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Stabilization of unstable steady states in an electrochemical system using derivative control

P. Parmananda, M. A. Rhode, G. A. Johnson, and R. W. Rollins
Condensed Matter and Surface Sciences Program, Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701-2979

H. D. Dewald
Condensed Matter and Surface Sciences Program, Department of Chemistry, Ohio University, Athens, Ohio 45701-2979

A. J. Markworth
Engineering Mechanics Department, Battelle Memorial Institute, Columbus, Ohio 43201-2693

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We report the stabilization of an unstable fixed point in both an electrochemical experiment and a model for electrochemical corrosion using a small control signal proportional to the derivative of a measurable function of system variables. Spontaneous periodic oscillations observed during the potentiostatic electrodissolution of a rotating copper disk in a sodium acetate–acetic acid buffer were suppressed to steady state behavior by adding to the anodic potential a feedback term proportional to the derivative of the electrical current passing through the cell. A general discussion of derivative control strategies shows that the steady state fixed points are left unchanged while, at the same time, the stability of the fixed points can be altered. We also show that, in general, the dimension of the state space of the system is increased when a derivative control strategy is applied.

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I. INTRODUCTION

It has been demonstrated in a number of different physical systems [1–5] that dynamical control of chaotic behavior can be achieved by judiciously applying small perturbations to an accessible control parameter. These experiments use flexible control strategies [6–8] to convert the observed chaotic behavior to periodic responses. Also, recently there have been reports of controlling the system dynamics on unstable fixed points (nonoscillatory solutions) [9–12] using feedback techniques [10,11]. Controlling the dynamics on a steady state fixed point is of practical importance in experimental situations where chaotic and/or periodic oscillations cause degradation in performance.

We report the stabilization of unstable fixed points in a numerical model [15,16] for aqueous electrochemical corrosion and in an electrochemical cell [17,18] using a derivative control strategy [10]. In the numerical model we were able to convert both chaotic and periodic oscillations to a steady state response, while in the experimental system we suppressed the observed periodic oscillations to obtain a dc output from the system. In the experimental system, the continuous perturbations required to stabilize the fixed point were largest (about 5% of the control parameter) when the derivative control was initially turned on.

II. CONTROL STRATEGY

In this section we provide a general theoretical framework for the derivative control strategy [10,11]. The discussion is based on the methods of control theory [13,14]. We apply a derivative control strategy to model systems of the form,

$$\dot{X} = F(X,P), \tag{1}$$

where $X \in \mathbb{R}^n$ and $P \in \mathbb{R}^m$. We assume that solutions of Eq. (1) exhibit chaotic or periodic dynamical behavior for some fixed parameter vector P_0 and have an unstable steady state fixed point X_0,

$$F(X_0,P_0) = 0. \tag{2}$$

Our goal is to stabilize the fixed point at (X_0,P_0) by applying a small control signal to some components of the parameter vector P. In real experiments the individual components of the state vector X and the parameter P are usually not accessible for measurement and control. Thus we assume that a single scalar $j = j(X,P)$ is measurable and that the parameter vector can be changed by adjusting a scalar (knob) v; $P = P(v)$. We take the zero of v such that $P(v=0) = P_0$. Now the general derivative control strategy of the type proposed by Biewalski *et al.* [10] is expressed by taking

$$\begin{aligned} v &= \alpha \frac{d}{dt} j(X,P) \\ &= \alpha \left(\sum_{i=1}^{n} \frac{\partial j}{\partial x_i}\dot{x}_i + \sum_{i=1}^{m} \frac{\partial j}{\partial p_i}\dot{p}_i \right), \end{aligned} \tag{3}$$

where α is a proportionality constant that adjusts the strength of the control signal. Note that since $v = 0$

when $\dot{X} = \dot{P} = 0$, the point (X_0, P_0) remains a fixed point of the system with control. Substituting Eq. (3) for v into $P(v)$ and solving for P gives

$$P = G(\dot{X}, X, \dot{P}, \alpha), \tag{4}$$

where G is such that $P = P_0$, when $X = X_0$ and $\dot{P} = 0$. Assuming G to be invertible with respect to $\dot{P}$ and substituting $\dot{X}$ using Eq. (1), the above equation leads to

