Producing methane from electrical current generated using renewable energy sources using methanogenic microorganisms

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Engineering Energy &
Environmental Institute

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H2E Center

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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 electrochemical technologies?
    - Microbial fuel cells
    - Microbial electrolysis cells for *electromethanogenesis*

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New Energy Sources Available using Microbial Electrochemical Technologies (METs)

- Wastewater organic matter (WW)
  - **15 GW** in wastewater (Savings 3x15 + 17 = 62 GW net)

- Cellulose Biomass Energy
  - **600 GW** available (based on 1.34 billion tons/yr of lignocellulose)
- Salinity Gradient Energy- Natural 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
  - **500 GW** from industrial waste heat
  - **1000 GW** from power production (33% efficient power plants)

(Does not include solar and geothermal energy sources)

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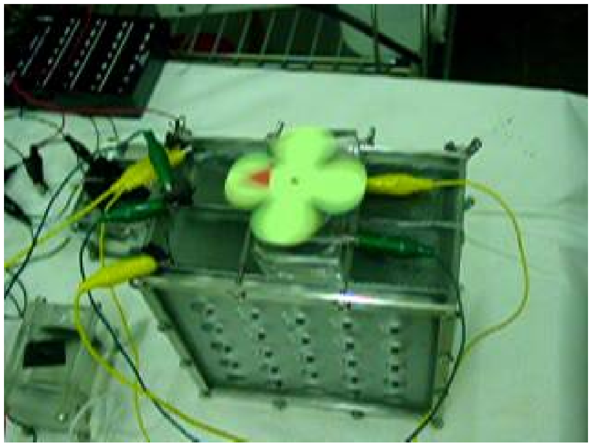
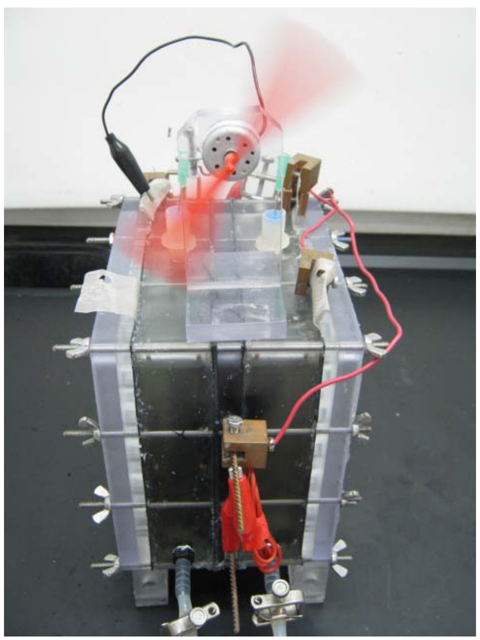
Logan and Rabaey (2012) *Science*
Logan and Elimelech (2012, *Nature*

Demonstration of a Microbial Fuel Cell (MFC)

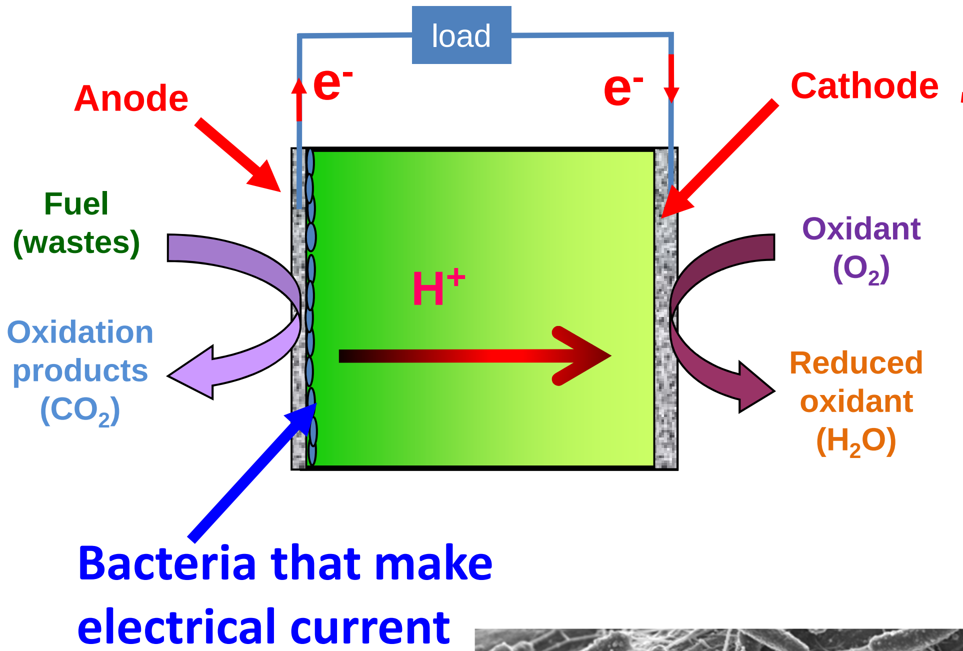


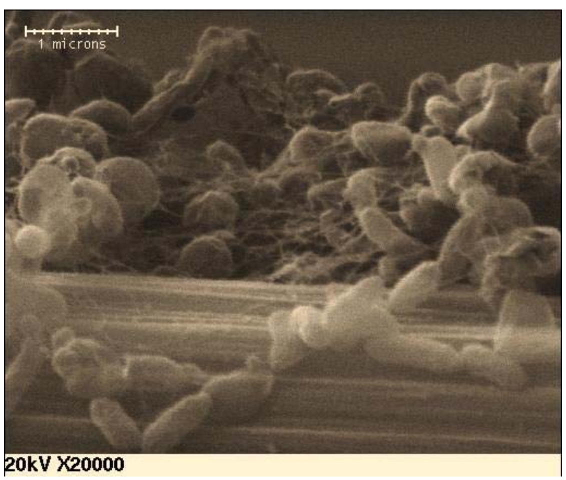


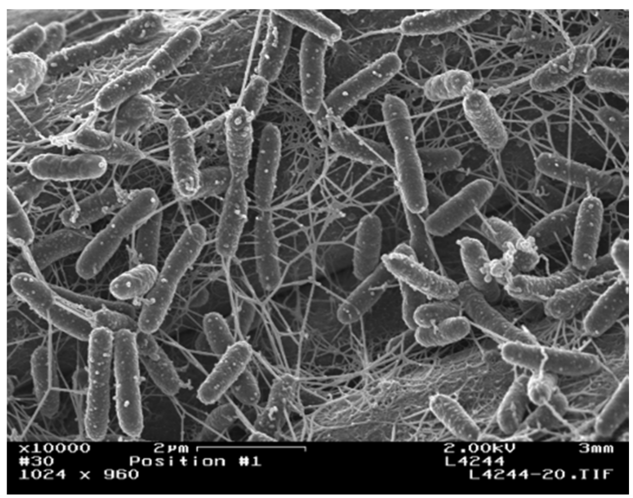
MFC webcam (live video of an MFC running a fan)

www.engr.psu.edu/mfccam

Electrical power generation in a microbial fuel cell (MFC) using exoelectrogenic microorganisms







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

Getting energy from food (biomass)

Oxidation

$C_6H_{12}O_6$ -> $6CO_2$ + 24 e- → NADH

(e^- transporter)

Reduction

NADH

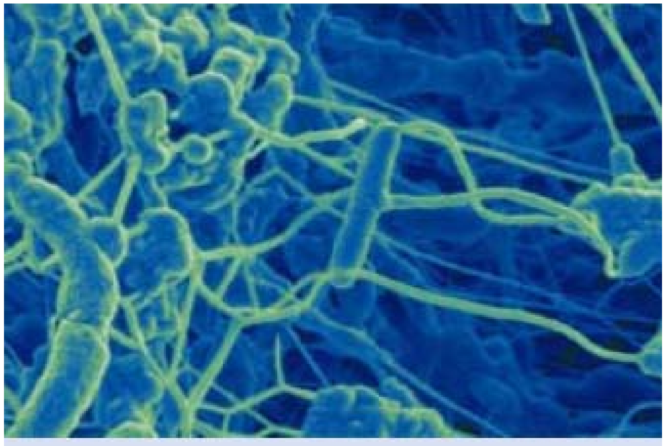
(Electron transfer)

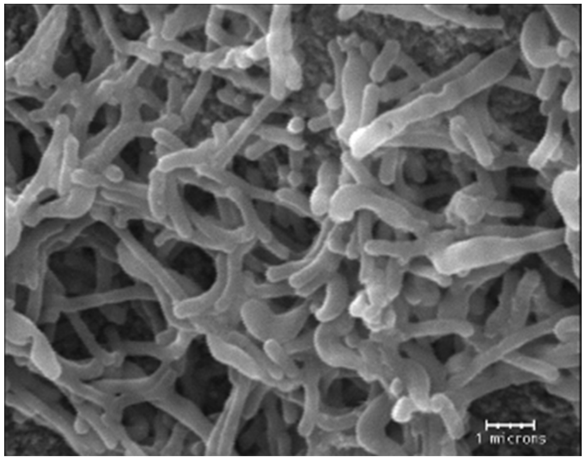
O_2 → H_2O

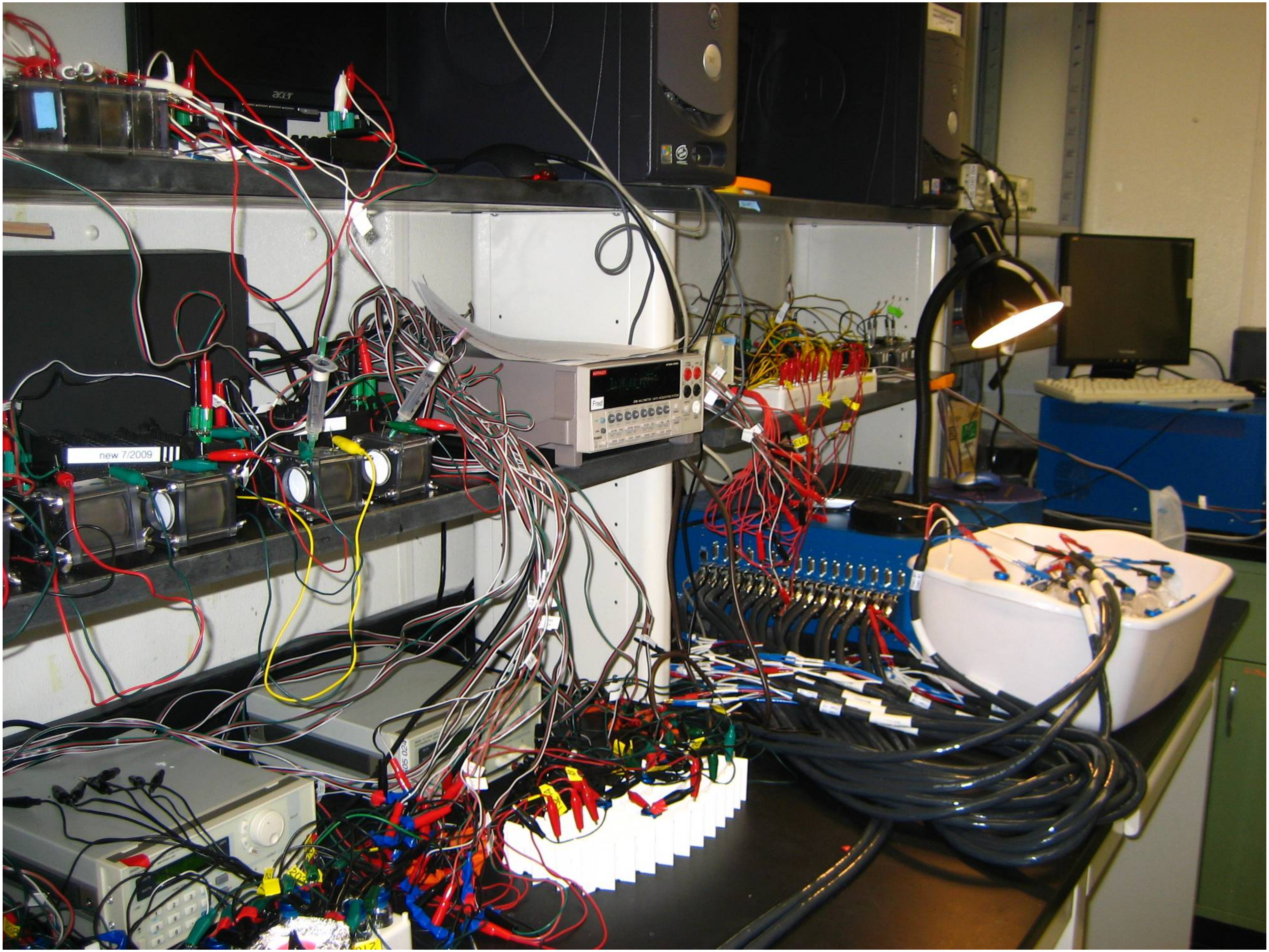
Respiration is the key for capturing energy from food... for humans and bacteria

