

# Evaluation and improvement of dynamic optimality in electrochemical reactors

B. Vijayasekaran, C. Ahmed Basha \*

*Central Electrochemical Research Institute, Karaikudi 630006, India*

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## Abstract

A systematic approach for the dynamic optimization problem statement to improve the dynamic optimality in electrochemical reactors is presented in this paper. The formulation takes an account of the diffusion phenomenon in the electrode/electrolyte interface. To demonstrate the present methodology, the optimal time-varying electrode potential for a coupled chemical–electrochemical reaction scheme, that maximizes the production of the desired product in a batch electrochemical reactor with/without recirculation are determined. The dynamic optimization problem statement, based upon this approach, is a nonlinear differential algebraic system, and its solution provides information about the optimal policy. Optimal control policy at different conditions is evaluated using the best-known Pontryagin's maximum principle. The two-point boundary value problem resulting from the application of the maximum principle is then solved using the control vector iteration technique. These optimal time-varying profiles of electrode potential are then compared to the best uniform operation through the relative improvements of the performance index. The application of the proposed approach to two electrochemical systems, described by ordinary differential equations, shows that the existing electrochemical process control strategy could be improved considerably when the proposed method is incorporated.

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## 1. Introduction

The quest for optimal design and control of electrochemical process plant has attracted much attention in recent years. Optimal-control theory has been introduced several years ago to calculate the dynamic temperature-control strategies for chemical reactors to enhance reaction selectivity [1–3], but it has not been extensively applied to electrochemical reactors, although static optimization of electrochemical reactors is a well-discussed topic. The traditional operating modes of electrochemical reactor with constant voltage or constant current are not always the best in a globally competitive electrochemical industry; emphasis must be placed to understand

the dynamic nature of electrochemical reactor engineering problems. The previous contributions to the literature in this area were sparse also; they are all focused on formulating and finding the solution for optimal control input trajectories in a batch electrochemical reactor without electrolyte recirculation.

Bakshi and Fedkiw [4] first determined the time-varying electrode potential that maximizes the desired product produced from a coupled, chemical–electrochemical reaction sequence occurring in a well-mixed batch reactor for a specified reaction time. Fournier et al. [5] presented a methodology of dynamic optimization and optimal control of a batch electrochemical reactor, where a series of two electrochemical reactions occurs. The sensitivity analysis of the optimization criterion and the main important steps that are worth to be analyzed prior to any on-line implementation, are also presented and discussed. Recently, Zhou et al. [6] followed

\* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779.  
E-mail addresses: [vijayasekaranb@yahoo.com](mailto:vijayasekaranb@yahoo.com) (B. Vijayasekaran),  
[cab\\_50@rediffmail.com](mailto:cab_50@rediffmail.com), [basha@cecri.res.in](mailto:basha@cecri.res.in) (C.A. Basha).

the same problem statement and proposed a control vector parameterization approach using the Karhunen–Loève expansion.

The assumption of steady-state approximation for the surface concentrations change with potential variation need not be true. The rate of change of surface concentration of the reactant shows a peak during the batch time; this peak is important to achieve the desired conditions at the end of batch process. This actuality can be evidenced by performing the computation, taking in a step simultaneous variation of the rates of change of both surface concentration and the concentration in the bulk solution. This effect plays an important role in many electrolytic cells [7,8], such as plating and electrochemical synthesis. Sometimes, the concentrations of the reactive species at the surface itself need to be maintained at specified conditions, as in the case of porous electrodes. Thus, concept of taking into account, the surface concentration variation for computing optimal control policy, will provide new insight into the electrochemical power sources that includes fuel cells and super capacitors. This paper further examines the effect of electrolyte recirculation through a continuous stirred tank reactor on optimal electrode potential profile. Scott [9] originally proposed the theoretical basis of the method. More recently, Jayaraman and Basha [10] applied the method for electrochemical reaction modeling in batch electrochemical reactors with/without recirculation.

The calculus of variation-based optimal control method [11–13] has been applied to determine extrema of the functionals. The newer techniques are variations on an old theme; the variations can be appreciated much more if the theme is recalled. The continuous-parameterized technique [14] is the one where a polynomial form approximates the optimal control profile, and the state vector is treated as continuous. The most frequently reported approximation continues on using zeroth-order spline functions to approximate the control profiles. In parameterised-parameterized technique [15], polynomial forms approximately both the state and control variables. Here, accurate approximations are obtained by the use of weighted residual methods, such as orthogonal collocation. These approaches have advantage of easy implementation by making use of existing parametric optimization techniques. One of the practical disadvantages of these two kinds of techniques is that the trial functions are chosen on a priority, based on one's experience, and are arbitrary to a large extent. One of the adverse effects of the arbitrariness is that, many terms or coefficients may be necessary to represent the control profile to an acceptable accuracy. The calculus of variation is a continuous-continuous technique, where both the state and the control solutions are continuous, which can obviously lead to the exact optimal solution for the given problem. This solution is, however, obtained at the expense of a long computational time, but it is not an issue for the latest high-speed computation processing technology.

