

Optimization of Electrochemical Reactors Using Genetic Algorithms

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Electrochemical reactor optimization using Genetic Algorithms (GAs) has been attempted in the present work. The objectives have been focused to determine the (i) optimal design parameters that maximize the yield of the product under specified conditions and (ii) optimal current density that minimizes the operating cost of the reactor. As a vehicle to do so, a reaction mechanism is considered in which the reactant is electrochemically reduced to a desired product and further reduced to an undesired product. Both, batch and continuous reactors have been considered for performance evaluation and simulation has been done at various kinetic parameters. To illustrate the potential utility of genetic search and to justify the use of GAs for this type of optimization problem, we begin our search for optimality with usual algorithms like Exhaustive search, Fibonacci search and Golden section search techniques. The comparative results of these techniques and experimental results show that GAs find optimal reactor cost and product yield, that is also found to agree with the reactors used in industries and in the reported literature. As a result, the need to obtain a good initial guess can be eliminated also with less number of generations to reach optimum level even for a large design problem.

Key words:

Genetic algorithms, electrochemical reactor optimization, simulation, yield, damköhler number.

Introduction

The design and optimization of electrochemical reactor play an important role in the development of electrochemical processes. Various search tools such as Fibonacci, Golden section and Nelder-Mead simplex search are adopted for optimizing electrochemical reactors. The objective of the paper is to illustrate the utility of GAs technique and potential benefits realized upon its application. As a vehicle to do so, the optimum yield that maximizes the production of the desired product of a multiple reaction are determined in, both, batch electrochemical reactor and continuous stirred tank electrochemical reactor (CSTER). The series of two electrochemical reactions involved in an electrochemical reactor is considered for the demonstration of GAs. The assumptions made in the present approach are (i) solvent decomposition does not occur and (ii) there is no variation in the parameters of the Tafel equations. Further, the effect of reversibility in the electrochemical kinetics is observed. Accordingly the mathematical models of complex electrochemical reaction schemes have been developed.^{1,2} The model is used to simulate the behavior of a potentially useful organic synthesis (the electro reduction of oxalic acid to glyoxylic acid).³

The mass transport of reactant and products from/to the electrode surface plays an important

role in describing overall reaction rates. Since the electricity required per unit of product greatly depend on the plant size, design, and on load rating, in the present investigation an optimum current density has been addressed with the objective of minimum cost of electrolytic cell. The reactor costing model expressions obtained for use in two ideal reactor configurations: batch and CSTER are also served as a model for application to other reaction systems.

Over last decade, GAs have enjoyed a large scale application for wide spectrum of engineering design problems.⁴⁻⁷ GAs are search and optimization procedure motivated by natural principles and selection in the quest of producing better and more suitable individuals. In principle, GAs are very different search algorithm than the traditional search and optimization techniques. The unique features of GAs are simplicity, global perspective, and parallel processing capability. These features make GAs to solve other search and optimization problems efficiently, including multimodal, multiobjective and scheduling problems, as well as fuzzy-GA and neuro-GA implementations. Detailed discussion of the working of GAs can be found in Goldberg.⁸ The aim of this paper is to extend the application of GAs for electrochemical reactor design and its optimization. The purpose of an optimization algorithm is to find a solution for which the function has optimum. Once the variable limits are bracketed, a more sophisticated algorithm needs to be used to

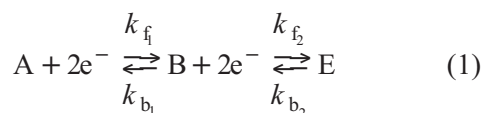
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improve the accuracy of the solution. For the mathematical problem under consideration, several algorithms are used that primarily work with the different principles. The results obtained from GAs in the present study are compared with those obtained from the traditional algorithms for optimization.⁹ This stochastic optimization method is highly robust and is very fast in terms of computation time when compared to the other methods and also it is well in predicting the exact solutions. The result show that in all cases the GAs have been able to converge closer to the optimal value.

