OPTIMAL STATE-FEEDBACK REGULATION OF THE HYDROGEN EVOLUTION REACTIONS

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Abstract— **A control strategy is developed in order to keep processes based on the hydrogen evolution reactions (HER) near operational steady states. The problem is treated in the context of Optimal Control for nonlinear systems subject to quadratic cost objectives. The original dynamics is shown to be accurately approximated by a bilinear model without increasing the dimension, so the state variables retain their physical meaning. Finite and infinite horizon optimal control strategies are developed, based on the Hamiltonian formalism, and introducing a novel approach for working on-line with generalized Riccati differential equations and the associated costate dynamics. When there exists a final penalty on the state deviation, then a first order quasilinear partial differential equation is discovered and solved for the Riccati matrix. The observability problem is also treated, since the natural state (electrode surface coverage) can not be measured continuously. The output variable (current density) is fed into a high-gain nonlinear observer based on Lyapunov's stability considerations. The whole approach allows for (in general time-dependent) state-feedback control.**

Keywords— **Optimal Control, Nonlinear Processes, Electrochemistry, Hydrogen Evolution Reaction, Hydrogen Technology.**

I. INTRODUCTION

Hydrogen Evolution Reactions (HER) refer to the kinetics of most electrochemical processes where hydrogen is produced or consumed. Hydrogen production is becoming increasingly relevant in the industrial world due to the recurrent crisis in oil prices, the international pressure to mitigate global warming, and the high rate of depletion of other natural fuels. A sufficiently general formulation of HER include the Volmer-Heyrovsky-Tafel (VHT) model studied below and described in Section 2. Since these reactions usually evolve on the surface of metallic electrodes, abundant empirical work has been carried out to determine kinetic parameters for different cathodes (Ni, Pt, Pd, Co_3O_4) and environments (acidic or alkaline solutions) (see Harrington and Conway, 1987). But also, as new applications of clean technologies are announced, interest is growing in the design, operation, and optimization of industrial devices based on HER systems, such as fuel cells, batteries (Vincent and Scrosati, 1997), H_2-decontamination and corrosion prevention processes for heavy metals (Al-Faqeer and Pickering, 2001), and cold nuclear fusion (Green and Britz, 1996; Yang and Pyun, 1996). The control of fuel cells operation has received special attention for non-isothermal proton exchange membrane prototypes (Golbert and Lewin, 2004; and the references therein), where the modeling aspects include pressure, heat, and mass transfer balances, so the problem takes a qualitatively different form. However, for conventional types of fuel cells with metallic electrodes where isothermal conditions are approximately maintained, the kinetics of set-point changes and steady-state operation install HER-VHT equations as the main object governing the process.

The dynamics of HER systems are irreducibly nonlinear. This is confirmed by the detection of solution trajectories whose characteristics are only possible for nonlinear systems (in fact, oscillatory behavior in reaction systems have appeared early and frequently in the electrochemical context; see the extensive review by Hudson and Tsotsis, 1994). Simulations and experiments have also shown hysteresis-like cyclic behaviors (Costanza *et al.*, 2003), bistability (see Costanza, 2005), strange attractors and chaos (Green *et al.*, 2000). These somehow unexpected results shed light on the theory of adsorption mechanisms, spatiotemporal patterns of catalytic electrodes, and related physical problems. Closer to the traditional control point of view, some parameter variation strategies have been developed to avoid or to cope with nonlinear complexities in electrochemical systems (see for instance Kiss *et al.*, 1997; Parmananda *et al.*, 1999), with the main objective to make safe the operation of emerging industrial applications. The optimal control of set-point changes for HER equations with fixed parameter values and power-spending restrictions has also been attacked recently (Costanza, 2005).

Regulation problems, more related to stability objectives, have an intrinsic local character, which allows the dynamics to be approximated by simpler control models. In this paper a bilinear model is proposed. The trajectories of the approximate system nearly coincide with those of the original equations for a wide range of control values. Bilinear approximations have theoretical advantages over classical linearization. They play the role of universal approximations to nonlinear systems (see for details Krener, 1975; and its references), analogously to polynomial approximations to continuous real functions in bounded domains guaranteed by the Stone-Weierstrass theorem. Also, since the analytical expression of bilinear equations is "almost linear", they represent an improvement concerning calculations with respect to the original dynamics. This simplification has allowed to the development of close solutions to several optimal control and tracking problems (Costanza and Neuman, 1995b) , including extensions to Kalman filtering (Costanza and Neuman, 1995a), some of which will be adapted to the situation at hand.

In the next Section the physical context of the dynamical system underlying the problem is succinctly presented through the main balance equations. In Section III different optimization criteria for evaluating the VHT electrochemical performance and their solutions are discussed. In Section IV the Hamiltonian approach is discussed in more detail and a novel solution for the steady-state problem is presented in Section V. The observability aspects are discussed in Section VI, and the conclusions are summarized in Section VIII.

