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Minimal-power control of hydrogen evolution reactions

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SUMMARY

An integral approach to solve finite-horizon optimal control problems posed by set-point changes in electrochemical hydrogen reactions is developed. The methodology extends to nonlinear problems with regular, convex Hamiltonians that cannot be explicitly minimized, i.e. where the functional dependence of the H-minimal control on the state and costate variables is not known. The Lagrangian functions determining trajectory costs will not have special restrictions other than positiveness, but for simplicity the final penalty will be assumed quadratic. The answer to the problem is constructed through the solution to a coupled system of three first-order quasi-linear partial differential equations (PDEs) for the missing boundary conditions $x(T), \lambda(0)$ of the Hamiltonian equations, and for the final value of the control variable $u(T)$. The independent variables of these PDEs are the time-duration T of the process and the characteristic parameter S of the final penalty. The solution provides information on the whole (T, S)-family of control problems, which can be used not only to construct the individual optimal control strategies online, but also for global design purposes. Copyright © 2009 John Wiley & Sons, Ltd.

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1. INTRODUCTION

An optimal control methodology to conduct set-point changes in some electrochemical systems usually called 'hydrogen evolution reactions' (HER) is the main purpose of this paper. HER are commonly referred to when electrochemical processes with hydrogen production or consumption are occurring. Typical HER processes are electrolysis, where electrical energy is supplied in order to decompose the water into H_2 and O_2; and fuel cells operation, where the reverse combination is conducted in a controlled setup to produce electricity. These processes are receiving increasing attention given the recurrent crisis in oil prices, the search for clean energy sources to mitigate global warming, and the current rate of depletion of natural fuels. There exists an extensive bibliography on other fields of research applying HER equations, like in cold nuclear fusion (see [1]), or in the H_2-decontamination and corrosion of heavy metals ([2] and references therein). As new applications of hydrogen technology are announced, interest is growing in the design, operation, and optimization of industrial devices based on HER systems.

The control of fuel cells operation has begun to be studied recently, specially for non-isothermal proton exchange membrane prototypes (see [3]). In all cases dynamic non-linearities have been confirmed experimentally, which suggests that fuel cell technology would

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require non-linear control techniques for conducting changes in their operational conditions. Other aspects of control of electrochemical reactions attempt to avoid chaotic behavior [4], or to minimize the dissipation of electrical power during the process [5].

Nonlinear optimal control problems are still a source of basic and applied research activity, increasingly dominated by geometrical and physical considerations (see for instance [6]). However, the Hamiltonian formalism has always been at the core of the development of modern optimal control theory [7]. When an optimal control problem involving an n-dimensional system and an additive cost objective is regular [8], i.e. when the Hamiltonian $H(t, x, u, \lambda)$ of the problem can be uniquely optimized by a control value u^0 depending on the remaining variables (t, x, λ), then the solution can be constructed from the trajectories of a set of $2n$ ordinary differential equations (ODEs) subject to two-point boundary conditions, known as Hamilton (or Hamiltonian) canonical equations. This boundary-value problem, if solvable, presents numerical difficulties due to the mixed-sign eigenvalues of its linear approximation [9, 10]. For the finite-horizon, linear-quadratic regulator problem, there exists at least a well-known method (see for instance [11]) to transform the boundary-value problem into a related initial-value one. But this kind of transformation does not apply in general to nonlinear systems.

In the infinite-horizon bilinear-quadratic case, for both the regulator and the change of set-point problems, a recent attempt to find the missing initial condition for the costate variable has been developed, which allows to integrate the equations online with the underlying control process (see [12–14]). In addition, a new procedure for finding initial costates in two-point boundary value situations (finite horizon) for bilinear-quadratic problems, along the lines of invariant imbedding [15], has been anticipated in [16] and applied to an explicitly regular nonlinear model with a quadratic Lagrangian in [17]. Here an extension to general nonlinear dynamics, subject to objective functions with arbitrary Lagrangians leading to regular (explicit or non-explicit) Hamiltonians, and in presence of quadratic final penalty functions, is developed and illustrated. Once the missing boundary conditions are calculated off-line for the whole range (T, S)-family of situations, then the 'Hamilton augmented canonical equations' (HACE) can be integrated online, in parallel with the process, and the optimal control can be constructed in real time from their solution. A system of first-order quasi-linear partial differential equations (PDEs) will be found to relate the boundary conditions for a family of optimal control situations including the original problem. The PDEs treatment of optimal control problems for nonlinear systems with Hamiltonians that cannot be explicitly minimized is novel in the literature.

The organization of the paper is as follows: Section 3 describes the electrochemical system, the main variables and its state-space model. Section 4 describes the objective function, then the (T, S)-optimal control problem is posed, including a differential equation for a control action, and the relevant PDEs to obtain the missing boundary conditions are introduced. Section 5 shows the results of PDEs integration and their application in constructing the optimal control strategy, and illustrates the potential use of (T, S) data at the objective design stage. The whole approach is reviewed and condensed in the Conclusions. An appendix is added to substantiate the general setup valid for the nonlinear case, and the corresponding equations for the implicit-control case are proved.

