifurcation diagram[26] obtained by varying a system parameter (rotation rate) exhibits alternating windows of periodic and chaotic dynamics. Using resonant control not only were be able to stabilize the target state in the chaotic windows of the bifurcation diagram but were also able to obtain control on the desired orbit when the natural dynamics were moved to the adjacent periodic windows (for example (Figure 1, Figure 3) and (Figure 2, Figure 4)). To reiterate, appropriate target dynamics could be stabilized for an extended

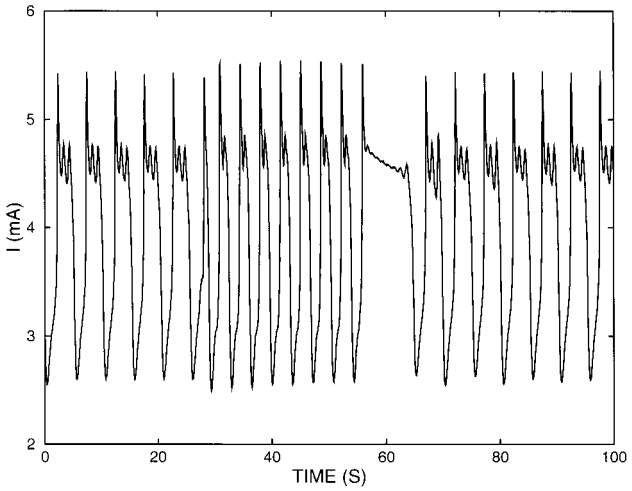

Figure 4. Stabilization of 1^1 type periodic orbit in the electrochemical system exhibiting (1^2) type mixed-mode oscillations. The rotation rate is 2800 rpm, while the anodic potential $V(0)$ is 0.720 V. The anodic current is plotted over a period during which control is switched off, on, and off again. The control parameters are $\gamma = 24$ mV and $\upsilon = 0.14$ Hz (obtained from the spectra of Figure 1b).

region of parameter space and not just for arbitrarily chosen system parameters.

All the results reported in the above section were robust to experimental noise. Apart from the natural drift all the control parameters regulating the electrochemical cell were well controlled and remained constant. This natural drift of the chemical dynamics at times resulted in the failure of the RCS in attaining target dynamics. In that case the appropriate tuning (perturbation) frequencies had to be recalculated.

IV. Discussion

Up until recently, most experimental reports on control of complexity have employed elegant yet sometimes hard-to-implement feedback strategies with complicated pre-control procedures. Using simple sinusoidal forcing (a nonfeedback method) to suppress deterministic complexity involves entrainment of the natural chaotic dynamics. In this article, we tested the so-called resonant control strategy, which besides being robust to experimental noise, has the advantage of calling for an extremely simple pre-control procedure that can be done on-the-fly as data are being acquired.

Our experiments involved corrosion of metal surfaces under electrochemical conditions. Our results indicate that resonant forcing can indeed be successfully applied to convert chaotic dynamics to periodic dynamics of lower complexity in dissipative electrochemical systems and that resonance between the oscillatory (either periodic or chaotic) system and the periodic perturbation might occur at certain frequencies. These frequencies correspond to the dominant peaks in the Fourier spectrum of the current of the *unperturbed* system. In addition, using the information from the Fourier-spectra of the low-dimensional chaotic systems as a first order estimate for the frequency the periodicity of some complex periodic motion can also be altered. Including Fourier analysis into the procedure thus eliminates the need for scanning a large frequency band so that the control procedure can be easily automated for real-world applications.

Clearly, the superimposed sinusoidal perturbation increases the dimension of the original dynamical system. Pyragas[28] has proposed that stabilization with RCS is achieved by utilizing this additional degree of freedom which, in turn, may result in a critical decrease of the largest Lyapunov-exponent of the originally unstable periodic orbit. Experiments with our simple electrochemical system provide the experimental validation/verification of the proposed theory. Furthermore, numerical modeling based on our simple system may also help in better understanding the mechanism of synchronization between a chaotic attractor and a periodic perturbation.

Control of the inherent chaotic dynamics provides useful insight into the underlying dynamics relevant to corrosion related problems. Moreover, control of unpredictable behavior in easily tractable electrochemical systems may prove to be important as a precursor to understanding and subsequently controlling complex responses of biological systems.

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