II. THE VOLMER-HEYROVSKY-TAFEL EQUATIONS

The dynamics of hydrogen adsorption, desorption, and chemical reactions over the surface of an electrode is usually modelled through a combination of three elementary "routes" or "steps" (Gennero de Chialvo and Chialvo, 1996, 1998), with corresponding velocities:

Volmer: $H_2O + e^- \rightleftharpoons H_{(ads)} + OH^-$

$$v_V = v_V^e \left\{ \frac{1-\theta}{1-\theta_e} e^{-(1-\alpha)f\eta} - \frac{\theta}{\theta_e} e^{\alpha f\eta} \right\} \quad (1)$$

Heyrovsky: $H_2O + H_{(ads)} + e^- \rightleftharpoons H_{2(g)} + OH^-$

$$v_H = v_H^e \left\{ \frac{\theta}{\theta_e} e^{-(1-\alpha)f\eta} - \frac{1-\theta}{1-\theta_e} e^{\alpha f\eta} \right\} \quad (2)$$

Tafel: $H_{(ads)} + H_{(ads)} \rightleftharpoons H_{2(g)}$

$$v_T = v_T^e \left\{ \left(\frac{\theta}{\theta_e}\right)^2 - \left(\frac{1-\theta}{1-\theta_e}\right)^2 \right\} \quad (3)$$

where the main variables involved are:

θ : surface coverage (the fraction of the electrode surface covered by adsorbed atomic hydrogen $H_{(ads)}$), and
η : the overpotential imposed on the system to run the reaction.

Other symbols and parameters used above mean:
$H_{2(g)}$: gaseous (desorbed) molecular hydrogen,
v_V^e, v_H^e, v_T^e : equilibrium reaction rates of each step
θ_e : specific equilibrium surface coverage ($\theta_e = 0.1$ in numerical calculations and graphics of this paper)
α : adsorption symmetric factor ($= 0.5$ in calculations)
$\mathbf{R}$: gas constant $= 8.3145$ Joule mol$^{-1\circ}K^{-1}$
F : Faraday constant $= 96484.6$ coulomb mol $^{-1}$
T : absolute temperature, here taken equal to 303.15 $^\circ K$
$f = \frac{F}{\mathbf{R}T} = 38.2795$ coulomb Joule^{-1}.

By taking all three routes into account, and assuming that the electrode's surface coverage is proportional to the number of atoms of $H_{(ads)}$, then the HER stoichiometric balance translates into a θ accumulation rate equation

$$\dot{\theta} = \frac{F}{\sigma}(v_V - v_H - 2v_T), (\doteq g(\theta, \eta)), \quad (4)$$

where σ is the experimentally measured surface density of electric charge needed to complete a monolayer coverage of $H_{(ads)}$. In the numerical results of this paper a value of $\sigma = 2.21 \times 10^{-4}$coulomb cm^{-2} will be adopted, corresponding to a standard Pt electrode (similar to Harrington and Conway, 1987).

Typical solutions for a small-amplitude toothed periodic path given to the forcing voltage η are illustrated in Fig. 1. Hysteresis loops appear because the state θ takes different values for the same value of η, depending on whether the voltage is in the ascending or in the descending part of the teeth of the forcing function. This behavior can be observed for most of the reference velocities used in these calculations, but such qualitative behavior is not present in other regions belonging to the range of admissible values for v_V^e, v_H^e, v_T^e. One of the reasons for improving regulation strategies might be to maintain the system far from regions where hysteresis can appear.

Sometimes a "double layer" capacitance is proposed to explain the overpotential decay when the circuit is opened. In this paper only close-circuit situations will be considered, so the overpotential behavior will be independent of the surface coverage.

III. THE OPTIMAL REGULATION PROBLEM

Since the overpotential evolution $\eta(.)$ is (within reasonable bounds) manipulated to influence the building of the hydrogen layer on the electrode surface, then η will be the natural *input* or *control* variable for the system Σ under study. On the contrary, the variable θ can not be directly handled from outside. However, once $\eta(.)$ is chosen and applied for $t \leq \tau$,

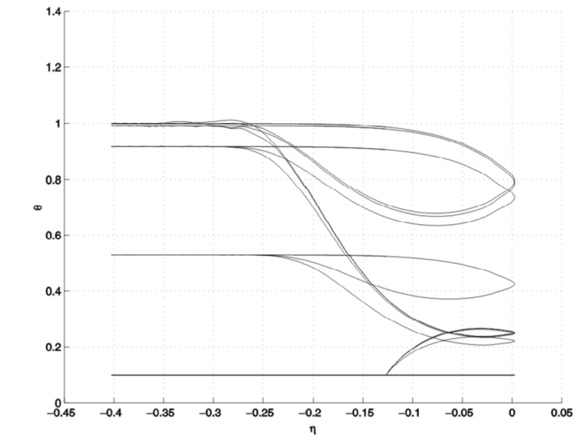

Figure 1. Solutions in phase space to toothed periodic forcings, with hysteresis loops. Parameter values: $v_V^e = 10^{-10}$, $v_T^e = 0$, $v_H^e = 10^{-10}$, $10^{-11}, 10^{-12}$, $10^{-13}, 10^{-14}$, (from top to bottom).