2. DESCRIPTION OF THE SYSTEM. THE VOLMER–HEYROVSKY–TAFEL STEPS

The dynamics of hydrogen adsorption and desorption over the surface of an electrode (HER) is usually modeled through a combination of three elementary 'steps' [18, 19], with corresponding velocities:

Volmer:

$$\mathrm{H_2O + e^- \rightleftharpoons H_{(ads)} + OH^-}$$
$$v_{\mathrm{V}} = v_{\mathrm{V}}^{\mathrm{e}} \left\{ \frac{1-\theta}{1-\theta_e} \mathrm{e}^{-(1-\alpha)d\eta} - \frac{\theta}{\theta_e} \mathrm{e}^{\alpha d\eta} \right\} \quad (1)$$

Heyrovsky:

$$\mathrm{H_2O + H_{(ads)} + e^- \rightleftharpoons H_{2(g)} + OH^-}$$
$$v_{\mathrm{H}} = v_{\mathrm{H}}^{\mathrm{e}} \left\{ \frac{\theta}{\theta_e} \mathrm{e}^{-(1-\alpha)d\eta} - \frac{1-\theta}{1-\theta_e} \mathrm{e}^{\alpha d\eta} \right\} \quad (2)$$

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Table I. HER's parameters.

Parameter/symbol	Description	Value
$H_{2(g)}$	Gaseous (desorbed) molecular hydrogen	
v_V^e	Equilibrium reaction rate of Volmer step	1×10^{-10}
v_H^e	Equilibrium reaction rate of Heyrovsky step	1×10^{-13}
v_T^e	Equilibrium reaction rate of Tafel step	1×10^{-12}
θ_e	Specific equilibrium surface coverage	0.1
α	Adsorption symmetry factor	0.5
R	Gas constant	$8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}$
F	Faraday constant	$96484.6\,\mathrm{Coulomb\,mol^{-1}}$
T	Absolute temperature	303.15 K
$d=F/RT$	Parameter	$38.2795\,\mathrm{Coulomb\,J^{-1}}$

Tafel:

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

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

where the main variables involved are the following: θ is the 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 are defined in Table I.

By taking all three routes (1)–(3) 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:

$$(\Sigma)\quad \dot{\theta}=\frac{F}{\gamma}(v_V-v_H-2v_T)\triangleq f(\theta,\eta) \tag{4}$$

where γ is the experimentally measured surface density of electric charge to complete a monolayer coverage of $H_{(ads)}$. In the numerical simulations of this paper a value of $\gamma=2.21\times10^{-4}\,\mathrm{Coulomb\,cm^{-2}}$ will be adopted, corresponding to a standard Pt electrode (similar to [20]).

The dynamics of HER are irreducibly nonlinear. This is confirmed by the detection of solution trajectories whose qualitative characteristics are only possible for nonlinear systems (see the extensive review by Hudson and Tsotsis [21]). Simulations and experiments have shown hysteresis-like cyclic behavior, bistability, strange attractors and chaos [22]. These somehow unexpected experimental results shed insight over the theory of adsorption mechanisms, spatiotemporal patterns of catalytic electrodes, and related physical problems. Emphasis will be put on the optimal control of the transient process occurring during set-point changes since these involve large departures of the state variables from one equilibrium (the original steady-state) towards another equilibrium (the target), hence, the nonlinearity of the dynamics will be wholly taken into account.

3. THE CONTROL SYSTEM

Since it is assumed that the overpotential evolution $\eta(\cdot)$ can be (within reasonable bounds) manipulated, then it will be the natural *input* or *control* variable for the system Σ given by (4). On the contrary, the variable θ cannot be directly handled from outside. Once $\eta(\cdot)$ is chosen and applied for $t\leqslant\tau$, then the value of $\theta(\tau)$ contains all the information needed to predict the (near) future evolution of system Σ, hence, θ is the natural *state* variable. The obvious smoothness of HER equations guarantees that for each piecewise continuously differentiable control trajectory $\{u(t)\triangleq\eta(t),\ 0\leqslant t\leqslant T\leqslant\infty\}$ and for each initial condition $x_0\triangleq\theta(0)=\theta_0\in[0,1]$, there exists a continuous solution trajectory $\{x(t)\triangleq\theta(t),\ 0\leqslant t\leqslant T\}$. Although

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knowledge of the state $x(t)$ is enough to describe the dynamics of Σ, x-values might not be continuously measured nor registered. The appropriate variable to be observed is the current density J, which in general is a known function $J=h(x,u)$. If values of J are continuously available, then J is called the *output* of the system Σ. The servo control problem will be able to find trajectories of $u(t)$ that will steer the system Σ from an initial equilibrium (x_0,u_0) into another final equilibrium $(\bar{x},\bar{u})$ with minimal power expense.

