Edited Version

Highly Efficient Microbe-mediated Energy Harvesting from Wastewater through Nanomaterial Decorated Three-dimensional Porous Matrix Electrode

International Faecal Sludge Management Conference
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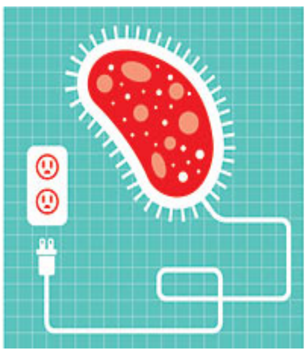
Microbe Power

Microbes Sweet on Making Power

Alternative energy is already a big business. Power plants that turn wastes into electric power... **But in the long run, the real potential is replacing biomass-burning with bugs**: It really simplifies the prospectus of using waste streams and biomass as fuel. ------ ***Vol. 301, September 2003, Science***



The Electric Microbe

…But we should be thankful for one **especially talented microbe,** Geobacter, which has tiny hairlike extensions called pili that it uses **to generate electricity from mud and wastewater**.-----***The 50 Best Inventions of 2009, Nov. 2009, Time***

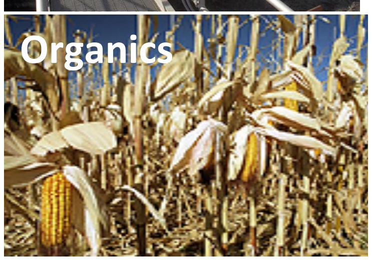
Top 10 New Water Technologies to Save the World

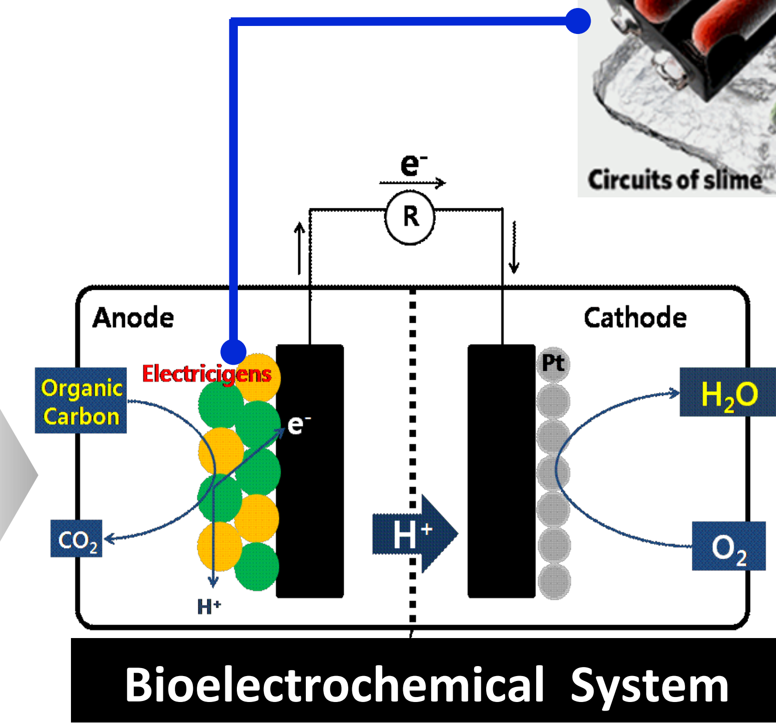
Aquaporins, …**Microbial fuel cells,** Vapor transfer irrigation, Phospho rus recovery …Decentralized wastewater treatment-----***Vol. 10, Global Water Intelligence, July 2009***

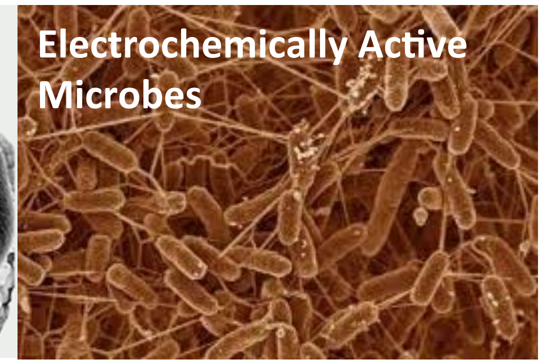
Bioelectrochemical System (BES)

What is a **Bioelectrochemical System?**

: an electrochemical system in which biocatalysts (such as microbes) perform oxidation and/or reduction at electrodes







- **Electricity Production**
- **Biohydrogen Production**
- **Chemical Production**

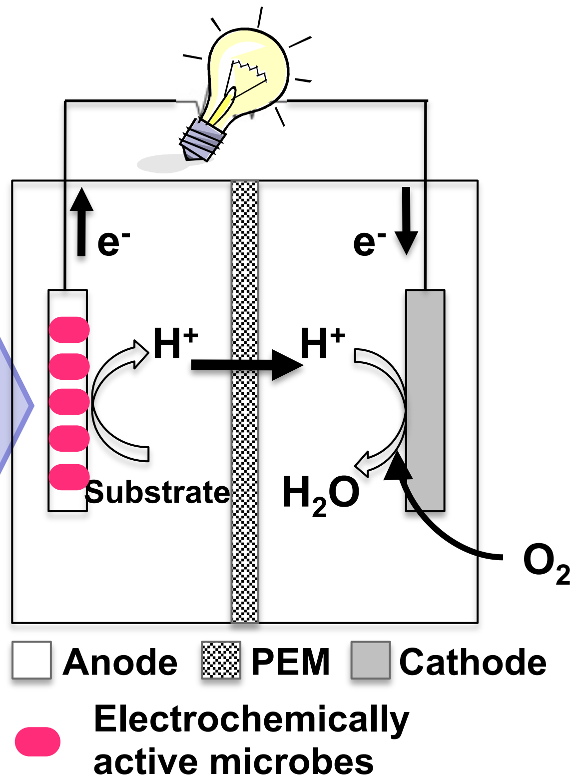
- **Wastewater Treatment**
- **Bioremediation**

- **Environmental Sensors**

Microbial Fuel Cell

Microbial Fuel Cell (MFC): A BES that produces net electrical power utilizing various organic substrates through direct electron transfer from microbes to electrodes

Natural Microbe Resources



*PEM: Proton exchange membrane

Anode: Organic oxidation

$HAc \rightarrow CO_2 + H^+ + e^-$

Cathode: Oxygen reduction

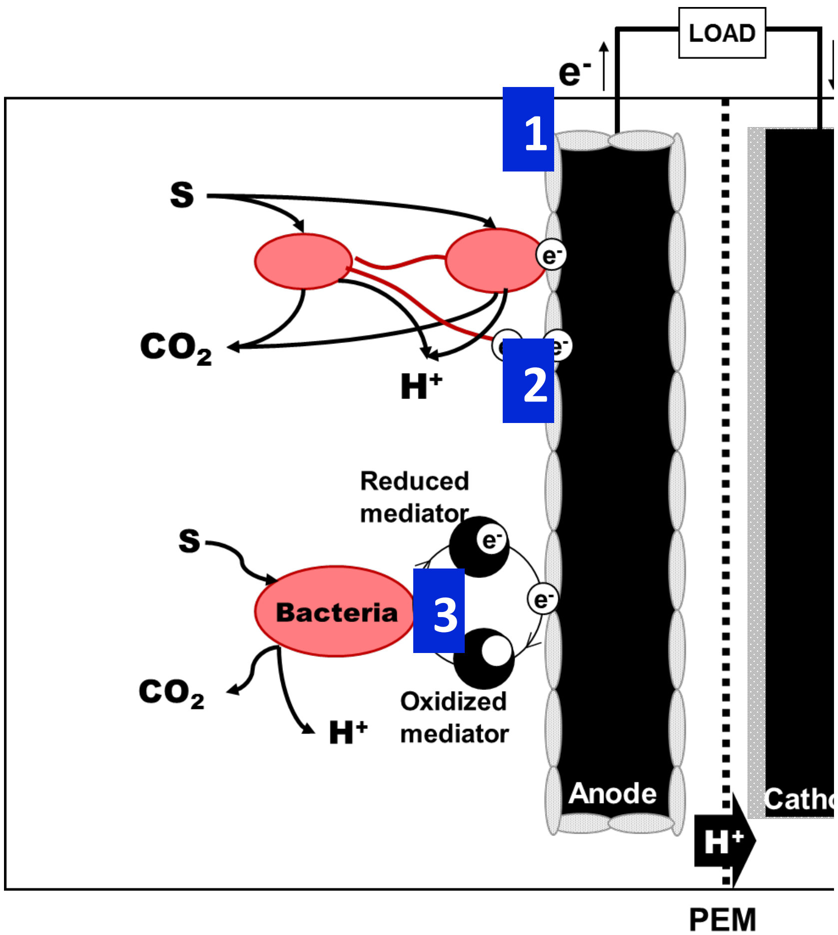
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

MFCs:

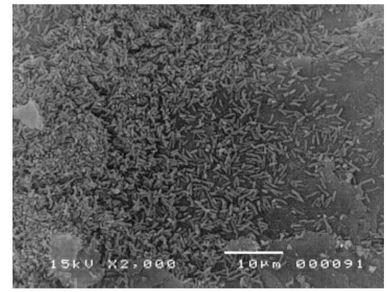
- Use bacteria as the catalysts to oxidize substrate and produce electrons
- Electrons produced by the bacteria are directly transferred to the anode and flow to the cathode, producing electricity

Mechanism of Electron Transfer by Microbes

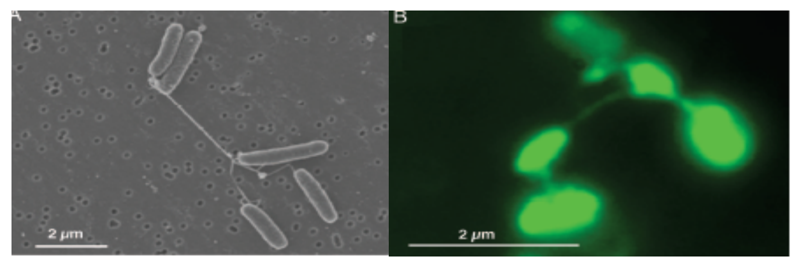
Not fully understood, but…



1. Direct electron transfer from microbes attached to electrodes



2. Highly conductive nanowires produced by specific microbes



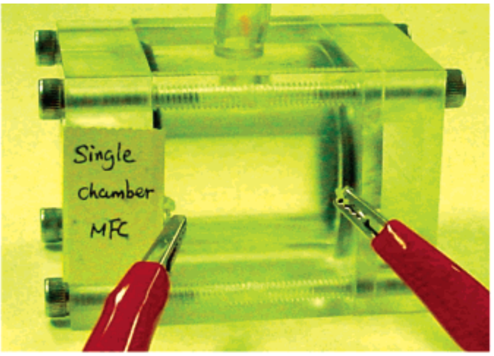
3. Exogenous mediators or microbial-origin mediator

Few known electricity-producing microbes: *Shewanella, Geobacter*

MFC Configurations: Lab-Scale

Lab-Scale MFCs

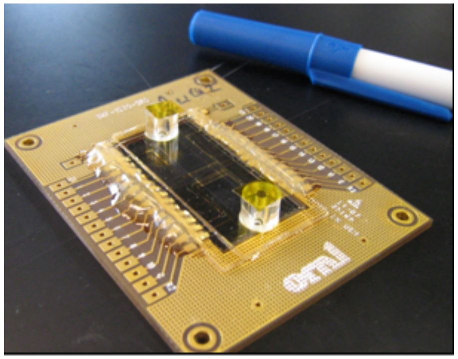
Two-Chamber MFC



Single-Chamber MFC

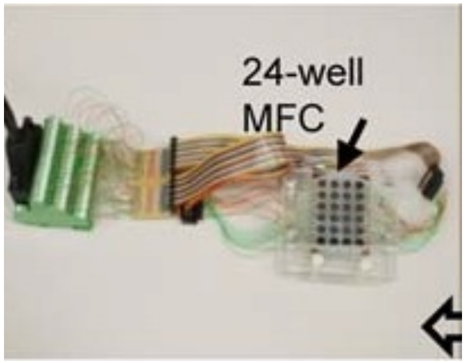
Min et al., 2005
Liu et al, 2004

Miniature Microbial Fuel Cells



Microfluidic MFC

The Gardner Lab in Boston University, USA



MFC Array (Our Lab)