## 2. Mathematical analysis

Calculus of variations, coupled with maximum principle, is used to calculate the optimal time-varying potential profile. In general, a controlled dynamic optimization process can be described by a set of ordinary differential equations.

$$\dot{\mathbf{x}} = f(\mathbf{x}(t), \mathbf{u}(t)) \quad (1)$$

where  $\mathbf{x}$  is a vector of state variables and  $\mathbf{u}$  is a vector of control or decision variables. The functions  $f_i$  are known for any values of the vector variables  $\mathbf{x} \in X$  and  $\mathbf{u} \in U$ , and are further assumed to be continuous, with respect to the set of variables  $\mathbf{x}$  and  $\mathbf{u}$ , and continuously differentiable with respect to the state variables  $\mathbf{x}$  for the given control  $\mathbf{u}(t)$  in the specified interval  $0 \leq t \leq t_f$ . The initial values of the state variables are:

$$\mathbf{x}(0) = \mathbf{x}_0 \quad (2)$$

Solution of the system Eq. (1) is uniquely defined. Now, the variational problem of interest is, for instance, to maximize an integral functional:

$$J_0 = J_0[\mathbf{x}(t_f)] \quad (3)$$

subject to the constraints Eqs. (1) and (2). For example,  $J_0 = C_D(t_f)$  or in dimensionless form  $J_0 = x_{7}(1)$  for the batch reactor without recirculation; here,  $C_D(t_f)$  is the final concentration of the desired compound. Similarly, for batch reactor with electrolyte recirculation,  $J_0 = x_{11}(1)$ . The constrained optimization problem (Eqs. (1)–(3)) can be transformed into a non-constrained optimization problem by defining an augmented performance index:

$$J = J_0 + \int_0^{t_f} \sum_{i=1}^n \gamma_i [-\dot{\mathbf{x}}_i + f_i(\mathbf{x}(t), \mathbf{u}(t))] dt \quad (4)$$

where  $\gamma_i$ 's are the Lagrange multipliers—they are determined optimally by the computational method used. The resulting problem (Eq. (4)) is then a standard unconstrained optimization problem, whose solution, if it exists, satisfies the following differential–algebraic system [16]. At this stage, it is convenient to introduce a new function  $H$  called 'Hamiltonian' which is defined as:

$$H = \sum_{i=1}^n \gamma_i f_i(\mathbf{x}(t), \mathbf{u}(t)) \quad (5)$$

with the help of  $H$ , we can write the system equations as:

$$\begin{aligned} \dot{\mathbf{x}} &= \frac{\partial H}{\partial \boldsymbol{\gamma}}, & \mathbf{x}(0) &= \mathbf{x}_0, \\ \dot{\boldsymbol{\gamma}} &= -\frac{\partial H}{\partial \mathbf{x}}, & \boldsymbol{\gamma}(t_f) &= \left[ \frac{\partial J_0}{\partial \mathbf{x}} \right]_{t_f} \\ \frac{\partial H}{\partial \mathbf{u}} &= 0 \end{aligned} \quad (6)$$

### 3. Computational scheme

Optimal control profiles under different conditions are determined by using Matlab. It can be seen that the boundary conditions of the state and adjoint variables are split. This is called a two-point boundary value problem and is not easy to solve analytically. This necessitates numerical procedures if all of the system equations are to be integrated in the same direction, either forward or backward in time. The following computational scheme is therefore followed to calculate the optimal profiles:

- (i) Assume an initial control policy  $\mathbf{u}(t) = \mathbf{u}^0(t)$  over the specified interval,  $0 \leq t \leq t_f$ .
- (ii) Integrate the system (Eq. (1)) forward in time from  $t = 0$  to  $t = t_f$ , using the initial value problem solver *ode45*, since  $\mathbf{x}(0) = \mathbf{x}_0$  is known from Eq. (2).
- (iii) Now with the computed trajectory  $\mathbf{x}(t)$ , integrate the adjoint Eq. (6) backward in time from  $t = t_f$  to  $t = 0$ , using the boundary value problem solver *bvp4c*, as  $\gamma(t_f)$  is known from Eq. (6). To improve the solver performance needed for some cases, default integration properties in the solver are altered using the function *bvpset*.
- (iv) Compute  $\mathbf{g}^i(t)$  from the following equation and obtain an improved control vector  $\mathbf{u}^{i+1}(t)$ .

$$\begin{aligned} \mathbf{g}^i(t) &= \frac{\partial H}{\partial \mathbf{u}}(t) \\ \mathbf{u}^{i+1}(t) &= \mathbf{u}^i(t) + \varepsilon \mathbf{g}^i(t) \end{aligned} \quad (7)$$

- (v) Repeat steps (ii) and (iii), until  $\mathbf{g}(t)$  becomes sufficiently small in which case  $\mathbf{u}(t)$  converges to the optimal control policy and further improvement in  $J$  would not be significant.

Stated in more specific terms, the method involves a successive approximation in the control domain, utilizing the gradient to compute a new control function in each iteration. When the control policy reaches the neighborhood of the optimal policy, the progress slows down due to  $\varepsilon$  being a small constant. Therefore, it is better to use varying  $\varepsilon$ , keeping it small in the beginning and gradually increasing it as the control policy is modified in each iteration.

### 4. Batch electrochemical reactor without electrolyte recirculation

The complex reaction scheme used to describe the present approach are coupled chemical–electrochemical reaction taking place in a batch electrochemical reactor; here the reactant A is electrochemically reduced to a stable intermediate, I, which itself is a reactant for two competing parallel reactions: a homogeneous chemical decomposition to the desired product D, or a further electrochemical reduction to an undesired product U. Batch electrochemical reactor [17] can

be operated in two modes, either without electrolyte recirculation or with the recirculation of electrolyte to enhance mass transport processes. For the cases of both with and without electrolyte recirculation through a continuous stirred tank reactor, the reaction scheme is studied. The E, C–E reaction sequence  $A \xrightarrow{E} I \xrightarrow{C} D, I \xrightarrow{E} U$  [18] is similar to that for the reduction of nitrobenzene (A) to the desired product *p*-aminophenol (D) and the undesired product aniline (U) through the intermediate phenylhydroxylamine (I).

