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Optimal time-varying potential profile for electro-hydro-dimerization reactions

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ABSTRACT

Optimal time-varying potential profile for batch electrochemical reactor is evaluated for a major industrial electro-organic synthesis, the electro-hydro-dimerization of acrylonitrile to adiponitrile. The control vector iteration technique is used for computing the optimal profiles. As the technique is continuous on both state and adjoint variables, it can give more accurate profile with no need for any polynomial approximation. A heterogeneous model of the reactor is uniquely used for the formulation of dynamic optimization problem statements by expressing the differential constraints in terms of concentration variations in bulk as well as at the electrode surface. In addition to taking an account of surface concentration variations, the separation of total current as faradic and non-faradic currents is also considered as an additional equality constraint. A path constraint on the electrode potential is imposed for safe reactor function and economical operation. The results of optimum time-varying potential profile are compared with those of applying a steady potential.

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1. Introduction

Batch operations offer some of the most interesting and challenging problems in modeling and process control because of their inherent dynamic nature. Consequently, modeling of batch reactor results in differential and algebraic equations and optimization of such reactors require the use of sophisticated dynamic optimization technique. A great number of industrially important electrochemical reactions in the area of electro-organic synthesis especially involve simultaneous mass transport with chemical reactions. However while performing either static or dynamic optimization; previous contributions [1–5] involve the assumption that electrochemical reactions are taking place with very fast surface electrochemical transformation. Likewise, the separability of total current into faradic and non-faradic current densities is also greatly ignored. As it is the principle characteristics for dynamic models to account for surface concentration dynamics, this investigation provides a new strategy for the optimal time-varying control of a batch electrochemical reactor in adiponitrile synthesis.

Recently, Boovaragavan and Basha [6–7] have discussed this class of problem extensively, indicating how to evaluate time-varying potential distribution in cells where the concentration variations in the bulk as well as at the electrode surface must be considered simultaneously. This work shows that an advanced dy-

namic optimization procedure is not necessary to optimize the rigorous reaction models and the control vector iteration can provide solutions with less computational and programming efforts once the adjoint equations are derived. Another difference in this paper compare to the earlier work is in addressing a different reaction mechanism that is complex and nonlinear due to the two intermediates formation with a total of seven species concentration variations. Thus the main feature of the proposed strategy includes the tasks of taking into account the surface dynamics at electrode surfaces and to keep a total current separation as a constant. Besides these, the results of applying the optimal control theory with those resulting from the best steady controls are also compared so as to realize the potential utility of optimal control policy evaluation. The electro-hydro-dimerization is an interesting example for the application of chemical reaction engineering techniques to electrochemical systems. A reaction scheme that represents the formation of all the products is shown in Fig. 1 which is one of the possible schemes for this synthesis [8–10]. In this system symbol E denotes the electrochemical reaction, symbol C denotes the chemical reaction step, P is propionitrile, T is trimer, D is adiponitrile, I and U are intermediates and B is the radical anion. It can be notice that, this scheme has both competing unimolecular and bimolecular steps leading to the various products.

In dealing with the practical computational solution of optimal control problems (or dynamic optimization problems) there are alternatives one can use [11], as for example complete parameterization of the control and state profiles, direct application of the solution of the necessary conditions of optimality, and control vector parameterization. Each method may be viewed to have its own advantages, as expected. In the last two decades, two main solution

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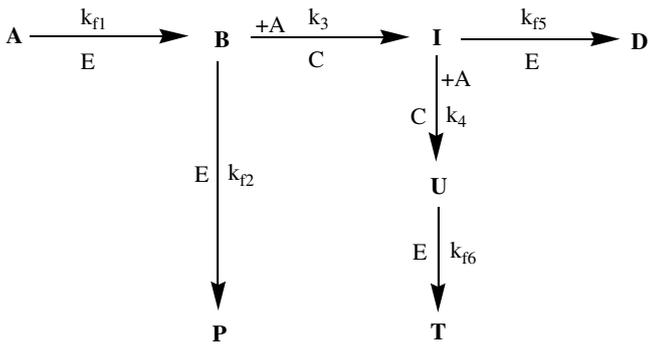


Fig. 1. The coupled chemical and electrochemical reaction scheme for electro-hydro-dimerization of acrylonitrile to adiponitrile.

methodologies have emerged to convert the dynamic optimization problem into a finite dimensional nonlinear programming problem. The key characteristics of the complete discretization approach are the fact that the optimization is carried out in the full space of discretised variables, and the discretised constraints are in general, satisfied at the solution of the optimization problem only. An alternative approach is to carry out the optimization in the state space or decision variables alone. In this article, the computation is carried out by control vector iteration technique, based on the maximum principle. The two point boundary value problem resulting by the application of maximum principle is solved by the assumption of initial control policy. It gives the exact control profiles as the technique treats both state variables as well as decision variables as continuous in their domain with no discretization approach [12].