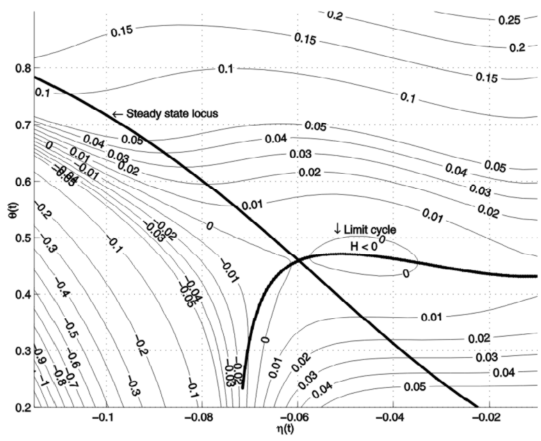

Figure 2. H-level curves for the minimun power optimal problem. H: Hamiltonian function.

then the value of $\theta(\tau)$ contains all the information needed to predict the (near) future evolution of the system, so θ is the natural *state* variable for Σ. The smoothness of HER equations guarantee that for each piecewise continuously differentiable control trajectory $\{\eta(t), 0 \le t \le t^* \le \infty\}$ and for each initial condition $\theta(0) = \theta_0 \in [0,1]$, there exists a continuous solution trajectory $\{\theta(t), 0 \le t \le t^*\}$. Mathematically, not more than piecewise continuous differentiability of the input is needed to ascertain the existence and uniqueness of state trajectories, but in what follows $\eta(.)$ will be assumed to belong to $C^1(0,t^*)$. Under such assumptions $\theta(.)$ will actually be not only continuous on $[0,t^*]$ but also continuously differentiable on $(0,t^*)$.

Regulation assumes that steady-state operation is desired. Admissible steady-states are equilibrium points of the HER coupled dynamics. In what follows $\theta_{equil}(\eta)$ denotes the only physically meaningful solution for θ to the equation $g(\theta,\eta) = 0$ (see Costanza, 2005).

The locus of admissible set-points is depicted in Fig. 2, together with typical power-optimal trajectories for one particular steady state, which coincides with the set-point used for illustration in the regulation examples below. The complex nonlinear qualitative behavior of the system is reaffirmed by Fig. 2, where a manifold (not a linear subspace) of equilibria, and a closed limit-cycle optimal orbit can be observed.

The original equations are however too involved for calculations. Without compromising the nonlinear treatment of the system, an acceptable simpler approximation is then sought for control engineering purposes. From its definition, the generating function g is analytical in both variables, and therefore its Taylor expansion exists and provides a basis for approximations

$$\begin{aligned} g(\theta,\eta) = g(\theta_0,\eta_0) + \left[\tfrac{\partial g}{\partial \theta}(\theta_0,\eta_0)\right](\theta-\theta_0) + \cdots \\ \left[\tfrac{\partial g}{\partial \eta}(\theta_0,\eta_0)\right](\eta-\eta_0) + \left[\tfrac{\partial^2 g}{\partial \theta\,\partial \eta}(\theta_0,\eta_0)\right] \cdots \\ (\theta-\theta_0)(\eta-\eta_0) + 2\left\{\left[\tfrac{\partial^2 g}{\partial \theta^2}(\theta_0,\eta_0)\right] \cdots \right. \\ \left. (\theta-\theta_0)^2 + \left[\tfrac{\partial^2 g}{\partial \eta^2}(\theta_0,\eta_0)\right](\eta-\eta_0)^2\right\} + \ldots \end{aligned} \tag{5}$$

Also, once the operational steady-state (θ_0,η_0) has been chosen, with $\theta_0 = \theta_{equil}(\eta_0)$, it is common practice in regulation situations to change variables to the differences $x := \theta - \theta_0 \quad u := \eta - \eta_0$. Then, in what follows the variable x will represent a deviation of the electrode surface coverage (denoted by $\theta_{absolute}$ when needed) from its steady state value θ_0, and similarly for the variable u. Since $g(\theta_0,\eta_0) = 0$, the best one-dimensional bilinear approximation is obtained by neglecting the terms after the mixed second derivative above.

So, in the regulation context the dynamics will be approximated by

$$\dot{x} \simeq Ax + Bu + xNu \doteq \bar{g}(x,u), \tag{6}$$

i.e. the system will be assumed bilinear around the operational steady state, with nominal parameter values

$$A \doteq \frac{\partial g}{\partial \theta}(\theta_0,\eta_0),\ B \doteq \frac{\partial g}{\partial \theta}(\theta_0,\eta_0), \qquad N \doteq \frac{\partial^2 g}{\partial \theta\,\partial \eta}(\theta_0,\eta_0). \tag{7}$$

A measure of the quality of the approximation may be derived from a result by Krener (1975): for any positive time T_1 there exists another positive constant M such that the state deviation trajectory $\bar{x}_\omega(.) = \theta_{\omega+\eta_0}(.) - \theta_0$ of the system corresponding to any admissible bounded input trajectory $\omega(.)$ will stay near

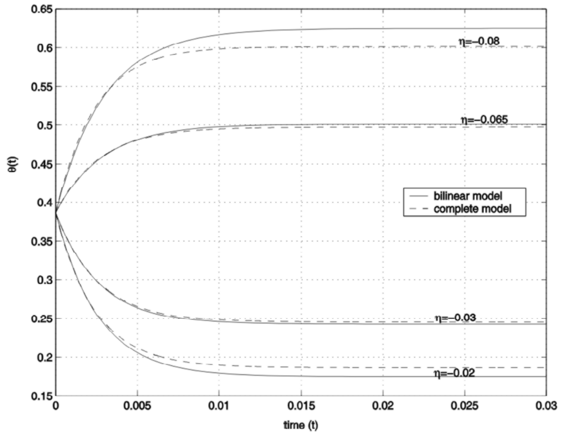

Figure 3. Responses to different step forcings applied to the original system and to its bilinear approximation.