The rest of this paper is organized as follows: First of all the formulation of the optimal electrochemical reactor problem is described. Thereafter, a brief description of the reactor-costing model is presented. Simulations using GAs has been compared with traditional optimization techniques. Finally, simulation results of GAs for different conditions are presented. Results show that the optimal yield and cost is well predicted by GAs while comparing with the traditional optimization techniques. Also, these results seem to be supporting the practice in industry as documented in Scott.¹⁰ The success story of GAs in this paper suggests further use of GAs in similar design problems.

Problem statement

The reactions involved in the electrochemical reactor, that is used for demonstration of the optimization using GAs, are consecutive:



where A denotes oxalic acid, B the product glyoxalic acid and E the byproduct glycolic acid. Although, there are other possible side reactions including hydrogen evolution, they are ignored for the sake of simplicity. The kinetics of the two reactions are assumed to be first order with the respect to the reactants and, both, forward and backward reaction rates are given by Arrhenius-type expressions. The rate equation may be written as¹¹

$$\frac{j_1 \cdot a}{n_1 F} = x_1 c_A^b + x_2 c_B^b + x_3 c_E^b \quad (2)$$

$$\frac{j_2 \cdot a}{n_2 F} = y_1 c_A^b + y_2 c_B^b + y_3 c_E^b \quad (3)$$

The rate coefficients of electrochemical reaction in equations (2) and (3) are given as (Table 1).

$$k_{f_i} = k_{f_{i0}} \exp\left(-\beta_i \frac{2F}{RT} E\right) \quad (4)$$

$$k_{b_i} = k_{b_{i0}} \exp\left(-\alpha_i \frac{2F}{RT} E\right) \quad (5)$$

Batch Electrochemical Reactor

For a series of reaction operating under batch conditions the material balances may be written as

$$-\frac{dc_A}{dt} = \frac{a j_1}{n_1 F} \quad (6)$$

$$\frac{dc_F}{dt} = \frac{a j_2}{n_2 F} \quad (7)$$

$$\frac{dc_B}{dt} = \frac{a}{F} \left(\frac{j_1}{n_1} - \frac{j_2}{n_2} \right) \quad (8)$$

From the stoichiometry, the overall material balance for the above reaction sequence can be written as

$$c_{A_0} = c_A + c_B + c_E \quad (9)$$

The reaction behavior can be obtained from the variation of c_B/c_{A_0} with fractional conversion. Considering the product distribution at high electrode potential, mass transfer resistance provides detrimental to intermediate product distribution. Substituting the equations (2) and (3) into equations (6) to (8), the system can be described by two simultaneous first order differential equations, which results the following solution (assuming $k_{LA} = k_{LB}$)

Table 1 – Expressions used for the Evaluation of Constants in the Equations (2) & (3)

$x_1 = \frac{k_{f_1} J k_{LB}^2}{J k_{LB}^2 - k_{f_2} k_{b_1}}$	$x_2 = \frac{k_{b_1} J k_{LB}^2 \left(\frac{k_{f_2}}{k_{LB} J} - 1 \right)}{J k_{LB}^2 - k_{f_2} k_{b_1}}$	$x_3 = -\frac{k_{b_1} k_{b_2} k_{LB}}{J k_{LB}^2 - k_{f_2} k_{b_1}}$	$I = 1 + \frac{k_{f_1}}{k_{LA}} + \frac{k_{b_1}}{k_{LB}}$
$y_1 = \frac{k_{f_2} a_1}{k_{LB} J}$	$y_2 = \frac{k_{f_2}}{J} \left(\frac{a_2}{k_{LB}} + 1 \right)$	$y_3 = \frac{k_{f_2} a_3}{k_{LB} J} - \frac{k_{b_2}}{J}$	$J = 1 + \frac{k_{f_2}}{k_{LB}} + \frac{k_{b_2}}{k_{LB}}$

$$\frac{c_B}{c_{A_0}} = \frac{1}{\left(\frac{k_{f_2}}{k_{f_1}} - 1\right)} [(1 - X) - (1 - X)^q] \quad (10)$$

