Microbial Fuel Cell and Reverse Electrodialysis Technologies for Renewable Power Generation From Biomass and Salinity Gradients

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Engineering Energy & Environmental Institute





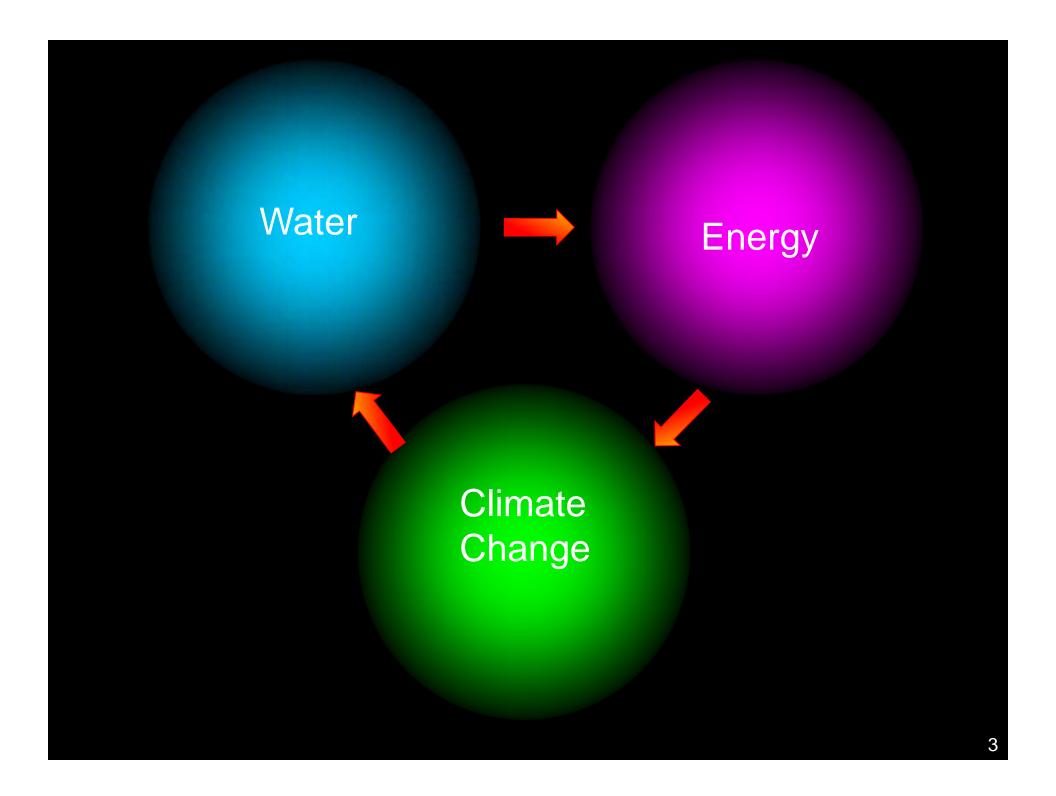




Global Water Demand

- 1 billion people lack adequate drinking water
- 2 billion people lack adequate sanitation
- By 2025, ¼ of all people could live in areas that face severe water shortages.







Energy Demands

- Global Energy Use (power = energy/time)
 - 13,500 GW (= 13.5 TW) (27,000 GW needed by 2050)
- Energy use in the USA
 - 3340 GW energy (continuous) currently used
 - 600 GW generated as electricity
 - → 1 large nuclear power plant produces ~ 1 GW





Power Consumption by People

2000 Calories/day

(2,000 kcal/d, 8.4 MJ/d)

100 W





25 W "down the drain" (2 MJ/d)







Energy & The Water Infrastructure



- Annual energy used for the water infrastructure
 - 30 GW (USA), or 5-6% of all electricity generated
- Wastewater treatment:
 - 15 GW
 - 0.6 kWh/m³ (0.12 to 1-2 kWh/m³)
- Drinking water treatment?
 - Desalination requires 3.7 650 kWh/m³



Goal of my research:

 Make our water infrastructure energysustainable in the next 20 to 25 years

How do I achieve this goal?

 Develop sustainable/green/CO₂ neutral renewable energy

Where do I get the energy from?

• Water... (??)





Energy & The Water Infrastructure



- Energy USED for wastewater treatment
 - 15 GW (USA)
 - 0.6 kWh/m³ (range: 0.12 to 1-2 kWh/m³)
- New energy SOURCE? (waste)water
 - Domestic & Industrial wastewaters contain 17 GW (USA)
 - Domestic wastewater contains (in the organic matter) about
 2-5 kWh/m³; or 4 10 times that needed using conventional treatment!

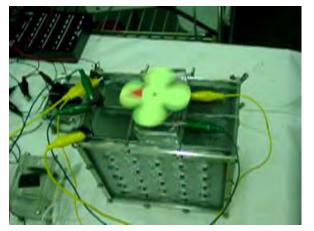


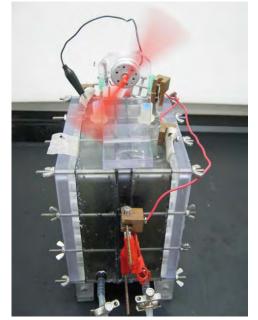
New Energy Sources Available using Microbial Electrochemical Technologies (METs)

- Wastewater : Organic matter in water (USA)
 - 17 GW in wastewater
 (Save 45 GW energy/yr used + produce 17 GW = 62 GW net change)
- Cellulose Biomass Energy: Get biomass → water
 - 600 GW available (based on 1.34 billion tons/yr of lignocellulose)
 (this is how much electrical power is produced in USA)
- Salinity Gradient Energy- Salt & Fresh-waters (global values)
 - 980 GW (from the 1900 GW available from river/ocean water)
 (20 GW available where WW flows into the ocean)
- Waste Heat Energy → Capture heat in "water" (USA)
 - 500 GW from industrial "waste heat"
 - 1000 GW from power plant waste heat
 (Does not include solar and geothermal energy sources)



Demonstration of a Microbial Fuel Cell (MFC)





PENNSTATE



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

www.engr.psu.edu/mfccam

New Water Technologies

- Every revolutionary idea moves through three stages
 - 1- It can't be done
 - 2- It's possible, but it's not worth doing (too \$\$)
 - 3- I said it was a good idea all along.
- Examples in water technologies
 - RO membranes for desalination
 - MBRs for wastewater treatment
 - Microbial fuel cells?





Anode

Microbial Electrochemical Technologies (METs)

Power Generated (P) P/PS Added (PS) **Cathode Microbes (Bioanode)** Microbes (Biocathode) **Abiotic (no microbes) Abiotic (no microbes)**

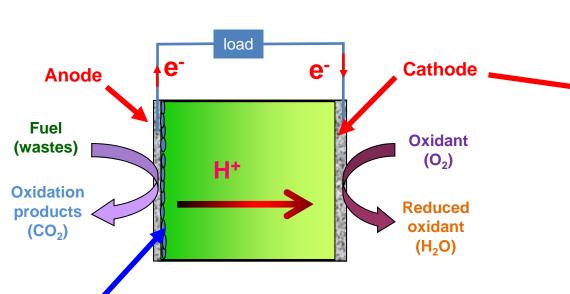
- None
- 1 or more

Membrane

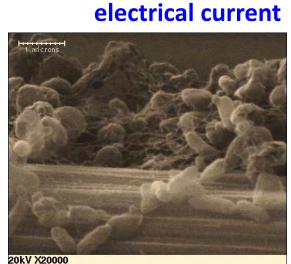


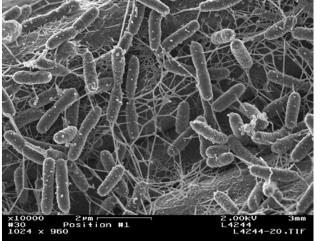


Electrical power generation in a Microbial Fuel Cell (MFC) using exoelectrogenic microorganisms



Bacteria that make





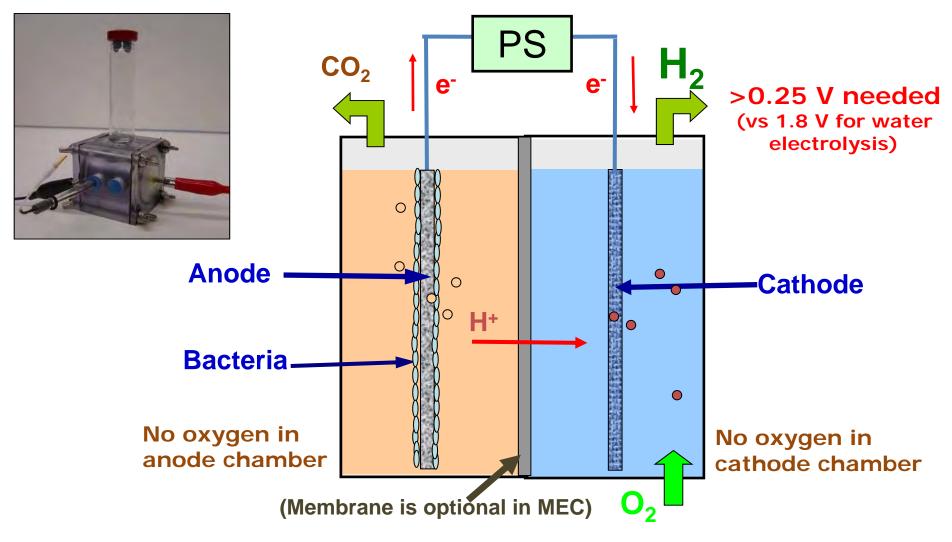




Liu et al. (2004) Environ. Sci. Technol.



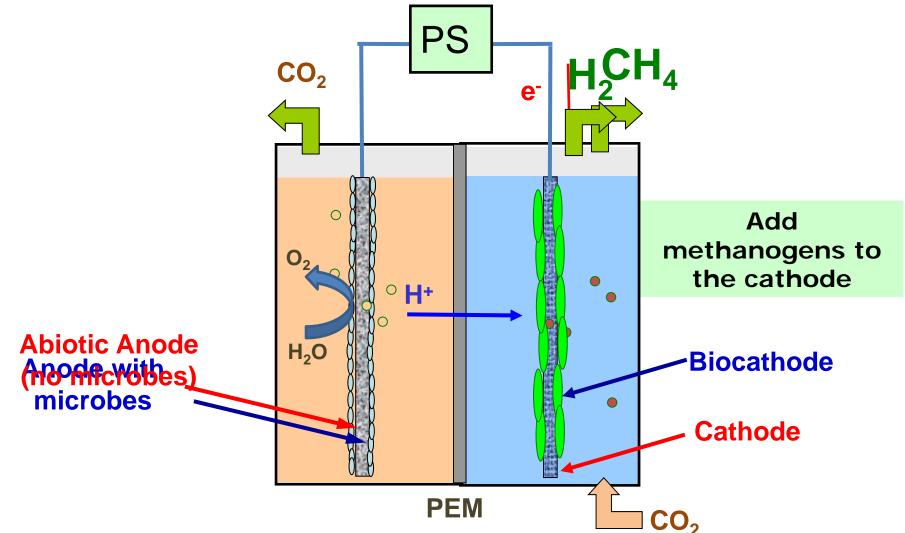
H₂ Production at the cathode using microbes on the anode in **M**icrobial **Electrolysis C**ells







CH₄ Production at the cathode using microbes on the cathode in Microbial Methanogenesis Cells





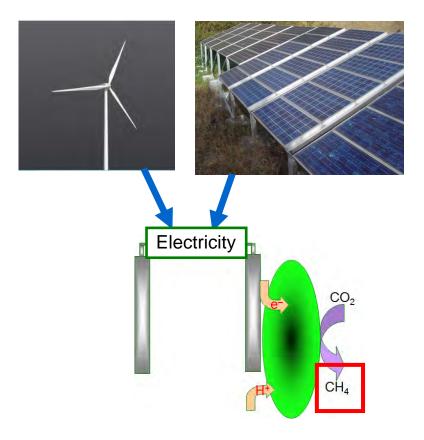
MECs used to harvest methane from renewable forms of electricity generation

Anaerobic digesters

(methane from organic matter)