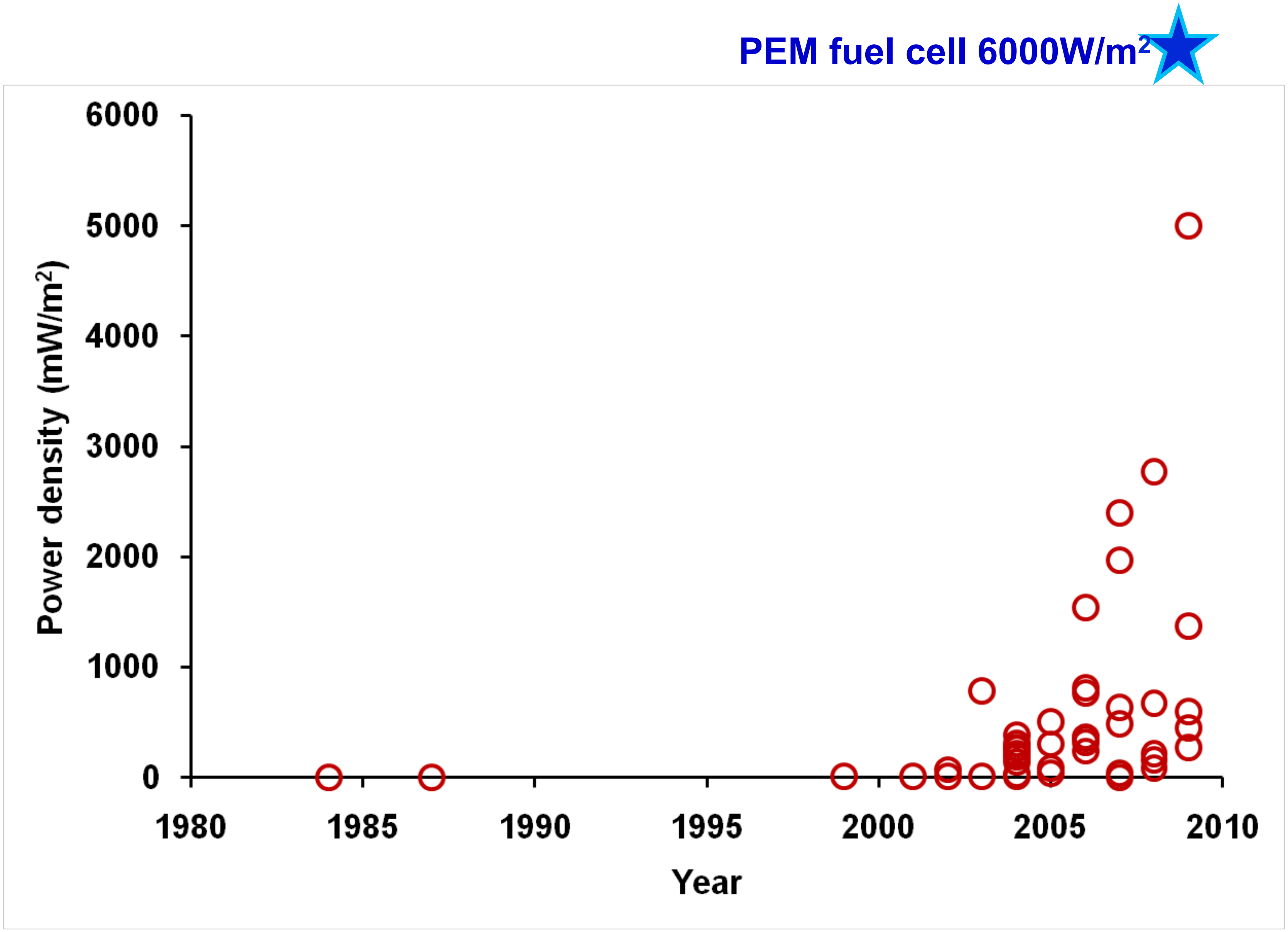
MFC Configurations: Pilot-Scale

Pilot Scale MFC for Brewery Waste Water Treatment
Advanced Water Management Centre, Australia

Electricity Production in Sea
Office of Naval Research

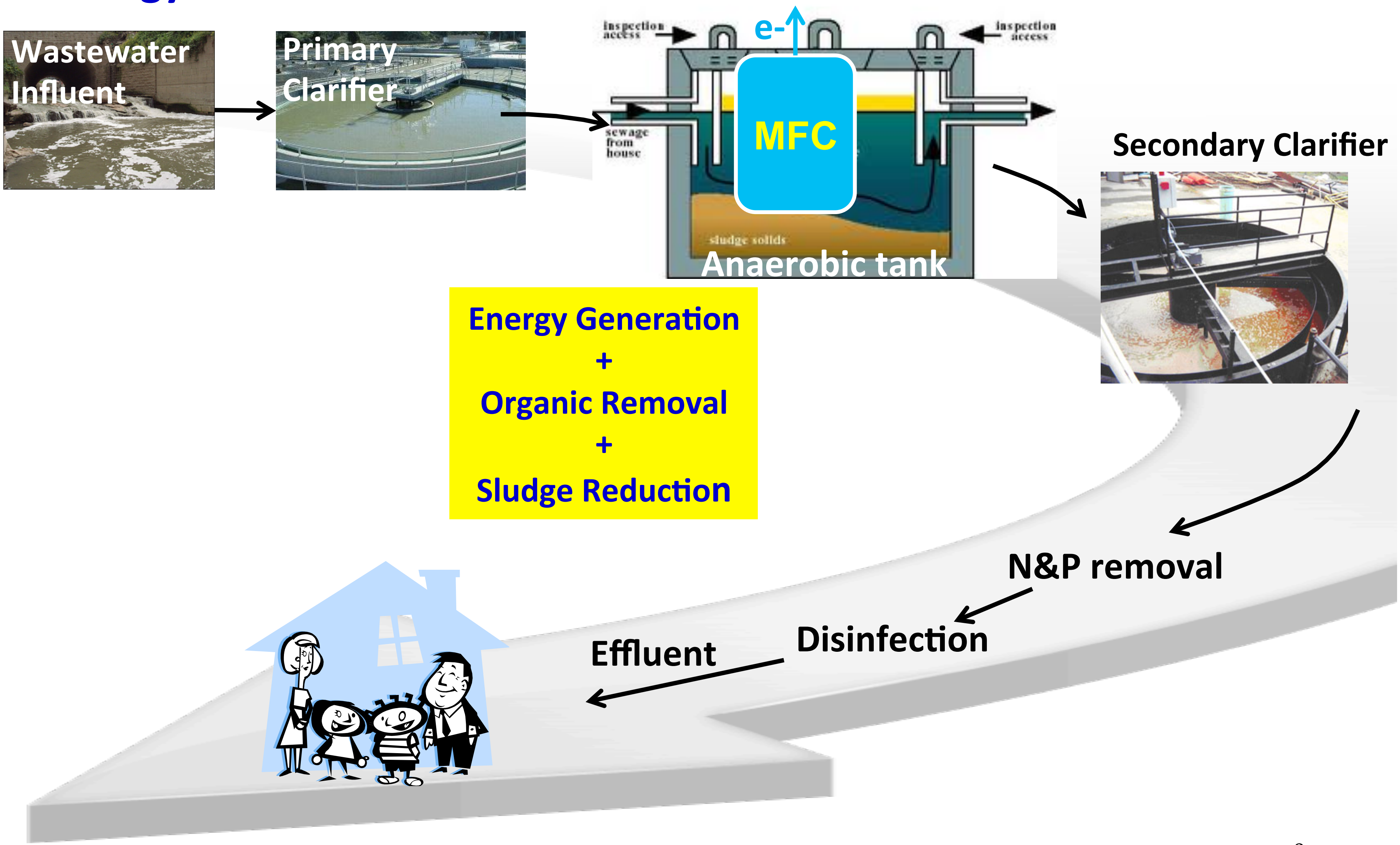
Biohydrogen Generation using Winery Waste
Penn State U., Logan Group

MFC Performances for Electricity Generation



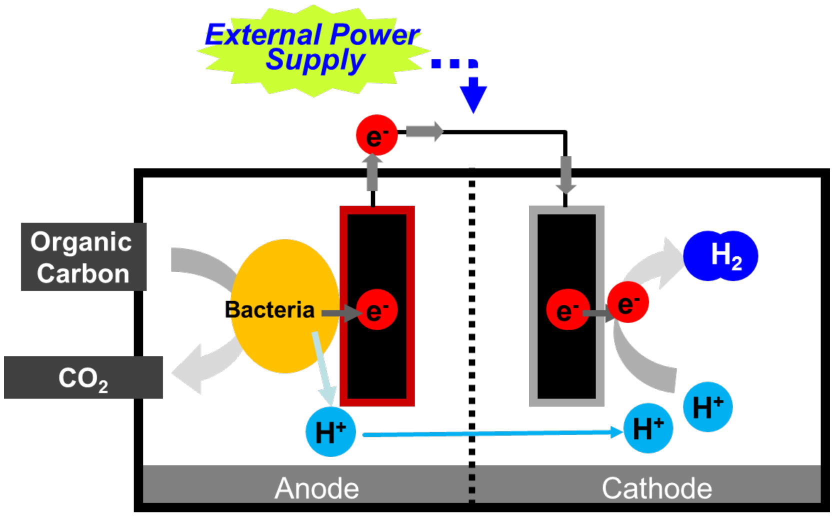
MFC in Wastewater Management Process

Energy Self-sufficient Wastewater Treatment Process with MFC



Microbial Electrolysis Cell (MEC)

Microbial Electrolysis Cell (MEC): A BES where minimal electrical power is provided to achieve hydrogen or chemical production



Anode: Organic oxidation

$HAc \rightarrow CO_2 + H^+ + e^-$

Cathode: Oxygen reduction

$2H^+ + 2e^- \rightarrow H_2$

	Anode (Substrate Oxidation)	Cathode (H^+ Reduction)
Redox potential	-280mV	-420mV
Overcoming Overpotential	Power augmented with > 140mV for H_2 generation	

Overpotential -0.14 V

VS. 1.2 V required for direct water electrolysis (in theory)

In practice, need ~0.25 V for H_2 production in MEC vs. ~1.8 V for water electrolysis

Why Hydrogen?

Hydrogen

Intensive energy carrier

- H_2: 33,890 kcal/kg
- CH_4: 9,500 kcal/kg
- Coal: 3,400 kcal/kg

No emission of greenhouse gas

- $2H_2 + O_2 \rightarrow 2H_2O + 571.6\ kJ$

Raw materials

- Fuel to power fuel cell and aerospace app.
- Production and fabrication of metals
- Recovery and refinery of fossil fuels
- Production of NH_3 as fertilizer

Hydrogen Production Costs

Cost comparison for the different H_2 production technologies

Process	Sources	Production scale (10^6 Nm^3/day)	Production costs ($/Kg)
Steam reforming	Natural gas	0.27~25.4	0.65~1.35
Coal gasification	Coal	2.30~6.78	1.18~1.39
Biomass gasification	Biomass	0.72~2.26	1.04~1.57
Biomass pyrolysis	Biomass	0.024~0.31	1.06~1.53
Electrolysis (general)	Water	0.1~6.75	2.47~3.44
Electrolysis (photovoltaic)	Water	0.195	5.02
Electrolysis (wind power)	Water	0.247	2.42

Water electrolysis vs. Microbial Electrolysis Cell

Technology	Energy efficiency (%)	Energy Demand (kWh/m^3-H_2)	Cost ($/kg-$H_2$)	Remarks
Water Electrolysis[a]	56	5.6	3.4	USDOE target cost for H_2 ($2~3/kg H_2)[c]
MEC[b]	350	0.9	0.62*	

[a] Ivy (2004) Summary of Electrolytic Hydrogen Production: Milestone Completion Report/ [b] Call et al. (2009) Environ. Sci. Technol./[c] DOE. Hydrogen, fuel cells & infrastructure technologies program. Multi-year research, development, and demonstration plan (2007)/ * single-chamber MEC at 0.4 V

Why MEC based H_2 Production?

- **H_2 can be biologically produced from bacterial fermentation**
- **Maximum 12 mol-H_2/mol-hexose**
- **However only 4 mol/mol (2 mol/mol in practice)**
  => How to recover the remaining 8 to 10 mol/mol?

