

Optimal potential–time programming in electrochemical batch reactors*

F. FOURNIER, M. A. LATIFI†

Laboratoire des Sciences du Génie Chimique, CNRS-ENSIC, B.P. 451, 1 rue Grandville, 54000 Nancy, France

Received 21 November 1996; revised 19 February 1997

In an electrochemical stirred batch reactor where a series of two reactions $A \rightleftharpoons B \rightleftharpoons D$ takes place, two practical dynamic optimization problems were analysed. More specifically, the optimal profiles of electrode potential which achieve the following performances are determined: (i) maximize the final concentration of product B in a specified batch period t_f and fixed final conversion rate of product A; (ii) minimize the terminal time t_f required to reach a specified selectivity of B. The reaction considered here is the reduction of oxalic acid (A) to glyoxilic acid (B) followed by the reduction of glyoxilic acid to glycollic acid (D). The optimization is carried out by means of Pontryagin's maximum principle and the computational technique used is the control vector iteration method. The influence of the liquid/solid mass transfer coefficients is mainly investigated. It is shown that, for low conversion rates, the optimized and static operating modes achieve the same performances. For high conversion rates however, the performances obtained in realistic operating conditions by applying optimized electrode potential profiles, are substantially improved with respect to best static electrode potential values.

Keywords: *electrochemical batch reactor, selectivity, batch period, dynamic optimization, maximum principle*

Nomenclature

A_e	electrode surface area (m^2)
C	concentration ($mol\ m^{-3}$)
E	electrode potential (V)
F	Faraday constant ($96\ 500\ C\ mol^{-1}$)
i	current density ($A\ m^{-2}$)
I	current (A)
k_b	backward rate constant ($m\ s^{-1}$)
k_d	liquid/solid mass transfer coefficient ($m\ s^{-1}$)
k_f	forward rate constant ($m\ s^{-1}$)
R	universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$)
T	temperature (K)
t_f	batch period (s)
V	reactor volume (m^3)
X	conversion rate

Greek symbols

α	electrochemical transfer coefficient of the direct reaction
β	electrochemical transfer coefficient of the reverse reaction
ν	number of electrons involved

Subscripts

0	initial conditions and constants
1	first reaction
2	second reaction
A	product A
B	product B
D	product D
e	surface
f	final
s	bulk

1. Introduction

Electrochemical reactions often proceed via several successive steps. In the presence of an electric field, some of these steps involve electron transfer and possibly chemical and catalytic reactions. Presently, several selective electrochemical reactions are being examined for industrial use [1–3]. The electrode potential does not play the simple role of a modifier of the rate constant for two steps but becomes an im-

portant optimization parameter. Thus, the selectivity and yield of a reaction intermediate can be improved in short periods and low potentials, depending on transfer coefficients, contrary to conventional kinetics [4]. However, despite recognition of the effect of potential on selectivity control, little information exists on *a priori* selection of optimal operating conditions for electrochemical reactors with multiple reactions.

Traditionally, the optimization of electrochemical processes, on the laboratory scale and on the

* This paper was presented at the Fourth European Symposium on Electrochemical Engineering, Prague, 28–30 August 1996.

† Author to whom all correspondence should be addressed.

industrial scale is carried out by studying the influence of different operating parameters such as current density, electrode potential, flowrates and concentrations, on a defined performance index. Naturally, this kind of optimization (i.e., static optimization) which provides uniform profiles of the control variables is not always optimal.

Optimization of electrochemical processes through the determination of the time varying control variables (i.e., dynamic optimization) is an interesting approach and requires the use of the optimal control theory [5, 6, 7]. The latter has already been applied to many chemical processes, such as simple continuous stirred tank [8], packed-bed catalytic reactors [9], biochemical production [10] and polymerization processes [11]. However, it has not been extensively applied to electrochemical reactors though some encouraging results have already been published [12, 13].

In the present paper, the maximum principle is used to determine the optimal profiles of electrode potential in a batch electrochemical reactor where a series of two cathodic reactions takes place. The objective is to point out the interest of optimal electrode potential-time programming with respect to the best static operating mode.