Electro-active Microorganisms

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



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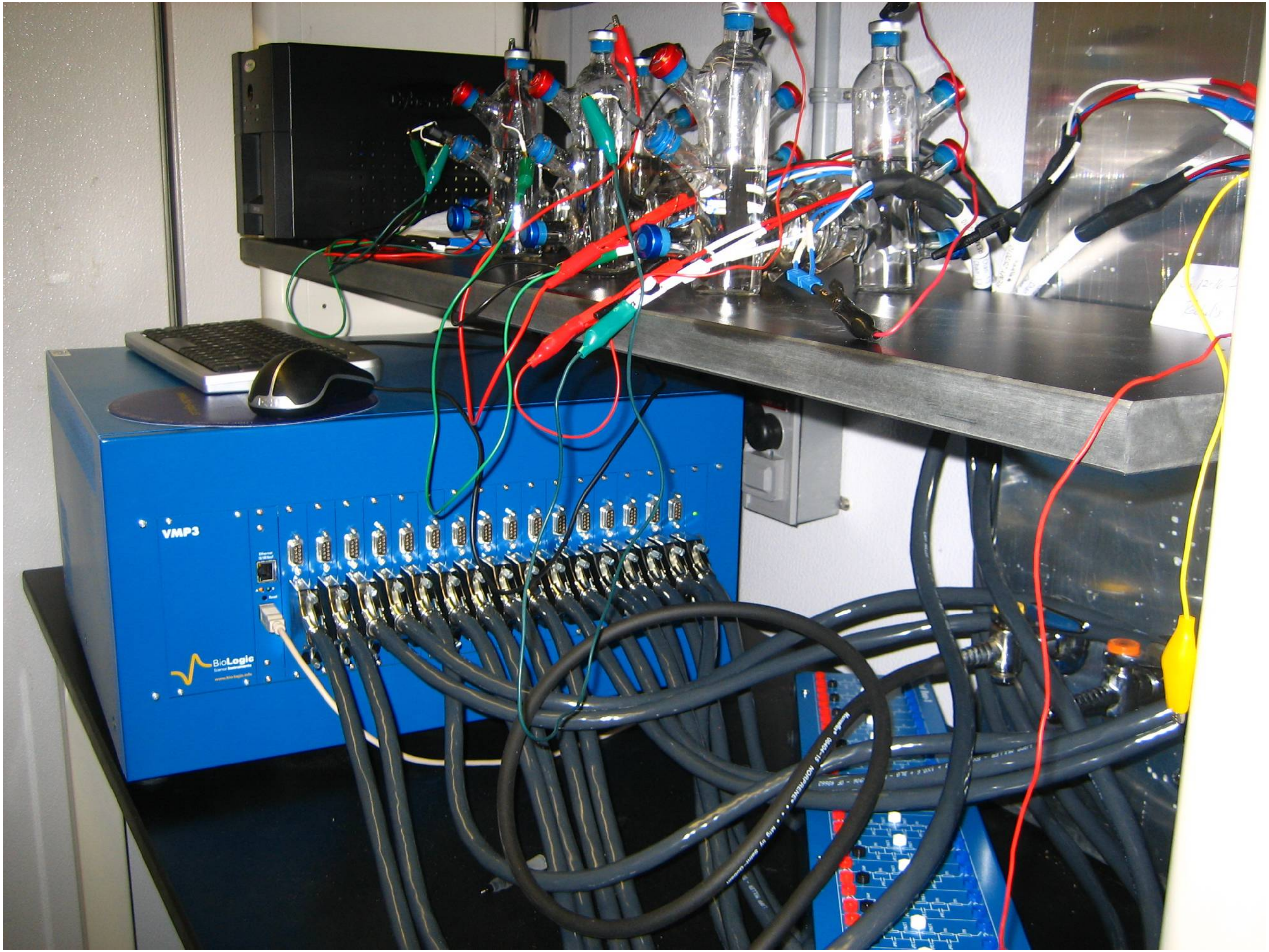
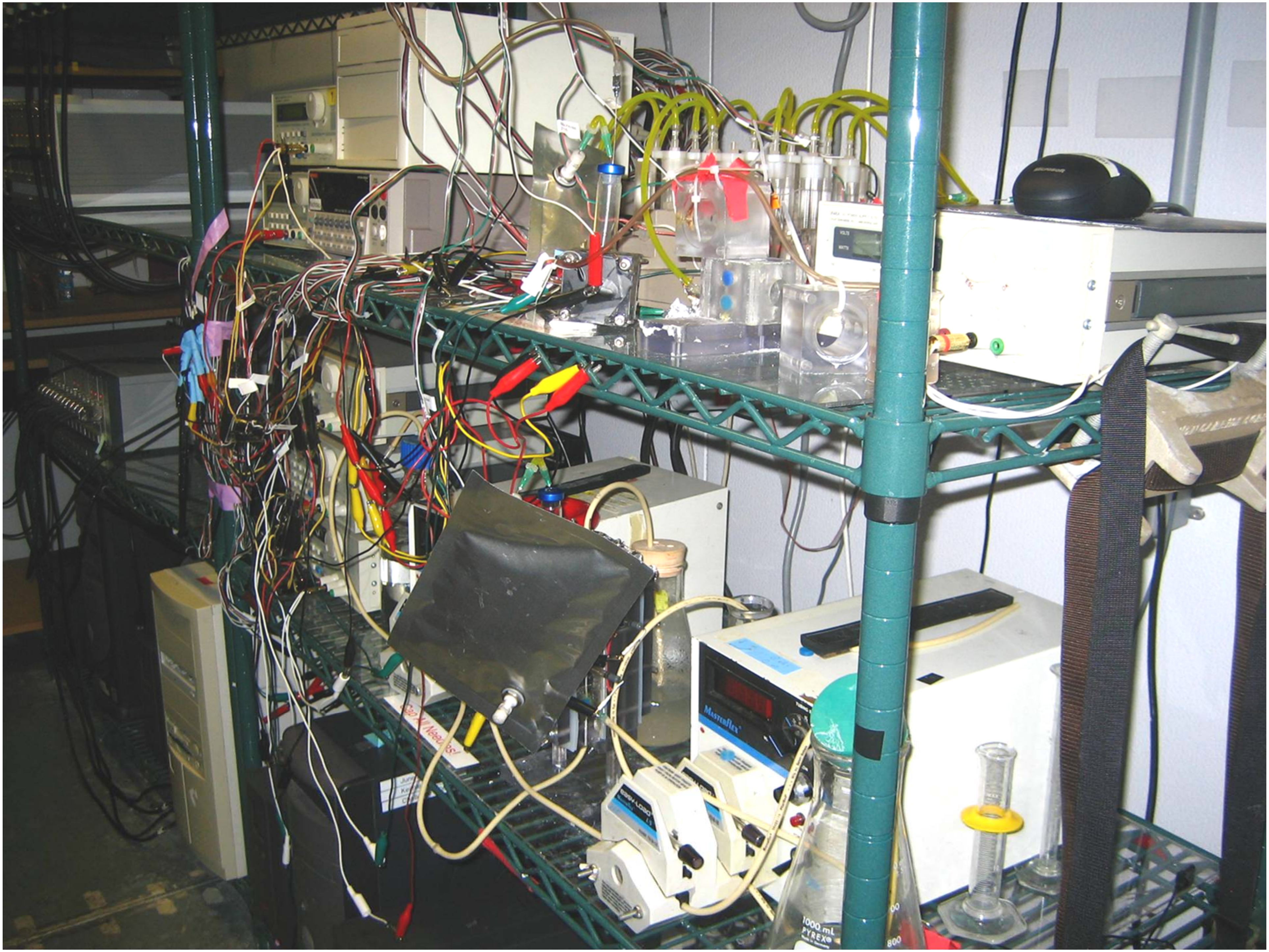
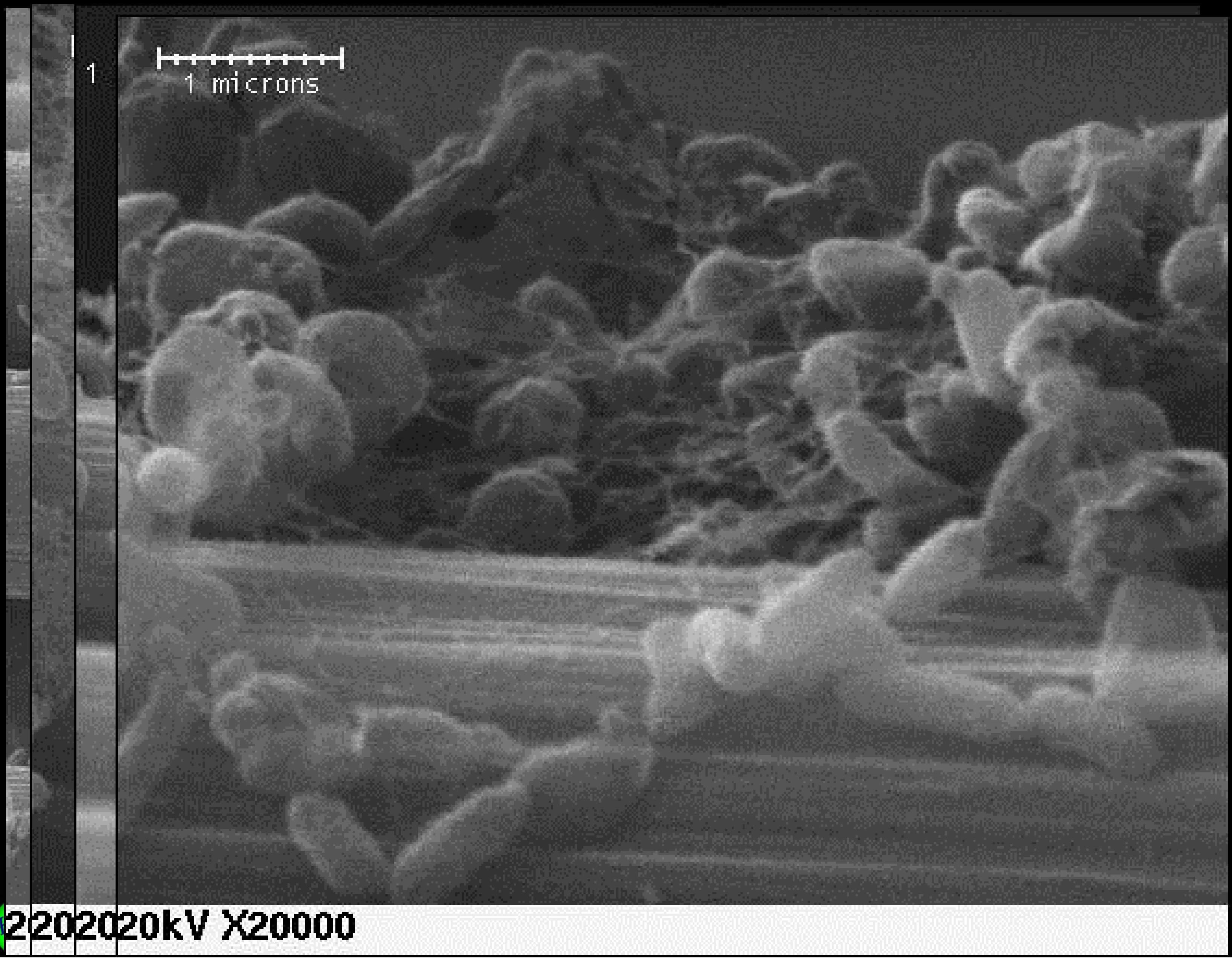

VMP3
BioLogic


Masterflex
1000 mL
PYREX

Electro-active Microorganisms

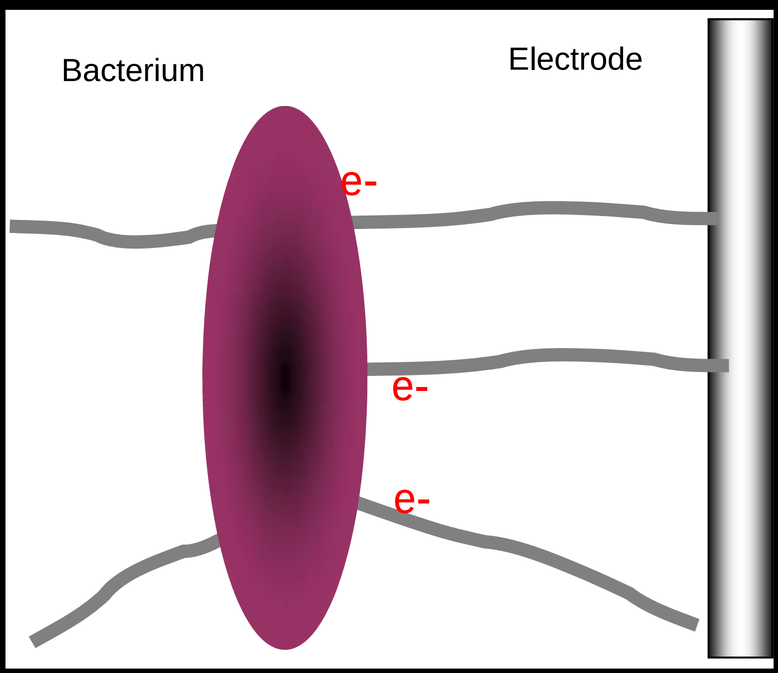
- Exoelectrogens
  - Microbes able to transfer electrons to the outside the cell
- Electrotrophs
  - Microbes that can accept electrons into the cell

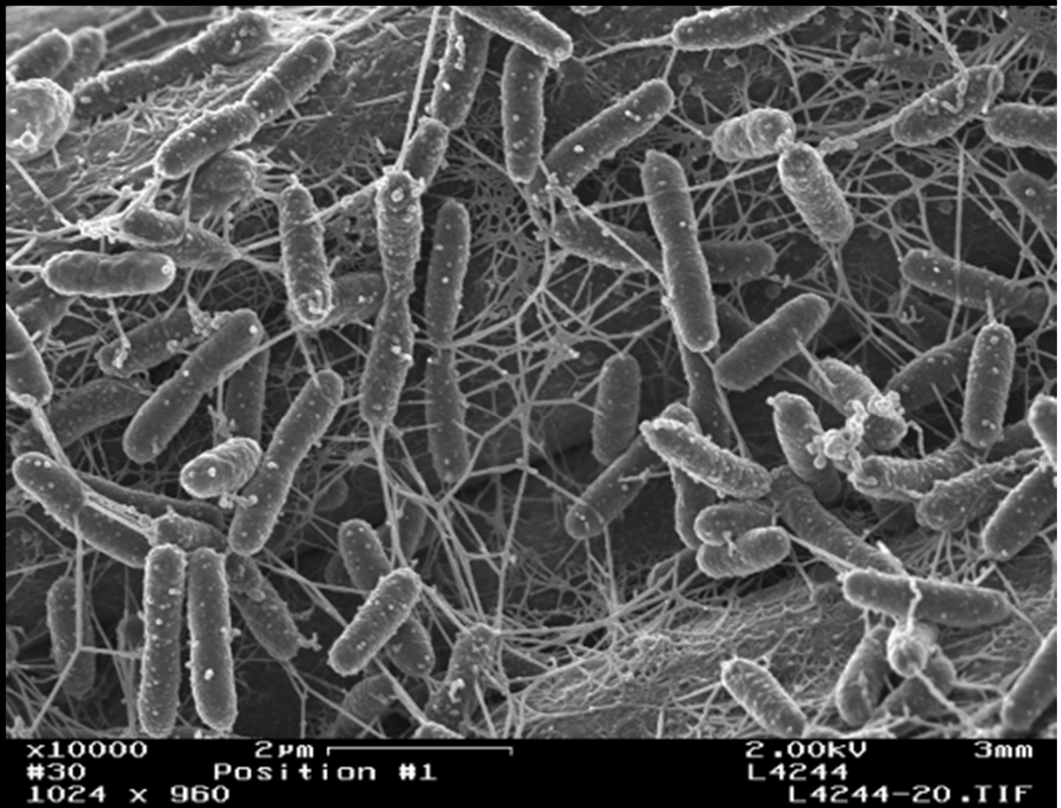
Exoelectrogens: Bacteria rapidly colonize the anode



Mechanisms of electron transfer in the biofilm:

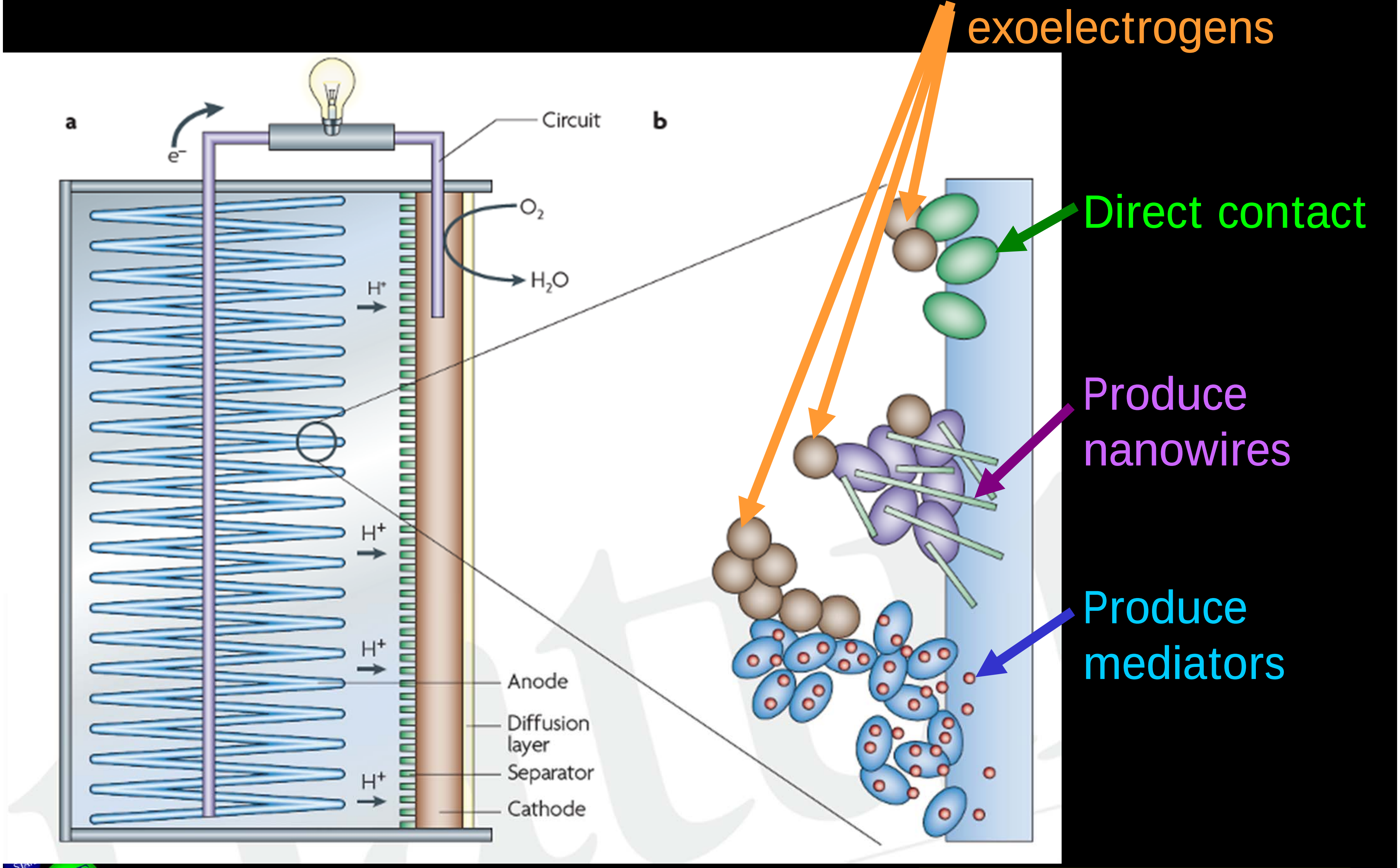
Nanowires produced by bacteria !?!





