Consideration of cathode specific surface area and hydrodynamics in scaling up microbial fuel cells

Bruce E. Logan
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What do we need to commercialize MFCs?

• Now have >1 decade of MFC research... why don’t we have commercialized MFCs?
• **Bacteria**: *Geobacter* sp
• **Materials**: both electrodes < $100 \text{ m}^{-2}$
  – Anode: many choices; brushes still superior
  – Cathode: activated carbon(s)
• **Architecture**: Tubular vs plate/frame?
• **Manufacturing**: Cathode production?
• Secondary processes needed!
What microbes are on the anodes?

- Tested reactors over 2 months from 3 sources
  - Penn State wastewater treatment plant (P)
  - UAJA wastewater treatment plant (U)
  - Freshwater bog sediments (B)
- Performance analysis: Power production
- Community analysis
  - Clone libraries
  - Pyrosequencing
  - DGGE
  - FISH

Wastewater Treatment plants:
P=PSU, U=UAJA

Yates, Kiely, Call, Rismani-Yadzi, Bibby, Peccia, Regan, Logan (2012) ISME J.
Pyrosequencing: mostly Delta Proteobacteria... and of those, almost all sequences most similar to *Geobacter sulfurreducens*
DGGE used to show changes in community diversity over time

Bog at start

Wastewater samples at start

END: Everything pretty similar

Conclusion:
High power requires *Geobacter* spp.

B=Bog, P=PSU, U=UAJA

Yates et al. (2012) *ISME J.*
Community composition unchanged at varied set potentials when different reactors used

MFCs

Influent

MFCs

Set anode potential

Open circuit

Much greater complexity of bacterial communities with domestic wastewater, but *Geobacter* still quite abundant

Isolate from MFC: *Geobacter anodireducens SD-1*

**Characteristics of *G. anodireducens SD-1* (Geobacter sulfurreducens PCA)**

- Isolated from MFC fed formate, 98% similarity to strain PCA
- DNA-DNA hybridizations show a relatedness of 61.6% with PCA (<70%)
- Tolerates up to 3% NaCl (vs 1.7% for PCA)
- Grows well in 200 mM phosphate buffer (PCA does not grow)
- *Cannot grow using fumarate as electron acceptor* (PCA can grow)

50 PBS: 50 mM phosphate buffer  
PBS-H: 200 mM PBS  
30 BCS: 30 mM bicarbonate buffer  
SW: 3% NaCl (like seawater)
Electrogenic Biofilms

- Dead biofilm (red) remains electrically conductive for active biofilm (yellow/green)
Scaling up MFCs
Bioelectrochemical Systems: An Outlook for Practical Applications

Tom H. J. A. Sleutel,[a] Annemiek Ter Heijne,[a,b] Cees J. N. Buisman,[a, b] and Hubertus V. M. Hamelers[a, b]

Bioelectrochemical systems (BESs) hold great promise for sustainable production of energy and chemicals. This review addresses the factors that are essential for practical application of BESs. First, we compare benefits (value of products and cleaning of wastewater) with costs (capital and operational costs). Based on this, we analyze the maximum internal resistance (in mΩ m²) and current density that is required to make microbial fuel cells (MFCs) and hydrogen-producing microbial electrolysis cells (MECs) cost effective. We compare these maximum resistances to reported internal resistances and current densities with special focus on cathodic resistances. Whereas the current densities of MFCs still need to be increased considerably (i.e., internal resistance needs to be decreased), MECs are closer to application as their current densities can be increased by increasing the applied voltage. For MFCs, the production of high-value products in combination with electricity production and wastewater treatment is a promising route.

Towards practical implementation of bioelectrochemical wastewater treatment


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Estimates for MFCs
- 100 € /m² or $130/m²

Estimates for MECs
- 100 € /m² or $130/m²
Design

• These are bad designs for treatment....Keep the electrodes close (but not too close!)
• You cannot design separate anode and cathode reactors!

Source: B.E. Logan, first MFCs built in 2003

Assessment of Microbial Fuel Cell Configurations and Power Densities

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Supporting Information
To Design your MFC:

• **Materials**
  – Anode: Flat (cloth, felt, etc.), brush, granules, or other?
  – Separator: fibrous or ion exchange membrane?
  – Cathode: Activated carbon + binder + diffusion layer

• **Architecture:**
  – Plate/frame or tubular?

