Hydrogen and Biogas Production using Microbial Electrolysis Cells

(Session 1-C) Biomass and Beyond: Challenges and Opportunities for Advanced Biofuels from Wet-Waste Feedstocks

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Cellulosic biomass $\rightarrow H_2$

1.34 billion tons of cellulose/yr
$= 2 \times 10^{11}$ kg/yr $H_2$

Need $10^{11}$ kg/yr $H_2$ for transportation by 2060 (light duty vehicles)
The cellulose “fermentation barrier”

Cellulose: 

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{H}_2\text{O} \rightarrow 12 \text{H}_2 + 6 \text{CO}_2 \]

2-4 \( \text{H}_2 \)

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 2 \text{H}_2\text{O} \rightarrow 4 \text{H}_2 + 2 \text{C}_2\text{H}_4\text{O}_2 + 2 \text{CO}_2 \]

Maximum of 4 mol/mol but only 2 mol/mol in practice.

8-10 \( \text{H}_2 \)?

How can we recover the remaining 8 to 10 mol/mol?

12 \( \text{H}_2 \)

Microbial Electrolysis Cells (MECs)
Penn State project with NREL

2 stage process:
Convert renewable lignocellulosic biomass resources to H₂ using fermentation + MEC

Approach overcomes 2 key barriers to making H₂ from other biomass sources
• Low feedstock cost of lignocellulose compared to corn/sugar
• Overcomes fermentation barrier:
  • Increases H₂ molar yield past 4 mol-hexose per mol-H₂ by using a microbial electrolysis cell (MEC)
Focus points

• Microbial electrolysis cells (MECs)
  – Electroactive microorganisms
• MECs for conversion of lignocellulose to $H_2$
• Avoiding the need for electricity in MECs
Electrical power generation in a **Microbial Fuel Cell (MFC)** using exoelectrogenic microorganisms.
Demonstration of a Microbial Fuel Cell (MFC)

MFC webcam
(live video of an MFC running a fan)

www.engr.psu.edu/mfccam
H₂ Production at the cathode using microbes on the anode in Microbial Electrolysis Cells

>0.25 V needed (vs 1.8 V for water electrolysis)

Anode

Bacteria

No oxygen in anode chamber

(Membrane is optional in MEC)

Cathode

CO₂

e⁻

e⁻

H₂

H⁺

O₂
H₂ production by MEC process: 

**Energy Yields**

\[ \eta_W = \frac{W_{H2}}{W_{in}} \]

Energy in H₂ produced

Energy in electricity required

200 – 400%

\[ \eta_{W+S} = \frac{W_{H2}}{W_{in} + W_s} \]

Energy in H₂ produced

Energy in electricity + substrate

65 – 89%
CH₄ Production at the cathode using microbes on the cathode in Microbial Methanogenesis Cells

Add methanogens to the cathode

Abiotic Anode (no microbes)
MECs used to harvest methane from renewable forms of electricity generation

Anaerobic digesters
(methane from organic matter)

MMCs
Methane from renewable electricity
Electro-active Microorganisms

- **Electromicrobiology**
  - New sub-discipline of microbiology examining exocellular electron transfer
Mechanisms of electron transfer in the biofilm:

Nanowires produced by bacteria!

Gorby & 23 co-authors (2010) *PNAS*

Figure 1. Colorized transmission electron micrograph of microbial nanowire networks secreted by *Geobacter sulfurreducens*. Scale bar, 100 nm.

Malvankar & Lovley (2012) *ChemSusChem*
Electrogenic biofilm ecology

Bacteria living off exoelectrogens

Direct contact

Produce nanowires (wired)

Produce mediators (wireless)

Electrogenic Biofilms

- Dead biofilm (red) remains electrically conductive for active biofilm (yellow/green)
Scaling up MFCs & MECs

MFCs = fuel cells, make electricity
MECs = electrolysis cells, make H₂
Towards practical implementation of bioelectrochemical wastewater treatment

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**Anode**: Graphite brush electrode

- **Graphite fibers** commercially available (used in tennis rackets, airplanes, etc.)

