Hydrogen and Biogas Production using Microbial Electrolysis Cells

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

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Engineering Energy &
Environmental Institute

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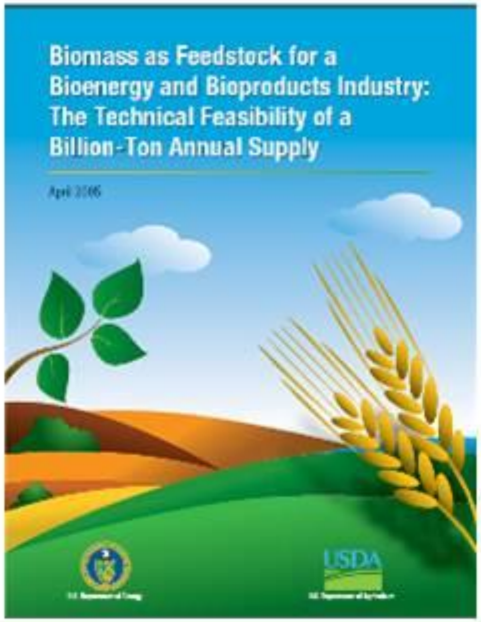
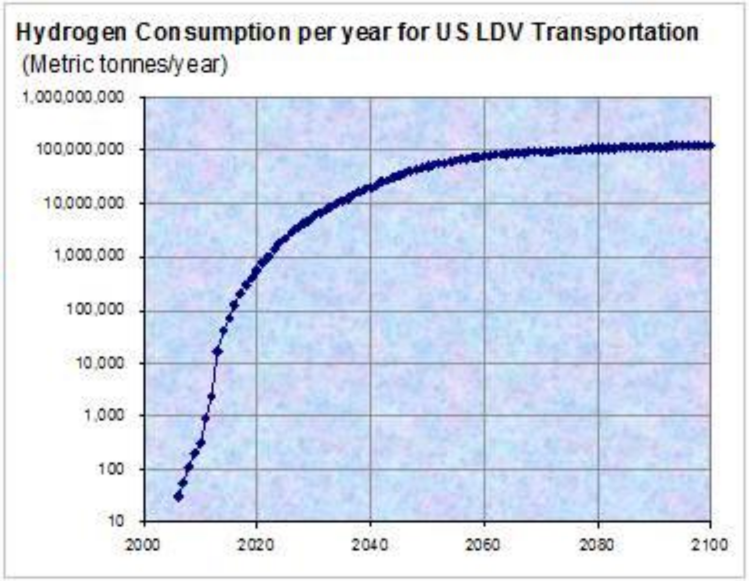
BIO
ENERGY
U.S. DEPARTMENT OF ENERGY
2015

Cellulosic biomass → H_2





1.34 billion tons of cellulose/yr

= 2 x 10^{11} kg/yr H_2

Need 10^{11} kg/yr H_2 for transportation by 2060(light duty vehicles)

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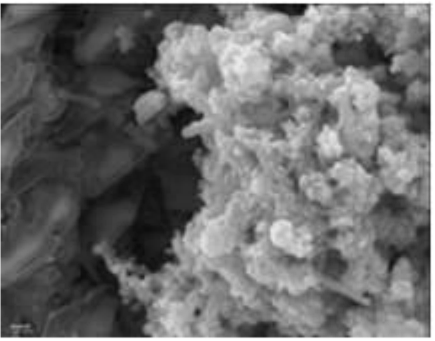

The cellulose "fermentation barrier"

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 12\ H_2 + 6\ CO_2$$

Cellulose → $12\ H_2$

$2\text{-}4\ H_2$ →

$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ C_2H_4O_2 + 2\ CO_2$

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

$8\text{-}10\ H_2$? →

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

→ Microbial Electrolysis Cells (MECs)

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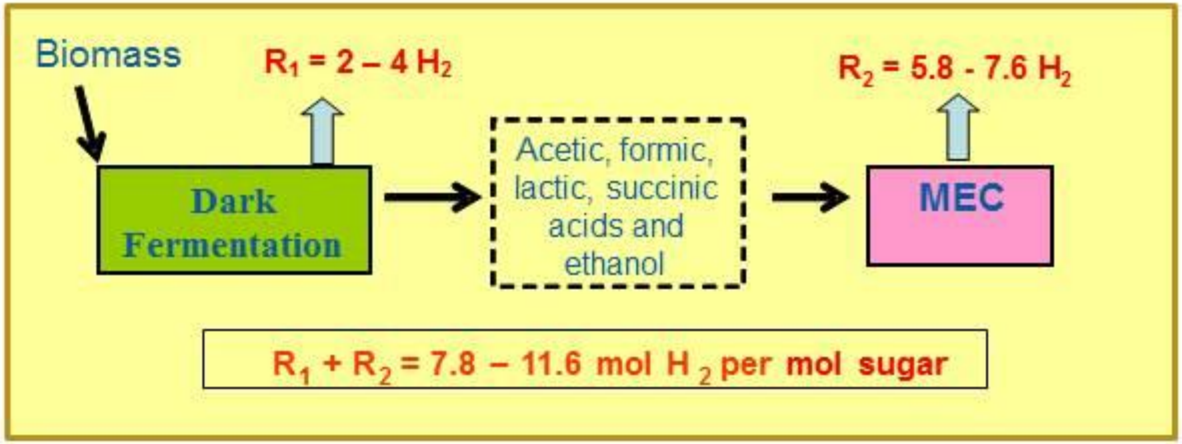
Penn State project with NREL

2 stage process :
Convert renewable lignocellulosic biomass resources to H_2 using fermentation + MEC



Approach overcomes 2 key barriers to making H_2 from other biomass sources

- Low feedstock cost of lignocellulose compared to corn/sugar
- Overcomes fermentation barrier:
    - Increases H_2 molar yield past 4 mol-hexose per mol-H_2 by using a microbial electrolysis cell (MEC)

Focus points

- Microbial electrolysis cells (MECs)
  - Electroactive microorganisms
- MECs for conversion of lignocellulose to H_2
- Avoiding the need for electricity in MECs

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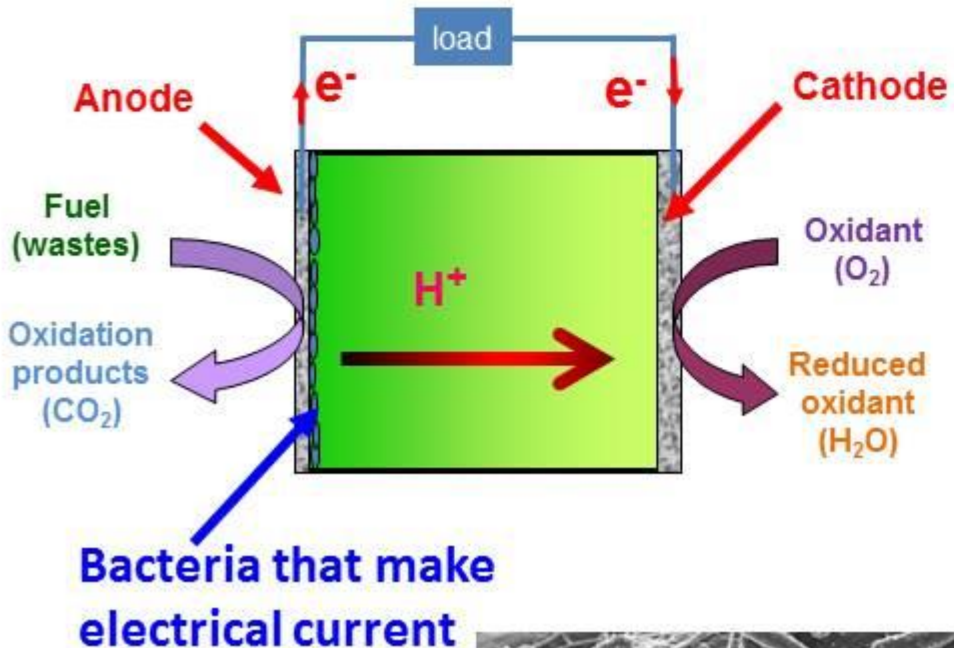
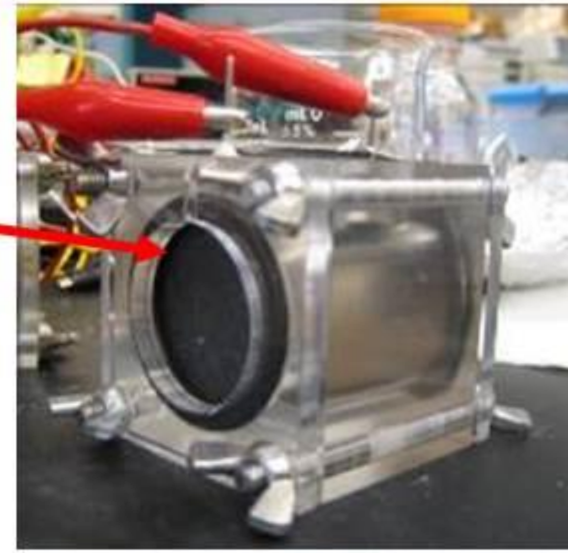
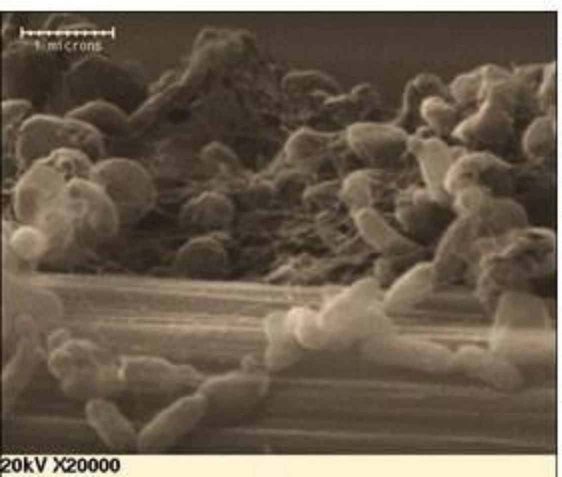
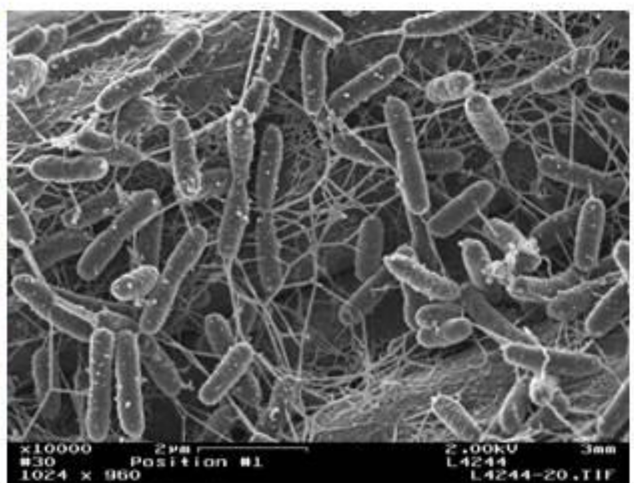
MFCs

Electrical power generation in a **M**icrobial **F**uel **C**ell (MFC) using exoelectrogenic microorganisms



