Optimal Current Paths for Model Electrochemical Systems

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Optimal control theory is used to determine process limits for a well-stirred fuel cell and a diffusive flow fuel cell, both operating with nonzero flows and in a finite time. Current paths and optimal end states are determined for cells constrained to provide either maximum work output, maximum effectiveness, or maximum profit. A constant current path is found to optimize these three criteria of process performance for the well-stirred fuel cell. In the diffusive flow fuel cell qualitatively different, nonmonotonic current trajectories are obtained for maximum work and maximum profit.

I. Introduction

In this paper we determine process limits, more realistic than reversible bounds, for electrochemical cells that operate at a nonzero rate and in a finite time. These cells deliver work and power through a fixed load and a variable resistance. The resistance can be adjusted to yield a time-parametrized current profile optimizing the different process variables of work output, effectiveness, and, as an economic measure, profit. Since the model systems include only current-dependent voltage losses and diffusive effects they serve as useful abstractions of realistic work-producing electrochemical cells, or fuel cells.

The performance of real systems frequently differs considerably from bounds based on equilibrium thermodynamics and reversible process paths. Previous works have investigated the effect of nonzero rate constraints and finite time operation have on performance bounds. More realistic performance limits have been found for Carnot-based heat engines, for general endoreversible heat engines, for internal combustion engines, for distillation process, and for intrinsically irreversible light-driven engines. The last system cited has no reversible counterpart; the engine is necessarily driven by nonzero flows.

An effective tool to determine limits on the performance of processes occurring in a finite time is optimal control theory. The value of this approach is that both the performance limit and the time path that yields this limit are obtained. All process variables associated with the operation of the system can be calculated once the time path is established.

The path optimization of the dynamic systems more appropriately falls under the heading of thermodynamics than do the parameter optimizations performed for processes in equilibrium or at steady state. These latter optimizations are best viewed as being within the domain of thermostatistics. The state variables are constant and a performance criteria is maximized with respect to the system’s parameters. The thermostatistic approach is used by Bockris and Srinivasan in their text of power and efficiency. As mentioned, the limits found in this paper apply to processes occurring in a finite time. Rather than looking for the bound on a time-invariant electrochemical system, we ask what are realistic and meaningful bounds on work output, effectiveness, and profit and what process paths achieve these bounds when we set out to drain a closed well-stirred fuel cell within a fixed time. We also ask these questions for the case of a permeable, diffusive flow fuel cell, in which we also optimize its performance. In both these systems the initial state is fixed. The final state is free to be chosen to optimize the performance. This differs from a classical thermodynamic analysis for maximum work output in which the fuel cell would be drained from the initial state to the equipotential equilibrium state in an infinite time interval and along a reversible path.

The models used for the well-stirred fuel cells and the diffusive flow fuel cells are described in section II. Section III details the optimal control analysis as applied to the well-stirred cell. Analytic solutions are obtained for the performance criteria of maximum work output, maximum effectiveness, and maximum profit. Section IV contains the optimal control analysis of the diffusive flow cell. Solutions for the optimal current path are given by a set of coupled, nonlinear differential equations with mixed boundary conditions. These equations are solved numerically. In section V we discuss the effects both the rate-dependent and non-rate-dependent parameters have on the process limits.

II. Description of the Model

Consider the model electrochemical system shown in Figure 1. The reducing and oxidizing electrolytic solutions are separated into distinct compartments by a semipermeable membrane. Only nonreacting ions pass through the membrane, ensuring the electroneutrality of each compartment. The inert electrodes in contact with the two solutions are connected through an external circuit consisting of a load and a variable resistance. Power output is delivered at the load; this electrochemical system operates as a fuel cell.

Section II, A and B, describes the well-stirred fuel cell. In section IIC we add a diffusive term to these model systems to form the diffusive flow fuel cell. Overvoltage losses occurring at the electrodes are not included in the models outlined in section IIA and C. Including these losses, as done in section IIB, does not affect the general form of the current time path providing maximum work output, effectiveness, or profit for the well-stirred system.

The model fuel cell discussed in this paper operates with the following assumptions:

(i) Current density is spatially uniform.

