Controlling Nonlinear Dynamics in Electrochemical Corrosion

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Abstract

Several electrochemical systems exhibits a variety of non-linear phenomena ranging form simple oscillations to deterministic chaos. In this work we examines simple feedback control laws to control the nonlinear behavior in electrochemical corrosion systems. The control laws are based on minimum system information. Numerical simulations shows the effectivity of the feedback control laws proposed.

Keywords: Nonlinear dynamics; electrochemical corrosion; feedback control; modeling error compensation; derivative control.

1. Introduction

Corrosion is either chemical or electrochemical in nature. Electrochemical corrosion is the dissolution of a metal through the oxidation process. Electrochemical systems have long been known to exhibit spontaneous oscillatory behavior under certain operating conditions [1]. Depending upon the nature of a given system and its operating conditions, its oscillations may be periodic, quasiperiodic, or chaotic [1-3]. Occurrence of oscillatory phenomena in electrochemical systems has been observed during different types of electrochemical reactions such as metal dissolution, electrocatalysis, electrodeposition, electropolishing, etc. [1].

Oscillatory metal electrodissolution-passivation and electrocatalytic reactions attracted special interest by many researchers [1-4]. Aside from the scientific point of view of exploring the dynamics of electrochemical systems, formation/dissolution of anodic films and alloys acquire a practical significance due to their applications in processes of technological importance such as pitting corrosion and electropolishing [2,5].

Interest has recently arisen in strategies for exerting control over this oscillatory behavior; for example, to make a chaotic electrochemical system oscillate periodically or even exhibit steady-state behavior, or to bring a periodically oscillating system to a steady state [2-4, 6-9]. For instance, it is recognized that the suppression of periodic and chaotic

oscillations plays an important role in the mechanism of prevention of pitting or localized corrosion [5]. Thus, there is a need to develop simple and effective methods to suppress and control the nonlinear dynamics in electrochemical corrosion systems. Success has been achieved in controlling oscillatory behavior in numerical models for electrochemical systems and in actual electrochemical cells. Parmananda *et al.*, [4], McCoy *et al.*, [6], and Kiss *et al.*, [7] have been reported both theoretical and experimentally a simple proportional feedback algorithm applied to simple accessible parameters of different electrochemical systems. A combined strategy, based on simple proportional actions and an ANN reference model is designed by Louvier-Hernandez *et al.*, [8] to maintain the transient chaos in an electrochemical system. In Parmananda [9] an electrochemical corrosion system is stabilized via a continuous delayed-feedback technique.

In this work, in the spirit of previous works [4,6-7] we examines the applicability of two simple feedback control laws [10,11] to eliminate the nonlinear behavior in electrochemical corrosion systems. Our main with this work is to test if two simple feedback controllers proposed recently can be used to control the nonlinear dynamics in electrochemical systems. We have focus on electrochemical corrosion systems as a first step to gain insights in the control of simple dynamical systems that displays a complex (oscillatory or chaotic behavior) nonlinear behavior, such as is found in metabolic processes that leads to corrosion processes [12].

2. Electrochemical corrosion models

We consider metal passivation processes that are described by two and three nonlinear differential equations that displays oscillatory and chaotic behavior respectively and an electrodissolution corrosion system described by three nonlinear differential equations that displays chaotic behavior.

2.1. Metal passivation in an aqueous medium

The phenomenon of passivation is one in which bifurcation seems to be consistent with the physical behavior. The system of equations which have been developed are non-linear, so that unstable behavior might be anticipated. These possibilities have been studied by Stringer and Markworth [3].
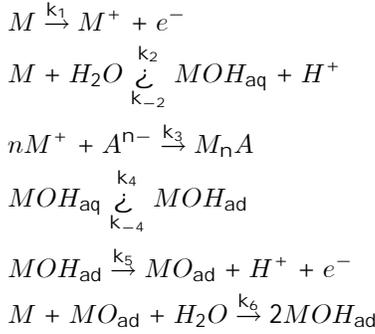
A metal M is dissolving in a solution. Any given point on the surface of the metal may be bare, covered with adsorbed