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

Electrogenic biofilm ecology



Logan, *Nature Rev. Microbiol.* (2009)

Electro-active Microorganisms

- Exoelectrogens
  - Microbes able to transfer electrons to the outside the cell
- Electrotrophs
  - Microbes that can accept electrons into the cell

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Examples of chemicals used by electrotrophs

- Dissolved oxygen
  - Current generation enhanced in the absence of a platinum catalyst
- Nitrate
- Metals (Copper)
- CO_2 reduction by methanogens

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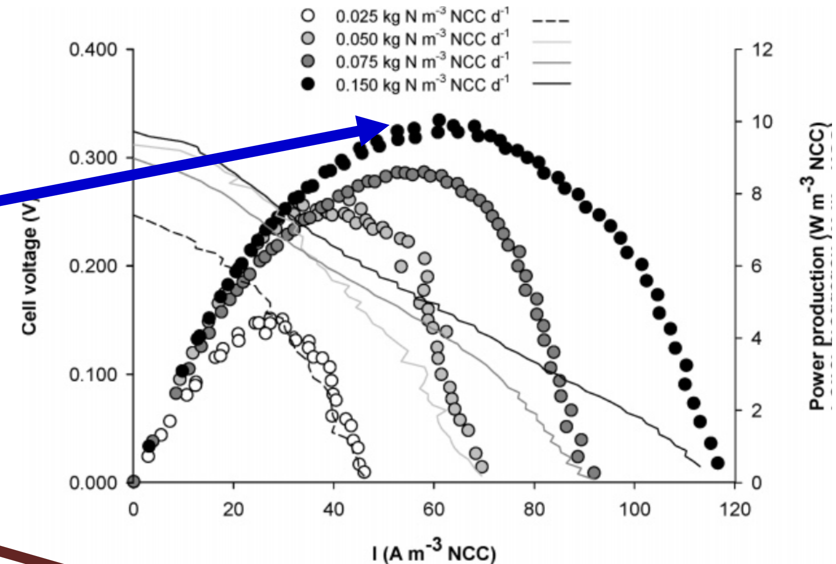
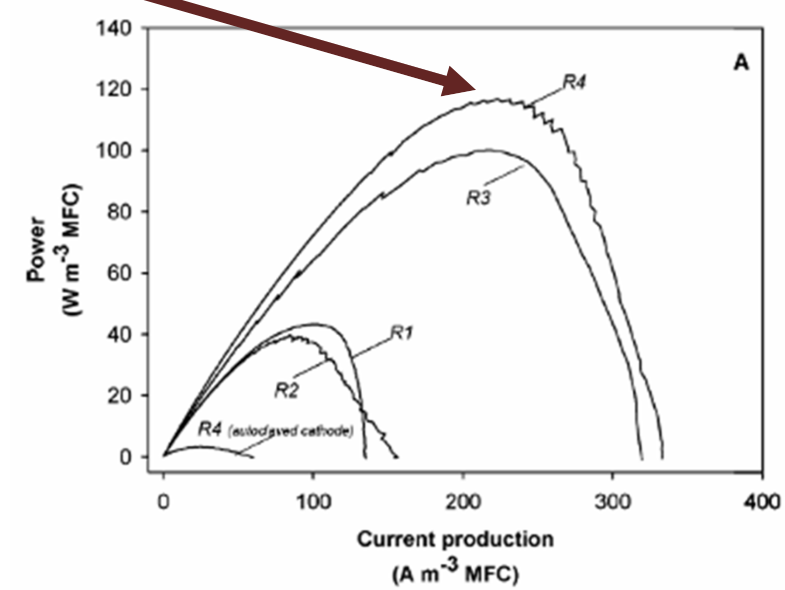
Electrotrophs: Biocathodes in MFCs

- Bacteria use
  - Nitrate (NO_3^-) 10 W/m^3
  - Oxygen (O_2) 120 W/m^3 (polarization) 83 W/m^3 (continuous)

Current higher compared to abiotic cathodes





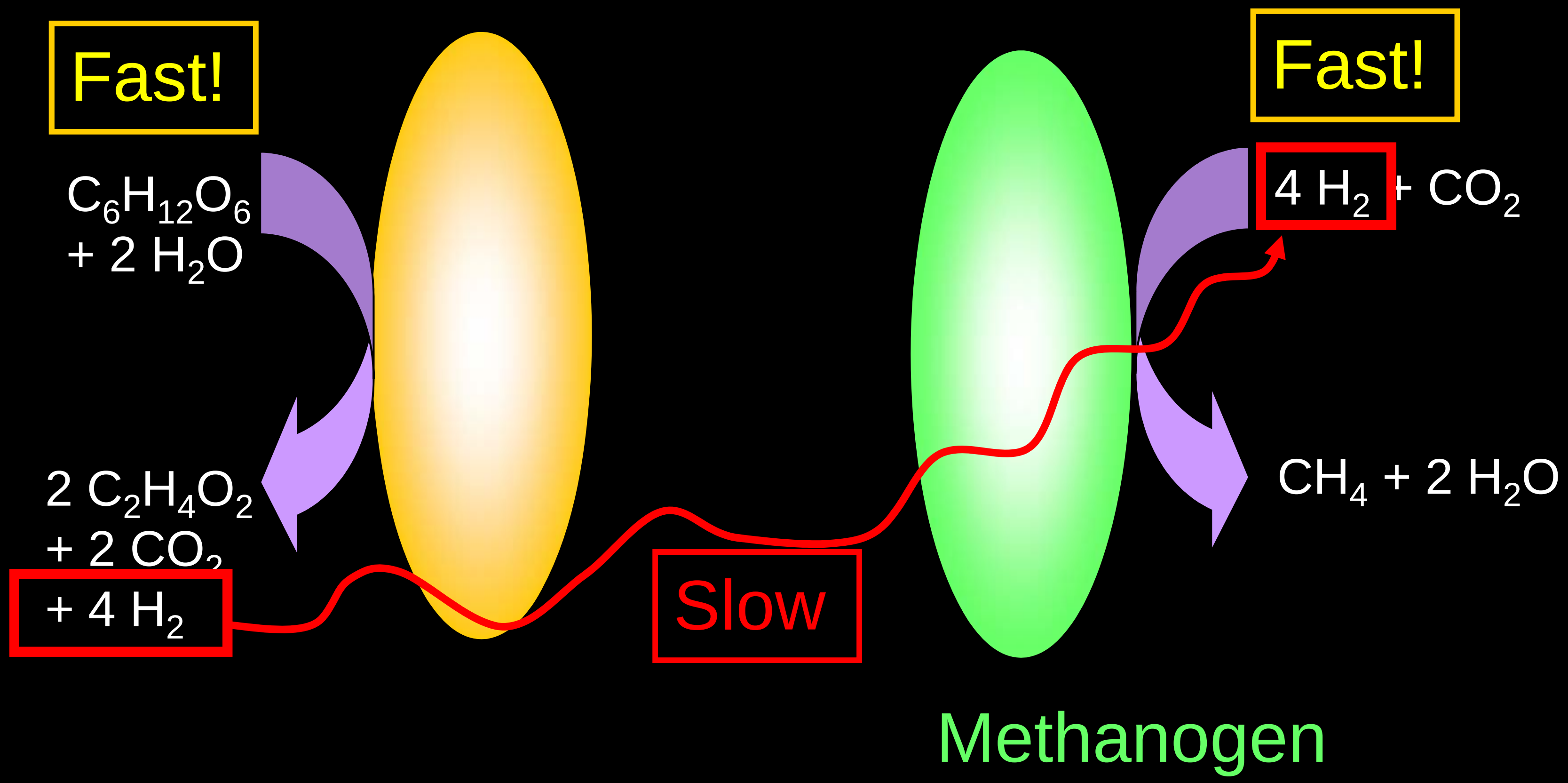
Sources (Ghent University group):

NO_3: Clauwert et al. (2007a), *Environ. Sci. Techonol.*
O_2: Caluwert et. Al. (2007b), *Environ. Sci. Technol.*

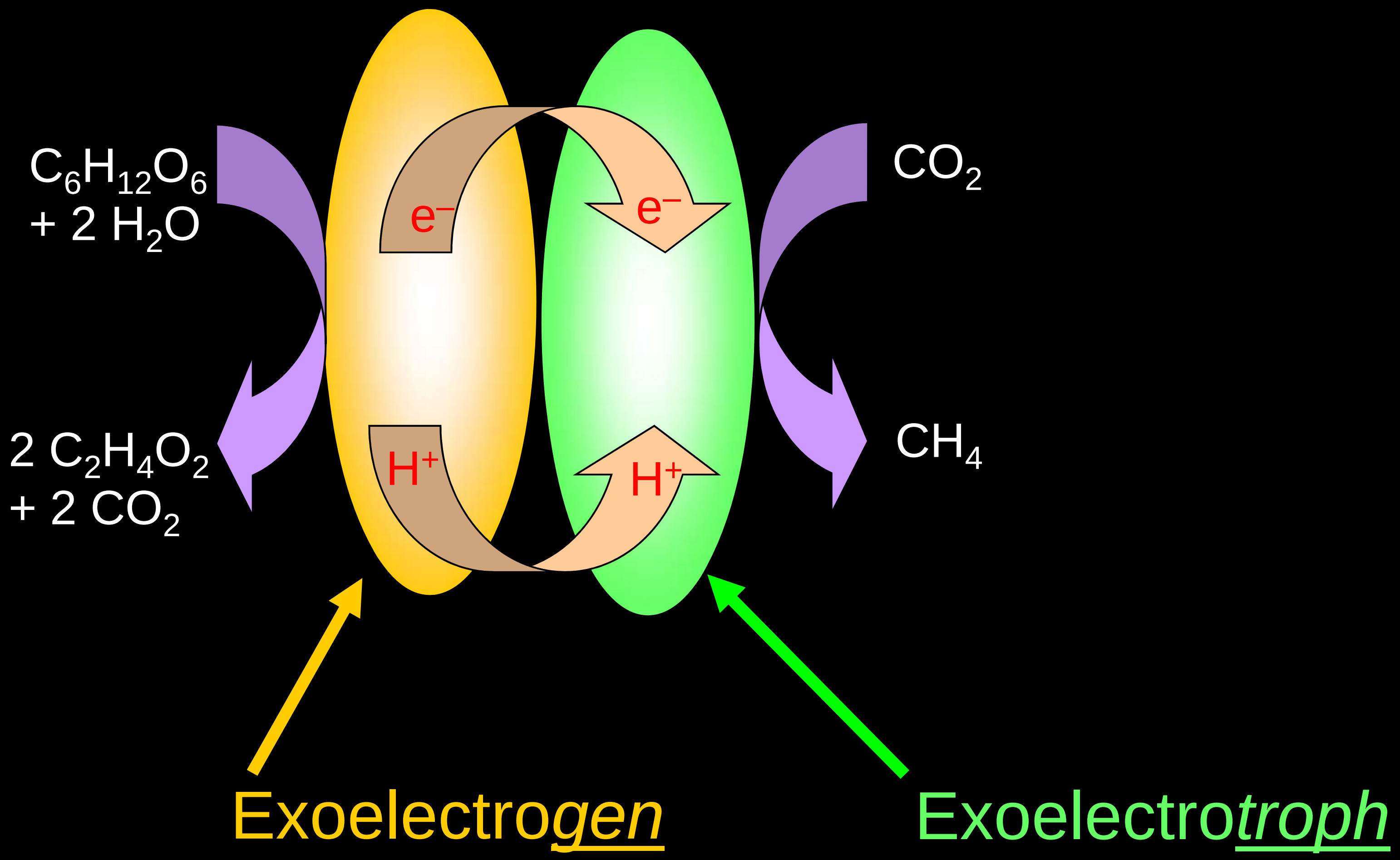
Examples of chemicals used by electrotrophs

- Dissolved oxygen
  - Current generation enhanced in the absence of a platinum catalyst
- Nitrate
- Metals (Copper)
- CO_2 reduction by methanogens

Methanogens: Conventional model based on interspecies *hydrogen* transfer



New model includes exoelectroactive microorganisms: electron transfer



What is the evidence for electromethanogensis?

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

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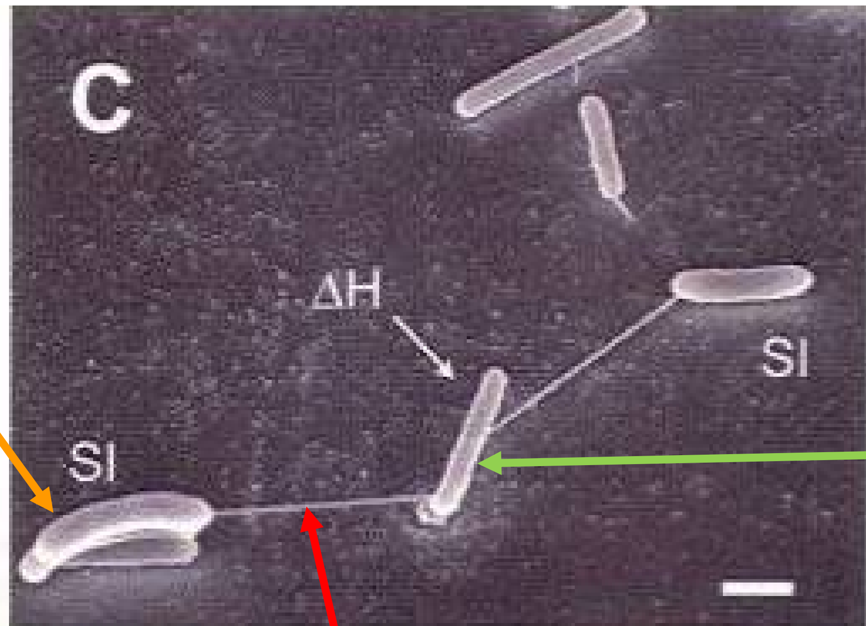
First evidence of direct interspecies *electron* transfer (2006)

SI- ferments propionate, releases electrons



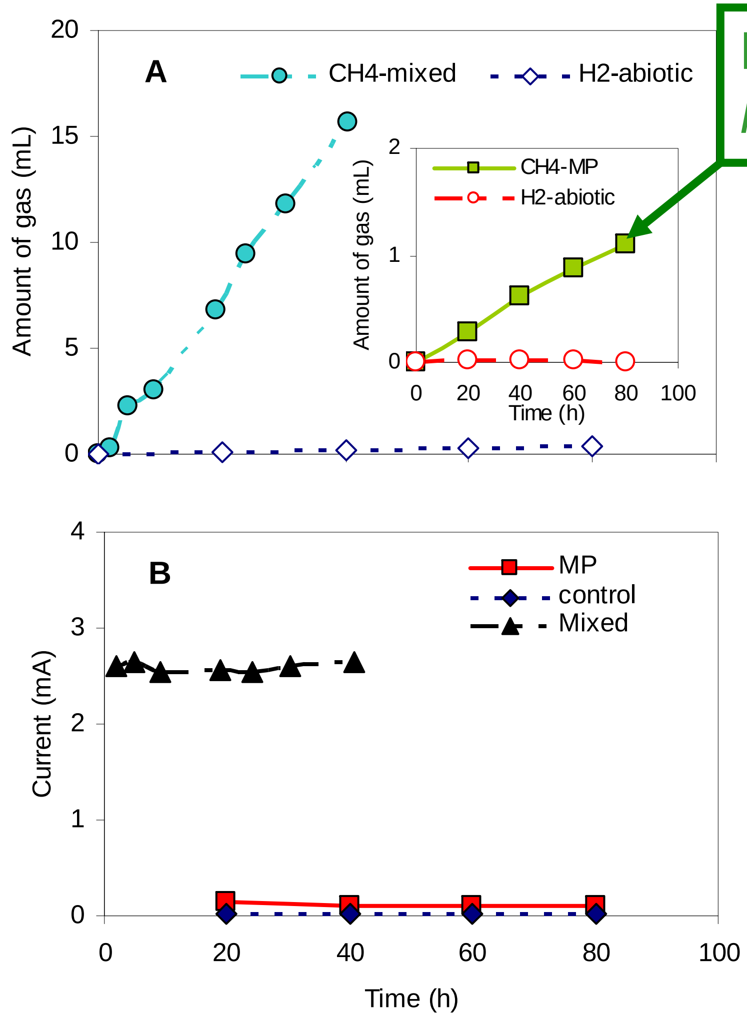
ΔH: Methanogen accepts electrons, makes methane

Nanowires connect fermentative and methanogenic microorganisms

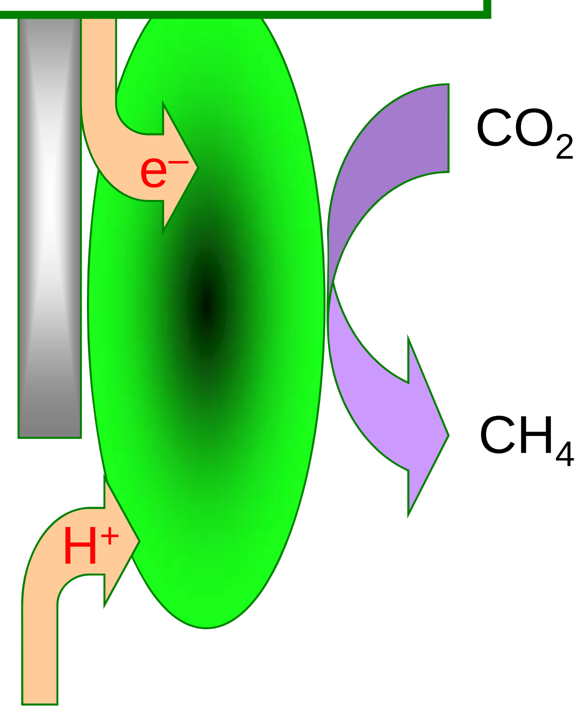
Figure source: Ishii et al. (2005) *Appl. Environ. Microbiol.*