$$\dot{P} = H(X, P, \alpha). \tag{5}$$

This control strategy results in a time dependence of P given by Eq. (5). Hence the vector P forms an added set of independent variables. We combine vectors X and P to form a new state vector Z,

$$Z^t = (x_1, \ldots, x_n, p_1, \ldots, p_m). \tag{6}$$

Similarly, Eq. (1) and Eq. (5) combine to give

$$\dot{Z} = \tilde{F}(Z, \alpha), \tag{7}$$

and the derivative control strategy has, in effect, increased the dimensionality of the system.

As mentioned above, $Z = Z_0$, with $X = X_0$ and $P = P_0$, is still a fixed point of Eq. (7), for any α. The derivative feedback does not change the fixed point solution of the system, since all time derivatives are zero there. However, the stability of the fixed point may be altered by the control parameter α. The eigenvalues of the Jacobian of $\tilde{F}$, evaluated at $Z = Z_0$, determine the stability of the controlled system. Our control strategy is successful provided α can be adjusted such that the real parts of all eigenvalues are negative. This will guarantee the stabilization of the steady state fixed point, but does not provide information about the basin of attraction in the state space for the (now stable) fixed point. In practice we have been able to numerically stabilize the steady state for a variety of models including the Lorenz equations and Chua's circuit using a simple feedback, where the control knob v affects only the kth parameter component $p_k = p_{k0} + v$, and the measured quantity j is a single component of the state vector; $j = x_l$. This simple additive control strategy does not increase the dimensionality of the system, since no components of $\dot{P}$ survive in Eq. (3). However, in the numerical model for electrochemical corrosion [15,16], the measured quantity j depends on a component of P, and the dimensionality of the system is increased as described in the section below.

III. APPLICATION OF THE CONTROL STRATEGY IN THE NUMERICAL MODEL

We apply derivative control to a model for aqueous electrochemical corrosion [15,16] described by three dimensionless differential equations:

$$\dot{Y} = p(1 - \theta_{\rm OH} - \theta_{\rm O}) - qY, \tag{8}$$

$$\begin{aligned}\dot{\theta}_{\rm OH} = {} & Y(1 - \theta_{\rm OH} - \theta_{\rm O}) \\ & -[\exp(-\beta\theta_{\rm OH}) + r]\theta_{\rm OH} \\ & +2s\theta_{\rm O}(1 - \theta_{\rm OH} - \theta_{\rm O}),\end{aligned} \tag{9}$$

$$\dot{\theta}_{\rm O} = r\theta_{\rm OH} - s\theta_{\rm O}(1 - \theta_{\rm OH} - \theta_{\rm O}). \tag{10}$$

The variables $\theta_{\rm O}$ and $\theta_{\rm OH}$ represent the fraction of the electrode surface covered by two different chemical species, while Y represents the concentration of metal ions in the electrolytic solution. The parameters p, q, r, s, and β are determined by chemical reaction rates in the model. Previous numerical studies [16] have shown that this model exhibits deterministic chaos for parameter set $\{p, q, r, s, \beta\}$ in the neighborhood of $\{2.0 \times 10^{-4}, 1.0 \times 10^{-3}, 2.0 \times 10^{-5}, 9.7 \times 10^{-5}, 5.0\}$. We numerically integrate these equations using a Runge-Kutta algorithm. In the actual electrochemical experiment, described in Sec. IV, the anodic potential V is available as a control parameter. The two parameters r and p in the model have an exponential dependence on this potential. To make the simulation realistic, we change r and p as a function of the changes in V. This control strategy results in adding an extra dimension to the system.