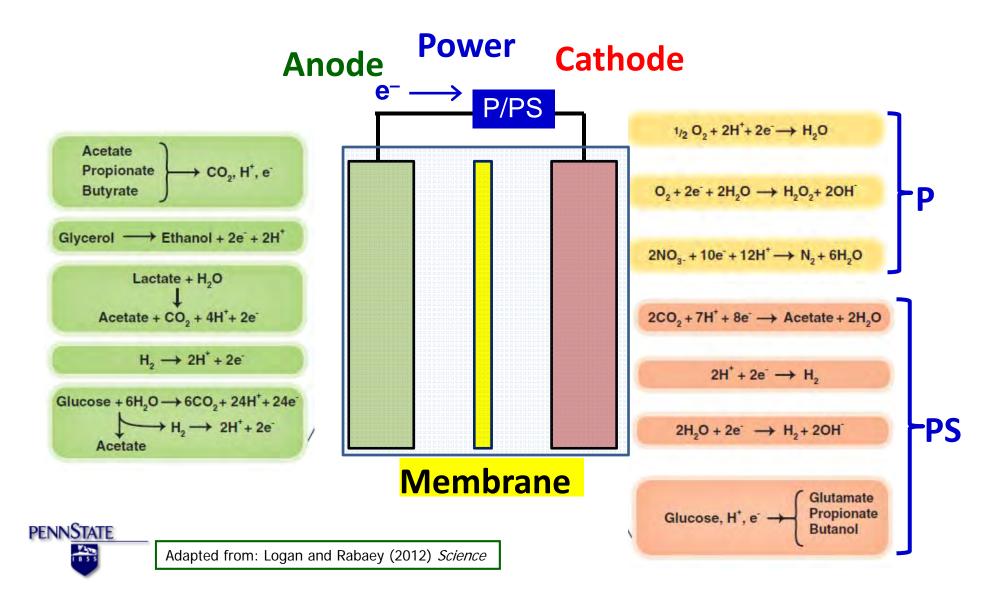
MMCs
Methane from renewable electricity







Microbial Electrochemical Technologies (METs)



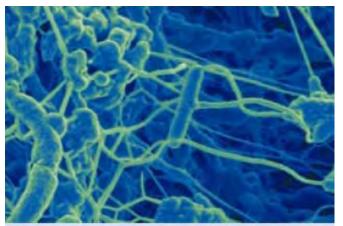
Focus points

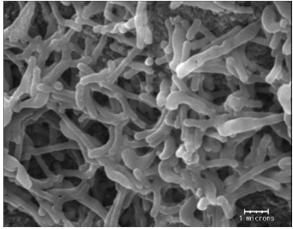
- Electromicrobiology
 - Bioanodes: Electron transfer from bacteria to electrodes
 - Biocathodes: Biofuel production via electromethanogensis
- Engineering: Microbial electrochemical technologies for wastewater treatment
 - Materials
 - Performance
- Salinity gradient energy
 - Methods of energy production
 - Combining MFCs with salinity gradient energy
- Conclusions and Acknowledgments



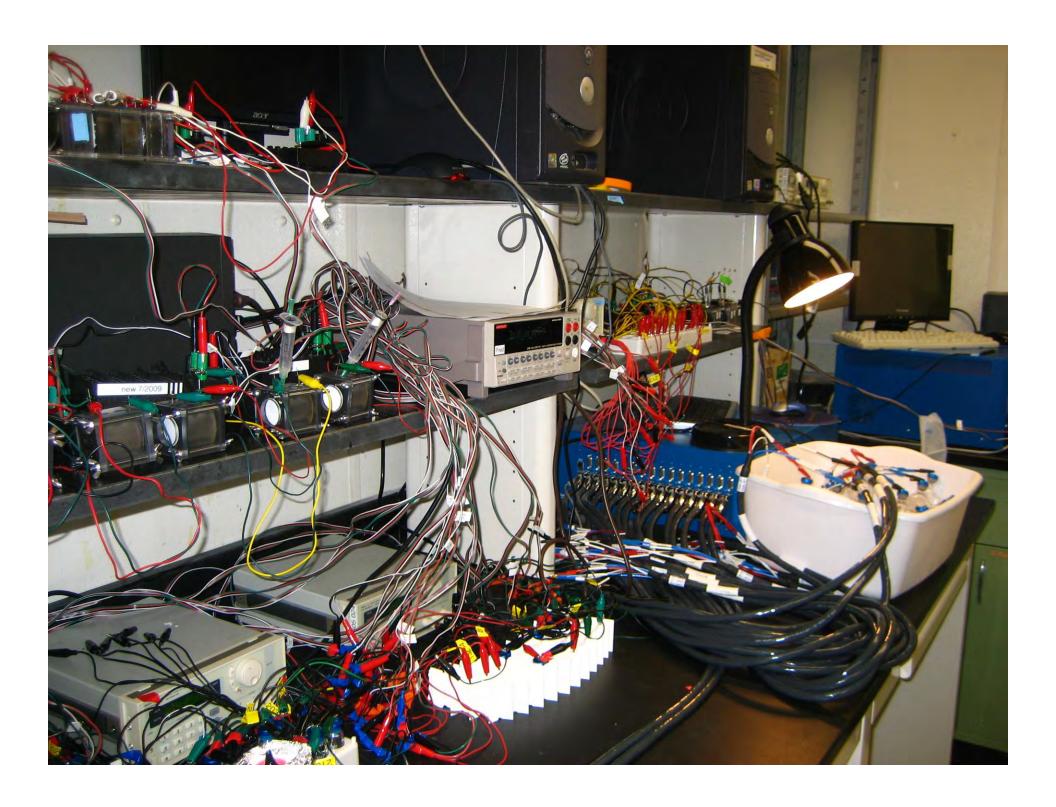
Electro-active Microorganisms

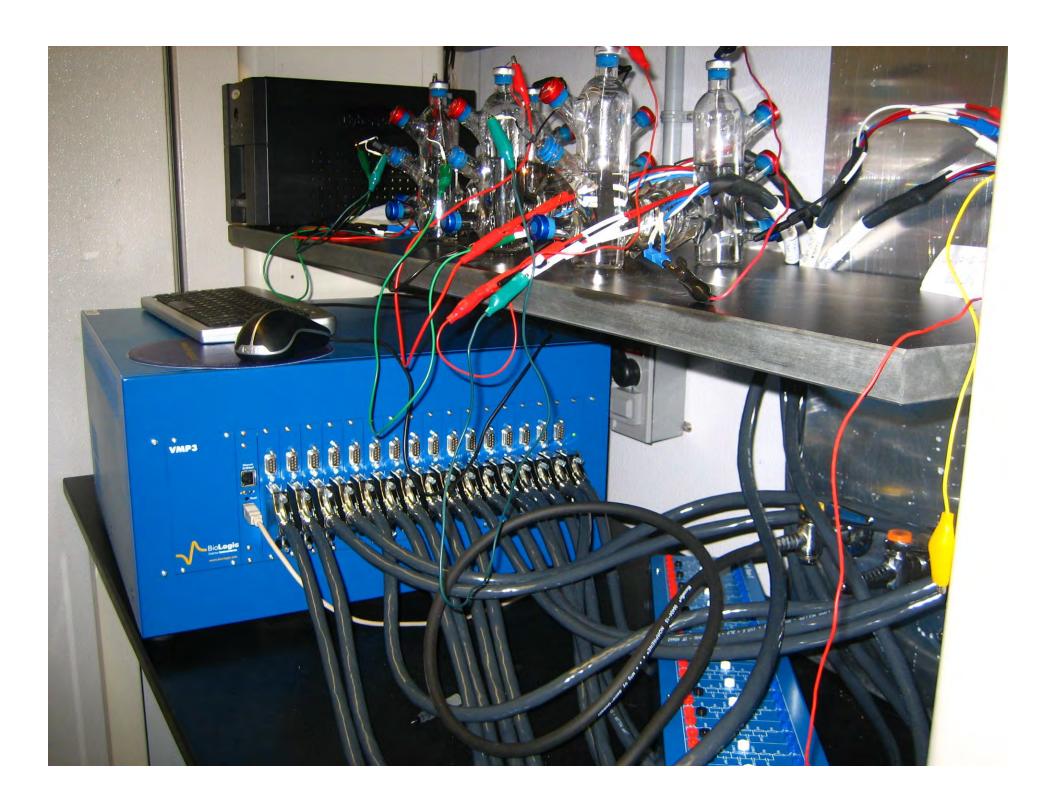
- Electromicrobiology
 - New sub-discipline of microbiology examining exocellular electron transfer