the state trajectory $x_\omega(.)$ of the bilinear approximation corresponding to the same control $\omega(.)$. In precise terms, for any admissible bounded control $\omega(.)$ the states' departure will be bounded by

$$|x_\omega(t) - \bar{x}_\omega(t)| \leq Mt^2 \; \forall t \in [0, T_1] \qquad (8)$$

where the constant M is related to the bounds on the control values and on the discarded second derivatives of the function g near the set-point. Therefore for small times a good approximation is expected. It should be noticed that for linear approximations the time T_1 can not be fixed in advance, so a linear approximation may be good for all control trajectories only during an uncertain time period T_1, eventually with $\inf_\omega T_1(\omega) = 0$. In the same paper Krener shows how to construct higher-dimension bilinear approximations to the original nonlinear system when the departure of solutions becomes unacceptable. The control strategy developed below can not be guaranteed to succeed in dimension one for arbitrary finite horizons. Here this situation will not be explored, but the results shown are extensible, via straightforward algebraic manipulations, to multiple-state models to meet accuracy requirements in the whole time-horizon.

Figure 3 shows the response to constant controls of the original system and its bilinear approximation, in absolute values, after a small perturbation of 0.001 applied to the states of both systems. The agreement is reasonably good, even for big step controls like $\eta(t) \equiv 0.8$ for $t > 0$. Different optimality criteria may be posed when searching for control strategies, since HER equations may be employed as a subsystem of industrial devices that consume electrical power in a variety of conditions. In the new variables, the global cost typically takes the form of an *objective functional* $\mathcal{J}$ of the form

$$\mathcal{J}(u) = \int_0^T \mathcal{L}(x(t), u(t))dt + \mathcal{K}(x(T)) \; ; \qquad (9)$$

where $\mathcal{L}$ is the *Lagrangian* of the optimal control problem, and $\mathcal{K}$ is the final penalty, eventually null. Finite or infinite horizons T give rise to different optimal control problems. Infinite horizon problems are more likely to accept state-feedback solutions than finite horizon situations. When set-point changes are to be optimized, usually the electrical power waste required by the whole operation is the cost to minimize (see Costanza, 2004). At each time, the electrical power is an involved nonlinear function of θ and η, so it is difficult to guess the incidence of changes on each individual variable over the total cost.

For the regulation problem typical quadratic optimization criteria will be adopted. Through the quadratic cost formulation the Lagrangian will take into consideration two conflictive objectives, each one corresponding to the trajectory of a unique variable. The desired accuracy in reaching the equilibrium value for θ is compromised by the amount of energy spent by the required manipulation of η, through

$$\mathcal{L}(x, u) = qx^2 + ru^2 \;\; \text{(quadratic cost).} \qquad (10)$$

The weight q may be chosen as a nonnegative constant but r must be strictly positive for the optimal control problem to make sense. Time-dependent parameters q and r may be treated without significant additional complication in finite horizon problems. In such cases the final penalty will also be quadratic

$$\mathcal{K}(x(T)) = s\,[x(T)]^2, \; s \geq 0. \qquad (11)$$

IV. THE HAMILTONIAN FORMALISM

The Hamiltonian of the approximated problem (bilinear model and quadratic cost) is

$$\begin{array}{c} \mathcal{H}(x, u, \lambda) \doteq \mathcal{L}(x, u) + \lambda \bar{g}(x, u) = \\ qx^2 + ru^2 + \lambda(Ax + Bu + xNu), \end{array} \qquad (12)$$

where λ is a real variable playing the role of a generalized Lagrange multiplier.

The Hamiltonian results to be regular in this case (see Kalman *et al.*, 1969; Sontag, 1998), *i.e.* that for all fixed pairs (x, λ) there exist a unique control value u^0 that minimizes $\mathcal{H}$ with respect to u, namely

$$u^0(\theta, \lambda) = -\frac{(B + Nx)\lambda}{2r}. \qquad (13)$$

For the one-dimensional infinite horizon case ($T = \infty$, $\mathcal{K} \equiv 0$) it is known (Cebuhar and Costanza, 1984) that the variable λ along the optimal trajectory $\tilde{x}(.)$ takes the form

$$\tilde{\lambda}(t) = 2\tilde{x}(t)\, p(\tilde{x}(t)), \qquad (14)$$

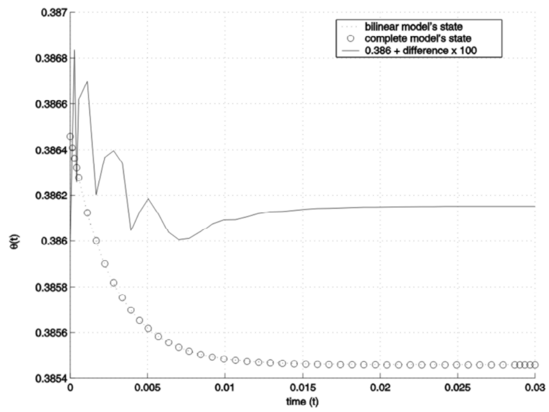

Figure 4. Responses to the optimal control. Differences are conveniently shifted and scaled, to be displayed in the same plot as the absolute values.