In a general case the variables take values $x(t)\in\mathbb{R}^n$, $u(t)\in\mathbb{R}^m$, $J(t)\in\mathbb{R}^m$, which will be maintained in derivations. The *objective functional* $\mathscr{J}$ will take the form

$$\mathscr{J}(u)=\int_0^T L(x(t),u(t))\,\mathrm{d}t + (x(T)-\bar{x})'S(x(T)-\bar{x}) \tag{5}$$

where $\mathscr{J}(u)$ is a short form for $\mathscr{J}(0,T,x_0,u(\cdot))$, i.e. the sum of the cost generated by the admissible control strategy $u(\cdot)$ and by the state trajectory $\{x(t)=\varphi(t,x_0,u(\cdot)),t\in[0,T]\}$ (with φ denoting the state-transition function or transition map of system (4) when $t_0=0$, see [8, 11]) measured by the integral of the Lagrangian $L(x,u)$, plus a quadratic final penalty weighted by some positive definite matrix S, namely

$$K(x)\triangleq(x-\bar{x})'S(x-\bar{x}) \tag{6}$$

This setup will be called a (T,S)-optimal control (or dynamic optimization) problem. Clearly, the desired final state is $\bar{x}$, hence, the problem aims to send x_0 as near as possible to $\bar{x}$ with optimal cost. The Hamiltonian of the problem is defined as usual

$$H(x,\lambda,u)\triangleq L+\lambda' f=L(x,u)+\lambda' f(x,u) \tag{7}$$

where λ is the adjoint or costate variable, with values in $\mathbb{R}^n$, in particular (see for instance [11])

$$\lambda(T)=\left(\frac{\partial K}{\partial x}\right)'(x(T))=2S(x(T)-\bar{x}) \tag{8}$$

H is assumed to be regular [8], i.e. H is uniquely minimized with respect to u (in the domain of operation) by some control value u^0, a continuous function of (x,λ). But the explicit dependence of u^0 on its variables may be unknown, then the usual 'Hamiltonian form' of the problem (in terms of the variables (x,λ) alone) cannot be posed. However, it is still required that the state and costate satisfy the boundary-value problem (see [11, p. 406])

$$\dot{x}=H_\lambda(x,\lambda,u)\triangleq\mathscr{F}(x,\lambda,u),\quad x(0)=x_0\neq 0 \tag{9}$$

$$-\dot{\lambda}=H_x(x,\lambda,u)\triangleq\mathscr{G}(x,\lambda,u),\quad \lambda(T)=2S(x(T)-\bar{x}) \tag{10}$$

Equation (9) is just the dynamics of system (4), and Equation (10) is called the 'adjoint equation'. In a general formulation the variable λ plays the role of a linear functional (therefore, a 'covector', 'costate', 'adjoint variable') on the dual of the tangent plane T_xX, where X is the appropriate state-space (usually a manifold). The Hamiltonian along the optimal trajectory should also verify [11, p. 403]

$$\hbar(t)\triangleq H_u(x^*(t),\lambda^*(t),u^*(t))=0\quad\forall t\in[0,T]$$

where the symbol * means 'optimal values'. Then, along these optimal trajectories

$$\begin{aligned}\dot{\hbar}(t)&=[H'_{ux}\dot{x}+H'_{u\lambda}\dot{\lambda}+H_{uu}\dot{u}]'\\&=[H'_{ux}f-H_{\lambda u}H'_x+H_{uu}\dot{u}]'\\&=[H'_{ux}f-f'_uH'_x+H_{uu}\dot{u}]'\equiv 0\end{aligned} \tag{11}$$

and since H is assumed strictly convex ($H_{uu}>0$), a necessary condition for the optimal control is readily obtained

$$\begin{aligned}\dot{u}&=H_{uu}^{-1}(x,\lambda,u)\{[H_x(x,\lambda,u)f_u(x,u)]'\\&\quad -H'_{ux}(x,\lambda,u)f(x,u)\}\\&\triangleq\mathscr{Y}(x,\lambda,u)\end{aligned} \tag{12}$$

Equations (9), (10), (12) are the announced HACE for the implicit regular problem. Neither initial nor final conditions can be naturally imposed on Equation (12), but constancy of the Hamiltonian along optimal paths (see [7, 11]) provides an additional algebraic restriction

$$\begin{aligned}&H(x^*(T),2S(x^*(T)-\bar{x}),u^*(T))\\&\quad=H(x_0,\lambda^*(0),u^*(0))\end{aligned} \tag{13}$$

which implies that for the three ODEs in Equations (9), (10), (12) there are essentially three missing boundary

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conditions: $x(T), \lambda(0)$, and either $u(0)$ or $u(T)$, the other control value can eventually be recovered from Equation (13).

3.1. Equations for missing boundary conditions

Let us call $\rho(T,S)$ to the optimal final value of the state $x^*(T)$, $\sigma(T,S)$ to the optimal initial value of the costate $\lambda^*(0)$, and $\mu(T,S)$, $v(T,S)$ to the optimal initial and final values of the control variable $(u^*(0), u^*(T))$, respectively, all corresponding to a fixed (T,S)-(optimal control) problem. Two-point boundary value problems for nonlinear ODEs have received much attention in applied mathematics and numerical analysis, and a variety of methods are commonly used to approximate their solution. Invariant imbedding, one of the findings of Richard Bellman, attempts to include the missing final value of the state as a new variable, and the time interval under consideration as a new parameter, into the flow of the original ODE (transition function for control systems), and take advantage of the smooth dependence of the flow on these variables and parameters whenever possible. Since the flow associated with a Cauchy problem is roughly C^k $(k \geqslant 1)$ with respect to state variables, initial conditions, and parameters whenever the vector field is C^k, then Bellman extrapolated this result and worked with the partial derivatives of the flow to obtain dynamic equations involving the boundary conditions and the optimization parameters. Here the missing initial value of the costate is added into the variables, and the final penalty coefficient into the parameters. In the Appendix an outline of the foundations for developing differential equations for the regulation problem, involving the augmented set of variables and parameters, is presented. The extension to the change-of-set-point problem requires replacing, in measuring costs, the values of intermediate and final states x, ρ, by their deviations from the target $x-\bar{x}, \rho-\bar{x}$. After defining