To implement control, we change the anodic potential proportional to the time derivative of the anodic current J,

$$\delta V = \alpha \frac{dJ}{dt}, \tag{11}$$

where the exact expression for the anodic current J from the rate equations in the model [15,16], can be approximated by

$$J = r\theta_{\rm OH}. \tag{12}$$

Using Eq. (12), δV can be rewritten as

$$\delta V = \alpha(\dot{r}\theta_{\rm OH} + r\dot{\theta}_{\rm OH}). \tag{13}$$

According to the rate equations, the time dependence in the parameters p and r is given by

$$p = p_0 \exp(\gamma\delta V) \tag{14}$$

and

$$r = r_0 \exp(\gamma\delta V). \tag{15}$$

The above equation can be written as

$$r = r_0 \exp[\gamma\alpha(\dot{r}\theta_{\rm OH} + r\dot{\theta}_{\rm OH})]. \tag{16}$$

Solving for $\dot{r}$ invariably adds an additional dimension to the model [Eqs. (8)–(10)],

$$\dot{r} = \frac{\ln(r/r_0)}{\gamma\alpha\theta_{\rm OH}} - \frac{r\dot{\theta}_{\rm OH}}{\theta_{\rm OH}}. \tag{17}$$

Equation (17) together with Eqs. (8)–(10) describe a new four dimensional system that represents the original model with the derivative control implemented. Since the current expression Eq. (12) is independent on p, the time dependent parameter p is determined from the system variables $\theta_{\rm OH}$ and r. The time evolution of the controlled system is obtained by numerical integration of Eqs. (8)–(10) and Eq. (17), using Eq. (13) and Eq. (14) to evaluate p. Since Eq. (17) depends only on the product of $\alpha\gamma$, we are free to assign an arbitrary value to one of the parameters. In our simulation, we chose γ such that α was of the order one when we achieved control.

Numerical results

For parameters $\{p, q, r, s, \beta\} = \{2.0\times10^{-4}, 1.0\times10^{-3}, 2.0 \times 10^{-5}, 9.7 \times 10^{-5}, 5.0\}$, the uncontrolled system shows its typical chaotic oscillation. It has a steady state fixed point at approximately $Y = 0.114$, $\theta_{\rm OH} = 0.315$, and $\theta_{\rm O} = 0.114$. For the stability analysis, we determined the Jacobian from the right-hand side of Eqs. (8)–(10) and used it to calculate the eigenvalues at the fixed point ($Y = 0.114$, $\theta_{\rm OH} = 0.315$, $\theta_{\rm O} = 0.114$). These eigenvalues were calculated to be $\lambda_1 = -1.0553 \times 10^{-4}$, $\lambda_2 = 0.00199 + 0.01044i$, and $\lambda_3 = 0.00199 - 0.01044i$, verifying that the fixed point is unstable, since two out of the three eigenvalues have non-negative real parts. The period of the chaotic oscillations is approximately 1000 time units. Thus the eigenvalues calculated in the natural time unit of this period are 1000 times larger than the values of λ_i quoted.

Adding the control stabilizes the steady state fixed point for a range of the proportionality constant α. Figure 1 shows the α dependence in the real parts of the eigenvalues for the new Jacobian in the four dimensional system [Eqs. (8)–(10) and Eq. (17)]. For small α, the eigenvalues λ_1, λ_2, and λ_3 approach the values listed above for the uncontrolled system. The real part of all eigenvalues must be negative for the fixed point to be stable. While λ_1 always stays negative [near (-10^{-4})], the real parts of λ_2 and λ_3 are negative only for a limited range in α. The new eigenvalue λ_4 corresponds to the additional dimension introduced by Eq. (17) and is always negative and real. It is interesting that there is an upper limit for α beyond which the derivative control will fail to stabilize the fixed point.