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MOH, or covered with adsorbed MO. The adsorbed MOH and MO passivate the underlying metal. The following reactions may occur [13,14];

$$M \xrightarrow{k_1} M^+ + e^-$$

$$M + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MOH_{aq} + H^+$$

$$nM^+ + A^{n-} \xrightarrow{k_3} M_nA$$

$$MOH_{aq} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} MOH_{ad}$$

$$MOH_{ad} \xrightarrow{k_5} MO_{ad} + H^+ + e^-$$

$$M + MO_{ad} + H_2O \xrightarrow{k_6} 2MOH_{ad}$$

where M is the metal species, A^{n-} is some anion in the aqueous medium other than OH^-. The adsorbed MOH_{ad} film passivates the metal surface, that is, prevents further dissolution of the metal. The following reduced variables are introduced: $\tau = k_{-4}t$, $Y = KC$, $K = k_4/k_{-4}$, $p = k_1K/k_{-4}$, $q = k_3/k_{-4}$, $r = k_5/k_{-4}$, $s = k_6/k_{-4}$, where C is the concentration of the metal in solution. The model for aqueous electrochemical corrosion is described by three dimensionless differential equations:

$$\dot{Y} = p(1 - \theta_{OH} - \theta_O) - qY$$
$$\dot{\theta}_{OH} = Y(1 - \theta_{OH} - \theta_O) - [\exp(-\beta\theta_{OH}) + r]\theta_{OH} + 2s\theta_O(1 - \theta_{OH} - \theta_O)$$
$$\dot{\theta}_O = r\theta_{OH} - s\theta_O(1 - \theta_{OH} - \theta_O)$$

where θ_O is the fractional surface coverage by MO and θ_{OH} is the fractional coverage by MOH. Previous numerical studies [6] have shown that this model exhibits period-3 dynamics for parameter set $p = 2.0 \times 10^{-4}, q = 1.0 \times 10^{-3}, r = 2.0 \times 10^{-5}, s = 9.8 \times 10^{-5}, \beta = 5.0$ and deterministic chaos in the parametric vicinity.

Taking the first four reactions, as essentially considered by Talbot and Oriani [14], and assuming that the hydrolysis reaction is always in equilibrium, the metal-passivation model can be expressed with two state variables: the fractional coverage θ_{OH}, of the passivating metal-hydroxide film and $[M^+]$, the concentration of metal in solution.

$$\dot{Y} = p(1 - \theta_{OH}) - qY$$
$$\dot{\theta}_{OH} = Y(1 - \theta_{OH}) - \theta_{OH}\exp(-\beta\theta_{OH})$$

Although the model is only two-dimensional, it has been shown to exhibit extremely complex dynamics due to its highly nonlinear character [3]. However, having only two dimensions, the model cannot exhibit chaotic oscillations, which require a minimum of three independent state variables. For the following set of values: $p = 0.0002$, $q = 0.001$, and $\beta = 5.0$, the stable dynamics consist of spontaneous, large-amplitude oscillations, characterized in state space by a large limit cycle. Inside the limit cycle is a fixed point (an unstable node), having coordinates $[Y = 0.072615, \theta_{OH} = 0.636924]$ [13].

2.2. Copper-Phosphoric acid system

The copper-phosphoric acid system consists in the potentiostatic electrodissolution of copper in an acetate buffer electrolyte solution of sodium acetate and acetic acid [2,7]. This is an electrochemical process in which copper dissolves into phosphoric acid from a rotating-disk electrode. The focus is on a set of states in which each member consists of a different combination of large and small oscillations (mixed-mode oscillations). The dynamics of the copper-phosphoric acid system under potentiostatic conditions has been studied extensively [2,4,7]. It has been shown that for an appropriate range of control parameters the system exhibits a variety of interesting behavior, such as simple oscillations, period-doubling cascades, mixed-mode transitions, and chaos [7].

The first-order differential equations of the copper-phosphoric acid system are given in a dimensionless form as [7].,

$$\dot{e} = -r^{-1}e - mk(e)\xi + r^{-1}v$$
$$\dot{\xi} = -1.25d^{1/2}k(e)\xi + 2d(\zeta - \xi)$$
$$\dot{\zeta} = -1.6d(2 - 3\zeta + \xi)$$

where v is the applied (circuit) potential, e is the "true" electrode potential appearing across the interfacial double layer, r is an adjustable series resistance, d is the rotation rate, and $k(e)$ is the heterogeneous rate constant determining the rate of electron transfer. Variables ξ and ζ are the normalized concentrations of the electroactive species, respectively, in the so-called "surface" and "diffusion" layers, while m is the concentrations in the bulk. The above equations are studied under potentiostatic conditions with circuit potential v as the control parameter.