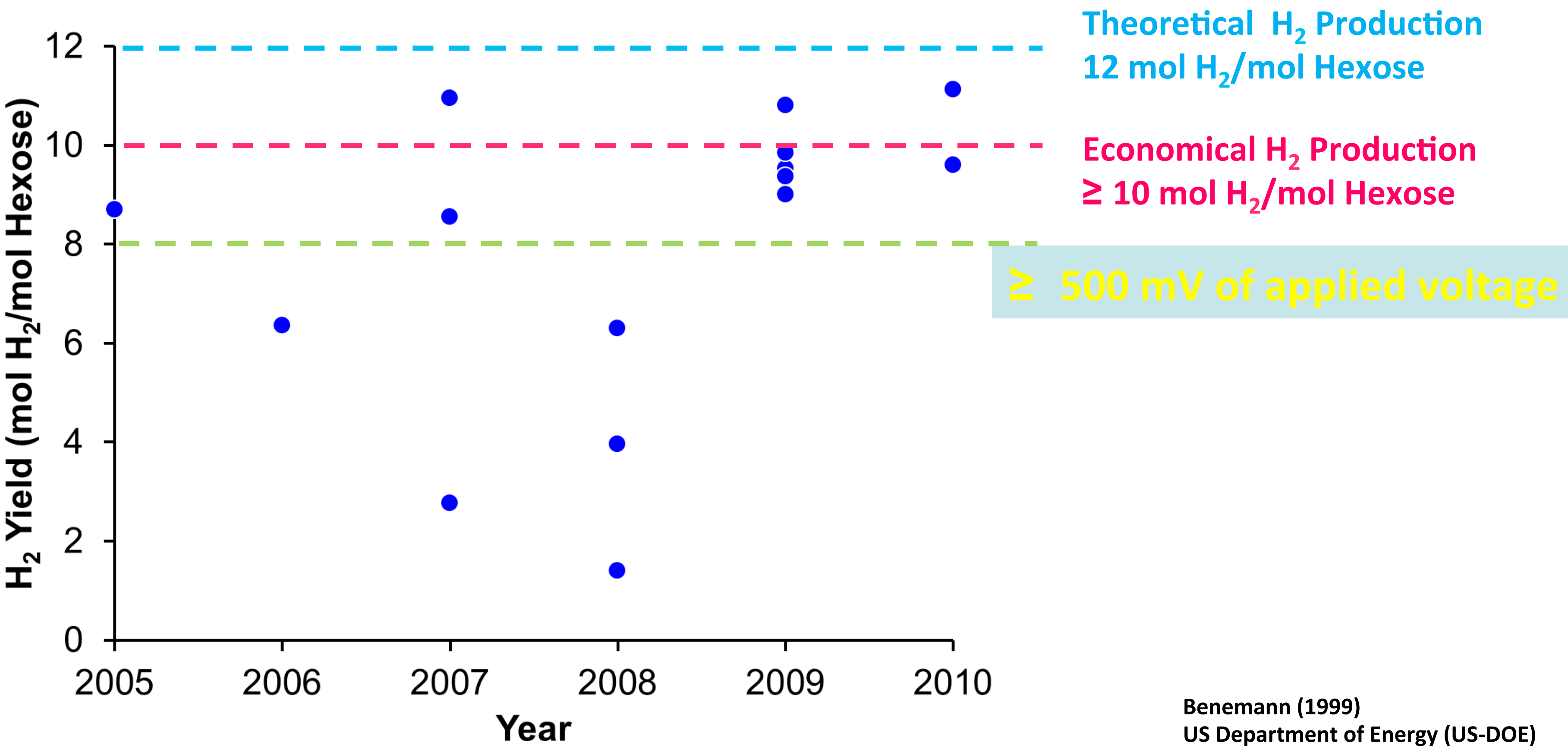
Biohydrogen from Hexose (dark fermentation)

Theoretical 12 mol H_2/mol Hexose	$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2$
Practical 2-3 mol H_2/mol Hexose	$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2CH_3COOH$
	$C_6H_{12}O_6 \rightarrow 2H_2 + 2CO_2 + CH_3CH_2CH_2COOH$

- **US DOE estimation for viable process: 10-12 mol H_2/mol Hexose**
- **DOE cost goal: reduce \$6 to \$2/kg H_2**

So, we need new technology

MEC Performances for H_2 Production



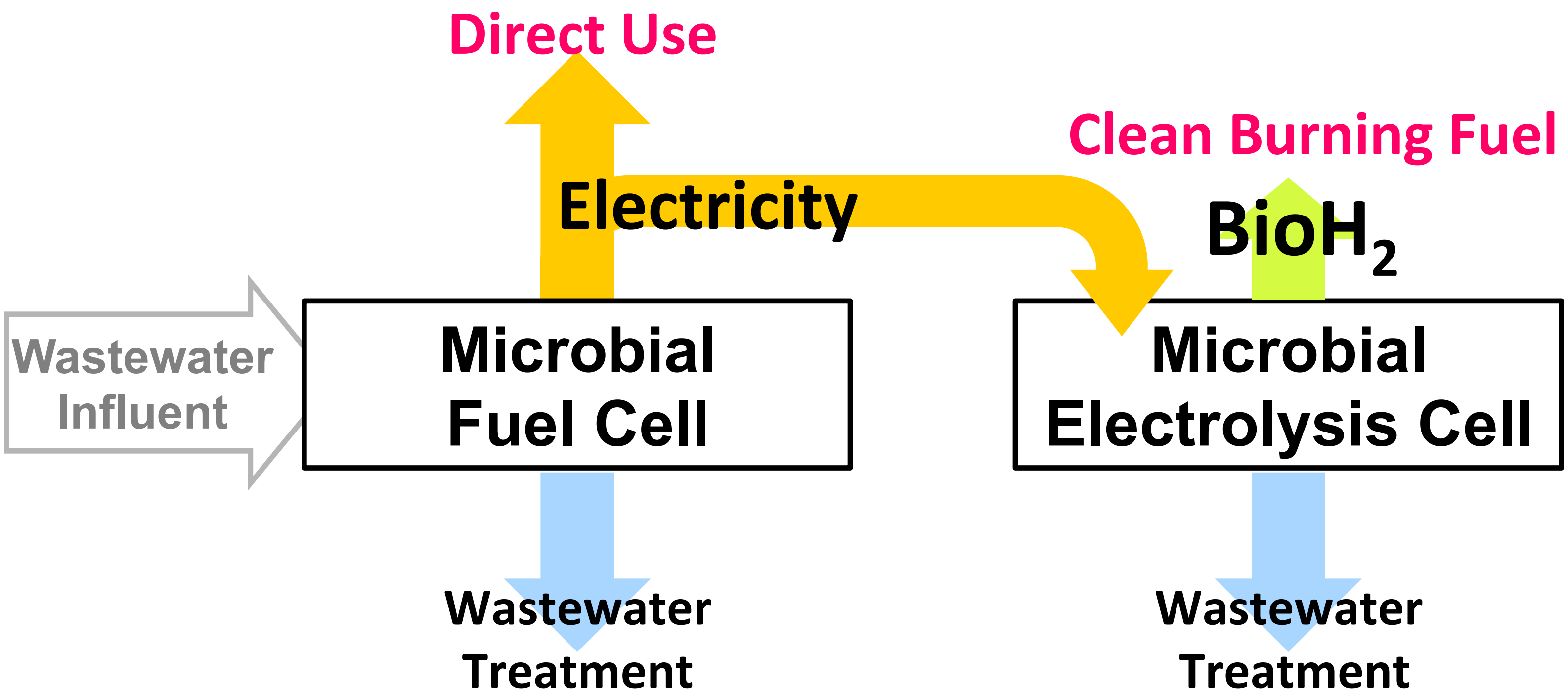
Benemann (1999)
US Department of Energy (US-DOE)

Still require external power to reach maximum H_2 production, however much lower than that needed for direct water electrolysis

Our Vision: MFC-MEC Coupled Hybrid System

for self-sustainable simultaneous wastewater treatment and electricity/biohydrogen generation

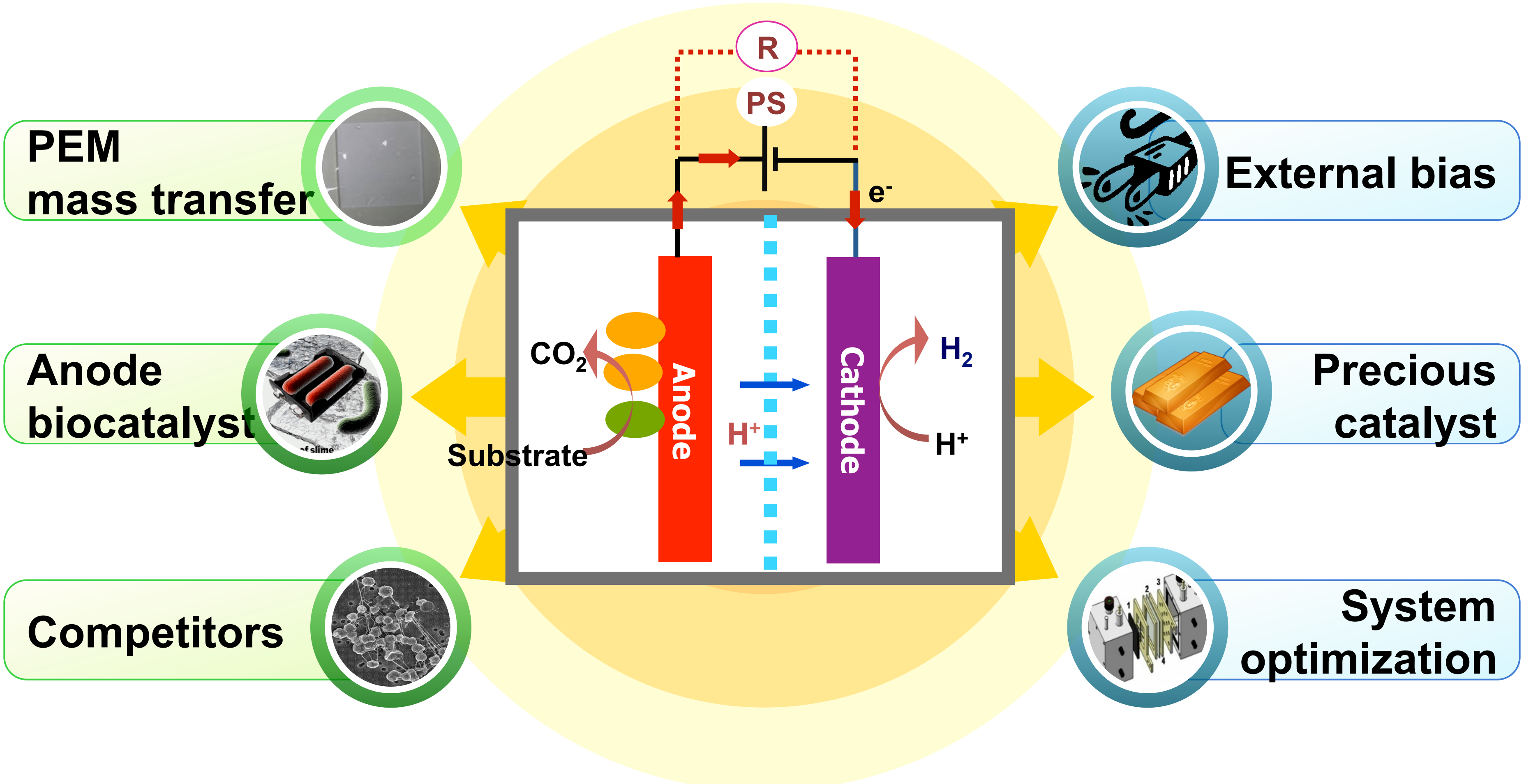
Goal for our BMGF Grand Challenge Exploration Grant (Round 7)



Need sufficient power output from MFCs at low cost

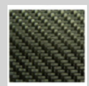
Development of high performance anode and cathode electrodes to significantly increase MFC performance to rapidly treat wastewater and generate sufficient energy for practical use at minimum cost

Challenges in BESs



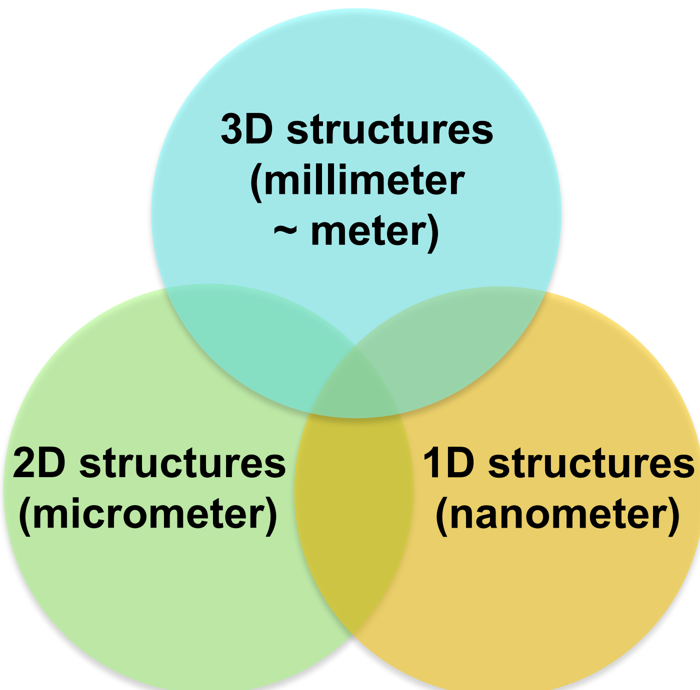
Cost and Efficiency

Cost Analysis of MFCs and MECs

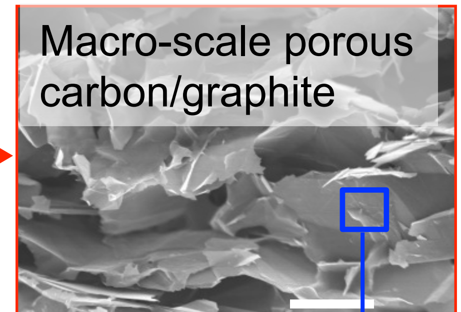
Components	Materials	Power (mW/m^2)	Cost ($\$/m^2$)	Reference/ Remark
Anode	Carbon Paper 	600	0.01	Logan et al. (2007) Environ. Sci. Technol.
	Carbon Cloth 	46 W/m^3	0.56-1.63	Zhang et al. (2009) Environ. Sci. Technol.
	Carbon mesh 	893	1.67-5	Wang et al (2009) Environ. Sci. Technol.
	Carbon Brush 	2400	0.57	Logan et al. (2007) Environ. Sci. Technol.
	Carbon Felt 	356 W/m^3	4.55-4.88	Aelterman et al. (2008) Bioresour. Technol.
	Granular Activated Carbon 	5 W/m^3	0.01 \$/kg	Jiang and Li (2009) Water Sci. Technol.
	Stainless steel Plate	23	0.09-0.63	Dumas et al. (2007) Electrochim. Acta
Ion Exchange Membrane	Cation/Anion Exchange Membrane	-	111.11	Membranes International Inc. CMI-7000S (1.2 m X 3.0 m) AMI-7001S (1.2 m X 3.0 m)
Cathode Catalysts	Pt	766	138.57 \$/g	Cheng et al. (2006) Electrochem. Commun.
	CoTMPP	286	49.90 \$/g	Zuo et al. (2008) Environ. Sci. Technol.
	MnO_2	86	10.88 \$/g	Zhuang et al.(2009) Biosens. Bioelectron.