(ii) The temperature of each system is spatially homogeneous and constant along the process path. This constraint assumes the entropy of reaction is zero, no phase changes occur, mixing effects are negligible, the heat capacity of the system remains constant, and heating from electrical work and stirring is negligible. If the heat capacity or the volume of the system is large, the Ohmic loss heating does not produce a temperature change. No heat transfer need occur either across the membrane or across the walls of the cell. Alternatively, the above constraints can be relaxed and the
cell could be placed in isothermal contact with a heat bath. The entropy production from heat flow between the bath and the cell compartments can then be incorporated into a minimization of entropy production.

(iii) No side reactions or electrode reactions (e.g., corrosion) occur. The anodic and cathodic reactions are respectively

\[

A = X + ne^- \\
B + ne^- = Y
\]

The initial concentrations of the reacting species are \( A_0, B_0, X_0 \), and \( Y_0 \).

(iv) The cell potential across the electrodes (neglecting overpotential losses) is

\[
E = E_r - IR_t
\]

where \( I \) is the current and \( E_r \) is the thermodynamic reversible potential of the cell given by

\[
E_r = E^\ominus - \frac{RT}{nF} \ln \left( \frac{N_A N_Y}{N_B N_X} \right)
\]

\( E^\ominus \) is the standard cell potential for the redox reaction \( A + B = X + Y \). The \( IR_t \) term is the voltage drop due to Ohmic losses from the internal cell resistance \( R_t \). The volume in each compartment of the cell is fixed at identical values.

These general considerations apply to each model electrochemical system discussed below. We now examine the specifics of each system, corresponding in turn to a well-stirred fuel cell, chemical system discussed below. We now examine the specifics

\[
\text{variable resistance}
\]

\begin{tikzpicture}
    \node (load) {load};
    \node (A) at (0,0) {A \ , \ X};
    \node (B) at (1,0) {B \ , \ Y};
    \draw[->] (load) -- (A);
    \draw[->] (load) -- (B);
\end{tikzpicture}

\text{compartment 1} \rightarrow \text{compartment 2}

Figure 1. Model fuel cell.

Figure 2. Contour plot of \( \xi_{\text{eq}} \) in \((\beta_1, \beta_2)\) parameter space. Contour interval of 0.10.

\( B_0 \) and \( n = 1 \). The dot notation is \( d()/dr \). The initial condition for eq 5 is \( \xi = 0 \) at \( t = 0 \).

The uppermost bound on work output for the well-stirred fuel cell is obtained by operating along a reversible path. Work output along this path is

\[
\Gamma_{\text{rev}} = \int_0^{E^\ominus(1)} \left[ 1 - 2\beta_1 \ln \left( \frac{\beta_2 + \xi}{1 - \xi} \right) \right] d\xi = \\
\xi(1) - 2\beta_1 [(\beta_2 + \xi)] \ln(\beta_2 + (\xi(1)) - \beta_2 \ln(\beta_2) + (1 - \xi))] \ln(1 - \xi(1))
\]

The end concentration \( \xi(1) \) maximizing \( \Gamma_{\text{rev}} \) is the equilibrium concentration \( \xi_{\text{eq}} \), given by

\[
\xi_{\text{eq}} = \left[ \exp \left( \frac{1}{2\beta_1} - \beta_2 \right) / \left( \exp \left( \frac{1}{2\beta_1} \right) + 1 \right) \right]
\]

The equilibrium concentration, plotted in Figure 2 as contours in \((\beta_1, \beta_2)\) parameter space, is a convenient base line against which to compare the end concentrations of optimized finite time processes. The dashed contours, representing negative values of \( \xi_{\text{eq}} \), delineate regions in parameter space where the reverse of reaction I occurs. As \( \beta_1 \) increases, \( \xi_{\text{eq}} \) decreases; the driving force due to the standard cell potential decreases and the equilibrium shifts to the left in reaction I. Likewise, \( \xi_{\text{eq}} \) decreases as \( \beta_2 \) increases; the driving force due to the initial concentration gradient decreases and the equilibrium again shifts to the left.

