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Optimal time-varying cell-voltage control of a parallel-plate reactor

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As a means to illustrate the calculation of an optimal cell-voltage control for a parallel-plate reactor, we determine the time-varying cell voltage that maximizes *p*-aminophenol produced from the electroreduction of nitrobenzene in a differential-conversion reactor operated in a batch mode; that is, the electrolyte is continuously recirculated from a batch holding tank through the reactor in which a low conversion per pass occurs. A rationale is given for restricting the search for the optimal control for this particular reaction network to a chattering-cell voltage that switches between *a priori* chosen minimum and maximum values. The optimal, time-varying duty cycle is computed using a gradient-search technique. The predicted concentrations are dependent upon the reaction time; for the conditions examined here, an improvement of twenty-five percent in the production and nine-hundred percent in the selectivity of *p*-aminophenol may be achieved by using the optimal, time-varying voltage in comparison to the best steady value. Since a chattering control is a mathematical construct, we illustrate that a rectangular, high-frequency waveform may be applied to yield results which are indistinguishable from those effected by a chattering cell voltage. The period of the waveform must be short enough so that surface concentrations are time invariant over it and yet, simultaneously, must be long enough so that double-layer charging does not account for a significant passage of coulombs.

List of symbols

a	cathode surface area per unit volume of electrolyte ($\mathrm{cm^{-1}}$)
C	electrode capacitance ($\mu\mathrm{F\,cm^{-2}}$)
c_i	bulk concentration of species i ($\mathrm{mol\,cm^{-3}}$)
c_i^0	initial concentration of species i ($\mathrm{mol\,cm^{-3}}$)
c_{is}	concentration of species i at electrode surface ($\mathrm{mol\,cm^{-3}}$)
E_a	anode potential (V)
E_c	cathode potential (V)
f	F/RT ($\mathrm{V^{-1}}$)
F	Faraday constant ($96\,487\,\mathrm{C\,mol^{-1}}$)
i	current density ($\mathrm{A\,cm^{-2}}$)
I	current (A)
I^k	kth value of a chattering current (A)
I_eff	current efficiency
i^k	kth value of a chattering i ($\mathrm{A\,cm^{-2}}$)
k_1	heterogeneous rate constant for the reaction NB $\rightarrow$ PHA ($\mathrm{cm\,s^{-1}}$)
k_2	heterogeneous rate constant for the reaction PHA $\rightarrow$ AN ($\mathrm{cm\,s^{-1}}$)
k_3	homogeneous rate constant for the reaction PHA $\rightarrow$ PAP ($\mathrm{s^{-1}}$)
$k_{\mathrm{m}i}$	mass-transfer coefficient of species i ($\mathrm{cm\,s^{-1}}$)
R	gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
R_j	kinetic resistance at electrode j ($\Omega\,\mathrm{cm^2}$)
R_Ω	ohmic resistance ($\Omega\,\mathrm{cm^2}$)
r_i	reaction rate for species i ($\mathrm{mol\,cm^{-3}\,s^{-1}}$ for homogeneous reaction, and $\mathrm{mol\,cm^{-2}\,s^{-1}}$ for heterogeneous reaction)
T	temperature (K)
t	time (s)
t_f	batch reaction time (s)
u_i	ith component of control vector u
$u_{\mathrm{c}i}$	$\exp(-\alpha_i f E_\mathrm{c})$
V	cell voltage (V)
V^k	kth value of a chattering-cell voltage (V)

Greek symbols

$\theta(t)$	duty cycle for a chattering control
Θ	duty cycle for a rectangular waveform
Δt	period of the rectangular waveform (s)
α	transfer coefficient (Equations 1–4)

Subscript

0	indicates exchange current
a	anode
c	cathode

1. Introduction

A significant impediment to the commercialization of many electroorganic processes is low-reaction selectivity due to the simultaneous occurrence of both desired and undesired charge-transfer reactions. However, it has been demonstrated that: (i) a time-varying electrode potential or current may

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be employed to enhance selectivity [1–4] and (ii) optimal-control theory can be applied to determine the electrode-potential profile that maximizes a desired objective, e.g., selectivity, production rate or current efficiency [5]. The intent of our previous communication [5] was to illustrate optimization concepts as applied to an electrochemical reactor and, to focus on these aspects, we assumed control of the working electrode potential was possible. Since potentiostatic control in an industrial setting is unlikely, the goal of this paper is to demonstrate how an optimal cell voltage or current may be determined for a parallel plate reactor. We focus only on the reactor, but clearly the entire reaction system, including reactant and product separation operations, must be considered ultimately in any process optimization – an objective beyond the scope of this communication.

Here we consider maximizing *p*-aminophenol (PAP) produced by the electroreduction of nitrobenzene (NB) in a parallel-plate reactor operated in a batch mode; i.e., the electrolyte with reactant is recirculated through the reactor from a batch holding tank. Figure 1 illustrates the NB reduction reaction sequence: NB is electrochemically reduced to phenylhydroxylamine (PHA), a stable intermediate, which may rearrange chemically to form PAP or undergo further electrochemical reduction to aniline (AN). The NB reaction is chosen because of the availability of kinetic rate equations [2] and experimental concentration data collected from a parallel-plate reactor [3, 4] under time-varying cell voltage with which to compare the present calculations. The optimal cell voltage or current can be determined for other objectives and reactions, as described by the general framework presented elsewhere [6].