• **Cathode specific surface area:** $A_{cat} \ (m^2/m^3)$
  – Defined as cathode area per volume
  – Maximize $A_{cat}$ based on MFC configuration
Tubular MFCs
Tubular/Cylindrical Designs

- $A_{cat}$ (m²/m³) based on a cylinder diameter, $d$
  - Area of the cathode is: $A_{cyl}$
  - Volume of the MFC is: $V_{cyl}$
  - $A_{Cat} = \frac{A_{cyl}}{V_{cyl}} = \frac{\pi d L}{\frac{\pi}{4} d^2 L} = \frac{4}{d}$

  - If $d = 5 cm$: $A_{Cat} = \frac{4}{d} = \frac{4}{(5 cm)} \frac{100 cm}{m} = 80 m^2/m^3$

- Tube designs need air flow around outside cylinder, so $d =$ tube diameter + air space
  - If $d = 5 cm + 2 cm$, $A_{Cat} = 57 m^2/m^3$
The Largest Tubular MFC

- $A_{\text{cat}} = 22 \text{ m}^2/\text{m}^3$ based $d = 18 \text{ cm}$ (volume around tubes not included)

- Performance not published in peer reviewed literature, but:
  - Tested brewery wastewater
  - Produced 330 mW/m$^2$ (8 W/m$^2$)
  - HRT = unknown

Small tube MFC

- Two tubes, each 2 L in volume (4 L total)
- $A_{\text{cat}} = 80 \text{ m}^2/\text{m}^3$ ($d=5 \text{ cm}$, just the tube; each 100 cm long)
- HRT = 11 h
- Power = 10-50 mW/m$^2$
- Final COD = 80–100 mg/L
- CE = 11%


Personal communication: Prof. Zhen He
Racks of many smaller tube MFCs

- 200 L based on 96 tubes, each ~2 L in volume
- $A_{\text{cat}} = 80 \text{ m}^2/\text{m}^3$ ($d=5 \text{ cm}$, just the tube; each 100 cm long)
- 6 – 9 mW/m² (84 - 130 mW, 15 m² cathode)
- HRT = 12 h
- Final COD= 33 mg/L

Personal communication: Prof. Zhen He
Serpentine MFC design

- $A_{\text{cat}} = 86 \text{ m}^2/\text{m}^3$ based estimated $d=4.6$; no volume around tubes
- $A_{\text{cat}} = 62 \text{ m}^2/\text{m}^3$ based on given summed electrode areas
- Produced 66 mW/m$^2$; HRT= ???; connector tube could clog

Wound stack electrodes

- Cylinder, but more similar to a plate design: more of a “wound plate”
- Not ww or air:
  - Acetate
  - Percarbamate cathode (O$_2$ release compound)
- 2 Designs (HRT=20 min)
  - 350 m$^2$/m$^3$; 94 mW/m$^2$
  - 700 m$^2$/m$^3$; 73 mW/m$^2$

Plate/Frame MFCs
Electrical power generation in a **Microbial Fuel Cell (MFC)** using exoelectrogenic microorganisms

**MFCs**

- **Anode**
- **Fuel (wastes)**
- **Oxidation products (CO₂)**

- **Cathode**
- **Oxidant (O₂)**
- **Reduced oxidant (H₂O)**

Bacteria that make electrical current

### MFC Materials

**Low cost $/m^2 (US)**

- **Anode (brushes)** $20
- **Separator (cloth)** $1
- **Cathode** $15
  - SS mesh
  - AC + PVDF Binder

- **TOTAL** $36
Key to cathode specific surface area is the “unit width”!