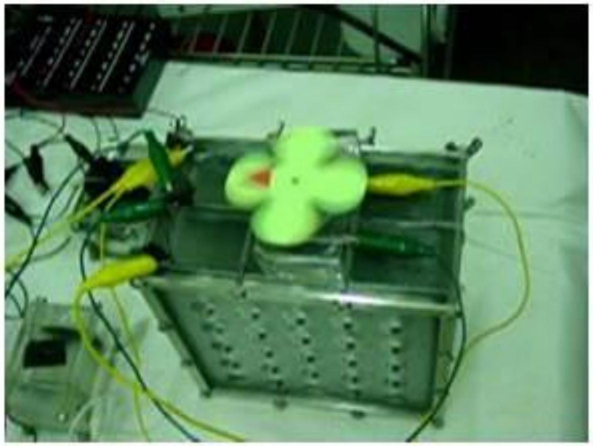


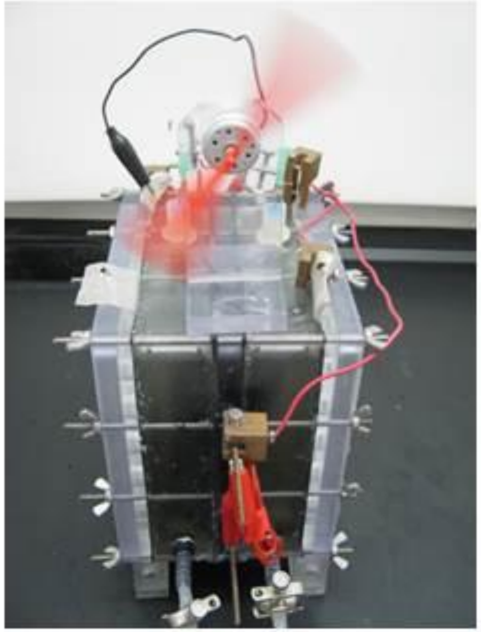




Liu et al. (2004) *Environ. Sci. Technol.*

Demonstration of a Microbial Fuel Cell (MFC)





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

www.engr.psu.edu/mfccam

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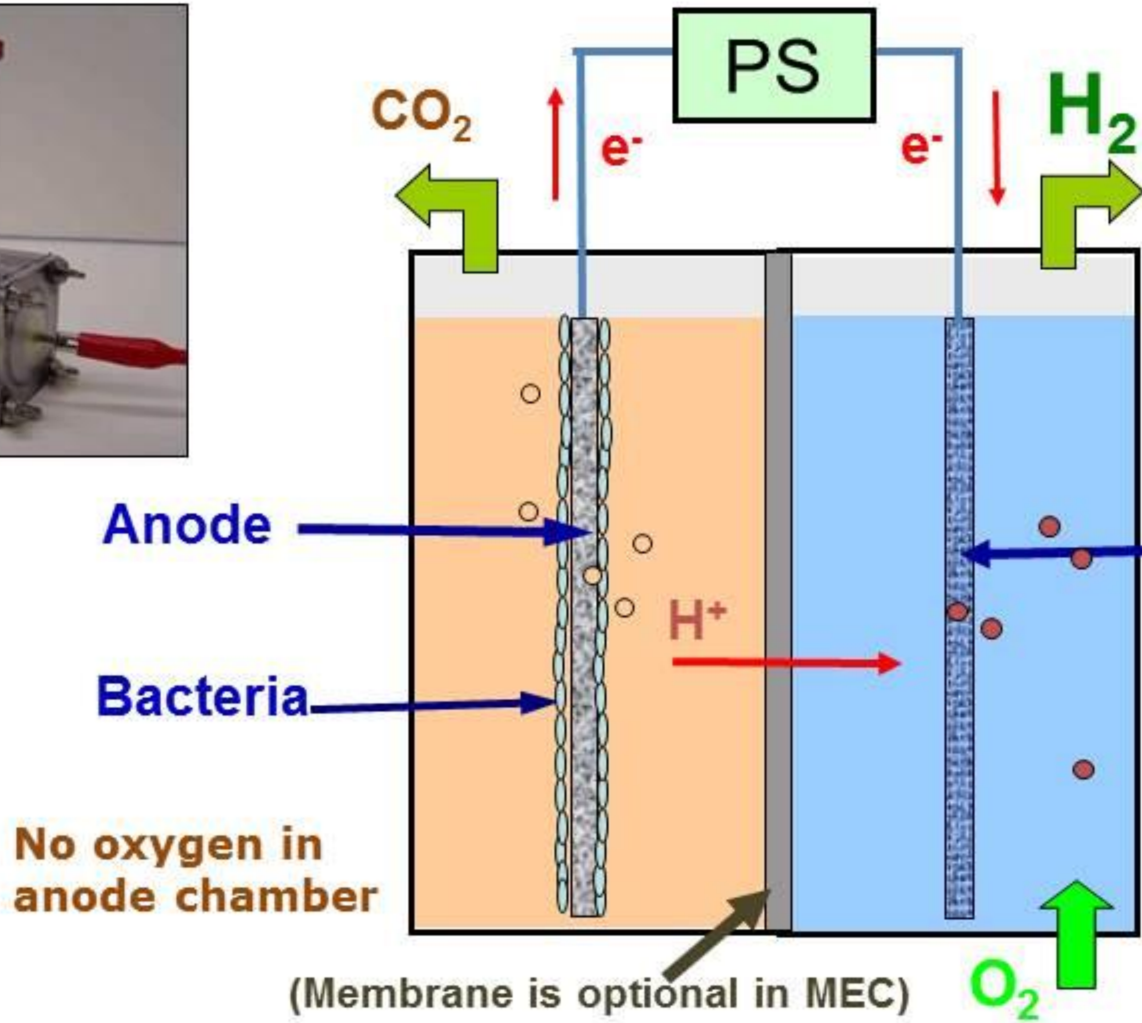
MECs

H_2 Production at the cathode using microbes on the anode in **M**icrobial **E**lectrolysis **C**ells



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

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

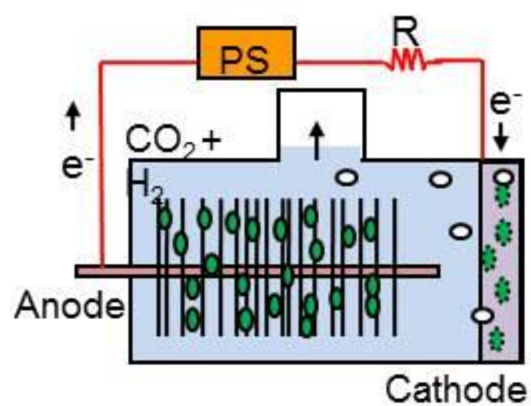
H_2 production by MEC process: Energy Yields

$$\eta_W = \frac{W_{H2}}{W_{in}}$$

$\frac{\text{Energy in } H_2 \text{ produced}}{\text{Energy in electricity required}}$ **200 – 400%**

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

$\frac{\text{Energy in } H_2 \text{ produced}}{\text{Energy in electricity + substrate}}$ **65 – 89%**



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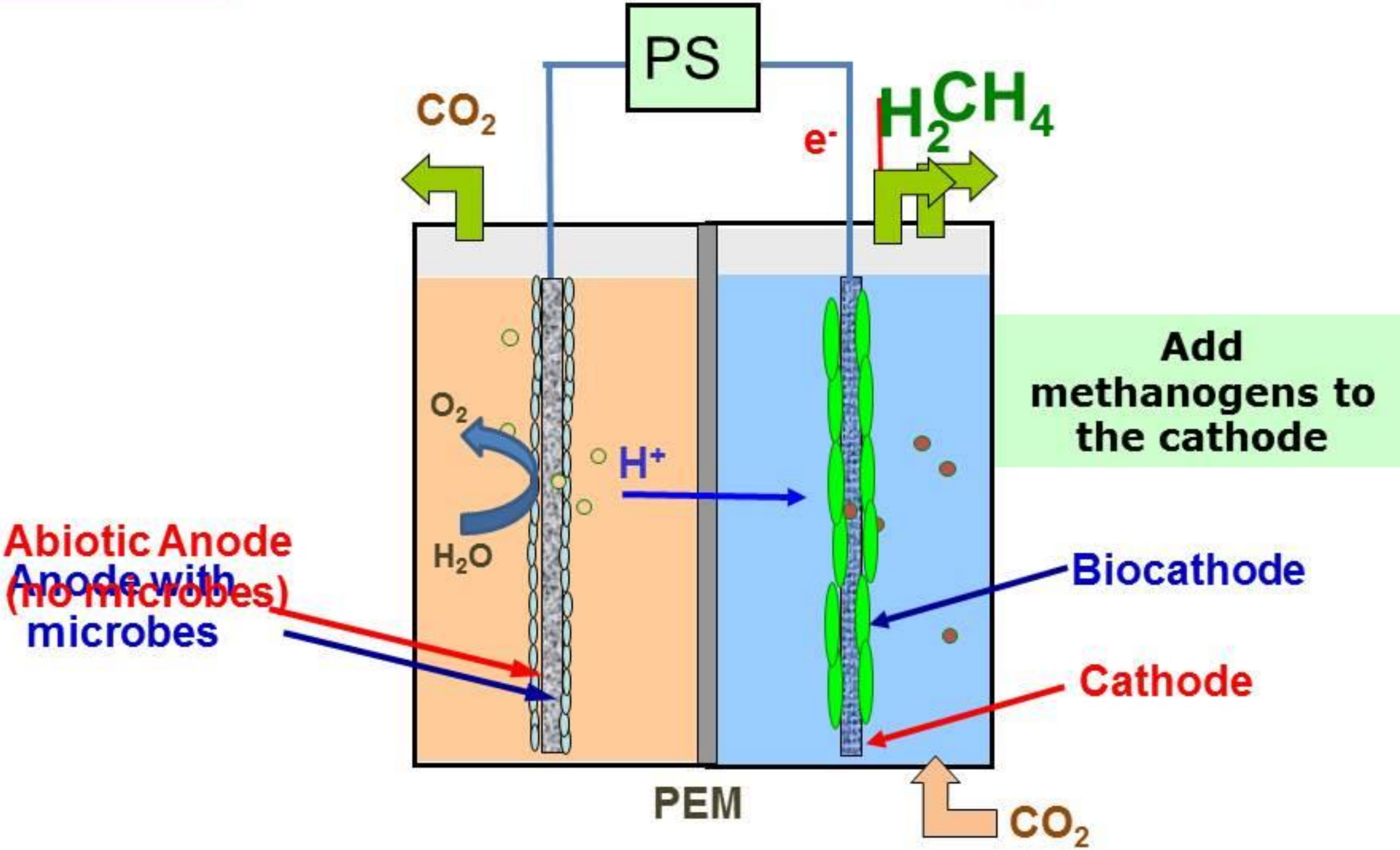
MMCs

CH_4 Production at the cathode using microbes on the cathode in **M**icrobial **Methanogenesis C**ells



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

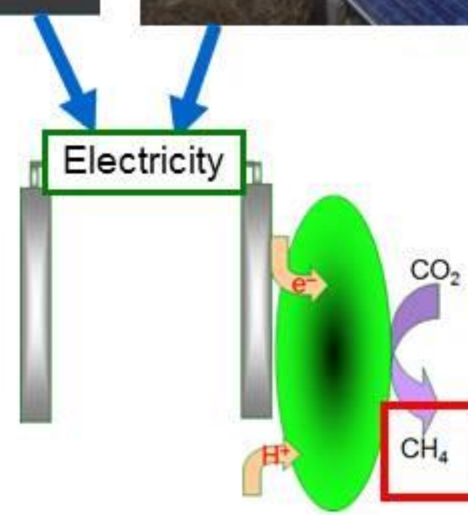
MECs used to harvest methane from renewable forms of electricity generation