2. Mathematical model and solution technique

Batch electrochemical processes are usually carried out in standard types of equipment as depicted in Fig. 2, this configuration

can easily be adapted and if necessary reconfigured to produce many other different products. A batch process is inherently an unsteady-state operation where compositions and temperature change with time. However, the common assumption is that all points in time the temperature throughout the reactor is uniform. Simplifying assumptions are also made about the transport and kinetic processes to reduce computational effort while still capturing the essential phenomena. In this manner, this investigation focuses on the improvements resulting from application of the optimal-potential control. The assumptions made are (i) 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, (ii) the homogeneous chemical reactions follows first-order kinetics in the bulk and consumes an inconsequential amount of reactant in the thin Nernst layer, (iii) no other reactions in addition to those shown in Fig. 1 occur, (iv) the current distribution is uniform and (v) the charge-transfer reactions are irreversible with a Tafel-potential behavior, first-order dependence on reactant concentration. Under these conditions the dynamic mass balance equation (Fig. 2) can be written as follows [10]:

$$-\dot{C}_A^b = k_{L_A} a(C_A^b - C_A^s) + k_3 a C_A^b C_B^b + k_4 a C_A^b C_I^b \quad (1)$$

$$\dot{C}_A^s = k_{L_A} a(C_A^b - C_A^s) - k_{f_1} a C_A^s \quad (2)$$

$$\dot{C}_B^b = k_{L_B} a(C_B^s - C_B^b) - k_3 a C_A^b C_B^b \quad (3)$$

$$\dot{C}_B^s = k_{f_1} a C_A^s - k_{L_B} a(C_B^s - C_B^b) - k_{f_1} a C_B^s \quad (4)$$

$$\dot{C}_P^b = k_{L_P} a(C_P^s - C_P^b) \quad (5)$$

$$\dot{C}_P^s = k_{f_2} a C_B^s - k_{L_P} a(C_P^s - C_P^b) \quad (6)$$

$$\dot{C}_I^b = k_3 a C_A^b C_B^b - k_{L_I} a(C_I^b - C_I^s) - k_4 a C_I^b C_A^b \quad (7)$$