$$\begin{aligned} &F \triangleq \mathscr{F}(\rho, 2S(\rho-\bar{x}), v), \quad G \triangleq \mathscr{G}(\rho, 2S(\rho-\bar{x}), v) \\ &Z \triangleq \mathscr{Z}(\rho, 2S(\rho-\bar{x}), v) \end{aligned} \tag{14}$$

and applying an invariant imbedding type of approach to the HACE's two-point boundary-value associated problem (see the Appendix below, [16] for foundations and [15] for the original idea), then the following equations arise:

$$(\rho-\bar{x})\rho_T - \left(SF + \frac{G}{2}\right)\rho_S = (\rho-\bar{x})F \tag{15}$$

$$(\rho-\bar{x})\sigma_T - \left(SF + \frac{G}{2}\right)\sigma_S = 0 \tag{16}$$

$$(\rho-\bar{x})v_T - \left(SF + \frac{G}{2}\right)v_S = (\rho-\bar{x})Z \tag{17}$$

where ρ_T and ρ_S are notations for the partial derivatives of ρ with respect to the first and second variable, respectively, and the same for σ, v. Expressions (15), (16), (17) form a coupled system of first-order, quasi-linear PDEs. Consideration of a 0-duration process $(x(T) = x_0)$ imposes the following boundary conditions on ρ, σ, v:

$$\rho(0,S) = x_0 \tag{18}$$

$$\sigma(0,S) = 2S(x_0-\bar{x}) \tag{19}$$

$$v(0,S) = g(S) \tag{20}$$

where the final value of the control is obtained, either analytically or numerically from

$$g(S) \triangleq \arg\min_v H(x_0, 2S(x_0-\bar{x}), v) \tag{21}$$

(Notice that x_0 is fixed, hence, g is a function of S only, and it is well defined according to the hypotheses stated in the formulation of the problem.) Finally, after the PDE system is solved, then the initial value μ of the control can be recovered, for each (T,S)- problem, from

$$H(\rho, 2S(\rho-\bar{x}), v) = H(x_0, \sigma, \mu) \tag{22}$$

This methodology will let us obtain (in a range of T and S) the missing boundary conditions in order to simulate the three ODEs (9), (10), (12), referred to as HACE, but it will also represent a large numerical effort since the control system needs to solve three additional PDE equations, including the interpolation method to calculate $g(S)$ and the method to find the roots of Equation (22). However, these computer calculations will be made off-line, that is to say, the computer effort will be made before the process is to be started.

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If the posed problem (4), (5) is solvable, the PDEs, the interpolation function $g(S)$, and the others could be carried out by standard software such as Mathematica or Matlab. In this paper all the simulations were developed in Mathematica 5.2.

4. OPTIMAL SET-POINT CHANGES IN HER SYSTEMS

An equilibrium $(\hat{x}, \hat{u})$—here also called a set-point—will be a pair of values for x and u such that, if they are simultaneously assumed at some time t, then $\dot{x}(t) = f(\hat{x}, \hat{u}) = 0$. The physical situation to be considered in this paper will ask for control trajectories forcing the system to evolve from one equilibrium condition:

$$\{(x(t), u(t)) = (x_0, u_0) = (0.3855, -0.05),\ t \leqslant 0\} \quad (23)$$

towards another equilibrium (the target),

$$\{(\bar{x}, \bar{u}) = (0.4603, -0.06)\} \quad (24)$$

through an admissible path.

When changing of set-points implies significant variations in the state variable, then the full nonlinearity of the system should be handled. Consequently, the original dynamics (4) will be considered together with the observation function

$$J = F(v_V + v_H) \triangleq h(x, u) \quad (25)$$

and the associated 'power density' $\mathscr{P}$ defined by

$$\mathscr{P}(t) \triangleq J(t)\eta(t) = h(x(t), u(t))u(t) \quad (26)$$

The Lagrangian in the generalized cost objective $\mathscr{J}(u)$ will be

$$L = -ku(t)(J(t) - J(0)) \quad (27)$$

where $J(0) = 2.9632 \times 10^{-6}$ V. L will describe the extra electrical power supply that Σ will need to reach the target state. Clearly, the function represented by (27) differs from the typical quadratic functional dependence of the Lagrangian. Since the voltage u is negative, the minus sign guarantees that L is in fact positive for the minimization of the Hamiltonian. Then, in this case H takes the form

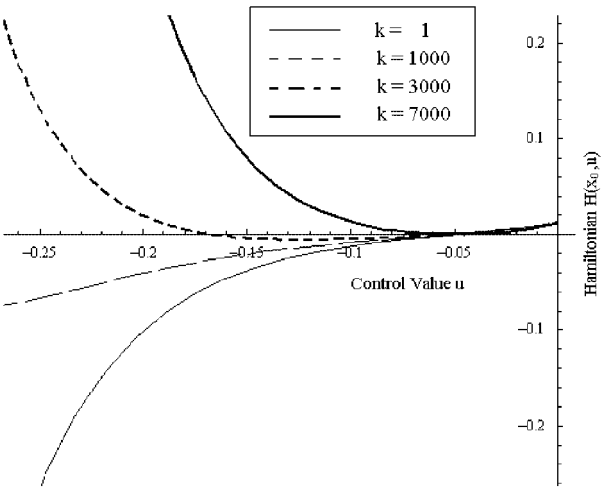

Figure 1. Scale factor k influence on the Hamiltonian. $S = 0.5,\ x = x_0$.