Simplifying assumptions are made about the transport and kinetic processes to reduce computational effort while still capturing the essential phenomena. In this manner, the problem statement focused on the improvements resulting from application of the optimal-potential control. The important assumptions in the analysis are as follows: (a) reactor operation is in the steady state, and hence, start-up criteria have been satisfied; (b) all the reaction steps have a first-order concentration dependency; (c) the reactor is well-mixed with mass-transfer resistance occurring by material diffusion through a Nernst diffusion layer, as quantified with a mass-transfer coefficient; (d) the capacitance of the double layer is negligible and the current distribution is uniform; and (e) constant volume conditions prevail and isothermal operation applies. Taking into account the dynamic concentration changes at the electrode surface, the component material balances are:

$$\begin{aligned} \frac{dC_A^b}{dt} &= -k_{m_A} a (C_A^b - C_A^s) \\ \frac{dC_A^s}{dt} &= k_{m_A} a (C_A^b - C_A^s) - k_{10} a e^{-\alpha_1 f E} C_A^s \\ \frac{dC_1^b}{dt} &= k_{m_1} a (C_1^s - C_1^b) - k_3 C_1^b \\ \frac{dC_1^s}{dt} &= -k_{m_1} a (C_1^s - C_1^b) + k_{10} a e^{-\alpha_1 f E} C_A^s - k_{20} a e^{-\alpha_2 f E} C_1^s \\ \frac{dC_U^b}{dt} &= k_{m_U} a (C_U^s - C_U^b) \\ \frac{dC_U^s}{dt} &= -k_{m_U} a (C_U^s - C_U^b) + k_{20} a e^{-\alpha_2 f E} C_1^s \\ \frac{dC_D^b}{dt} &= k_3 C_1^b \end{aligned} \quad (8)$$

Here,  $C_i^b$  is the bulk concentration of the species  $i$ ,  $C_i^s$  is the concentration at the electrode surface, which differs from the bulk concentration  $C_i^b$ , because of the presence of mass-transfer resistance,  $k_{m_i}$  is the mass-transfer coefficient of species  $i$ ;  $f = F/RT$ ,  $\alpha$  is the transfer coefficient, and  $a$  is the specific electrode area. The performance index associated with this reactor–reaction system is:

$$J_0[E(t)] = C_D(t_f) \quad (9)$$

The objective is to determine the time-varying electrode potential that maximizes the  $C_D(t_f)$ , the concentration of the desired product at the end of the specified batch period  $t_f$ . In

a more general sense, we want to determine the control  $E(t)$  which maximize the functional  $J[E(t)]$ , where  $E(t)$  is some function of potential. Eq. (8) can be written in dimensionless form as:

$$\begin{aligned}\dot{x}_1 &= -k_{m_A}^*(x_1 - x_2) \\ \dot{x}_2 &= k_{m_A}^*(x_1 - x_2) - k_1^*x_2 \\ \dot{x}_3 &= k_{m_i}^*(x_4 - x_3) - k_3^*x_3 \\ \dot{x}_4 &= -k_{m_i}^*(x_4 - x_3) + k_1^*x_2 - k_2^*x_4 \\ \dot{x}_5 &= k_{m_U}^*(x_6 - x_5) \\ \dot{x}_6 &= -k_{m_U}^*(x_6 - x_5) + k_2^*x_4 \\ \dot{x}_7 &= k_3^*x_3\end{aligned}\quad (10)$$

where  $x = C/C_{A0}^b$  is the dimensionless concentration of species  $i$ ,  $k_i^* = ak_it_f$  for  $i = 1$  or  $2$ ,  $k_3^* = k_3t_f$ ,  $k_{m_i}^* = ak_{m_i}t_f$  is the dimensionless mass-transfer coefficient of species  $i$ ,  $\dot{x}_i = dx_i/dt^*$  is the dimensionless reaction velocity, and  $t^* = t/t_f$  is the dimensionless time. Only reactant A is present initially, which results in the initial conditions:

$$x_1(0) = 1.0, \quad x_i(0) = 0, \quad \text{where } i = 2, 3, \dots, 7 \quad (11)$$

To restrict the number of variables to be optimized, the electrode potential is a priori mentioned between the lower and upper bounds.

$$E_{\min} \leq E(t) \leq E_{\max} \quad (12)$$

Introducing the seven Lagrange multiplier functions, one for each of the system equations, the unconstrained maximization function can be written as:

$$J = x_7(1) + \int_0^{t_f} \left[ \begin{aligned} &\gamma_1(-\dot{x}_1 - k_{m_A}^*(x_1 - x_2)) + \gamma_2(-\dot{x}_2 + k_{m_A}^*(x_1 - x_2) - k_1^*x_2) \\ &+ \gamma_3(-\dot{x}_3 + k_{m_i}^*(x_4 - x_3) - k_3^*x_3) \\ &+ \gamma_4(-\dot{x}_4 - k_{m_i}^*(x_4 - x_3) + k_1^*x_2 - k_2^*x_4) + \gamma_5(-\dot{x}_5 + k_{m_U}^*(x_6 - x_5)) \\ &+ \gamma_6(-\dot{x}_6 - k_{m_U}^*(x_6 - x_5) + k_2^*x_4) + \gamma_7(-\dot{x}_7 + k_3^*x_3) \end{aligned} \right] dt \quad (13)$$