Gorby & 25 others (2006) *Proc. Nat. Academy Sci.*

Electrophic Methanogens



Pure culture of ATCC
Methanobacterium palustre



Mixed culture
(*Methanobacterium palustre*)

Cheng, Call & Logan (2009) *Environ. Sci. Technol.*

Electrically conductive granules in anaerobic digesters

Potential for Direct Interspecies Electron Transfer in Methanogenic Wastewater Digester Aggregates

Masahiko Morita,[a,b] Nikhil S. Malvankar,[a,c] Ashley E. Franks,[a] Zarath M. Summers,[a] Ludovic Giloteaux,[a] Amelia E. Rotaru,[a] Camelia Rotaru,[d] and Derek R. Lovley[a]

Department of Microbiology, University of Massachusetts, Amherst, Massachusetts, USA[a]; Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), Abiko, Chiba, Japan[b]; Department of Physics, University of Massachusetts, Amherst, Massachusetts, USA[c]; and Civil and Environmental Engineering Department, University of Massachusetts, Amherst, Massachusetts, USA[d]

"*The aggregates were electrically conductive,* with conductivities 3-fold higher than the conductivities previously reported for dual-species aggregates of *Geobacter* species in which the two species appeared to exchange electrons via interspecies electron transfer."
(Morita et al. 2011; mBio)

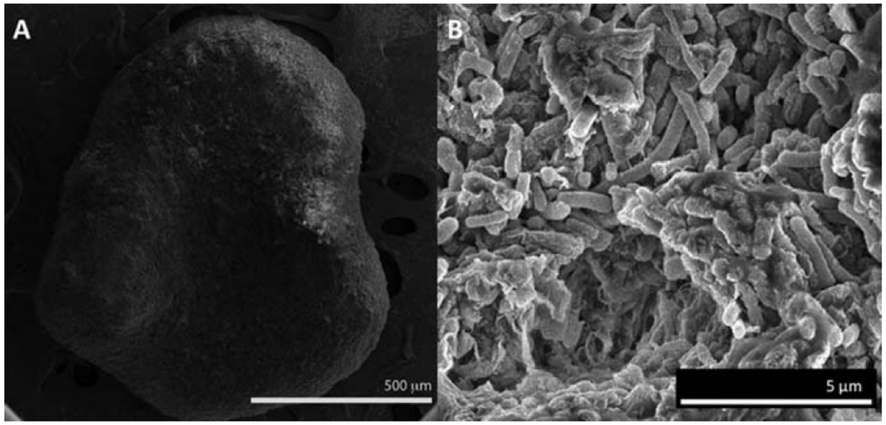


FIG 1 Scanning electron micrographs of an entire aggregate (A) and higher magnification of the aggregate surface (B).

Enhanced methane production in anaerobic digesters

Energy & Environmental Science

Dynamic Article Links

Cite this: *Energy Environ. Sci.*, 2012, **5**, 8982

www.rsc.org/ees

PAPER

Promoting direct interspecies electron transfer with activated carbon

Fanghua Liu,* Amelia-Elena Rotaru, Pravin M. Shrestha, Nikhil S. Malvankar, Kelly P. Nevin and Derek R. Lovley

- It is known that adding activated carbon, which is electrically conductive, to anaerobic digesters increases methane production.

- "GAC also greatly stimulated ethanol metabolism and methane production in co-cultures of *G. metallireducens* and *Methanosarcina barkeri*" (Liu et al., 2012, Energy Env. Sci.)

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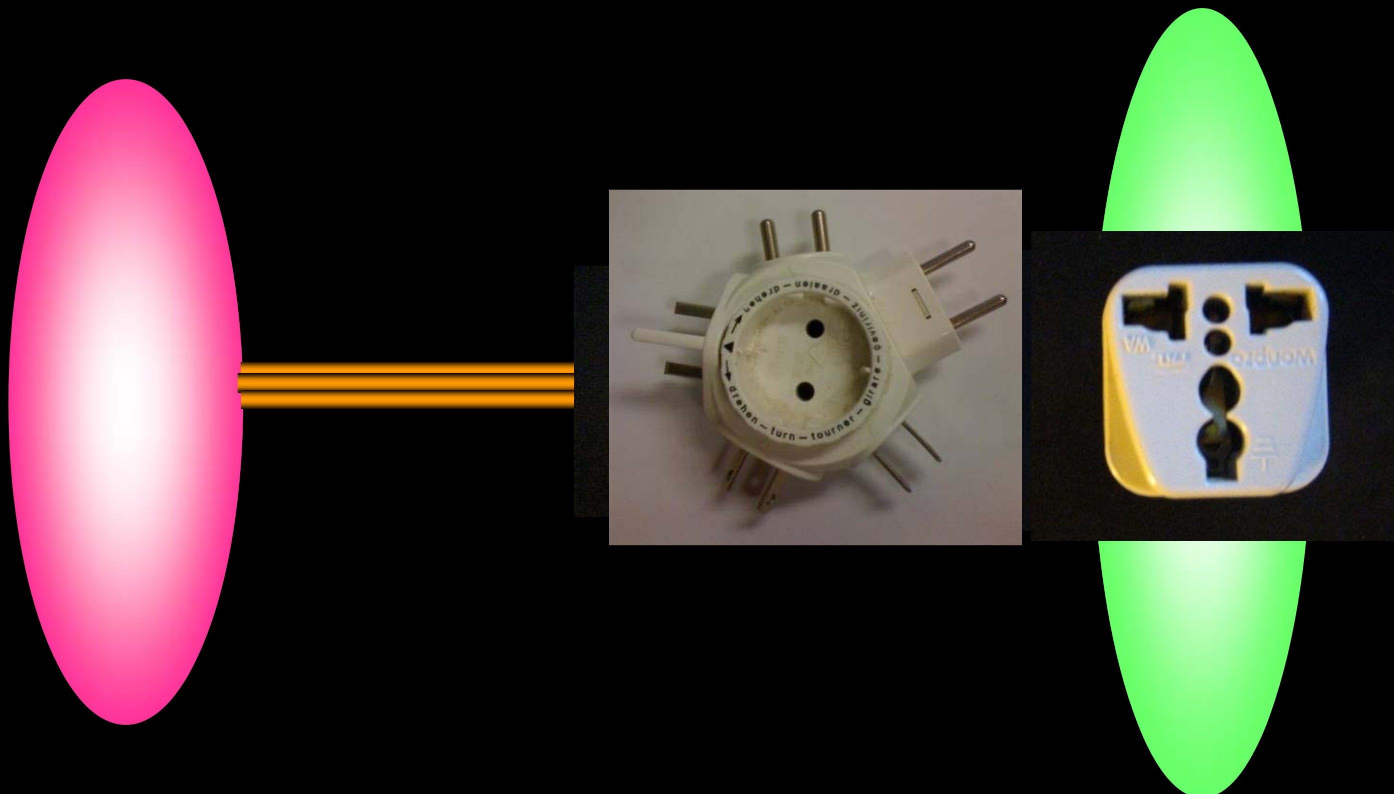
Connections between microbes- Specific or non-specific?



Exoelectro*gen*   Exoelectro*troph*

GCEP PROJECT
Methane production in MECs by *Electrochemical Methanogenesis*

Microbial Electrolysis Cell (MEC):

– Produces hydrogen or methane

– Non-spontaneous reaction (energy needed)

– Completely anaerobic (no oxygen in reactor)

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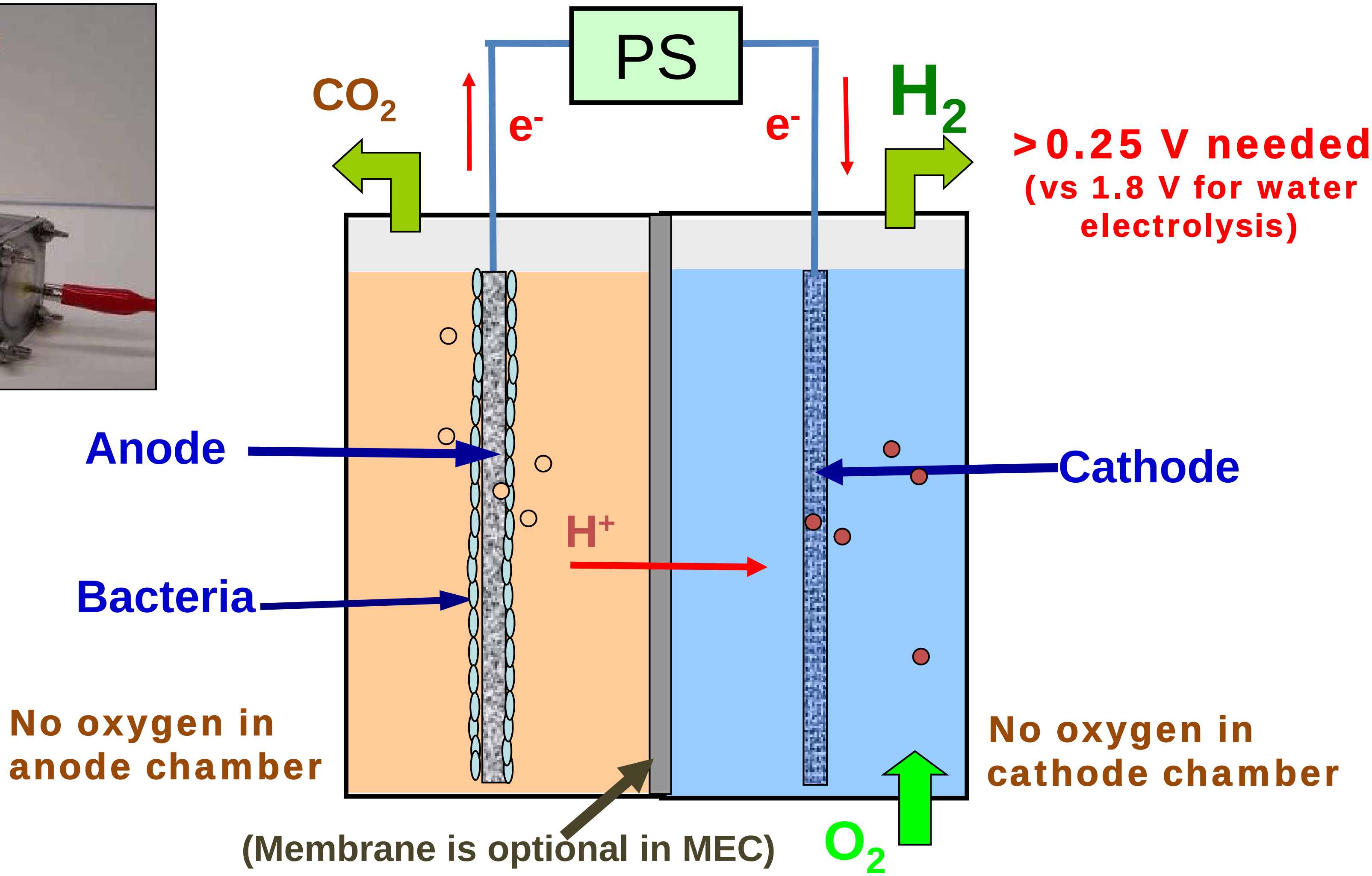
MECs H_2 Production Using Microbial Electrolysis Cells



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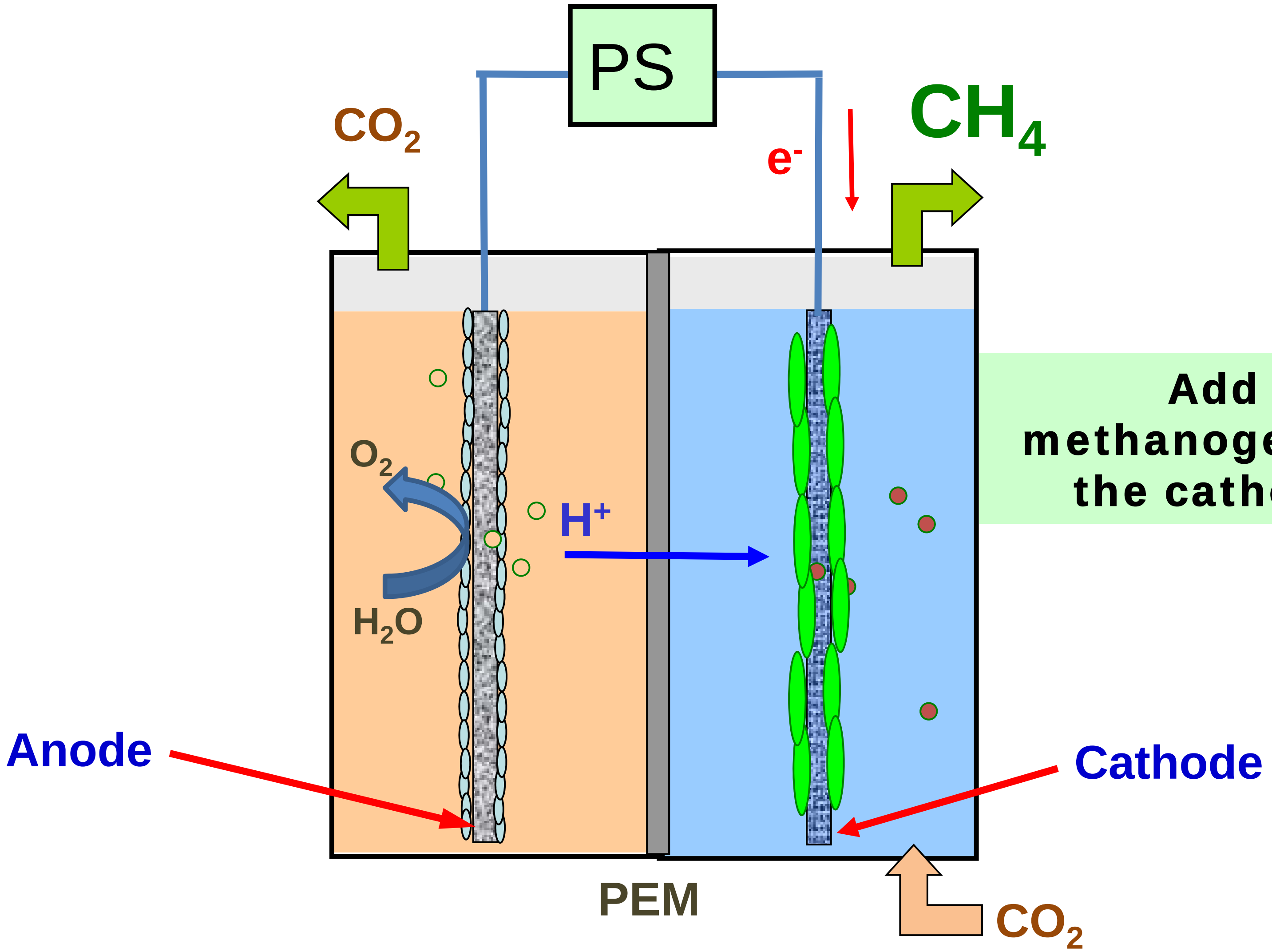
Liu, Grot & Logan (2008) *Environ. Sci. Technol.*

CH_4 from electrical current using an MEC



Add methanogens to the cathode

Cheng, Xing, Call & Logan (2009) *Environ. Sci. Technol.*

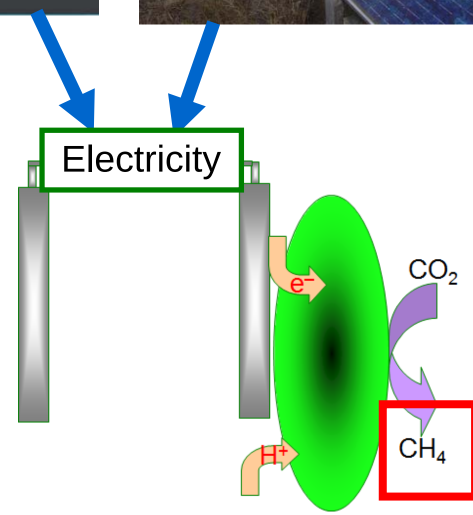
MECs used to harvest methane from renewable forms of electricity generation

Anaerobic digesters

(methane from organic matter)

MECs

Methane from renewable electricity



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Methanogens in various METs

- Basic types of methanogens
  - Hydrogenotrophic (use H_2)
  - Acetoclastic (use acetate)

- Hydrogenotrophic methanogens predominate in:
  - MECs for H_2 production from acetate
  - MFCs with electricity generation from acetate
  - MEC with direct electron transfer to methanogens with minimal H_2 evolution (buffer)

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Reduce overpotential using non-precious metal cathode catalyts

- Goal in MEC is to reduce total applied potential:
  - Total Voltage = Cathode – Anode
- Anode:
  - (Biotic anode produces 0.3 V)
  - Abiotic anode needs: –0.8 V to split water, releasing O_2
- Cathode
  - Direct electron transfer: –1 V
  - H_2 evolution: No catalyst, need <u>more</u> than – 1V
  - H_2 evolution: with Catalyst, need <u>less</u> than – 1V