The potential-dependent rate constant $k(e)$ is given by a prototype function,

$$k(e) = k_1\theta^2 + k_2\exp\left[n\alpha(e - e^0)\right]$$

where e^0 is the dimensionless standard potential, α is the transfer coefficient, and θ is related to the surface coverage by some electroactive species. The value of θ is approximated by a sigmoidal function,

$$\theta = \left\{ \begin{array}{ll} 1 & for\ e \leq e_d \\ \exp\left[-b(e - e_d)^2\right] & for\ e > e_d \end{array} \right\}$$

For the following parameter values, $r = 0.02$, $m = 120$, $d = 0.11915$, $k_1 = 2.5$, $k_2 = 0.01$, $n\alpha = 0.5$, $e^0 = 30.0$, $e_d = 35.0$, $b = 5.0$, and $s = 36.74$, the system exhibits chaotic behavior.

The following comments are in order:

- Most cases of oscillatory behavior in electrochemical systems have been observed during the electrodissolution of certain metals. In this case, the oscillatory behavior occurs as the result of the active-passive transition of metallic electrodes. During this process, a

passive film of metal salts (mainly oxides) forms on the electrode surface, which causes an increase in the system resistance and decrease in current. After appearance of the active site, the generated film dissolves into the acidic media and this is accompanied by a decrease of the resistance and by an increase in the current. These two steps repeat all over again for several times when oscillatory behavior in the current is observed [1,2].

- Electrochemical systems can be monitored by the generated behavior in electricity properties such as current and potential and the data can be easily recorded [2].

3. Feedback Control in Electrochemical Corrosion

We consider minimum phase, nonlinear systems describing electrochemical corrosion systems given by

$$
\begin{aligned}
\overset{\bullet}{y} &= f_1(y,z) \\
\overset{\bullet}{z} &= f_2(y,z)
\end{aligned}
\tag{1}
$$

where $f_1(y,z) \in \mathsf{R}$ and $f_2(y,z) \in \mathsf{R}^{n-1}$ can be linear or nonlinear functions, and $y \in \mathsf{R}$ is the measured output of the system. Moreover $f_i(t)$ are Lipschitz functions. Assume that is physically plausible to introduce an external input u, which can be used for control purposes, then equation (1) is changed by

$$
\begin{aligned}
\overset{\bullet}{y} &= f_1(y,z) + \gamma u \\
\overset{\bullet}{z} &= f_2(y,z)
\end{aligned}
\tag{2}
$$

where γ is a positive constant.

In electrochemical corrosion systems only measurements of potential, voltage, or current are available on-line for control purposes. Hence, our main objective is to design simple feedback control laws with minimum system information. We examines the applicability of two recently proposed control designs [10,11] that employs the minimum system information. The first one is based on modeling error compensation (MEC) techniques while the second one is a derivative-type control which feedback a filtered version of the time-derivative of a given measured state.

3.1. MEC control design

Since our feedback control law does not use measurements of z and neither of the functions $f_1(y,z)$ and $f_2(y,z)$, we define the modeling error as

$$
\eta = f_1(y,z)
$$

such that

$$
\overset{\bullet}{y} = \eta + \gamma u
\tag{3}
$$

let y_r be a reference set point, consider the inverse dynamics control law,

$$
u = -\gamma^{-1}[\eta + \tau_c^{-1}(y - y_r)]
\tag{4}
$$

where $\tau_c > 0$ is a closed-time constant. Under this feedback control law it is noted that the dynamics (5) are stable and $y \to y_r$ asymptotically with τ_c as the mean convergence time.

$$
\overset{\bullet}{y} = -\tau_c^{-1}(y - y_r)
\tag{5}
$$

Since the modeling error signal η is unknown, for practical implementation purposes, the modeling error is viewed as an extra state that is estimated using a high-gain reduced-order observer. We introduce the observer,

$$
\overset{\bullet}{\overline{\eta}} = \tau_e^{-1}(\eta - \overline{\eta})
\tag{6}
$$

where τ_e is the estimation time constant. From (3), we know that $\eta = \overset{\bullet}{y} - \gamma u$. Hence

$$
\overset{\bullet}{\overline{\eta}} = \tau_e^{-1}(\overset{\bullet}{y} - \gamma u - \overline{\eta})
\tag{7}
$$

introduce the variable $w \overset{\text{def}}{=} \tau_e \overline{\eta}_t - y$. Then, the estimator (7) can be realized as follows:

$$
\begin{aligned}
\overset{\bullet}{w} &= -\gamma u - \overline{\eta} \\
\overline{\eta} &= \tau_e^{-1}(w + y)
\end{aligned}
\tag{8}
$$

which is initialized as follows. Since η is unknown, we have that $\overline{\eta}_0 = 0$. Therefore, $w_0 = -y_0$.