B. Overpotential Losses. The difference in potential across the electrodes when current is flowing and when the circuit is open is the overpotential. With overpotential losses the voltage across the electrodes can be expressed as

\[
E = E_r - \eta_{\text{act},c} - \eta_{\text{conc},c} - \eta_{\text{act},a} - \eta_{\text{conc},a} - R_t I
\]

The subscripts act and conc denote the contributions from activation overpotential and concentration overpotential, respectively. Activation overpotential is the extra potential needed to reduce the energy barrier of the rate-determining step of reaction I. Concentration overpotential is the loss resulting from limits on diffusion transfer of the reactants to, or products from, the electrode. The subscripts c and a reference reactions at the cathode and anode, respectively. In the linear Tafel region

\[
\eta_{\text{act},c} = \frac{RT}{\alpha_c F} \ln \left( \frac{I}{A_d I_c} \right)
\]

and

\[
\eta_{\text{conc},c} = -\frac{RT}{nF} \ln \left( 1 - \frac{I}{A_d I_c} \right)
\]

\( A_c \) is the cathode surface area, \( \alpha_c \) is the transfer coefficient for
the cathodic reaction, $i_{0c}$, is the exchange current density (i.e.,
the velocity of the cathodic reaction at equilibrium), and $i_{Lc}$ is
the limiting current density at the cathode. Similar expressions
hold for the anodic reaction. In terms of the dimensionless
variables introduced earlier

$$\nu = 1 - 2\beta_i \ln \left( \frac{\beta_i + \xi}{1 - \xi} \right) - \beta_s \ln (\gamma_s t) + 2\beta_i \ln (1 - \gamma_i) -$$

$$\beta_s \ln (\gamma_s t) - \beta_d t \quad (7)$$

where

$$\beta_s = RT/(\alpha_s F \theta) \quad \beta_a = RT/(\alpha_a F \theta)$$

$$\gamma_s = A_0 n F/(\gamma_s A_0) \quad \gamma_a = A_0 n F/(\gamma_a A_0)$$

and

$$\gamma = A_0 n F/(\gamma A_1)$$

We have set $A_s = A_a = A$ and $i_{0s} = i_{0a} = i_{0c}$.

In eq 7 the potential difference is a function of only the extent
of reaction and current flow. It may be expressed as the sum of
two univariable functions

$$\nu = \nu(\xi_1) + \nu(\xi_2) \quad (8)$$

In section III we show that the functional form of the optimal
current path for the well-stirred cell is the same for electrochemical
systems with overpotential losses and without overpotential losses.

C. Diffusive Flow Fuel Cell. In this section we probe the effect
of a nonzero diffusion rate on the behavior of the model electrochemical
system. The potential difference across the electrodes is
given by eq 4; overpotential losses are not included in this model.
We assume the electrodes are immersed in infinite reservoir
compartments. The concentration of species A in the bulk in
compartment 1 of Figure 1 is $X_1$; if no current flow occurs in the
cell then $X_1 = X_0$ at every point in compartment 1. Similarly for
species X in compartment 1; $X_{1x} = X_0$ and $X_{1x} = X_0$ at all points
when no current flows. Assuming diffusion is proportional to the
difference in concentration at the electrode surface and in the bulk,
the time evolution of species A in compartment 1 can be written as

$$\dot{\xi}_1 = 1 - \delta \xi_1 \quad (9)$$

where $\delta$ is the dimensionless diffusion coefficient. This Fick's law
approximation neglects contributions to concentration flux from
convection and migration in the electric field. For simplicity, each
reacting species in reaction I may be described by an expression
similar to eq 9.

The well-stirred electrochemical cell has no steady-state position
from which work, let alone power, can be extracted. However, the
diffusion flow fuel cell bridges two infinite reservoirs of differ-
fering electrochemical potential. If unconstrained, the fuel cell
would evolve to a steady state. The resulting current flow across
the potential gradient would generate both work and power.