2. Reactor model

2.1. Mass balance equations

Here a batch electrochemical reactor in which a series of cathodic reactions takes place is considered. The following simplifying assumptions are made: (i) the reactor is perfectly stirred, (ii) the mass transfer resistance occurs by material diffusion through a Nernst diffusion layer and is characterized by a mass transfer coefficient, (iii) no other reactions in addition to those occur, (iv) the capacitance of the double layer is negligible, and (v) the current distribution is uniform.

For a series of two electrochemical reactions $A \leftrightarrow B \leftrightarrow D$, the mass balance equations, subject to the listed assumptions, may be written as

$$V \frac{dC_{As}}{dt} = -\frac{i_1 A_e}{v_1 F} \quad (1)$$

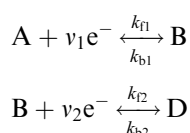
$$V \frac{dC_{Bs}}{dt} = \frac{i_1 A_e}{v_1 F} - \frac{i_2 A_e}{v_2 F} \quad (2)$$

with

$$C_{As}(0) = C_{A0} \text{ and } C_{Bs}(0) = C_{B0} \quad (3)$$

2.2. Kinetic equations

The reaction scheme considered here is the following [14]:



The reactions are assumed to be first order with respect to the reactants. Thus, the reaction rates for both steps are

$$\frac{i_1}{v_1 F} = k_{f1} C_{Ae} - k_{b1} C_{Be} \quad (4)$$

$$\frac{i_2}{v_2 F} = k_{f2} C_{Be} - k_{b2} C_{De} \quad (5)$$

which can be written in terms of mass transfer coefficient as

$$\frac{i_1}{v_1 F} = k_{dA} (C_{As} - C_{Ae}) \quad (6)$$

$$\frac{i_2}{v_2 F} = k_{dD} (C_{De} - C_{Ds}) \quad (7)$$

$$\frac{i_1}{v_1 F} - \frac{i_2}{v_2 F} = k_{dB} (C_{Be} - C_{Bs}) \quad (8)$$

By combining these equations to eliminate the surface concentrations, the reaction rates for both steps become as follows:

$$\frac{i_1}{v_1 F} = a_1 C_{As} + a_2 C_{Bs} + a_3 C_{Ds} \quad (9)$$

$$\frac{i_2}{v_2 F} = b_1 C_{As} + b_2 C_{Bs} + b_3 C_{Ds} \quad (10)$$

where

$$a_1 = \frac{k_{f1} Y k_{dB}^2}{\Delta}$$

$$a_2 = \frac{k_{b1} k_{dB} (k_{f2} - Y k_{dB})}{\Delta}$$

$$a_3 = -\frac{k_{b1} k_{b2} k_{dB}}{\Delta}$$

$$b_1 = \frac{k_{f2} a_1}{k_{dB} Y}$$

$$b_2 = \frac{k_{f2}}{Y} \left(\frac{a_2}{k_{dB}} + 1 \right) \quad (11)$$

$$b_3 = \frac{k_{f2} a_3 - k_{dB} k_{b2}}{k_{dB} Y}$$

$$X = 1 + \frac{k_{f1}}{k_{dA}} + \frac{k_{b1}}{k_{dB}}$$

$$Y = 1 + \frac{k_{f2}}{k_{dB}} + \frac{k_{b2}}{k_{dD}}$$

$$\Delta = XY k_{dB}^2 - k_{f2} k_{b1}$$

The rate constants are defined as

$$k_{fi} = k_{fi0} \exp\left(-\alpha_i \frac{v_i F}{RT} E\right) \text{ for } i = 1, 2 \quad (12)$$

$$k_{bi} = k_{bi0} \exp\left(\beta_i \frac{v_i F}{RT} E\right) \text{ for } i = 1, 2 \quad (13)$$

2.3. Characteristic criteria

Through the paper, two criteria will be used:

(i) Final conversion rate of A:

$$X_{Af} = \frac{C_{A0} - C_{Af}}{C_{A0}} \quad (14)$$

(ii) Selectivity (overall) of B:

$$S_B = \frac{C_{Bf}}{C_{A0} - C_{Af}} \quad (15)$$

The determination of these two variables requires the specification of C_{Af} for X_{Af} and C_{Af} and C_{Bf} for S_B . C_{A0} is being the concentration of the product initially present in the reactor, that is, product A.