2. Background

2.1. *Reaction kinetics*

The rate equations for the reactions of Fig. 1 are shown below, along with those for hydrogen evolution at the cathode and oxygen evolution at the anode

NB consumption [2]:

$$r_{\mathrm{NB}} = k_1 c_{\mathrm{NB_s}} \exp(-\alpha_1 f E_{\mathrm{c}}) \equiv k_1 c_{\mathrm{NB_s}} u_{\mathrm{c1}} \qquad (1)$$

AN production [2]:

$$r_{\mathrm{AN}} = k_2 c_{\mathrm{PHA_s}} \exp(-\alpha_2 f E_{\mathrm{c}}) \equiv k_2 c_{\mathrm{PHA_s}} u_{\mathrm{c2}} \qquad (2)$$

PAP production [2]: $r_{\mathrm{PAP}} = k_3 c_{\mathrm{PHA}}$ (3)

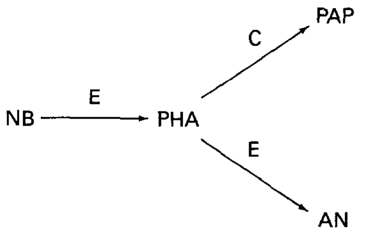


Fig. 1. E–C,E reaction sequence for the reduction of nitrobenzene (NB). The stable reaction products are phenylhydroxylamine (PHA), *p*-aminophenol (PAP) and aniline (AN).

Table 1. Parameters used in the computation [*2–4*]

$k_1 = 6.03 \times 10^{-8}\,\mathrm{cm\,s^{-1}}$	$\alpha_1 = 0.693$
$k_2 = 2.71 \times 10^{-8}\,\mathrm{cm\,s^{-1}}$	$\alpha_2 = 0.398$
$i_{\mathrm{H},0} = 2.81 \times 10^{-7}\,\mathrm{A\,cm^{-2}}$	$\alpha_2 = 0.328$
$i_{\mathrm{Ox},0} = 2.59 \times 10^{-12}\,\mathrm{A\,cm^{-2}}$	$\alpha_{\mathrm{a}} = 0.39$
$k_3 = 4.77 \times 10^{-6}\,\mathrm{s^{-1}}$	
$k_{\mathrm{mNB}} = 2.84 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$	$k_{\mathrm{mPHA}} = 1.73 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$
$R_{\Omega} = 20.6\,\Omega\,\mathrm{cm^2}$	$a = 0.02\,\mathrm{cm^{-1}}$
$c^0_{\mathrm{NB}} = 50 \times 10^{-6}\,\mathrm{mol\,cm^{-3}}$	$c^0_i = 0,\ i \neq \mathrm{NB}$
$V^{\max} = 3.2\,\mathrm{V}$	$V^{\min} = 1.0\,\mathrm{V}$
$t_f = 4\,\mathrm{h}$	$f = 38.66\,\mathrm{V^{-1}}$

Hydrogen evolution [2]:

$$i_{\mathrm{H}} = i_{\mathrm{H},0} \exp(-\alpha_3 f E_{\mathrm{c}}) \equiv i_{\mathrm{H},0} u_{\mathrm{c3}} \qquad (4)$$

Oxygen evolution [3]: $i_{\mathrm{Ox}} = i_{\mathrm{Ox},0} \exp(\alpha_{\mathrm{a}} f E_{\mathrm{a}})$ (5)

where r_{NB} and r_{AN} are the electrochemical rates of NB consumption and AN production per unit electrode area, r_{PAP} is the PAP volumetric production rate by first order chemical decomposition of PHA, c_i and $c_{i\mathrm{s}}$ are the concentrations of species i in the bulk and at the electrode surface, i_{H} is the current density due to hydrogen evolution, i_{Ox} is the current density due to oxygen evolution, E_{c} is the cathode potential and E_{a} is the anode potential with both measured with respect to a SCE, $f = F/RT$, and $u_{\mathrm{c}i} = \exp(-\alpha_i f E_{\mathrm{c}})$ is component i of the three-element vector u_{c}. (In [5] we demonstrated how the optimal, time-varying cathode potential can be calculated by use of u_{c}.) The kinetic constants in Equations 1–5 are given in the top portion of Table 1.

2.2. *Mathematical model of a parallel-plate reactor*

The model utilized here is that described by Smeltzer and Fedkiw [3] who showed that it predicted PAP concentrations which matched experimentally measured values during a batch reduction of NB in a parallel-plate reactor using steady or time-varying, cell voltage control [4]. The following assumptions are made about the transport and kinetic processes: (i) The flow rate of the electrolyte through the reactor is sufficiently large that streamwise concentration variations are negligible. (ii) Edge effects in fluid flow and potential distribution are neglected because the electrodes are separated by a distance much smaller than their length. (iii) Mass-transfer resistance from the bulk solution to the electrode surface can be quantified by a constant mass-transfer coefficient. The reaction distribution is uniform as a result of these three assumptions. (iv) The homogeneous chemical reaction does not occur to a significant extent within the Nernst layer.