$$\dot{C}_I^s = k_{L_I} a(C_I^b - C_I^s) - k_{f_5} a C_I^s \quad (8)$$

$$\dot{C}_D^b = k_{L_D} a(C_D^s - C_D^b) \quad (9)$$

$$\dot{C}_D^s = k_{f_5} a C_I^s - k_{L_D} a(C_D^s - C_D^b) \quad (10)$$

$$\dot{C}_U^b = k_4 a C_A^b C_I^b - k_{L_U} a(C_U^b - C_U^s) \quad (11)$$

$$\dot{C}_U^s = k_{L_U} a(C_U^b - C_U^s) - k_{f_6} a C_U^s \quad (12)$$

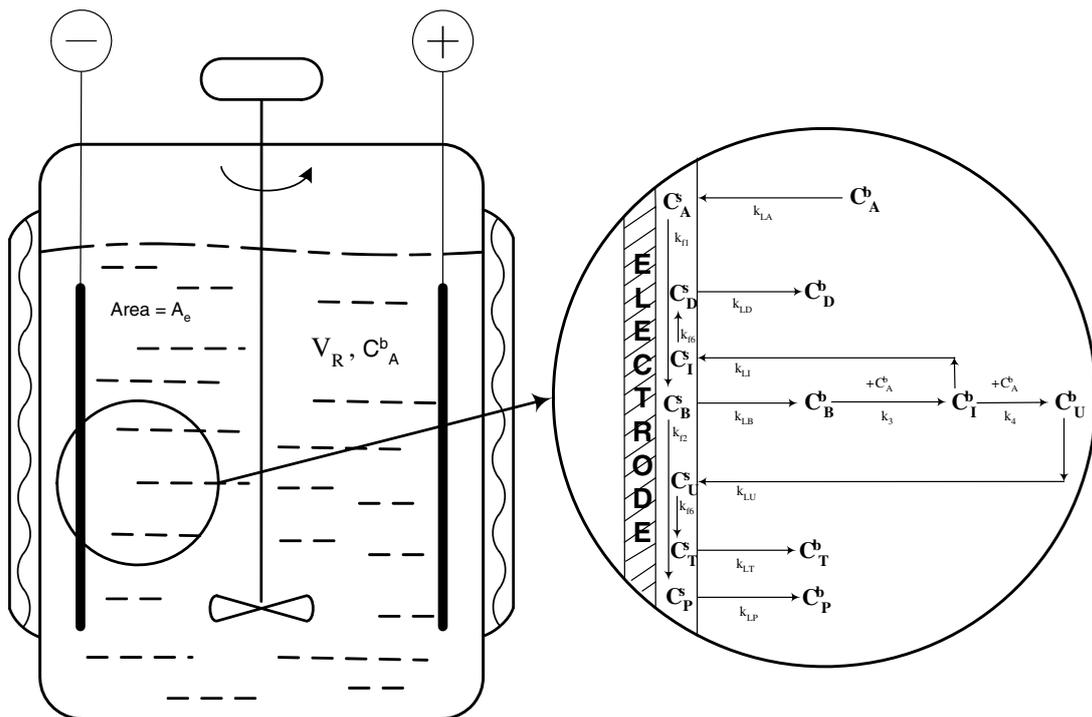


Fig. 2. Schematic representation of the batch electrochemical reactor and species dynamics.

$$\dot{C}_T^b = k_{L_T} a (C_T^s - C_T^b) \quad (13)$$

$$\dot{C}_T^s = k_{f_6} a C_U^s - k_{L_T} a (C_T^s - C_T^b) \quad (14)$$

Here \dot{C}_i^b is time derivative of the bulk concentration of species i , C_i^s is time derivative of the concentration at the electrode surface, k_{L_i} is mass-transfer coefficient of species i and a is the specific electrode area. The forward reaction rates are given by Arrhenius-type expressions where the reaction potential is the electrode potential, $k_{f_i} = k_{f_{i0}} \exp(-\alpha_i f E(t))$ (15)

α is the transfer coefficient and $f = F/RT$. E , the electrode potential is the only control variable. The additional constraints may be of different types: lower and upper bounds of control, interior-point and terminal-point equality and inequality constraints. All these constraints, particularly involved in this dynamic optimization problem, can be written as

$$E_{\min} \leq E(t) \leq E_{\max} \quad (16)$$

$$i_T = C_{dl} \frac{dE}{dt} + i_F \quad (17)$$

Eq. (17) represents the separation of the total current (i_T) into faradic and non-faradic current densities, where C_{dl} is the double layer capacitance and i_F is the faradic current i.e. reaction current and it is given as

$$i_F = k_{f_1} C_A^s + k_{f_2} C_B^s + k_{f_5} C_U^s + k_{f_6} C_I^s \quad (18)$$

The objective is to maximize the conversion of the desired product D subjected to Eqs. (1)–(17) while optimizing the electrode potential profile $E(t)$ within safe bounds. The objective function is

$$J_0[E(t)] = C_D(t_f) \quad (19)$$

The resulting problem is solved using the control vector iteration technique. Step-by-step details of the computation technique and the dynamic optimization algorithm are explained in our previous publications [6–7]. It can be summarized here as follows:

1. Introduce the adjoint variables and write the unconstrained dynamic optimization statement using the differential constraints and their initial conditions.

2. Use the Euler–Lagrangian equation to find out expressions for each adjoint variable and evaluate its boundary condition.
3. Differentiate the state variables forward in time and adjoint variables backward in time till the difference in the converged optimal profile does not differ significantly with the previous iteration.

Some more techniques to solve the simultaneous/coupled system of equations are also introduced and/or explained in [13–14].