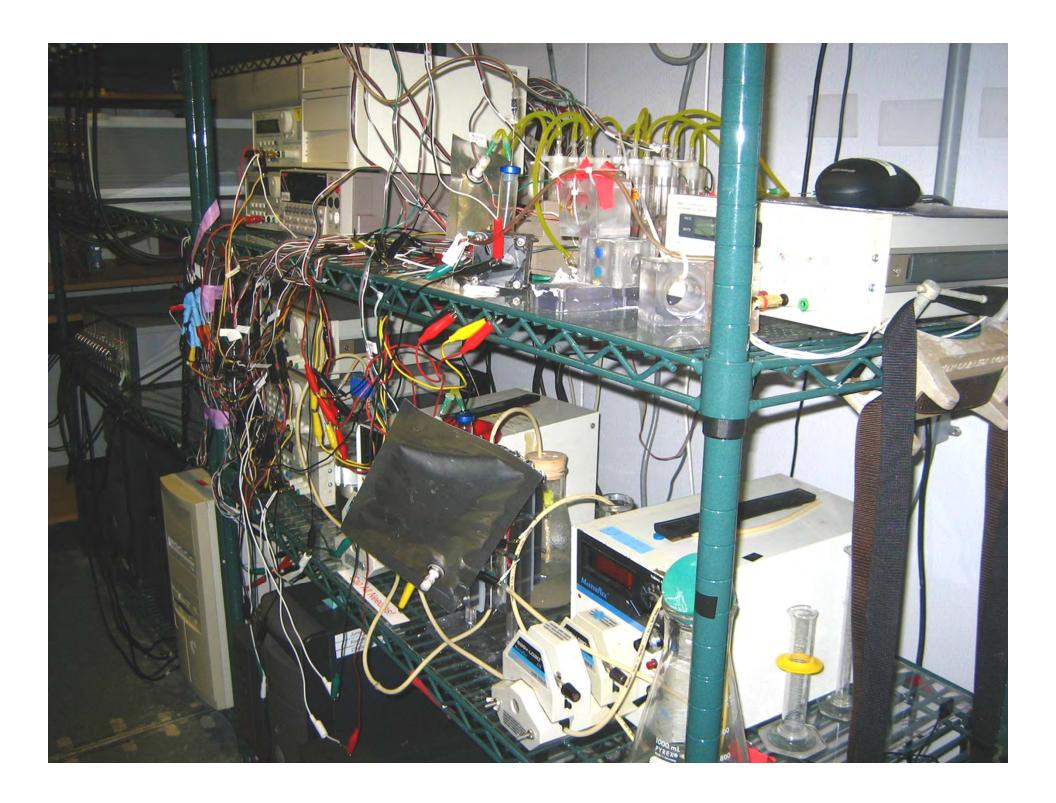








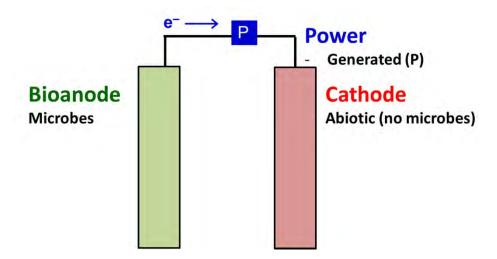




Electro-active Microorganisms

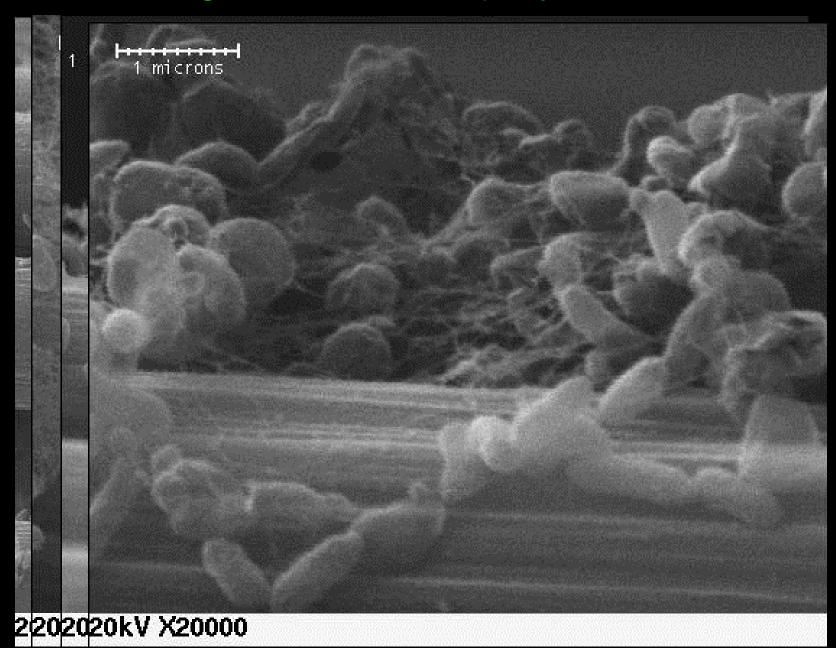
Exoelectrogens

Microbes able to transfer electrons to the outside the cell



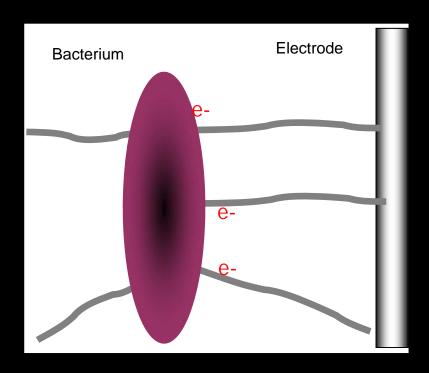


Exoelectrogens: Bacteria rapidly colonize the anode



Mechanisms of electron transfer in the biofilm:

Nanowires produced by bacteria!



Gorby & 23 co-authors (2010) PNAS

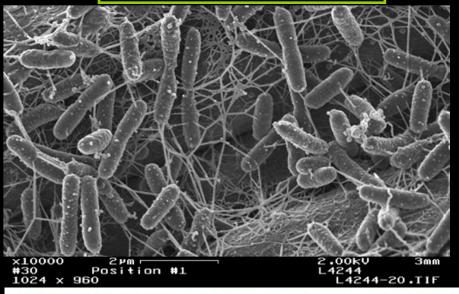
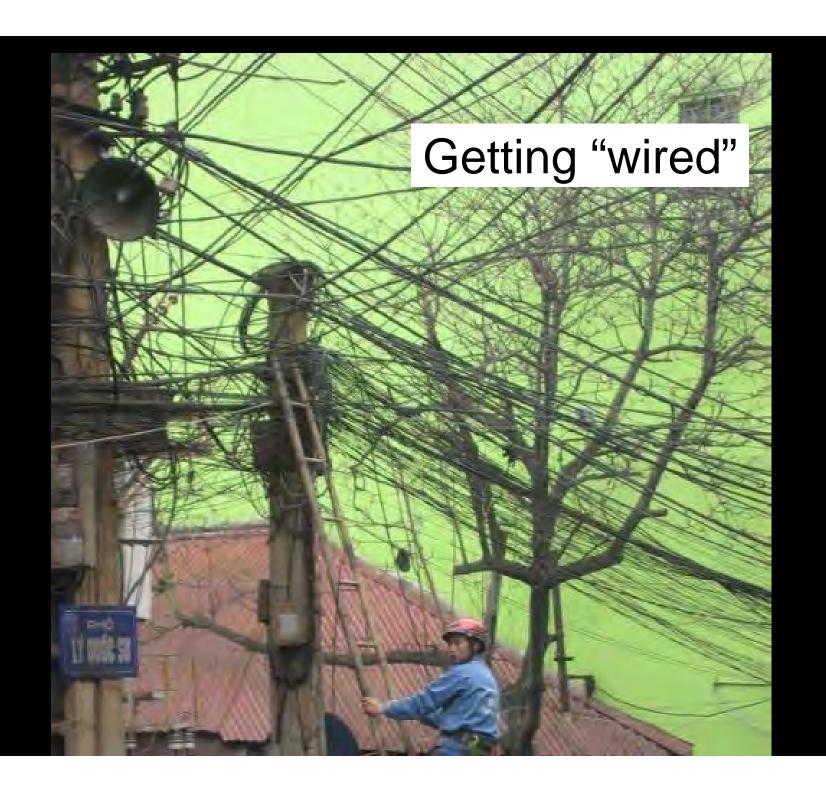


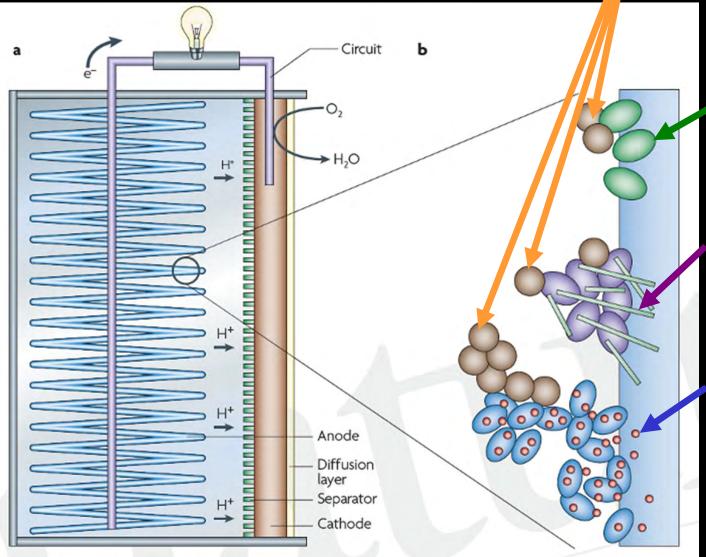


Figure 1. Colorized transmission electron micrograph of microbial nanowire networks secreted by *Geobacter sulfurreducens*. Scale bar, 100 nm.



Electrogenic biofilm ecology

Bacteria living off exoelectrogens



Direct contact

Produce nanowires (wired)

Produce mediators (wireless)

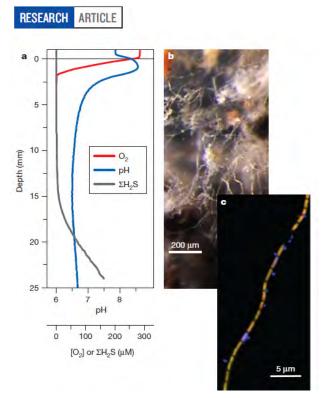
How long are the wires?

Nanowires in Nature- Ocean sediments "wired" over unprecedented length scales

doi:10.1038/nature11586

Filamentous bacteria transport electrons over centimetre distances

Christian Pfeffer¹, Steffen Larsen², Jie Song³, Mingdong Dong³, Flemming Besenbacher³, Rikke Louise Meyer^{2,3}, Kasper Urup Kjeldsen¹, Lars Schreiber¹, Yuri A. Gorby⁴, Mohamed Y. El-Naggar⁵, Kar Man Leung^{4,5}, Andreas Schramm^{1,2}, Nils Risgaard-Petersen¹ & Lars Peter Nielsen^{1,2}



- Individual nanowires that connect cells are individually 10-100 nanometers (nm=10⁻⁹ m)
- <u>Biofilms</u> on electrodes 10-50 micrometers (μm=10⁻⁶ m)
- <u>Filamentous bacteria</u> can help wire up cells over distances of 40 millimeters (mm=10⁻³ m)

Pfeffer et al. (2012) *Nature*

Electrical conductivity of "nanowires" can span across the biofilm length (cm? meters?)

LETTERS NATURE NANOTECHNOLOGY DOI: 10.1038/NNANO.2011.119 100 µm Influent Distance above gold surface: 8 µm Cathode Control Split anode Effluent 100 µm Biofilm Distance above gold surface: 20 µm 100 µm electrode substrate Non-conductive gap

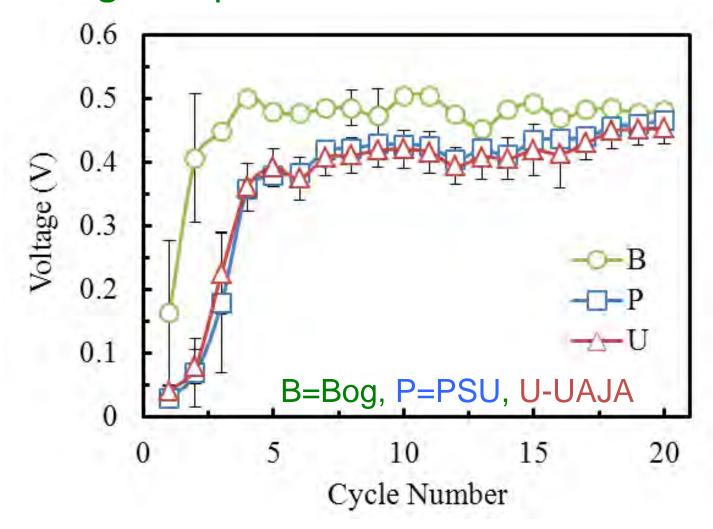


What microbes are on the anodes?

- 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

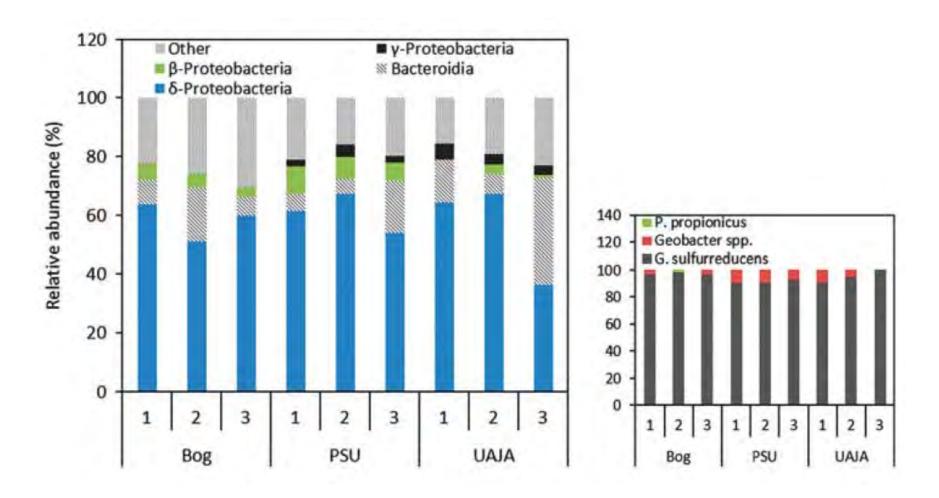


Bog produced power most rapidly but all inocula converged in power



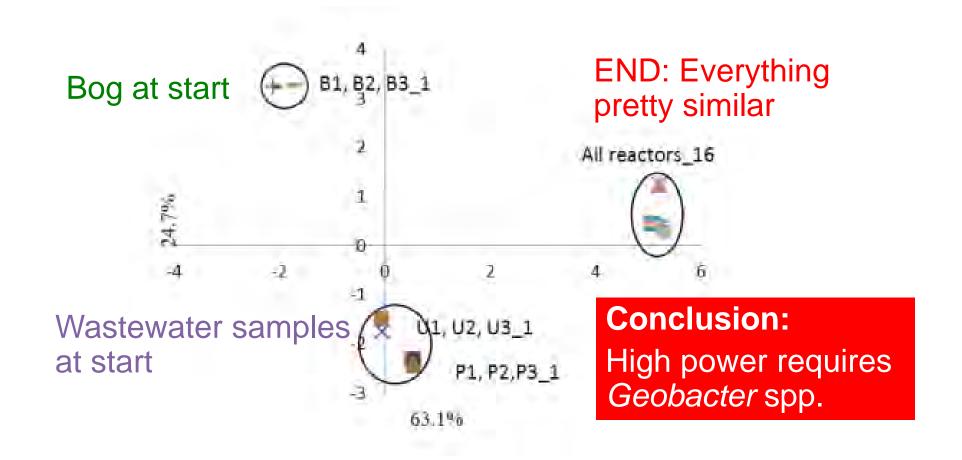


<u>Pyrosequencing:</u> mostly Delta Proteobacteria... and of those, almost all sequences most similar to *Geobacter sulfurreducens*