Assuming the external load and resistance across the electrodes
can be set arbitrarily, it is useful to determine the maximum power
obtainable from operating the cell at a steady state. This value
provides a measure against which to compare the work output from
optimized diffusive flow fuel cells. From eq 9 the steady-state
current is

$$i_s = \delta \dot{\xi}_1$$

Power output $\Phi$ at the steady state is

$$\Phi_s = \nu_i i_s$$

Maximizing $\Phi_s$ with respect to $\xi_1$ gives

$$1 - 2\beta_i \dot{\xi}_1 = 2\beta_i (1 + \beta_i) \xi_1 (1 - \xi_1) - 2\beta_i \ln \left( \frac{\beta_i + \xi_1}{1 - \xi_1} \right)$$

where $\dot{\xi}_1$ is the optimal steady-state concentration at the electrode
surface. In Figure 3a and b, contours of $\xi_1$ and $\Phi_s$, respectively,
are plotted in $(\beta_i, \beta_s)$ parameter space. Increasing either $\beta_s$ or

$\delta$ shifts the contours up and to the right, decreasing both $\xi_1$ and
$\Phi_s$. However, the contour $\xi_1 = 0$ in Figure 3a remains invariant,
cutting the parameter space at $\beta_3 = \exp(1/(2\beta_i))$, regardless of
the $\beta_3$ and $\delta$ values. The contours $\xi_1 = 0$, $\xi_3 = 0$, and $\Phi_s = 0$ are
identical.

III. Optimal Control of the Well-Stirred Cell

A. Maximum Work Output. In this section we determine both
the current path and the end concentration that yield maximum
work output from the well-stirred fuel cell operating in a finite
time interval. The form of the current path is shown to be the
same for all systems where the potential losses are functions of
only the current. Thus, the current paths are the same for the
two models of the well-stirred fuel cell looked at in this paper.

The objective function for maximum work output is

$$\Gamma = \int_0^T \nu_i \nu_e \, dt \quad (10)$$

The integration limits are $\tau_i = 0$ and $\tau_e = 1$. The scale for work
output is $\Gamma = W/\beta_i$ where $\beta_i = E^*/A_0 n F$. With eq 5 as a
differential constraint on the state variable $\xi$, the Hamiltonian for
this system is written as

$$H = \nu_i + \lambda i_s \quad (11)$$

The functional form of the control variable $i$ is

$$\frac{\partial H}{\partial i_s} = 0 = 1 - 2\beta_i \ln \left( \frac{\beta_i + \xi_3}{1 - \xi_3} \right)$$

The time evolution of the Lagrange multiplier $\lambda$ is
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\[ \dot{\lambda} = -\frac{\partial H}{\partial \xi} = \frac{2\beta_1(1 + \beta_2)i}{(\beta_2 + \xi)(1 - \xi)} \]  (13)

Equations 5 and 13 can be solved simultaneously to give

\[ \lambda = 2\beta_1 \ln \left( \frac{\beta_2 + \xi}{1 - \xi} \right) + c_0 \]  (14)

Substituting this expression into eq 12 gives

\[ i = \frac{c_0 + 1}{2a_4} \]  (15)

Since \( i \) is a function of constants, maximum work output occurs when the current is constant. Equation 5, describing the time evolution of the concentration, can be solved to give

\[ \xi = \frac{(c_0 + 1)r}{2a_4} \]  (16)

From this expression we find \( c_0 = 2a_4\xi(1) - 1 \). Equation 10 can now be integrated along the optimal current path to give

\[ \Gamma = \xi(1) - 2\beta_1[(\beta_2 + \xi(1)) \ln (\beta_2 + \xi(1)) + (1 - \xi(1)) \ln (1 - \xi(1)) - \beta_2 \ln (\beta_2)] - \beta_4\xi(1)^2 \]  (17)

as the upper bound on work output from a well-stirred fuel cell being drained from \( \xi(0) = 0 \) to \( \xi(1) \) in a finite time interval.

