Microbial Fuel Cells: Principles and Optimization

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Outline

I. On-Line Optimization with Multiple Units

II. Microbial Fuel Cells (MFC) Principles

III. Experimental Results

IV. Conclusion and Perspectives
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Static optimization of continuous processes

- System is dynamic, optimization of steady-state is considered:
  
  \[
  \min_u \ J(x, u) \\
  s.t. \quad \dot{x} = F(x, u) \equiv 0
  \]  

- Optimization = necessary condition of optimality \( \rightarrow \frac{dJ}{du}|_{u^*} = 0 \)
• System is dynamic, optimization of steady-state is considered:

\[
\min_u J(x, u) \quad \text{(1)}
\]

\[
s.t. \quad \dot{x} = F(x, u) \equiv 0 \quad \text{(2)}
\]

• Optimization = necessary condition of optimality \( \rightarrow \frac{dJ}{du}|_{u^*} = 0 \)

• Real-time optimization \( \rightarrow \) track optimum using measurements
General structure of extremum-seeking control
The Perturbation Method: Krstic and Wang, 2000
Multi-Unit Optimization Method with Two Identical Units. Srinivasan, 2006

\[ u_1 = u - \Delta \]

\[ u_2 = u + \Delta \]

\[ \dot{u} = k \left( J_2(u_2) - J_1(x_1, u_1) \right) \]

\[ \dot{u} = k \frac{J_2 - J_1}{\Delta} \]
Evolution of multi-unit optimization method: one input, 2 units

\[ \delta J = J_2 - J_1 \]

\[ \delta u = \Delta \]
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![Graph showing the evolution of the optimization method with one input and two units. The graph is a curve that starts from a point and increases towards a higher value as the input variable u changes from -2.5 to 0.5.](image)
Evolution of multi-unit optimization method: one input, 2 units
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Extremum-seeking: multi-unit optimization method

- Process with multiple identical or similar units
- Each unit operated at different operating points: difference between operating points is constant
- Difference in performance used to compute gradient
- Perturbation in the unit dimension: decoupled from the system dynamics
Illustrative Example: Maximization of the Productivity of Green-Fluorescent Protein (GFP) by E. Coli Cells

\[
\begin{align*}
\text{max}_{F} \quad & FP \\
\text{s.t.} \quad & \dot{X} = \mu X - \left( \frac{F}{V} \right) X \\
& \dot{P} = \left( \frac{Y_P}{S} \mu + \beta \right) X - \frac{F}{V} P \\
& \dot{S} = \left( \frac{F}{V} \right) (S_f - S) - \frac{\mu X}{Y_{X/S}} - \frac{\left( \frac{Y_P}{X} \mu + \beta \right) X}{Y_{P/S}} \\
& \quad - m_s \left( \frac{S}{K_{sm} + S} \right) X \\
& \mu = \frac{\mu_{\text{max}} S}{K_s + S}
\end{align*}
\]
Static characteristics of the two identical bioreactors:
\[ F_{1}^{\text{opt}} = F_{2}^{\text{opt}} = 16.9 \ \frac{L}{h}, \ \ J_{1}^{\text{opt}} = J_{2}^{\text{opt}} = 15040 \ \frac{mg}{h} \]
Multi-Unit Method vs Perturbation Method

![Graphs showing GFP and Flow over time for unit 1 and unit 2.](image)
Multi-unit optimization

Advantages:

- Faster convergence than the perturbation method
- No oscillations around the optimum

Disadvantages:

- Processes must have several identical units
- The number of units needed is related to the number of manipulated variables
Convergence of the Multi-Unit Method with Non-Identical Units

\[ J_2(u) = J_1(u + \beta) + \gamma + \bar{J}(u) \]

**Stability:**
\[ \Delta(\Delta + \beta) > 0 \]

**Equilibrium point:**
\[ u^* \simeq \frac{u_1^{opt} + u_2^{opt}}{2} - \frac{\gamma}{(\Delta + \beta) \frac{\partial J_1}{\partial u^2}} \]
Static Characteristics of the two units: \( F_{1}^{opt} = 16.9 \frac{L}{h}, \)
\( F_{2}^{opt} = 18.4 \frac{L}{h}, \)
\( J_{1}^{opt} = 15040 \frac{mg}{h}, J_{2}^{opt} = 17780 \frac{mg}{h} \)
Static Characteristics of the two units \( F_{1}^{opt} = 16.9 \frac{L}{h} \), \( F_{2}^{opt} = 18.4 \frac{L}{h} \), \( J_{1}^{opt} = 15040 \frac{mg}{h} \), \( J_{2}^{opt} = 17780 \frac{mg}{h} \)