$$\text{with } p(x) = \frac{A}{w(x)}\left[1 + sign(A)\sqrt{1+\frac{q\,w(x)}{A^2}}\right], \quad (15)$$

$$\text{and } \; w(x) \doteq \frac{(B+Nx)^2}{r}. \quad (16)$$

Knowledge of $p(x)$ renders the optimal control in the desired feedback form through:

$$\tilde{u} = u^0(x, 2x\,p(x)). \quad (17)$$

Figure 4 shows the performance of this control applied to the original system and to its bilinear approximation around the steady state $(\theta_0, \eta_0) = (0.38545805, -0.05)$, with

$A \doteq \frac{\partial g}{\partial \theta}(\theta_0, \eta_0) = -363.7724$,
$B \doteq \frac{\partial g}{\partial \theta}(\theta_0, \eta_0) = -2714.1$,
$N \doteq \frac{\partial^2 g}{\partial \theta\, \partial \eta}(\theta_0, \eta_0) = -770.1951$
and the parameter values
$v^e_T = 10^{-9}$
$v^e_H = 10^{-10}$
$v^e_V = 10^{-7}$.

Notice that $B + Nx = 0$ for $|x| = \left|-\frac{B}{N}\right| > 1$, so $p(x)$ is always well defined since $|\theta - \theta_0|$ must be less than 1 to have any physical meaning.

V. INTEGRATING THE COSTATE ON-LINE

The generalized multiplier λ is usually referred to as the *costate*, or *adjoint variable* in the Hamiltonian formalism of optimal control theory. It is well known that along the optimal trajectory it coincides with the gradient

$$\tilde{\lambda}(t) = \frac{\partial V}{\partial x}(t, \tilde{x}(t)) \quad (18)$$

of the *"value function"* V (also called the *"Bellman function"*) associated with the optimal control problem at hand, defined in terms of the cost functional as the total cost associated to the optimal trajectory that starts at time τ from the state x_τ, *i.e.*

$$V(\tau, x_\tau) \doteq \inf_{u(.)} \mathcal{J}_{x_\tau}(u) =$$

$$\inf_{u(.)}\left\{\int_\tau^T \mathcal{L}(x(t), u(t))dt + \mathcal{K}(x(T))\right\}, \; \tau \in [0, T]. \quad (19)$$

Then, in particular for $\tau = 0$, the value of $\tilde{\lambda}(0) = \frac{\partial V}{\partial x}(0, x_0)$ is approximately equal to the variation of the (optimal) cost due to an unitary increase in the initial state condition, consequently called *"marginal cost"* in Economics. Therefore, knowledge of the costate λ may help to take economical decisions when considering the magnitude of eventual changes in set-point for the state x.

But also, when the Hamiltonian is regular, the costate allows to evaluate the optimal control in simplest terms, which will be used here. By defining

$$\mathcal{H}^0(x, \lambda) \doteq \mathcal{H}(x, u^0(x, \lambda), \lambda), \quad (20)$$

then the optimal costate satisfies the *adjoint equation* obtained from

$$\dot{\lambda} = -\frac{\partial \mathcal{H}^0}{\partial x} = -\frac{\partial \mathcal{L}}{\partial x}(x, u^0(x,\lambda)) - \lambda\frac{\partial \bar{g}}{\partial x}(x, u^0(x,\lambda)) =$$

$$-\frac{\partial \mathcal{H}}{\partial x}(x, u^0(x,\lambda), \lambda) - \frac{\partial \mathcal{H}}{\partial u}(x, u^0(x,\lambda), \lambda)\frac{\partial u^0}{\partial x}(x, \lambda)$$

$$\dot{\lambda} = -2qx - A\lambda + \frac{N(B+Nx)}{2r}\lambda^2 \quad (21)$$

with its natural $(final)$ condition

$$\lambda(T) = \frac{\partial V}{\partial x}(T, x(T)) = \frac{\partial \mathcal{K}}{\partial x}(x(T)) \quad (22)$$

Also, the optimal state trajectory is a solution to

$$\dot{x} = \frac{\partial \mathcal{H}^0}{\partial \lambda} = \left[\frac{\partial \mathcal{L}}{\partial u}(x, u^0(x,\lambda)) + \lambda\frac{\partial \bar{g}}{\partial u}(x, u0(x,\lambda))\right]$$

$$\frac{\partial u^0}{\partial \lambda}(x, \lambda) + \bar{g}(x, u^0(x,\lambda)) = \bar{g}(x, u^0(x,\lambda)), \quad (23)$$

i.e.