Wei et al. (2011) Bioresour. Technol. http://www.sigmaaldrich.com

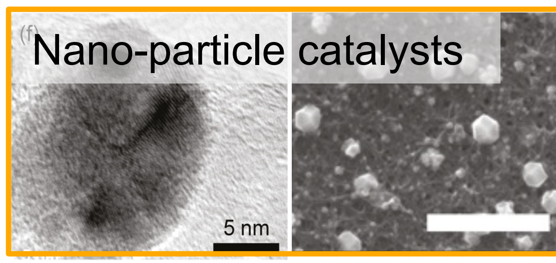
Maximizing reactions & electricity generation by using multi-dimensional macro/nano-scale electrodes



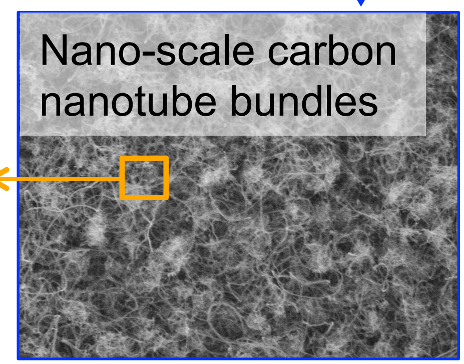
3D structures (mm~meter)



2D (micrometer)



0D (nanometer)



1D (nanometer)

- ***Extremely large surfaces for high reactions***
- ***Multi-scale/dimensions for excellent electricity generation/collection***

Overcoming Bottlenecks of BESs

1. **Potential losses at anode compartment**
2. **Charge and ion transports in electrolyte**
3. **Membrane resistance, selectivity and O_2 permeability**
4. **Structure of the anode**
5. **Role of the cathode performance**
6. **Scaling up problems**

Biofuels for Fuel Cells (2005) IWA Publishing

- Catalysts on the electrode decreasing the activation losses
- Increasing the roughness and specific surface area of the electrode
- Decreasing the activation losses at the bacteria

- Free flow of influent and effluent through the electrode matrix
- Adequate surface for growth of a biofilm, which will perform most of the electron transfer
- Sufficient support and conductive surface
- Sufficient turbulence for adequate proton diffusion towards the membrane and the cathode

Our Approach

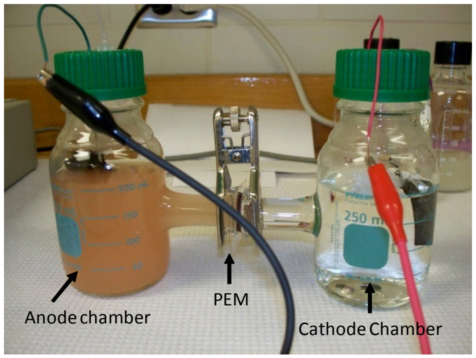
Problem (need): Lots of testing needed at every step of MFC and MEC development

1. Develop a high-throughput screening BES system that will allow parallel analysis of many different microbes, operating conditions, anode materials, cathode materials, etc.

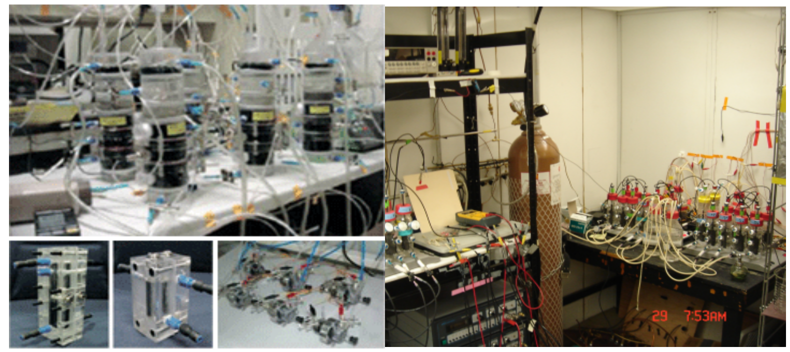
2. Utilize this screening system for rapid development of low-cost high-efficient anode materials and non-platinum catalyst cathode materials

Microbial Fuel Cell (MFC) Array

A Single H-type MFC



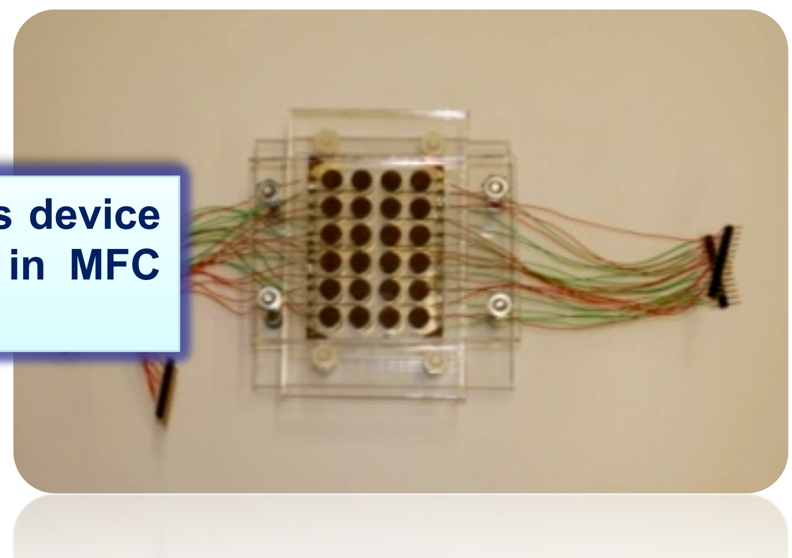
Multiple H-type MFCs or miniature MFCs



http://www.mfc-conference.kr/

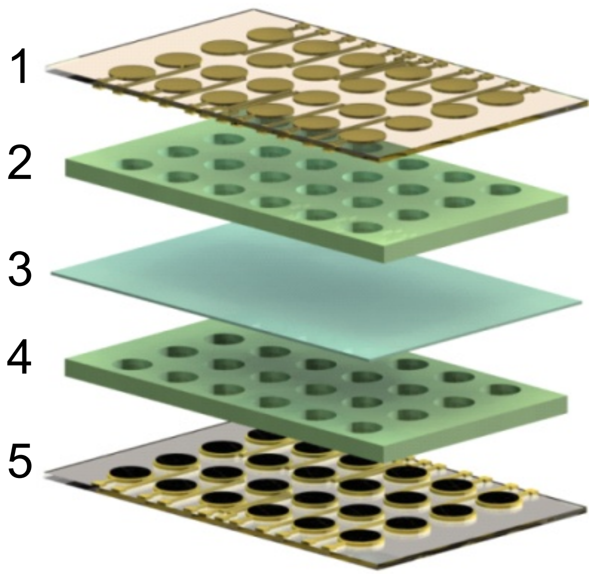
http://geobacter.org/wiki/pmwiki.php/LabMembers/HannoRichter

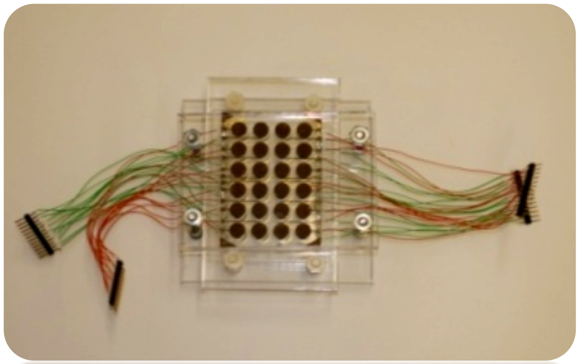
Microfabricated MFC array



A high throughput screening/analysis device for parallel studies of electricigens in MFC applications!

24-Well Microbial Fuel Cell Array (MFCA)





DESIGN

- **Anodes (1)**: 24 individually addressable Ti/Au electrodes patterned on a glass substrate
- **Anode & cathode chambers (2&4)**: 24 miniaturized PDMS chambers (600 µl)
- **Proton exchange membrane (PEM) (3)**
- **Cathodes (5):** 24 individually addressable Pt loaded carbon electrodes

FEATURES

- 24 integrated independent miniature MFCs
- Power output monitored from each MFC in parallel
- Less reagents consumption (380 times smaller)
- Low well to well variations (< 8% std)
- Highly repeatible
- Reusable and easy to assemble

Application 1: Environmental Microbe Screening

Step 1 → Step 2 → Step 3 → Step 4 → Step 5

Sample collection & pre-screening

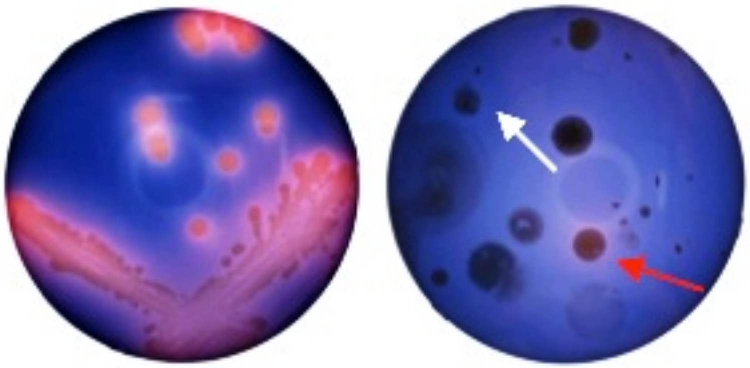
Environmental sample from water and soil

Brazos River, TX

Brazos River, TX

Lake Somerville, TX

Prescreening of electrogenic microbes

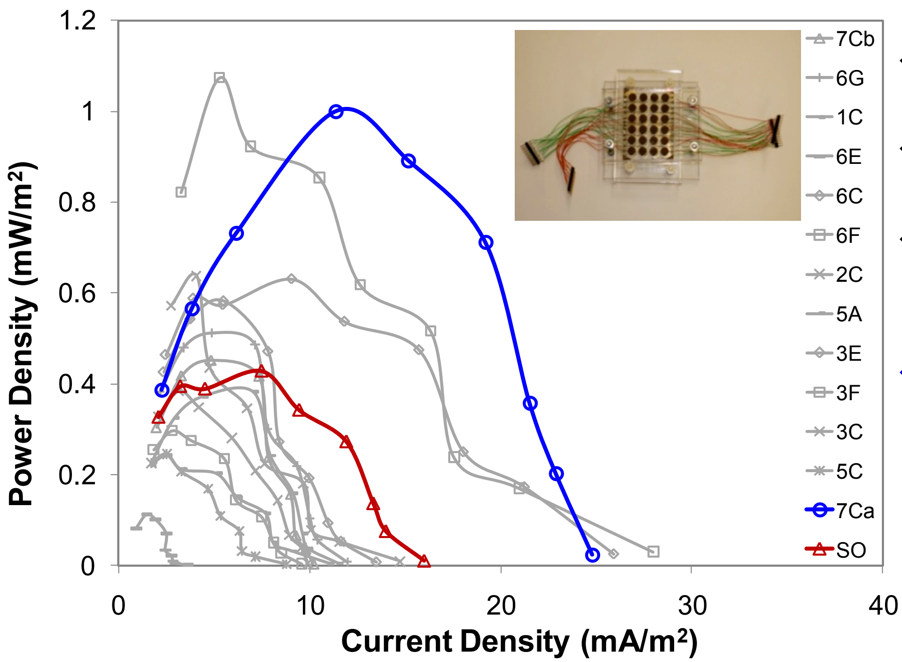


- Use Reaction Black 5, an azo dye that indicates electrochemically active organisms
- 26 hits