Anaerobic digesters

(methane from organic matter)

MMCs

Methane from renewable electricity



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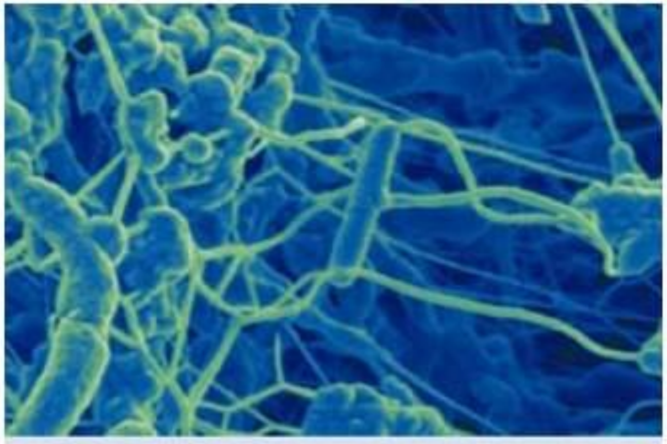
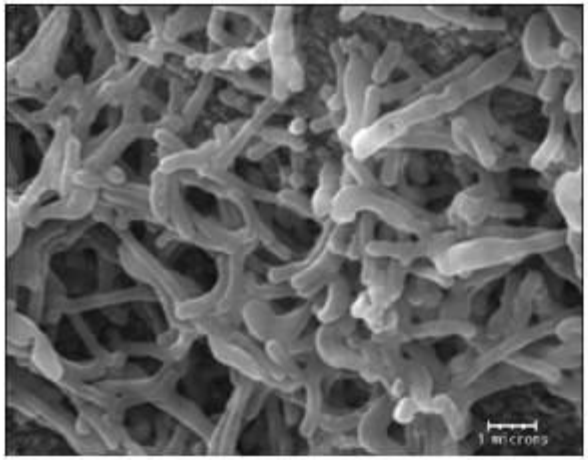
Electro-active Microorganisms

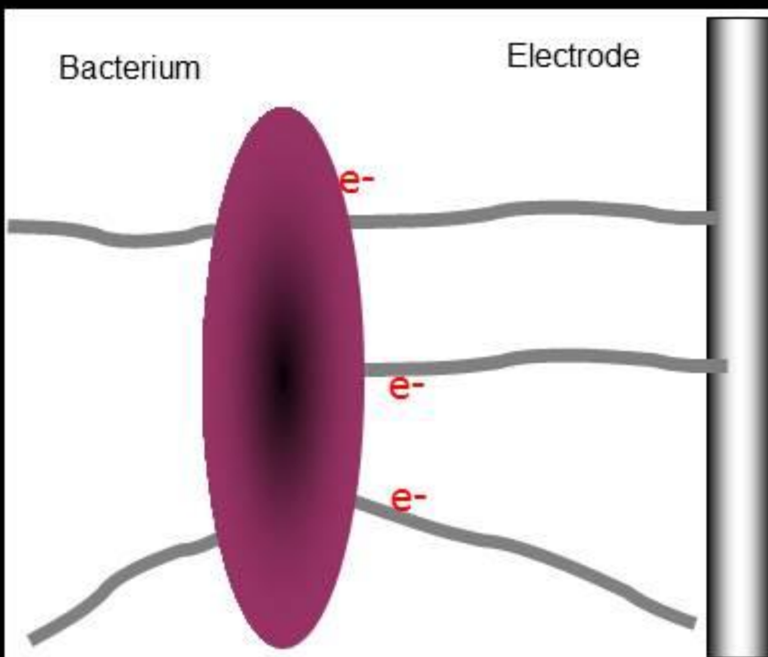
- Electromicrobiology
  - New sub-discipline of microbiology examining exocellular electron transfer



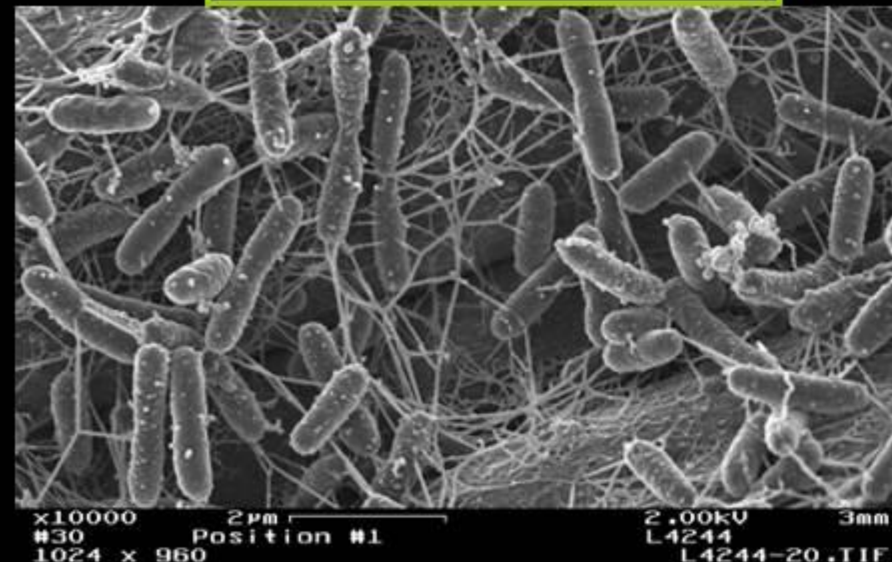


Mechanisms of electron transfer in the biofilm:

Nanowires produced by bacteria !



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



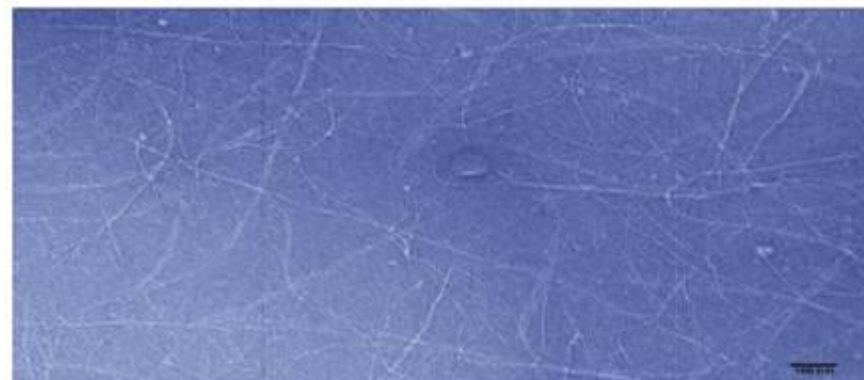
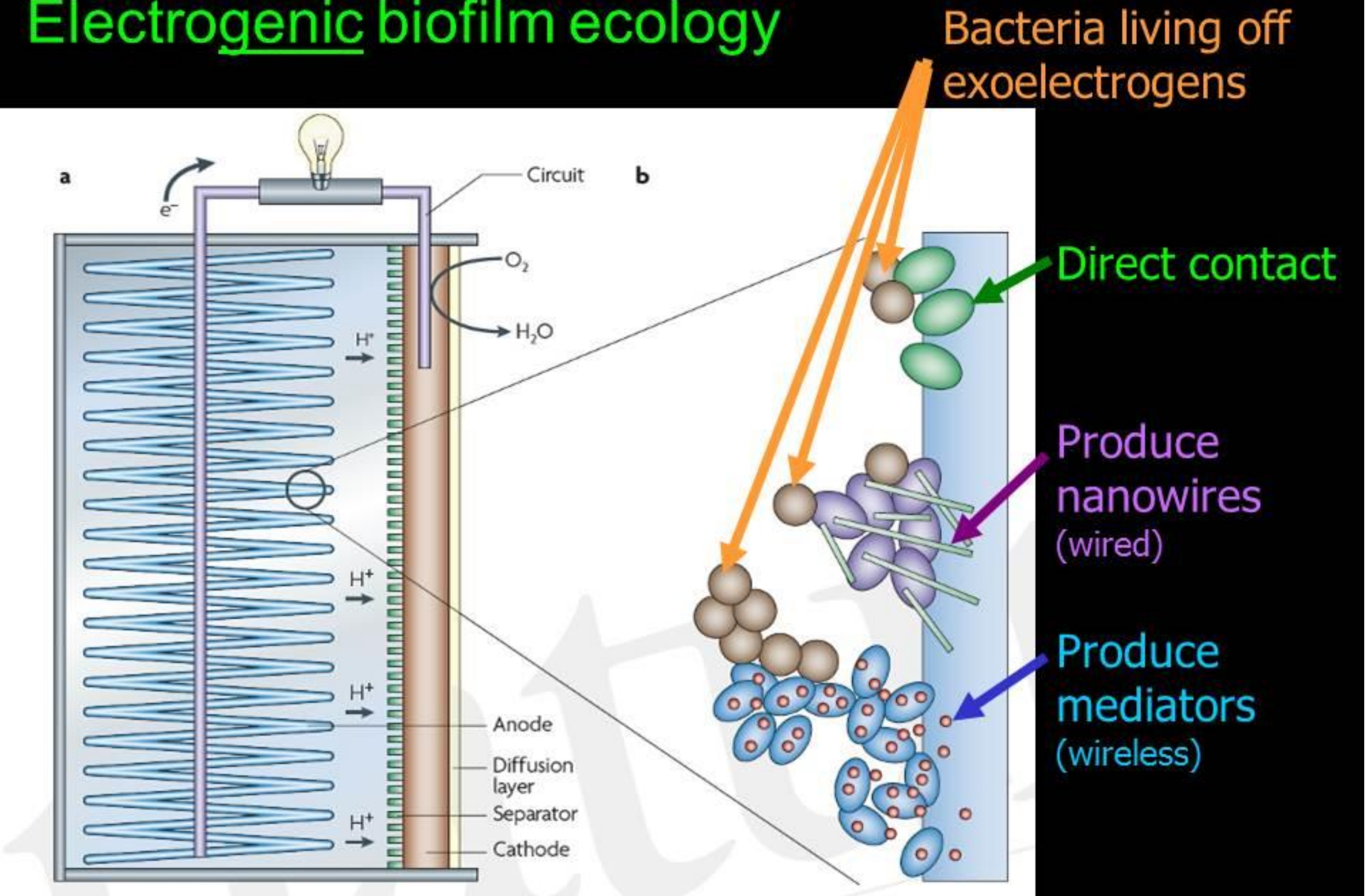


Figure 1. Colorized transmission electron micrograph of microbial nanowire networks secreted by *Geobacter sulfurreducens*. Scale bar, 100 nm.