3. Results and discussion

In order to ensure high accuracy and consistent results, the default properties of the solver performance (dsolve command in Maple) are adjusted. All computations were done in double precision. It can be noted that different IVP solvers are possible using dsolve: from a Runge–Kutta type method, suitable for the solution of non stiff or mildly stiff systems, to the one based on the BDF approach, using the ‘stiff=true’ option (rosenbrock) suitable for solving stiff ODEs/DAEs. The physical data used for the computation are given as $k_{f_1} = 10^{-2} \text{ m s}^{-1}$, $k_{f_2} = 10^{-4} \text{ m s}^{-1}$, $k_3 = 1.0 \text{ m s}^{-1}$, $k_4 = 0.5 \text{ m s}^{-1}$, $k_{f_5} = 10^{-2} \text{ m s}^{-1}$, $k_{f_6} = 10^{-5} \text{ m s}^{-1}$, $t_f = 3600 \text{ s}$, $E_{\min} = -2.5 \text{ V}$, $E_{\max} = -1.0 \text{ V}$, $f = 38.68 \text{ V}^{-1}$, $a = 140.1 \text{ m}^{-1}$, $C_{A_0} = 17.9 \times 10^{-3} \text{ M}$, $k_{L_A} = 2k_{L_B} = 3k_{L_P} = k_{L_I}/2 = 4k_{L_U} = 3k_{L_T} = 2k_{L_D} = 4k_{L_I}$ where k_L is the parameter varied during the computations from 0.025 to 2500 m s^{-1} .

The profiles in Fig. 3 show the dynamic optimization results obtained at different mass transport levels. The profile shows a mixed kinetics behavior: partly controlled by mass-transfer and partly controlled by kinetics. The steep fall in the potential that appears at about -1.65 V is due to avoid the unwanted electron transfer reaction leading to P, by product. Vijayasekaran and Basha [6] reported a similar situation in the electrochemical reduction of nitrobenzene to *p*-aminophenol. The underlying cause for the increase in electrode potential after a certain period of time is that the transfer coefficient for the reaction $I \rightarrow D$ is larger than that for the reaction $U \rightarrow T$; that is, high potential kinetically favor the reaction leading to D. In between these two dynamic phases the process is kept at some constant low potential for certain period

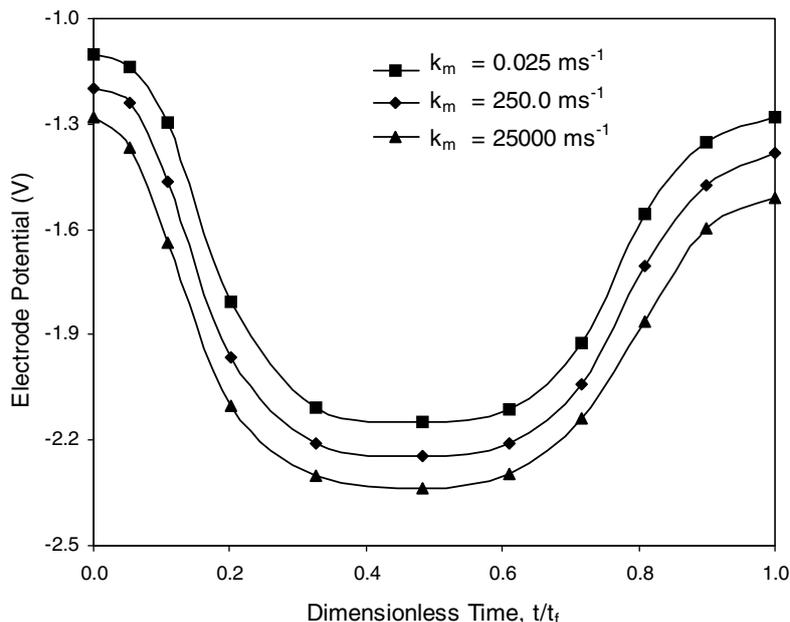


Fig. 3. Plots of optimal operation policy at various mass transport levels.

of time so as to enhance the chemical transformation of $B \rightarrow I$. But under steady control the diffusion layer becomes depleted out of I at large cell voltages with a commensurate increase of the fraction of the current going to reduction of U. From this perspective, it is seen that this approach towards the problem statement can produce an effective optimal control policy. A very minimal part of this optimal control work was presented and discussed during the annual meeting of the electrochemical society [15].

Fig. 4 shows the response of optimal control policy for the case where the overall process is controlled by both mass-transfer and kinetics ($k_L = 250 \text{ m s}^{-1}$). Fig. 5 presents the concentration distributions under steady control; this case is included for comparison and was found by solving numerically the IVPs, Eqs. (1)–(14) using

dsolve command for potentials differing by 0.01 V from -1.0 to -2.5 V and locating that corresponding to the maximum $C_D(t_f)$ satisfying the Eqs. (16)–(18). At the end of the reaction period, a substantial amount of the A is reduced in both steady control and continuous control. But it has not successfully reacted further to form $I \rightarrow D$ during steady electrode potential, the selectivity is high but the production is low. The drop in the production is due to the depletion of A in the cathode diffusion layer and the simultaneous increase of P or T. Consequently, an increasing fraction of the current goes to the electrochemical reductions of $B \rightarrow P$ and $U \rightarrow T$.