Application 1: Environmental Microbe Screening

Step 1 ⇨ Step 2 ⇨ Step 3 ⇨ Step 4 ⇨ Step 5

MFC array primary screening

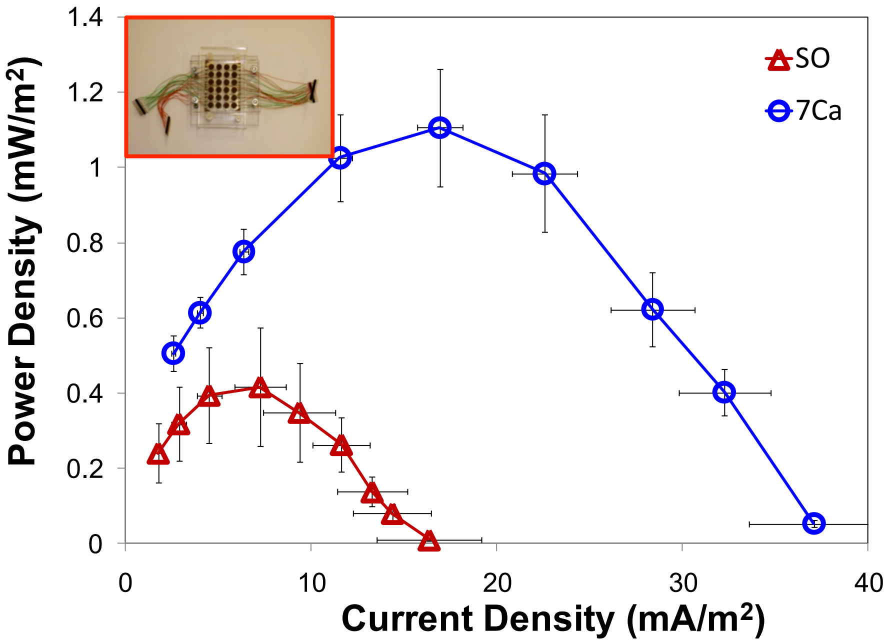


- **13** environmental samples (*n* = 2)
- **Control**: *S. oneidensis* MR-1(SO)
- **7Ca** vs. ***S. oneidensis* MR-1 (SO)**: 1 mW/m^2 vs. 0.43 mW/m^2, 233% higher
- **=> Select 7Ca strain**

Environmental Microbe Screening

Step 1 ⇨ Step 2 ⇨ Step 3 ⇨ Step 4 ⇨ Step 5

MFC array confirmation screening

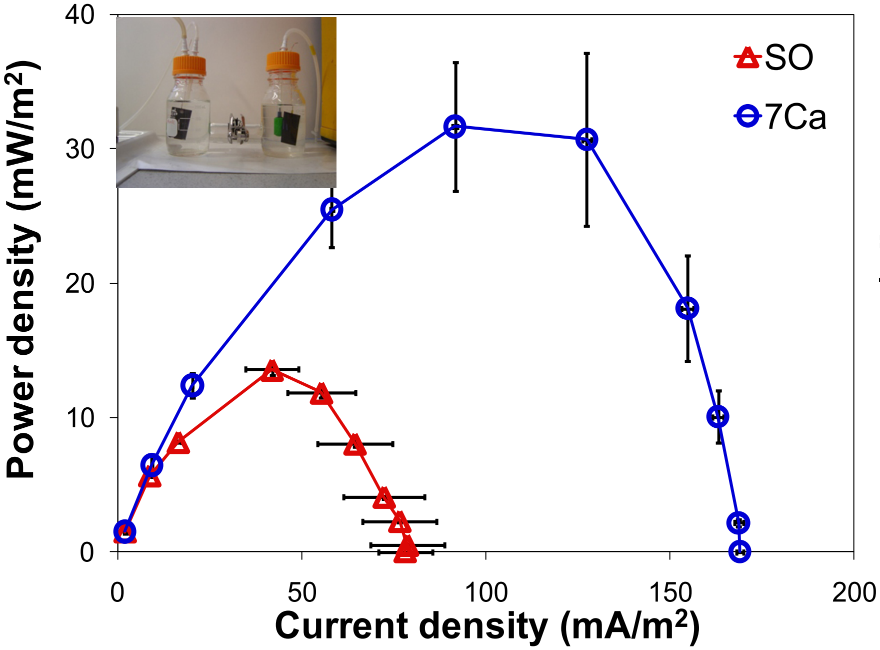


- 7Ca and SO with more repeats (*n* = *8*)
- **7Ca showed 266% higher than the SO**

Environmental Microbe Screening

Step 1 → Step 2 → Step 3 → Step 4 → Step 5

H-type MFC validation



n = 4

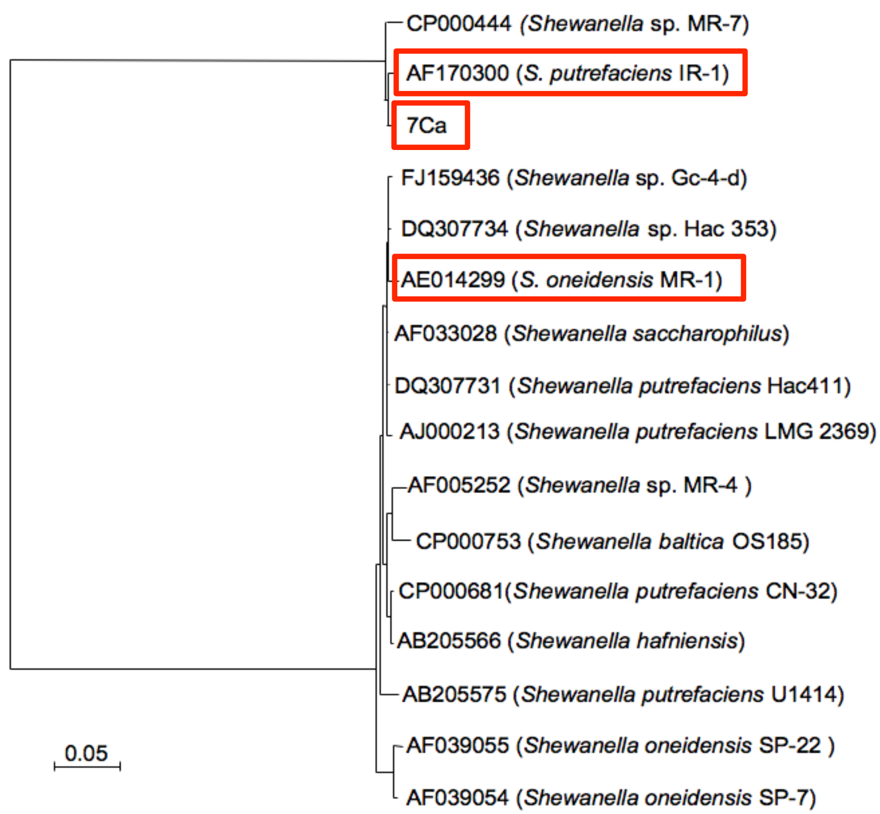
- Maximum power density:
  7Ca showed 233% higher SO (MFC array: 266%)

=>Findings in our MFC array system can be translated to larger scale conventional systems

Environmental Microbe Screening

Step 1 → Step 2 → Step 3 → Step 4 → Step 5

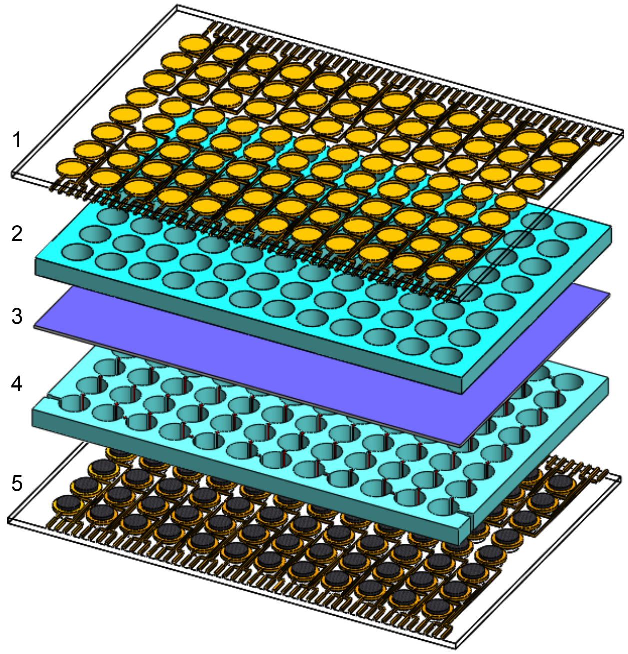
16S rDNA Sequencing & Phylogenetic analysis

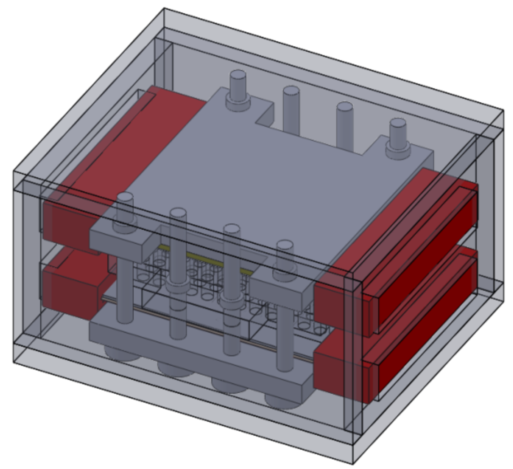


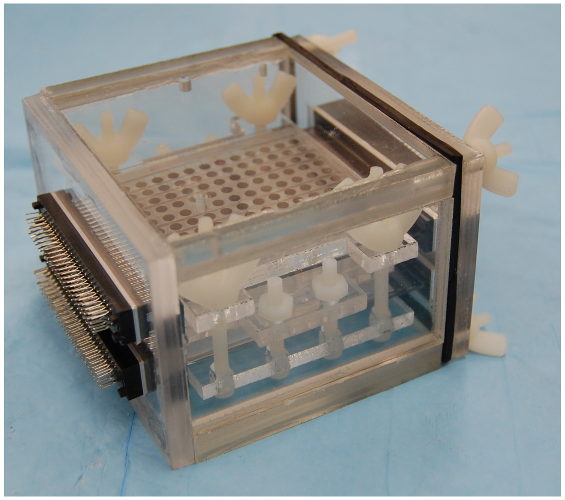
- 7Ca was most closely related to *S. putrefaciens* IR-1 (98% sequence similarity) and *Shewanella* sp. MR-7 (98% sequence similarity)

H. Hou et al., *PLoS ONE*, 2009
H. Hou et al., Biosensors & Bioelectronics, 2011

96-Well Microfluidic MFC Array (MMFCA)





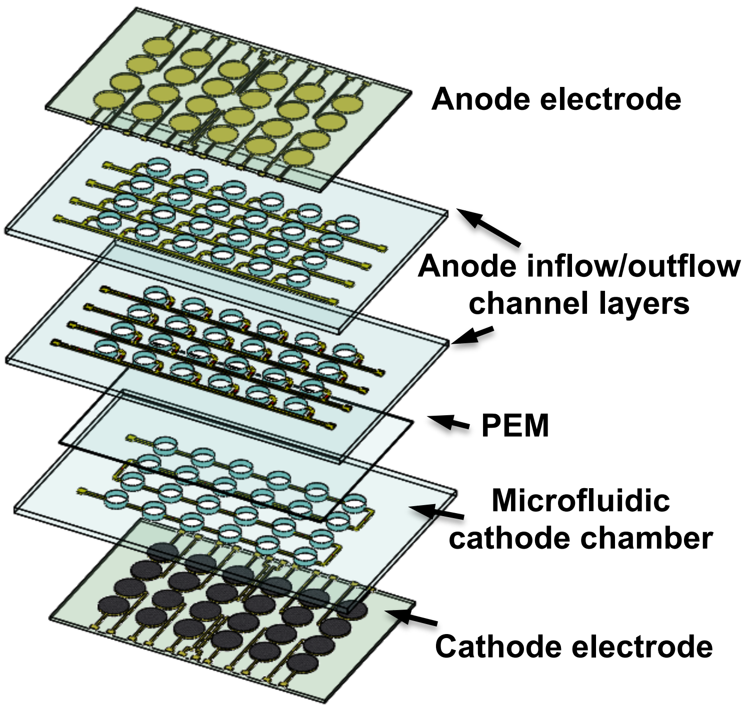


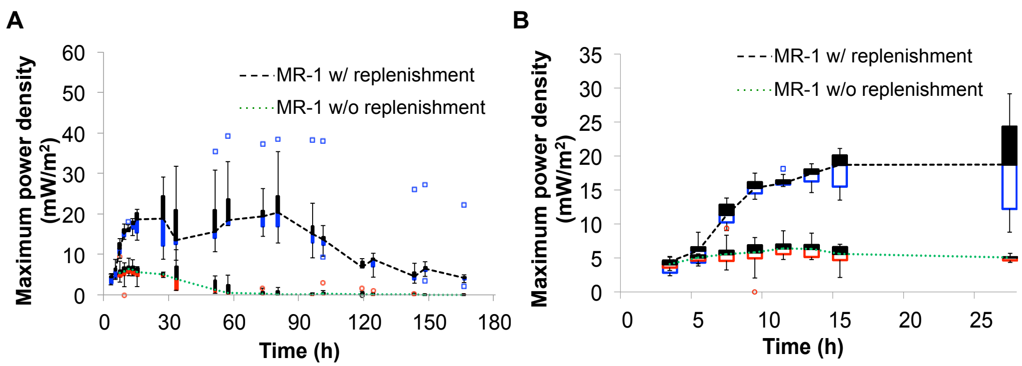
FEATURES

- Same design concept as the 24-well microfluidic MFCA
- Higher throughput (24 => 96)
- Can accommodate multi-channel pipettors
- Both fully anaerobic and aerobic environment can be tested

