Electricity and hydrogen production using microbial fuel cell-based technologies

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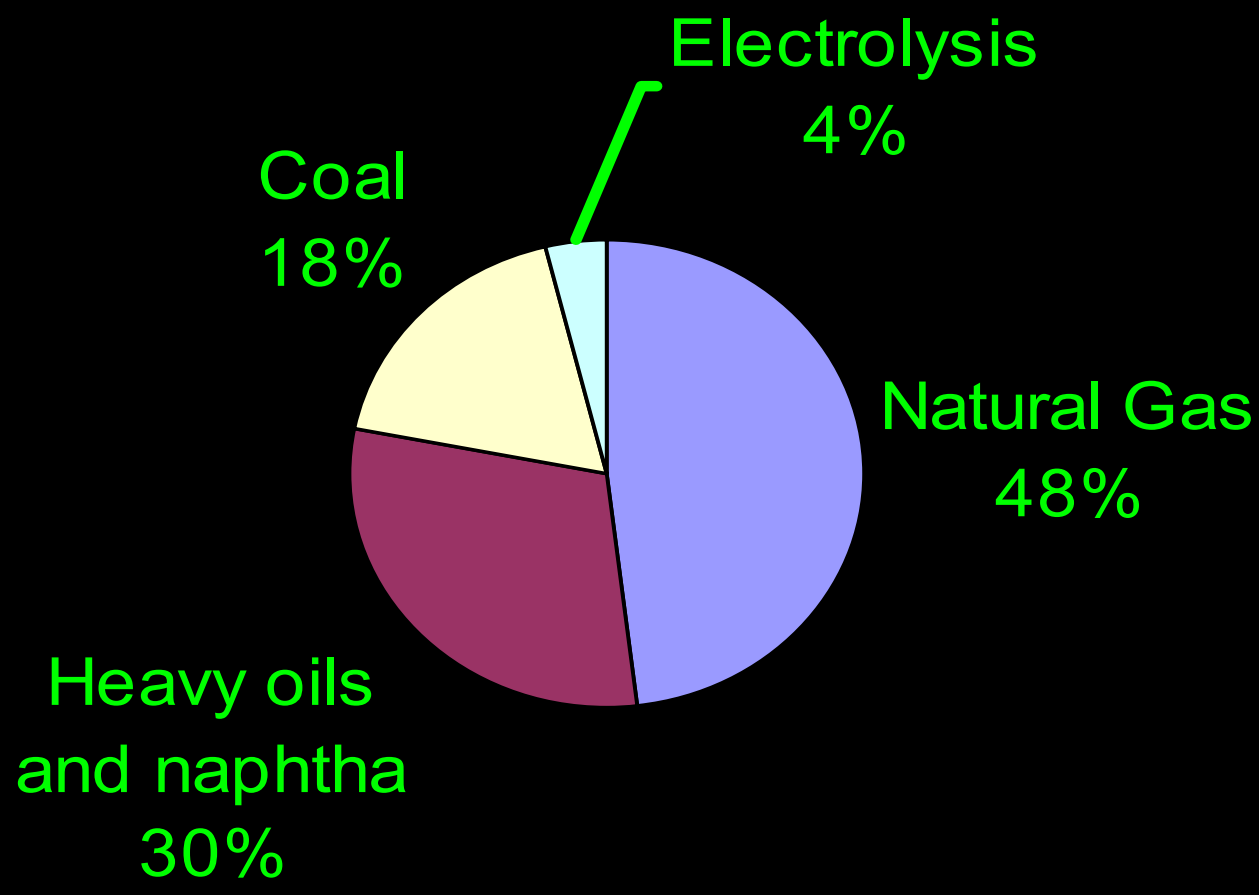
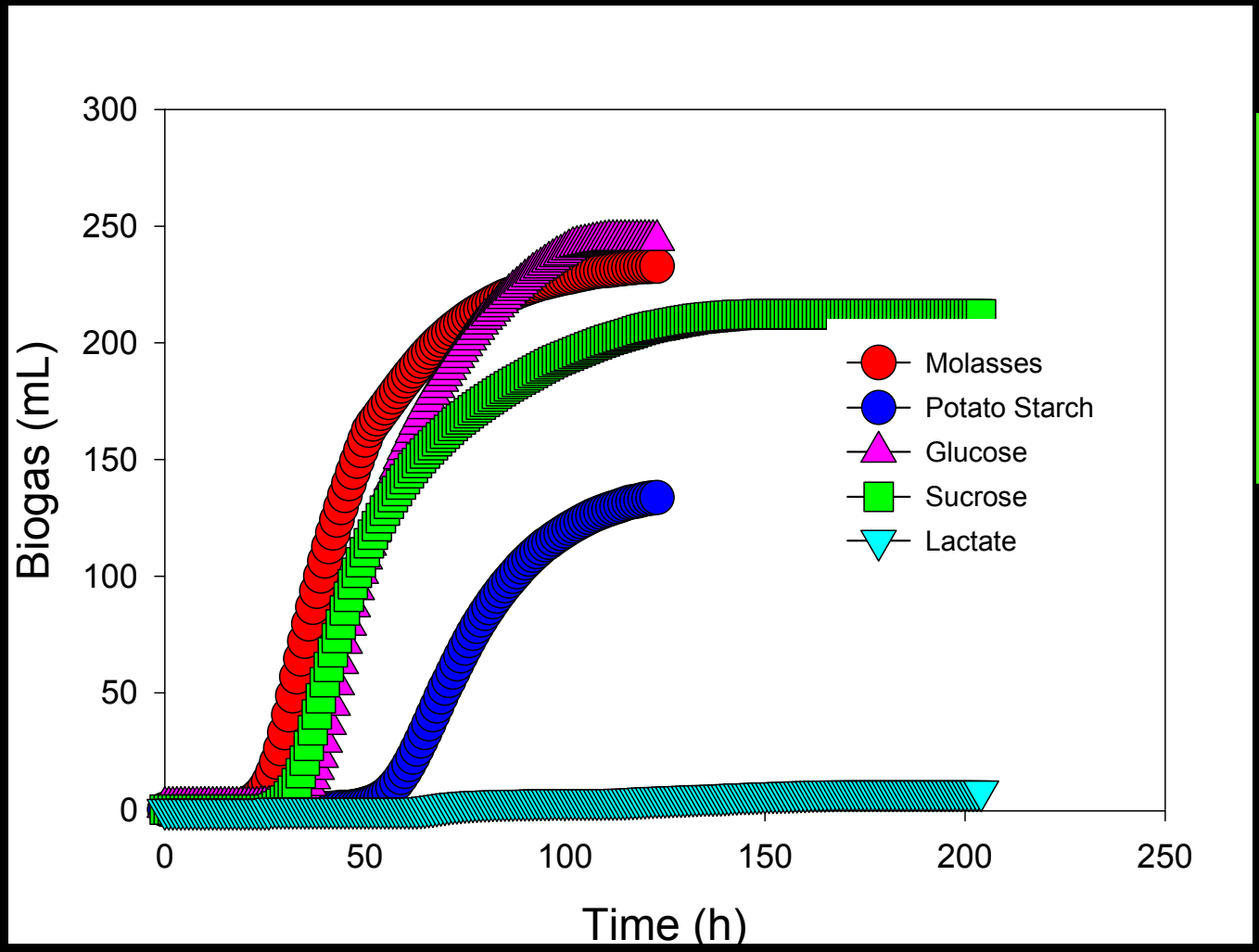
Ethanol versus H_2 from Glucose