$$\begin{aligned} H(x, \lambda, u) &\triangleq L + \lambda' f \\ &= -ku(t)(F(v_V + v_H) - J(0)) \\ &\quad + \lambda' f(x, u) \end{aligned} \quad (28)$$

The presence of k is required to assure that H is regular and it will also work as a scale factor. It plays a role similar to the constants q and r in a quadratic functional. The value of k used here is 6500. Figure 1 shows the Hamiltonian's behavior for various k. It can be observed that for $k \gtrapprox 2500$, $H(x_0, u)$ becomes regular.

The exact 'invariant imbedding' approach is applicable to this change of set-point problem. The resulting PDEs applied to HER for the missing boundary conditions are given by (15), (16), and (17). In order to solve the PDEs, the missing boundary condition in (20) denoted by $g(S)$, which represents the initial condition for a 0-duration process, must be found. The physical system imposes a constraint over the admissible u^0-values, namely $u^0(T, S) \geqslant u_0$, otherwise, the system would generate electrical power instead of expending it, then the only accepted values are: $v(0, S) < -0.05$. Figure 2 shows that the adopted values of $S \geqslant 0.5$ are compatible with the restriction. The interval used in simulation was then $0.5 \leqslant S \leqslant 5$.

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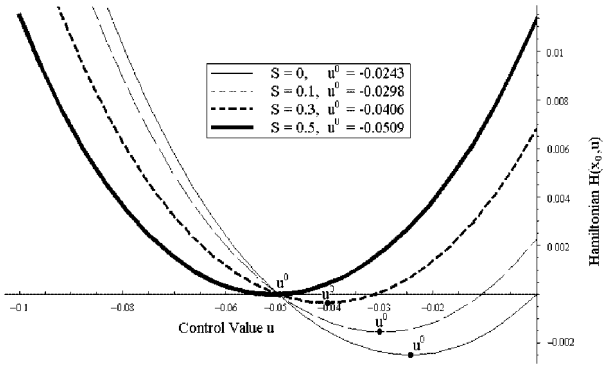

Figure 2. $g(S)$ boundary condition for 0-duration process.

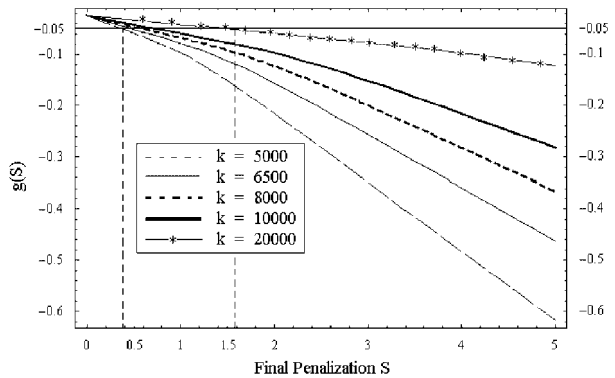

Figure 3. $g(S)$ dependence on k. Admissible S-values.

In Figure 3 the dependence of functions $g(S)$ on the design parameter k is illustrated. The admissible final penalizations S for each k are those that correspond to u values smaller than -0.05, i.e. $g(S) \leqslant -0.05$. Only S greater than those at the intersections $g(S) = -0.05$ will be admissible.

Having found $g(S)$, the PDEs were integrated. Figures 4–6 reveal the solutions for ρ, σ, and v in a range of (T, S) values. It can be observed that, in the range of time-horizons $T \in [0, 1]$, for mild final penalties the attainable final states are far from the target, and for even smaller S-values ρ hardly differs from its initial state $x_0 = 0.3855$ despite the target being bigger ($\bar{x} = 0.4603$). This shows that having the whole family of solutions for a region in the (T, S)-plane is useful to assess, and eventually to modify, the original

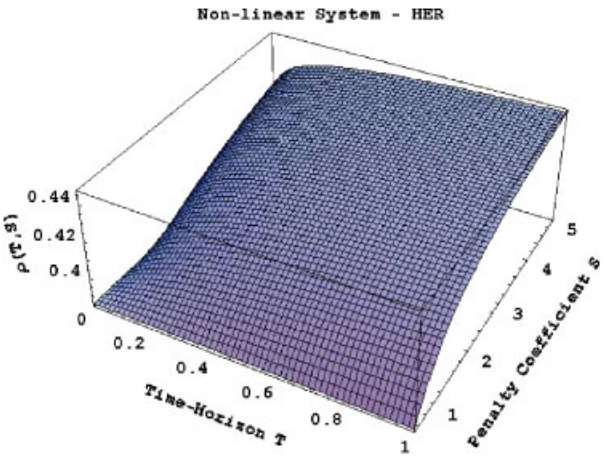

Figure 4. $\rho(T, S)$. Final state, solution to PDEs.