(v) The electrode kinetics are irreversible and are described by Equations 1, 2, 4 and 5. (vi) Double-layer charging/discharging is negligible compared to the charge consumed by the electrochemical reactions.

With the above assumptions, the cell voltage $V(t)$ can be written as

$$V(t) = -E_c(t) + E_a(t) + i(t)R_\Omega \qquad (6)$$

where E_c is negative and E_a is positive for the reactions considered, R_Ω is the ohmic resistance ($\Omega\,\mathrm{cm}^2$), and i is the current density. At the cathode, the current density is the sum of NB consumption, AN production and hydrogen evolution

$$i(t) = i_{\mathrm{NB}}(t) + i_{\mathrm{AN}}(t) + i_{\mathrm{H}}(t) \qquad (7)$$

where $i_{\mathrm{NB}} = 4Fr_{\mathrm{NB}}$ and $i_{\mathrm{AN}} = 2Fr_{\mathrm{AN}}$. At the anode, oxygen evolution is the only reaction, therefore

$$i(t) = i_{\mathrm{Ox}}(t) \qquad (8)$$

All reaction currents are taken as positive.

2.3. *Rationale for the optimal cell voltage*

For an E–C,E reaction sequence, such as the NB reaction of Fig. 1, we demonstrated [5] that a chattering cathode potential switching between two limits maximized the species produced by the chemical reaction if the electrochemical reaction forming the intermediate has a larger transfer coefficient than the reaction consuming it. The NB reaction meets this transfer coefficient criterion; that is, PHA is an electrochemically produced intermediate with $\alpha_1 > \alpha_2$ (Table 1). Hence, a chattering cathode potential switching between minimum and maximum values would maximize the concentration of PAP at the end of a batch period t_f. Because cathode potential can be effected by the cell voltage, a chattering cell voltage is optimal. The minimum and maximum cell voltages are set *a priori* in our calculations; for example, the minimum may be set to prevent electrode corrosion and the maximum may be set to prevent significant solvent electrolysis or, alternatively, by power supply capability. (We discuss elsewhere how these limit values may be determined as part of the optimization calculation [6].)

Side reactions at the working electrode such as hydrogen evolution, which lowers current efficiency but does not affect selectivity, were also neglected in our previous communication [5]. We show below that a chattering cathode potential (and, hence, cell voltage) switching between two limits maximizes, not only the concentration of PAP, but also the current efficiency if the transfer coefficient for the reaction NB → PHA is greater than that for hydrogen evolution (i.e., $\alpha_1 > \alpha_3$, Table 1). We first demonstrate that, for any given rate of the reaction NB → PHA, a chattering potential maximizes both the differential conversion to PHA and the differential current efficiency. Consequently, the integral conversion to PAP (i.e., $c_{\mathrm{PAP}}(t_f)$) is maximized, as is the integral current efficiency, since PAP is formed by a first-order decomposition of PHA.

Using a chattering cathode potential, the rate of NB decomposition $\bar{r}_{\mathrm{NB}}$, AN formation $\bar{r}_{\mathrm{AN}}$, and hydrogen evolution current density $\bar{i}_{\mathrm{H}}$ are given by [5]

$$\bar{r}_{\mathrm{NB}} = k_1\bar{c}_{\mathrm{NBs}}\bar{u}_{c1} \qquad (9)$$

$$\bar{r}_{\mathrm{AN}} = k_2\bar{c}_{\mathrm{PHAs}}\bar{u}_{c2} \qquad (10)$$

$$\bar{i}_{\mathrm{H}} = i_{\mathrm{H},0}\bar{u}_{c3} \qquad (11)$$

where $\bar{u}_{ci}$ is the average value of u_{ci} when the cathode potential rapidly switches between $E_c^{\min}$ and $E_c^{\max}$

$$\bar{u}_{ci} = (1-\theta)u_{ci}^{\min} + \theta u_{ci}^{\max} \qquad (12)$$

with θ being the fraction of an infinitesimal interval δt for which the potential is held at $E_c^{\max}$ and $u_{ci}^k = \exp(-\alpha_i f E_c^k)$ [5, 7, 8]. (The overbar designates a quantity evaluated under chattering control conditions.) The surface concentrations $\bar{c}_{is}$ do not vary during δt since, because of mass-transfer resistance, they cannot track the rapidly varying potential and are at a so called *relaxed state*. The surface concentrations, however, are expressible in terms of the bulk concentrations by equating the mass-transfer rates of NB and PHA through the Nernst film to their respective reaction rates at the electrode; this balance yields