3. Optimization problem

The objective is to determine the optimal profiles of electrode potential required to achieve specified performances. Two different and practical problems (P1 and P2) are considered in this study:

P1: Minimize the operating time t_f for a specified selectivity of product B (the final concentrations of both product A and B are fixed). Thus the performance index J (cost functional) to be optimized is defined as

$$J[E(t)] = t_f \quad (16)$$

and the selectivity of B is guaranteed by the following terminal-point constraints:

$$C_{As}(t_f) - C_{Af} = 0 \quad (17)$$

$$C_{Bs}(t_f) - C_{Bf} = 0 \quad (18)$$

P2: Maximize the final concentration of the intermediate product B, in a fixed batch period t_f , for a specified final conversion rate of A. In this case the performance index is defined as

$$J[E(t)] = C_{Bs}(t_f) \quad (19)$$

and the final conversion rate of A is specified through the terminal-point constraint (Equation 17). These two optimization problems are subjected to the following additional constraints:

(i) the potential bounds:

$$E_{\min} \leq E(t) \leq E_{\max} \quad (20)$$

(ii) the mass balance equations (Equations 1–3).

4. Optimization method

The optimization method used is based on Pontryagin's maximum principle [5, 6]. This principle provides a necessary condition to determine control profiles which

(i) optimize the general performance index, J ,

$$J(u) = G[x(t_f), t_f] + \int_0^{t_f} F(x, u) dt \quad (21)$$

(ii) satisfy the state equations,

$$\frac{dx(t)}{dt} = f[x(t), u(t)]; \quad x(0) = x_0; \quad \text{for } 0 \leq t \leq t_f \quad (22)$$

(iii) and satisfy the terminal state constraints,

$$x_i(t_f) - x_{if} = 0 \quad \text{for } i = 1, \dots, nc; \quad nc \leq 2 \quad (23)$$

where $x(t)$ is a n -dimensional state vector (here $n = 2$) and $u(t) [= E(t)]$ is a scalar control variable.

The computational technique used is the control vector iteration (CVI) approach [6]. It attempts to construct a control profile history that simultaneously decreases or increases the performance index, J and satisfies the terminal constraints.

4.1. Minimization of the batch period t_f (Problem P1)

In this case both concentrations of A and B are specified ($nc = 2$) at an unspecified batch period t_f . This is well known as a minimum time problem.

The choice of the following $\delta u(t)$ history and value for dt_f [6]:

$$\delta u = -w \left[\left(\frac{\partial F}{\partial u} \right)^T + \left(\frac{\partial f}{\partial u} \right)^T \left(\psi^{(j)} + \sum_{i=1}^{nc} \mu_i \psi^{(i)} \right) \right] \quad (24)$$

$$dt_f = -b \left\{ \frac{\partial G}{\partial t} + F + \left[\psi^{(j)} \right]^T f + \sum_{i=1}^{nc} \mu_i f_i \right\}_{t=t_f} \quad (25)$$

produces $dJ < 0$, and satisfies $dx_i(t_f) = 0$, for $i = 1, 2, \dots, nc$.

Where:

$$\frac{d\psi^{(j)}}{dt} = - \left(\frac{\partial F}{\partial x} \right)^T - \left(\frac{\partial f}{\partial x} \right)^T \psi^{(j)} \quad (26)$$

$$\psi_j^{(j)}(t_f) = \begin{cases} 0, & \text{for } j = 1, 2, \dots, nc \\ \left(\frac{\partial G}{\partial x_j} \right)_{t=t_f} & \text{for } j = nc + 3, \dots, n \end{cases} \quad (27)$$

and

$$\frac{d\psi^{(i)}}{dt} = - \left(\frac{\partial f}{\partial x} \right)^T \psi^{(i)} \quad \text{for } i = 1, 2, \dots, nc \quad (28)$$

$$\psi_j^{(i)}(t_f) = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases} \quad (29)$$