- Glucose: ΔH_c= 2808 kJ/mol
- Ethanol
  - Produce 2 ethanol per glucose by fermentation
  - $2\times\Delta H_c$= 2× 1367 kJ/mol => ΔH_c= 2734 kJ/mol
- Hydrogen
  - Produce up to 12 H_2 per glucose
  - $12\times\Delta H_c$ = 12× 286 kJ/mol => ΔH_c = 3430 kJ/mol
- DOE
  - 10-12 mol-H_2/mol-glucose needed to make biological H_2 production feasible (9.6 mol H_2= ΔH_c for 2 ethanol from glucose)

Current sources of H_2 Production



H_2 can be biologically produced from bacterial fermentation of sugars

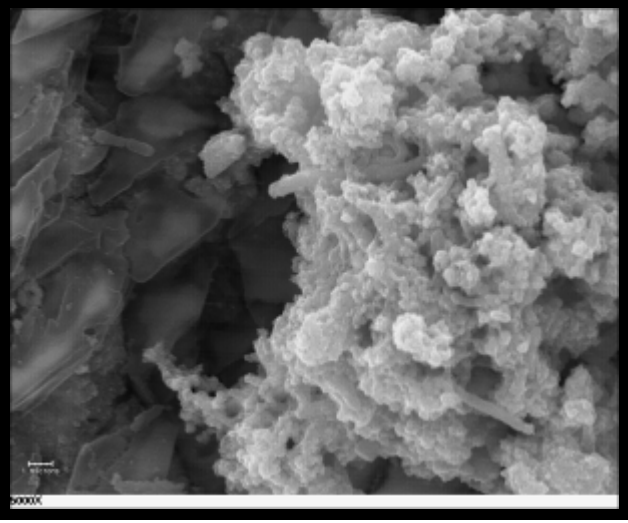


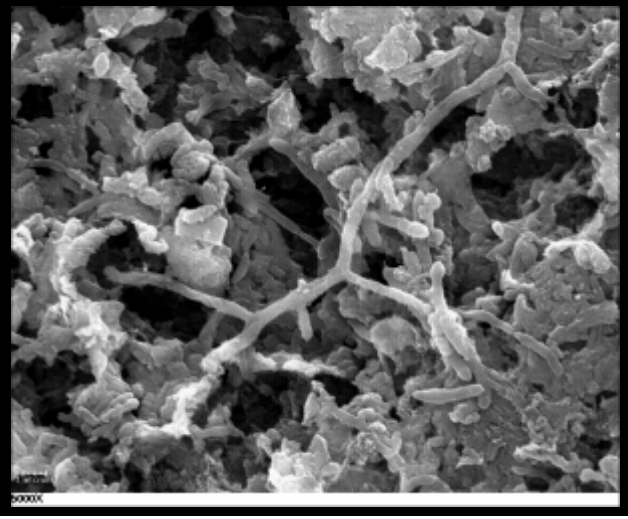
Biogas:

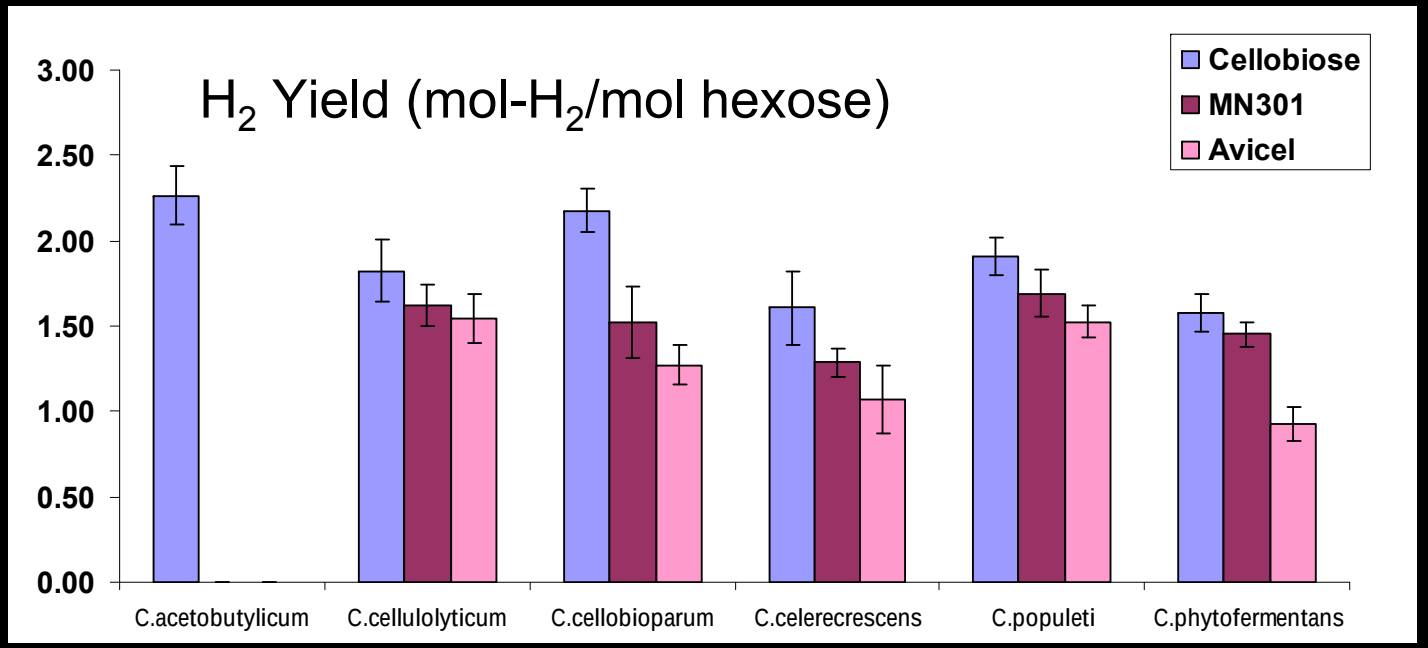
- 60% H_2
- 40% CO_2

Source: Logan, VanGinkel & Oh *Environ. Sci. Technol.* (2002)

H_2 can be produced by *cellulose fermentation*







Source: Ren et al., *J. Appl. Microbiol.* (2007)

The “fermentation barrier” limits H_2 yields

Maximum: 12 mol-H_2/mol-hexose

$C_6H_{12}O_6 \rightarrow 2\ H_2 + C_4H_8O_2 + 2\ CO_2$

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

Maximum of 4 mol/mol
(2 mol/mol in practice)

?