Since the end concentration \( \xi(1) \) is not constrained, a necessary boundary condition at \( \tau = 0 \) is \( \lambda(1) = 0 \). Given the boundary conditions, the optimal end concentration \( \xi(1) \) is found by solving

\[ 1 - 2\beta_4\xi(1) = 2\beta_1 \ln \left( \frac{\beta_2 + \xi(1)}{1 - \xi(1)} \right) \]  (18)

Equation 18 can be solved numerically or \( \xi(1) \) can be approximated by

\[ \xi(1) = \frac{1 - 2\beta_1 \ln (\beta_2)}{2\beta_1 + 2\beta_2 + \frac{2\beta_1}{\beta_2}} \]

Alternatively, the optimal end concentration can be related to the equilibrium concentration of the system as

\[ \frac{\beta_2 + \xi_{eq}}{1 - \xi_{eq}} / \frac{\beta_2 + \xi(1)}{1 - \xi(1)} = \exp \left( \frac{\beta_4\xi(1)}{\beta_1} \right) \]

In Figure 4 are plotted contours of optimal \( \xi(1) \) in \( (\beta_1, \beta_2) \) parameter space. In Figure 5 are plotted contours of maximum work output, eq 17, in \( (\beta_1, \beta_2) \) space. The end values \( \xi(1) \) in these curves were found by solving eq 18. In these figures the contour lines move down and to the left as \( \beta_2 \) increases. Higher Ohmic resistance \( R_i \), or shorter operating interval \( t_f \), shifts the optimal end concentration, and hence the work output, to smaller values. This reduces the current flowing through the cell and minimizes Ohmic losses. At low \( \beta_2 \), values the optimal \( \xi(1) \) and \( \Gamma \) decrease as \( \beta_1 \) and \( \beta_2 \) increase, not unlike the behavior noted for the reversible cell. However, as \( \beta_2 \) increases, the \( (\beta_1, \beta_2) \) space separates into two regimes; at small \( \beta_2 \) \( \partial \Gamma / \partial \beta_1 > 0 \), while at large \( \beta_2 \), \( \partial \Gamma / \partial \beta_1 < 0 \). The region where \( \partial \Gamma / \partial \beta_1 > 0 \) is termed the favored work region. The unfavored work region occurs where \( \partial \Gamma / \partial \beta_1 < 0 \).

Additional current-dependent losses (e.g., overpotential losses), if included in the expression for the potential difference across the electrode, do not change the form of the current path generating optimal work output. The potential difference in this case is given by eq 8. The Hamiltonian is given by eq 11. The control variable \( \dot{i} \) is implicitly determined by

\[ \frac{\partial H}{\partial \dot{i}} = 0 = f(\xi) + g(i) + \dot{i} \frac{dg(i)}{dt} + \lambda \]  (19)

The Lagrange multiplier evolves as

\[ \dot{\lambda} = -\lambda_0 \frac{dF(\xi)}{d\xi} \]  (20)

Solving eq 5 and 20 simultaneously yields

\[ \lambda = -f(\xi) + c_1 \]  (21)

and

\[ g(i) + \dot{i} \frac{dg(i)}{dt} = c_1 \]  (22)

With the boundary condition \( \lambda(1) = 0 \) this equation simplifies to

\[ g(i) + \dot{i} \frac{dg(i)}{dt} + f(\xi(1)) = 0 \]

The current is constant along the path that maximizes work output and depends upon the final concentration.

B. Maximum Effectiveness. Effectiveness, or the second-law efficiency, can be expressed as

\[ \epsilon = \frac{\Gamma}{\Gamma_{rev}} \]

where \( \Gamma_{rev} \) is given by eq 6 and is a function of \( \xi(1) \) alone. Both the reversible process and the process occurring in finite time operate between the same initial and final states. The maximum possible work output for the well-stirred fuel cell is given by eq 17. We can rewrite the effectiveness as

\[ \epsilon = 1 - \frac{\beta_4\xi(1)^2}{\Gamma_{rev}} \]

The maximum path problem simplifies to an optimization of \( \epsilon \) with respect to \( \xi(1) \). The effectiveness is optimized along the boundary maximum \( \epsilon = 0 \) and \( \xi(1) = 0 \), at which point \( \epsilon = 1 \). For the parameter sets studied, no interior, local maximum is found.