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Find non-precious metal catalysts that are alternatives to Pt

- Pt
  - Works great for H_2 evolution reaction (HER) but it is expensive and a precious metal
- Stainless steel (SS)
  - Inexpensive, but it has a high overpotential (large energy penalty)
  - Therefore, a low capital cost, but high operating cost
- Molybdenum disulfide (MoS_2)
  - Proposed to be a suitable HER catalyst, but not tested under MEC-like conditions

    (Reference: Hinnemann et al., J. Am. Chem. Soc., 2005, 127, 5308)

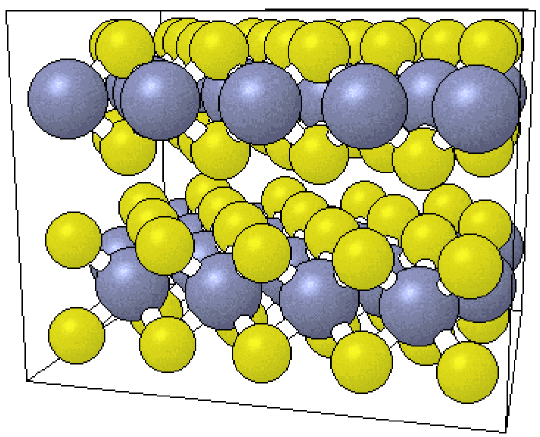
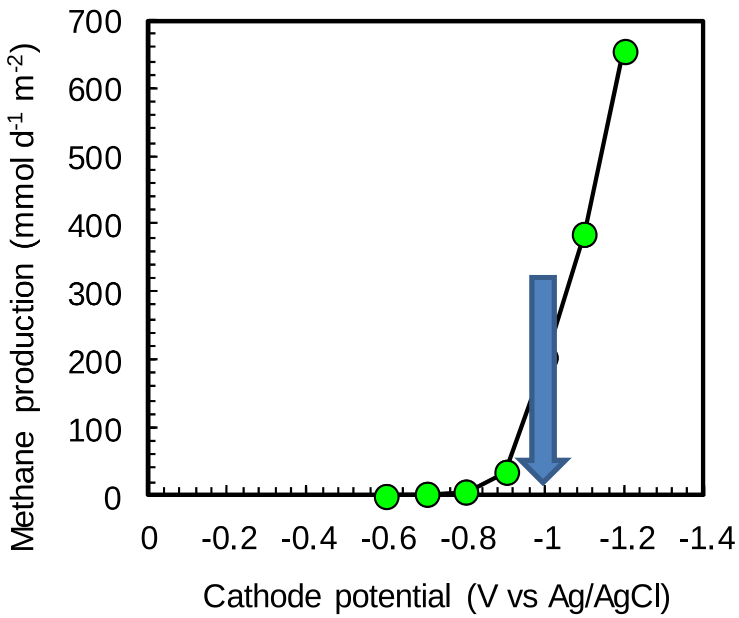
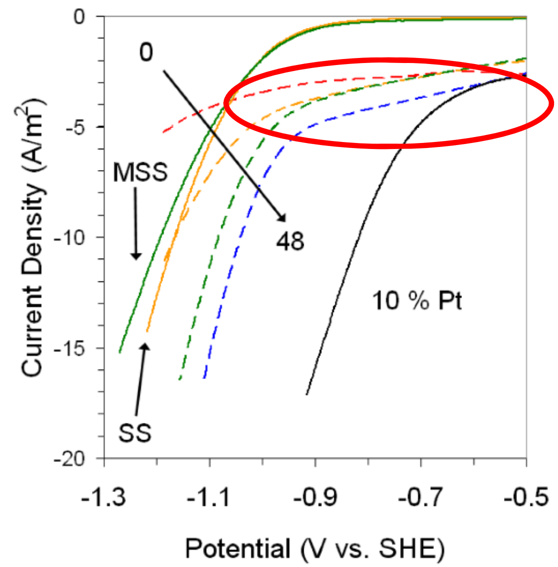


Image: NIST Standard Reference Database No. 42 by P. R. Watson, M. A. Van Hove, and K. Hermann.

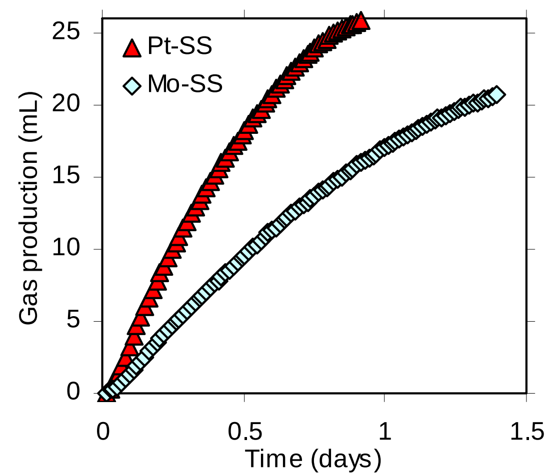
Direct electron transfer



H_2 Evolution with MoS_2 (0-48 g/m^2)



Region of operation



Comparison at same applied potential

Cheng, Xing, Call & Logan (2009) *Environ. Sci. Technol.*

Tokash & Logan (2011) *Int. J. Hydrogen Energy*

Kim & Logan (2011) *Proc. Nat. Academy Sci.*

Tests underway with cathodes

Scaling up MFCs

- This **2-Liter** MFC is in on display at the London Science museum, with the help of:
  - KAUST, Saudi Arabia
  - University of Newcastle, UK
  - VITO, Belgium

- See also the MFC webcam (live video of an MFC running a fan)
  - www.engr.psu.edu/mfccam

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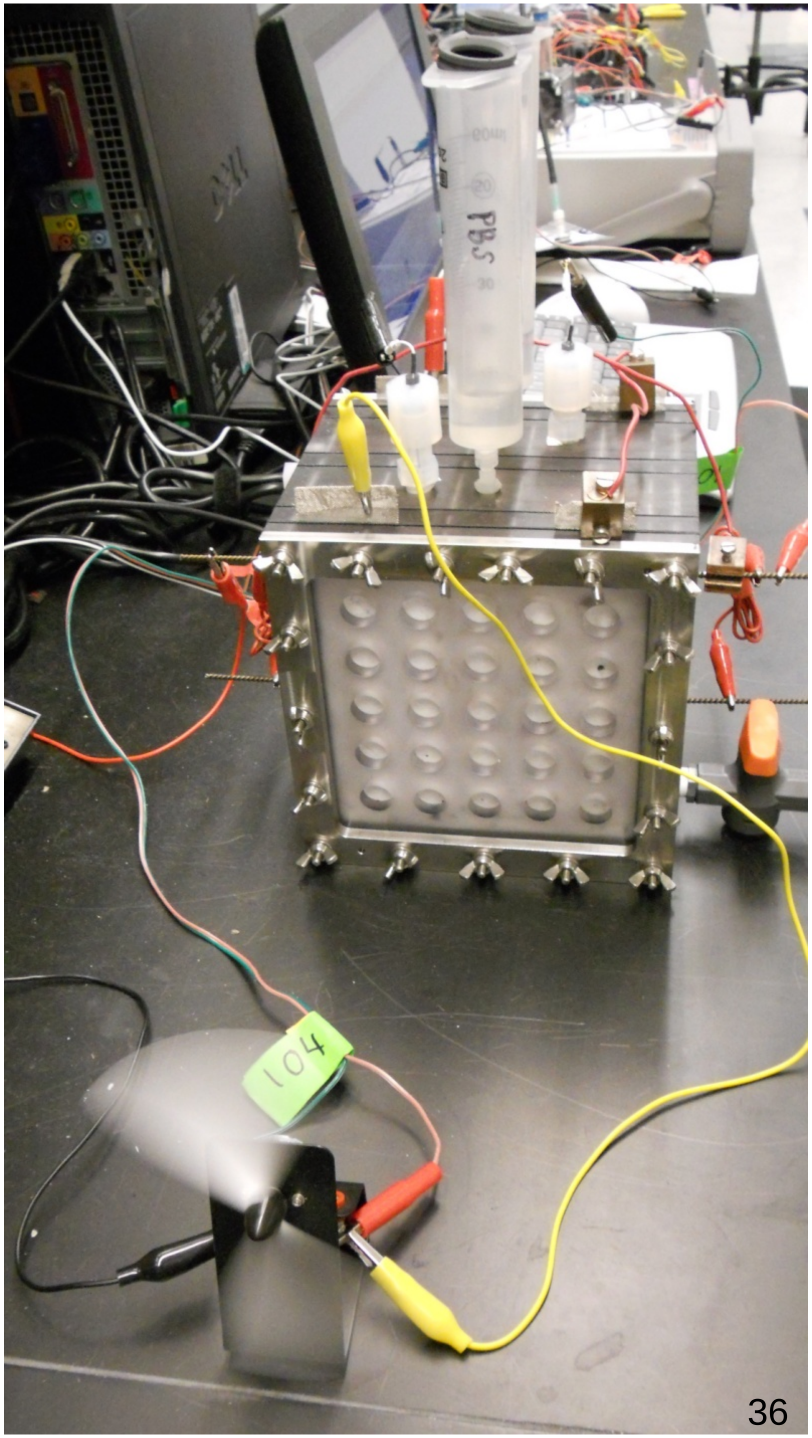
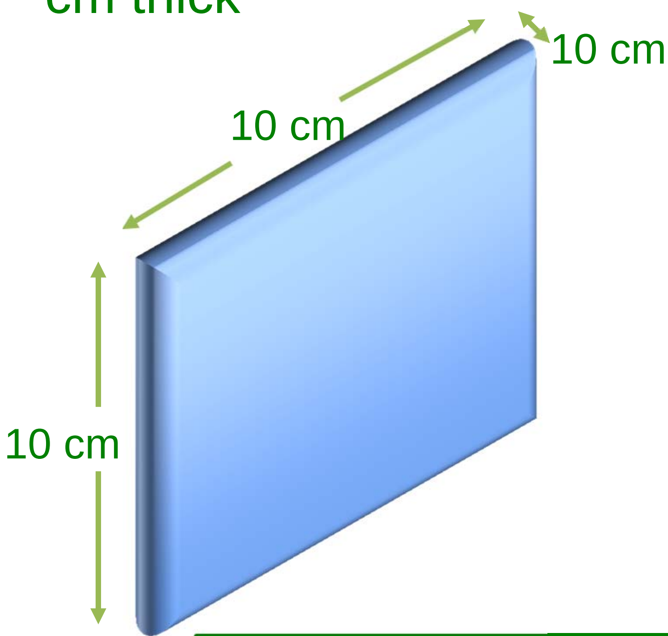
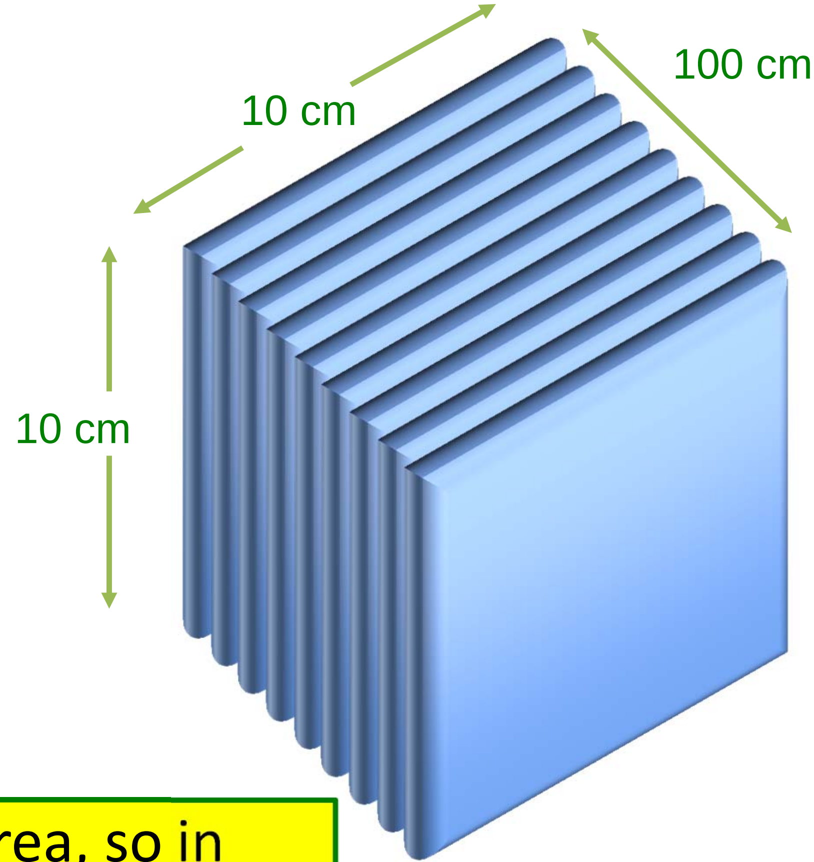


Overall goal: compact reactor design

Assume: One anode-cathode module is 1 m^2 projected area (height x width) and 10 cm thick



Result: 10 modules = 10 m^2



Design: Limited by cathode area, so in this example we achieve 10 m^2/m^3

Logan (2012) *Chem. Sus. Chem.*

MFC Architecture

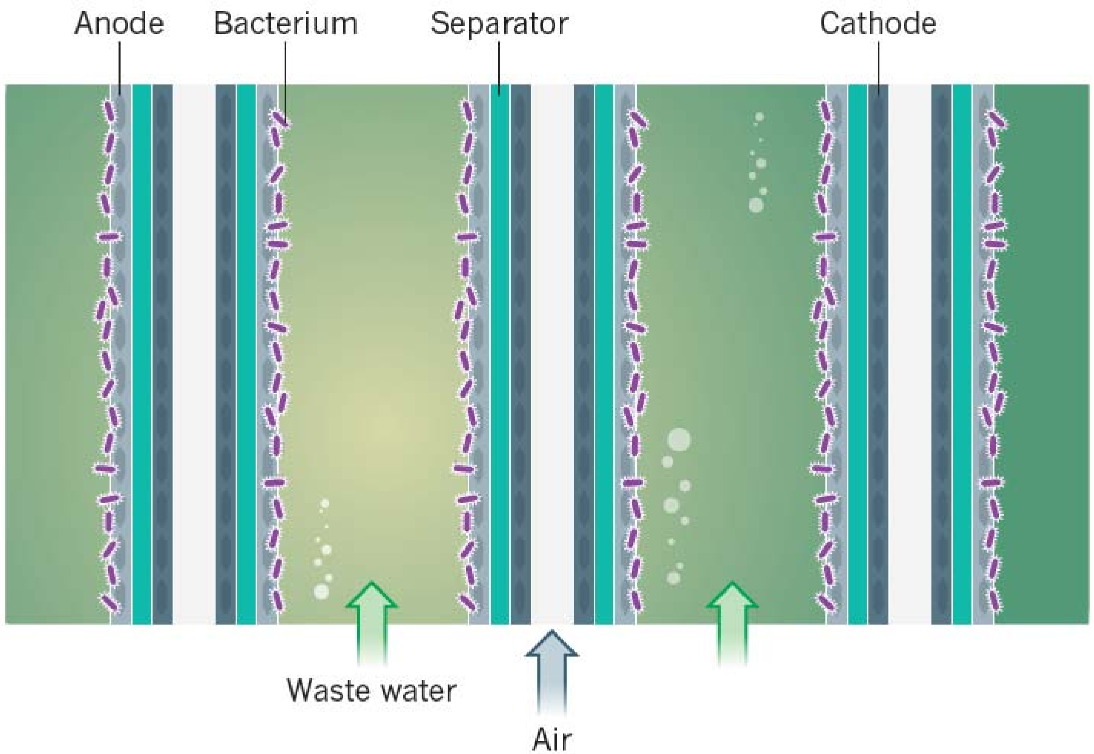


Figure 3 | An MFC stack. MFCs are arranged close together to reduce internal resistance and form compact reactors. Within the stack the electrodes consist of repeating units of an anode coated in a mat of bacteria, or biofilm, an insulating separator and a cathode. Waste water flows over the anodes and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