The computed control law is then given by

$$
u^C = --\gamma^{-1}[\overline{\eta} + \tau_c^{-1}(y - y_r)]
\tag{9}
$$

for consider possible physical restrictions in the magnitude of external stimulus we include a saturation function given by

$$
u_{real} = Sat(u^C)
\tag{10}
$$

where

$$
Sat(u^C) = \begin{cases} u_{min} & if \quad u \le u_{min} \\ u & if \quad u_{min} < u < u_{max} \\ u_{max} & if \quad u \ge u_{max} \end{cases}
$$

thus, the control input is limited by u_{min} for the minimum external signal and u_{max} for the maximum external signal.

The proposed control law is composed by the feedback function (9),(10) and the modeling error estimator (8).

3.2. Derivative-type control

The derivative-type control law is a simple feedback control strategy that makes use only of measurements of the available state

$$
u = -K\gamma^{-1}\overset{\bullet}{y}
\tag{11}
$$

3

where K is a positive constant, which is called the controller gain. The aim of the feedback (11) is to speed down the system trajectories. Notice that the implementation of the feedback function (11) does not require the specification of any exogenous signal (*i.e.*, of any reference signal to be tracked by the controlled system). In this way, the feedback control strategy (11) can be seen as a self-controlling strategy because it is driven only by measured (endogenous) system signals. The feedback function (11) can lead to excessively large control actions, which can not be available in practice. To avoid this situation, and since the dynamics of the chaotic system are constrained to evolve within a bounded region, the following bounded feedback function is proposed:

$$u = u_{\mathsf{KE}} = u_{\mathsf{max}} \tanh\left(-K\gamma^{-1}\dot{y}\right) \tag{12}$$

Notice that $|u_{\mathsf{KE}}| \leq u_{\mathsf{max}}$, so that u_{max} defines the maximum amplitude of the control action.

For practical implementation of the control law (12), the idea is to use an estimate $\dot{y}_{\mathsf{e}}$ of $\dot{y}$ obtained from measures of y, so that the practical feedback function becomes

$$u = u_{\mathsf{max}} \tanh\left(-K\gamma^{-1}\dot{y}_{\mathsf{e}}\right) \tag{13}$$

One can obtain a continuous-time approximation $\dot{y}_{\mathsf{e}}$ by taking a causal approximation of the time-derivative operator s (*i.e.*, $s = \frac{\mathsf{d}}{\mathsf{dt}}$) in the following form: $\dot{y}_{\mathsf{e}} = F(s)s$, where $F(s)$ is a filtering operator satisfying $F(0) = 1$. The simplest one is $F(s) = \omega_{\mathsf{c}}/(s + \omega_{\mathsf{c}})$ where ω_{c} is called as the cutting frequency. In this way, one obtains

$$\dot{y}_{\mathsf{e}} = \frac{\omega_{\mathsf{c}}s}{s + \omega_{\mathsf{c}}}y(t) \tag{14}$$

A realization of (14) in terms of a differential system can be made as follows. Expression (14) implies that $\frac{\mathsf{d}\dot{y}_{\mathsf{e}}}{\mathsf{dt}} + \omega_{\mathsf{c}}\dot{y}_{\mathsf{e}} = \omega_{\mathsf{c}}\dot{y}$. Introducing the variable $z = \dot{y}_{\mathsf{e}} - \omega_{\mathsf{c}}y$, so that

$$\dot{z} = -\omega_{\mathsf{c}}(z + \omega_{\mathsf{c}}y), \; z(0) = z_0 \tag{15}$$
$$\dot{y}_{\mathsf{e}} = z + \omega_{\mathsf{c}}y$$

Observe that the estimate $\dot{y}_{\mathsf{e}}$ is obtained on the basis of measures of the state $y(t)$ only.

The following comments are in order:

- System (2) is of relative grade one. However, straight extensions of the MEC and derivative type control designs to both autonomous third and second order chaotic systems can be found in Puebla *et al.*, [15] and Alvarez-Ramirez *et al.*, [11] respectively.

- The stability analysis of the MEC and derivative control designs are beyond of the scope of this paper, however the stability analysis of the MEC design can be found in Alvarez-Ramirez [10] and the stability of the derivative-type control can be derived from stability results of perturbed systems.