- **Cathode specific surface area**: $A_{cat} \text{ (m}^2/\text{m}^3\text{)}$
  - Defined as cathode area per volume
  - Maximize based on MFC configuration

- **Plate/Frame**:
  - Width of anode chamber is: $W_{An}$
  - Width of cathode chamber is: $W_{Cat}$

  $$A_{Cat} = \frac{1}{W_{An} + W_{Cat}}$$

- If $W_{an} = 3 \text{ cm}$, $W_{cat} = 1 \text{ cm}$
  $$A_{cat} = 25 \text{ m}^2/\text{m}^3$$

Figure 3 | An MFC stack. MFCs are arranged close together to reduce internal resistance and form compact reactors. Within the stack the electrodes consist of repeating units of an anode coated in a mat of bacteria, or biofilm, an insulating separator and a cathode. Waste water flows over the anodes and air over the cathodes. The individual anode and cathode are connected by a wire (not shown).

Logan & Elimelech (2012) *Nature*
How close can electrodes be?

- Need room for electrodes, wastewater, air
- Acetate = no particles like real wastewater
- Too little space for wastewater → clogging

25 m²/m³ (25 mL reactor)
Acetate: 2.8 W/m² (2.1 kW/m³)
WW: 0.5 W/m²

680 m²/m³ (30 mL reactor)
Acetate: 3.1 W/m² (2.1 kW/m³)
WW: (not tested)

Fan et al. (2013) *Energy Env. Sci.*
Range of power densities

• For MFCs treating single substrates area power density:
  – decreases with larger size reactors (left figure)
  – Shows an increase with volumetric density
• For MFCs treating wastewater, no trends!

Cathode specific surface area decreases with reactor size

Electrode spacing?

- Flat electrodes: ≥ 2 cm
- Brush electrodes: Is closer is OK?

Oxygen leakage through the cathode

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**Increased Power Generation in a Continuous Flow MFC with Advective Flow through the Porous Anode and Reduced Electrode Spacing**

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*Department of Civil and Environmental Engineering and The Penn State Hydrogen Energy (H2E) Center, The Pennsylvania State University, University Park, Pennsylvania 16802*

The maximum power generated in a single-chamber air-cathode microbial fuel cell (MFC) has previously been shown to increase when the spacing between the electrodes is decreased from 4 to 2 cm. However, the maximum power from a MFC with glucose (500 mg/L) decreased from 811 mW/m² ($R_{st} = 200$ Ω, Coulombic efficiency of CE = 28%) to 423 mW/m² ($R_{st} = 500$ Ω, CE = 18%) when the electrode spacing was decreased from 2 to 1 cm (batch mode operation, power normalized by cathode projected area).

with both electrode. One of the main wastewater treatment generating electricity. Power densities pro larger than those ob differences in power tration and form (se kinetics, and the cor the biofilm that is ne (9).

Power densities; modifying the an performance using produce high conce the PEM in systems et al. (14) achieved; mediator-producing. However, ferricyanide for wastewater treat An advantage of w reaction is self-sustaining cathodes, and al reduced to as little generation (16). P alternatives such as MPP or iron(II) ph treatment.
Brush to cathode distance

- Brush edge: 0.4, 0.8 or 1.4 cm
  - Closer brush works better, even up to 0.4 cm!
- 30-80% of brush removed from most distant side of the brush
  - No decrease in power until 80% of the brush removed. **Brushes near the cathode are okay!**

Hutchinson, Tokash, Logan (2011) *J. Power Sources*
Voltage Production:
Mesh vs Brushes (domestic ww)

B = Brush anode
M = Mesh (flat) anode

Hays and Logan (2011) J. Power Sources
Multi-electrode MFCs

3 brushes (R3)
3500 m²/m³

5 brushes (R5)
2800 m²/m³

8 brushes (R8)
2900 m²/m³

Electrode area (2.5 cm diameter brush/chamber width = 40 m²/m³)

Lanas & Logan (2013) J. Power Sources
Smaller, closer brushes work best with acetate

(Continuous flow, acetate in buffer)

Maximum power densities
R8C = 1020 mW/m²
R8 = 280 mW/m²
(R3 = 560 mW/m²)
(not shown)

Lanas & Logan (2013) J. Power Sources
Reactor instability smaller brushes: wastewater

Continuous flow, 4 h HRT, domestic ww

Maximum power quite different:
260 mW/m² vs 150 mW/m²
Not possible to get true “duplicates”

**Conclusion:** Avoid the use of very thin brushes
(it produces conditions similar to “flat anodes”)

Stager & Logan, *Unpublished*
Reactor Designs

**Gen 0**: 0.025 L, 25 m²/m³

**Gen 1**: ~0.13 L, 25 m²/m³

**Gen 2**: 2 L, 2 chambers, 25 m²/m³

**Gen 3**: 5.7 L, 4 chambers
Gen 1 MFCs: Separator or no separator?

Separator (Separator Electrode Assembly, SEA)

No-separator (Spaced electrode assembly, SPA)

Tests using domestic wastewater

Maximum power densities similar for SEA & SPA

Ahn, Hatzell, Zhang, Logan (2014) J. Power Sources
Gen 1 MFCs: 1 or 2 Cathodes?