Logan & Elimelech (2012) *Nature*

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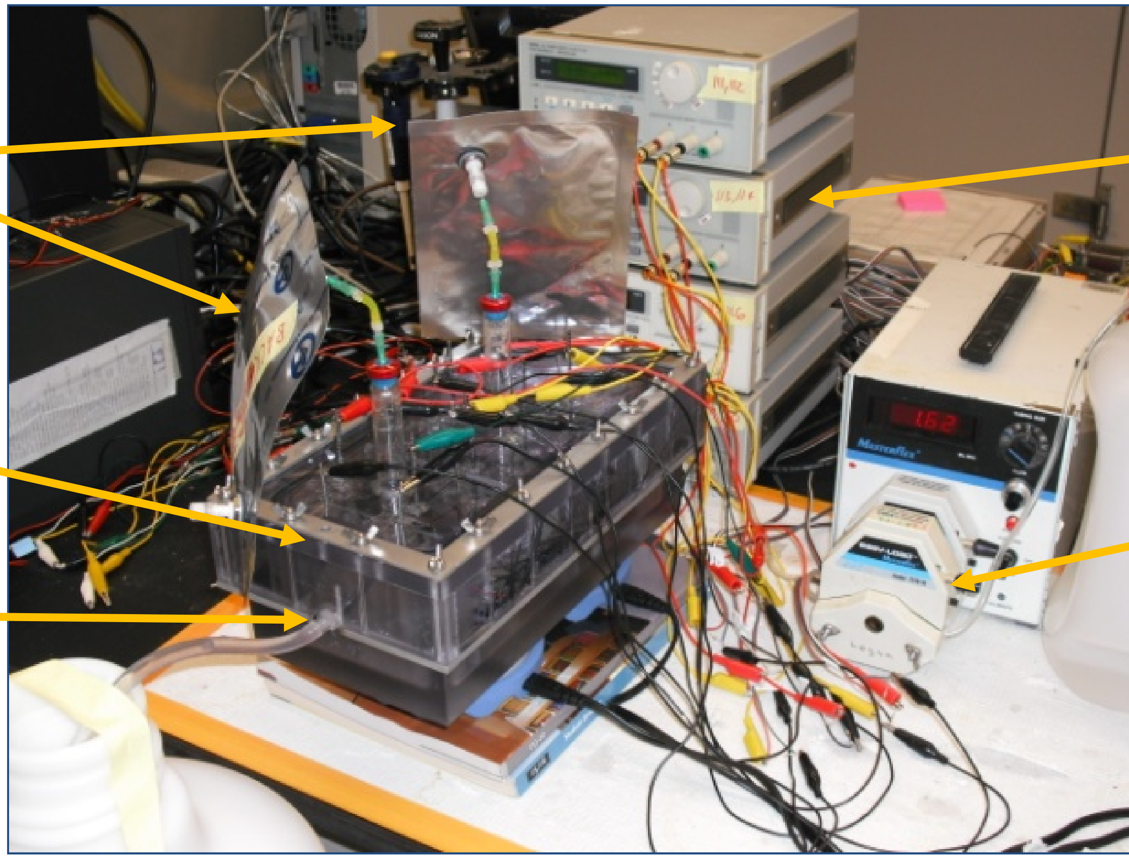
Scaling up MECs

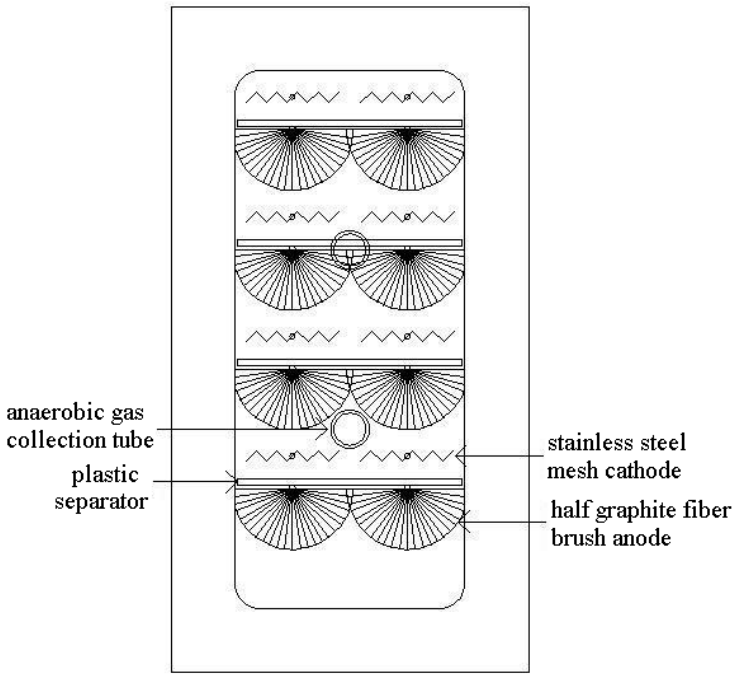
MECs: Bench scale, Continuous flow

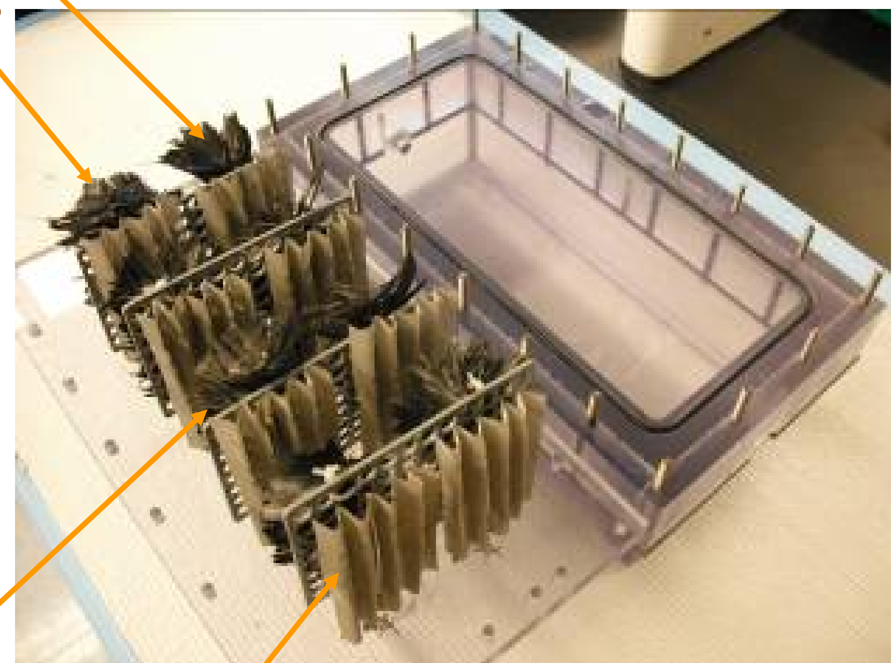


2.5 L with 1 day HRT (acetate fed)

MEC components (2.5 L reactor)

Schematic





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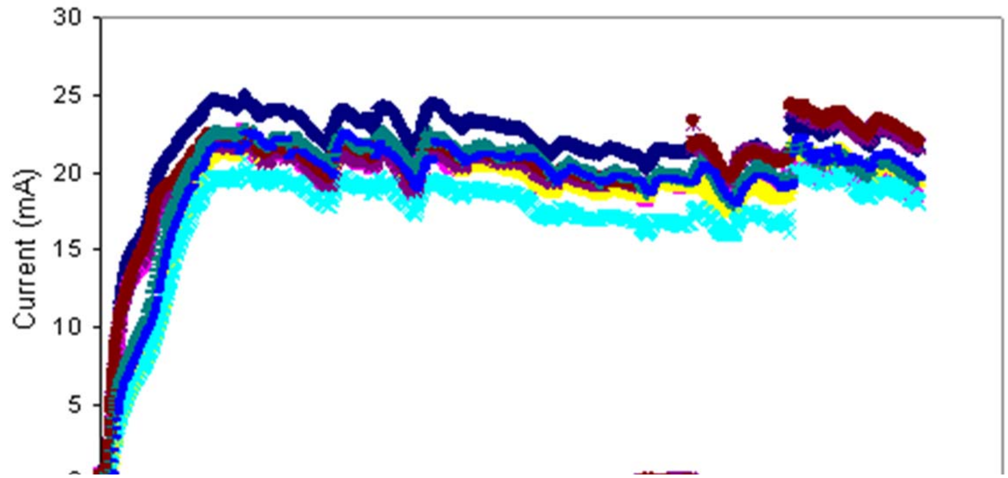
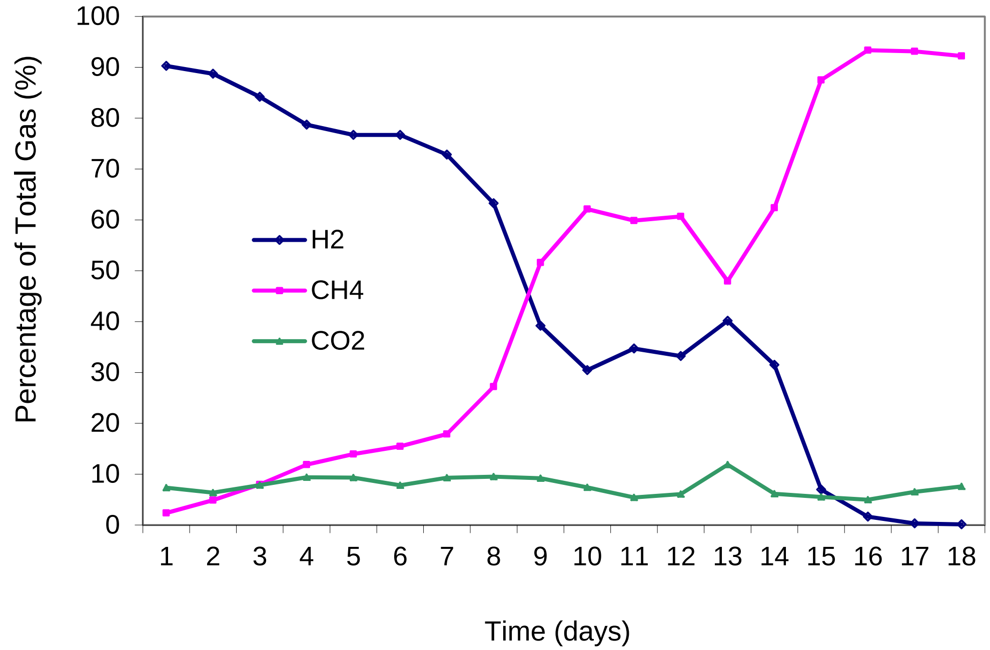
MEC Performance- 2.5 L reactor

Current monitored through each anode, resulted in consistent performance



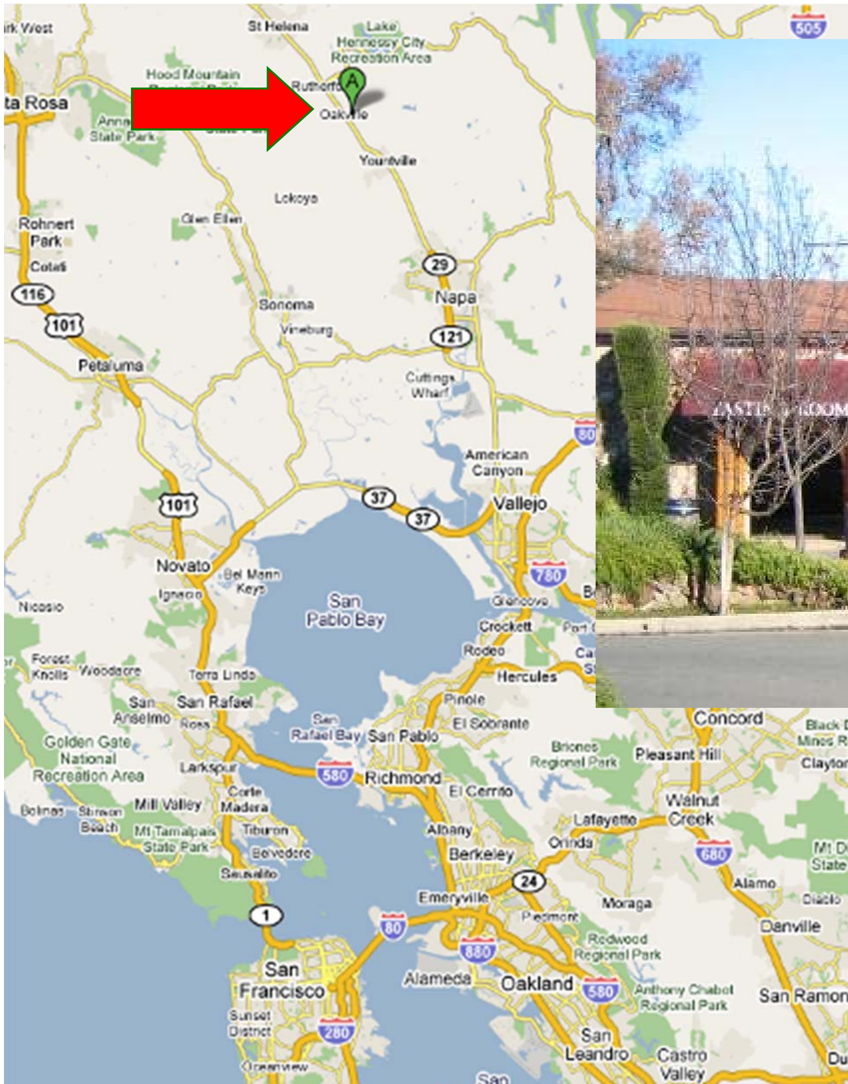
H_2 intially produced, but it all was converted to CH_4



Rader & Logan (2011) *Int. J. Hydrogen Energy*

MEC Field test :

Penn State University @ Napa Wine Company



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

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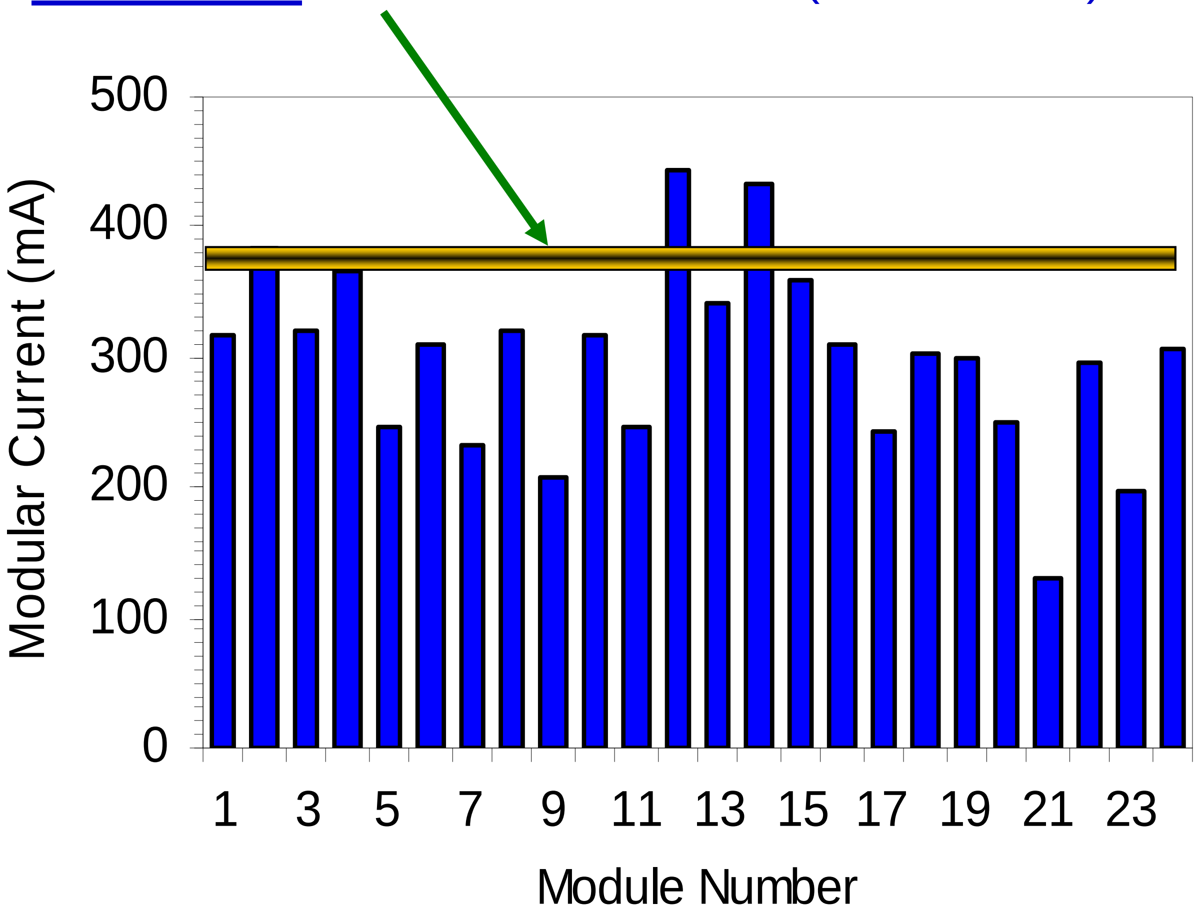
Cusick et al. (2011) *Appl. Microbiol. Biotechnol.*

Individual module performance of the MEC treating Wastewater

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



H_2 intially produced, but it all was converted to CH_4

Cusick et al. (2011) *Appl. Microbiol. Biotechnol.*

New Frontiers in Bioelectrochemical Technologies

- Reverse Electrodialysis Cells (RED) meeting MFCs & MECs→ MRCs
- Phosphorus/struvite recovery
- Microbial desalination cells
  [for water desalination without electrical grid energy]

