Synthesis of Biofuels on Biocathodes

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Current bioenergy efforts on nontraditional biomass

Source: The National Academies
http://needtoknow.nas.edu/energy/interactive/energy-system.php

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Microbial electrosynthesis

Source: The National Academies
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Synthesis of CO$_2$-neutral Electrofuels

Solar
Wind
Nuclear

H$_2$O, waste

$e^-$

CO$_2$
(atmospheric)

Microbial Cathodic Biofuel Reactors

CO$_2$-neutral Transportation fuels
Commodity/Fine Chemicals

Usage
Energetics of Bio-Electrochemical Systems

Microbial fuel cell

![Diagram of a microbial fuel cell with reactions and energy production](image)

- Anode: \( \text{CH}_2\text{O} \) to \( \text{CO}_2 \)
- Cathode: \( \frac{1}{2} \text{O}_2 \) to \( \text{H}_2\text{O} \)

Redox potentials:
- \( \Delta G < 0 \) (useful)
- \( \Delta G > 0 \)

Energy production

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Energetics of Bio-Electrochemical Systems

**Microbial fuel cell**

\[
<\text{CH}_2\text{O}> \xrightarrow{\Delta G<0, \text{(useful)}} \text{CO}_2 \\
\text{Anode} \xrightarrow{e^-} \text{Cathode} \\
\frac{1}{2} \text{O}_2 \xrightarrow{\Delta G<0} \text{H}_2\text{O}
\]

*Energy production*

**Microbial electrosynthesis**

\[
<\text{CH}_2\text{O}> \xrightarrow{\Delta G>0} \text{CO}_2 \\
\text{Cathode} \xrightarrow{e^-} \text{Anode A} \\
\text{H}_2\text{O} \xrightarrow{\Delta G>0, \text{(solar, renewable, nuclear)}} \frac{1}{2} \text{O}_2
\]

*Energy consumption*

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**Exoelectrogenic Bacteria**

**Actinobacillus succinogenes**

-325mV (vs SHE)

**Sporomusa ovata**

-400mV (vs SHE)

**Methanobacterium palustre**

- 700mV
- 900mV (vs SHE)

Coulombic Efficiency:

- Sporomusa ovata: 85% (Nevin et al. 2010)
- Methanobacterium palustre: 80-96% (Cheng et al. 2010, Vilano et al. 2010)

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Research Focus in Microbial Electrosynthesis

- Uptake of cathodic electrons and integration into cellular metabolism
- CO₂ reduction and designer fuels/chemicals pathways
- Engineering stable microbial communities
- Delivery and activation of electrons to cathode
Our research platform

**Methanogenic archaea**
- Cathode
- CO₂
- Methane

**Homoacetogenic bacteria**
- Cathode
- CO₂
- Acetate

**Shewanella oneidensis**
- Cathode
- Med<sub>ox</sub>
- Med<sub>red</sub>
- Fumarate (Surrogate)
- Succinate
- -500mV (vs SHE)

**Escherichia coli**
- Cathode
- Med<sub>ox</sub>
- Med<sub>red</sub>
- Fumarate (Surrogate)
- Succinate
- -600mV (vs SHE)

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Mediator-controlled cathodic electron consumption by *S. oneidensis* MR1

Expected stoichiometry:  
\[ \text{Fumarate} + 2e^- + 2H^+ \rightarrow \text{Succinate} \]
Electrode attached biofilm of *S. oneidensis* MR1

Current consumption coupled to fumarate reduction

**Graph:**
- **Y-axis:** Current [mA]
- **X-axis:** Time [h]
- **Key Points:**
  - **Fumarate addition:** -360 mV vs. SHE
  - **Discontinued for CV measurement:**
Electrode attached biofilm of *S. oneidensis* MR1

Current consumption coupled to fumarate reduction

Expected stoichiometry: \( \text{Fumarate} + 2e^- + 2H^+ \rightarrow \text{Succinate} \)

-360 mV vs. SHE

![Graph showing succinate recovered and electrons consumed](image-url)
Electrode attached biofilm of *S. oneidensis* MR1

Cyclic voltammetry of abiotic and biofilm electrode with fumarate
Mediator-controlled cathodic electron consumption by *E. coli* using fumarate