where

$$Y = \frac{1 + Da_1}{\frac{k_{f_1}}{k_{f_2}} + Da_1}$$

It can be noticed from the equation (10) that the Damkohler number and the ratio of rate constants affect the product yield. The Damkohler number and reaction rate constants are subjected to change within the given limit. The physical data and operating conditions, that have been considered for the simulation, are given below¹²

$$\begin{aligned} k_L = k_{LA} = k_{LB} &= 2.0 \cdot 10^{-4} \text{ m s}^{-1}, \\ k_{f1} = 10^{-5} \text{ m s}^{-1}, \quad k_{f2} &= k_{f1}/10, \quad k_{b1} = k_{b2} = 0, \\ T &= 293.15 \text{ K}, \quad p = 101325 \text{ Pa}. \end{aligned}$$

Continuous Stirred Tank Electrochemical Reactor

The governing material balance for a consecutive reaction in a CSTER can be written as

$$c_B = a\tau \left(\frac{j_1}{n_1 F} - \frac{j_2}{n_2 F} \right) \quad (11)$$

$$\frac{c_A}{c_{A_0}} = \frac{1}{1 + \frac{a\tau k_{f_1}}{1 + Da_1}} \quad (12)$$

The current density j_2 is expressed as

$$\frac{j_2 a}{n_2 F} = \frac{k_{f_1} Da_1 c_A}{(1 + Da_1)(1 + Da_2)} + \frac{k_{f_2} c_B}{(1 + Da_2)} \quad (13)$$

Combining equations (11) to (13), concentration of c_B can be obtained as a function of electrode potential. Thus the relationship between c_B/c_{A_0} and conversion is given as

$$\frac{c_B}{c_{A_0}} = \frac{X_A}{\left\{ 1 + Da_2 + \frac{(1 + Da_1)X_A}{k_{f_1}(1 - X_A)} \right\}} \quad (14)$$

It can be seen from the above equation that mass transport rate reduces the maximum yield of product B at a fixed electrode potential. The physical data and operating conditions used in the simulation of CSTER are the followings.

$$\begin{aligned} a &= 140.1 \text{ m}^{-1}, \quad k_L = k_{LA} = 10 \text{ m s}^{-1}, \quad k_{LB} = 10^{-4} \text{ m s}^{-1}, \\ k_{f10} &= 10^{-13} \text{ m s}^{-1}, \quad k_{f20} = k_{f10}/3, \\ k_{b10} = k_{b20} &= 0, \quad \beta_1 = 0.162, \quad \beta_2 = 0.157, \\ \alpha_1 = \alpha_2 &= 0, \quad T = 298.15 \text{ K}, \quad p = 101325 \text{ Pa} \end{aligned}$$

Reactor Costing Model

The costs analysis of electrolytic reactor can be divided into three components namely, the investment cost, energy cost, and fixed cost.

Investment costs: the cost per unit electrode area including depreciation and interest on the capital. The specific investment cost associated with the electrochemical reactor ' C_R ' is directly proportional to electrode area and inversely proportional to current density, i.e

$$C_R = a \cdot A \cdot t$$

Electrical Energy Costs: The energy cost is directly proportional to the current density and other electrical equipments used. Thus energy cost can be given by

$$C_E = b V I t$$

where V is the voltage, the overall voltage balance may be written as

$$V = V_D + IR + \sum_j |\eta_j|$$

Fixed Costs: The fixed cost consists of amortization and interest on fixed investment cost and costs of the wages of personnel whose number is independent of the current density. It is assumed that the fixed cost equals the 10 % of this sum. Finally, the cost of the process operating per unit time can be conveniently expressed as ampere-hour of energy supplied, which can be expressed as

$$\begin{aligned} C_T &= \frac{a z F P}{\epsilon_j} + b \left\{ \frac{-\Delta G^0}{nF} + i \frac{1}{\kappa} + a_a + b_a \log j + \right. \\ &\left. + a_c + b_c \log j + \frac{RT}{nF} \ln \frac{j_L - j}{j_L} \right\} \frac{z F P}{\epsilon_c} + C_F \quad (15) \end{aligned}$$

The first term on the right hand side represents the electrochemical reactor cost, followed by the cost associated with the energy requirement and the fixed investment cost. The data used for the simulation are given in Table 2.