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New Energy Sources Available using Microbial Electrochemical Technologies (METs)

- Cellulose Biomass Energy
  - **600 GW** available (based on 1.34 billion tons/yr of lignocellulose)
- Wastewater organic matter (WW)
  - **17 GW** in wastewaters (Savings 3x15 + 17 = 62 GW net)
    - **2-5 kWh/m³** for "typical" domestic wastewater
- Salinity Gradient Energy- Natural Waters (global values)
  - **980 GW** (from the 1900 GW available from river/ocean water)
  - **20 GW** available where WW flows into the ocean
    - **0.75 kWh/m³** for Typical Seawater-Freshwater
    - **1 kWh/m³** using Ammonium Bicarbonate (waste heat)
    - **14.1 kWh/m³** for Dead Sea-Freshwater
- Waste Heat Energy
  - **500 GW** from industrial waste heat
  - **1000 GW** from power production (33% efficient power plants)

(Does not include solar and geothermal energy sources)

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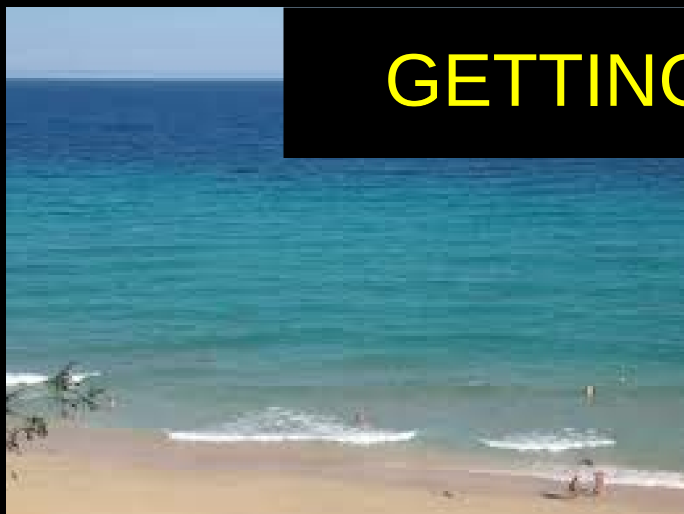
Logan and Rabaey (2012) *Science*
Logan and Elimelech (2012, *Nature*

Salinity Gradient Energy

GETTING MORE ENERGY



+

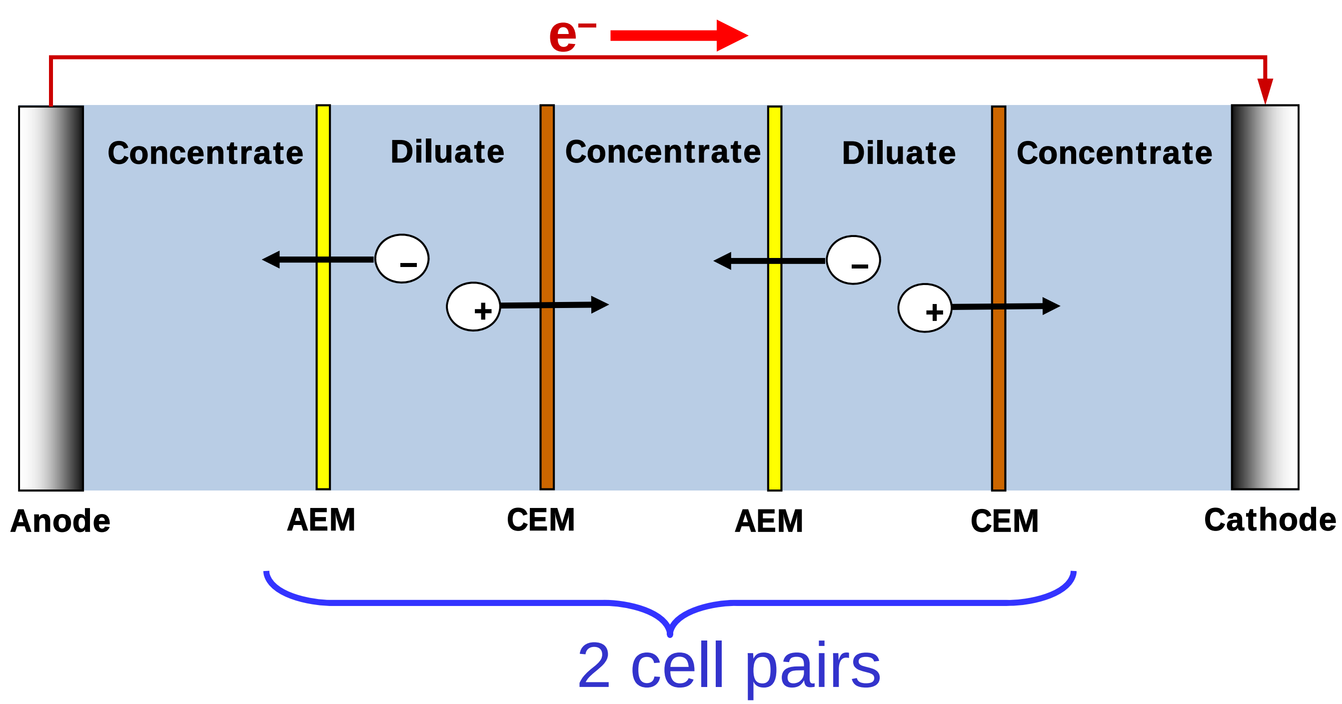
=

270 m of
Hydraulic Head

Oceanside WWTPs and Rivers could produce 980 GW

Electrodialysis (ED) stack

1 cell pair = Diluate cell + Concentrate cell

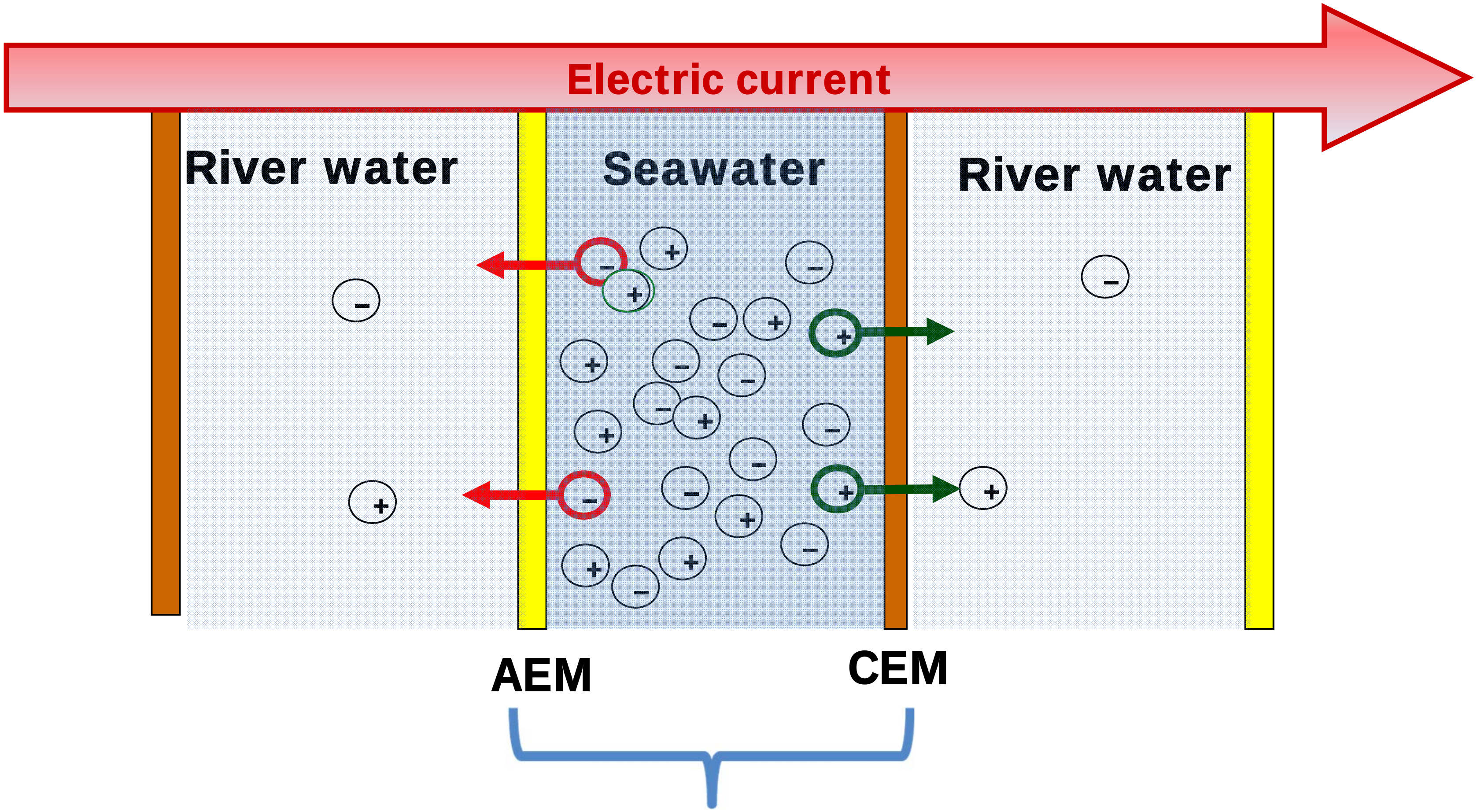


2-cell pair system: 1 e^- → 2 cations and 2 anions

5-cell pair system: 1 e^- → 5 cations and 5 anions

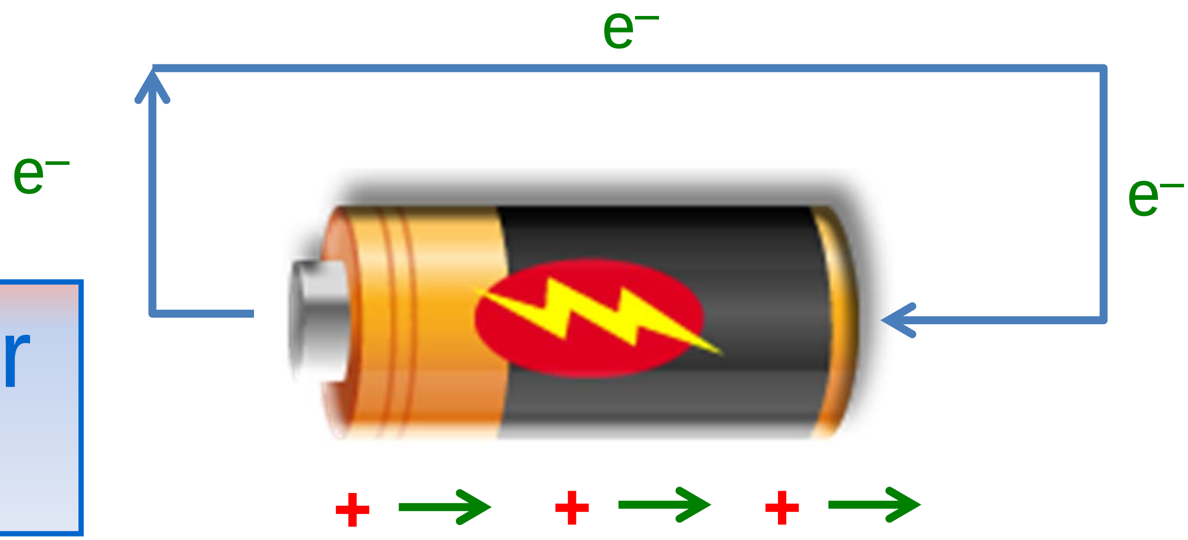
Reverse electrodialysis (RED)

Salinity difference produces ion transport → electrical current

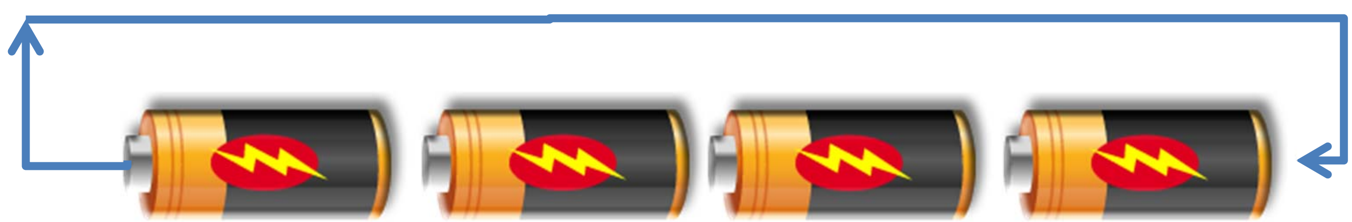


Each pair of seawater + river water cells→ **~0.1 – 0.2 V**

Batteries = motion of ions & electrons

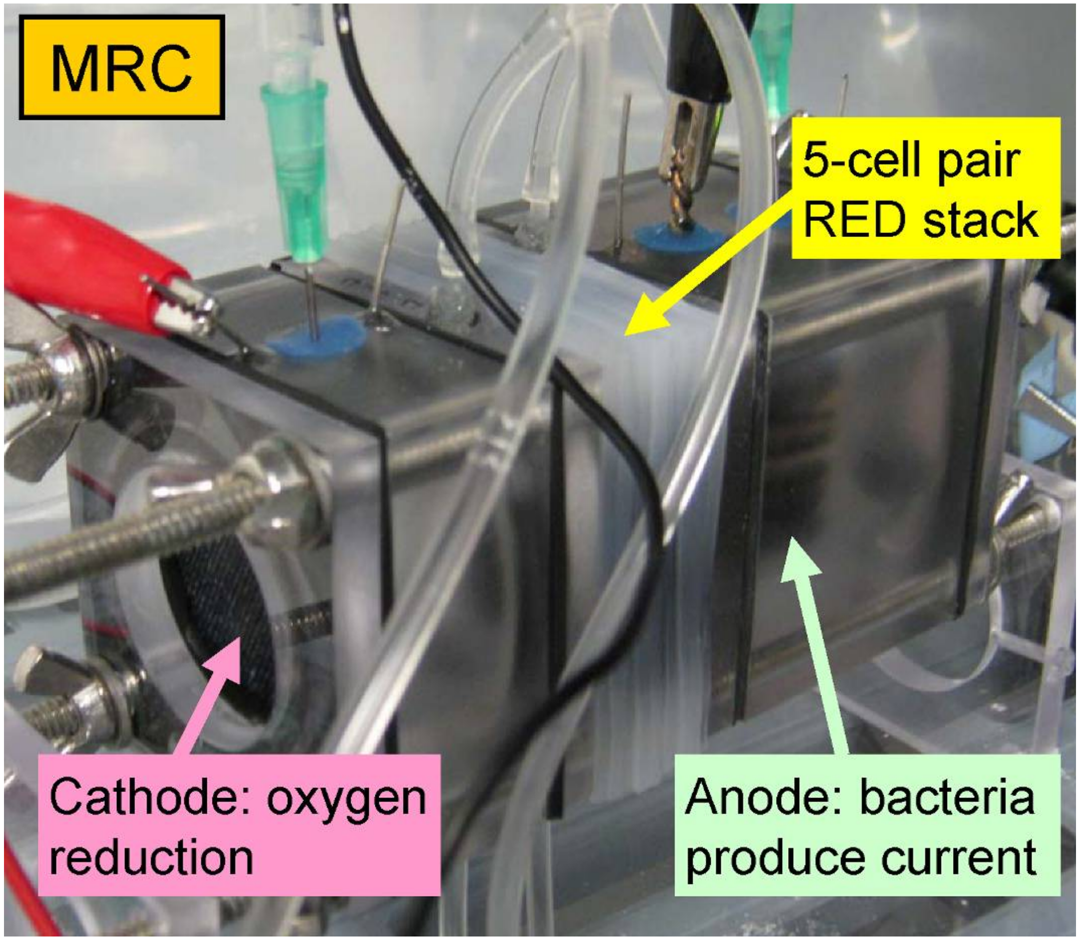


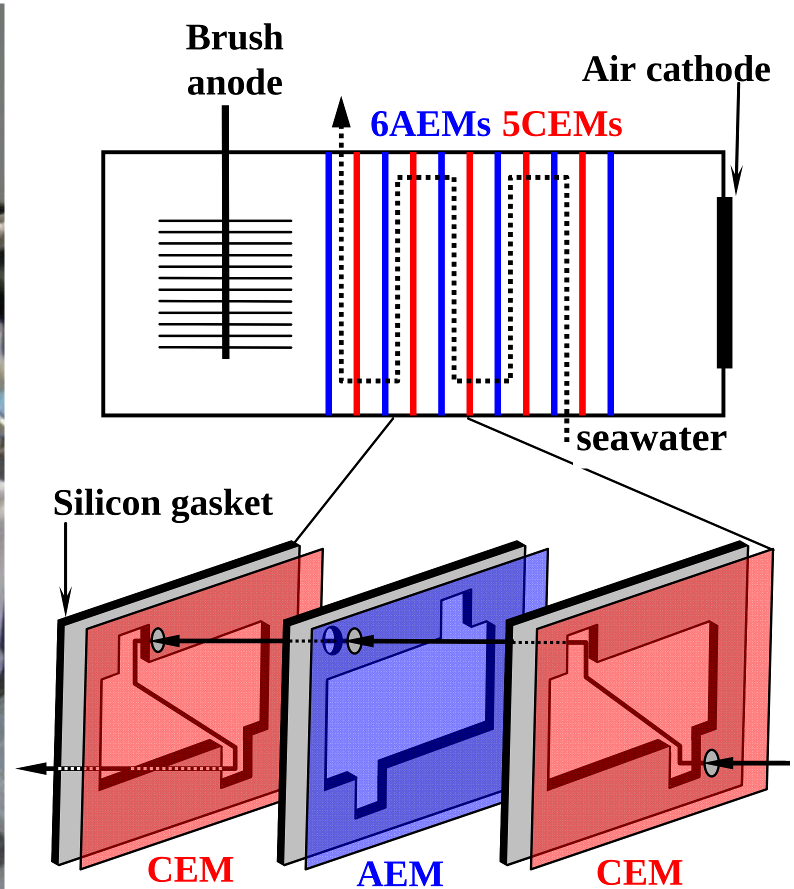
1.5 V per battery



6 V (4 batteries)

MFC + RED = MRC (Microbial RED Cell)