It can be seen that significantly higher D selectivity and production are obtained if the electrolyte is allowed to go through a dy-

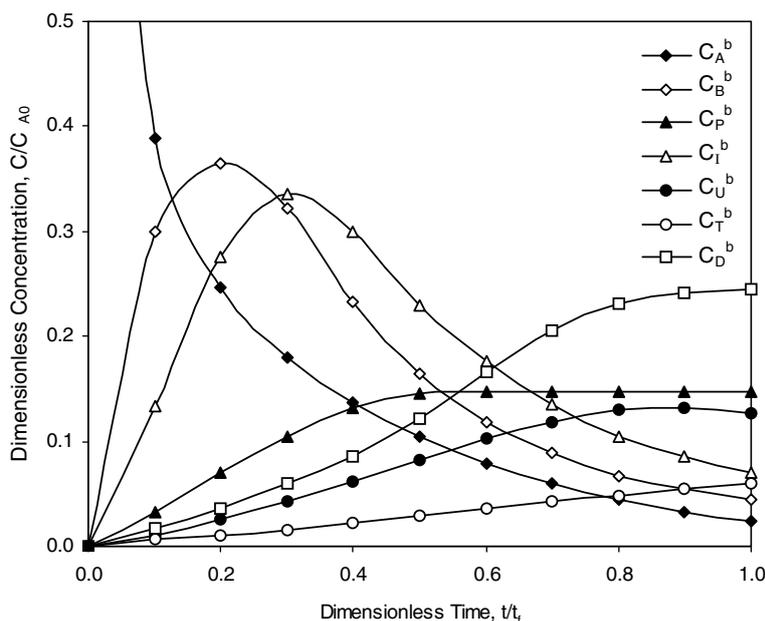


Fig. 4. Variations of dimensionless concentration on applying the optimal time-varying potential in batch electrochemical reactor for electro-hydro-dimerization.

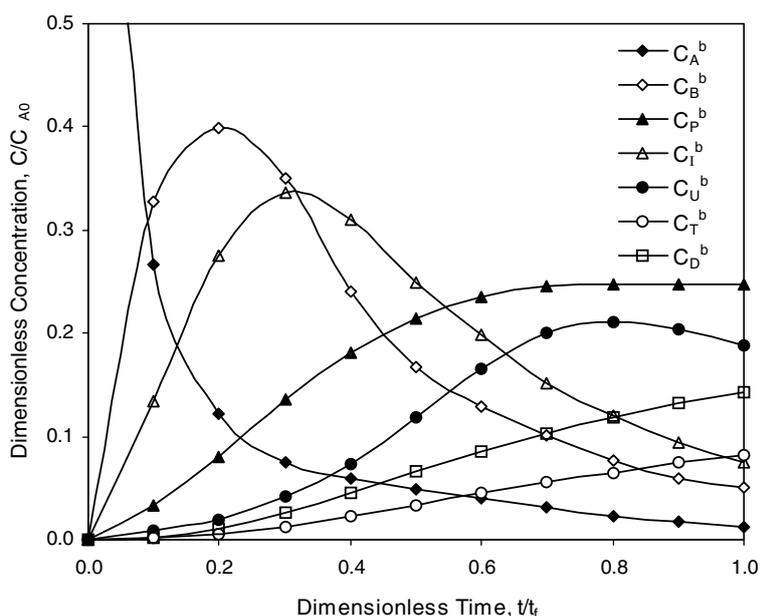


Fig. 5. Variations of dimensionless concentration on applying the best steady potential.