Malvankar & Lovley (2012) *ChemSusChem*

Electrogenic biofilm ecology

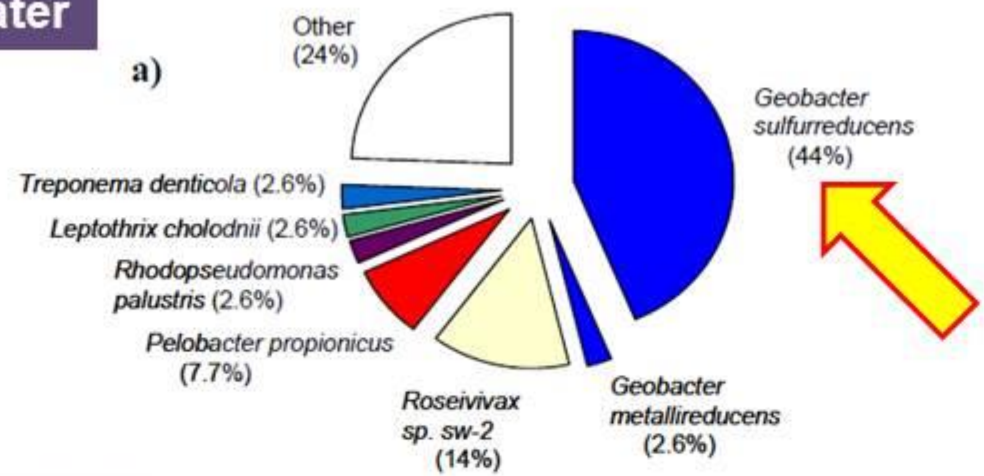


Logan, *Nature Rev. Microbiol.* (2009)

Bacteria on the anodes

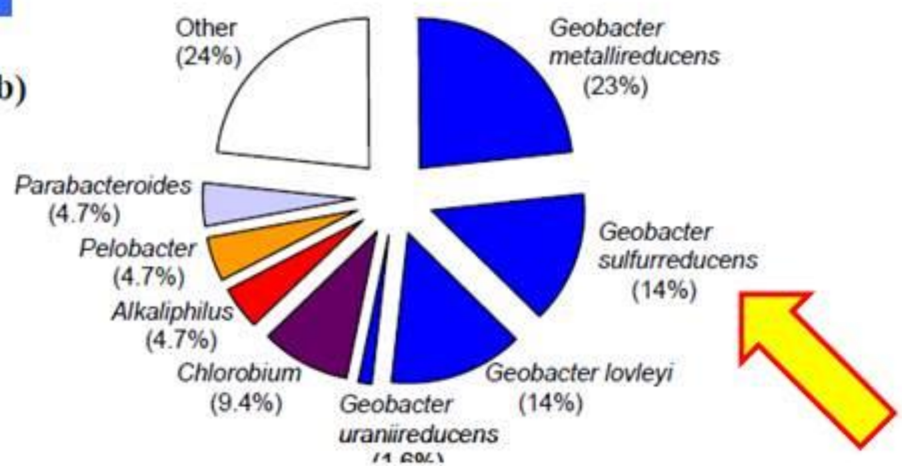
Winery Wastewater

a)



Domestic Wastewater

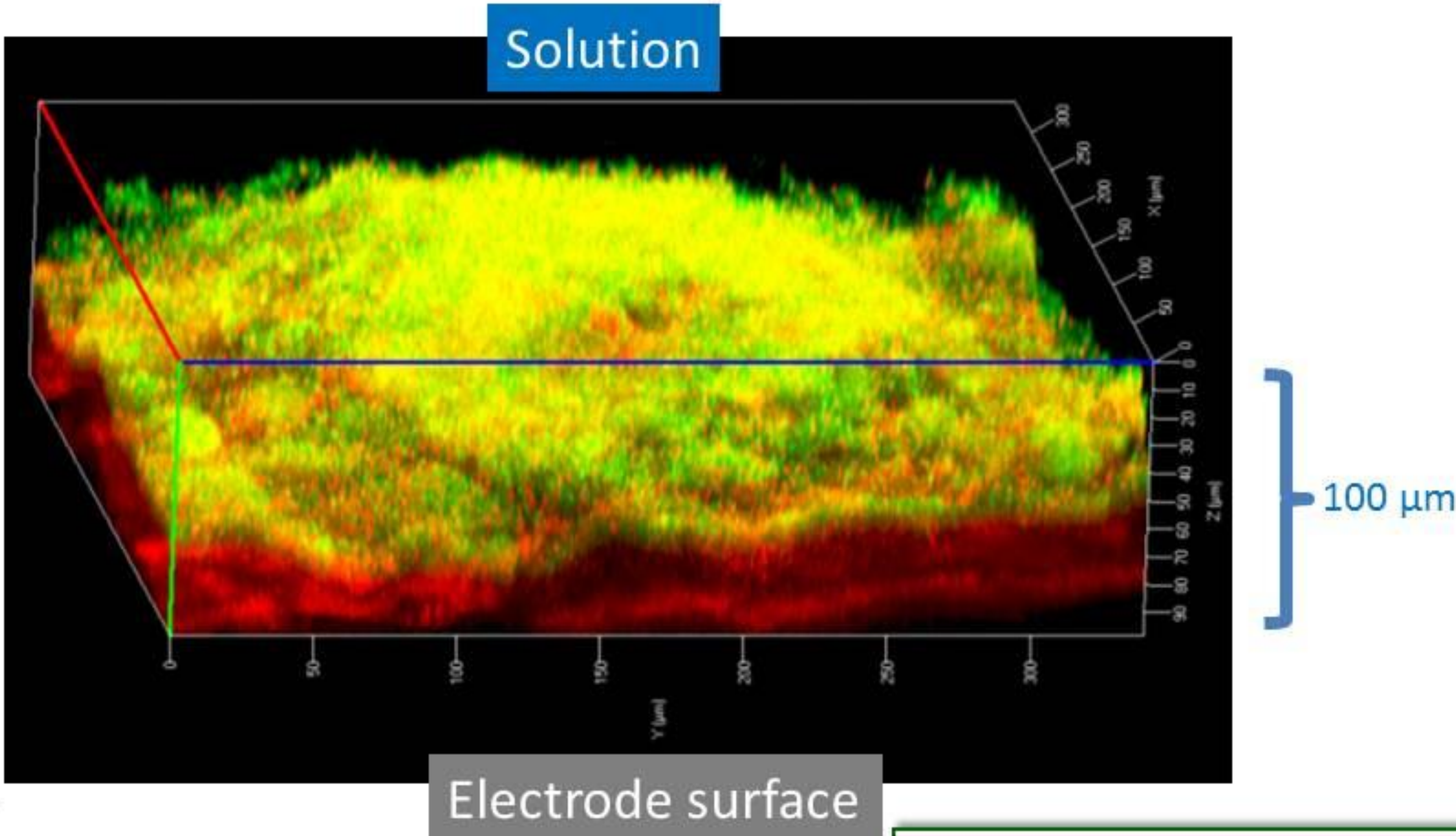
b)



Cusick, Kiely, Logan (2010) *IJHE*

Electrogenic Biofilms

- Dead biofilm (red) remains electrically conductive for active biofilm (yellow/green)

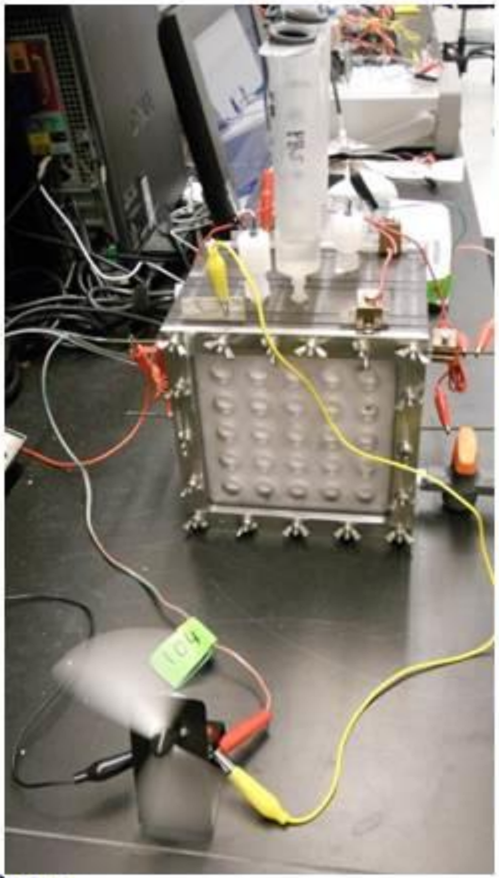


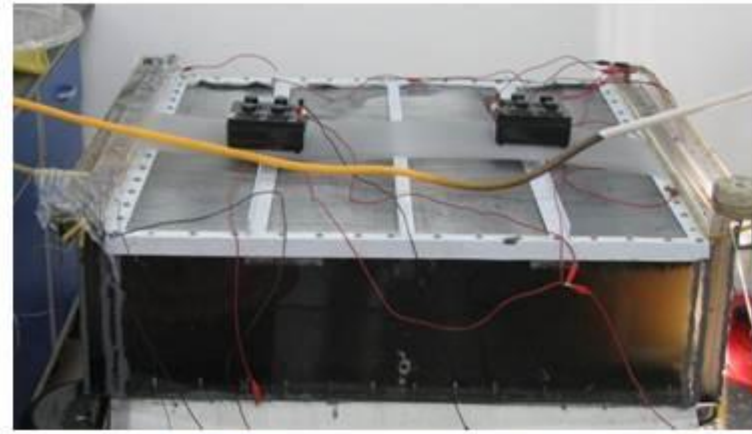
Sun, Cheng, Wang, Li, Logan, Cen (2015) *ES&T*

Scaling up MFCs & MECs

M**F**Cs= fuel cells, make electricity

M**E**Cs= electrolysis cells, make H_2





MxC Architecture

CHEMSUSCHEM ChemPubSoc Europe

DOI: 10.1002/cssc.201100732

Bioelectrochemical Systems: An Outlook for Practical Applications

Tom H. J. A. Sleutels,[a] Annemiek Ter Heijne,*[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 mΩm²) and current density that is required to make microbial fuel cells (MFCs) and hydrogen-producing microbial electrolysis cells (MECs) cost effective. We compare these maximum resistances to reported internal resistances and current densities with special focus on cathodic resistances. Whereas the current densities of MFCs still need to be increased considerably (i.e., internal resistance needs to be decreased), MECs are closer to application as their current densities can be increased by increasing the applied voltage. For MFCs, the production of high-value products in combination with electricity production and wastewater treatment is a promising route.

Review — Cell Press

Towards practical implementation of bioelectrochemical wastewater treatment

René A. Rozendal[1,2,3], Hubertus V.M. Hamelers[2], Korneel Rabaey[1], Jurg Keller[1] and Cees J.N. Buisman[2,3]

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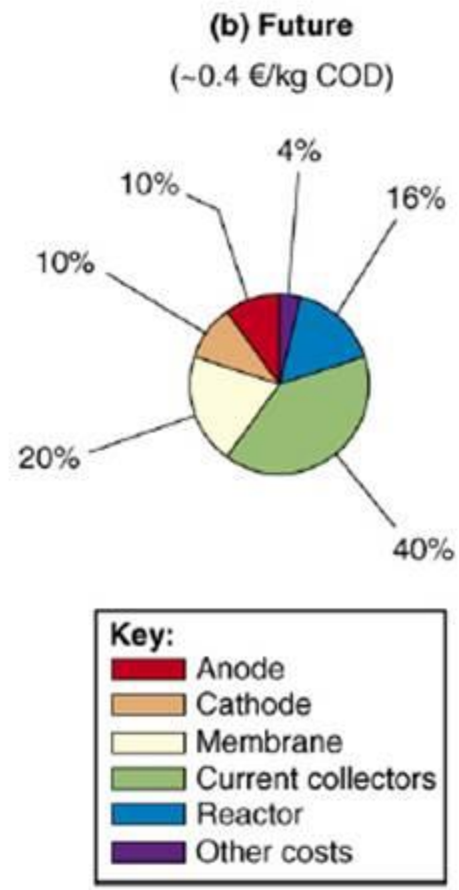
Estimates for MFCs