The appropriate choice of μ is

$$\mu = - \left[Q + \frac{b}{w} S \right]^{-1} \left(g + \frac{b}{w} r \right) \quad (30)$$

where

$$Q_{ij} = \int_0^{t_f} (\psi^{(i)})^T \left(\frac{\partial f}{\partial u} \right) \left(\frac{\partial f}{\partial u} \right)^T \psi^{(j)} dt \quad \text{for } i, j = 1, 2, \dots, nc \quad (31)$$

$$S_{ij} = (f_i f_j)_{t=t_f} \quad (32)$$

$$g_i = \int_0^{t_f} (\psi^{(i)})^T \left(\frac{\partial f}{\partial u} \right) \left[\left(\frac{\partial F}{\partial u} \right)^T + \left(\frac{\partial f}{\partial u} \right)^T \psi^{(j)} \right] dt \quad (33)$$

$$r_i = \left\{ f_i \left[\frac{\partial G}{\partial t} + F + \left(\psi^{(j)} \right)^T f \right] \right\}_{t=t_f} \quad (34)$$

b and w are positive weighting constants. The choice w is very important as far as the conver-

gence is concerned. A very satisfactory value of w is the following function:

$$w^{-1} = \varepsilon \frac{\partial^2 H}{\partial u^2} \quad \text{with } 0 < \varepsilon \leq 1 \quad (35)$$

(where $H = F + (\psi^{(j)} + \sum_{i=1}^{nc} \mu_i \psi^{(i)})^T f$) provided that the involved second derivative is positive [6]. In this case Q and g depend on w .

It is worth noticing that $\psi^{(j)}$ and $\psi^{(i)}$, for $i = 1, 2, \dots, nc$, are different n -dimensional vectors. μ , g and r are nc -dimensional vectors and Q and S $nc \times nc$ matrices.

4.2. Maximization of the final concentration of B (Problem P2)

In this case only the concentration of A is specified ($nc = 1$) at a fixed batch period t_f . A $\delta u(t)$ history that produces $dJ > 0$ and satisfies $dx_i(t_f) = 0$, for $i = 1, 2, \dots, nc$, is also given by Equation 24. In these conditions, the appropriate choice of μ is

$$\mu = -Q^{-1}g \quad (36)$$

The existence Q^{-1} is the controllability condition of the process under consideration [6].

5. Simulations and discussions

The physical data are given in Table 1. The kinetic, mass transfer and operating parameters are chosen to represent an electrochemical system suiting the electroreduction of oxalic acid to glyoxilic acid followed by the electroreduction of glyoxilic acid to glycollic acid [2, 14]. (A = COOHCOOH, B = CHOCOOH, D = CH₂OHCOOH). To point out the optimality of the results, they are compared with those of the best static operations.

5.1. Maximization of the final concentration of B (Problem P2)

Typical convergence rate of the electrode potential profile is shown in Fig. 1. No change in the values of $E(t)$ can be seen after the fourth iteration. One of the main features of the control vector iteration method

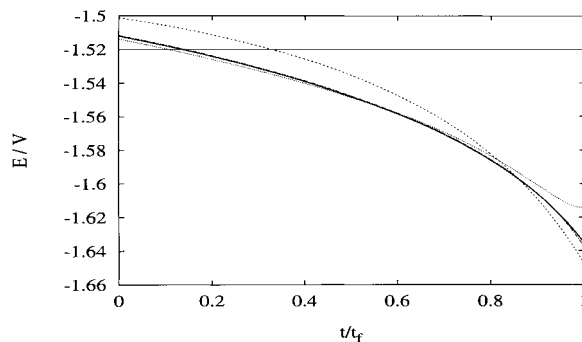


Fig. 1. Convergence rate of the electrode potential profile. Iteration: (1) —; (2) - - - -; (3); (4) - · - · - ·; (14) ———. $X_{Af} = 0.80$; $k_{dA} = 10.0 \times 10^{-5} \text{ m s}^{-1}$.

is to provide a good estimation of $E(t)$ in a very few number of iterations. Another interesting feature of the computational method lies in its ability to provide a simple mean to check whether the system under consideration is controllable. Figure 2 which presents the controllability condition, Q^{-1} , shows that the system remains controllable during the whole iterative process.