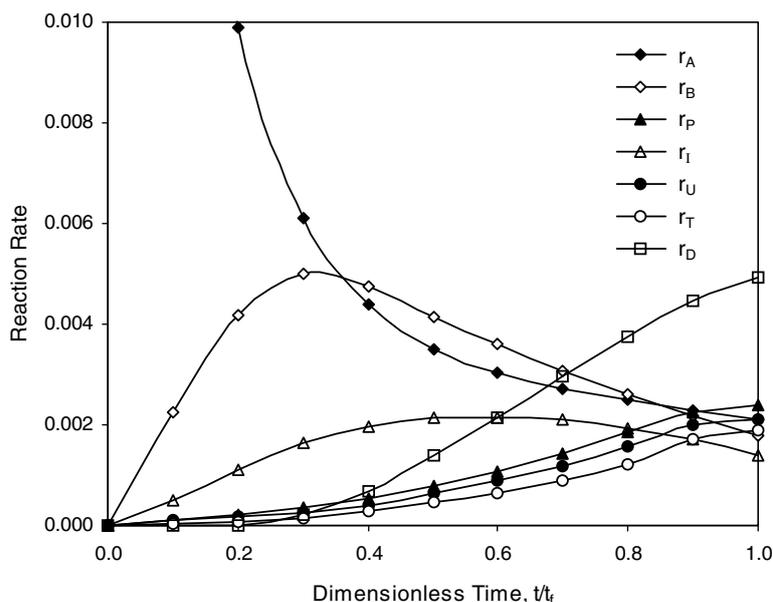


Fig. 6. The electrochemical reaction rate curve for the electro-hydro-dimerization reaction.

dynamic variation in applied potential. The maximum production of the desired product is obtained by applying rate of low potential during the intermediate period of the reaction, thereby allowing maximum diffusion of the bulk concentration of B and a consecutive decrease in the bulk concentration of I. Also it is interesting to note that these optimal trends are resulted irrespective of the mass transport rate and the results are obtained by applying minimum energy.

The aim of electrochemical industries is to produce high quality and purity product. Therefore, the dynamic optimization of batch operating conditions such as electrode potential is more efficient approach to obtain a maximum yield in a minimum cost, as well as to reach the specific final conditions of the product in terms of quality and quantity. In contrast to chemical reactors, the dynamic manipulation of voltage or current is much easier than temperature or concentration, flow rate, pressure, etc., such an investigation offers fascinating possibilities for electrochemical reaction engineering. Fig. 6 shows the electrochemical reaction rate distribution, this high rate of desired reaction is achieved by following the best optimal time-varying potential profile ($k_L = 250 \text{ m s}^{-1}$). Thus the control over electrode potential in electrochemical reactor is ultimately a control over the reaction rate occurring inside the electrochemical reactor. Such a strong controlling capability for chemical reactions taking place in a chemical vessel is not possible.

Though the treatment of unsteady-state concentration dynamics for this reactor-reaction system is efficiently handled, the main objective here has been to evaluate the optimal time-varying potential profile for the electro-hydro-dimerization of acrylonitrile to adiponitrile. This significant reaction mechanism has a six-step sequence composed of both series and parallel chemical and electrochemical reactions. Strictly looking into the system, the side reactions such as anodic gas evolution and more exact parameter values should also be considered. This complex and strongly coupled reaction scheme should be completely incorporated into a process control model for an efficient control.

4. Conclusion

If electro-organic process is to move forward, a better understanding of the role of the surface concentration dynamics

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 control

$k_m \text{ (m s}^{-1}\text{)}$	Static control			Dynamic control		
	C_D^b/C_{A_0}	C_P^b/C_{A_0}	C_T^b/C_{A_0}	C_D^b/C_{A_0}	C_P^b/C_{A_0}	C_T^b/C_{A_0}
25,000	0.1761	0.2753	0.1121	0.2819	0.1881	0.0853
250.0	0.1423	0.2476	0.0821	0.2451	0.1481	0.0600
0.025	0.1030	0.2242	0.0591	0.2310	0.1217	0.0435

and non-faradic contribution in electrochemical synthesis is required. Hence, a precise optimal time-varying electrode potential profile was obtained using control vector iteration technique. This optimal profile can greatly enhance the process control strategy in electrochemical synthesis. The evaluated optimal profiles of the electrode potential are realistic since the most important physico-chemical phenomena are considered. To facilitate solutions with adequate accuracy, efficient ODEs solvers are used in the solution of the state and control variables. The performances of the optimized operating modes are compared to those of the best static modes. The resulting improvements rise to a significant percentage, hence showing the economical interest of dynamic operating mode.

Once the optimal operation policies are obtained, these controls can be implemented by designing appropriate controllers. It is clear that in on-line optimization, all these important steps are required prior to any experimental validation. As an important effort has been paid to physical evaluation of the numerical results, the dynamic operating mode of the electrochemical reactor seems to be very encouraging (see Table 1).

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