It should be noted that the multipliers are analogous to the impulse functions in the maximum principle. The Euler–Lagrange equation is expressed as:

$$\frac{d}{dt} \frac{\partial F}{\partial \dot{x}_i} - \frac{\partial F}{\partial x_i} = 0, \quad i = 1, \dots, n \quad (14)$$

where  $n$  represents the number of dependent variables and  $F$  represents the integrand function. The multiplier rule can now be obtained by applying the Euler–Lagrange equation to Eq. (13) for the seven state variables and one control variable  $E(t)$  by considering the integrand in the equation as

function  $F$ .

$$\begin{aligned}\dot{\gamma}_1 &= k_{m_A}^*(\gamma_1 - \gamma_2) \\ \dot{\gamma}_2 &= (k_{m_A}^* + k_1^*)\gamma_2 - k_{m_A}^*\gamma_1 - k_1^*\gamma_4 \\ \dot{\gamma}_3 &= k_{m_i}^*(\gamma_3 - \gamma_4) + k_3^*(\gamma_3 - \gamma_7) \\ \dot{\gamma}_4 &= k_2^*(\gamma_4 - \gamma_6) + k_{m_i}^*(\gamma_4 - \gamma_3) \\ \dot{\gamma}_5 &= k_{m_U}^*(\gamma_5 - \gamma_6) \\ \dot{\gamma}_6 &= k_{m_U}^*(\gamma_6 - \gamma_5) \\ \dot{\gamma}_7 &= 0\end{aligned}\quad (15)$$

$$E(t) = \frac{1}{(\alpha_1 - \alpha_2)f} \ln \left[ \frac{\alpha_1 k_{10} x_2 (\gamma_4 - \gamma_2)}{\alpha_2 k_{20} x_4 (\gamma_4 - \gamma_6)} \right] \quad (16)$$

Thus, the system (Eq. (8)) is already given. The adjoint Eq. (15) is derived. The Hamiltonian and the boundary conditions for the system are:

$$\begin{aligned}H &= \gamma_1[-k_{m_A}^*(x_1 - x_2)] + \gamma_2[k_{m_A}^*(x_1 - x_2) - k_1^*x_2] \\ &+ \gamma_3[k_{m_i}^*(x_4 - x_3) - k_3^*x_3] + \gamma_4[-k_{m_i}^*(x_4 - x_3) \\ &+ k_1^*x_2 - k_2^*x_4] + \gamma_5[k_{m_U}^*(x_6 - x_5)] \\ &+ \gamma_6[-k_{m_U}^*(x_6 - x_5) + k_2^*x_4] + \gamma_7[k_3^*x_3]\end{aligned}\quad (17)$$

The boundary conditions for the adjoint equations are obtained at  $t = t_f$  by applying the second of system Eq. (6), giving  $\gamma_7(t_f) = 1.0$  and other  $\gamma$ 's equal to zero. The dimensionless form of the boundary conditions can be written as:

$$\gamma_i(1) = 0, \quad \text{where } i = 1, \dots, 6 \quad \text{and} \quad \gamma_7(1) = 1.0 \quad (18)$$

Now, starting with an initial guess of the assumed vectorized electrode potential, the iterative procedure as outlined in Section 3 has been followed. The physical data used for the computation are as follows:  $k_1^* = 10^{-4}$ ,  $k_2^* = 10^{-2}$ ,

$$k_3^* = 1.0, \quad \alpha_1 = 0.693, \quad \alpha_2 = 0.398, \quad \tau_1 = 104.58, \quad \tau_2 = 167.33, \\ t_f = 3600 \text{ s}, \quad E_{\min} = -1.0 \text{ V}, \quad E_{\max} = 1.0 \text{ V}, \quad f = 38.68 \text{ V}^{-1}.$$

The converged state trajectories, as well as the control profile obtained, are shown in Figs. 1a and 2, respectively. To illustrate the effect of mass-transfer resistance on the optimal-potential profile,  $k_m$  is varied in the range of  $1-10^5 \text{ cm h}^{-1}$ . To show the importance and need of dynamic optimisation, the resultant concentration profiles over the batch period for the best steady-potential control is also given in Fig. 2b. The best steady potential was found by numerically solving the material balance equations for potentials differing by  $0.001 \text{ V}$