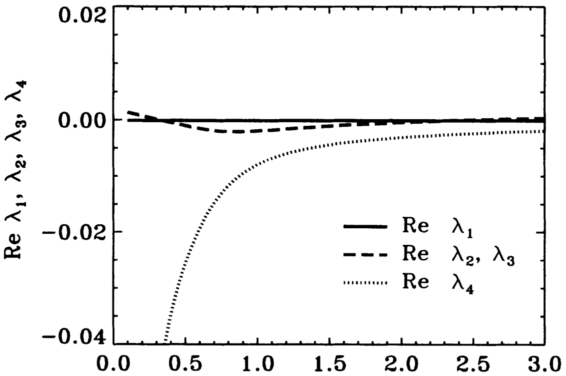

FIG. 1. Real part of the eigenvalues λ_1–λ_4 of the Jacobian of the electrochemical model system Eqs. (8)–(10) for the steady state fixed point including the additional fourth dimension Eq. (17), neccessary to implement the derivative feedback control. The dashed line represents two complex conjugate eigenvalues. For the proportional constant α in the range $0.4 < \alpha < 2.4$ the real part of all the eigenvalues is negative. This indicates a maximum range for α, where the derivate control stabilizes the steady state fixed point.

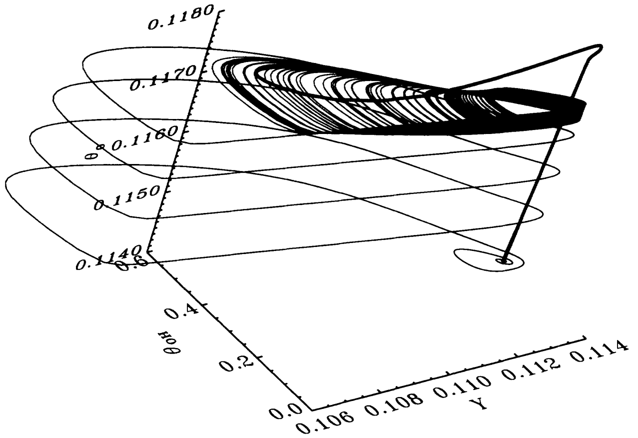

FIG. 2. Numerical integration of the electrochemical model Eqs. (8)–(10). After the derivative control is switched on [Eq. (14)–(17)], the system leaves its attractor and approaches a steady state fixed point (thick line). Subsequently, when the control is turned off the system leaves the fixed point by spiraling outward and returns to the chaotic attractor.

Figures 2–4 demonstrate the successful control on the steady state of the model [Eqs. (8)–(10)] by application of derivative control Eqs. (14)–(17) for above parameters and $\{\gamma, p_0, r_0\} = \{-1.0\times10^{7}, 2.0\times10^{-4}, 2.0\times10^{-5}\}$. After integrating 10^5 time units of the uncontrolled system, we switch the derivative control on setting $\alpha = 1$ (thick line). The system leaves the chaotic attractor and goes to the steady state. Figure 4 illustrates that the control perturbation on r is very small, except for a sharp peak at the moment of its initialization. At $t = 5.0 \times 10^5$ we turn control off again. After some delay the system spirals out and returns to its attractor. We also controlled the steady state for other system parameters, in particular for parameters where the uncontrolled system is periodic. In all cases the system moved towards the steady state immediately after control was initialized.

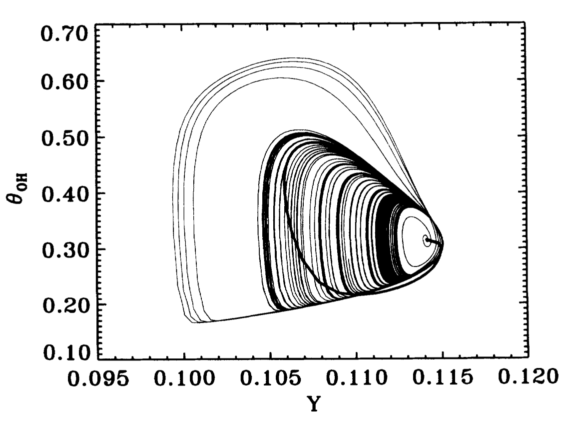

FIG. 3. The dynamics of the numerical model projected in two dimensions. After the control is turned on the system leaves the attractor. The thick line indicates the trajectory the system follows to reach the fixed point.