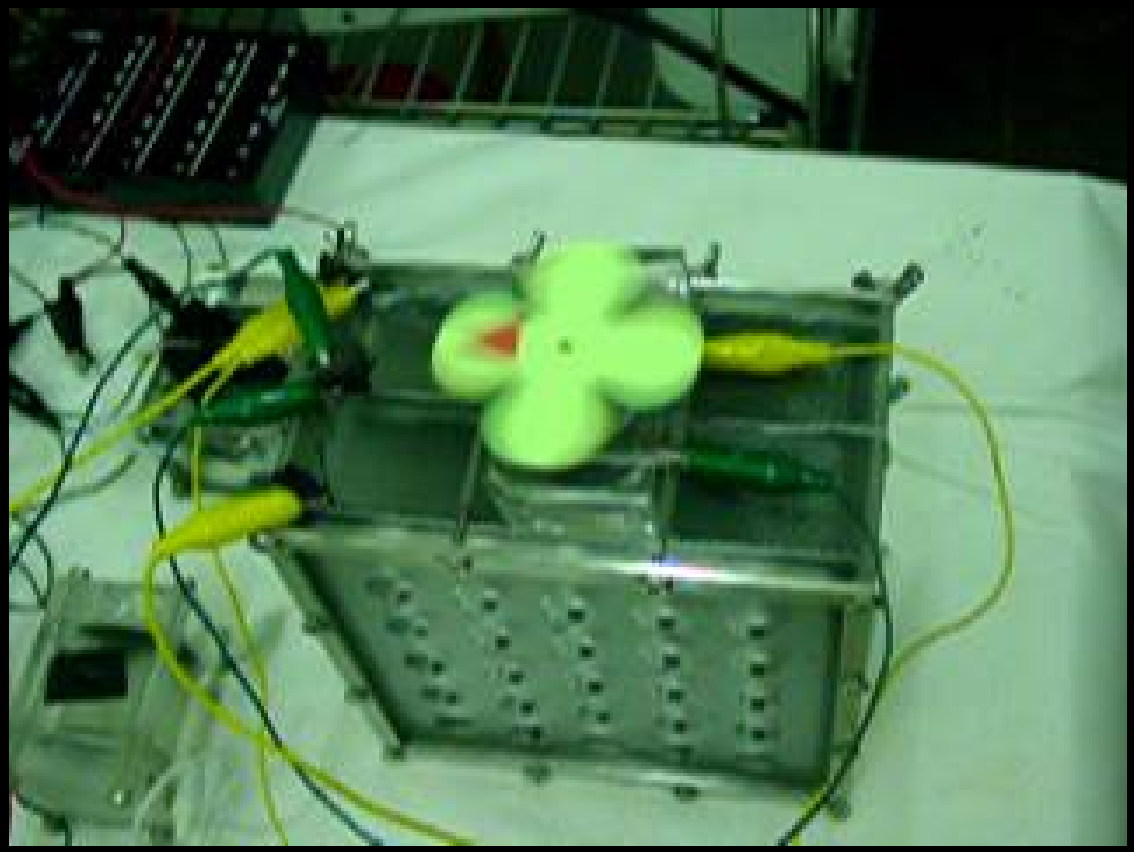
How can we recover the remaining 8 to 10 mol/mol?

...use the MEC/BEAMR process

Energy Production using MFC technologies

- Electricity production using microbial fuel cells (MFCs)
- H_2 Production from biomass using the MEC/BEAMR process: overcoming the "fermentation barrier"
- A path to renewable energy

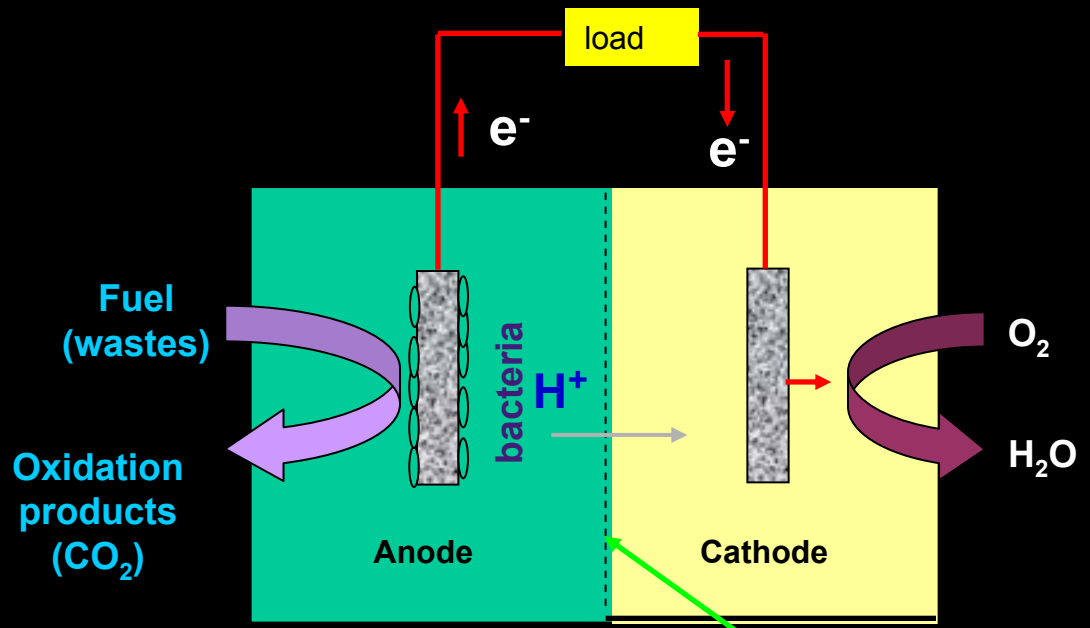
Demonstration of a Microbial Fuel Cell (MFC)