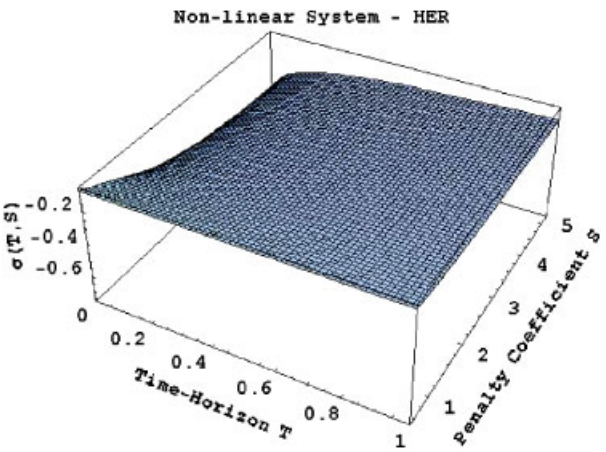

Figure 5. $\sigma(T, S)$. Initial costate, solution to PDEs.

optimization criterion, i.e. the information concerning ρ, σ, and v is also a design tool. It should be stressed that these figures do not show an evolution of the final state, initial costate, and final control action, but just the values of ρ, σ, and v for processes of duration T and final penalization S. In order to obtain the evolution from the fixed initial state chosen in (23) towards the desired final state (24), the Hamiltonian problem for an individual pair (T, S) must be solved. The election of the time interval of duration T, and the final penalization S is related to economic criteria. In this paper we chose $(T, S) = (5, 10)$, the only purpose

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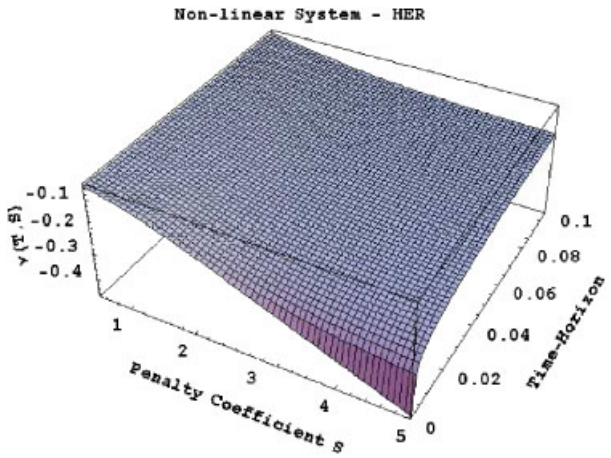

Figure 6. $v(T, S)$. Final control-value, solution to PDEs.

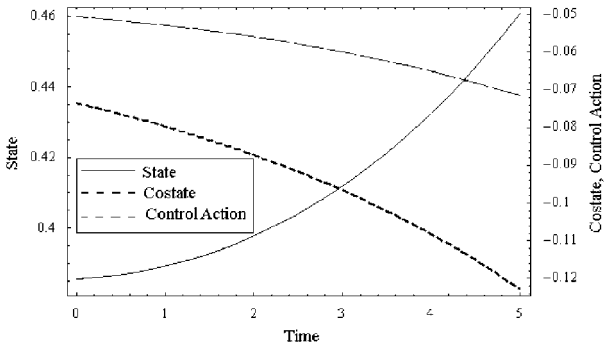

Figure 7. Solution (x, λ) to HCE, and optimal control strategy.

being to show that this change of set-point is possible. The missing boundary conditions for this (T, S)-problem can be extracted from the PDEs' solution as

$$\rho(5, 10) = 0.4590 \tag{29}$$

$$\sigma(5, 10) = -0.0723 \tag{30}$$

$$v(5, 10) = g(10) = -0.0699 \approx -0.07 \tag{31}$$

However, the integration of Equation (12) cannot be started since only a final condition $v(5, 10) \triangleq u^*(5)$ was found. But the unchangeability of Hamiltonian values at end-points lets us to recover the initial condition μ of the control for the pair (T, S) from

$$H(\rho, 2S(\rho - \bar{x}), v) = 1.062117 \times 10^{-6} = H(x_0, \sigma, \mu)$$

$$\Longrightarrow \mu(5, 10) = -0.050047$$

Notice that x_0 and σ are fixed, therefore, $H(x_0, \sigma, \mu)$ is a function only of $\mu(T, S)$. Figure 7 shows the time-evolution of solutions to Hamiltonian equations. The left axis represents the state $x(t)$, while the right axis shows the costate $\lambda(t)$ and the control action $u(t)$. The state trajectory approaches the target with increasing velocity (qualitatively different from the behavior of classical steady-state control results, which steer the state to the target asymptotically, with a decreasing velocity). Correspondingly, the optimal manipulated variable increases in absolute value and surpasses the equilibrium value $\bar{u} = -0.06$. In practical situations, whatever the optimal value $u^*(T)$ results, immediately afterwards the target control value $\bar{u} = -0.06$ is adopted, driving the system to the desired set-point, unless additional optimization criteria are present for $t > T$.