Table 2 – Parameters used in the Costing Model

Reactions	
Cathodic reaction	$A + 2e^- \xrightleftharpoons[k_{b_1}]{k_{f_1}} B + 2e^- \xrightleftharpoons[k_{b_2}]{k_{f_2}} E$
Anodic reaction	$H_2O - 2e^- \rightarrow 2H^+ + 0.5O_2$
Production flow rate	1.0 kmol h ⁻¹ of product B
Process data	
Initial reactant concentration	1.0 kmol m ⁻³
Required conversion	0.99
Temperature	298.15 K
Pressure	101325 Pa
Electrolyte resistance (l/κ)	500 Ω m
Availability	12 hours per day
Reaction data (298.15 K)	
	$a_a = a_c = 0.059V$
	$b_c = 200$ mV/decade
	$b_a = 150$ mV/decade
	$\varepsilon_c = 95\%$
	$\Delta G^0 = -222.74475$ KJ mol ⁻¹
	$j_L = 0.325$ A m ⁻²
Costs	
Batch reactor	
Capital cost coefficient of the reactor, a	5 MU m ⁻² h ⁻¹
Electricity cost, b	0.00541 MU m ⁻² h ⁻¹
CSTER	
Capital cost coefficient of the reactor, a	6 MU m ⁻² h ⁻¹
Electricity cost, b	0.00941 MU m ⁻² h ⁻¹
Nominal reactor life	10 years

Numerical simulation and results

Coding GAs using MATLAB® 6.0 in a 1.8GHz Pentium IV processor solves the formulated problems. The other search techniques are used to solve the problem by a custom C coding. The other techniques include the Exhaustive search, Fibonacci search, and Golden section search algorithms. To have a high accuracy of simulated process variables, the floating-point representation of variable has been chosen. Roulette wheel proportionate selection is applied for the reproduction operation. A single-point crossover operator and a bit-wise mutation operator are used. Table 3 gives the GA parameters used in the present study. The simulation

Table 3 – Values of GA Parameters Used in the Present Work

Number of generations	50
Selection mechanism	Roulette method selection
Crossover	Simple
Crossover probability	0.6
Mutation	Binary
Mutation probability	0.05
Representation of variables	Floating point
Coding of simple genetic algorithm	MATLAB® 6.0

results are given in Figure 1. It can be seen from the figure that the GAs are quite more powerful than the traditional algorithms. In all cases, the search has been carried out in the same interval of uncertainty. In Fibonacci and Golden Section methods the same shrinkage has been produced, resulting into a greater number of function evaluations in the case of latter which obviously produces a better result. One difficulty of Fibonacci search method is that the Fibonacci numbers have to be calculated and the total number of experiments to be conducted has to be specified before beginning the simulation. In order to overcome these two problems and yet calculate one new function evaluation per iteration, the golden section search method (Golden number = 0.618) is used. The Exhaustive search method is a simultaneous search method in which all the experiments are conducted before any judgment is made regarding the location of the optimum point. On the other hand GAs are found to have surprising speed of convergence to near-optimal solutions. The last two columns in Table 4 compare the performance of various traditional optimization algorithms based on the results obtained from the GAs.