- 100 € /m² or $130/m²

Estimates for MECs

- 100 € /m² or $130/m²



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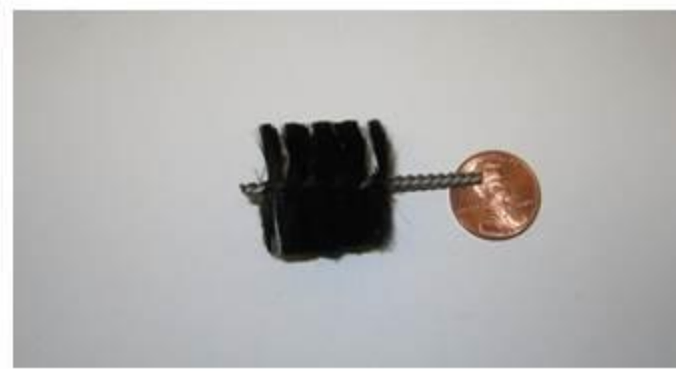
MxC Materials

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 m^2/m^3



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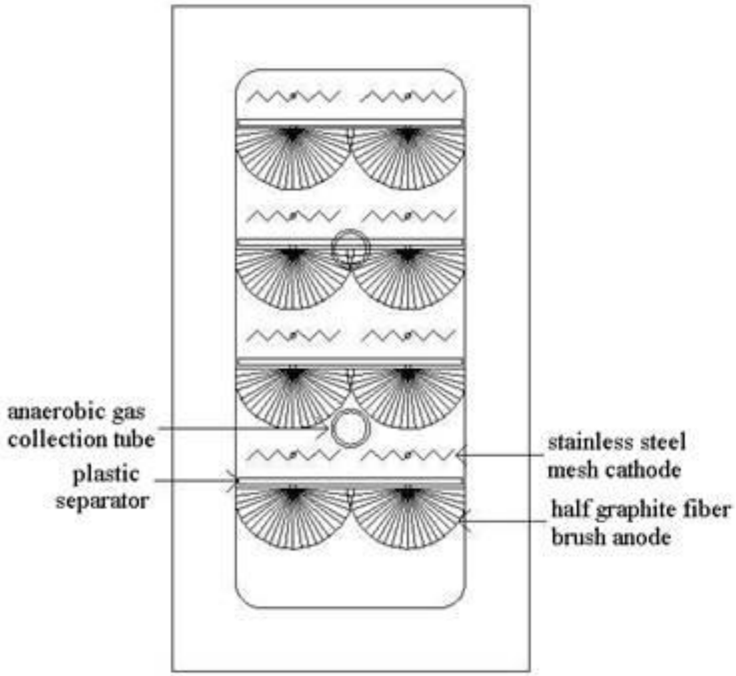
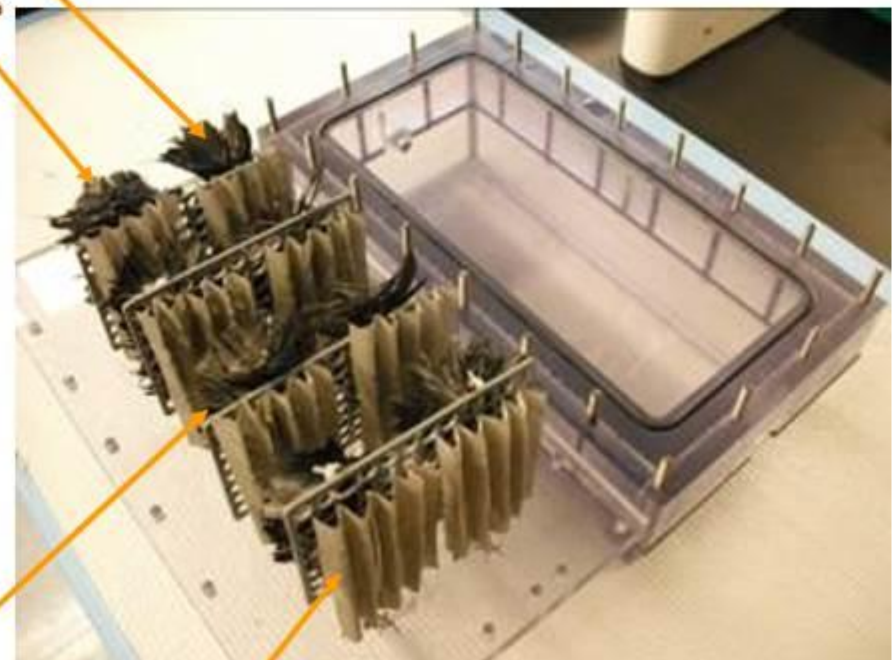
Logan et al. (2007) *Environ. Sci. Technol.*

MEC components (2.5 L reactor)

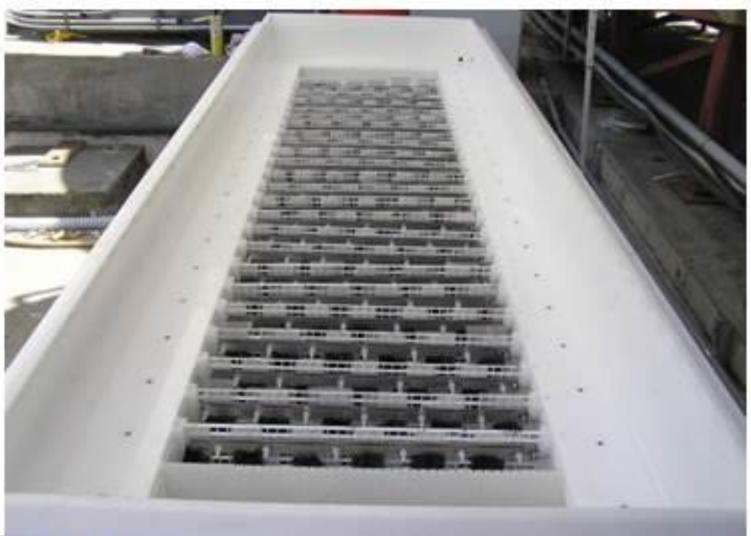
Schematic





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

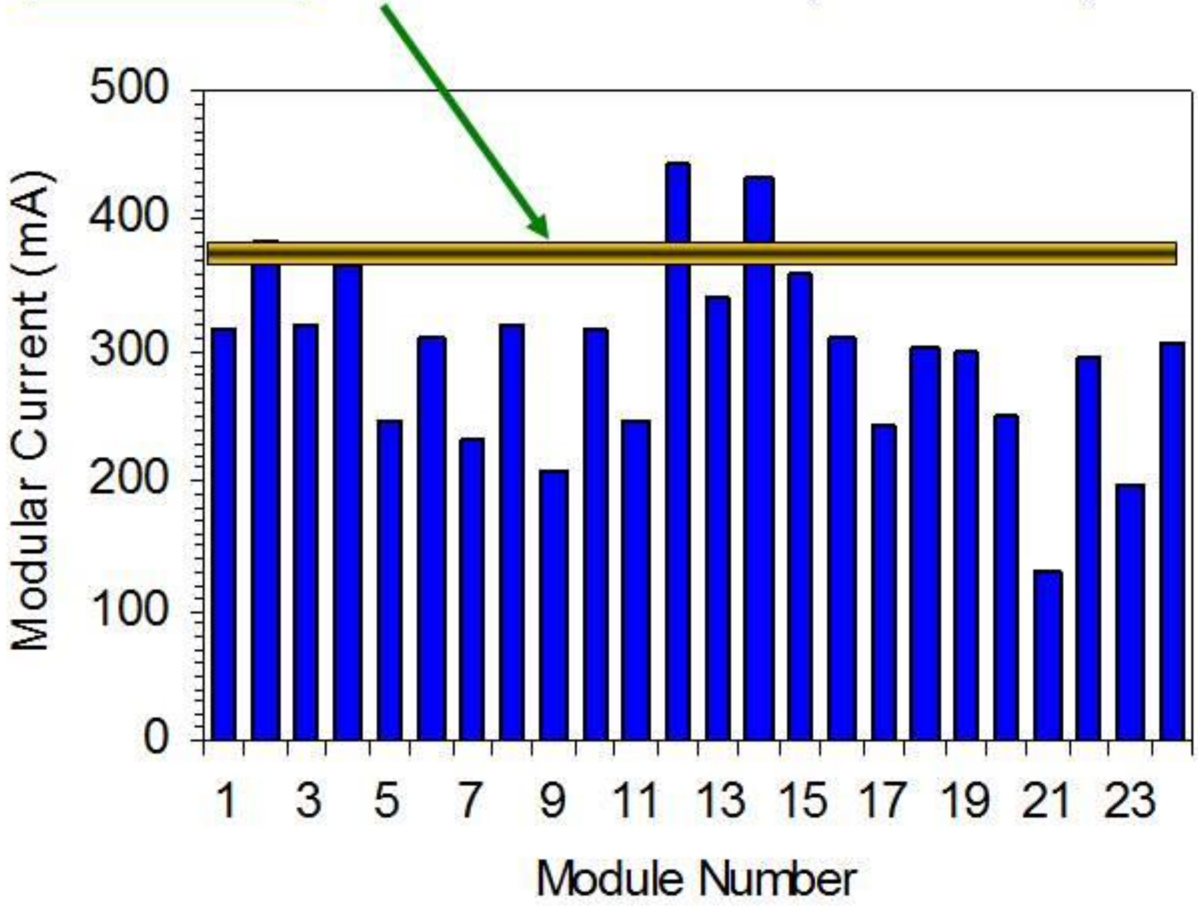
MEC Reactor that has 24 modules with a total of 144 electrode pairs (1000 L)