- Easy to manufacture

- **Fiber diameter**: 6-10 μm a good match to bacteria (~1 μm)

- **High surface area per volume**: Up to 15,000 m²/m³
MEC components (2.5 L reactor)

Schematic:
- Anaerobic gas collection tube
- Plastic separator
- Stainless steel mesh cathode
- Half graphite fiber brush anodes

Imagery:
- Plastic separator
- Stainless steel mesh cathodes
- Half graphite fiber brush anodes

MEC Reactor that has 24 modules with a total of 144 electrode pairs (1000 L)
Individual module performance of the MEC treating Wastewater

**Predicted:** 380 mA/module (total of 9.2 A)

- H₂ initially produced, but it all was converted to CH₄
- Elec. Energy input = 6 W/m³
- Energy Out = 99 W/m³

16× more energy recovered than electrical energy put into the process

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NEW Module Design to capture $\text{H}_2$ from the cathode $\rightarrow$ Needs a separator or membrane
Task 3.1 – Technical Accomplishments
Hydrogen Generation from Fermentation Wastewater

Fermentation Effluent Composition

- **Current**: Synthetic ww = 51 A/m³; Fermented ww = 44 A/m³ (no protein in synthetic ww).
- **Gas production rates**: Synthetic, 0.6 L-H₂ L⁻¹ d⁻¹; Fermented, 0.5 L-H₂ L⁻¹ d⁻¹.
- **COD (chemical oxygen demand) removal**: Synthetic ww = 87%; Fermented ww = 73%.
  - Removals in fermented ww: Alcohols and VFAs >90%; Carbohydrates = 89%, Protein = 48%.
Avoiding the need for electricity (PS)

Use waste heat as an “energy source” for MECs rather than a power source (PS). Two options being examined

1. Thermal regenerative ammonia batteries \textit{(new, not tested)}
   - Waste heat used to produce ammonia, which is the “fuel” in a metal-salt solution battery

2. Reverse electrodialysis (RED) stacks incorporated into the MEC \textit{(works!)}
   - RED stacks can produce electricity from salinity gradient energy (SGE)
   - Both \textit{natural} and \textit{engineered} salinity gradients can be used.
Natural Salinity Gradient Energy (SGE)

+  

=  

270 m of Hydraulic Head

Oceanside WWTPs and Rivers could produce 980 GW
Reverse electrodialysis (RED)

Salinity difference produces electrical current

Electric current

River water  Seawater  River water

AEM  CEM

Each pair of seawater + river water cells $\rightarrow \sim 0.1 - 0.2$ V
Reverse electrodialysis (RED) stack produces electrical current (here also makes H₂)
... but you need a lot of membranes

Each pair of high salt (HC) + low salt (LC) cells = \( \sim 0.1 - 0.2 \) V

Logan and Elimelech (2012) Nature
What if we move the RED stack into an MFC?
MEC + RED = MREC (Microbial RED Elec. Cell)
Engineered SGE: Use waste heat to create artificial "salinity gradient" energy using ammonium bicarbonate.

\[ \text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_4\text{HCO}_3 \]

Low concentration (LC) of \( \text{NH}_4\text{HCO}_3 \)

High concentration (HC) of \( \text{NH}_4\text{HCO}_3 \)

370 m

\[ \text{NH}_4\text{HCO}_3 \]

270 m

\[ \text{NaCl} \]

Freshwater

Cusick, Kim & Logan (2012) Science
MRFC Using Ammonium Bicarbonate

Brush Anode

COD → CO₂ + 4H⁺

Pt/CC Cathode

H₂O → O₂ + 2H⁺

HC

Distillation

Waste heat

LC
Challenges & Opportunities

- **Challenges- Big picture**
  - Renewable $\text{H}_2$ production at high yields possible from lignocellulose
  - Microbial electrolysis cells have not been widely recognized as a method for $\text{H}_2$ production

- **Challenges-Technical**
  - Reactions at electrodes/materials/kinetics need to be improved (but without use of any precious metals)
  - Rates of $\text{H}_2$ production need to be increased
  - Cost of membranes will be a key factor in overall economics
  - Use of osmotic/heat energy systems needs to be further explored

- **Opportunities**
  - $\text{H}_2$ production is carbon neutral ($\text{CO}_2$ in plants is fixed and not fossil)
  - Incentives for “green” $\text{H}_2$ production could speed development and applications.
Conclusions

• New **green/renewable** energy technologies can be created using electro-active microorganisms in different microbial electrochemical technologies:
  – MFCs= Electrical power
  – MECs= $H_2$ or $CH_4$ gases

• MECs can be combined with **Blue energy** technologies based on salinity gradient and waste heat energy sources
  – TRABs- thermal regenerable ammonia batteries using waste heat
  – MRECs = RED stacks incorporated into MECs
Thanks to students and researchers in the MxC team at Penn State!

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