To improve convergence process the weighting function $w(t)$ (Equation 35) is used rather than a positive constant. The shapes of these functions, obtained for $\varepsilon = 0.95$ and depicted in Fig. 3, can be easily justified from the convergence rate of $E(t)$ presented in Fig. 1. In fact, at each iteration, in the beginning of the operation and from a uniform initial guess of $E(t)$, the control does not require that much correction as at the end of the operation where the optimal profile exhibits a more rapid decrease.

Various time-varying profiles of the electrode potential are presented in Fig. 4 for different specified final conversion rates of A. It can be seen that the optimal profiles are quasiuniform when low conversion rates are required, showing thus the optimality of static operating mode under such operating conditions.

When high conversion rates are required, the optimal profile is no longer uniform. In the beginning of the operation, the absolute value of the electrode potential is relatively low allowing hence to convert more A into B than B into D since α_1 is greater than

Table 1. Physical data used

Parameter	Value	Unit
A_e	22×10^{-4}	m^2
V	157×10^{-6}	m^3
T	293.15	K
C_{A0}	680	mol m^{-3}
C_{B0}	0	mol m^{-3}
C_{D0}	0	mol m^{-3}
k_{dB}	$0.1 k_{dA}$	m s^{-1}
kf_{10}	1.0×10^{-13}	m s^{-1}
kf_{20}	3.33×10^{-14}	m s^{-1}
kb_{10}	0	m s^{-1}
kb_{20}	0	m s^{-1}
α_1	0.162	—
α_2	0.157	—

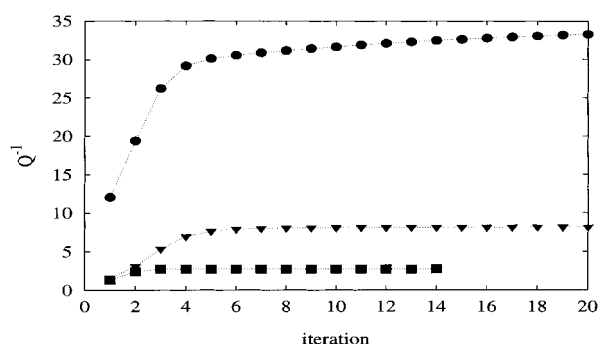


Fig. 2. Controllability condition. k_{dA} : (■) $10.0 \times 10^{-5} \text{ m s}^{-1}$; (●) $7.0 \times 10^{-5} \text{ m s}^{-1}$; (▼) $5.0 \times 10^{-5} \text{ m s}^{-1}$. $X_{Af} = 0.80$.

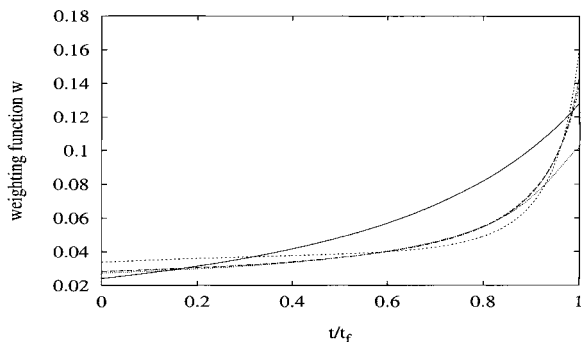


Fig. 3. Weighting function $w(t)$. Iteration: (1) —; (2) - - - -; (3); (4) - · - · - ·; (14) - - - - - - - - . $X_{Af} = 0.80$; $k_{dA} = 10.0 \times 10^{-5} \text{ m s}^{-1}$.

α_2 . At the end of the operation, the absolute value of electrode potential increases in order to ensure the desired conversion rate of A. The optimized profiles of the electrode potential are therefore consistent with the desired performances.