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

Individual module performance of the MEC treating Wastewater

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



H_2 intially produced, but it all was converted to CH_4

Elec. Energy input= 6 W/m^3

Energy Out = 99 W/m^3

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

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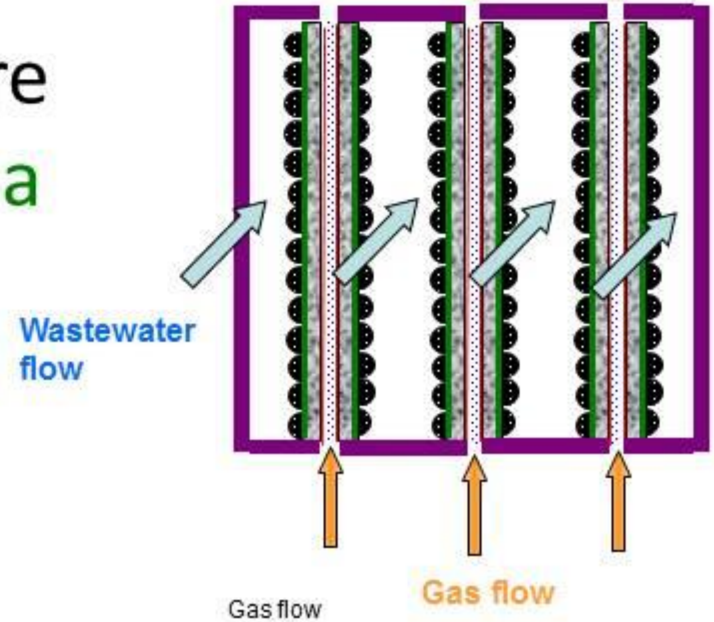
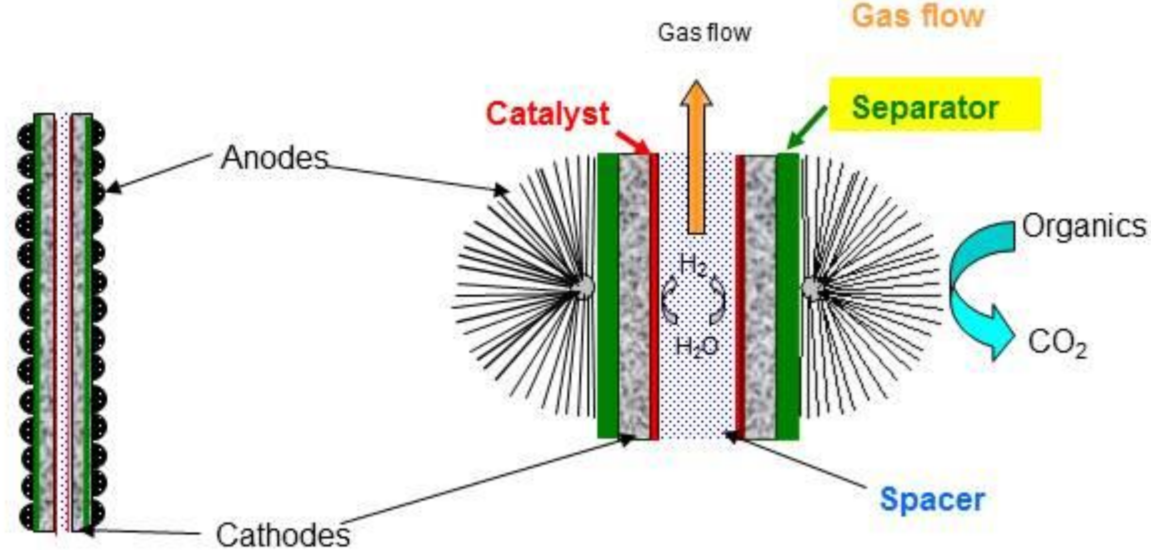
Cusick et al. (2011) *Appl. Microbiol. Biotechnol.*

NEW Module Design to capture H_2 from the cathode → Needs a separator or membrane



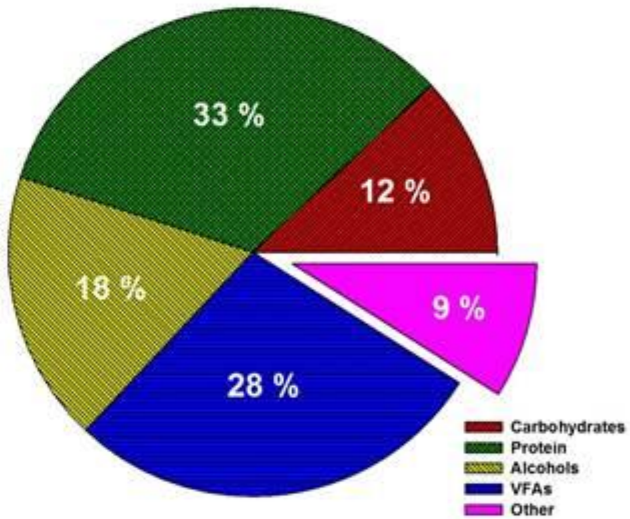


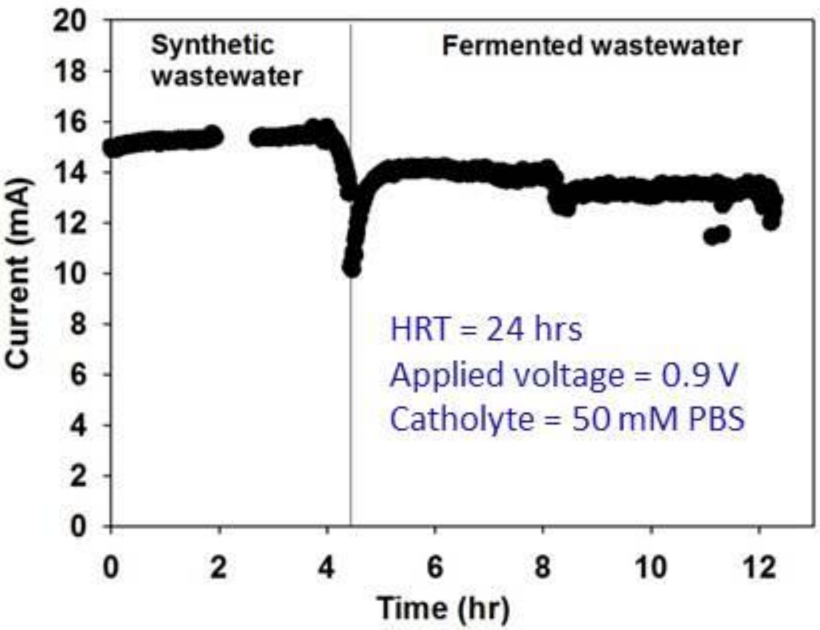
Side View

Close up view

Hydrogen Generation from Fermentation Wastewater

Fermentation Effluent Composition



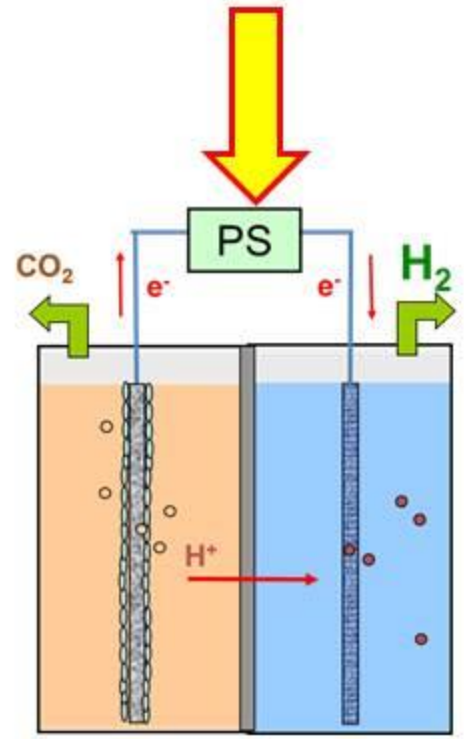


- **Current**: Synthetic ww = 51 A/m^3; Fermented ww = 44 A/m^3 (no protein in synthetic ww).
- **Gas production rates**: Synthetic, 0.6 L-H_2 L^{-1} d^{-1} ; Fermented, 0.5 L-H_2 L^{-1} d^{-1}.
- **COD (chemical oxygen demand) removal**: Synthetic ww = 87%; Fermented ww = 73%.
  - Removals in fermented ww: Alcohols and VFAs >90%; Carbohydrates= 89 %, Protein= 48%.

Avoiding the need for electricity (PS)

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

- 1: Thermal regenerative ammonia batteries (new, not tested)
  - Waste heat used to produce ammonia, which is the "fuel" in a metal-salt solution battery
- 2: Reverse electrodialysis (RED) stacks incorporated into the MEC (works!)
  - RED stacks can produce electricity from salinity gradient energy (SGE)
  - Both natural and engineered salinity gradients can be used.



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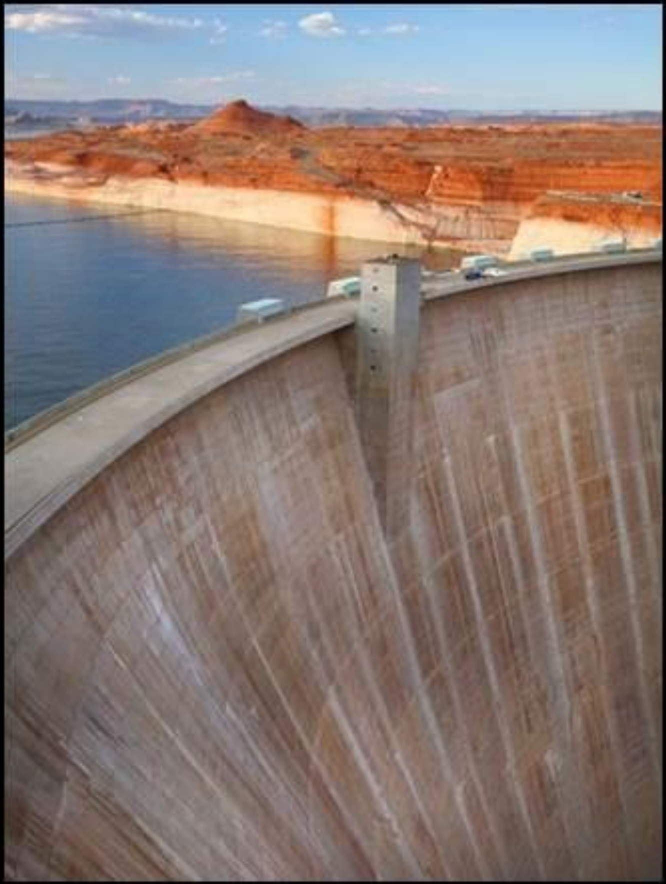
Natural Salinity Gradient Energy (SGE)

+

=

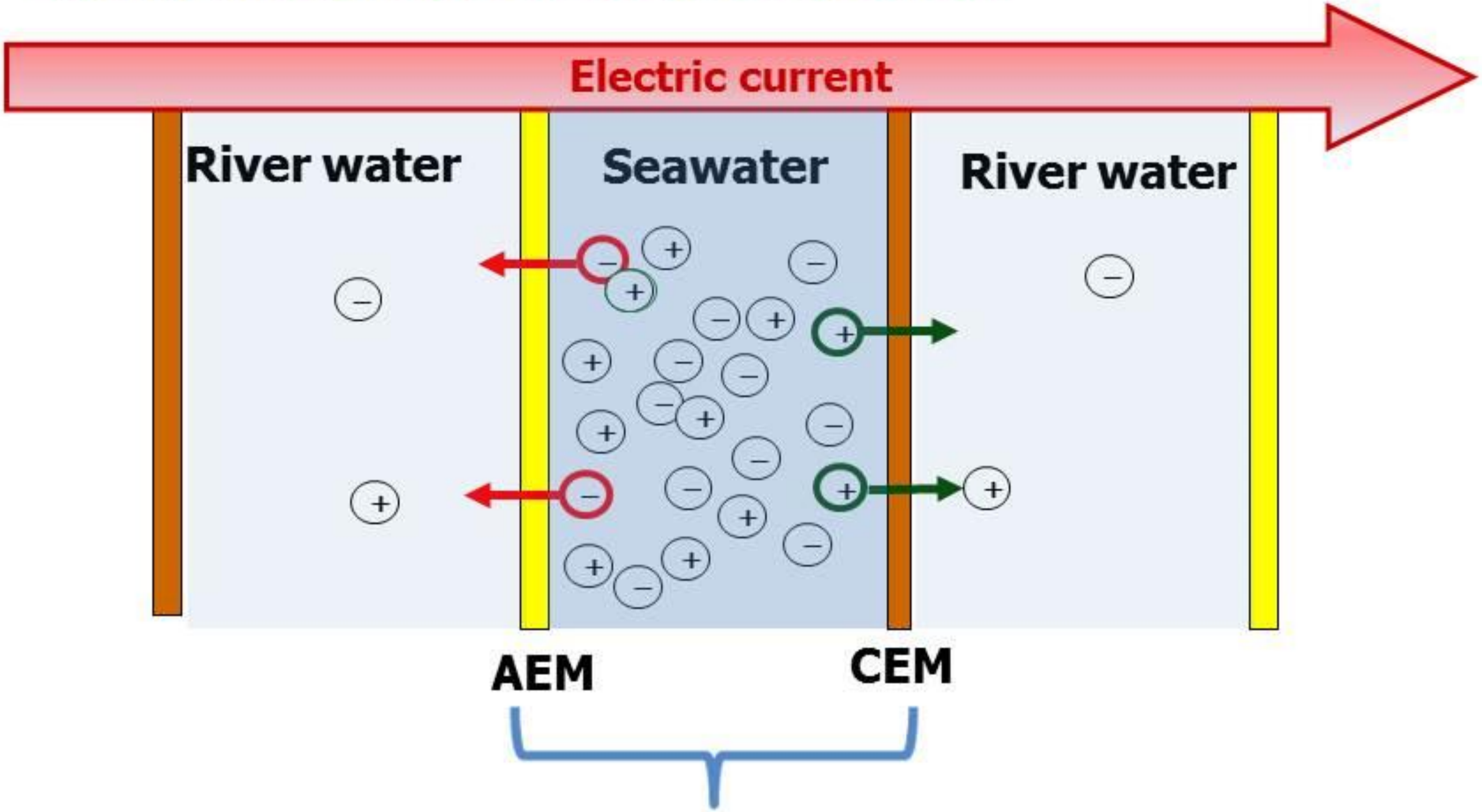


270 m of
Hydraulic Head

Oceanside WWTPs and Rivers could produce 980 GW

Reverse electrodialysis (RED)