DGGE used to show changes in community diversity over time

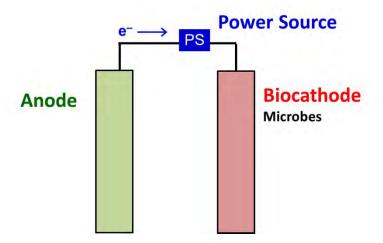




Electro-active Microorganisms

Electrotrophs

Microbes that can accept electrons into the cell

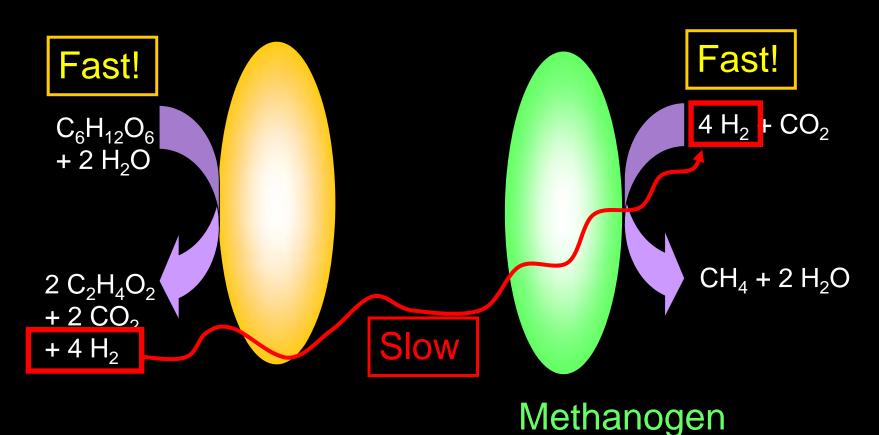


Chemicals used (examples)

- Dissolved oxygen
- Nitrate
- CO₂ Reduction by methanogens, called "Electromethanogenesis"

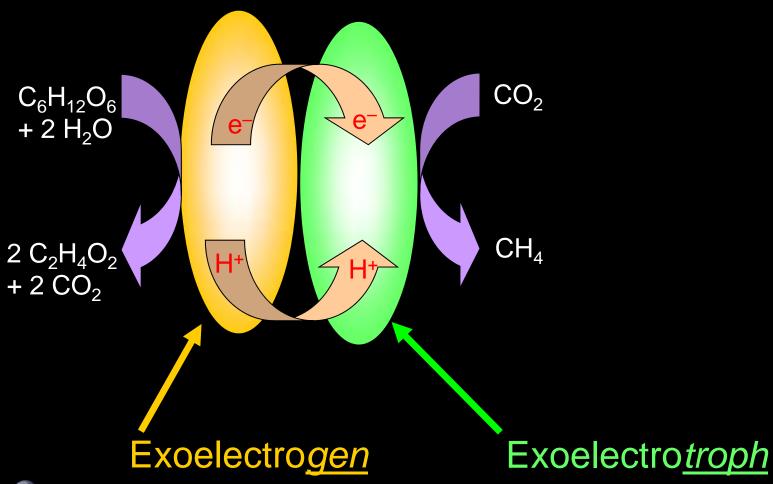


Methanogens: Conventional model based on interspecies <u>hydrogen</u> transfer





New model includes exoelectroactive microorganisms: <u>electron</u> transfer





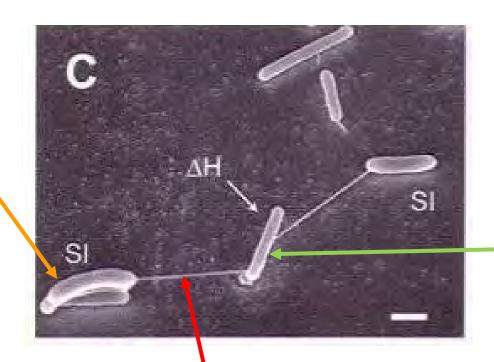
What is the evidence for electromethanogensis?

- Nanowire connections
- Experiments:
 - Mixed cultures
 - Pure cultures
- New studies on methane production



First evidence of direct <u>interspecies</u> <u>electron</u> transfer (2006)

SI- ferments propionate, releases electrons



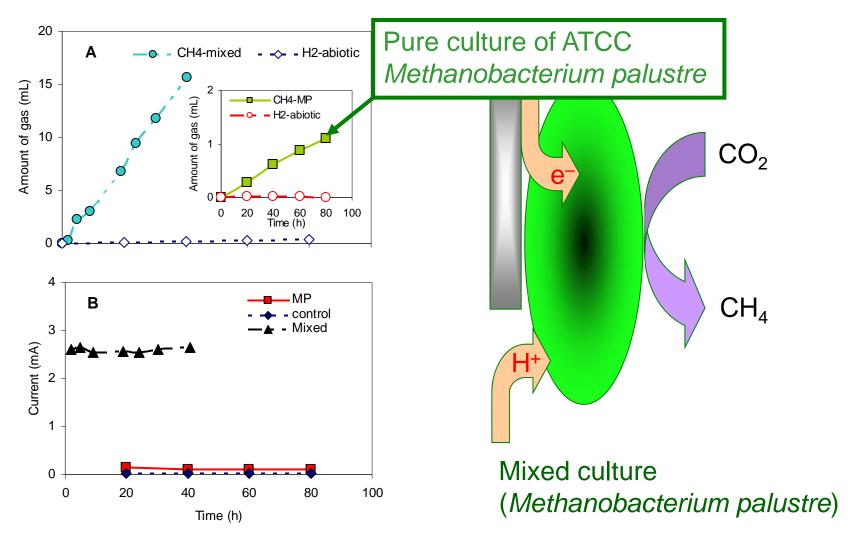
ΔH: Methanogen accepts electrons, makes methane

Nanowires connect fermentative and methanogenic microorganisms



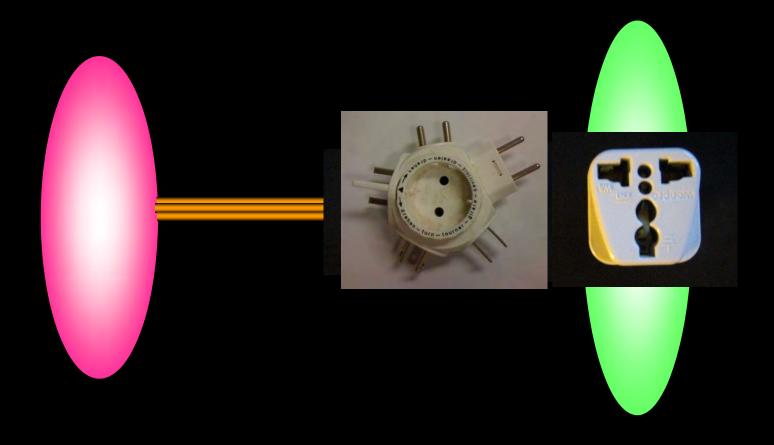


Electrotrophic Methanogens





Connections between microbes-Specific or non-specific?



Exoelectro*gen*

Exoelectro<u>troph</u>



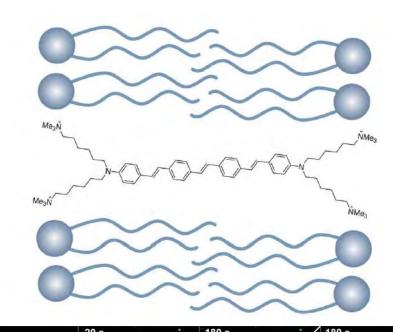
Can "we" make artificial bio-nanowires?

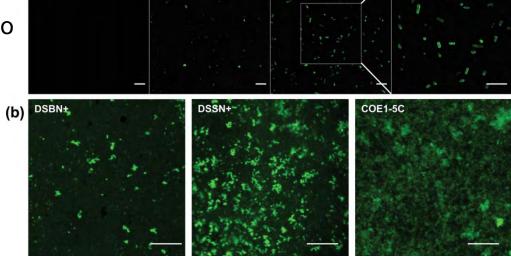
Yes!

"Conjugated oligoelectrolytes (COEs) are synthetic molecules described by a π -conjugated backbone bearing ionic pendant substituents."

Research group: Guillermo (Gui) Bazan, University of California, Santa Barbara

> COEs spontaneously insert into the membrane, and fluoresce only when in the cells





Addition of COEs increase power production in Escherichia coli

E. coli often used as a "negative control" as it produces little current in a microbial fuel cell.

COE1 series

I = 1 DSBN+

n = 2 DSSN+

n = 3 COE1-5C

COE2 series

COE2 series

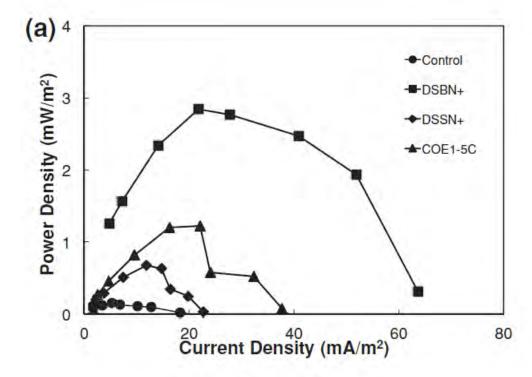
COE2 series

COE2 series

Scheme 1. Molecular structures of conjugated oligoelectrolytes used in this study. COE1 series: DSBN+ DSSN+ and COE1-5C: COE2 series: COE2-3C COE2-4C COE2-5C.

Addition of 2 different COEs shown to increase power production (but power density is still relatively low)

Hou, Chen, Thomas, Catania, Kirchhofer, Garner, Han, and Bazan (2013) *Adv. Materials*



Scaling up MFCs

MFCs= fuel cells, make electricity

Scaling up MECs

MECs= electrolysis cells, make H₂



How can we make large-scale MFCs?

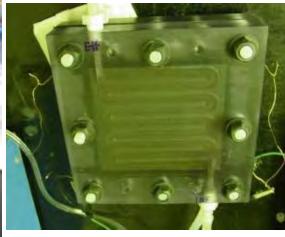
- Reactor design- MFCs, MECs
- Materials and performance-- Costs are the key!

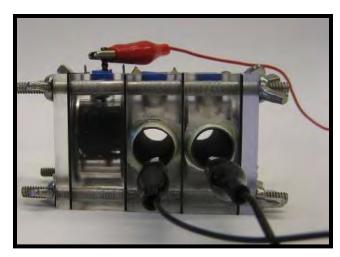


REACTOR ENGINEERING

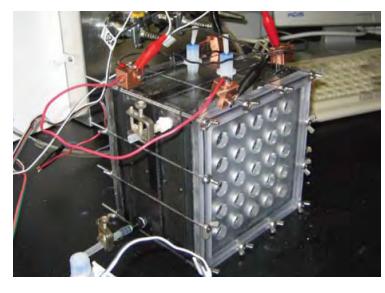
Air cathode MFCs developed at Penn State













CHEMSUSCHEM



DOI: 10.1002/cssc.201100732

Bioelectrochemical Systems: An Outlook for Practical Applications

Tom H. J. A. Sleutels, [a] Annemiek Ter Heijne, \star [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 $m\Omega m^2$) 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 resis-

tances 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.