$$\dot{x} = Ax - \frac{(B+Nx)^2}{2r}\lambda, \quad (24)$$

with the *initial* condition

$$x(0) = x_\sigma \; (= \theta_{absolute}(0) - \theta_0) \quad (25)$$

Equations 24 and 21, together with their respectively initial and final conditions, give rise to a two-point boundary value problem, usually analytically unsolvable and difficult to treat numerically. It is

known that in the linear-quadratic case the two-point boundary value situation may be transformed into an initial-value problem (see for instance Sontag, 1998). It is shown below that such a useful result may also be obtained for the bilinear-quadratic problem. For simplicity, the algebraic manipulations will be made explicit only for the one-dimensional case.
(i) The infinite horizon (steady-state) case. By proposing

$$\frac{\partial V}{\partial x}(t,x) = 2xp(x); \ \frac{\partial V}{\partial t}(t,x) = 0, \qquad (26)$$

then the Hamilton-Jacobi-Bellman (HJB) equation for the bilinear-quadratic problem reads:

$$0 = \mathcal{H}^0(x, \frac{\partial V}{\partial x}) = qx^2 + r\left[u^0(x, \frac{\partial V}{\partial x})\right]^2 + \qquad (27)$$

$$\frac{\partial V}{\partial x}\left[Ax + (B + xN)u^0(x, \frac{\partial V}{\partial x})\right] =$$

$$= qx^2 + \frac{\partial V}{\partial x}Ax - \frac{1}{4}\frac{(B+Nx)^2}{r}\left(\frac{\partial V}{\partial x}\right)^2 =$$

$$= qx^2 + 2Apx^2 - \frac{(B+Nx)^2}{r}p^2x^2$$

Then, for any nontrivial state x (for instance for an initial condition $x_0 \neq 0$), the proposed form for $\frac{\partial V}{\partial x}$ will be valid provided that $p(x)$ is a solution to the generalized ($x-$dependent) algebraic Riccati equation (GARE)

$$q + 2A\,p(x) - \frac{(B+Nx)^2}{r}[p(x)]^2 = 0. \qquad (28)$$

Keeping t fixed, the value function will not decrease with $|x|$ (the cost should increase as the state departs from zero), then for $x \neq 0$ the sign of the variables would require

$$p(x) = \frac{1}{2x}\frac{\partial V}{\partial x} = \frac{1}{2x}\frac{\partial V}{\partial |x|}sign(x) = \frac{1}{2|x|}\frac{\partial V}{\partial |x|} \geq 0. \qquad (29)$$

Then, finding the nonnegative solution to the GARE equation would be equivalent to obtain the missing initial condition for the adjoint equation, namely

$$\lambda(0) = 2x_0p(x_0) \qquad (30)$$

Therefore the adjoint equation 21 can be integrated on-line and at each time the optimal control can be implemented as a state feedback from equations 17 and 13.

Figure 5 shows that on-line integration of the costate is really efficient, since it is compared against the exact value calculated from equations 14. Calculations were performed with the following values of the cost-weight parameters: $q = 1$; $r = 5$.

Figure 6 shows the evolution of a 0.1 perturbation in the state x with and without control. The control was generated by on-line integration of the costate equation. It is clear that regulation is necessary, since the free-state evolution, even when heading to equilibrium, after some time departs and diverges.

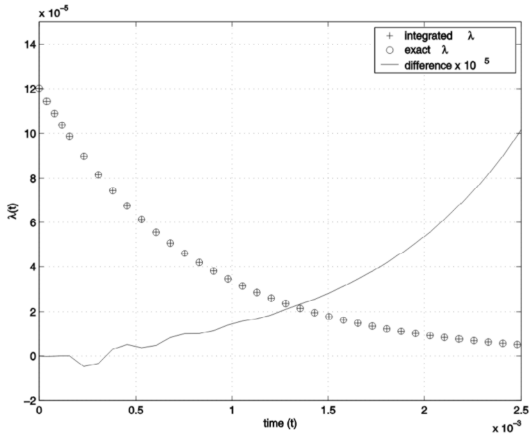

Figure 5. Costates λ, evaluated on-line (integrated), and calculated from equations 14-16 (exact). Differences between both curves are appropriately scaled.

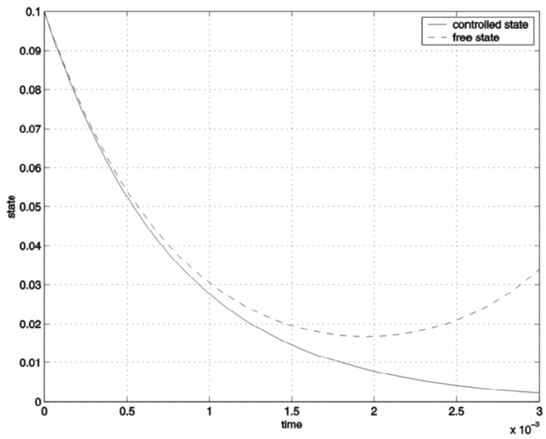

Figure 6. State trajectories after a big perturbation. Comparison between the free evolution ($u \equiv 0$), and the controlled evolution (u optimal).

(ii) Finite horizon problem. In this case the quadratic cost objective takes the form

$$\mathcal{J}(u) = \int_0^T \left\{q[x(t)]^2 + r[u(t)]^2\right\}dt + s[x(T)]^2\ , \ (31)$$

with $q, s \geq 0$, and $r > 0$.