$$\bar{c}_{\mathrm{NBs}} = \frac{k_{\mathrm{mNB}}\bar{c}_{\mathrm{NB}}}{k_{\mathrm{mNB}} + k_1\bar{u}_{c1}} \qquad (13)$$

$$\bar{c}_{\mathrm{PHAs}} = \frac{1}{k_{\mathrm{mPHA}} + k_2\bar{u}_{c2}} \times \left(k_{\mathrm{mPHA}}\bar{c}_{\mathrm{PHA}} + k_1\bar{u}_{c1}\frac{k_{\mathrm{mNB}}\bar{c}_{\mathrm{NB}}}{k_{\mathrm{mNB}} + k_1\bar{u}_{c1}}\right) \qquad (14)$$

where $k_{\mathrm{m}i}$ is the mass-transfer coefficient for species i. Equations 9 and 10 can be rewritten using Equations 13 and 14 as

$$\bar{r}_{\mathrm{NB}} = k_1\bar{u}_{c1}\frac{k_{\mathrm{mNB}}c_{\mathrm{NB}}}{k_{\mathrm{mNB}} + k_1\bar{u}_{c1}} \qquad (15)$$

$$\bar{r}_{\mathrm{AN}} = \frac{k_2\bar{u}_{c2}}{k_{\mathrm{mPHA}} + k_2\bar{u}_{c2}} \times \left(k_{\mathrm{mPHA}}c_{\mathrm{PHA}} + k_1\bar{u}_{c1}\frac{k_{\mathrm{mNB}}c_{\mathrm{NB}}}{k_{\mathrm{mNB}} + k_1\bar{u}_{c1}}\right) \qquad (16)$$

The differential-conversion rate of NB to PHA is the difference in the above two equations, and the differential current efficiency, $\bar{I}_{\mathrm{Eff}}$, is

$$\bar{I}_{\mathrm{Eff}} = \frac{\bar{i}_{\mathrm{NB}} - \bar{i}_{\mathrm{AN}}}{\bar{i}_{\mathrm{NB}} + \bar{i}_{\mathrm{AN}} + \bar{i}_{\mathrm{H}}} \qquad (17)$$

It is apparent from the above discussion and examination of Equations 15, 16 and 17 that, in order to maximize both the differential conversion and the current efficiency at a specified $\bar{r}_{\mathrm{NB}}$, it suffices to demonstrate that $\bar{u}_{c2}$ and $\bar{u}_{c3}$ resulting from the corresponding $\bar{u}_{c1}$ are the minimum attainable. The solid

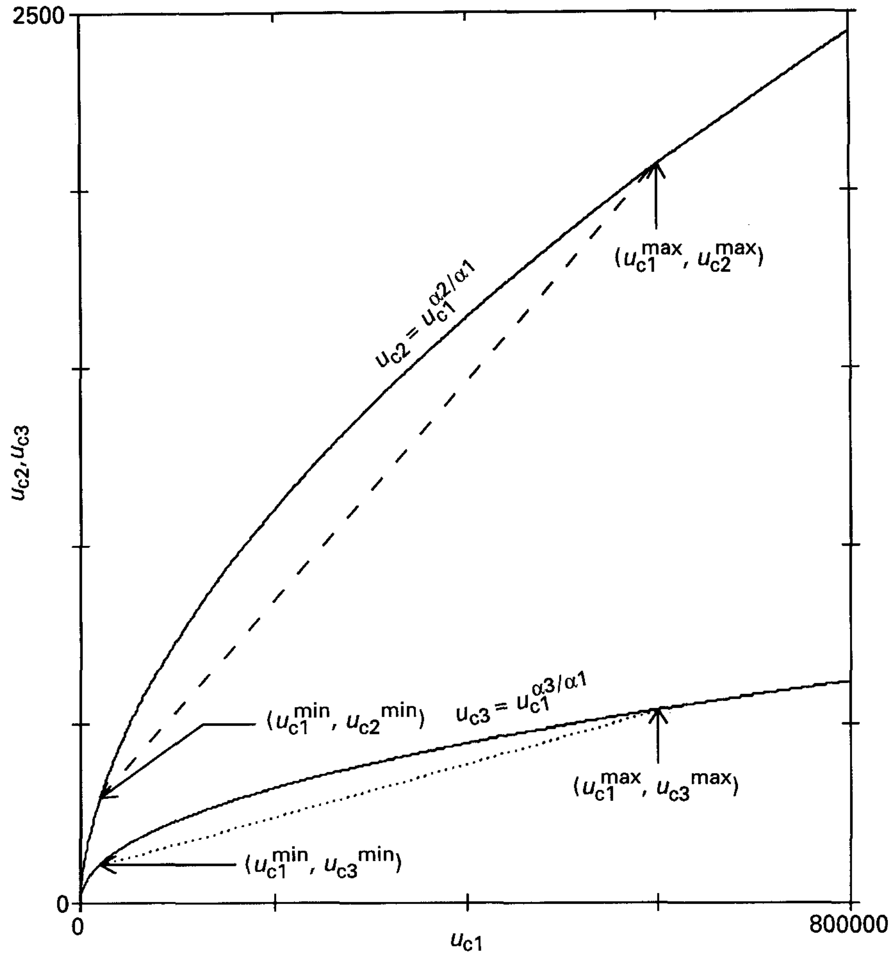


Fig. 2. The broken lines show the locus of attainable ($\bar{u}_{c1}$, $\bar{u}_{ci}$) for a chattering cathode potential switching between E_c^{max} and E_c^{min} where $u_{ci} = \exp(-\alpha_i f E_c)$.