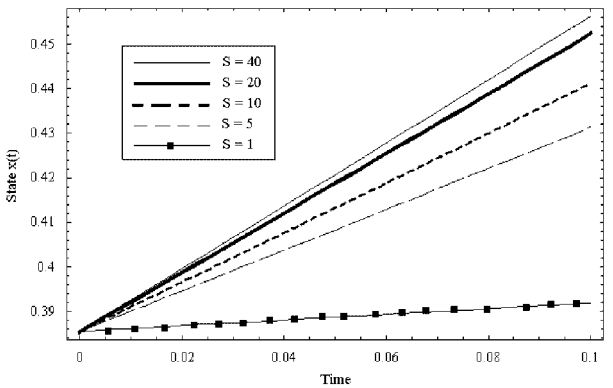

Figure 8. The influence of final penalization S on the optimal state trajectory.

In Figures 8 and 9 it can be seen the effect of varying the penalty coefficient S, the time of optimization being fixed $(T = 0.1)$. For $S = 1$, the system barely moves from the initial state and for $S = 40$ the system arrives very near the set-point.

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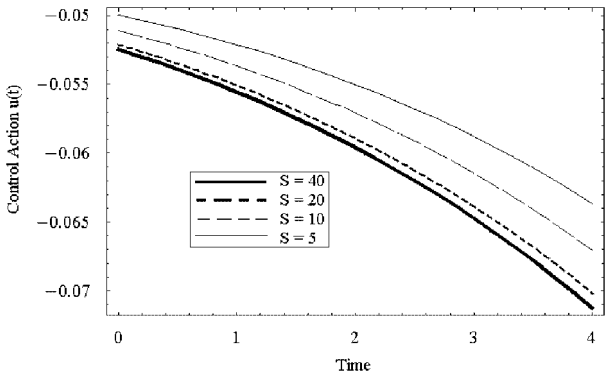

Figure 9. The influence of final penalization S on the optimal control strategy.

5. CONCLUSIONS

An effective procedure for constructing optimal control strategies during set-point changes operations is devised and illustrated through a highly nonlinear problem in electrochemistry. The manipulated variable can be evaluated at each time-instant from the online integration of the Hamilton equations for the problem. This integration turns possible thanks to a previous (off-line) calculation of missing boundary conditions, performed for a family of (T, S) problems governed by three coupled, first-order, quasi-linear PDEs, presented here for the first time.

The information obtained from the PDEs' solution is also important from the design point of view, since the optimal final state ρ reachable for each (T, S) combination becomes accessible from their solutions, hence, appropriate values for the parameters can be chosen before starting the process, in order to obtain a ρ as near to the target state as desired.

A step-by-step procedure for the optimal control of nonlinear systems with regular Hamiltonians, in case the H-minimal control u^0 is not explicitly known, would be:

- Pose Hamilton ODEs as in Equations (9)–(10) and derive an additional ODE for the control variable (12). The functions $\mathscr{F}, \mathscr{G}, \mathscr{Z}$ of (x, λ, u) become explicit.
- From $\mathscr{F}, \mathscr{G}, \mathscr{Z}$ construct (F, G, Z) (14) and obtain the expressions for the PDEs governing the missing boundary conditions (ρ, σ, υ) (15)–(17).
- Find (analytically or numerically) the function $g(S)$ (21), which completes the required boundary conditions (18)–(20) for the relevant PDEs.
- Solve the PDEs plus boundary conditions problem for a range of parameter values (T, S) allowing the desired flexibility in design objectives.
- Obtain the initial control value $\mu(T, S)$ from the Hamiltonian constancy property (22).
- Select the appropriate pair (T, S) and start the control process in parallel with the integration of Equations (9), (10), (12) with initial conditions:

$$x(0) = x_0$$
$$\lambda(0) = \sigma(T, S)$$
$$u(0) = \mu(T, S)$$

The value $u(t)$ resulting from this integration is the (approximate) optimal control to be applied to the physical system.

APPENDIX A: PDEs FOR MISSING BOUNDARY CONDITIONS IN THE IMPLICIT H-OPTIMAL CONTROL CASE

It is assumed that for each combination of parameters (T, S) the boundary-value problem corresponding to the optimal regulation case (target state $\bar{x} = 0$), i.e.

$$\begin{aligned} \dot{x} &= \mathscr{F}(x, \lambda, u), \quad x(0) = x_0 \\ \dot{\lambda} &= -\mathscr{G}(x, \lambda, u), \quad \lambda(T) = 2Sx(T) \\ \dot{u} &= \mathscr{Z}(x, \lambda, u), \quad u(T) = \upsilon \end{aligned} \tag{A1}$$

has a unique solution, varying smoothly with smooth changes in parameters, initial and final conditions. For the (in general nonlinear) system it will also be assumed that there exists a smooth flow $\phi : \mathbb{R} \times O \to \mathbb{R}^n \times \mathbb{R}^n \times \mathbb{R}^m$ (with O denoting some sufficiently large open set in $\mathbb{R}^n \times \mathbb{R}^n \times \mathbb{R}^m$) such that $\phi(t, x, \lambda, u)$ will render the values of the state, costate, and control at time t, along the trajectory that starts (when $t = 0$) at the generic value (x, λ, u). The mathematical soundness of the relevant PDEs will be proved here for the one-dimensional