Figure 5 shows the influence of the desired final conversion rate of A, X_{Af} , on the final concentration of B, $C_{Bs}(t_f)$, in both static and dynamic operations. This influence is presented for three different values of the mass transfer coefficient k_{dA} . This figure exhibits a maximum for the two operating modes and for each liquid/solid mass transfer coefficient. This maximum is due to the competition between the two

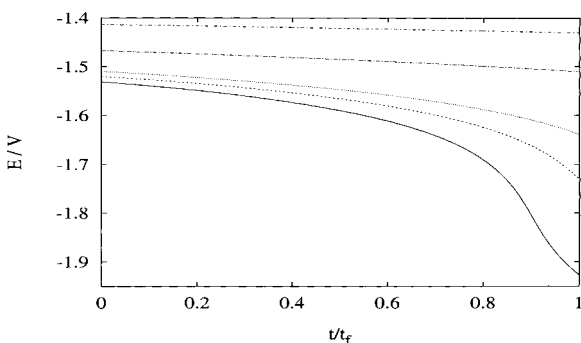


Fig. 4. Optimal profiles of the electrode potential (Problem P2). $k_{dA} = 5.0 \times 10^{-5} \text{ m s}^{-1}$. X_{Af} : (—) 0.80; (- - - -) 0.75; (.....) 0.60; (- · - · - ·) 0.50; (- - - - - - - -) 0.30.

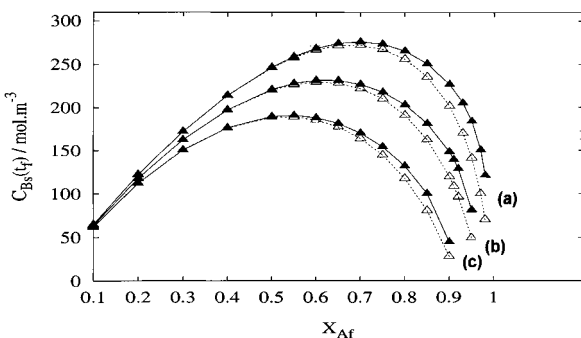


Fig. 5. Final concentration of B against final conversion rate of A for different liquid/solid mass transfer coefficients (static and optimized operations). Key: (\blacktriangle) optimal operation; (\triangle) static operation. k_{dA} : (a) $10.0 \times 10^{-5} \text{ m s}^{-1}$; (b) $7.0 \times 10^{-5} \text{ m s}^{-1}$; (c) $5.0 \times 10^{-5} \text{ m s}^{-1}$.

reactions. Before the maximum value, both static and optimal operations lead to the same results. In these conditions, it is not necessary to operate at optimized electrode potential. This result is in agreement with the quasiuniform optimal profiles of electrode potential in Fig. 4.

On the other hand, when high conversion rates are imposed, the conversion rate of A is achieved at the expense of the production of B. The optimized potential then provides a higher final product concentration (performance index) with respect to the best static operation. This is clearly shown in Fig. 6 which presents the relative improvements of the performance index due to the optimized potential with respect to the best constant values.

It is worth noticing that the best improvements (more than 30%) are obtained for unrealistic potential values since the experimental bounds are $E_{\min} = -1.7 \text{ V}$ and $E_{\max} = -1.0 \text{ V}$ [2]. It is however not easy to account for these limits by means of the maximum principle method. Nevertheless, by using the control vector parametrization (CVP) method [15], which allows to easily handle different types of constraints, the resulting improvements turns out to be lower but still interesting since they rise up to 25%.

5.2. Minimization of the batch period t_f (Problem P1)

The objective here is to minimize the terminal time required to reach a specified selectivity of product B. In the study of the problem P2 (Section 5.1) we used the control vector iteration method and pointed out its major features. Unfortunately, this method has a main drawback. Like all first-order gradient methods, control vector iteration shows great improvements in the first few iterations but has poor convergence characteristics as the optimal solution is approached. It is the case for minimum time problems where the method must be combined with efficient and powerful other methods, especially close to the optimum. For this specific optimization problem, we used the CVI method in the first iterations to have a good initial guess of different variables for another computational method, that is, boundary condition iteration (BCI) [16].