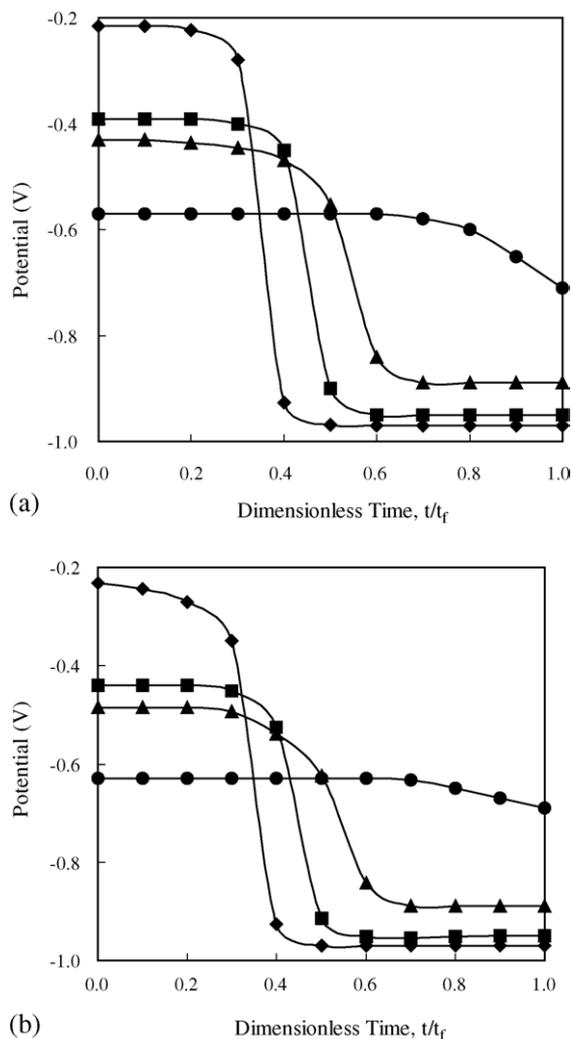


Fig. 1. Optimal control policy obtained for the E–C, E reaction sequence taking place in: (a) batch electrochemical reactor; (b) batch with electrolyte recirculation processes. ( $\blacklozenge$ )  $k_m = 100000 \text{ cm s}^{-1}$ , ( $\blacksquare$ )  $k_m = 1000 \text{ cm s}^{-1}$ , ( $\blacktriangle$ )  $k_m = 100 \text{ cm s}^{-1}$ , ( $\bullet$ )  $k_m = 1 \text{ cm s}^{-1}$ .

from 1 to  $-1 \text{ V}$  and locating that corresponding to the maximum  $x_D(t_f)$ . The extent of the improvement in production above the best steady control will, however, depend upon the values of  $k_i^*$ .

There are considerable differences in the optimal control policies between the steady-state and unsteady-state problem statement. Performance indices resulting from the present approach are exact than the earlier studies on optimal control of batch electrochemical reactor due to the incorporation of concentration dynamics. This improvement points out two major results. First, for some operating conditions ( $k_m \leq 10^3 \text{ cm h}^{-1}$ ), the same performance index is achieved with both operating modes of batch electrochemical reactor, i.e. static and dynamic. It is then not necessary to operate at optimal transient control profiles in that case. Under some other operating conditions, however ( $k_m \geq 10^3 \text{ cm h}^{-1}$ ), the improvements rise up when the optimal control policy is accounted. But this improvement (maximum of 15%) is not

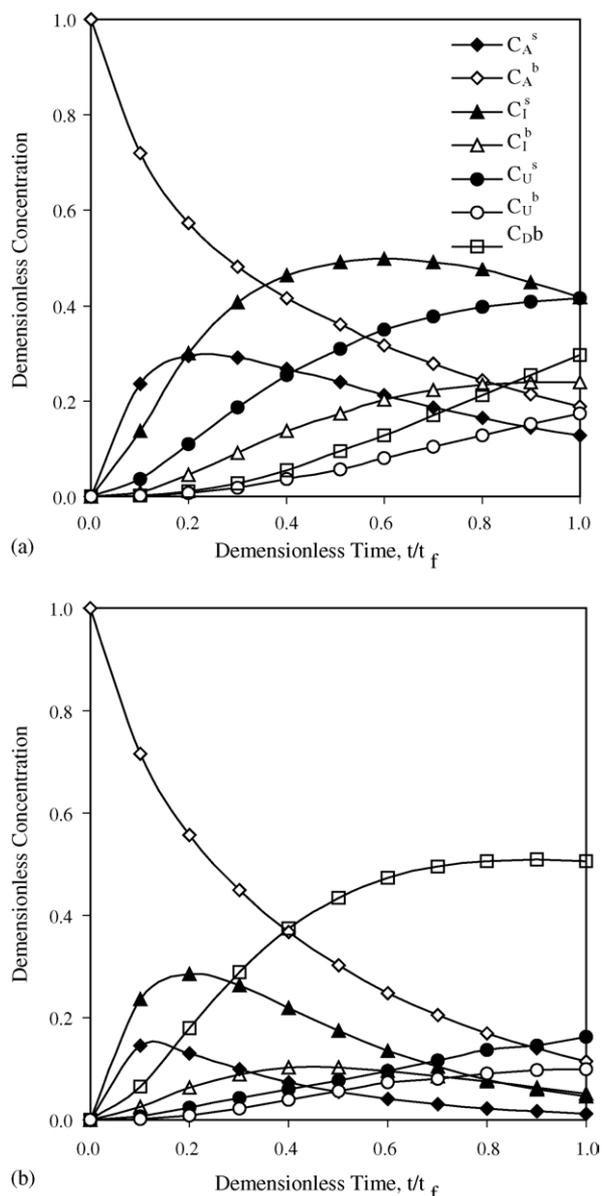


Fig. 2. Dimensionless concentration profiles obtained during the batch period on applying the (a) best steady potential, and (b) optimal time-varying potential in batch electrochemical reactor.

significant; emphasize need for different operating modes of reactor. Thus, for batch operation where the chemical reaction step is desired, the real benefits of using the optimal control theory can be realized by the use of electrolyte recirculation through a stirred tank chemical reactor.