1 cathode

2 cathodes

N1C=SEA (previous terminology)

COD Removals vs actual HRTs

HRTs: N1C > S2C

• Same theoretical HRT set for reactor comparisons
• N1C > S2C

It is important to measure actual HRTs

Regression line (dashed) based on measured HRT (not theoretical)

R² = 0.9931

• **Modular MFC**
  - Gen II reactor has 2 banks of 8 anodes; 2 cathodes
  - Cathode specific surface area: 29 m² m⁻³ based on total liquid volume (1.4 L), or 20 m² m⁻³ based on total reactor volume (2 L).
  - Not a “cassette” (anode+cathode) but separate anode and cathode modules.
Gen 2 MFCs: Power production

- Modular MFC
  - Shown with 2 anodes, 2 cathodes; 20 m² m⁻³ (total volume)
  - Produced ~ **400 mW/m²** with domestic wastewater, highest to date for this source

He, Zhang, Logan (2014) *Submitted*
Gen 2 MFCs: Performance

Fed batch: Long cycle times, high COD removal

Continuous flow (8 h HRT):
Influent: $480 \pm 25$ mg L$^{-1}$
COD removal: $57 \pm 5\%$

He, Zhang, Logan (2014) Submitted
## Power density comparisons: WW

<table>
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<th>Substrate</th>
<th>Notes</th>
<th>Power (mW/m²)</th>
<th>Reference</th>
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<td>180 mL, Cont flow</td>
<td>280-330</td>
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<td>Domestic WW</td>
<td>Cassette</td>
<td>150</td>
<td>Yu et al. (2012)</td>
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</table>

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Gen 3 MFCs (in progress)
Final thoughts on using MFCs for Domestic Wastewater Treatment

• COD cannot be removed to < 30 mg/L with electricity generation
• A second process must be added after the MFC to further reduce COD
• Nutrient removal of anaerobic effluents is a research frontier (not just MFCs)
Current generation shifts more substrate to electricity generation in MFCs (acetate)

Current density vs soluble COD (sCOD)

Current rapidly drops off at ~100 mg/L sCOD

In both cases, current rapidly decreases when sCOD is still high (~100 mg/L)

MFC + AFMBR
(Anaerobic Fluidized Bed Membrane Bioreactor)
AFMBR Construction

- Idea of AFMBR first published by Chae et al. (ES&T). Used as a second stage to granular fluidized bed anaerobic digester
- AFMBR consists of a reactor body + ultrafiltration membrane + granular activated carbon (GAC)
- GAC fluidized by recirculation
- In tests here, used with a hydraulic retention time of 1 hour

Effluent reduced to 16 mg/L tCOD

- Two trains of MFC (HRT = 4 h) to AFMBR (HRT = 1 h)
- Membrane flux 16 L/m²/h
- 50 days performance
- Energy balanced
  (MFC produced = AFMBR used)

- Effluent COD = 16 mg/L
- Effluent TSS <1 mg/L
Conclusions

• MFCs can be used for domestic wastewater treatment
  – Cost of electrodes reduce: to < $40 m\(^{-2}\)
  – High performance for brush anodes and activated carbon cathodes
  – Cathode specific surface area must be maintained as reactor sizes are increased

• A second process is needed for COD removal
  – Adding an AFMBR increased COD removal to achieve <20 mg/L
  – TSS < 1 mg/L, so no secondary clarifier needed
  – Nutrients need to be solved.
Thanks to students and researchers in the MxC team at Penn State!

Current research sponsors
International Collaborations

King Abdullah University of Science and Technology

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Universiteit Gent

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Stanford University

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