Salinity difference **produces** electrical current



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

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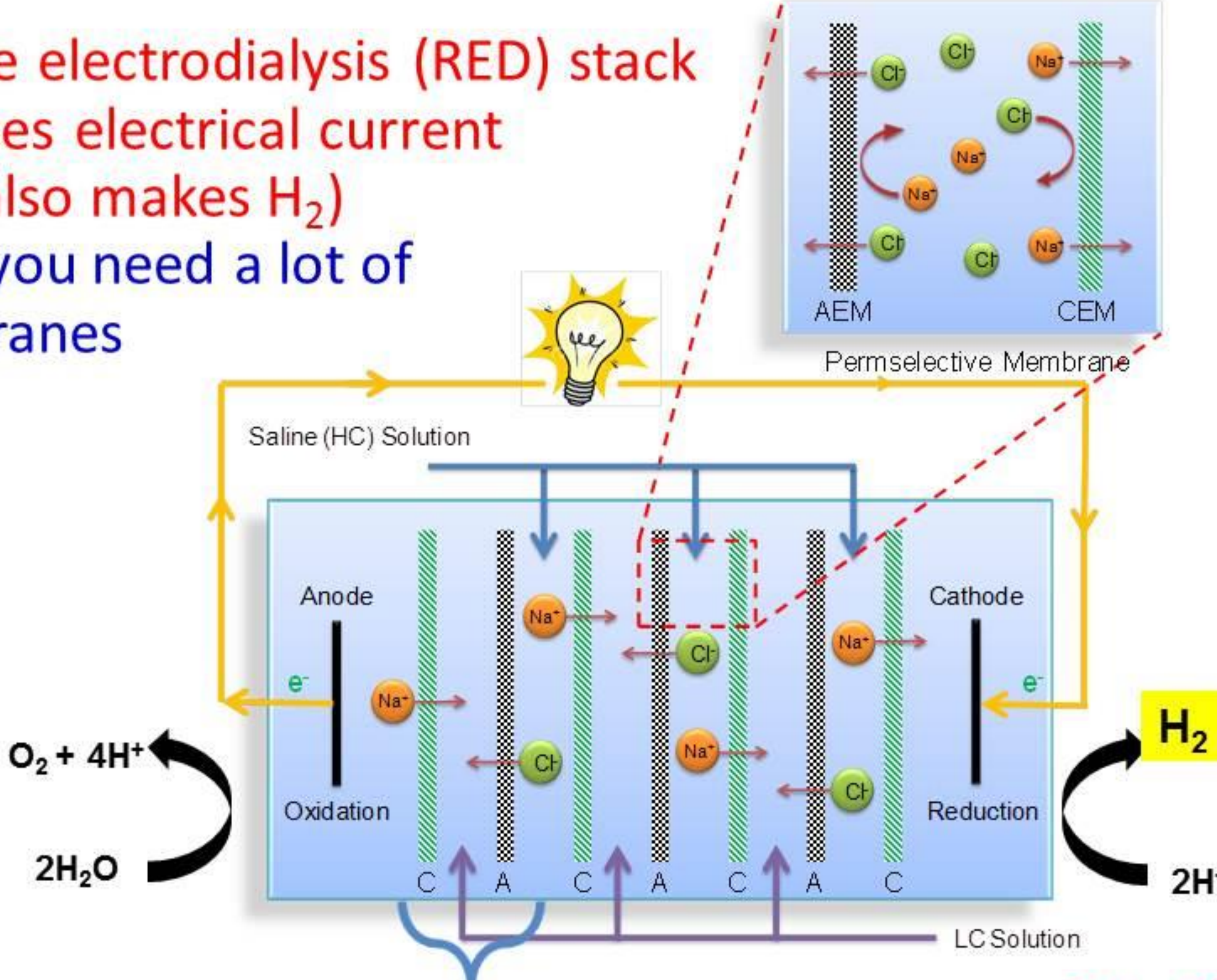
Reverse electrodialysis (RED) stack produces electrical current (here also makes H_2)

… but you need a lot of membranes



Each pair of high salt (HC) + low salt (LC) cells = **~0.1 – 0.2 V**

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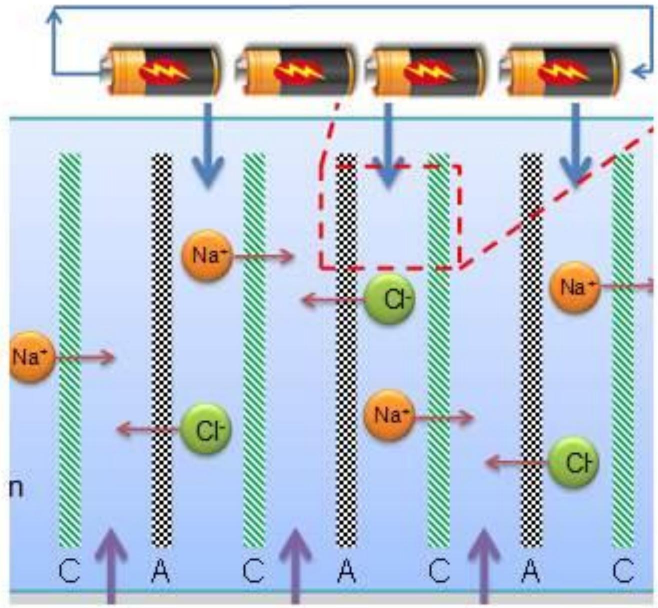
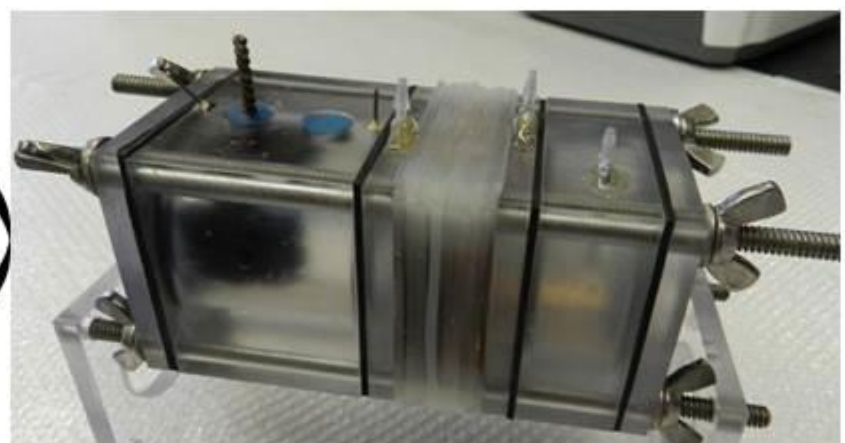
Logan and Elimelech (2012) Nature

What if we move the RED stack into an MFC?