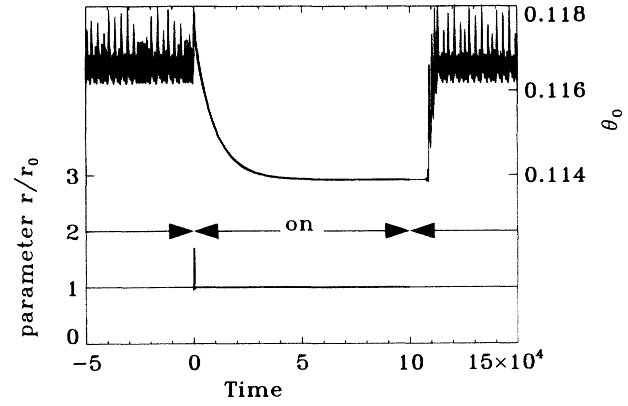

FIG. 4. At $t = 0$, control is initiated (thick line). The control parameter r (see bottom graph) undergoes a sharp peak and then returns immediately back near its original value r_0. The system represented by θ_O (upper graph) quits its chaotic oscillations and reaches the steady state. At $t = 10 \times 10^4$ we release control. After a delay the system returns to its original chaotic state.

For all investigated models, we succeeded in forcing the system to leave its attractor and stay on the steady state fixed point after implementing an appropriate derivative control. We did not find the success of the derivative control to depend on the initial condition of the system. With the same control parameter and proportionality constant, we could bring the system to the steady state fixed point even from regions far away in state space.

IV. APPLICATION OF THE CONTROL STRATEGY IN THE EXPERIMENTAL SYSTEM

We applied the derivative control strategy discussed in Sec. II to stabilize spontaneous oscillations in an electrochemical cell.

A. Experimental system

The experimental system was a PAR Model K60066 (Princeton Applied Research) three electrode electrochemical cell set up to study the potentiostatic electrodissolution of copper in an acetate buffer. The electrochemical behavior of this system has been studied in some detail by Dewald, Parmananda, and Rollins [17,18]. Under appropriate parameter conditions, this electrochemical system exhibits both periodic and chaotic current oscillations [17,18]. A schematic diagram for the electrochemical cell is presented in Fig. 5.

The anode is a rotating copper disk (5 mm diameter) shrouded by Teflon. The electrolyte solution was an acetate buffer, a mixture, comprising of 60 parts of glacial acetic acid and 35 parts of 2M sodium acetate. A volume of about 100 ml was maintained in the cell. The anodic potential measured relative to a saturated calomel reference electrode was used as our control parameter. The cathode was 2.5 cm^2 platinum foil disk. The emf of the circuit was continuously adjusted by a potentiostat to maintain a desired set value of the anodic potential (the potential between the anode and the reference), and the oscillation in anodic current (the current between the anode and the cathode) was recorded. For recording purposes time series data was collected by sampling the anodic current at 50 ms intervals using a Nicolet model 3091 digital storage oscilloscope. Typical period for the anodic current (periodic) oscillations ranged between 2–4 sec, hence it was ensured that the sampling interval is small compared to the period of the oscillations.

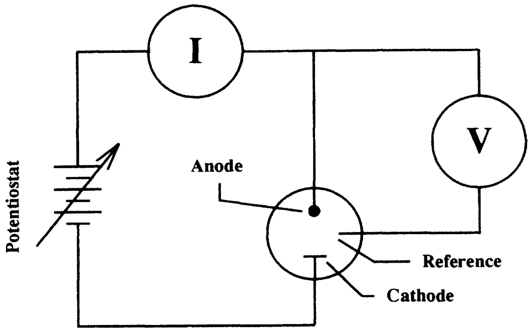

FIG. 5. Schematic representation of the three-electrode electrochemical cell. V is the anodic potential and I is the anodic current. The potentiostat adjusts the emf to hold V at the desired set value.

An analog differentiator circuit, shown in Fig. 6, was used to generate a continuous feedback signal proportional to the time derivative of the anodic current (system variable). This feedback signal was then used to continuously perturb the anodic potential (control parameter) in order to stabilize a fixed point of the system.