In the simulation process, it is observed that when the value of  $k_m$  is higher than  $10^5 \text{ cm h}^{-1}$ , all the fourteen differential equations become numerically unstable. Therefore, it becomes difficult to solve those ODEs for the entire span of batch process time. Moreover, the solutions obtained from the ODEs violate the conservation of mass even nearer the higher limit of  $k_m$ . To overcome these difficulties, the default integration properties of the ODEs solver performance are increased. The biggest startup cost occurs as the solver attempts

to find a step-size appropriate to the scale of the problem. The solvers for stiff problems are suggested with initial step-size using the function *odeset*. Initial step sets an upper bound on the magnitude of the first step-size the solver tries. Though, use of this option will slow down the computation in most cases, it is necessary for ODE systems which are stiff.

### 5. Batch electrochemical reactor with circulation through a stirred tank reactor

The previous analysis is limited with respect to the reduction in overall rate due to mass-transport restrictions. An overall view of the physicochemical phenomena is that of a series of events, i.e. mass transport–electrode reaction–mass transport. The use of electrolyte recirculation in electrochemical reactor operation is adopted for one or more of the reasons, such as: (a) a high overall conversion of reactant; (b) high degree of flexibility regarding the amount of reactant charge to the reactor; (c) when coupled electrochemical reaction and slow chemical reaction occur, large holding volumes are required to achieve the desired degree of chemical transformation. The simplifying assumptions made regarding kinetics, mechanisms and transport properties are the same as in previous analysis. The model system is that of batch electrochemical reactor with the recirculation of product stream back to the reactor through a continuous stirred tank reactor to achieve a high overall conversion of reactant. The dimensionless component material balance equations for this type of system are:

$$\begin{aligned}
 \dot{x}_1 &= \tau_1^*(x_3 - x_1) \\
 \dot{x}_2 &= k_{m_A}^*(x_3 - x_2) - k_1^*x_2 \\
 \dot{x}_3 &= -k_{m_A}^*(x_3 - x_2) + \tau_2^*(x_1 - x_3) \\
 \dot{x}_4 &= -k_3^*x_4 + \tau_1^*(x_6 - x_4) \\
 \dot{x}_5 &= k_1^*x_2 - k_2^*x_5 - k_{m_1}^*(x_5 - x_6) \\
 \dot{x}_6 &= k_{m_1}^*(x_5 - x_6) - k_3^*x_6 + \tau_2^*(x_4 - x_6) \\
 \dot{x}_7 &= \tau_1^*(x_9 - x_7) \\
 \dot{x}_8 &= -k_{m_U}^*(x_8 - x_9) + k_2^*x_5 \\
 \dot{x}_9 &= k_{m_U}^*(x_8 - x_9) + \tau_2^*(x_7 - x_9) \\
 \dot{x}_{10} &= \tau_1^*(x_{11} - x_{10}) + k_3^*x_4 \\
 \dot{x}_{11} &= \tau_2^*(x_{10} - x_{11}) + k_3^*x_6
 \end{aligned} \tag{19}$$

Here  $\tau_1^* = t_f/\tau_1$ ,  $\tau_2^* = t_f/\tau_2$ ,  $\tau_1 = V_m/q$ ,  $\tau_2 = V_R/q$ ;  $q$  is the volumetric flow rate of the reticulating electrolyte,  $V_R$  and  $V_m$  are the volumes of electrochemical reactor and stirred tank, respectively. The objective here is to determine optimal time-varying electrode potential that maximizes  $C_D(t_f)$ , subject to the listed material balance equations:

$$J_0[E(t)] = x_{11}(1) \tag{20}$$

Only reactant A is present at  $t=0$ , which results in the initial conditions:

$$x_1(0) = 1.0, \quad x_i(0) = 0, \quad \text{where } i = 2, 3, \dots, 11 \tag{21}$$

Introducing the Lagrange multipliers, the problem can be transformed as an unconstrained optimization problem. Using the Euler–Lagrange equation, the multipliers can be expressed as:

$$\begin{aligned}
 \dot{\gamma}_1 &= \tau_1^*\gamma_1 - \tau_2^*\gamma_3 \\
 \dot{\gamma}_2 &= (k_{m_A}^* + k_1^*)\gamma_2 - k_{m_A}^*\gamma_3 - k_1^*\gamma_5 \\
 \dot{\gamma}_3 &= (k_{m_A}^* + \tau_2^*)\gamma_3 - k_{m_A}^*\gamma_2 - \tau_1^*\gamma_1 \\
 \dot{\gamma}_4 &= (k_3^* + \tau_1^*)\gamma_4 - k_3^*\gamma_{10} - \tau_2^*\gamma_6 \\
 \dot{\gamma}_5 &= (k_{m_1}^* + k_2^*)\gamma_5 - k_{m_1}^*\gamma_6 - k_2^*\gamma_8 \\
 \dot{\gamma}_6 &= -\tau_1^*\gamma_4 - k_{m_1}^*\gamma_5 + (k_m^* + \tau_2^* + k_3^*)\gamma_6 - k_3^*\gamma_{11} \\
 \dot{\gamma}_7 &= \tau_1^*\gamma_7 - \tau_2^*\gamma_9 \\
 \dot{\gamma}_8 &= k_{m_U}^*\gamma_8 - k_{m_U}^*\gamma_9 \\
 \dot{\gamma}_9 &= -\tau_1^*\gamma_7 - k_{m_U}^*\gamma_8 + (k_{m_U}^* + \tau_2^*)\gamma_9 \\
 \dot{\gamma}_{10} &= \tau_1^*\gamma_{10} - \tau_2^*\gamma_{11} \\
 \dot{\gamma}_{11} &= -\tau_1^*\gamma_{10} + \tau_2^*\gamma_{11}
 \end{aligned} \tag{22}$$