In Figure 6 are overlaid contours of effectiveness on maximum work output contours in \( (\beta_1, \beta_2) \) space. The end concentrations maximize work output. The contours of effectiveness move up and to the left as \( \beta_2 \) decreases; smaller Ohmic losses are possible at lower values of \( \beta_2 \). Of particular interest is the magnitude of the effectiveness; the effectiveness remains in the range 0.49-0.65 for 0.5 \( \leq \beta_1 \leq 10.0 \). In the unfavored work region effectiveness increases as work decreases. In the favored work region both the effectiveness and work output increase as \( \beta_1 \) increases.

C. Maximum Profit. Following Salamon and Nitzan we view the fuel cell as a production process with work as an output and species A and B as inputs. Given an initial input of the reacting species, the problem we face is to operate the fuel cell within a finite time period while maximizing a profit function. The profit function is the difference between revenue and costs, which for a simple system with perfect competition is

\[ P = R - C = p_sF_{eq} - p(A_0 - A) \]  (23)

The prices per unit of input and output, \( p_i \) and \( p_o \) respectively, are constant in an economic model assuming perfect competition. Costs incurred in the process are assumed to depend only on the quantity of inputs consumed. This model neglects long-term costs associated with maintenance, depreciation, and capital investment. The short-run optimization performed below treats the system parameters as constants in the time period considered.

In the dimensionless variables, eq 23 can be scaled to give

\[ \Pi = \int_0^1 (\beta_2 - \dot{i}) \, dr \]  (24)

where \( \Pi = P/A_0p_o, \beta_2 = p_iE^2nF/p_o \), and \( \nu \) is given by eq 4. The Hamiltonian for this objective function is

\[ H = (\nu - 1/\beta_2)\beta_2 + \lambda \]

In this form it is easily seen that profit maximization can be treated as a special case of overvoltage loss; the potential difference is

Figure 4. (a) Contour plot of optimal $\xi(1)$ for maximum work output from the well-stirred fuel cell in $(\beta_1, \beta_2)$ parameter space. Contour interval of 5.0E-2. $\beta_1 = 0.5$. (b) Contour plot of optimal $\xi(1)$ for maximum work output from the well-stirred fuel cell in $(\beta_1, \beta_2)$ parameter space. Contour interval of 1.0E-2. $\beta_1 = 2.0$.

Figure 5. (a) Contour plot of $\Gamma$ for maximum work output from the well-stirred fuel cell in $(\beta_1, \beta_2)$ parameter space. Contour interval of 3.0E-2. $\beta_1 = 0.5$. (b) Contour plot of $\Gamma$ for maximum work output from the well-stirred fuel cell in $(\beta_1, \beta_2)$ parameter space. Contour interval of 1.0E-2. $\beta_1 = 2.0$.

Figure 6. Contour plots of $\Gamma$ for maximum work output from the well-stirred fuel cell in $(\beta_1, \beta_2)$ parameter space. Contour interval of 3.0E-2. $\beta_1 = 0.5$.

The time evolution of the adjoint variable $\lambda$ is

$$\lambda = \frac{2\beta_1(1 + \beta_2)}{(\beta_2 + \xi)(1 - \xi)} + \delta\lambda$$

Maximizing the Hamiltonian by setting $\partial H / \partial \lambda = 0$ gives...
The constant current operation is similar to optimal process paths for several parameter sets. As \( \beta_1 \) is increased, the end concentration, current level, and work output drop. The optimal current path shifts dramatically from a left skewed parabola for \( \beta_2 = 0.5 \), to a roughly symmetric parabola for \( \beta_2 = 1.0 \), to a right skewed parabola for \( \beta_2 = 2.0 \).

**V. Discussion and Summary**

Work output, effectiveness, and profit are maximized in the well-stirred fuel cell when the current through an external load is held constant during the finite time interval of operation. This path occurs for all current-dependent losses. In cells maximizing work output and profit such a path minimizes the overpotential losses while sustaining the highest possible power production. Maximum effectiveness occurs for the boundary optimum \( i = 0 \). The constant current operation is similar to optimal process paths reported by Mozurkewich and Berry\(^4\) and by Salamon et al.\(^6\).