Organic matter

CO_2 & H^+



$O_2 + 4H^+$

$2H_2O$

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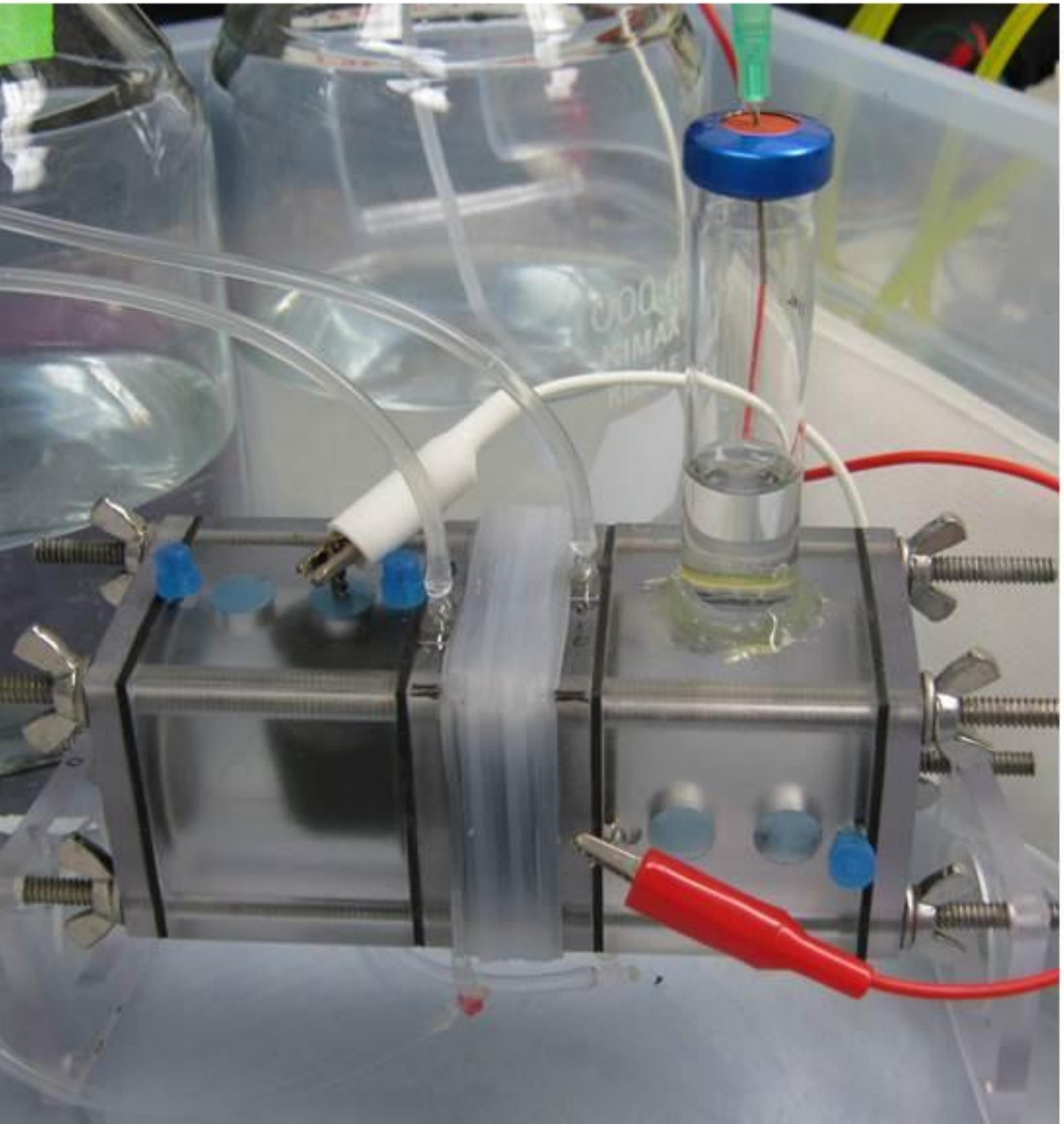
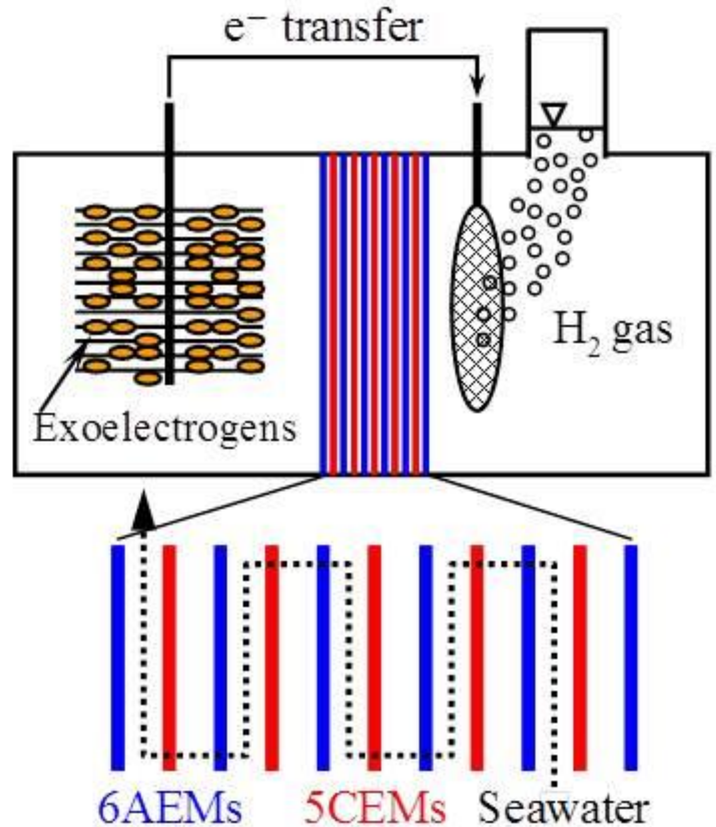
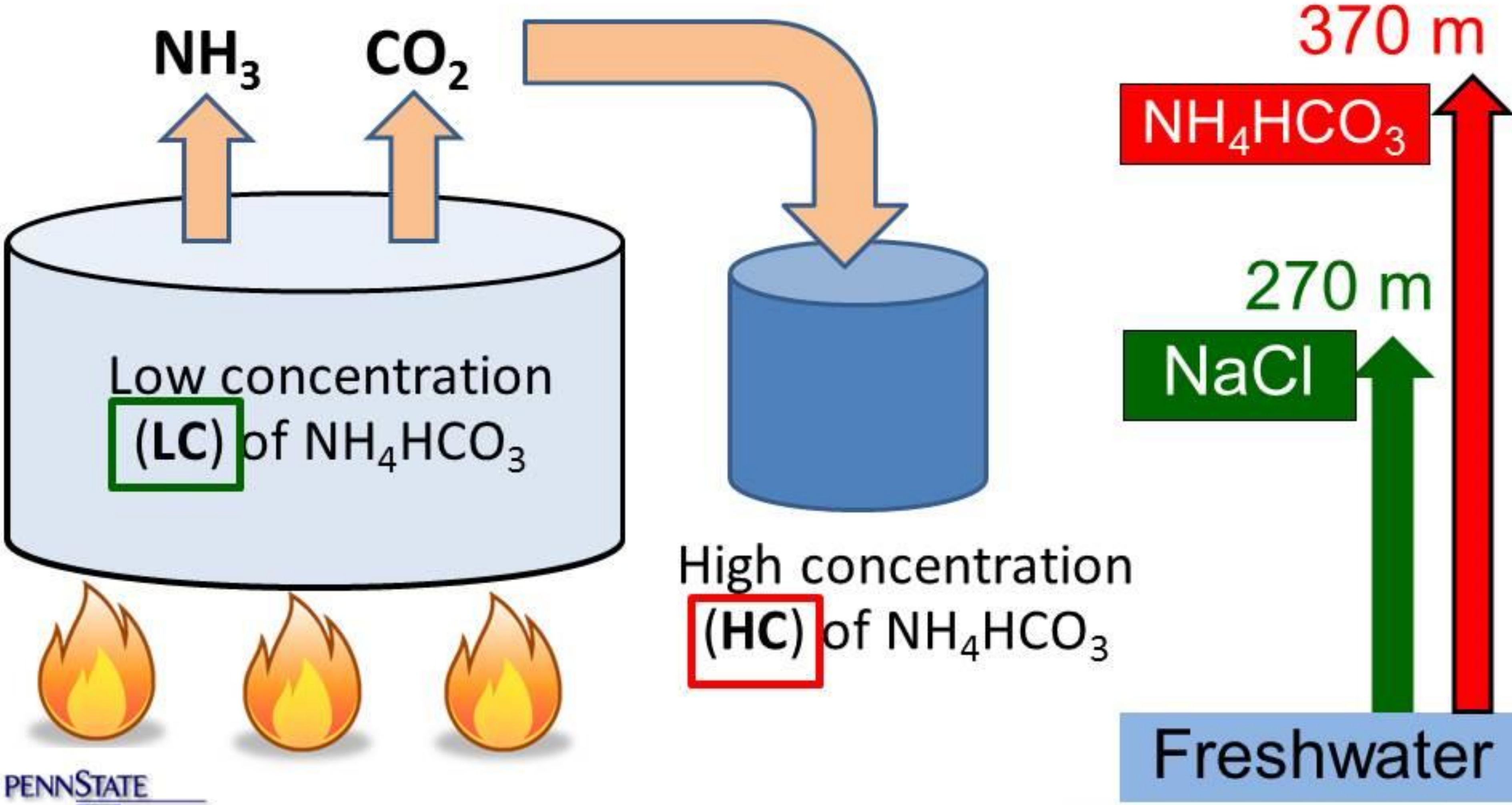
MEC + RED = MREC (Microbial RED Elec. Cell)





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

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



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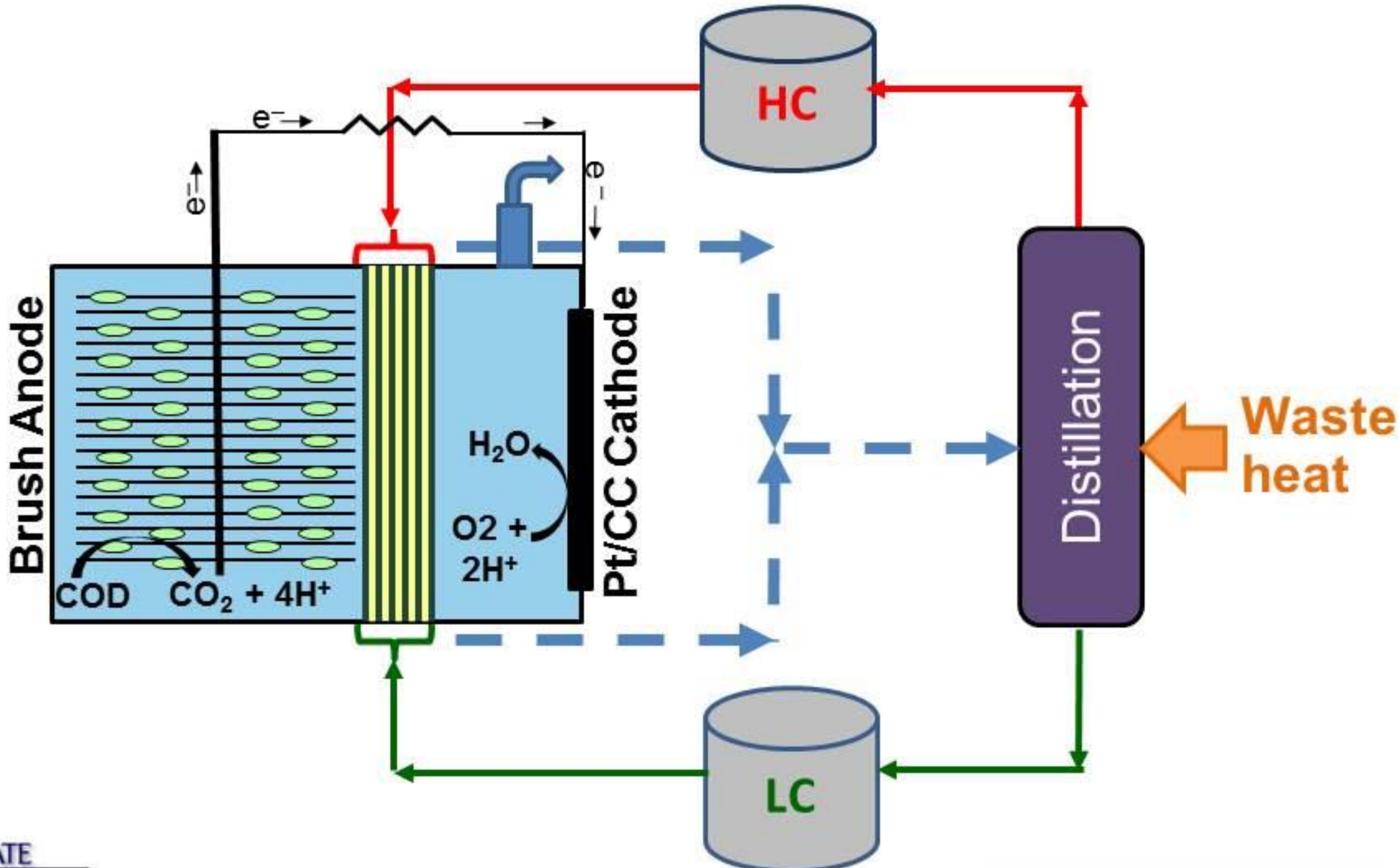
Cusick, Kim & Logan (2012) *Science*

MRFC Using Ammonium Bicarbonate



Cusick, Kim & Logan (2012) *Science*

Challenges & Opportunities

- Challenges- Big picture
  - Renewable H_2 production at high yields possible from lignocellulose
  - Microbial electrolysis cells have not been widely recognized as a method for H_2 production
- Challenges-Technical
  - Reactions at electrodes/materials/kinetics need to be improved (but without use of any precious metals)
  - Rates of H_2 production need to be increased
  - Cost of membranes will be a key factor in overall economics
  - Use of osmotic/heat energy systems needs to be further explored
- Opportunities
  - H_2 production is carbon neutral (CO_2 in plants is fixed and not fossil)
  - Incentives for "green" H_2 production could speed development and applications.

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Conclusions

- New green/renewable energy technologies can be created using electro-active microorganisms in different microbial electrochemical technologies:
  - MFCs= Electrical power
  - MECs= H_2 or CH_4 gases
- MECs can be combined with Blue energy technologies based on salinity gradient and waste heat energy sources
  - TRABs- thermal regenerable ammonia batteries using waste heat
  - MRECs = RED stacks incorporated into MECs

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International Collaborations

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للعلوم والتقنية
King Abdullah University of
Science and Technology

Water Desalination and
Reuse Center

UNIVERSITEIT
GENT

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NATIONAL RENEWABLE ENERGY LABORATORY

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