Review



Towards practical implementation of bioelectrochemical wastewater treatment

René A. Rozendal^{1,2,3}, Hubertus V.M. Hamelers², Korneel Rabaey¹, Jurg Keller¹ and Cees J.N. Buisman^{2,3}

PENNSTATE

SIAIL

Estimates for MFCs

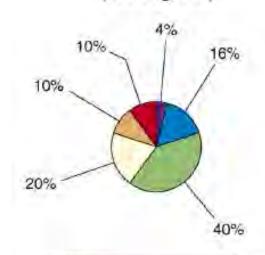
• 100 € /m² or \$130/m²

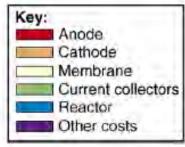
Estimates for MECs

• 100 € /m² or \$130/m²

(b) Future

(~0.4 €/kg COD)

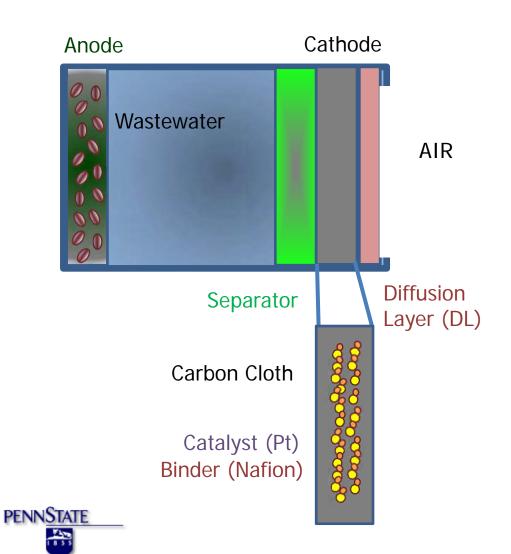




¹ Advanced Water Management Centre, The University of Queensland, St. Lucia, QLD 4072, Australia

² Sub-department of Environmental Technology, Wageningen University, Bomenweg 2, P.O. Box 8129, 6700 EV Wageningen, The Netherlands

Wetsus, Centre for Sustainable Water Technology, Agora 1, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands



Original systems: \$/m² (US)

- Carbon cloth~ \$1,000
- Pt catalyst~ \$ 500
- Binder~ \$ 700
- DL (PTFE)~ \$ 0.30
- Separator~ \$ 1
- TOTAL \$2200

New systems: \$/m² (US)

- Anode \$20
- Cathode \$22
 - SS + CB= \$20
 - Catalyst (AC)=\$0.40
 - Binder= \$1.5
 - DL (PDMS)= \$0.15
- Separator \$ 1
- TOTAL \$43



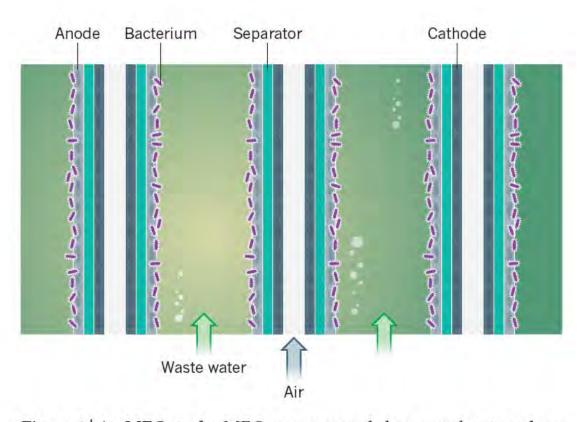
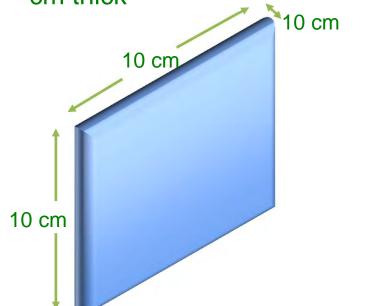


Figure 3 | **An MFC stack.** MFCs are arranged close together to reduce internal resistance and form compact reactors. Within the stack the electrodes consist of repeating units of an anode coated in a mat of bacteria, or biofilm, an insulating separator and a cathode. Waste water flows over the anodes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

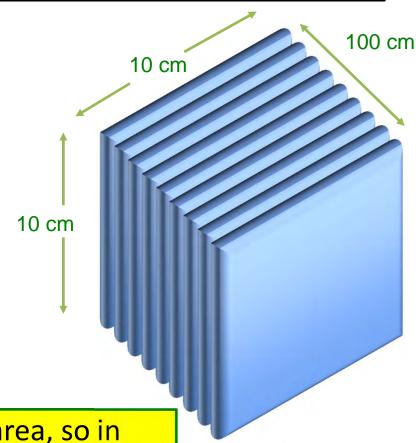


Overall goal: compact reactor design

Assume: One anode-cathode module is 1 m² projected area (height x width) and 10 cm thick

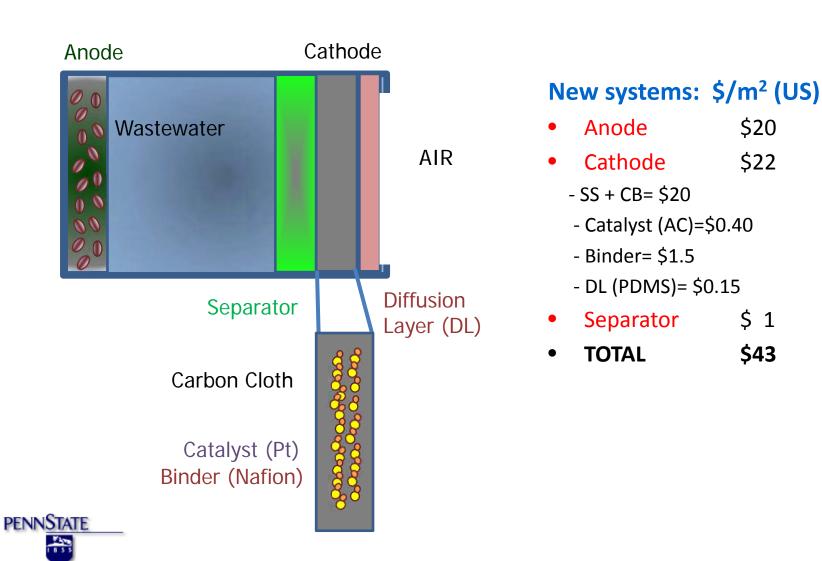


Result: 10 modules = 10 m^2



<u>Design</u>: Limited by cathode area, so in this example we achieve 10 m²/m³





\$20

\$22

\$ 1

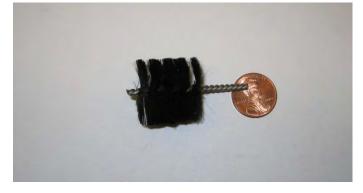
\$43

MFC Materials

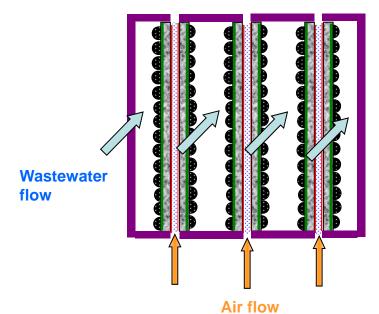
Anode: Graphite brush electrode

- 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

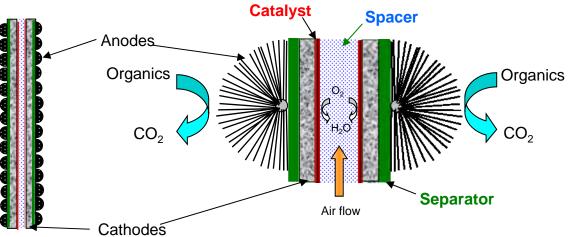








Brush Module Design





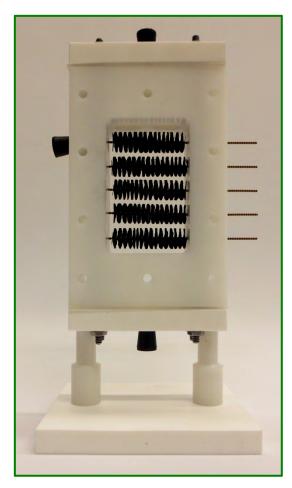
Side View

Close up view

Multi-electrode MFCs



3 brushes (**R3**) 3500 m²/m³



5 brushes (**R5**) 2800 m²/m³

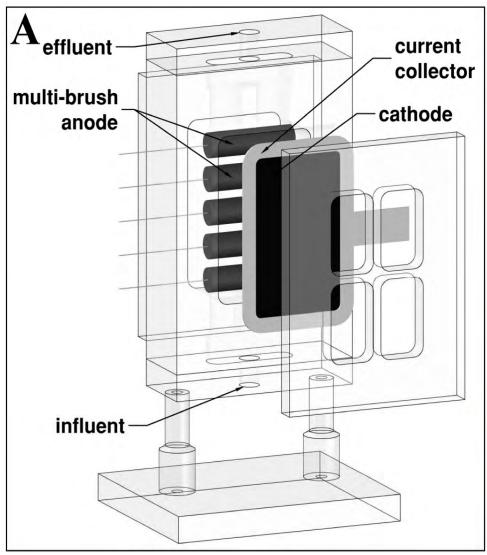


8 brushes (**R8**) 2900 m²/m³



Electrode area (2.5 cm diameter brush/chamber width = $40 \text{ m}^2/\text{m}^3$

MFCs with 5 (left) or 8 anodes (right)

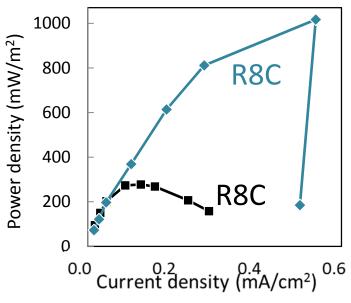






Smaller, closer brushes work best

(Continuous flow, acetate in buffer)



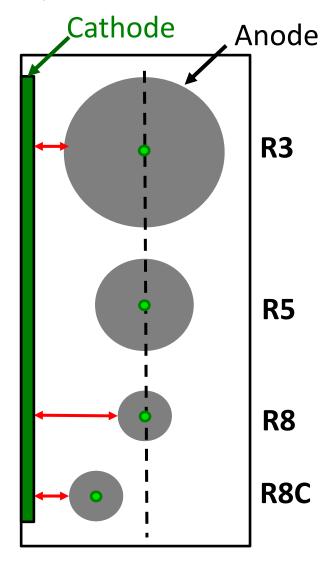


Maximum power densities

R8C= 1020 mW/m²

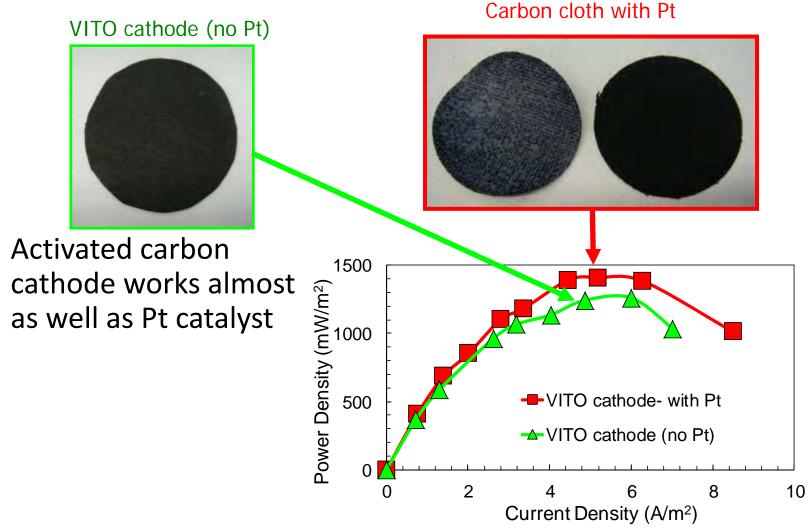
 $R8 = 280 \text{ mW/m}^2$

(R3= 560 mW/m^2) (not shown)