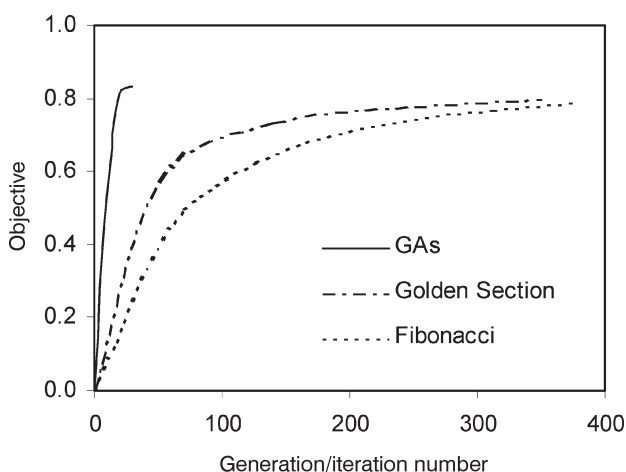


Fig. 1 – Comparison of various search techniques

Table 4 – Comparison of Results for Yield Optimization

Method	Conversion, X		Yield, Y		Function evaluation		% deviation			
	batch	CSTER	batch	CSTER	batch	CSTER	conversion		yield	
							batch	CSTER	batch	CSTER
GAs	0.9487	0.8712	0.8303	0.5646	30	30	0	0	0	0
Fibonacci	0.9031	0.8205	0.7997	0.5416	350	375	-4.81	-5.82	-3.66	-4.07
Golden Section	0.8910	0.8122	0.7879	0.5397	377	392	-6.08	-6.77	-5.11	-4.41
Exhaustive	0.7529	0.6749	0.6319	0.4337	957	1156	-20.64	-22.53	-23.89	-23.18

The yields obtained at different conditions using GAs for the fitness function of yield are given in Table 5; it can be noticed that GAs predict the real situation more accurately and the yield of the desired compound for the reaction scheme lies in the range of 0.52 to 0.83. It has been observed that the optimum yield of the desired product increases with decreasing Damkohler number. It has also been observed that the increasing Damkohler number enhances reverse reaction. It can be noticed from Table 6 that the maximum profit expected from CSTER is less due to poor yield and high operating cost. From the present observation and that reported in literature, it can be reiterated,¹³ that the performance of the CSTER is inferior to that of the batch electrochemical reactor. The electrochemical

reactor optimization methodology used in the present investigation can also be applicable to plug flow electrochemical reactors, where the batch real time is replaced by space–time. Three different initial populations (initial population of 10, 20 and 30) have been applied to investigate the effect of GA parameters on the optimum yield. The results show that in all cases GAs have been able to converge closer to the same tabulated values. In other simulations with different GA parameter values (population number = 50; crossover probability = 0.9; mutation probability = 0.01) identical results were obtained. GA can be used in the modeling of reactors, even in the presence of poor information of reactor performance. All these GAs results are consistent with previous theoretical predictions of glyoxylic acid production.^{3,10}

Table 5 – GA Based Optimal Parameters for Batch Electrochemical Reactor at $k_f/k_r = 8.5$

Da	Conversion	Yield	Number of generations
0.05	0.9084 (0.9080)	0.7410 (0.7395)	20
0.50	0.8835 (0.8812)	0.6598 (0.6589)	20
1.00	0.8615 (0.8599)	0.5904 (0.5896)	20

Values in the parentheses represent the experimental data^{3,10}

Table 6 – GA Based Optimal Parameters for Batch Electrochemical Reactor ($Da = 0.05$) and CSTER ($Da_1 = 1748.0$ & $Da_2 = 0.3483$)

k_{f_1}/k_{f_2}	Conversion		Yield		Number of generations
	batch	CSTER	batch	CSTER	
2.5	0.7788 (0.7779)	0.7859 (0.6729)	0.4581 (0.5254)	0.6738 (0.3952)	30
8.5	0.9084 (0.9075)	0.8527 (0.7720)	0.5393 (0.7398)	0.7229 (0.4876)	30
17.0	0.9487 (0.9475)	0.8727 (0.8705)	0.5648 (0.8297)	0.8717 (0.5639)	30

Values in the parentheses represent the experimental data^{3,10}

$$\min \Psi = (C_T) + \lambda \left[\sum_{K \in LVC}^K |C_{T_K} - C_{T_{K(Limit)}}| \right] \quad (16)$$