In the first case a constant velocity piston path maximized work output along the nonpower strokes of an Otto engine. In the second case a constant-temperature path minimized entropy production in a endoreversible heat engine.
output increases as the standard cell potential of the reacting electrolytic species. This can be obtained from the well-stirred fuel cell by reducing the concentration potential decreases, as the driving force from either the standard cell potential or the concentration potential (increase as increases. As results for increases in work output and profit are not found for the diffusive flow fuel cell. The optimal current paths are not constant over the finite time interval that the cell operates in. Instead, the current approaches a constant only in the work-favored region; elsewhere changes in involve a tradeoff between increased optimal work output and decreased effectiveness.

At low $\beta_5$ values the profit-optimized well-stirred fuel cell displays a bifurcation similar to that between the work-unfavored and the work-favored region. Asymptotically increasing $\xi(1)$ and profit $\Pi$ result for increases in $\beta_1$. This occurs most strongly at low $\beta_4$ and low $\beta_5$, where the price per unit input dominates the price per unit output. In this region we can decrease both the standard cell potential and the concentration potential (increase $\beta_1$ and $\beta_2$) and remain at the same profit level.

The effectiveness of the well-stirred cells maximizing work output increases as $\beta_1$ increases and $\beta_2$ decreases. The $\Gamma$ and $\varepsilon$ curves in Figures 5 and 6 can guide future, more detailed studies aimed at improving fuel cells. Research should concentrate on the $\beta_2$ parameter since this analysis implies that it is possible to increase both the optimal work output and the effectiveness of the cell by decreasing $\beta_2$. A similar situation occurs for the $\beta_1$ only in the work-favored region; elsewhere changes in $\beta_1$ involve a tradeoff between increased optimal work output and decreased effectiveness.

The magnitude of the constant current path differs for the three performance criteria. The optimal $\xi(1)$ for maximum work output and effectiveness serve as natural bounds on the optimal $\xi(1)$ for maximum profit. Contour curves in $(\beta_1, \beta_2)$ parameter space for $\xi(1)$ optimizing work output and profit approach the curves of $\xi_{\text{opt}}$ when $\beta_1$ is low and $\beta_2$ is high. Optimal $\xi(1)$ for work and profit maximization is less than $\xi_{\text{opt}}$, implying that the well-stirred fuel cell is not completely drained.

The gradient of $\xi(1)$ in $(\beta_1, \beta_2)$ space is much steeper for maximum work output than the gradient of $\xi_{\text{opt}}$ in the same space. For low $\beta_4$ values both contours decrease as $\beta_1$ and $\beta_2$ increase; as the driving force from either the standard cell potential or the concentration potential decreases, $\xi(1)$ and $\Gamma$ decrease. However, at large $\beta_4$ values a bifurcation occurs in the contours of optimal $\xi(1)$ and $\Gamma$ for maximum work output and maximum profit. For constant $\beta_5$, a low $\beta_1$ region exists where both optimal $\xi(1)$ and $\Gamma$ increase as $\beta_1$ increases. Thus a region, the work-favored region, exists in parameter space where increased work output and profit can be obtained from the well-stirred fuel cell by reducing the standard cell potential of the reacting electrolytic species. This effect is more pronounced at higher $\beta_1$ values.

Figure 9. Time-parametrized curves of potential difference vs. current for maximum work output from the diffusive flow fuel cell. $\beta_1 = 0.25$, $\beta_2 = 0.15$. Curve assignments: $\beta_4 = 0.5$ and $\delta = 1.0$ (A), $\beta_4 = 1.0$ and $\delta = 1.0$ (B), $\beta_4 = 0.5$ and $\delta = 0.1$ (C).

Figure 10. Optimal $\xi(1)$ plotted against $\delta$ for maximum work output from the diffusive flow fuel cell. $\beta_1 = 0.25$, $\beta_2 = 0.15$. Curve assignments: $\beta_4 = 0.5$ (A), $\beta_4 = 1.0$ (B), and $\beta_4 = 2.0$ (C).

Figure 11. Work output $\Gamma$ (solid curve) and effectiveness $\varepsilon$ (dashed curve) plotted against $\delta$ for the diffusive flow fuel cell maximizing work output. $\beta_1 = 0.25$, $\beta_2 = 0.15$. Curve assignments: $\beta_4 = 0.5$ (A), $\beta_4 = 1.0$ (B), and $\beta_4 = 2.0$ (C).