With boundary conditions:

$$\gamma_i(1) = 0, \quad \text{where } i = 1, \dots, 10 \quad \text{and} \quad \gamma_{11}(1) = 1.0 \tag{23}$$

The control variable is expressed in terms of state and adjoint variables as:

$$E(t) = \frac{1}{(\alpha_1 - \alpha_2)f} \ln \left[ \frac{\alpha_1 k_{1_0} x_2 (\gamma_2 - \gamma_5)}{\alpha_2 k_{2_0} x_5 (\gamma_8 - \gamma_5)} \right] \tag{24}$$

The Hamiltonian derivative of the system is:

$$\frac{\partial H}{\partial E} = \alpha_1 k_1^* f x_2 (\gamma_2 - \gamma_5) - \alpha_2 k_2^* f x_5 (\gamma_8 - \gamma_5) \tag{25}$$

Fig. 1b shows the optimal electrode potential–time profiles obtained by the above computational method. Fig. 3a and 3b compares the concentrations of the reactant and products obtained by dynamic optimization with the traditional operating mode of batch electrochemical reactors, i.e. constant voltage. It is clear that the concentration of desired product at the end of batch time under different mass-transport conditions are superior in case of electrolyte recirculation. Table 1 lists the resultant dimensionless concentrations of the desired and undesired species at the end of batch period for all the four cases of batch—batch with recirculation and steady control of these reactor system.

The greatest production of the desired product is obtained by the optimal potential control of batch electrochemical reactor, with recirculation of electrolyte through a continuously stirred tank reactor. Regardless of the value of  $k_m$ , this system

Table 1

Dimensionless concentrations of the desired and undesired products at the end of the batch period for the best steady potential and optimal time-varying potential operations in Batch and Batch with electrolyte recirculation processes at various mass transport limits

$k_m$	Batch electrochemical reactor				Batch with electrolyte recirculation			
	Static control		Dynamic control		Static control		Dynamic control	
	$x_D$	$x_U$	$x_D$	$x_U$	$x_D$	$x_U$	$x_D$	$x_U$
10000	0.47	0.45	0.58	0.25	0.47	0.43	0.63	0.23
1000	0.30	0.42	0.51	0.16	0.31	0.37	0.54	0.13
100	0.25	0.31	0.47	0.15	0.32	0.34	0.51	0.12
1	0.18	0.24	0.40	0.12	0.19	0.28	0.48	0.10

produces the concentration of D always greater than that of U. It is because of the reactor configuration and time-varying potential that favors the decomposition of the intermediate to the desired product while keeping the undesired electro reduction of I to U, low. Of course, the same trend is also aimed in batch electrochemical reactor without electrolyte recirculation

through the use of optimal control policy. But the production is lowered due to the continuous growth of diffusion layer. Thus, the electron-transfer step is more pronounced than the chemical step. In contrast, under steady-potential control, it is not possible to restrict the formation of U, and its concentration continues to increase by consuming I, which otherwise could have been used to form the desired product D. Obviously, the production rate of the desired product D decreases for all the cases with increasing mass-transfer resistance.

It is only the electrochemical reactor, where we can have a direct control over the reaction velocities, unlike chemical kinetics. Even though, the analogous optimum temperature progression in chemical reactor can have some control over reaction rate, it has been recognized that reaction rates and selectivities control in ordinary chemical reactors are not significantly affected as in electrochemical industry. Because the large thermal inertia associated with the reactor wall, catalyst support, and solvent can notably dampen temperature fluctuations. But the potential or current modulation is particularly sensitive to electro-organic reactions. Fig. 4 illustrates the