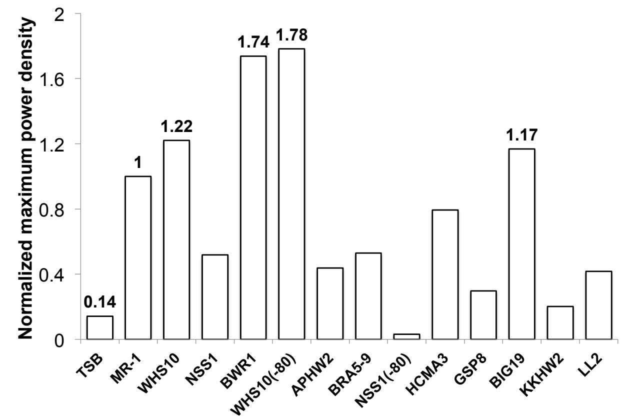
Microfluidic Microbial Fuel Cell Array

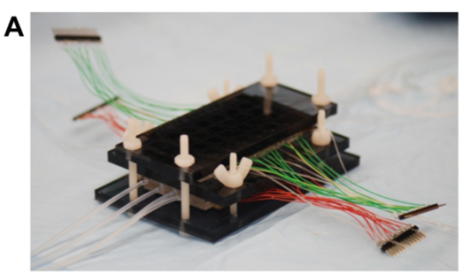
Microfluidic MFC array with individual control of anode & cathode chambers for high-throughput and long-term MFC experiments

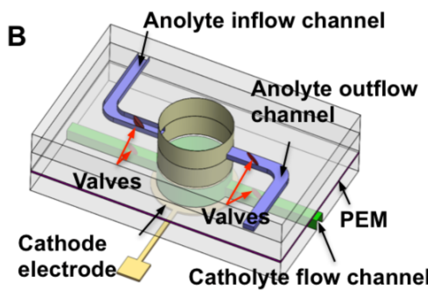




- With catholyte replenishment, power generation of ***Shewanella oneidensis*** **MR-1 increased by 3.6-fold, with lifetime increased by 7-fold. (batch-mode anode)**







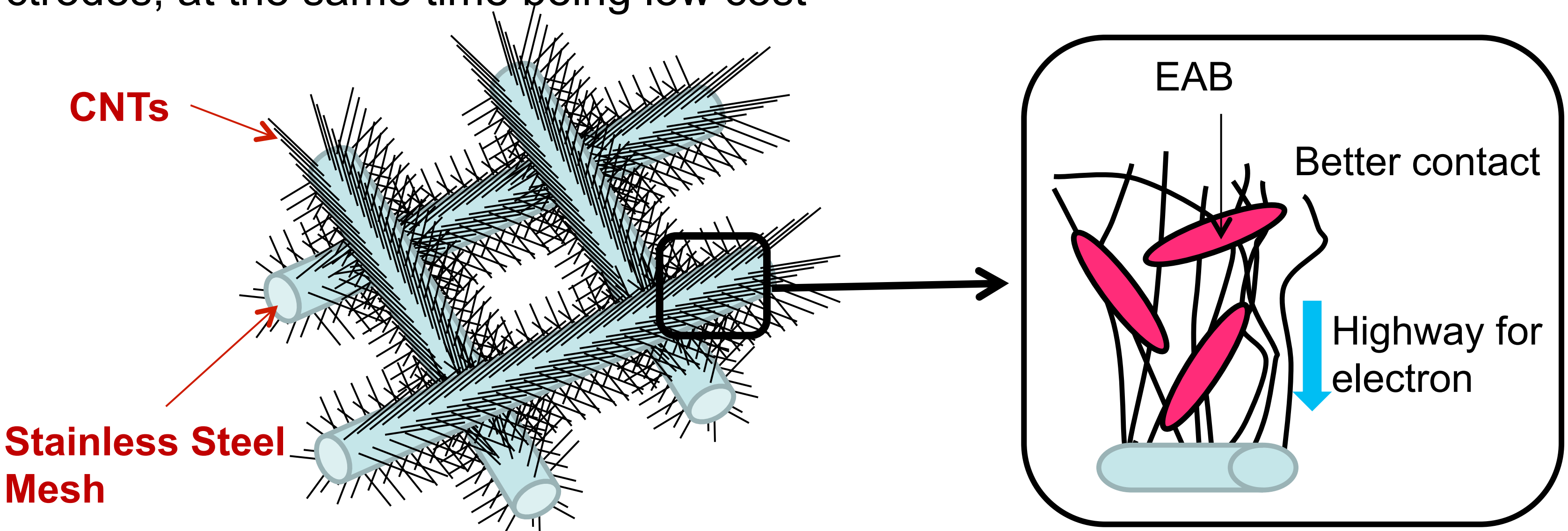
- **Environmental soil sample screening for high-electiricity producing electricigens using the microfluidic MFC array.**

H. Hou et al., *Lab Chip, 2012*

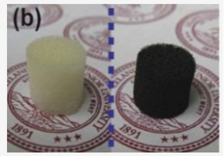
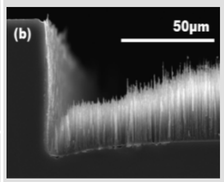
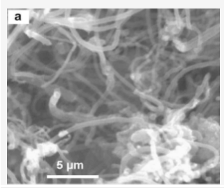
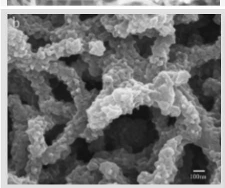
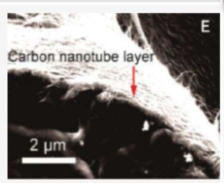
3D Multi-Length Scale Porous Matrix Electrodes

- **Excellent Connections between Microbes and Electrodes**
  - **Three-dimensional porous structures** → Large surface to volume ratios for improved macro-scale microbe-electrode interactions
  - **Nanomaterial-synthesized electrodes** → Improved electron transfer route from microbes to electrodes, both in terms of higher conductivity and more conduits for electron transfer with extremely high surface area

Method: Directly synthesize MWCNTs on low-cost macroporous stainless steel (SS) mesh electrodes. Advantages of both 3D structures and nanomaterial-decorated electrodes, at the same time being low cost



Nanomaterial-Based Anodes

References	Anode Material/ Structure		Power Density (mW/m^2)	Improvement	MFC configuration
Xie et al. (2012)	CNT on Sponge		2130 mA/m^2	47 %	H-shaped MFC (150 mL)
	Sponge		1440 mA/m^2		
Mink et al. (2012)	MWCNTs with a nickel silicide		19.6	390 %	Microsized MFCs (125 μL)
	Gold [a]		4		
Sharma et al. (2008)	MWCNTs		2470	763 %	Dual-chambered MFC (250 mL)
	Graphite		286		
Qiao et al. (2008)	CNT/PANI on Nickel foam		42	1515%	-
	Woven graphite [b]		2.6		
Xie et al (2011)	CNT on textile fibers		1098	68 %	H-shaped MFC (200 mL)
	carbon cloth		655		

[a] Siu et al. (2008) J. Microelectromech. S./ [b] Part et al. (2003) Biotechnol.Bioeng

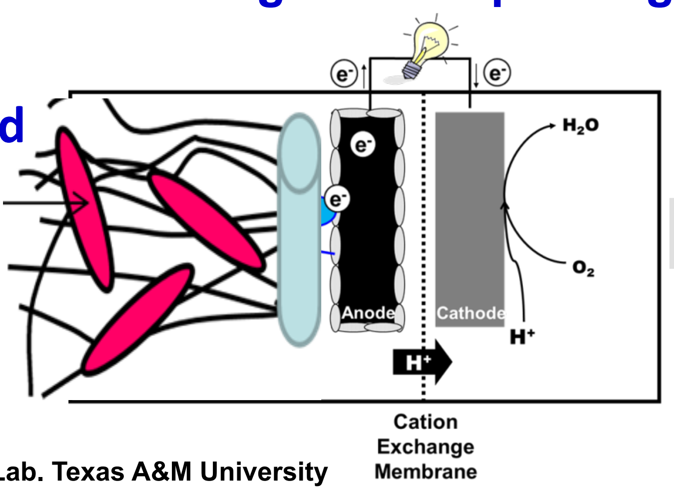
Carbon Nanotubes on Stainless Steel Mesh

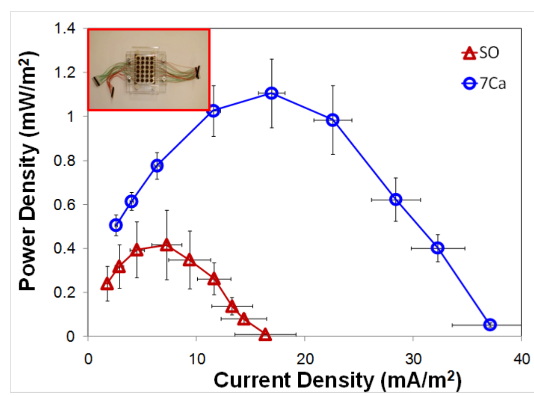
- **Why Carbon Nanotubes (CNT)?**
  - ❑ Excellent electrical conductivity: ~10^4 S/cm at 300 K (metal-like conductivity)
  - ❑ Extremely large surface area: Sites for various reactions

Our hypothesis is that directly synthesizing MWCNTs on low-cost macroporous SS mesh can establish a tighter linkage with the underlying electrodes and produce higher power due to enhanced microbe-electrode coupling

❑ **Systematically study what physical properties of CNT-based electrodes contribute to higher MFC power generation**