It can be shown (Cebuhar and Costanza, 1984) that in this case

$$\frac{\partial V}{\partial x}(t,x) = 2xp(t,x) \qquad (32)$$

with p an analytical function of x and smooth on t. Local controllability and observability will be assumed true in what follows. Then, along the optimal trajectory, a necessary condition stemming from 18, 32, and 21 must be met, namely

$$\dot{\lambda} = 2[\dot{x}p + x(\frac{\partial p}{\partial t} + \frac{\partial p}{\partial x}\dot{x})] =$$

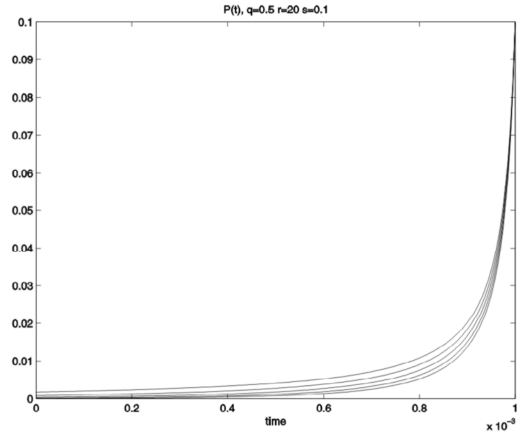

Figure 7. $P(t) = p(t, \tilde{x}(t))$ for several optimal state trajectories ending near zero. $\tilde{x}(T)$ decreasing from top to bottom.

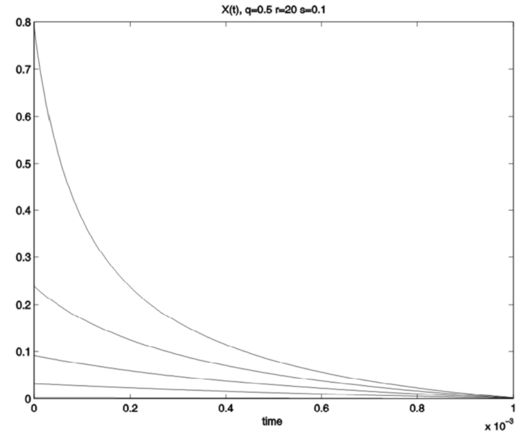

Figure 8. State trajectories corresponding to the generalized Riccati solutions depicted in Fig. 7. $P(0)$ decreasing from top to bottom.

$$-2qx - A\lambda + \frac{N(B+Nx)}{2r}\lambda^2 = \tag{33}$$
$$-2\left\{x\left[q + Ap - \frac{N(B+Nx)}{r}xp^2\right]\right\}$$

Now using 24 and the equations for λ again, the following PDE for the optimal p is obtained

$$\frac{\partial p}{\partial t} + [A - \frac{(B+Nx)^2}{r}p]x\,\frac{\partial p}{\partial x} =$$
$$-q - 2Ap + \frac{(B+2Nx)(B+Nx)}{r}p^2\ , \tag{34}$$

which can be considered as a generalized differential Riccati equation (GDRE), with boundary condition

$$p(T,x) = \frac{1}{2x}\frac{\partial V}{\partial x}(T,x) = \frac{1}{2x}\frac{\partial \mathcal{K}}{\partial x}(x) = s\ . \tag{35}$$

The GDRE has been solved by using the method of characteristics and a value of $s = 0.1$. The variable x has been discretized. Results are illustrated in Fig. 7 and 8. In Fig. 7 the values of $p(t, \tilde{x}(t))$ are shown for several optimal trajectories, each one corresponding to a different final state value $\tilde{x}(T)$ (and resulting then in different values of $\tilde{x}(0)$). The final value $p(T, \tilde{x}(T))$ is constant and equals s.

Figure 8 illustrates the optimal state trajectories departing from different initial conditions, that can be obtained as a collateral result from the numerical integration of p in the reverse direction (Eqs. 34 and 35). It is clear that the solution to the optimization problem stabilizes this system, since all perturbations are abated.

As before, the optimal control can then be readily constructed if all values of $p(t,x)$ have been saved, from

$$\tilde{u}(t) = -\frac{[B + Nx(t)]x(t)}{r}p(t, x(t))\ , \tag{36}$$

or by integrating Eq. 21 on-line, starting with the condition

$$\lambda(0) = 2p(0, x_0)x_0\ . \tag{37}$$

VI. OBSERVABILITY ASPECTS

Although knowledge of the state $x(t)$ is enough to describe and control the dynamics of Σ, θ-values are not continuously available in general. The natural *output* of the system is the current density J, which in the present case is a known function $J = h(\theta, \eta)$. Nonlinear observers for a vast kind of nonlinear systems (Isidori, 1989; García, 1993, 2004; Gauthier and Kupka, 1994) have been devised to recuperate the value of the state from input-output information when necessary.

When local approximations are not sufficiently accurate, or when changing of set-points imply significant variations in the state variable, then the full nonlinearity of the system should be handled. Consequently, the original dynamics 4 will be considered in this Section, together with the observation function

$$J = F(v_V + v_H)\ (\doteq h(\theta, \eta)) \tag{38}$$

An efficient nonlinear observer has been adopted for this case. The following intermediate definitions are needed to illustrate the structure of such a device,