Kim & Logan (2011) *ES&T* (MRCs)

New Energy Sources Available using Microbial Electrochemical Technologies (METs)

- Wastewater organic matter (WW)
  - **17 GW** in wastewater (Savings 3x15 + 17 = 62 GW net)

- Cellulose Biomass Energy
  - **600 GW** available (based on 1.34 billion tons/yr of lignocellulose)
- Salinity Gradient Energy- Natural 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
  - **500 GW** from industrial waste heat
  - **1000 GW** from power production (33% efficient power plants)

(Does not include solar and geothermal energy sources)

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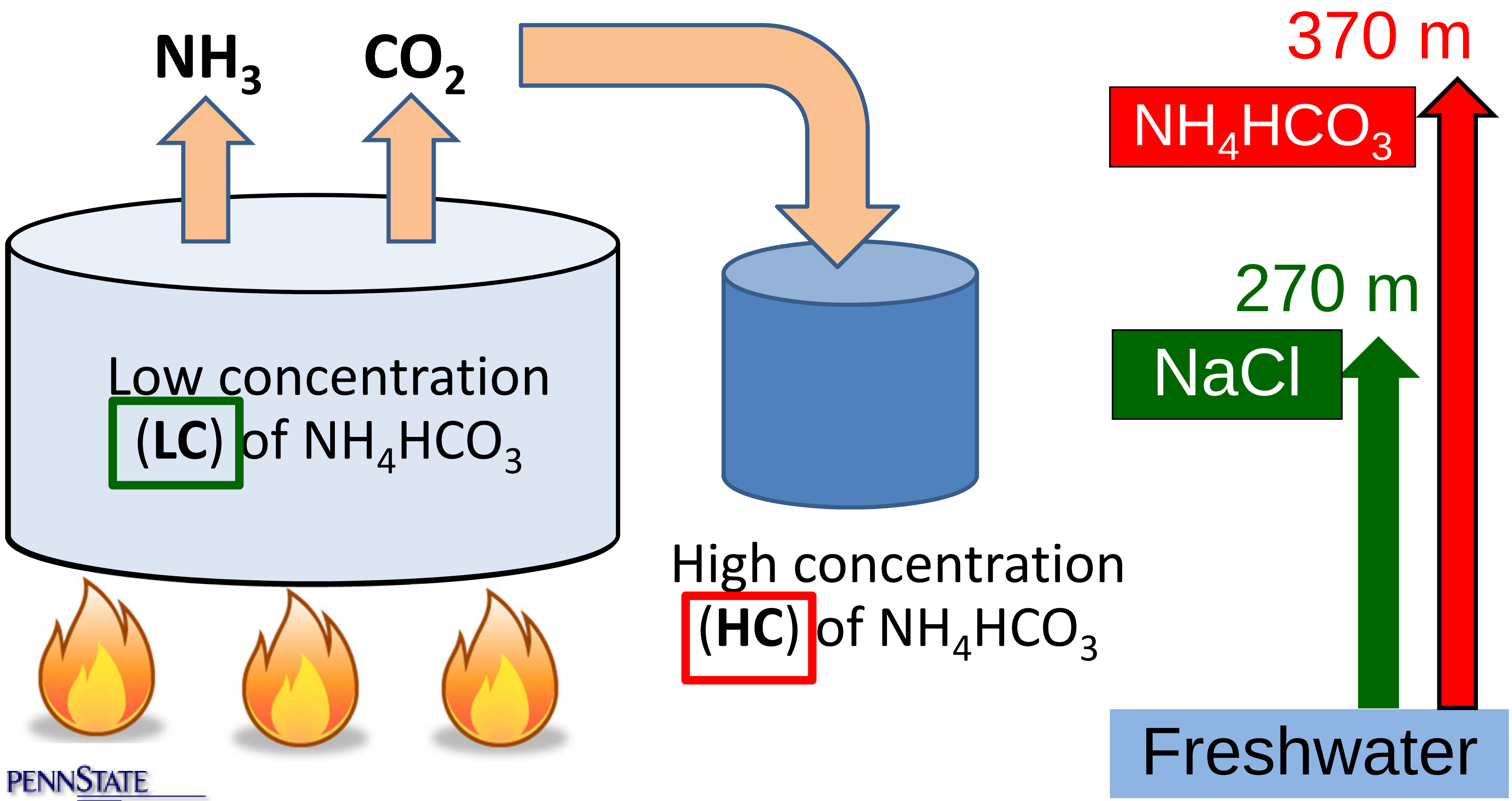
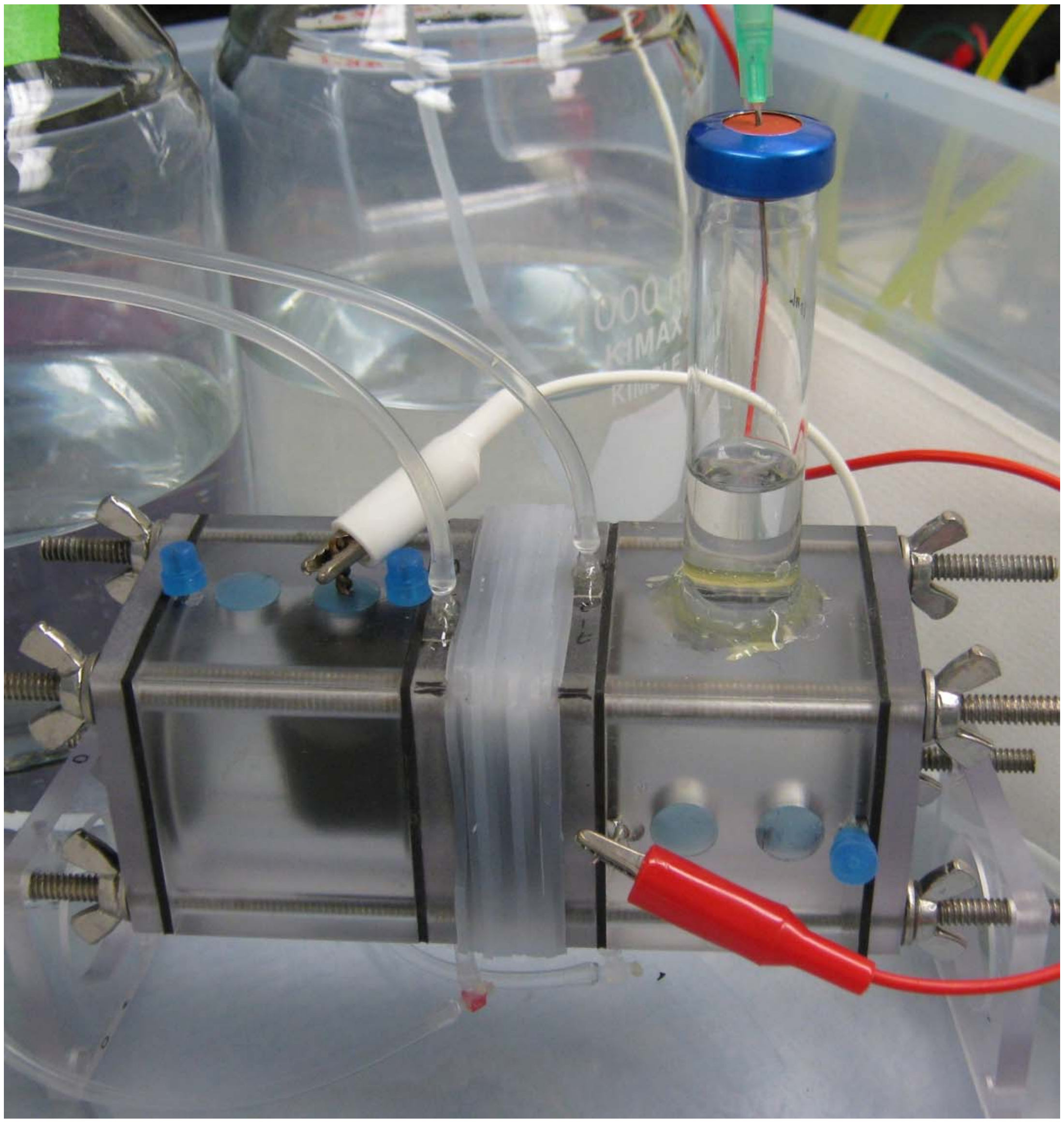
Logan and Rabaey (2012) *Science*
Logan and Elimelech (2012, *Nature*

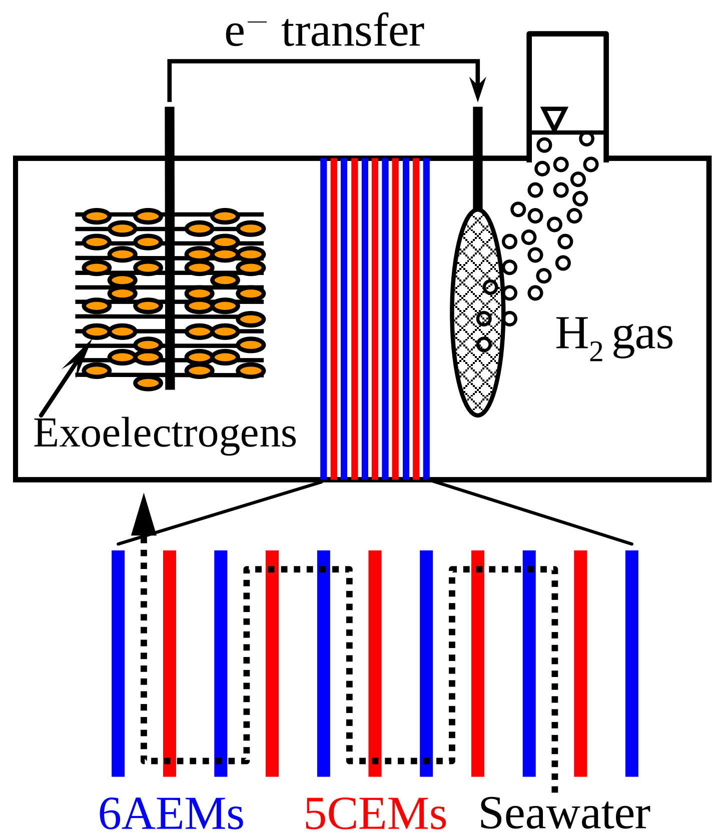
Use waste heat to create artificial “salintity gradient” energy using ammonium bicarbonate



Cusick, Kim & Logan (2011) *Science*

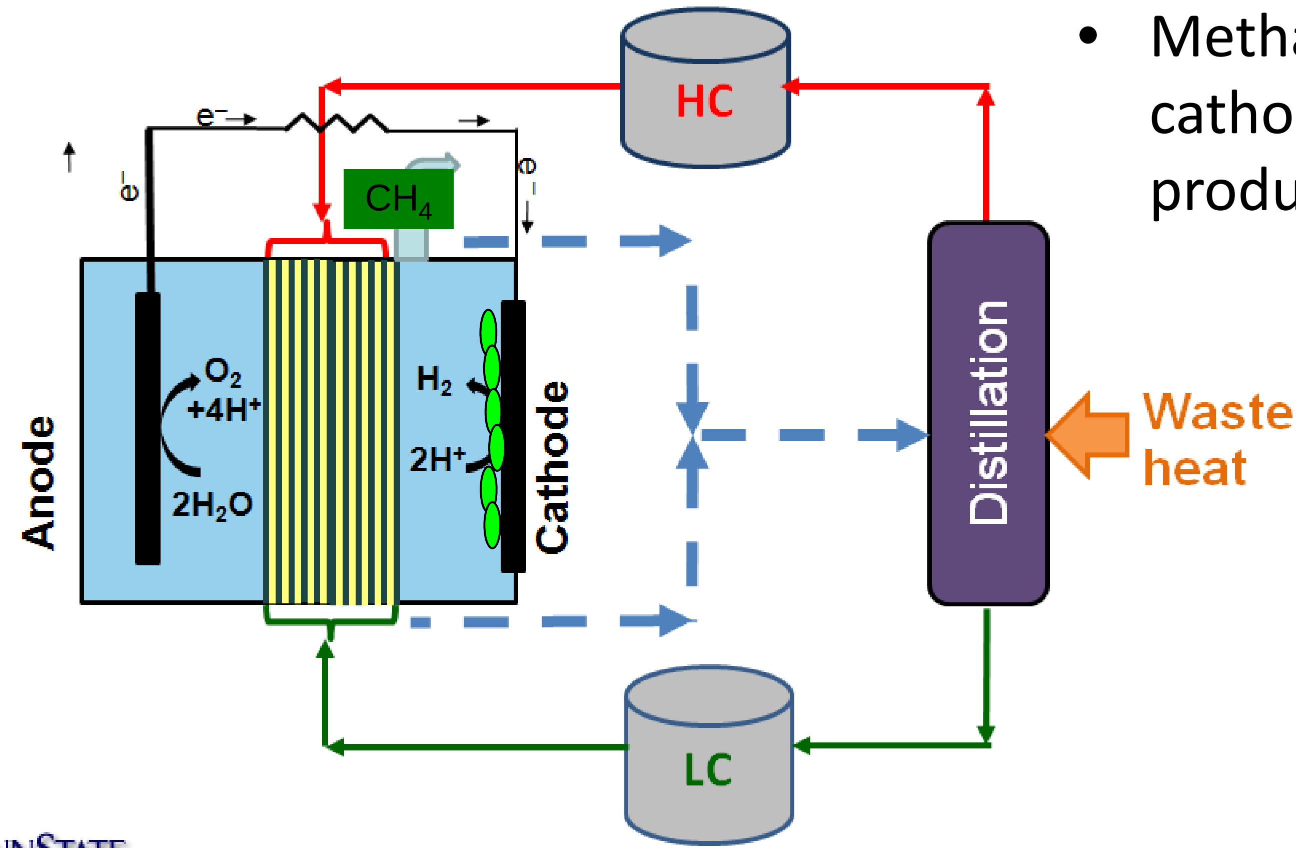
MREC: Microbial RED Electrolysis Cell





Kim & Logan (2011) *Proc. Nat. Academy Sci.*

RED Stack (abiotic) with NH_4HCO_3 Could be used as Energy Source for CH_4 Production



- Abiotic anode with water splitting
- Methanogens on cathode to use H_2 gas produced

Cusick, Kim & Logan (2011) *Science*

Thanks to students and researchers in the MFC team at Penn State!

Current research sponsors

KAUST (2008-2013); Air Products and Chemicals, Inc. (2006-2012); DOE-NREL (2008-2012); Chevron (2012-2013); Arpa-E (2013); DOE (2012-2015); DOD/SERDP (2012-2015); GCEP/Stanford (2012-2014)

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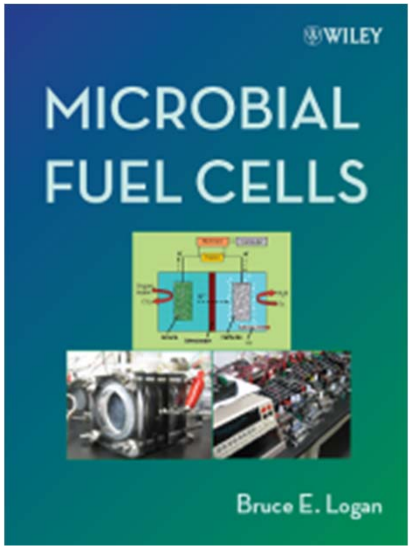
International MFC site: www.IS-MET.org

YouTube: YouTube/user/MFCTechnology
Twitter: MFCTechnology



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

(live video of an MFC running a fan)

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