Cathode: Activated Carbon Catalysts







Catalytic Activity of ACs







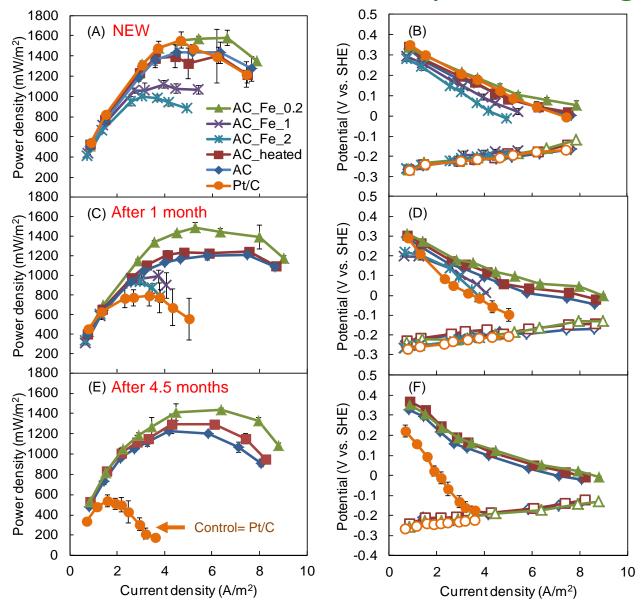




Precursor	Sample
Hardwood	W1- MWV1500
Phenol resin	R1- Kuraray RP-20
Peat	P1- Norit SX1
Peat	P2- Norit SX Plus
Peat	P3- Norit SX Ultra
Coconut shell	C1- Kuraray YP-50
Coconut shell	C2- CR8325C
Coconut shell	C3- ACP1250
Bituminous Coal	B1- CR325B



Activated Carbon Cathodes- improved longevity



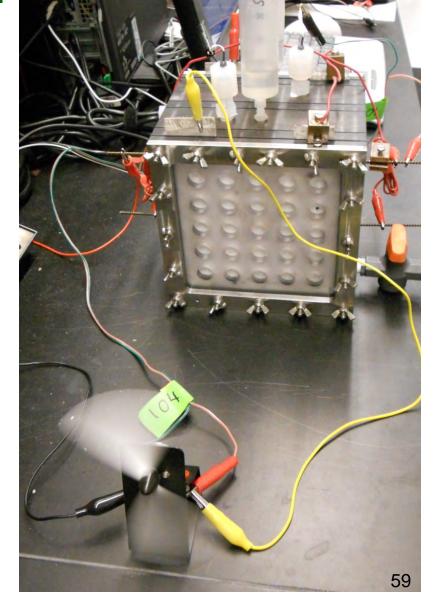


Scaling up MFCs

MFCs= fuel cells, make electricity

This 2-Liter MFC has been "viewed by the public for several years:

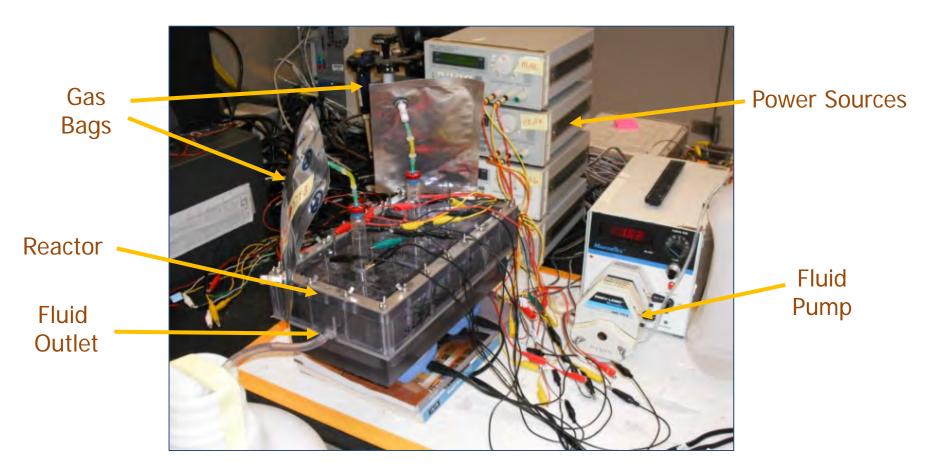
- See the MFC webcam (live video of an MFC running a fan)
 - www.engr.psu.edu/mfccam
- Display at the London Science museum (2012), with the help of:
 - KAUST (Saudi Arabia)
 - University of Newcastle (UK)
 - VITO (Belgium)





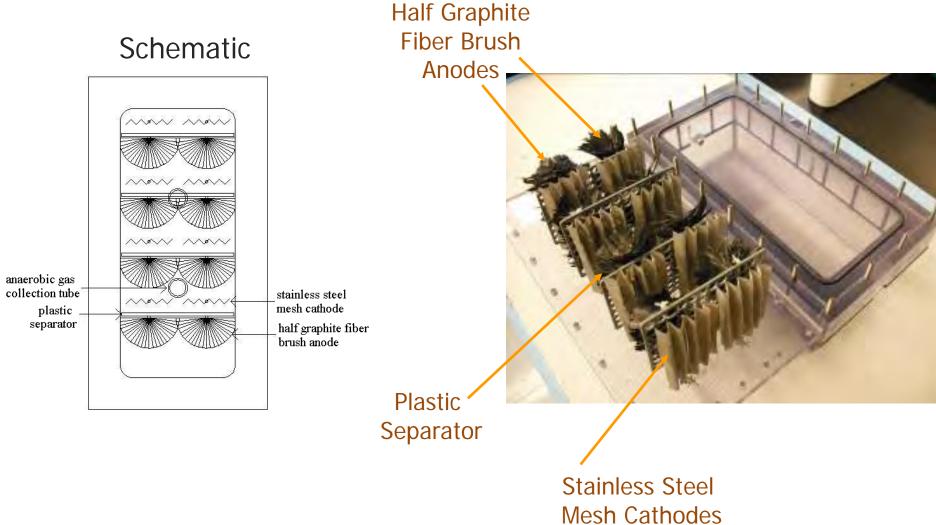
Scaling up MECs

MECs= electrolysis cells, make H₂





MEC components (2.5 L reactor)





MEC Reactor that has 24 modules with a total of 144 electrode pairs (1000 L)







Wastewater Evaluation for Pilot-Scale Tests: Choosing the best WW

Four Waste Waters:

- 1. Domestic (MFC, MEC)
- 2. Winery (MFC, MEC)
- 3. Dairy (MFC)
- 4. Potato Chip (MFC)





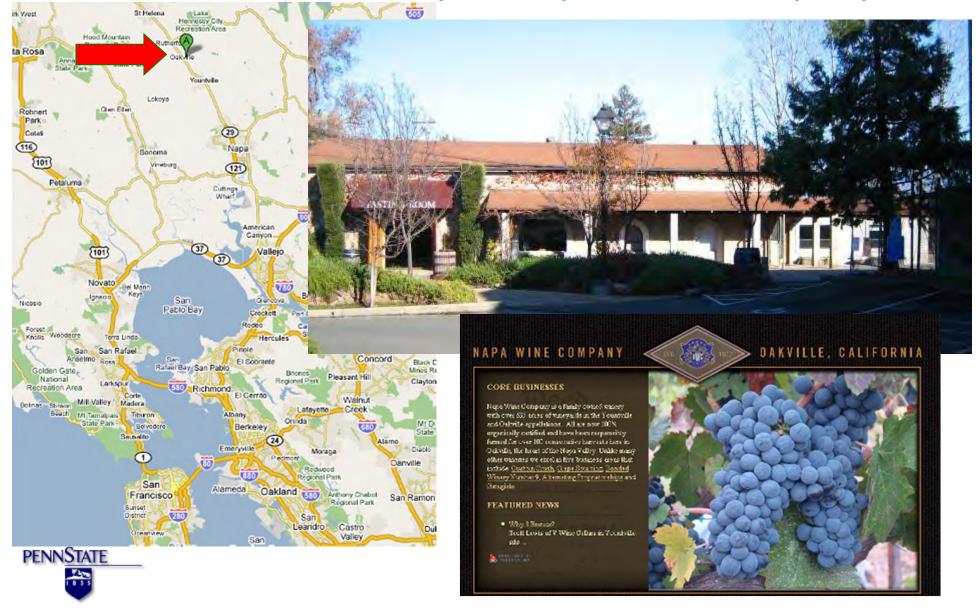
Summary of Results

Waste Water	COD (g/L)	Power Density (mW/m²)	MFC CE (%)	Q (m³/m³-d)	MEC CE (%)
Domestic	0.32	147	13	0.16	35
Winery	2.5	260	18	0.35	26
Dairy	2.8	189	12		
Potato Chip	7.7	217	21	0.48 0.74	50 78



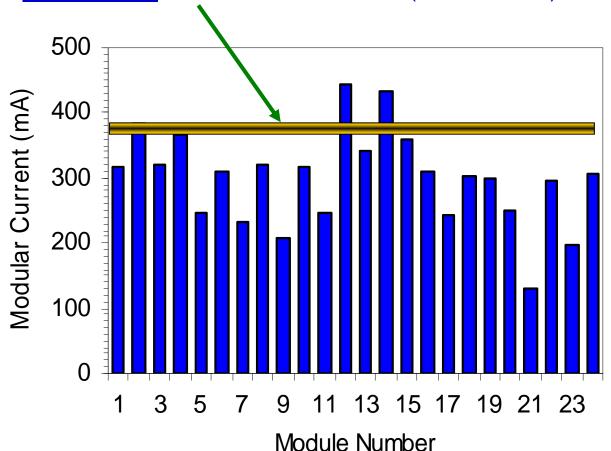
MEC Field test:

Penn State University @ Napa Wine Company



Individual module performance of the MEC treating Wastewater

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



H₂ intially 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



MEC at a Domestic WWTP (120 L)

(University of Newcastle, UK)

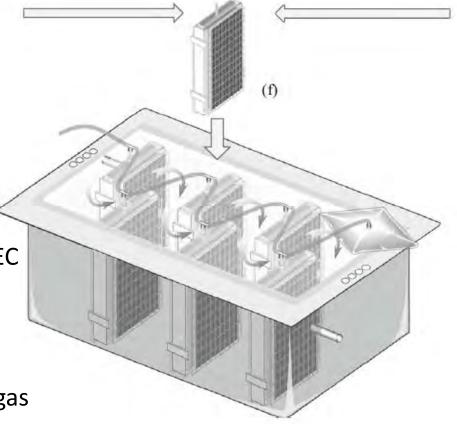


Produced pure H₂ using 2-chamber MEC cassettes

 2.3 kJ/gCOD used compared to 2.5-7.2 kJ/gCOD for activated sludge

Recovered ~70% of energy used in H₂ gas

Incomplete COD removal



Other Microbial Electrochemical Technologies

- MDCs: Microbial desalination cells [for water desalination without electrical grid energy]
- MSCs: Phosphorus (struvite) recovery from wastewaters
- MES: Electrofuels and organic substrates [Microbial ElectroSynthesis]
- Energy production from salinity gradient and waste heat energy using MRECs and MRFCs



New Energy Sources Available using Microbial Electrochemical Technologies (METs)

- Wastewater : Organic matter in water (USA)
 - 17 GW in wastewater
 (Save 45 GW energy/yr used + produce 17 GW = 62 GW net change)
- Cellulose Biomass Energy: Get biomass → water
 - 600 GW available (based on 1.34 billion tons/yr of lignocellulose)
 (this is how much electrical power is produced in USA)
- Salinity Gradient Energy- Salt & Fresh-waters (global values)
 - 980 GW (from the 1900 GW available from river/ocean water)
 (20 GW available where WW flows into the ocean)
- Waste Heat Energy → Capture heat in "water" (USA)
 - 500 GW from industrial "waste heat"
 - 1000 GW from power plant waste heat
 (Does not include solar and geothermal energy sources)

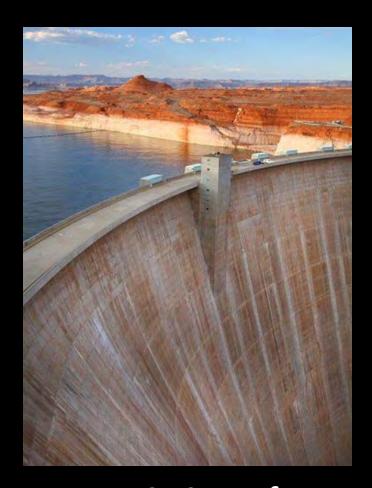


Salinity Gradient Energy









270 m of Hydraulic Head

Oceanside WWTPs and Rivers could produce 980 GW

3 Methods to capture Salinity Gradient Energy

- 1) Pressure retarded osmosis (PRO)
- 2) Reverse electrodialysis (RED)
- 3) Capacitive layer expansion ("Capmix")
 (Variation uses battery like reactions, "Battmix")

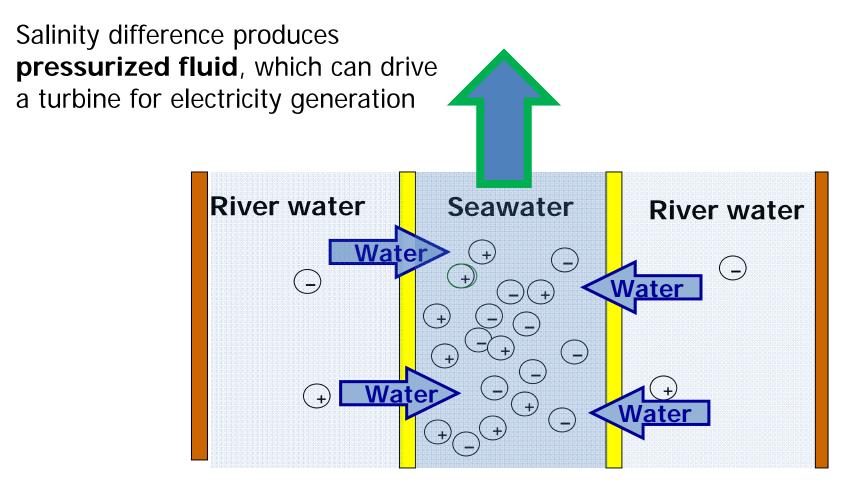


Combining MFCs with salinity gradient energy technologies??