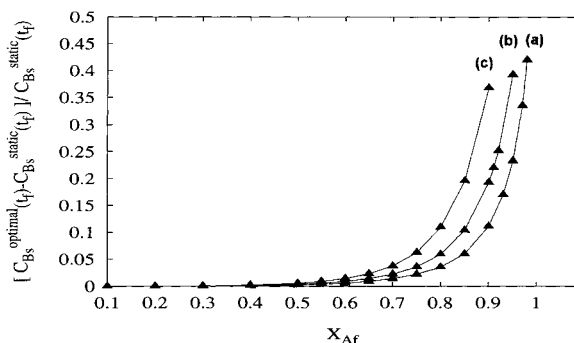


Fig. 6. Final concentration improvement against conversion rate of A for different liquid/solid mass transfer coefficients. k_{dA} : (a) $10.0 \times 10^{-5} \text{ m s}^{-1}$; (b) $7.0 \times 10^{-5} \text{ m s}^{-1}$; (c) $5.0 \times 10^{-5} \text{ m s}^{-1}$.

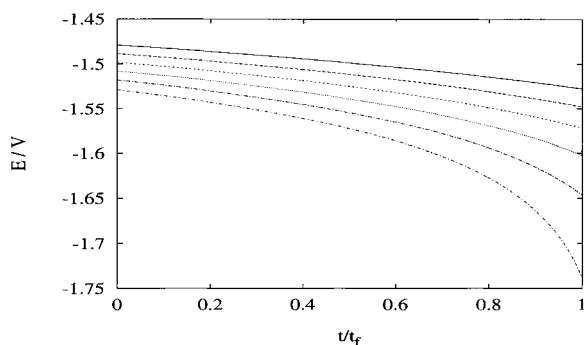


Fig. 7. Optimal profiles of the electrode potential (Problem P1). $k_{dA} = 10.0 \times 10^{-5} \text{ m s}^{-1}$; Key for (X_{Af}, t_f) from top to bottom: (0.60, 3535 s); (0.65, 3514 s); (0.70, 3485 s); (0.75, 3445 s); (0.80, 3388 s); (0.85, 3303 s).

It has to be clear that the combination of these two methods is not the best, but allows us to determine an optimal solution in reasonable computational time.

Typical optimal profiles of electrode potential required to reach a specified selectivity of B in a minimum time are presented in Fig. 7 for different final conversion rates of A ($\varepsilon = 0.95$; $b = 100$). The specified selectivity of B, that is, final concentrations of A and B, to be reached is obtained from the best static operations for a batch period t_f fixed at 3600 s. In fact, the conversion rates of A are limited to the range where the static operation is no longer optimal, that is, between the value which maximizes the final concentration of B and unity, and Fig. 5 provides the corresponding concentration of B. The operating conditions are summarized in Table 2.

Figure 8 shows the optimized time obtained for various final conversion rates of A and for different liquid/solid mass transfer coefficients. It can be seen that since the mass transfer coefficient is used to determine the final concentration of B in static operations, its influence on the optimal terminal time is not significant. It is clearly shown that the batch period can be substantially reduced when the electrode potential is optimized with respect to best static potential values. The improvement of the terminal time with respect to the best static operation (i.e., $t_f = 3600$ s) increases with the conversion rate of A and naturally the reached selectivity of B decreases. The latter may be maintained at a higher level provided that the electrode potential is no longer inside the control bounds.

Table 2. Different operating conditions

X_{Af}	$C_{Af} / \text{mol m}^{-3}$	$k_{dA} =$	$k_{dA} =$	$k_{dA} =$
		$5 \times 10^{-5} \text{ m s}^{-1}$	$7 \times 10^{-5} \text{ m s}^{-1}$	$10 \times 10^{-5} \text{ m s}^{-1}$
		$C_{Bf} / \text{mol m}^{-3}$		
0.60	272	185.6	229.8	266.6
0.65	238	177.5	228.5	271.3
0.70	204	164.0	221.7	272.0
0.75	170	144.8	210.1	267.2
0.80	136	117.6	191.1	255.7
0.85	102	80.2	162.5	235.3