CNT-based electrode

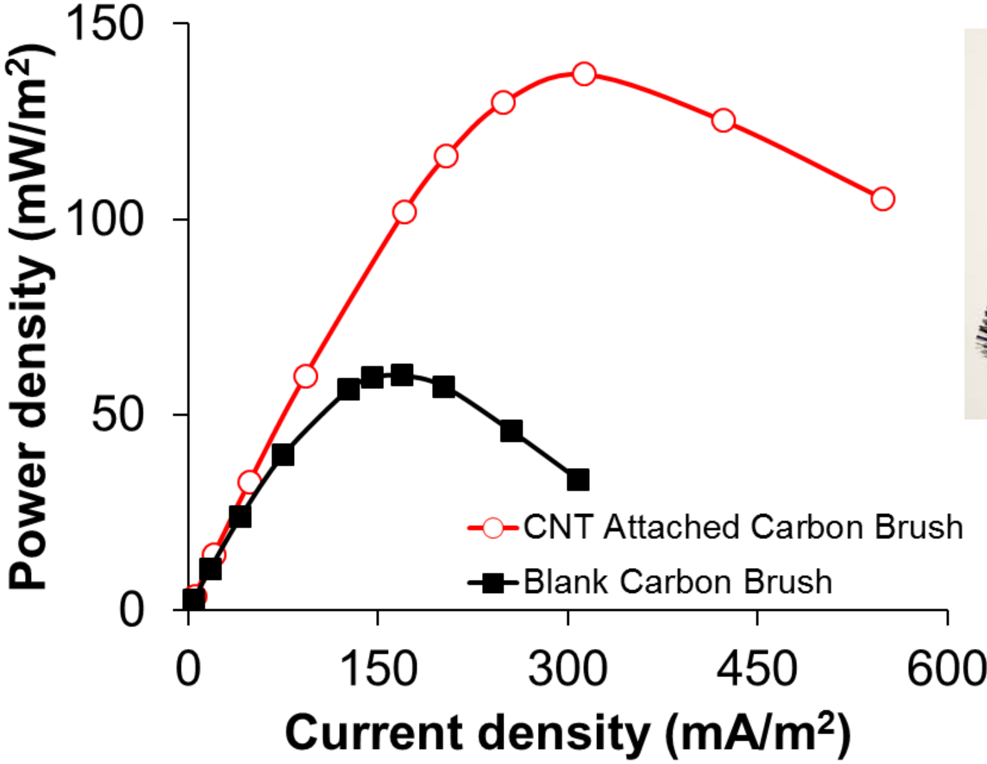


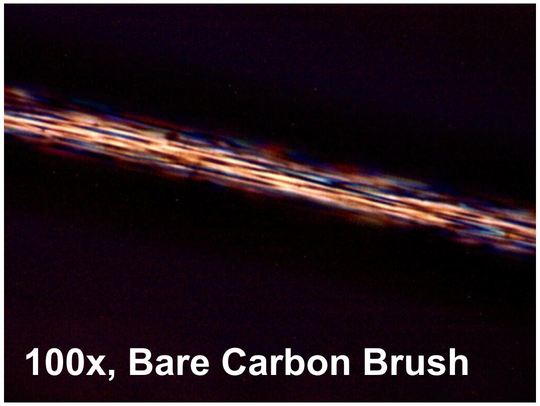


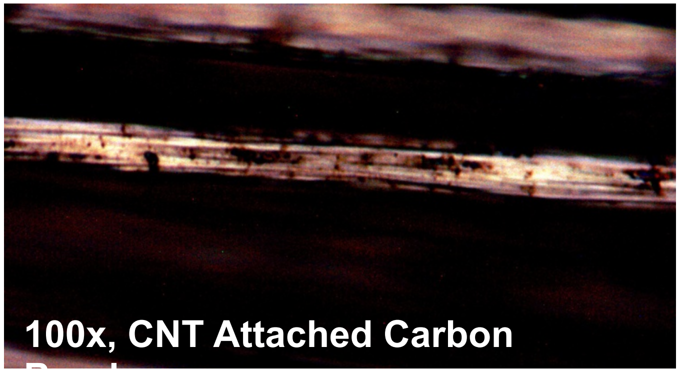
Carbon Nanotubes Attached on Carbon Brush

Direct Attachment through Dipping, NOT Direct Synthesis

Using pure culture (*Shewanella Oneidensis* MR-1)







- ✓ CNT Loaded Carbon Brush: 137 mW/m^2
- ✓ Bare Carbon Brush: 60 mW/m^2
- ✓ Improvement: 128%

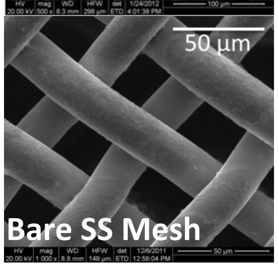
Improved electricity production, but not sufficient

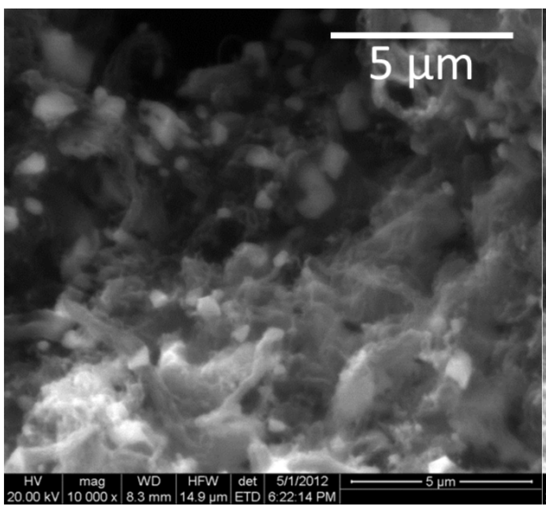
CNTs Directly Synthesized on Stainless Steel Mesh

- **MWCNTs grown on SS Mesh by Chemical Vapor Deposition**

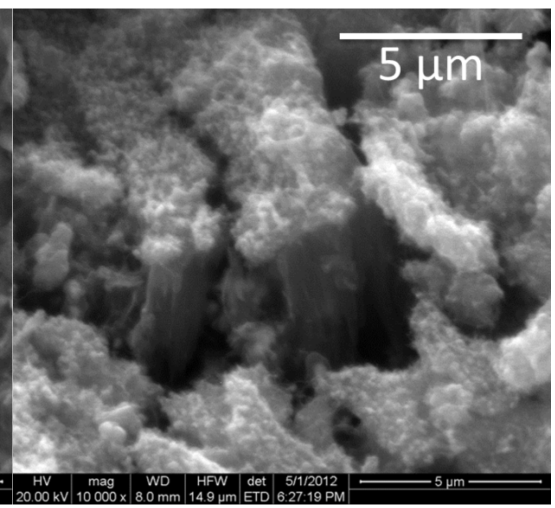
Synthesis Conditions: C_2H_4 and H_2 with moisture (800 ºC, 30min)

Sample Name	Length	Diameter	Distribution
CNT-SSM1	~15 µm	~200 nm	Random
CNT-SSM2	~20 µm	~50 nm	Aligned
CNT-SSM3	~20 µm	~200 nm	Random

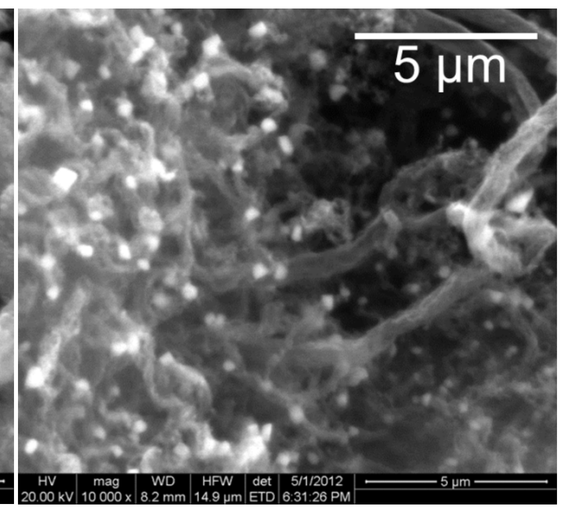




CNT-SSM1



CNT-SSM2

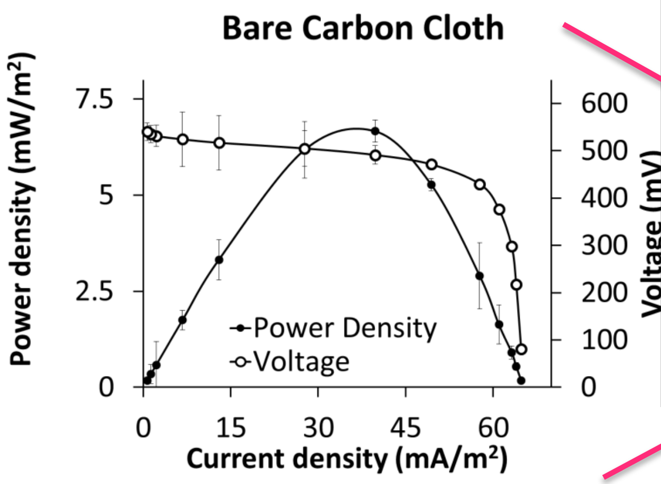


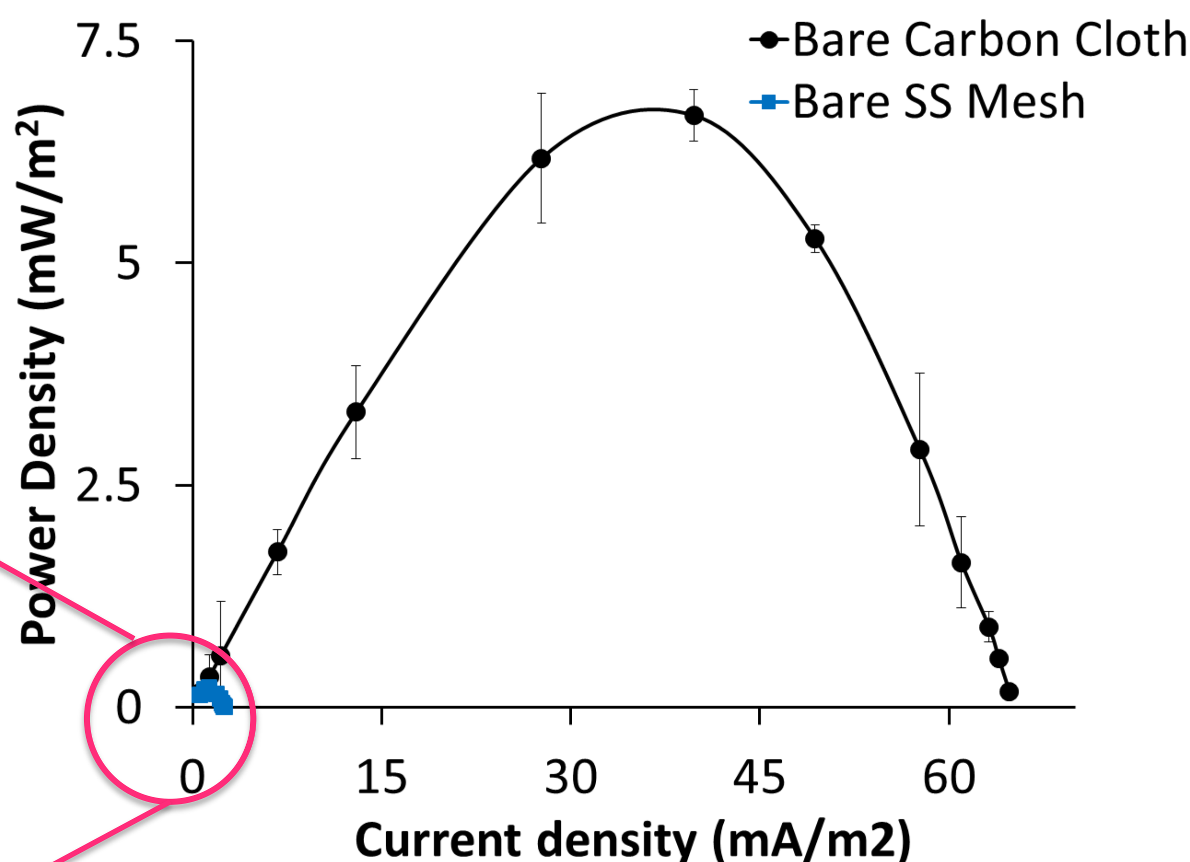
CNT-SSM3

Power Generation of 3D vs 2D Electrodes

Bare SS Mesh (3D) vs Bare Carbon Cloth (2D)

Using pure culture (*Shewanella Oneidensis* MR-1)





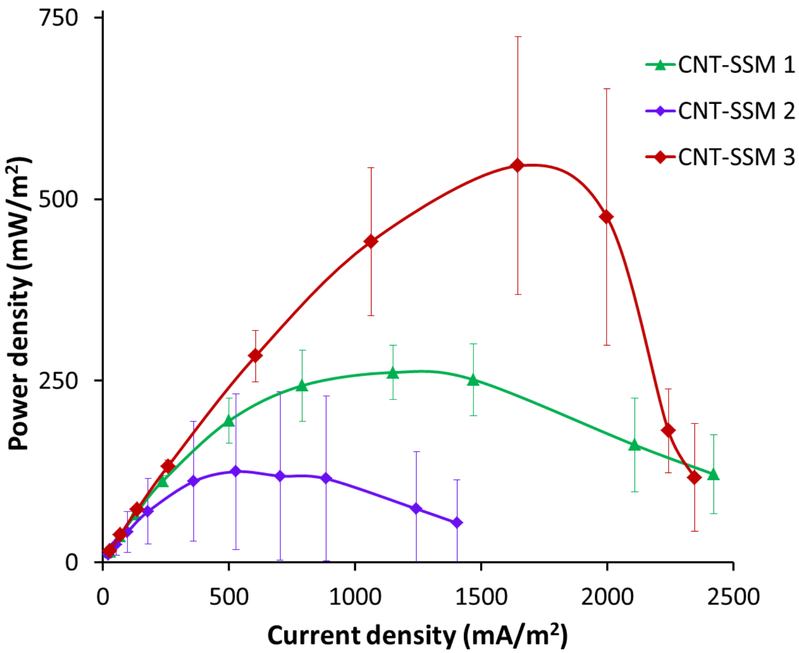
- ✓ **Bare Carbon Cloth: 6.6 mw/m²**
- ✓ **Bare SS Mesh: 0.2 mw/m²**

3D is better than 2D

Power Generation with CNT on SS mesh

Power Density Comparison with Different CNTs on SS Mesh

Using pure culture (*Shewanella Oneidensis* MR-1)