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case (x, λ, and u scalars), the multidimensional version being discussed in a forthcoming paper. The following notation indicates that the three 'components' of the flow, referring to the state (denoted by ϕ_1 below), the costate (denoted ϕ_2), and the control (denoted ϕ_3), each one in $\mathbb{R}$, will be considered separately

$$\phi(t,x,\lambda,u)=\begin{pmatrix}\phi_1(t,x,\lambda,u)\\ \phi_2(t,x,\lambda,u)\\ \phi_3(t,x,\lambda,u)\end{pmatrix} \tag{A2}$$

and, accordingly, the following identities become clear:

$$\rho(T,S)=\phi_1(T,x_0,\sigma(T,S),\mu(T,S)) \tag{A3}$$

$$\lambda^*(T)=2S\rho=\phi_2(T,x_0,\sigma(T,S),\mu(T,S)) \tag{A4}$$

$$u^*(T)=v=\phi_3(T,x_0,\sigma(T,S),\mu(T,S)) \tag{A5}$$

and where $(x^*(\cdot),\lambda^*(\cdot),u^*(\cdot))'$ is the optimal state-costate-control trajectory corresponding to a fixed horizon duration T and a fixed penalty weight S. The point symbol in $(\cdot)$ stands for the independent variable, in this case time $t\in[0,T]$.

By taking partial derivatives with respect to the first variable in Equation (A3) (the notation $D_1=\partial/\partial t$, $D_2=\partial/\partial x$, $D_3=\partial/\partial\lambda$, $D_4=\partial/\partial u$, following the order of appearance in $\phi(t,x,\lambda,u)$, is adopted to avoid confusion with the values of the involved variables),

$$\begin{aligned}&D_1\rho(T,S)\\ &\quad=D_1\phi_1(T,x_0,\sigma(T,S),\mu(T,S))\\ &\qquad+D_3\phi_1(T,x_0,\sigma(T,S),\mu(T,S))D_1\sigma(T,S)\\ &\qquad+D_4\phi_1(T,x_0,\sigma(T,S),\mu(T,S))D_1\mu(T,S))\end{aligned} \tag{A6}$$

Since the existence of the flow implies

$$D_1\phi(t,x,\lambda,u)=\begin{pmatrix}\mathscr{F}\phi(t,x,\lambda,u))\\ -\mathscr{G}(\phi(t,x,\lambda,u))\\ \mathscr{L}(\phi(t,x,\lambda,u))\end{pmatrix} \tag{A7}$$

i.e. it 'verifies' the original ODEs (A1); then, at the final time T,

$$\begin{aligned}&D_1\phi_1(T,x_0,\sigma(T,S),\mu(T,S))\\ &\quad=\frac{\partial\phi_1}{\partial t}(T,x_0,\sigma,\mu)\\ &\quad=\mathscr{F}(\phi(T,x_0,\sigma(T,S),\mu(T,S)))\\ &\quad=\mathscr{F}(x(T),\lambda(T),u(T))\\ &\quad=\mathscr{F}(\rho(T,S),2S\rho(T,S),v(T,S))\end{aligned} \tag{A8}$$

which in simplified notation leads to

$$\rho_T=F+\phi_{1_\lambda}\sigma_T+\phi_{1_u}\mu_T \tag{A9}$$

Now, the derivative of Equation (A3) with respect to S gives

$$\rho_S=\phi_{1_\lambda}\sigma_S+\phi_{1_u}\mu_S \tag{A10}$$

and repeating the procedure $(\partial/\partial T,\partial/\partial S)$ with Equations (A4)–(A5) renders

$$2S\rho_T=-G+\phi_{2_\lambda}\sigma_T+\phi_{2_u}\mu_T \tag{A11}$$

$$2(\rho+S\rho_S)=\phi_{2_\lambda}\sigma_S+\phi_{2_u}\mu_S \tag{A12}$$

$$v_T=Z+\phi_{3_\lambda}\sigma_T+\phi_{3_u}\mu_T \tag{A13}$$

$$v_S=\phi_{3_\lambda}\sigma_S+\phi_{3_u}\mu_S \tag{A14}$$

Now, the existence of $u^0(x,\lambda)$ allows to write

$$\mu(T,S)=u^0(x_0,\sigma(T,S)) \tag{A15}$$

which then implies, successively

$$\mu_T=u^0_\lambda\sigma_T,\quad \mu_S=u^0_\lambda\sigma_S \tag{A16}$$

$$\mu_T\sigma_S=\mu_S\sigma_T \tag{A17}$$

$$v_T\sigma_S-v_S\sigma_T=Z\sigma_S \tag{A18}$$

The same procedure applied to the two pairs of Equations (A9), (A10) and (A11), (A12) results in

$$\rho_T\sigma_S-\rho_S\sigma_T=F\sigma_S \tag{A19}$$

$$2S\rho_T\sigma_S-2(\rho+S\rho_S)\sigma_T=-G\sigma_S \tag{A20}$$

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and then, in order to have a nontrivial solution in the unknowns (σ_T, σ_S), the determinant of the linear system relating the unknowns must be zero, from which the relevant equation (15) for ρ is obtained.

Similarly, eliminating ρ_S from Equations (A19), (15) the PDE for σ, Equation (16) results.

Finally, by starting again with the pair of Equations (A18), (A20), then after replicating the operational scheme done for σ an analogous PDE is found for v, specifically Equation (17), which is published for the first time in this paper.

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