![Graph showing static characteristic of each unit: J(u)](image)

\[ \beta = F_{1}^{*} - F_{2}^{*} = -1.5 \text{ L/h} \]

\[ \gamma = J_{2}^{*} - J_{1}^{*} = 2740 \text{ mg/h} \]
Stability does not necessarily mean good performance.
Multi-Unit with Correctors: Simultaneous Adaptation
• Microbial Fuel Cell Principle
• Definition of the optimization problem
• Algorithms usually used
• Multi-unit Optimization Structure
• Experimental Results
• Conclusions
Basic electrochemistry

- An electrochemical reaction couples...
  - An electron (e⁻) producing reaction (anode)
  - An electron (e⁻) consuming reaction (cathode)

- E.g., car battery:
Bioelectrochemistry

Electrochemically active bacteria
Bioanode: electrons from waste

• Glucose:
  – $\text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{H}_2\text{O} \rightarrow 6 \text{CO}_2 + 24 \text{H}^+ + 24 \text{e}^-$

• Acetic Acid:
  – $\text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^-$

• COD:
  – 1 g COD $\rightarrow$ 0.125 mol e$^-$

• These electrons are released with high energy!
Bioanode

- Organic Material
- CO₂
- H⁺
- e⁻
Microbial Fuel Cell

Glucose/CO₂ (-0.41 Volt)
Acetic Acid/CO₂ (-0.27 Volt)

Energie Opbrengst Bacteriën
O₂/H₂O (0.82 Volt)

Bio-electricity (+1.02 Volt)

Anode Potential loss

Biological Anode Potential (~ -0.2 Volt)

Bio-Anode

Cathode

Advanced Water Management Centre

The University of Queensland Australia
Microbial fuel cell

- Anode = Electrode (e.g., graphite)
- 0 = Electrochemically active microorganisms
- । = Cation exchange membrane
- e⁻ = Electron
- H⁺ = Proton
- o = Air bubble

Membrane

Cathode

Wastewater

CO₂

Effluent

Spent air

CO₂

Air (oxygen)

Organic Material

H⁺
Conventional Anaerobic Treatment

Wastewater (COD) → Biogas Production → Biogas Treatment (a.o. H₂S removal) → Electricity Production (gasmotor) → Electricity

Source: www.paques.nl

Efficiency: +/- 30%

# of Units: At least 3
Microbial Fuel Cell

Efficiency: +/- 60%

# of Units: Only 1
Beyond MFCs

- Glucose/ CO₂ (-0.41 Volt)
- Acetic Acid/ CO₂ (-0.27 Volt)
- H⁺/ H₂ (-0.42 Volt)

Hydrogen production requires an input of electricity (-0.22 Volt)

Biological Anode Potential (~ -0.2 Volt)

Advanced Water Management Centre

The University Of Queensland
Australia
Hydrogen from acetic acid

• Anode:
  \[ \text{CH}_3\text{COOH} + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ CO}_2 + 8 \text{ H}^+ + 8 \text{ e}^- \]

• Cathode:
  \[ 8 \text{ H}^+ + 8 \text{ e}^- \rightarrow 4 \text{ H}_2 \]

• Overall:
  \[ \text{CH}_3\text{COOH} + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ CO}_2 + 4 \text{ H}_2 \]
  – In theory: 0.14-0.22 Volt required
  – In practice: ~0.5 Volt required
Parallel development

BEAMR
(Bruce Logan)

Biocatalyzed Electrolysis
Proof of principle experiment

Dark Fermentation

• Yield in practice (~15%):  
  – Stoichiometry: Glucose $\rightarrow$ 12 H$_2$  
  – Theory: Glucose $\rightarrow$ 4 H$_2$ + 2 acetic acid  
  – Practice: Glucose $\rightarrow$ 1.8 H$_2$ + byproducts

• Most of the substrate is lost for H$_2$ production!