lines in Fig. 2 show the dependence of u_{c2} and u_{c3} on u_{c1}. (Recall that the cathode potential varies along these lines.) In view of Equation 12, the attainable values of $\bar{u}_{c2}$ lie on the dashed line joining the points (u_{c1}^{min}, u_{c2}^{min}) and (u_{c1}^{max}, u_{c2}^{max}), and the attainable values of $\bar{u}_{c3}$ likewise lie on the dotted line joining (u_{c1}^{min}, u_{c3}^{min}) and (u_{c1}^{max}, u_{c3}^{max}). Since both broken lines are below the corresponding solid lines, it is evident that a chattering cathode potential switching between the minimum and maximum values leads to the minimum attainable $\bar{u}_{c2}$ and $\bar{u}_{c3}$ at any given $\bar{u}_{c1}$; that is, both the differential selectivity and current efficiency are greatest for a given rate of nitrobenzene consumption using a chattering control. If $\alpha_3 > \alpha_1$, however, the curvature of the lower solid line would be in the opposite sense and this conclusion would be invalid.

3. Calculation of the optimal chattering-cell voltage

For a chattering cell voltage switching between two fixed limits over an infinitesimal time δt, the controlled variable is the duty cycle $\theta(t)$. The optimal $\theta(t)$ is computed iteratively such that $\bar{c}_{PAP}(t_f)$ increases at each iteration. We summarize the manipulations necessary to carry out this iterative calculation. In Section 3.1 we first describe the method to compute the resulting bulk species concentrations for a known $\theta(t)$; in Section 3.2, we describe the iterative method to compute the optimal $\theta(t)$ and the manner to calculate the jth duty cycle Θ_j of the approximating, high-frequency rectangular waveform.

3.1. *Bulk concentrations resulting from chattering cell-voltage control*

Within the framework of the reactor model, the concentrations in the batch holding tank are determined by solving the material-balance equations

$$\frac{d\bar{c}_{NB}}{dt} = -ak_1\bar{c}_{NBs}\bar{u}_{c1} \tag{18}$$

$$\frac{d\bar{c}_{PHA}}{dt} = ak_1\bar{c}_{NBs}\bar{u}_{c1} - ak_2\bar{c}_{PHAs}\bar{u}_{c2} - k_3\bar{c}_{PHA} \tag{19}$$

$$\frac{d\bar{c}_{PAP}}{dt} = k_3\bar{c}_{PHA} \tag{20}$$

$$\frac{d\bar{c}_{AN}}{dt} = ak_1\bar{c}_{PHAs}\bar{u}_{c2} \tag{21}$$

where a is the cathode surface area per unit volume of electrolyte (catholyte in a divided cell, otherwise catholyte plus anolyte), and $\bar{c}_{NBs}$ and $\bar{c}_{PHAs}$ are given by Equations 13 and 14, respectively. In the above balances, it is assumed that the volume of electrolyte within the reactor is much less than that of the holding tank. To solve these state equations numerically (using the IMSL routine DGEAR [9]), $u_{ci}(t)$ must be expressed in terms of $\bar{c}_i(t)$ and/or $\theta(t)$, where $\theta(t)$ is known from an initial guess or a previous iteration.

In view of Equation 12, it is clear that to determine

$\bar{u}_{c1}(t)$ and $\bar{u}_{c2}(t)$ for a given $\theta(t)$, the minimum and maximum cathode potentials, $E_c^{\min}(t)$ and $E_c^{\max}(t)$, must be found. When the cell voltage switches to V^k ($k = \min$ or max), the anode potential, cathode potential, and current density all instantaneously switch to $E_a^k(t)$, $E_c^k(t)$, and $i^k(t)$ because transient capacitive and mass-transfer effects are assumed unimportant. We calculate $E_c^k(t)$ by the following two-step procedure:

1. For each V^k:
(a) In Equation 6, express $E_a^k(t)$ in terms of $i^k(t)$ using Equations 5 and 8.
(b) In Equation 7, write the reaction current densities i_{NB}^k, i_{AN}^k, and i_{H}^k using Equations 1, 2, and 4, respectively, to obtain an expression for $i^k(t)$ in terms of $E_c^k(t)$, $\bar{c}_{\mathrm{NBs}}(t)$, and $\bar{c}_{\mathrm{PHAs}}(t)$.
(c) In the equation resulting from step (b), employ Equations 13 and 14 to express $\bar{c}_{\mathrm{NBs}}(t)$ and $\bar{c}_{\mathrm{PHAs}}(t)$ in terms of bulk concentrations, $E_c^{\max}(t)$, and $E_c^{\min}(t)$.
2. Carrying through step 1 results in a nonlinear algebraic equation at each V^k which relates $\theta(t)$, $\bar{c}_{\mathrm{NB}}(t)$, and $\bar{c}_{\mathrm{PHA}}(t)$ to the unknowns $E_c^{\max}(t)$ and $E_c^{\min}(t)$. To obtain $E_c^{\max}(t)$ and $E_c^{\min}(t)$, set $k = \min$ and max and solve numerically the two resulting nonlinear algebraic equations.