- The following tuning guidelines can be borrowed from Alvarez-Ramirez [10] and Alvarez-Ramirez *et al.*, [11]: (i) MEC design. In a first stage, set the value of the closed-loop time constant $\tau_{\mathsf{c}} > 0$. τ_{c} can be chosen as the mean time of the dominant corrosion processes. In a second stage, set the estimation time constant $\tau_{\mathsf{e}} > 0$. (ii) Derivative-type control. In a first stage, set the value of the closed-loop constant gain $K > 0$. In a second stage, set the cutting frequency ω_{c}. Finally, the control amplitude u_{max} is determined by the capacities of the control mechanisms, notice that for large values of the gain K, the controller injects the maximum damping $\pm u_{\mathsf{max}}$. The closed-loop time constant τ_{e} and the cutting frequency determines the smoothness of the modeling error and the velocity of the time-derivative estimation respectively.

4. Numerical Simulations

We consider the three electrochemical systems descibed above to test both MEC and derivative type control laws. In general, to establish a control structure, one must look at the location of the control input u, corresponding to an accessible physical parameter.

4.1. Metal passivation control

In the two-dimensional case we examines the possibility to inject a control input in the Y coordinate according to:

$$\dot{Y} = p(1 - \theta_{\mathsf{OH}}) - qY + \gamma u$$

following the methodology described in the above section we have,

$$
\begin{aligned}
u &= \gamma^{-1}\left[-\overline{\eta} - \tau_{\mathsf{c}}^{-1}(Y - Y_{\mathsf{ref}})\right] \\
\dot{w} &= -\gamma u - \overline{\eta} \\
\overline{\eta} &= \tau_{\mathsf{c}}^{-1}(w + Y)
\end{aligned}
$$

In the three-dimensional case we examines the possibility to inject a control input in the θ_{O} coordinate according to:

$$\dot{\theta}_{\mathsf{O}} = r\theta_{\mathsf{OH}} - s\theta_{\mathsf{O}}(1 - \theta_{\mathsf{OH}} - \theta_{\mathsf{O}}) + \gamma u$$

the control law is given by,

$$
\begin{aligned}
u &= \gamma^{-1}\left[-\overline{\eta} - \tau_{\mathsf{c}}^{-1}(\theta_{\mathsf{O}} - \theta_{\mathsf{Oref}})\right] \\
\dot{w} &= -\gamma u - \overline{\eta} \\
\overline{\eta} &= \tau_{\mathsf{c}}^{-1}(w + \theta_{\mathsf{O}})
\end{aligned}
$$

Figure 4.1 and Figure 4.2 shows the performance of the above simple feedback MEC control laws. It can be seen that successful oscillation and chaotic suppression can be achieved with the proposed feedback control laws.
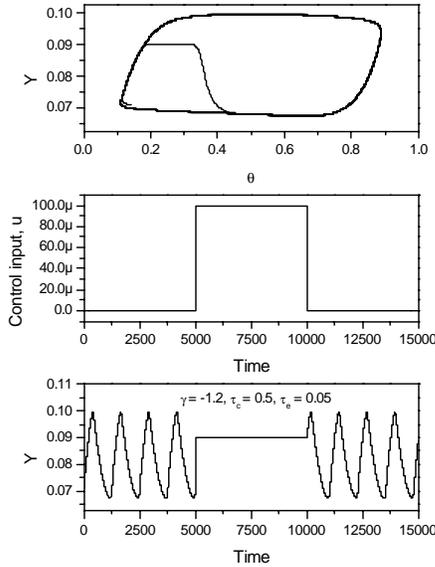
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Figure 4.1: Limit cycle of the two-dimensional model for the metal passivation process and performance of the MEC control law.
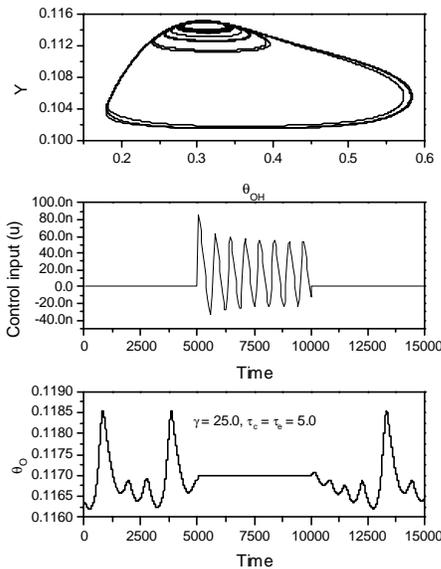