B. Experimental results

The control strategy was implemented while the system was exhibiting periodic oscillations. Figure 7 shows the time series of the anodic current while the control is off, turned on, and then shut off again. The anodic potential with the control off was 0.715 V and the anode rotation rate was 1400 rpm. During successful control, the anodic current oscillations decay eventually yielding a dc response from the system. When the control is shut off

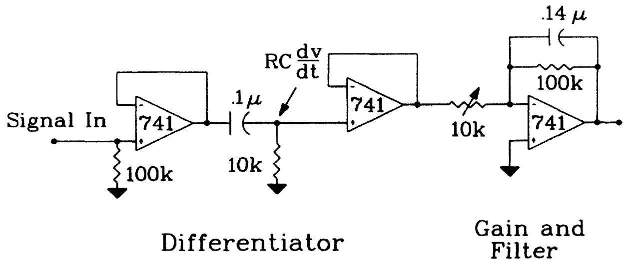

FIG. 6. The analog circuit used to obtain the continuous time derivative of the anodic current.

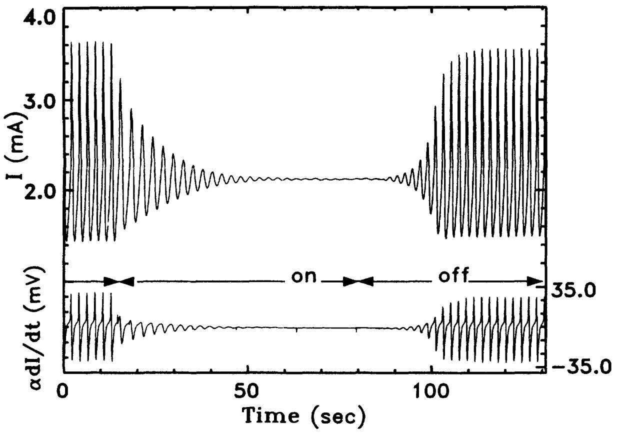

FIG. 7. The time series of anodic current plotted continuously over a time during which the control is switched on and then turned off. The derivative signal used to achieve control is superimposed on the bottom graph. The rotation rate = 1400 (rpm), the anodic potential with control off is $V_0 = 0.715$ V.

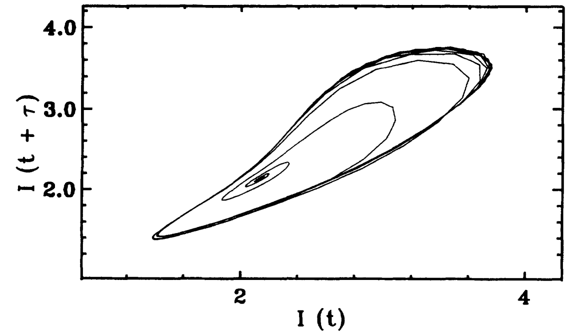

FIG. 8. The phase space reconstruction for a segment of the time series data shown in Fig. 7. After the control is turned on, the system dynamics spiral in, and eventually settle on the stabilized fixed point.

the system moves away from the fixed point and reverts to executing periodic oscillations again. The feedback signal proportional to the time derivative of the anodic current is superimposed on the bottom graph to illustrate the fact that the corrections (maximum) are about 5% of the applied potential, and go to zero as the system stabilizes itself on the fixed point. Figure 8 depicts the dynamics in a reconstructed phase space for a segment of the time series in Fig. 7. As the control is turned on, the system leaves the limit cycle, spirals in, and eventually settles down on the stabilized fixed point.

V. CONCLUSIONS

The derivative feedback technique extends the stability regime of unstable steady states observed in oscillating chemical systems. This could be of practical importance in chemical reactors where oscillations are undesirable as they cause degradation in system performance. In the numerical model, we studied the robustness of this control strategy and the range of proportionality constants for which the stabilization could be attained. In the experimental system we show that this control strategy requires no prior knowledge of the system dynamics, and the simplicity in its implementation makes it an effective technique for stabilization of chemical systems which are inherently unstable. Experiments in application of the derivative control strategy to convert the chaotic oscillations to a steady state fixed point response in the electrochemical cell are underway. We also plan to investigate the possibility of stabilizing the dynamics of other chemical systems exhibiting oscillatory behavior.

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