• Byproducts need to be converted to H$_2$ as well!!!  
  – Photofermentation  
  – **Microbial electrolysis**
Byproduct conversion

• Photofermentation:
  – Fatty acids + sunlight $\rightarrow$ H$_2$ + CO$_2$
  – Low conversion efficiencies
  – Sunlight is diffuse $\rightarrow$ Enormous reactor surface areas required
  – No production at night
  – Not regarded economically feasible!

• Microbial electrolysis:
  – Fatty acids + electricity $\rightarrow$ H$_2$ + CO$_2$
  – High conversion efficiencies
  – H$_2$ production independent from the reactor surface area
  – 24/7 production
  – Prospects for economic feasibility look promising!
Perspectives

• Status
  – ~1 Nm³ H₂/m³ reactor/day
  – 90 % efficiency
  – At 0.6 to 1.0 Volt

• Perspectives
  – > 10 Nm³ H₂/m³ reactor/day
  – 90 % efficiency
  – At 0.5 Volt

These conversion rates are comparable to other wastewater treatment technologies, but now we clean wastewater AND produce hydrogen!
Biocathode

Wastewater

Effluent

Power Supply

CO₂

H₂

H₂CO₂

H⁺

H₂
Stacked systems

Power Supply

Wastewater

CO₂ H₂ CO₂ H₂ CO₂ H₂ CO₂ H₂ CO₂ H₂ CO₂ H₂ CO₂ H₂ CO₂ H₂

e− e− e− e− e− e− e− e−
Novel biocathodes

E.g. Glycerol → 1,3 propanediol
$0.60/kg → $1.68/kg
Microbial Fuel Cells Principle

- Bacteria used as catalysts
- Source of carbon as substrate: glucose, acetate
- Micro-organisms use energy to grow, to maintain their metabolism and to transfer electricity from the anode to the cathode

From Rabaey and Verstraete, Trends in biotechnology, 2005
The optimization problem:

\[
\max_R P
\]

1. \( R^* = R_{int} \)
2. Source has variable internal resistance
3. Use of MPPT to track the internal resistance in real time
Different algorithms for MPPT

Perturbation and Observation method

\[ R(k + 2) = \begin{cases} 
R(k + 1) + \Delta R & \text{if} \quad \frac{P(k+1) - P(k)}{R(k+1) - R(k)} \geq 0 \\
R(k + 1) - \Delta R & \text{if} \quad \frac{P(k+1) - P(k)}{R(k+1) - R(k)} < 0 
\end{cases} \]  

Gradient method

\[ R(k + 1) = R(k) + \Delta R \]  
\[ R(k + 2) = R(k + 1) + \alpha \frac{P(k + 1) - P(k)}{R(k + 1) - R(k)} \]  

- temporal perturbation: wait for steady-state
- persistent perturbation: oscillation around the optimum
Microbial Fuel Cells: a variable source of electricity

- Variable internal resistance
- Biological system with slow dynamics
- Power density delivered is relatively low: stack of MFC may be needed
Extremum-seeking: multi-unit optimization method.
Srinivasan, 2006

\[ \dot{u} = k \frac{J_2 - J_1}{\Delta} \]
Experimental Set-up
Polarization curves: $R_1^* \approx R_1^* \approx 45\,\Omega$, $P_1^* \approx 85\,mW/L_A$, $P_2^* \approx 76\,mW/L_A$, $\gamma = P_2^* - P_1^* = -9\,mW/L_A$
MFC Dynamics from two sources: electrochemical reactions and biological processes

Below the optimum: inverse response system

![Graph showing power density and resistance over time](graph.png)
MFC Dynamics from two sources: electrochemical reactions and biological processes

Above the optimum: non-inverse response system
Multi-unit algorithm applied to the MFC set-up

\[ R_1 = R - \frac{\Delta}{2} d_{mu} \]
\[ R_2 = R + \frac{\Delta}{2} d_{mu} \]
\[ \dot{R} = k \frac{dP}{dR} = k \frac{P_2 - P_1 - \hat{\gamma}}{\Delta R} \]
\[ \dot{\hat{\gamma}} = -k_\gamma (P_2 - P_1 - \hat{\gamma})(1 - d_{mu}) \]
\[ d_{mu}(t) = \begin{cases} 
1 & \text{if} \quad i(T_1 + T_2) \leq t \leq i(T_1 + T_2) + T_1 \\
0 & \text{if} \quad i(T_1 + T_2) + T_1 \leq t \leq (i + 1)(T_1 + T_2)
\end{cases} \]
\[ T_1 = T_2 = 3\text{min.}, \Delta R = 2.5\Omega, \quad k = 90 \frac{\Omega^2}{mW}, \quad k_\gamma = 1 \]
Optimization Results:

\[ R_1^* = 34\,\Omega \quad P_1^* = 81.8\,\frac{mW}{L_A} \quad R_2^* = 36\,\Omega \quad P_2^* = 84.4\,\frac{mW}{L_A} \]
Comments on the results