$$\begin{aligned}
v_V^0 &\doteq \tfrac{\check{E}}{1-\theta_e};\ v_V^1 \doteq v_V^0 + \tfrac{\hat{E}}{\theta_e};\\
v_H^0 &\doteq \tfrac{\hat{E}}{1-\theta_e};\ v_H^1 \doteq v_H^0 + \tfrac{\check{E}}{\theta_e};\\
\breve{A}(\eta) &\doteq -\tfrac{F}{\sigma}\left[v_V^e v_V^1 + v_H^e v_H^1 + \tfrac{4v_T^e}{(1-\theta_e)^2}\right];\\
\breve{B} &\doteq -\tfrac{2Fv_T^e}{\sigma}\left[\tfrac{1}{\theta_e^2} - \tfrac{1}{(1-\theta_e)^2}\right];\\
\breve{D}(\eta) &\doteq \tfrac{F}{\sigma}\left[v_V^e v_V^0 + v_H^e v_H^0 + \tfrac{2v_T^e}{(1-\theta_e)^2}\right];\\
\breve{C}(\eta) &\doteq F[v_H^e v_H^1 - v_V^e v_V^1];\\
\breve{E}(\eta) &\doteq F[v_V^e v_V^0 - v_H^e v_H^0]
\end{aligned} \tag{39}$$

The original system reads now

$$\dot{\theta} = \breve{A}(\eta)\theta + \breve{B}\theta^2 + \breve{D}(\eta) \tag{40}$$
$$J = \breve{C}(\eta)\theta + \breve{E}(\eta)\ , \tag{41}$$

and the proposed observer has the following form

$$\dot{\Theta} = \breve{A}(\eta)\Theta + \breve{B}\Theta^2 + \breve{D}(\eta) + \frac{\breve{C}(\eta)}{\zeta} \{J - \breve{C}(\eta)\Theta - \breve{E}(\eta)\}, \Theta(0) = \theta_0; \quad (42)$$

$$\dot{\zeta} = -\mu\zeta - 2\breve{A}(\eta)\zeta + 2[\breve{C}(\eta)]^2 \ , \ \zeta(0) = \zeta_0 > 0. \quad (43)$$

where Θ stands for the observed values of θ, obtained from on-line input/output (η/J) data, and the ODE for the correction factor ζ is found from the requirement that the observation error

$$e(.) \doteq \Theta(.) - \theta(.) \quad (44)$$

tend to zero for any control strategy, which in turn is guaranteed provided that

$$W(t,e) \doteq \frac{1}{2}\zeta(t)e^2 \quad (45)$$

be a time-dependent Lyapunov function, i.e., a smooth positive-definite function of e with negative derivative along $e-$trajectories. Notice that from equations 43 and 45, and by defining

$$\mathcal{W}(t) \doteq W(t, e(t)), \quad (46)$$

then the following result can be obtained

$$\dot{\mathcal{W}}(t) = -k(t)\mathcal{W}(t)\,, \quad (47)$$

with

$$k(t) \doteq \mu - 2\breve{B}(\Theta(t) + \theta(t))\,, \quad (48)$$

and since the state and its observation are bounded (in this case $0 \leq \Theta, \theta \leq 1$), then μ can be chosen to make k always positive. Actually, an estimation of the type

$$\bar{\zeta}e(t)\dot{e}(t) \approx \dot{\mathcal{W}}(t) \approx -\bar{k}\mathcal{W}(t) \approx -\frac{1}{2}\bar{k}\bar{\zeta}[e(t)]^2\,, \quad (49)$$

where $\bar{\zeta}$ and $\bar{k}$ are characteristic values for the corresponding variables in the time interval under consideration, indicates that the error will tend exponentially-like to zero with parameter $-\frac{\bar{k}}{2} < 0$.

Figure 9 illustrates the performance of the observer after a simulated perturbation of 0.02 in the (unknown) state, a value of $\mu = 1$ (in this case, $\breve{B} < 0$, so any positive μ will do), and $\zeta_0 = 1$. The observer catches the state in a very small time, so the control variable will not be affected in any perceptible way when calculated from $\Theta-$values instead than from the physical state θ.

VII. CONCLUSIONS

In this paper an integral approach to the regulation problem for the Hydrogen Evolution Reactions of Electrochemistry has been developed and the extension to a class of nonlinear processes discussed and illustrated. The quadratic-cost optimal regulation problem was

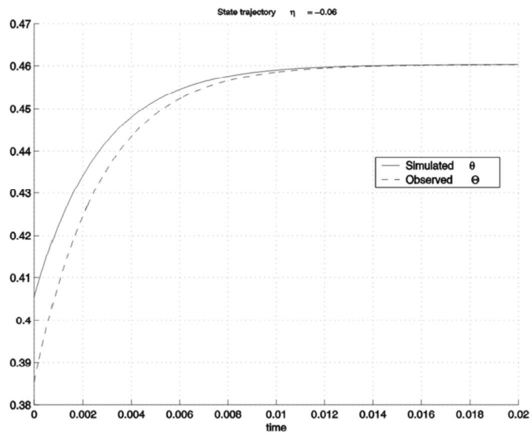

Figure 9. Observer performance.

posed for finite and infinite time horizons, and their solutions were substantiated and calculated. Classical linear-quadratic theory was discarded since there exist qualitative features of HER equations that are irreducibly nonlinear, like hysteresis loops and closed periodic orbits far from the origin. The optimization of these processes has an increasing practical interest in the light of the energy crisis recurrently appearing in contemporary industrialized world.

In steady-state situations the proposed strategy results suboptimal, though accurate enough for engineering purposes. The basic equations for an alternative treatment of finite-time restrictions based on the Hamiltonian formalism are presented but not applied to the present problem due to its numerical involvement.

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