The two equations resulting from step 2 are solved at each time step t_j to determine $u_{c1}(t_j)$ and $u_{c2}(t_j)$ which are used in the right side of Equations 18–21 to integrate to the next time step. The concentrations $\bar{c}_i(t_j)$ are known in this calculation since the initial conditions $c_i(0)$ are specified and DGEAR is used to calculate $\bar{c}_i(t_j)$ in a sequential manner to the final reaction time t_j.

3.2. *Computing the optimal duty cycle*

By using Equations 12, 13 and 14 and the two-step procedure described above the state equations (Equations 18–21) can be rewritten in terms of $E_c^{\max}(t)$, $E_c^{\min}(t)$, $\bar{c}_i(t)$, and $\theta(t)$, and the optimal $\theta(t)(0 \leqslant \theta(t) \leqslant 1)$ is determined using the gradient-projection method [5, 10, 11]. In each ith iteration of this method, an improved $\theta^i(t)$ is calculated such that $\bar{c}_{\mathrm{PAP}}^{(i)}(t_f) > \bar{c}_{\mathrm{PAP}}^{(i-1)}(t_f)$, and the iterations are terminated when the increase in $\bar{c}_{\mathrm{PAP}}^{(i)}(t_f)$ over $\bar{c}_{\mathrm{PAP}}^{(i-1)}(t_f)$ is less than 0.001%.

It is, of course, impossible to actually apply a chattering control. It is possible, however, to impose a high frequency, rectangular wave-form such that the resultant effects are indistinguishable from those of a chattering control. In Section 4.2 we present criteria to choose the frequency of this rectangular waveform. Furthermore, the $\theta(t)$ for a chattering control is continuous, but it can only be varied discretely when the approximating rectangular waveform is applied. These discrete values are calculated by dividing the batch period t_f into small, equally-spaced intervals Δt where $\Delta t \ll t_f$ and is equal to the period of the rectangular waveform. In each Δt interval the duty cycle Θ_j of the rectangular waveform is calculated as

$$\Theta_j = \frac{1}{\Delta t}\int_{t_{j-1}}^{t_j} \theta(t)\,\mathrm{d}t \tag{22}$$

4. Results and discussion

4.1. *Optimal cell-voltage for NB reduction*

Table 1 lists the parameters used in the computations. These values describe the reaction kinetics, ohmic resistance, mass-transfer resistance, and operating conditions for the NB reduction experiments carried out by Smeltzer and Fedkiw [4] in a parallel-plate reactor under time-varying (but not optimal) cell voltage control.