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Synthesis of CO$_2$-neutral Electrofuels

- Solar
- Wind
- Nuclear

H$_2$O, waste $\rightarrow$ e$^-$ $\rightarrow$ Microbial Cathodic Biofuel Reactors $\rightarrow$ CO$_2$ (atmospheric) $\rightarrow$ Usage

CO$_2$-neutral Transportation fuels
Commodity/Fine Chemicals
Spormann bioelectrofuels team

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Funding: GCEP

Dr. Bruce Logan
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Power densities reported on MFCs
(normalized to electrode-projected surface)

Logan 2009
Shewanella oneidensis MR-1 (AS84)
Cell suspension, 0, 0.1, 0.5 mM MV (prereduced)

Current [mA] vs. Time [h]

0 mM MV
0.05/0.1 mM MV
0.1 mM MV
0.5 mM MV

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Exoelectrogenic Bacteria

Sporomusa ovata

Coulombic Efficiency: 85%
(Nevin et al. 2010)

Geobacter sulfurreducens

Coulombic Efficiency: 65%
(Dumas et al. 2010)

Methanobacterium palustre

Coulombic Efficiency: 80-96%
(Cheng et al. 2010)
(Vilano et al. 2010)
Expected Data

Addition of e⁻-acceptor

Current

Time

Concentration

Reactant, Product

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Escherichia coli: $e^- + \text{fumarate}$
**Shewanella oneidensis – Electron Balance**

- **Electrons [mmol]**
  - 0.5
  - 0.4
  - 0.3
  - 0.2
  - 0.1
  - 0.0

- **Time [h]**
  - 0
  - 2
  - 4
  - 6

- e\(^{-}\) consumed by fumarate reduction
- Cathodic e\(^{-}\) consumed
Future Work - Outlook

• Identify molecular mechanism of electron transport into the cell
• Optimize shuttle mediated electron transport
• Explore other mediators & cathode potentials
• Work with other (engineered) target microorganisms
• Construct microbial communities, interspecies electron transfer
• Scale up
Bio-Electrochemical Systems

Microbial Fuel Cell

- Microbially catalyzed
- Chemically catalyzed

Anode

- CO₂
- Organics

Energy production

Cathode

- O₂
- H₂O
- H⁺
- H₂

Microbial Electrosynthesis

- Chemically catalyzed
- Microbially catalyzed

Cathode

- Product
- Electron acceptor
- CO₂

Energy consumption

adapted from Rabaey & Rozendal, 2010
**Mediators/Electron shuttles**

**Methyl Viologen**

\[ \text{H}_3\text{C}-\text{N}^+\text{N}^+-\text{CH}_3 \]

Redox potential: -440mV

Oxidized: Transparent

Reduced: Blue

**Neutral Red**

\[ \text{N} \]

Redox potential: -330mV

Oxidized: Red

Reduced: Transparent
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**Shewanella oneidensis – Electron Balance**

- **Electrons [mmol]**
  - 0.4
  - 0.8
  - 1.2
  - 1.6

- **Time [h]**
  - 0
  - 5
  - 10
  - 15
  - 20
  - 25

- **e⁻ consumed by fumarate reduction**
- **Cathodic e⁻ consumed**
Methanothermobacter marburgensis measured results

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Shewanella oneidensis MR-1 WT (AS579)

Cell suspension, 0.5 mM MV (added last)

Pregrown on 50mM lactate, 70mM + CAA fumarate anaerobically for app. 18h, OD: app. 0.8, -700mV vs Ag/AgCl
Candidate Microorganisms for Microbial Electrosynthesis

**Homoacetogens**
- CO₂
- H₃C — COO⁻ (Acetate)
- alkane precursor

**Engineered microorganisms**
- Butanol
- Isobutanol
- Isoprenes

**Methanogens**
- CO₂
- CH₄ (Methane)

**Construct microorganisms communities**
- Biofuels
- Intermediate Products

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Exoelectrogenic Bacteria

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- Acetate
- CO₂

Coulombic Efficiency: 85%
(Nevin et al. 2010)

**Shewanella oneidensis**

-500 mV (vs SHE)

- Medox
- Medred
- Fumarate (Surrogate)
- Succinate

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**Escherichia coli**

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