Figure 4.2: Chaotic attractor of the three-dimensional model for the metal passivation process and performance of the MEC control law.
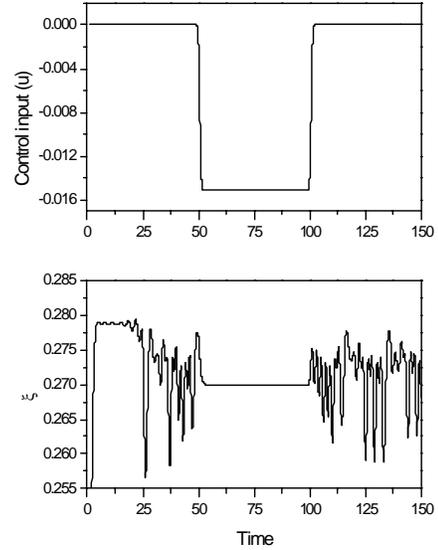

Figure 4.3: Performance of the MEC control law in electrodissolution of copper.

4.2. Electrodissolution control

We examines the possibility to inject a control input in the ξ coordinate according to:

$$\dot{\xi} = -1.25d^{1/2}k(e)\xi + 2d(\zeta - \xi) + \gamma u$$

again following the methodology described in the above section we have,

$$
\begin{aligned}
u &= \gamma^{-1}\left[-\overline{\eta} - \tau_{\mathsf{c}}^{-1}(\xi - \xi_{\mathsf{ref}})\right] \\
\dot{w} &= -\gamma u - \overline{\eta} \\
\overline{\eta} &= \tau_{\mathsf{c}}^{-1}(w + \xi)
\end{aligned}
$$

Figure 4.3 shows the performance of this simple feedback control law. Successful chaotic suppression can be achieved with the proposed feedback control law.

Consider the derivative-type control design. We have,

$$
\begin{aligned}
u &= u_{\mathsf{max}}\tanh\left(-K\gamma^{-1}\dot{y}_{\mathsf{e}}\right) \\
\dot{z} &= -\omega_{\mathsf{c}}\left(z + \omega_{\mathsf{c}}\xi\right),\, z(0) = z_0 \\
\dot{y}_{\mathsf{e}} &= z + \omega_{\mathsf{c}}\xi
\end{aligned}
$$

Figure 4.4 shows the derivative-type control capabilities. Depending of the closed-loop gain value we can successfully perform both periodic and steady-state behavior. Notice that in this case we only uses the measurement available for the control design. Although chaos eliminations or reduction can be obtained, the use of bounded control signal can
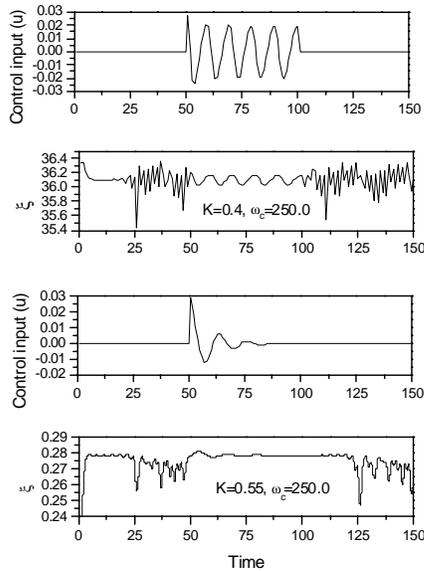
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Figure 4.4: Derivative-type control behavior for two values of the closed-loop gain K.

limit seriously the achievable convergence rate. In fact, the smaller the value of u_{max}, the smaller the energy dissipation rate [11]. In the above simulations it can be seen that after the external input has been turned off the natural dynamics of the corrosion systems will arise to its open-loop behavior.

The feedback control law tested numerically in this work could be implemented experimentally in electrochemical corrosion systems via the introduction of certain external actions. For instance, using an anodic current input, potential changes, and dosage of metal ions [9,13].

5. Conclusions

In this work, we have presented two simple feedback control laws to control electrochemical corrosion systems. We have examined two control laws which uses only the available measured state. We have shown via numerical simulations how the nonlinear behavior of different electrochemical system can be stabilized to either periodic or steady-state behavior. In spite that our results have been obtained for two and three dimensional electrochemical corrosion systems, we expect that our conclusions will be valid for any model describing electrochemical corrosion. We plan to investigate the application of different simple control laws to control corrosion processes generated by basic metabolic processes which display a rich variety of nonlinear behaviors [12].

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6