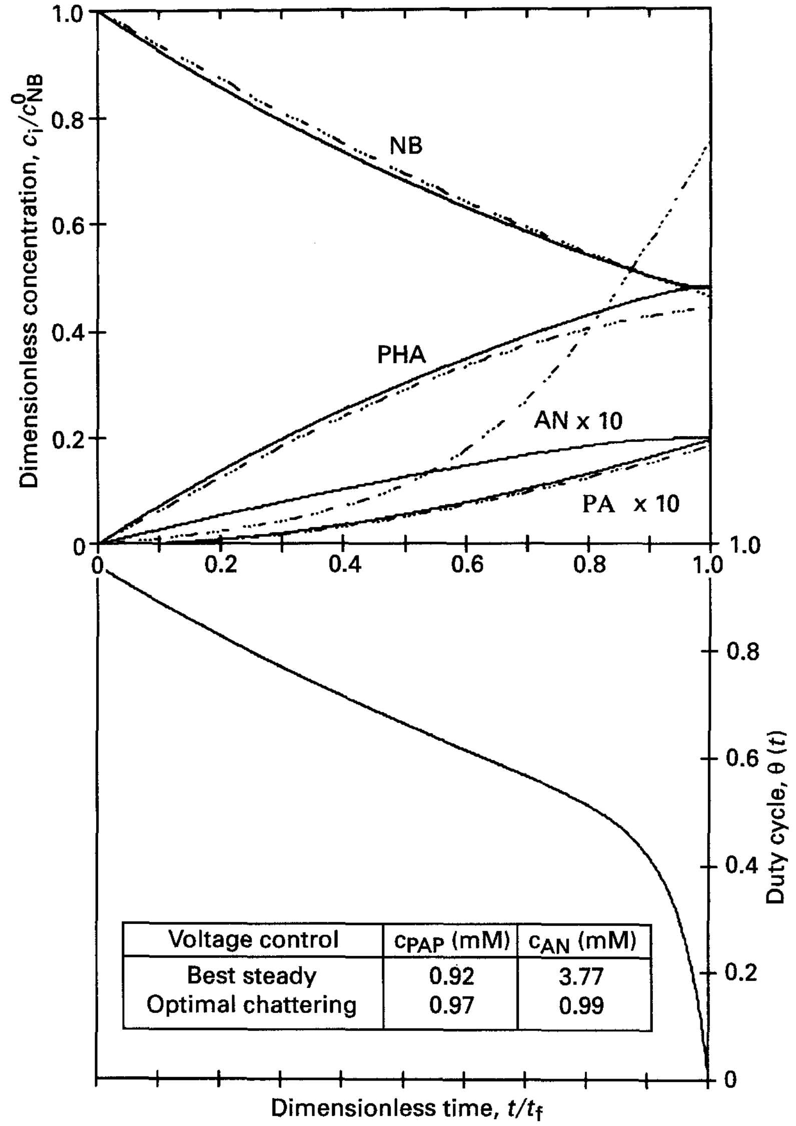
The lower panel in Fig. 3 shows the optimal duty cycle $\theta(t)$ computed for the chattering cell voltage. The solid lines in the upper panel show the corresponding concentration profiles over the batch period, and the dashed lines show the concentration profiles at the best steady voltage of 2.90 V which maximized $\bar{c}_{\mathrm{PAP}}(t_f)$ [4]. The predicted trend in $\theta(t)$ can be qualitatively explained as follows. Since PHA is not present initially, the duty cycle is largest at the start of the batch during which little AN can form; however, because the PHA concentration increases with time, the duty cycle commensurately decreases so that the rate of the undesired reaction PHA → AN is minimized. The inset Table in Fig. 3 compares the predicted PAP and AN concentration for steady and chattering control at the end of the batch period; the results show that the optimal cell voltage increases the production of PAP by 4% and decreases the production of AN by 72% over the best steady voltage. These improvements become more pronounced for a longer batch period because of the increased conversion of PHA to PAP; for example, if the reaction is extended to 20 h, Table 2 shows that applying the optimal chattering voltage instead of the best steady voltage of 2.32 V increases the production of PAP by 22% and lowers the production of AN by 83%. The underlying physicochemical mechanisms by which these improvements are produced have been discussed [1–4].

4.2. *Considerations in approximating a chattering-cell voltage by a rectangular waveform*

It can be shown [6] that, when capacitive and transient mass-transfer effects are unimportant, the integral of the state equations (Equations 18–21) over a finite

Table 2. Concentration of PAP and AN at the end of a twenty-hour batch period resulting from applying the best steady cell voltage of 2.32 V and the optimal chattering cell voltage switching between 1.0 and 3.2 V

Voltage control	c_{PAP}/mM	c_{AN}/mM
Best steady	8.56	13.19
Optimal chattering	10.65	1.84



Voltage control	c_{PAP} (mM)	c_{AN} (mM)
Best steady	0.92	3.77
Optimal chattering	0.97	0.99

Fig. 3. The optimal duty cycle $\theta(t)$ for chattering cell voltage control and the resulting dimensionless concentrations $\bar{c}_i/c^0_{NB}$ (solid lines). The broken lines show the dimensionless concentrations resulting on applying the best steady voltage of 2.90 V [4]. The inset table shows the resulting concentrations of PAP and AN using both controls at the end of the 4 h batch period.

but small Δt are essentially identical for a chattering control and a rectangular control of frequency of $1/\Delta t$. As a verification of this equality, the theoretical calculations and experimental results of Smeltzer and Fedkiw [3, 4], who applied a 100 Hz square wave ($\Theta = 0.5$) cell voltage to a parallel-plate reactor in which NB reduction occurred, are considered. Table 3 compares the predicted PAP and AN concentrations under the two strategies and are seen to be nearly identical. Smeltzer accounted for time-dependent mass-transfer effects by solving the transient-diffusion equation within the Nernst layer, but assumed double-layer charging was unimportant. (We illustrate below that for a 100 Hz square waveform, double-layer charging is indeed unimportant.) A PAP concentration of 0.75 mM was experimentally measured which is only four percent higher than the two predicted values. The conclusion is that a 100 Hz square wave cell voltage results in essentially the same product outcome as that of a chattering control for this particular set of reaction conditions. Also, the chattering-control calculations are simpler to execute computationally than those performed by Smeltzer and Fedkiw for two reasons: (i) Their Fourier series approach requires an increasingly greater number of terms as the frequency increases, and (ii) the number of cycles in their iterative calculations concurrently increases with frequency.