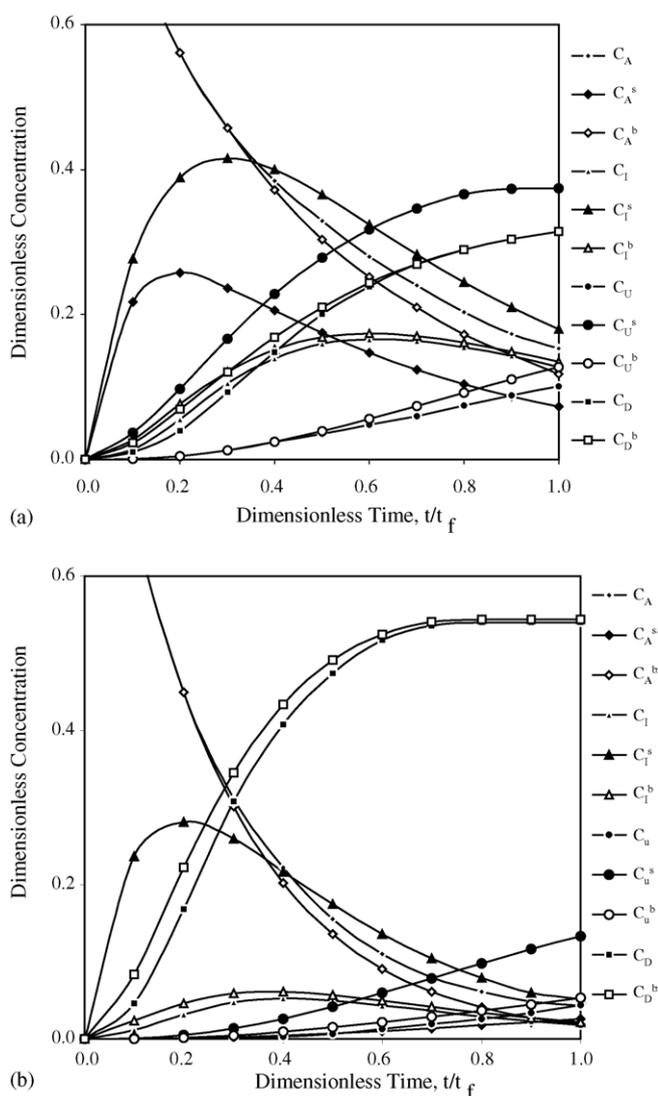


Fig. 3. Dimensionless concentration profiles obtained during the batch period on applying the (a) best steady potential, and (b) optimal time-varying potential in batch electrochemical reactor with electrolyte recirculation.

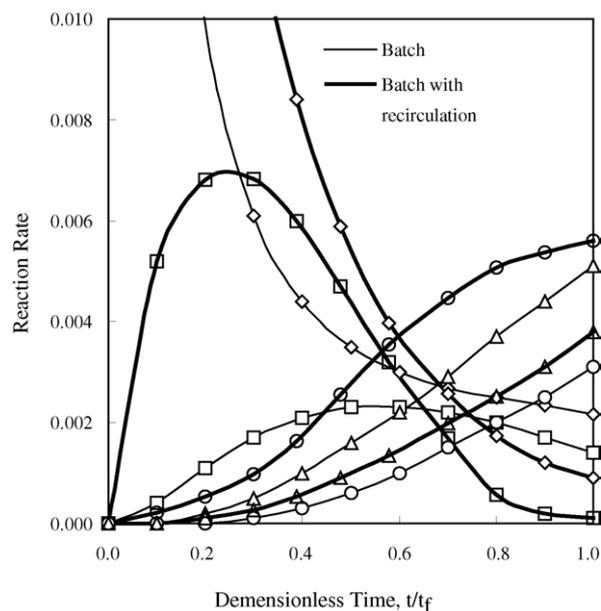


Fig. 4. Representation of the general shape of the electrochemical reaction rate curve for E–C, E reaction mechanism in the two reactor systems. ( $\diamond$ ) Rate of disappearance of the reactant A; ( $\square$ ) rate of appearance and disappearance of the intermediate I; ( $\triangle$ ) rate of appearance of the undesired product U; ( $\circ$ ) rate of appearance of the desired product D.

qualitative nature of the two reaction velocities for the E–C, E reaction scheme under kinetic control. This representation is very much important, as the decision of choosing the best reactor system solely depends on the reaction rate curve. Also, it is clear from the figure, that the rate of formation of D is superior for the case of reactor with recirculation system. Based on the nature of the decomposition rate of the reactant A, the other possible reactor system for the reaction scheme can be decided and worked out for the maximum production of D.

The computational difficulty becomes even more pronounced when reactor with recirculation system is considered. Matlab numerical IVP and BVP solvers control the errors by means of the options RelTol, AbsTol and NormControl. At each step, the solver makes a truncation and/or discretization error that depends on the method and the length of the step. The cumulative effect of these errors depends on the stability of the ODEs near the solution. If the given system of ODEs is stable near the solution (solutions with nearby initial data do not diverge from one another), errors are not amplified, but if the ODEs are unstable near the solution (solutions with nearby initial data diverge), errors are amplified. The default error tolerance property,  $1e-3$ , corresponds to 0.1% accuracy. To achieve the desired accuracy in convergence of assumed profile  $E(t)$ , this error tolerance in solver performance is adjusted to some extent, without sacrificing much accuracy in the exact solution of the ODEs. But this will not diminish the main results. On the other hand, the whole problem of handling the differential equations can be attempted by symbolic inversion technique or successive substitution method using Maple [19,20]. The former technique solves the BVPs for the values at the boundaries as unknown constants, and hence, the solutions once obtained cover various boundary conditions and geometries. The later method gives the series solutions for the BVPs as a function of independent variable and the parameters that appear in the governing equations.

A simple kinetic model is shown to adequately describe the observed phenomena. Thus, the presented methodology can be used to enhance and perk up the process control strategy, currently practiced in electrochemical industries. However, the methodology employed in the examples is general and should also be very useful in simplifying the analysis of other electrochemical reaction systems [21]. Moreover, this methodology is readily extendable to the case where the reactors are connected in series or other complicated electrochemical cell geometries. It is an elegant approach that can be expanded in latter communication. Therefore, it is anticipated that these practice in electrochemical processes will find considerable use in realizing the improved optimal time-varying potential control of electrochemical reactors.

## 6. Conclusion

Surface concentration is one of the most important variables that govern the performance of electrochemical sys-

tems, and hence, it is logical to strive for an increase in reactant conversion to the desired product via precise optimal control policy. In this manner, this paper addresses a dynamic optimization approach, that takes into account, the surface concentration changes during the electrochemical process. In order to obtain solutions with adequate accuracy, efficient ODEs solvers are used in the solution of the state and adjoint system equations. These results are hopeful and put forward the use of this methodology to other reactor–reaction systems.

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