Figure 12. Current (solid curve) and concentration (dashed curve) profiles for profit maximization of the diffusive flow fuel cell. $\beta_1 = 0.25$, $\beta_2 = 0.15$, $\beta_4 = 0.5$, $\delta = 1.0$. Curve assignments: $\beta_5 = 0.5$ (A), $\beta_5 = 1.0$ (B), and $\beta_5 = 2.0$ (C).
output decreases and the effectiveness increases.

The optimized diffusive flow fuel cell can deliver twice the work as the steady-state diffusive flow cell. This result suggests novel designs for fuel cells constructed to provide maximum work output. For example, if the reactants are inexpensive, one can run a cell along an optimal work path followed by a recharge of the cell at the end of the cycle interval. Such a cyclic operation would deliver more work and average power than a diffusive cell in a steady-state operation.

It should be possible to construct both the well-stirred fuel cell and the diffusive flow fuel cell. A variable resistance can be programmed to constrain the current to the optimal path. Work output from fuel cells following the work-optimized current paths can be compared to the predicted optimal work output. This would provide a measure of how realistic and applicable the upper work bounds provided by the modeled fuel cells are to real processes. Additionally, the work-favored region predicted for the well-stirred fuel cell can be probed to determine if it exists in real electrochemical systems.

This paper extends the application of thermodynamics to simple electrochemical systems that can serve as generic models for fuel cells operating in a finite time and with nonzero flows. Several interesting behaviors are revealed in this analysis, not the least of which is the parabolic current path for maximum work output from the dissipative flow fuel cell. This work provides useful directions for the future study of performance limits of realistic models of fuel cells and photoelectrochemical cells. In more detailed models heat flows, side reactions, finite reaction rates, and electrode surface effects can be introduced. The inclusion of heat flows would allow the investigation of bounds on minimum entropy production.

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CHEMICAL KINETICS

Subharmonic Response of a Heterogeneous Catalytic Oscillator, the "Cantabrator", to a Periodic Input

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The oscillatory reaction between oxygen and carbon monoxide/propane mixtures, the Cantabrator, has been studied with periodic feed switching in order to investigate the interactions of complex reaction dynamics with a time-varying concentration input. A supported platinum catalyst was used in a continuously stirred tank reactor (CSTR) at 1 bar total pressure at temperatures in the range 408-423 K. Two instances of subharmonic response (in which the output oscillation has twice the input period), rarely discussed in heterogeneous catalytic oscillators, are reported. Our elementary step model, previously proposed to account for the spontaneous concentration oscillations of this and other CO/alkene systems under steady-feed conditions, is used to obtain qualitative and some quantitative insights into the occurrence of subharmonic response.

Introduction

The study of periodic feed switching in catalytic reactors is a specific example of the wider topic of "forcing" a system, mechanical, chemical, electrical or environmental, which may have a natural frequency of its own. Work to date has been mainly concerned with devising optimum switching schemes that could enhance reactor performance, as measured in terms of time-averaged conversion or reaction selectivity.

A plethora of reactions have been examined under conditions where the reactor feed concentration varies with time. These include the oxidation of sulfur dioxide on \( \text{V}_2\text{O}_5 \), the oxidation of ethene on Ag, the hydrogenation of butadiene on Ni, the synthesis of ammonia, the addition of ethene to acetic acid catalyzed by \( \text{H}_2\text{SO}_4 \), the Fischer-Tropsch synthesis reaction, and, last but not least, the oxidation of carbon monoxide. Hawkins and Cutlip reported significantly increased reaction rates of CO oxidation compared to the steady-state rate when two streams consisting of CO/argon and O\(_2\)/argon mixtures are alternatively fed to the reactor. The oxidation of CO on \( \text{V}_2\text{O}_5 \) has also been examined as well as the oxidation of CO/NO mixtures.

The work reported here is concerned with the more fundamental problem of the interaction of a time-varying reactor feed with the complex kinetics of the heterogeneous catalytic oxidation of a...