Table 3. Calculated bulk concentrations at the end of a 4 h batch reduction of NB using a chattering cell voltage and a 100 Hz rectangular cell voltage waveform. Both switch between 1.0 and 3.2 V with a duty cycle of 0.5

Voltage control	c_{PAP}/mM	c_{AN}/mM
Chattering	0.72	0.25
Rectangular [4]	0.72	0.27

With the assumption that capacitive and transient mass-transfer effects are the only phenomena that must be considered, there are two questions to address in determining if a high-frequency, rectangular control can approximate well a chattering control: (i) How high a frequency is necessary to ensure that transient mass-transfer effects are unimportant? That is, the surface concentrations c_{is} are at a relaxed steady state. (ii) How low must the frequency be to ensure that a significant fraction of the coulombs passed during application of V^{max} will not be utilized in double-layer charging? Considering first the mass transfer question, if the characteristic time for transport across the Nernst layer is much greater than the period, Δt, of the rectangular waveform, then the surface concentrations will be at a relaxed state. That is, the criterion may be written

$$\sqrt{D/(k_m^2 \Delta t)} \gg 1 \tag{23}$$

with the square root dependency arising from considerations of the analytical solution to Fick's second law. For example, for a 100 Hz waveform applied to the NB system [3, 4], this ratio is approximately 5 when using the k_m values in Table 1 and assuming $D = 2 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$. Although five is not extremely large in comparison to unity, Bailey [12] has noted that systems typically approach a relaxed steady state more rapidly with a variation in the ratio of time constants than they approach a quasisteady state.

The effect of capacitance is unimportant if the charge associated with the double layer is much less than that of the faradaic reactions during the application of $V^{\max}$ in time $\theta\Delta t$. (The majority of the faradaic coulombs are passed during this time in the Δt cycle.) This qualitative criterion may also be quantified with order-of-magnitude arguments as [6]

$$\theta\Delta t \gg R_a C_a \quad \text{and} \quad \theta\Delta t \gg R_c C_c \tag{24}$$

where R_j is the effective kinetic resistance at electrode j and C_j is the electrode capacitance. If m parallel faradaic reactions are present, as occurs for NB and PHA reduction, then $R_j^{-1} = \sum_{i=1}^{m} R_{ji}^{-1}$ where R_{ji} is the kinetic resistance of reaction i at electrode j; for example, the resistance for the NB reduction reaction according to Equation 1 is $(i_{NB}\alpha_1 f)^{-1}$. If the cell current is controlled, similar considerations [6] show that the criterion may be expressed as

$$\theta\Delta t \gg R_c C_c \tag{25}$$

Puippe and Ibl [13] previously arrived at the same criterion in their study of double layer effects in pulsed current plating. As an illustration of these criteria, we again consider NB reduction. Using the parameters in Table 1, the electrode resistances at $V^{\max}$ are $R_a = 1.1\,\Omega\,\text{cm}^2$ and $R_c = 0.6\,\Omega\,\text{cm}^2$. Assuming $C_a = C_c = 20\,\mu\text{F}\,\text{cm}^{-2}$, leads to the criterion $\theta\Delta t \gg 23\,\mu\text{s}$. Hence, double-layer effects should be unimportant for a 100 Hz square wave since $\theta\Delta t$ for it is $5000\,\mu\text{s}$.

4.3. *Optimal current control*

The optimal, time-varying current that maximizes $c_{PAP}(t_f)$ can, alternatively, be computed. As with a chattering cell voltage, a chattering current switching between maximum and minimum values also results in the cathode potential switching in a like manner. Hence, the search for the optimal current can also be restricted to a chattering control switching between *a priori* fixed maximum ($I^{\max}$) and minimum ($I^{\min}$) values which may be set by other considerations (e.g., those already discussed for cell-voltage limits). The control variable is again the duty cycle $\theta(t)$, the fraction of an infinitesimal δt for which the current is held at $I^{\max}$. The optimal $\theta(t)$ can be determined by an iterative method nearly identical to that presented earlier. Under chattering current control, the state dynamics are still governed by Equations 18–21, except that $\bar{u}_{ci}$ are now induced by the chattering current. The two-step procedure outlined in Section 3.1 to compute $E_c^{\max}$ and $E_c^{\min}$ must be slightly modified: I^k replaces V_c^k, and step 1(a) is not needed since the current density i^k is known.

A chattering current could not actually be applied, but its effect can be approximated with a rectangular, high frequency current control. The approximating waveform would switch between $I^{\max}$ and $I^{\min}$ with a duty cycle given by Equation 22 and a frequency such that both transient mass-transfer and capacitive effects are negligible following the criteria given in Section 4.2.

5. Summary

We have computed the optimal, time-varying cell voltage that maximizes p-aminophenol produced by the electroreduction of nitrobenzene in a differential-conversion, parallel-plate reactor operated in the batch mode. A rationale was given for restricting the search for the optimal cell voltage to a chattering control which switches between *a priori* fixed maximum and minimum values at an infinite frequency. These limits may be determined by practical considerations, such as preventing significant solvent electrolysis and electrode corrosion. The computations show that improvement in the selectivity and production of p-aminophenol can be obtained by using the optimal, time-varying cell voltage instead of the best steady voltage. Because an infinite-frequency control cannot actually be implemented, it was shown that the results effected by a chattering cell voltage can be obtained by applying a rectangular voltage waveform having a frequency such that both transient mass-transfer and capacitive effects are negligible. A method was also presented to compute the optimal current control.

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