- MFC + PRO = MOFC (Microbial osmotic fuel cell)
 - (Envisioned more for water desalination than power generation)
- MFC + RED = MRFC (Microbial reverse electrodialysis fuel cell)
 - Single circuit enhanced power
- MFC + CapMix = CMFC (CapMix MFC)
 - Two circuit system for energy capture



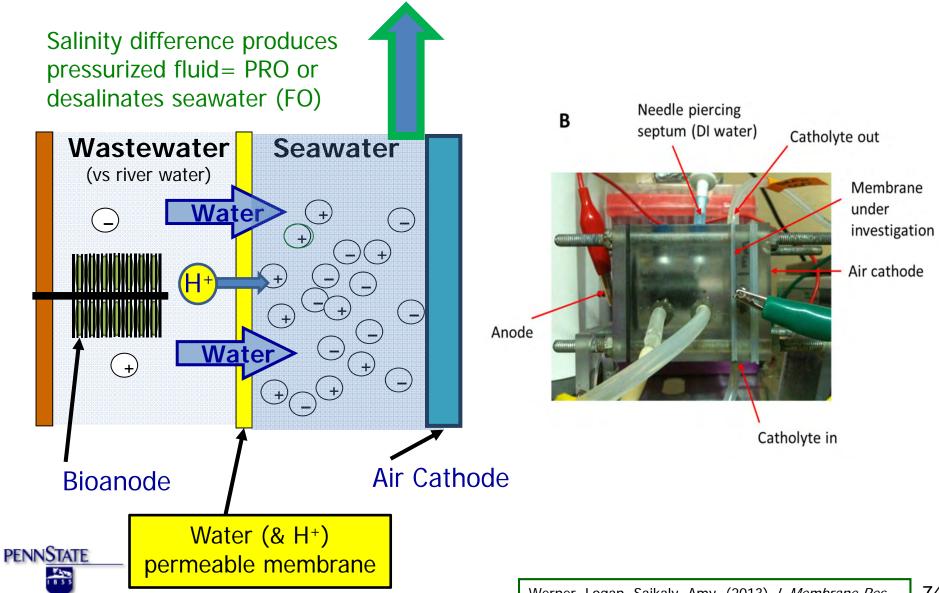
#1- Pressure Retarded Osmosis (PRO)



Water permeable membranes- "Forward Osmosis" (FO)membrane



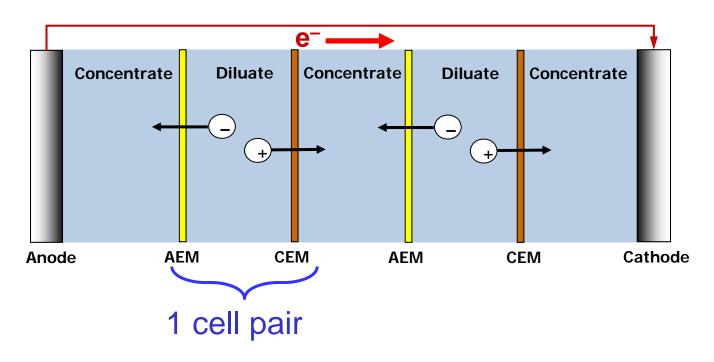
MFC + PRO = MOFC (Microbial Osmotic Fuel Cell)



#2- Reverse Electrodialysis (RED)

What is Electrodialysis (ED)?

Method to use electricity to desalinate water



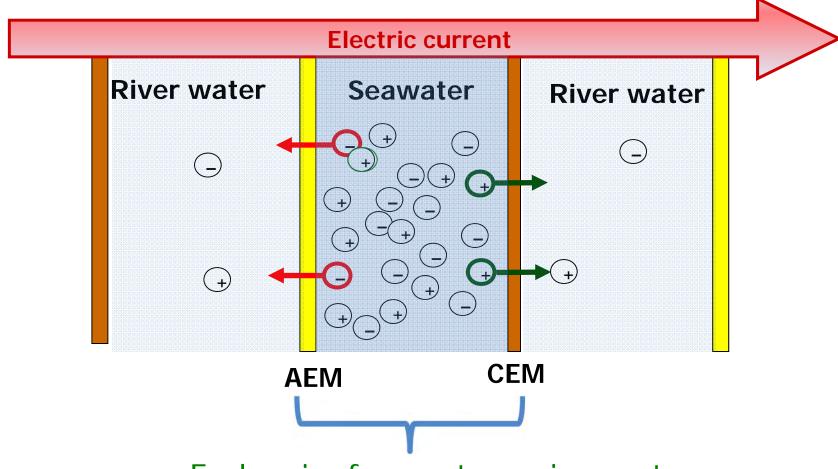
1-cell pair system: 1 e⁻ → 1 cation and 1 anions

2-cell pair system: 1 $e^- \rightarrow 2$ cations and 2 anions



Reverse electrodialysis (RED)

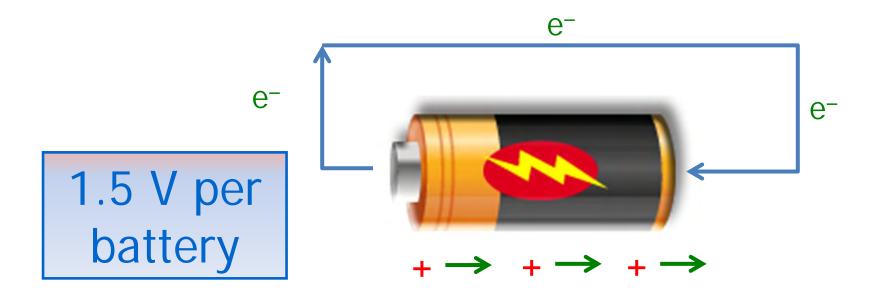
Salinity difference **produces** electrical current

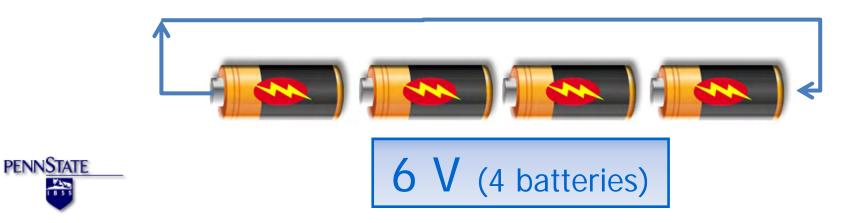


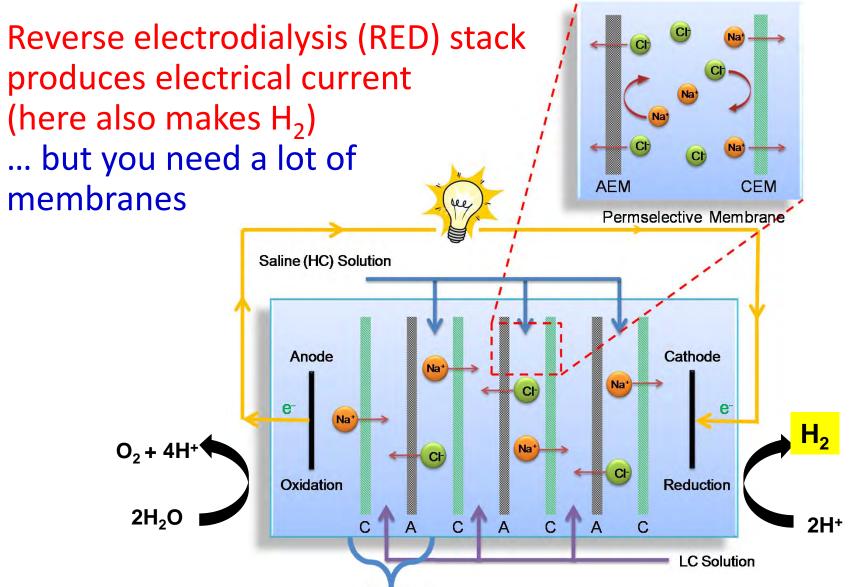
Each pair of seawater + river water cells → ~0.1 - 0.2 V



Batteries = motion of ions & electrons





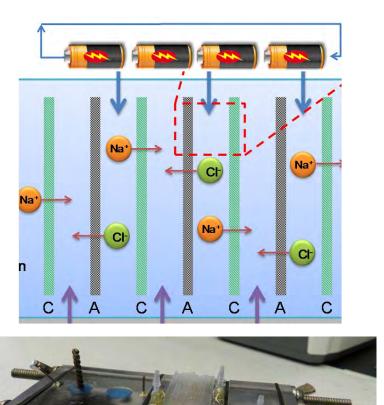








What if we move the RED stack into an MFC?

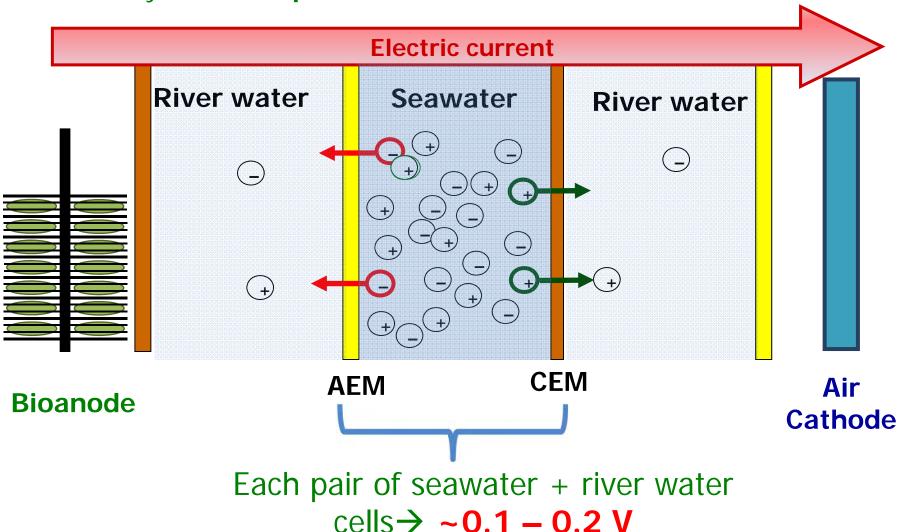




PENN<u>STATE</u>

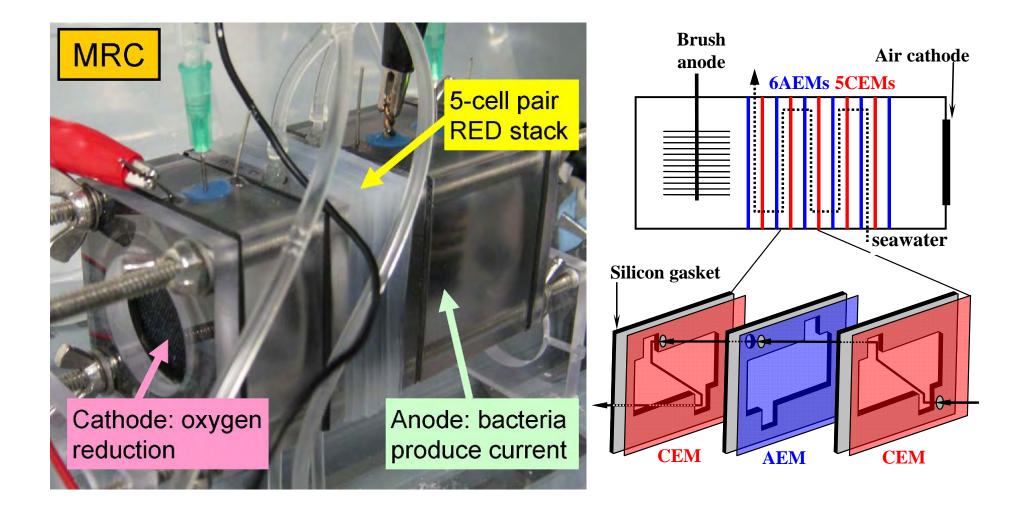
Reverse electrodialysis (RED)