Table 7 – Comparison of Results for Cost Optimization

Method	Current density, $j / \text{A m}^{-2}$		Total cost $\times 10^{-5}$ (Rupees)		Function evaluation		% deviation			
	batch	CSTER	batch	CSTER	batch	CSTER	current density		Total cost	
							batch	CSTER	batch	CSTER
GAs	5.9348 (6.00)	4.0451 (4.25)	5.1815	7.7749	30	30	0	0	0	0
Golden Section	5.8310	3.9852	5.0841	7.6536	423	486	-1.75	-1.48	-1.88	-1.56
Fibonacci	5.816	3.9680	5.0774	7.6349	400	450	-1.99	-1.91	-2.01	-1.80
Exhaustive	4.9437	3.4469	4.2354	6.5572	1115	1218	-16.69	-14.79	-18.26	-15.66

Values in the parentheses represent the experimental data¹⁴

Here C_T is given by the equation (15) and the fitness is obtained by transforming the minimization problem into a maximization problem as

$$\text{FIT} = \frac{1}{1 + \Psi} \quad (17)$$

A comparison of near-optimal solutions generated by GAs with the best result of a number of traditional optimization methods and experimental data are also shown in the table. Among the most striking features of these results is a fact that the GAs found an optimal solution that optimally satisfies the experimental and documented values. The second most striking feature of the GAs results is the high performance with quick convergence; it also requires the less number of total function evaluations. It has to be noted that the near-optimal solutions generated by traditional algorithms are obtained after only about 350 iterations. Though not much of information except the objective function values are used, GAs quickly simulate a solution which is comparable with experimental and documented results.¹⁴ From the set of simulation data used, GA based optimum current density of 5.9348 A m^{-2} is obtained for a batch electrochemical reactor. For CSTER, the optimum value of current density is 4.0451 A m^{-2} . These results are encouraging and suggest the use of GAs in similar reactor design problems.

One of the advantages of using GAs is that they usually do not get trapped into local solutions. In order to show the inherent capability to better solve noisy and non-stationary problems in the search space of the above problem, we have also plotted the cost versus current density in Figure 2 for batch electrochemical reactor. The total cost curve exhibits a flat curvature around the true minimum indicating that even suboptimal converge at

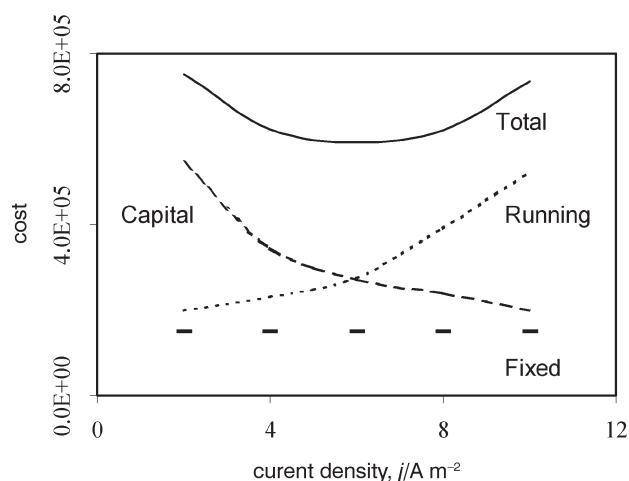


Fig. 2 – Minimization of total cost as a function of current density

current densities at some distance from global optimum. But the results obtained for both reactor configurations show that GAs did not get trapped into one of those local optimum solutions as evident from the industrial practice. This distinguishes GAs from other search techniques used. It is worth mentioning here that, if a gradient-based optimization technique is used and an initial guess of the current density is assumed, the algorithm may have got struck at a solution with a much lower profit.

Conclusion

GAs have been used to optimize the electrochemical reactors for the potentially useful organic synthesis. A simple GA with reproduction, crossover, and mutation operators is able to converge fast to near-optimal design parameters, after examining only a small fraction of the search space.