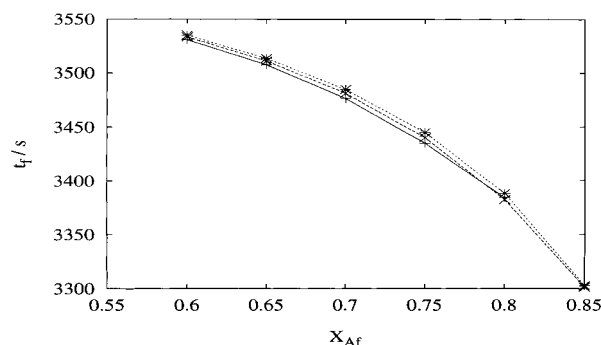


Fig. 8. Minimum time against final conversion rate of A for different liquid/solid mass transfer coefficients. k_{dA} : (+) $5.0 \times 10^{-5} \text{ m s}^{-1}$ (lower curve); (x) $7.0 \times 10^{-5} \text{ m s}^{-1}$; (*) $10.0 \times 10^{-5} \text{ m s}^{-1}$ (upper curve).

6. Conclusions

In the two practical dynamic optimization problems studied here, it is interesting to notice the benefits of optimized operation over constant operation in the case of a nonlinear electrochemical reactor where the model is supposed to be perfect. Despite the fact that perfect models are rare in practical applications, solution of the nominal optimization problems is the most frequent approach, both in academic research contributions and industrial applications. In practical cases, the parameters of the nominal model will be chosen at or near their mean value over the modelling runs. The resultant optimization given this nominal model and neglecting its uncertainty does not necessarily yield poor results in practical problems for at least two reasons [17]. One is that many technical problems, also in the optimization of batch reactors, exhibit very flat, that is, insensitive, optima. The other is that there are cases where the influence of variations on the objective cannot be reduced by appropriately choosing an operating policy, that is, the best strategy found by taking into account the uncertainty is similar to the best strategy ignoring the uncertainty.

Acknowledgement

The authors are grateful to the Ministère de l'Enseignement Supérieur et de la Recherche (MESR) for its partial financial support.

References

- [1] T. Doco, G. Valentin and A. Storck, Récents Progrès en Génie Chimique, Phénomènes fondamentaux, Vol. 3., Tec & Doc, Lavoisier, Paris (1989), p. 164.
- [2] D. J. Pickett and Y. Yap, *J. Appl. Electrochem.* **4** (1974) 17.
- [3] L. Weise, Thèse de doctorat de l'INPL, LSGC-ENSIC, Nancy, France (1987).
- [4] G. P. Sakellariopoulos, *AIChE J.* **25** (1979) 781.
- [5] L. S. Pontryagin, V. G. Boltyanskii, R. V. Gamkrelidze and E. F. Mishchenko, 'The Mathematical Theory of Optimal Processes', Pergamon Press, New York (1964).
- [6] A. E. Bryson and Y. C. Ho, *Applied Optimal Control*, Hemisphere Publishing Corporation, Washington (1975).

-
- [7] W. H. Ray and J. Szekely, 'Process Optimisation', J. Wiley & Sons, New York (1973).
- [8] E. S. Lee, *AIChE J.* **10** (1964) 309.
- [9] M. T. Asrar and A. S. Moharir, *Computers & Chem. Engng* **15** (1991) 533.
- [10] J. Lee and W. F. Ramirez, *AIChE J.* **40** (1994) 899.
- [11] D. Tieu, W. R. Cluett and A. Penlidis, *Polym. React. Engng* **2** (1994) 275.
- [12] M. A. Latifi, S. Risson, and A. Storck, *Entropie* **163** (1991) 37.
- [13] P. S. Fedkiw and R. Bakshi, *J. Appl. Electrochem.* **23** (1993) 715.
- [14] K. Scott, *Electrochim. Acta.* **30** (1985) 235.
- [15] F. Fournier and M. A. Latifi, The 5th World Congress of Chemical Engineering, Vol 1, 14-18 July (1996) San Diego, CA, p. 9.
- [16] F. Fournier and M. A. Latifi, *Chem. Engng Comm.* (1996) in press.
- [17] P. Terwiesch, M. Agarwal and D. W. T. Rippin, *J. Proc. Control.* **4** (1994) 238.