Salinity difference **produces** electrical current





MFC + RED = MRFC (Microbial RED Fuel Cell)





MRFC performance

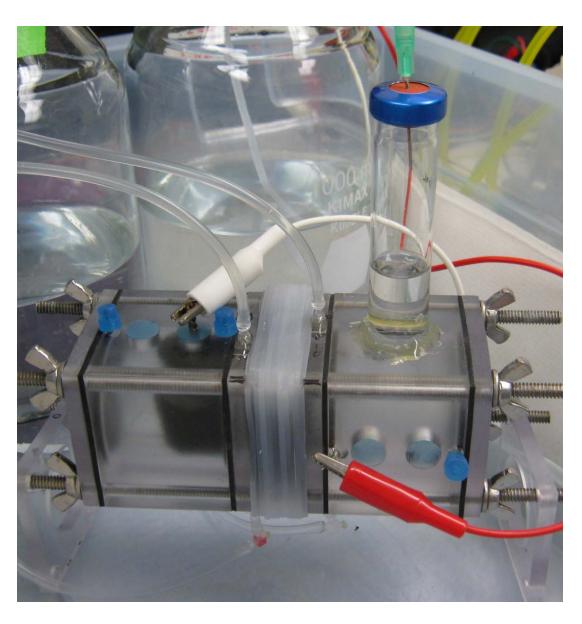
Cathode: oxygen reduction

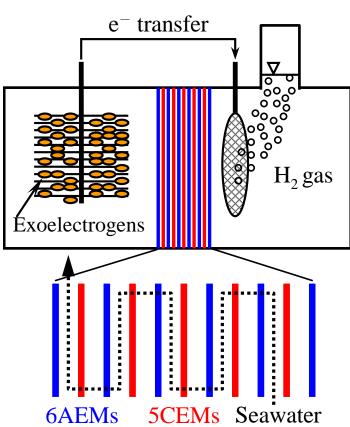
Anode: bacteria produce current

- Higher voltages
 - -1.3 V (vs. MFC alone = 0.5 V)
- Higher power
 - $-4.3 \text{ W/m}^2 \text{ (vs. MFC} = 0.7 \text{ W/m}^2 + \text{RED} < 0.15 \text{ W/m}^2)$
- Higher energy efficiency
 - 42% (obtained vs entering and leaving):



MEC + RED = MREC (Microbial RED Elec. Cell)





#3- Capacitive/Battery Mixing Techniques



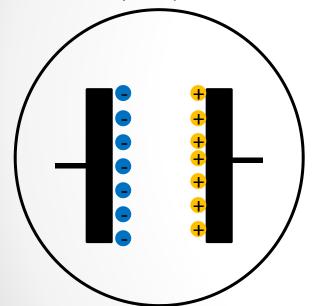




Capacitive energy extraction through Double Layer Expansion

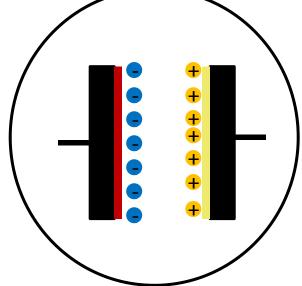
Capacitive energy extraction based through Donnan Potential (membranes)

Battery-like energy extraction with oxidation/reduction (intercalation based) electrodes



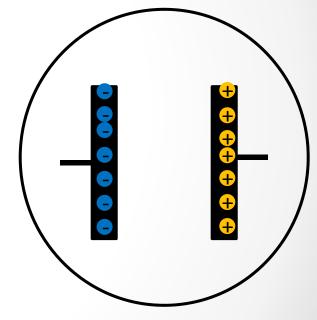
Capmix CDLE:

Capacitive- Double Layer Expansion



Capmix CDP:

Capacitive- Donnan Potential

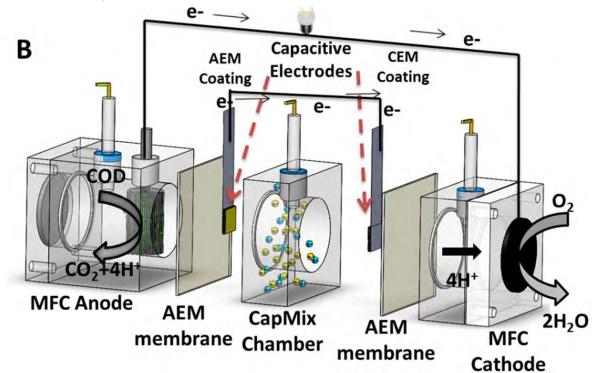


Battmix:

Battery reactions or an entropy battery

MFC + CapMix = CMFC

- Two separate circuits are used to capture energy from the MFC circuit, and separately from the CapMix circuit
- The central chamber is cycled with seawater and freshwater.
- Insertion of electrodes in MFC (CMFC) increased energy capture 65×, power production 46× compared to CapMix alone (up to ~1 W/m² based on CapMix electrodes)





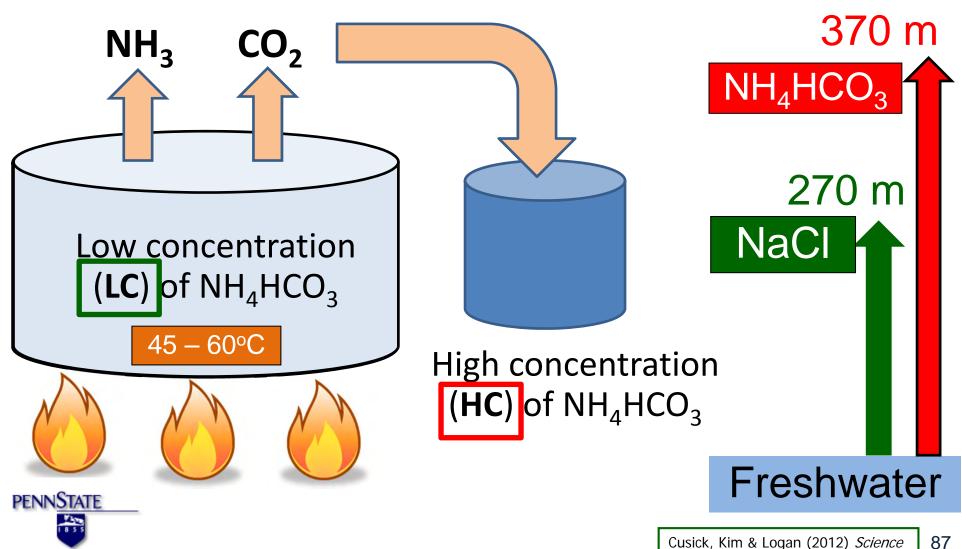
Hatzell et al. (2013) Submitted

New Energy Sources Available using Microbial Electrochemical Technologies (METs)

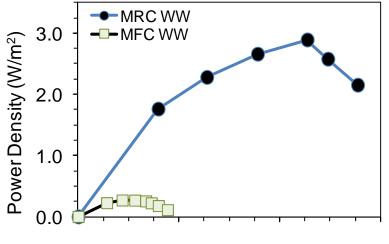
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 (this is how much electrical power is produced in USA)
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 (20 GW available where WW flows into the ocean)
- Waste Heat Energy → Capture heat in "water" (USA)
 - 500 GW from industrial "waste heat"
 - 1000 GW from power plant waste heat
 (Does not include solar and geothermal energy sources)



Use waste heat to create artificial "salintity gradient" energy using ammonium bicarbonate



MRFC with: Domestic Wastewater, AmB

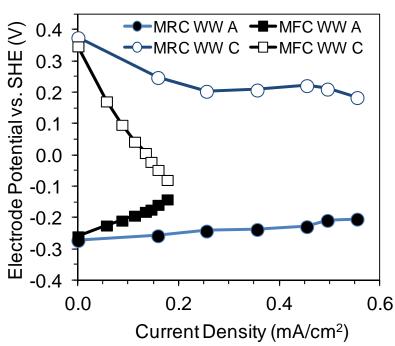


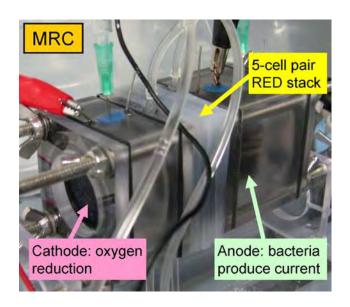
MHRC Peak Power = 2.8 W/m²

= 10× versus MFC with wastewater

Electrodes: 1.8 W/m²

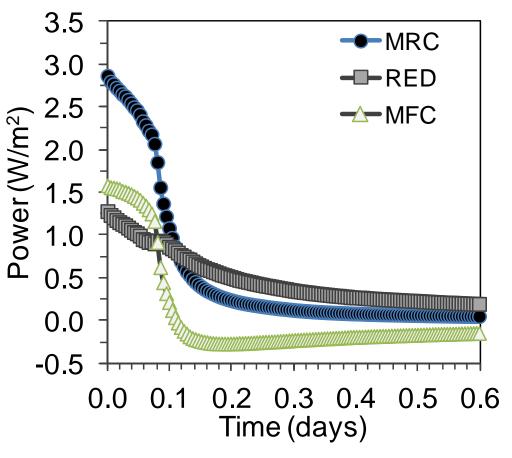
RED: 1.0 W/m^2







Improved performance with Domestic Wastewater Time for treatment greatly reduced



Short Cycle Time:

- 40% COD removal per cycle
- 25% COD removal in 2 hrs (suggests only sCOD removal) (typical of biofilm processes)



Conclusions

- New renewable energy technologies can be created using electro-active microorganisms:
 - Exoelectrogens- make electrical current
 - Electrotrophs- consume electrons, make H₂ and CH₄
- METs
 - MFCs= electrical power
 - MECs= H₂ gas
 - MRCs = Just add (salt) water to supply extra power
 - CMFCs= Using electrochemical fields to enhance energy production
- Pilot scale METs
 - MECs= it worked! (although CH₄ recovered not H₂)
 - MFCs- On the way...
 - MRCs- Still a bit in the future.
- Stay tuned!

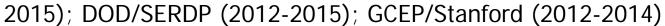


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- The Francqui Foundation, for their support of:
 - Sabbatical at Ghent University, Fall 2013
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 - Universiteit Antwerpen, Prof. Ludo Diels
 - Université Catholique de Louvain (UCL), Prof. Laurent Francis
- My collaborators at the universities and institutes listed below















Water Desalination and Reuse Center



DeTao Masters Academy

Additional Information

Email: blogan@psu.edu

Logan webpage: www.engr.psu.edu/ce/enve/logan/

International MFC site: www.IS-MET.org

YouTube: YouTube/user/MFCTechnology

Twitter: MFCTechnology

MFC webcam: www.engr.psu.edu/mfccam

(live video of an MFC running a fan)