Computations using documented data were performed that demonstrates the GAs ability to obtain optimal parameter estimation. The major application of the work lies in the prediction of the performance of electrochemical processes during industrial operation. The optimum current density for maximum yield has been evaluated. The optimum yield and current density observed in the present investigation are invariant with respect to the conversion, which agrees with the industrial practice. Process economics are particularly sensitive to the values assigned to the process variables, which would therefore be given a high priority in any supporting research programme directed towards the measurement of physical data. For some batch operations where the end-time constraints should be met tightly (i.e. for tight control of the product quality), this approach may be necessary. Thus GAs has been investigated for its potential use as an optimization tool in electrochemical reactor engineering. As a result, there is no need to obtain a good initial guess to ensure reasonable solution. The total number of generations to reach optimum can also be decreased to a surprising level.

The primary advantages of GAs are that no gradient or other auxiliary problem information is required in the search process. Moreover, the implicit parallel processing of the problem information makes GAs less likely to converge to a sub optimal solution. Because of their simplicity in operation and minimal requirements, GAs are finding increasing popularity across a broad section of engineering problems. The successful operation in this particular application, which represents a large class of similar reactor engineering problems, will broaden GAs applicability to a wider spectrum of disciplines.

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Nomenclature

a	– area, m^2
a	– electrode area per unit volume, $m^2 m^{-3}$
c_a	– specific investment cost, $MU m^{-2} h^{-1}$
A	– electrode area, m^2
a_a, a_c	– Tafel parameter, V
c_b	– energy cost, $MU m^{-2} h^{-1}$
b_a, b_c	– Tafel parameter, V
C_E	– energy cost, $MU m^{-2} h^{-1}$
C_F	– fixed cost, MU

c_j	– concentration of the species j , $mol m^{-3}$
C_R	– investment cost of reactor, $MU m^{-2} h^{-1}$
C_T	– total cost of operating the process per unit time, $MU m^2 h^{-1}$
Da	– Damköhler number
E	– electrode potential, V
F	– Faraday's constant, $96\,487 C mol^{-1}$
FIT	– fitness function
j	– current density, $A m^{-2}$
I	– current, A
j_L	– limiting current density, $A m^{-2}$
κ	– conductivity, $\Omega^{-1} m^{-1}$
k_{bi}	– backward electrochemical rate coefficient of step i , $m s^{-1}$
k_{bi0}	– standard backward rate constant of step i (potential independent), $m s^{-1}$
k_{fi}	– forward electrochemical rate coefficient of step i , $m s^{-1}$
k_{fi0}	– standard forward rate constant of step i (potential independent), $m s^{-1}$
k_L	– mass transfer coefficient for liquid, $m s^{-1}$
k_{Lj}	– mass transfer coefficient for species j , $m s^{-1}$
l	– inter electrode distance, m
LVC	– Limit Violated Constraint
MU	– monetary units
n	– electrons exchanged in electrode reaction
P	– productivity, $mol h^{-1}$
R	– Perfect gas constant, $J K^{-1} mol^{-1}$
t	– time, h
V	– Total Voltage, V
V_D	– decomposition voltage, V
X	– conversion
Y	– yield
β_i	– potential dependency of forward reaction rate coefficient, V^{-1}
α_i	– potential dependency of backward reaction rate constant, V^{-1}
η_{act}	– activation overpotential, V
η_{Conc}	– concentration overpotential, V
ε_c	– current efficiency
τ	– residence time, h
ΔG^0	– Gibbs free energy change, $J mol^{-1}$
Ψ	– objective function to be minimized for total cost minimization
λ	– penalty factor

Subscripts

0	– initial condition
a	– anode
c	– cathode
j	– compound j
K	– constraint function Portia Matseke {WITS}
Limit	– constraint limit

Superscript

b – bulk condition

Subscripts 1 and 2 refer to the reactions $A \rightleftharpoons B$ and $B \rightleftharpoons C$ respectively.

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