• $R_{mu}^* \approx 35\Omega < R_1^* = R_2^* = 45\Omega$

• $T_2 = 3\text{m.}$ too short. Bad estimation of $\gamma$ affects the convergence point.

Estimated time to reach the optimum with the P-O method:

$$t_{PO} \approx \frac{140 - 45}{2.5} \times 10 = 380\text{ m} \approx 6\text{ h}$$

$$t_{MU} \approx 1\text{ h}$$
Conclusions

• Multi-unit optimization to maximize power from MFC motivated by two main reasons:
  1. slow dynamics of the MFC
  2. low power density ⇒ need to optimize, stack of MFC is often available

• Fast convergence to the optimum
• Good response to a temperature perturbation
• Improvement of $\gamma$ estimation needed ($T_2$ should be increased)
• Further work: more tests to compare MU performance with other MPPT algorithms.
Future work

- Prove the convergence of the Multi-unit with simultaneous correctors adaptation
- Application of Multi-unit method with simultaneous correctors adaptation to maximize power delivered by Microbial Fuel Cells.
- Apply Multi-unit optimization Method to problems under inequality constraints (using a gradient projection onto active constraints algorithm)
Static Characteristics of the two units 

\[ F_{opt}^1 = 16.9 \frac{L}{h}, \quad F_{opt}^2 = 18.4 \frac{L}{h}, \quad J_{opt}^1 = 15040 \frac{mg}{h}, \quad J_{opt}^2 = 17780 \frac{mg}{h} \]

**Static characteristic of each unit : J(u)**

\[ \beta = F_1^* - F_2^* = -1.5 \frac{L}{h} \]
\[ \gamma = J_2^* - J_1^* = 2740 \frac{mg}{h} \]
Multi-Unit with Correctors: Simultaneous Adaptation

\[ \hat{J}_1 = \Phi_1^T \theta_1 \]
\[ e_1 = J_1 - \hat{J}_1 \]
\[ \Phi_1 = [1 \quad F_1 \quad F_1^2] \]
\[ \dot{\theta}_1 = R_1^{-1} \Phi_1^T e_1 \]
\[ \dot{R}_1 = \Phi_1 \Phi_1^T - \lambda R_1 \]
\[ \hat{J}_2 = \ldots \]

\[ F_1 = F - \frac{\Delta}{2} \]
\[ F_2 = F + \frac{\Delta}{2} - \hat{\beta} \]
\[ \hat{F} = \frac{k_{mu}}{\Delta} (J_2 - J_1 - \hat{\gamma}) + a \sin(\omega t) \]
\[ \dot{\hat{F}} = \frac{k_{\beta}}{a^2} \left( \frac{d \hat{J}_2}{dF_2} - \frac{d \hat{J}_1}{dF_1} - \delta \exp(-t/t_0) \right) \]
\[ \dot{\hat{\beta}} = \frac{k_{\hat{\beta}}}{a^2} (J_2(F) - \hat{J}_1(F) - \hat{\gamma}) \]
\[ \dot{\hat{\gamma}} = \frac{k_{\gamma}}{a^2} (J_2(F) - \hat{J}_1(F) - \hat{\gamma}) \]

\( \delta \) parameter is necessary to avoid a compensation of \( \Delta \) by the \( \beta \) corrector.
Multi-Unit with Correctors: Simultaneous Adaptation

Graphs showing the relationship between time and GFP (mg/h) and flow (L/h) for $J_1$, $J_2$, $F_1$, and $F_2$. The graphs illustrate the adaptation process over time.
Multi-Unit with Correctors: Simultaneous Adaptation

\[ \beta \]

\[ \gamma \]

\[ \text{mg/h} \]
Thank you for your attention!