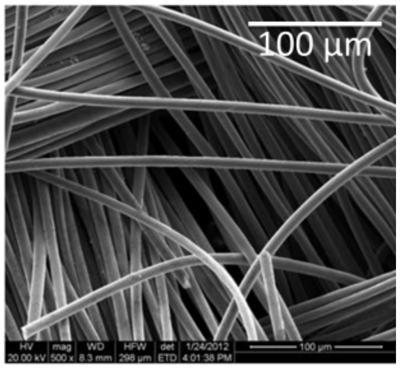
Sample Name	Length (µm)	Diameter (nm)	Distribution	Power (mW/m^2)
CNT-SSM1	~15	~200	Random	**261.4**
CNT-SSM2	~20	~50	Aligned	**124.9**
CNT-SSM3	~20	~200	Random	**545.8**

CNTs grown directly on SSM (CNT-SSM3) **shows 2725 times and 82 time higher** power generation than bare SS mesh and bare carbon cloth

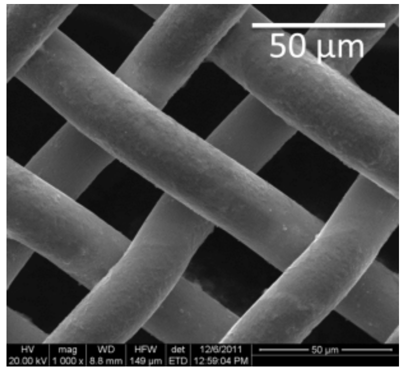
Biofilm Growth on CNT Anode Electrodes

- **Before MFC Run**

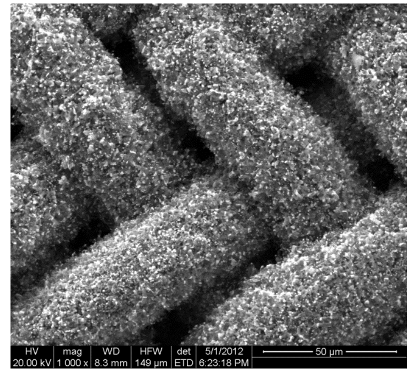
Bare Carbon Cloth

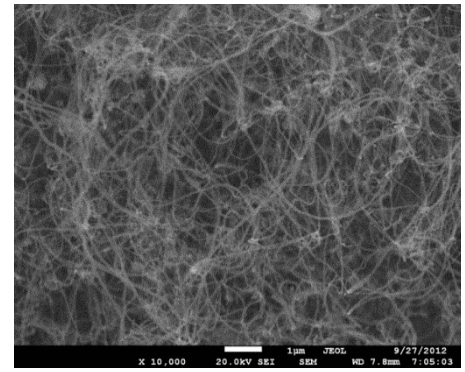


Bare SS Mesh



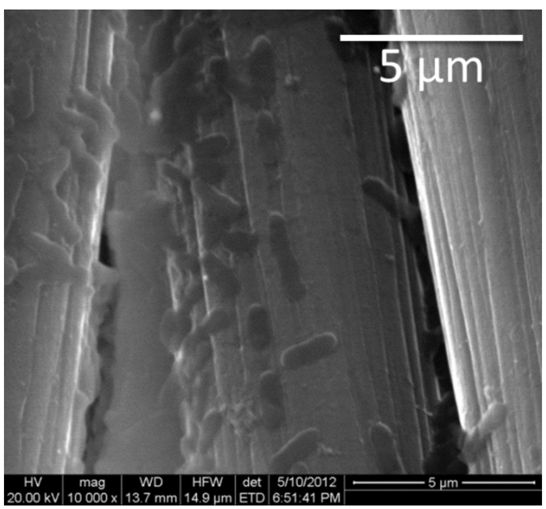
Bare CNT on SS Mesh



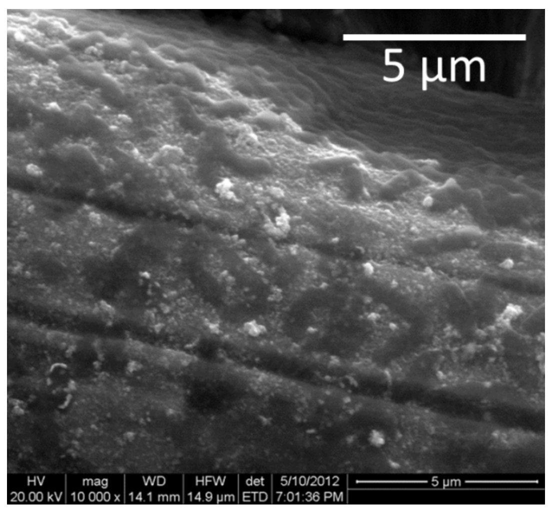


- **After MFC Run**

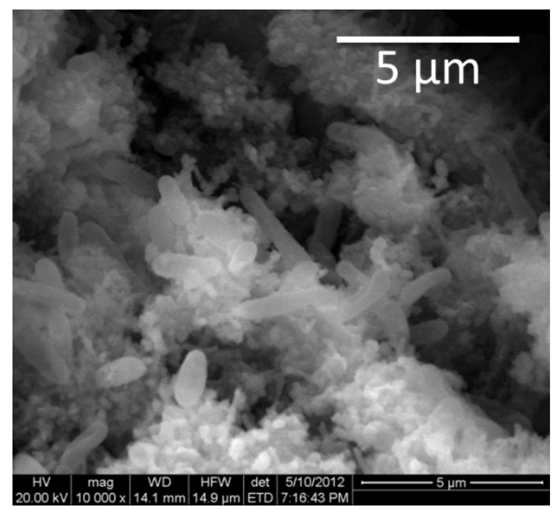
Bare Carbon Cloth



Bare SS Mesh



CNT on SS Mesh



What to Expect when using Wastewater

- **Mixed microbial culture from wastewater typically results in significantly higher power output**

Culture/ Innoculum	Power Density (mW/m^2)	Coulombic efficiency (%)	Current Density (mA/m^2)	Anode Materials	Cathode Materials	References
Shewanella oneidensis	9.3	56.2	50	Solid graphite	Graphite	Lanthier et al. (2007)
Geobacter sulfurreducens	13.1	95	65.4	Solid graphite	Solid graphite	Bond and Lovley (2003)
Pseudomonas aeroginosa	1.67	-	130	Solid graphite	Solid graphite	Rabaey et al. (2005)
Anaerobic digestor Sludge	170	0.7-8.1	516	Carbon fiber	Carbon fiber	He et al. (2005)
Wastewater	766	32	1050	Carbon cloth	Carbon cloth	Min and Logan (2004)
Anaerobic & aerobic digestor sludge	280 W/m^3	29	-	Graphite granules	Graphite granules	Aelterman et al. (2006)

Conclusion

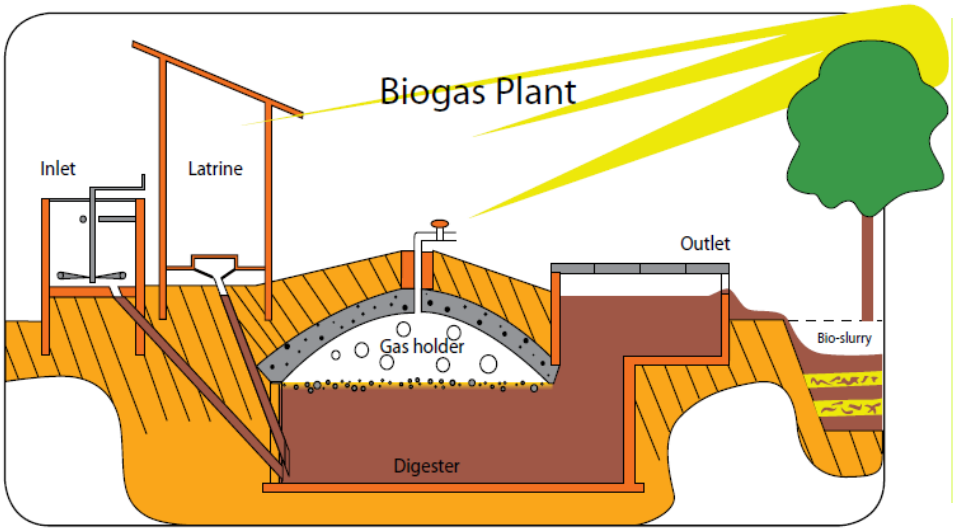
- Unique microfluidic system approach allowed high-throughput screening of various microbes and anode materials
- Carbon nanotubes (CNTs) directly grown on SS mesh electrodes significantly improve the power density compared to bare SS mesh electrodes (2725 times) and carbon cloth electrodes (82 times)
- Modest cost increase for MWCNT synthesis process in cathode (in current lab scale < $\$10/m^2$) results in high power output

Future Works (for next 6 - 9 months)

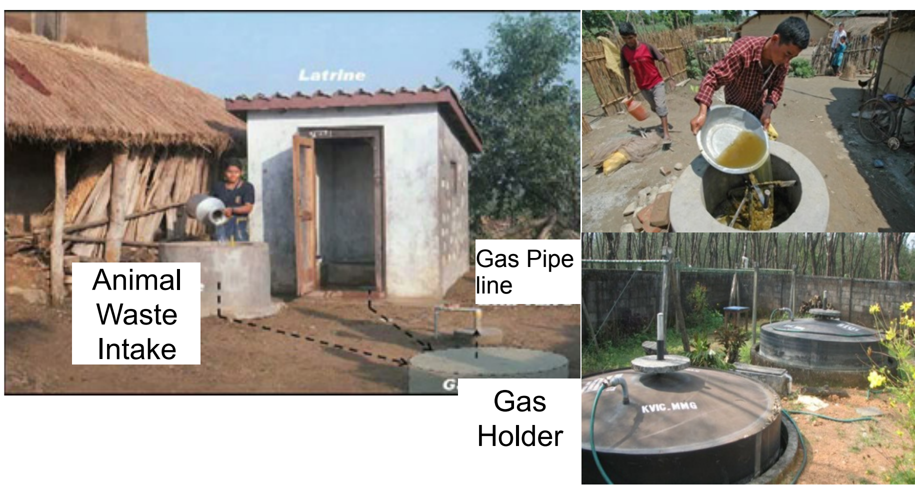
- Currently at TRL 3 - 4
- Further systematic analysis of physical properties of CNTs influencing MFC power output
- Apply the system using wastewater
- Apply the unique CNT-based anode for MEC hydrogen production
- Non-platinum catalyst cathodes based on nanomaterial-electrodes are being developed and tested

Future Works

Where do we see this technology in developing world?



- ❑ **the Biogas Support Programm (BSP)**
  - ✓ the Government of Nepal & SNV with financial support from the Netherlands Ministry of Foreign Affairs (DGIS)
  - ✓ In 1989: started in Nepal
  - ✓ In 2010: 330,000 household in Asia (nearly 2 million people)



https://www.engineeringforchange.org
http://www.snvworld.org/sites/www.snvworld.org
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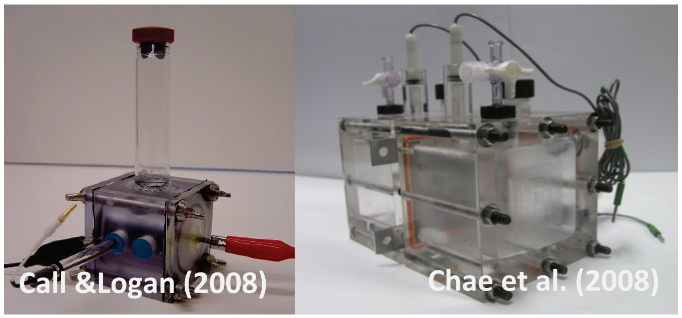
Future of MEC

Lab scale MEC



Pilot scale MEC

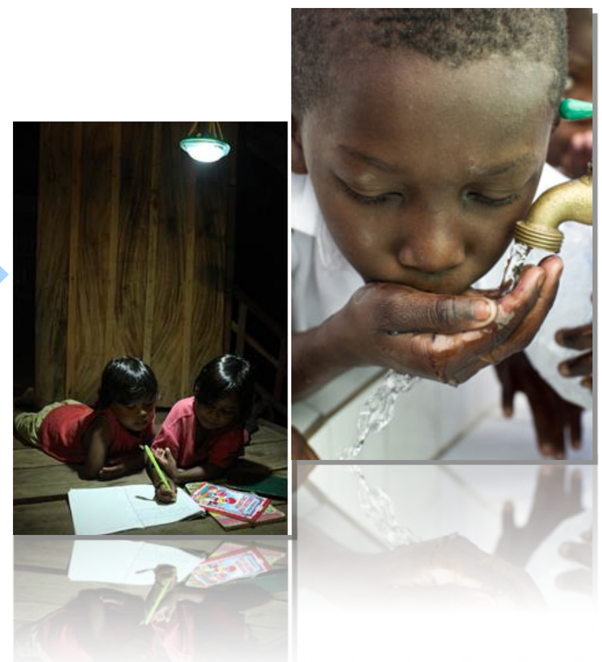
Microbial Fuel Cell

+

Microbial Electrolysis Cell

Electricity

Hydrogen



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- Prof. Won-Bo Shim (TAMU, Plant Pathology)
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