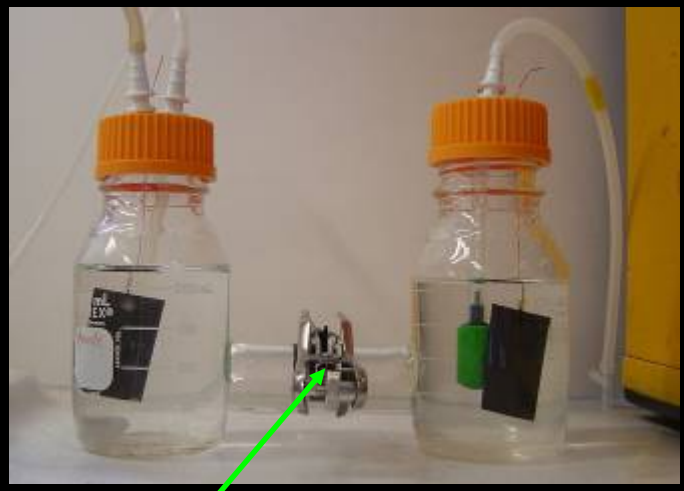


MFC webcam (live video of an MFC running a fan)

www.engr.psu.edu/mfccam

Microbial Fuel Cells: Aqueous cathode





Proton exchange membrane (PEM)

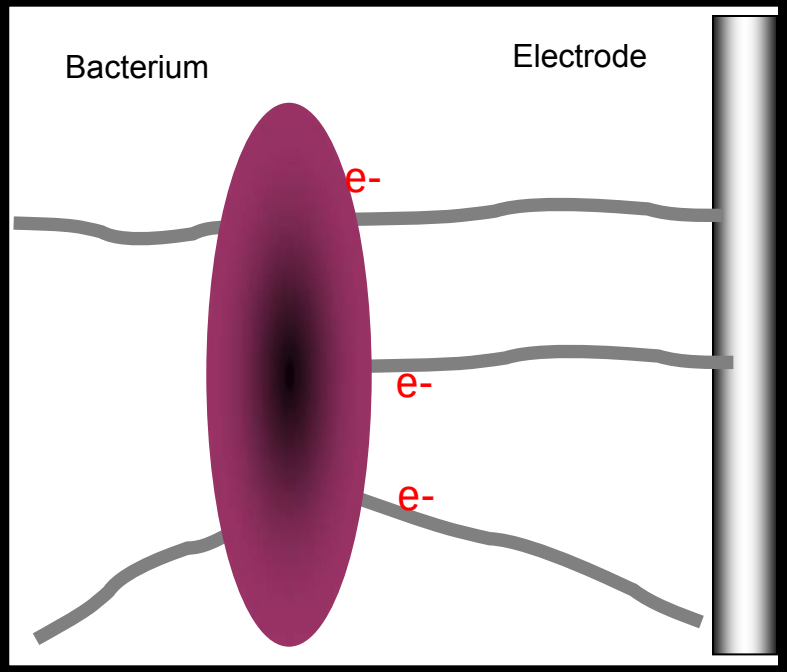
- *Methanogenesis*
  - Generation of methane
  - Methanogens
  - Anaerobic digesters

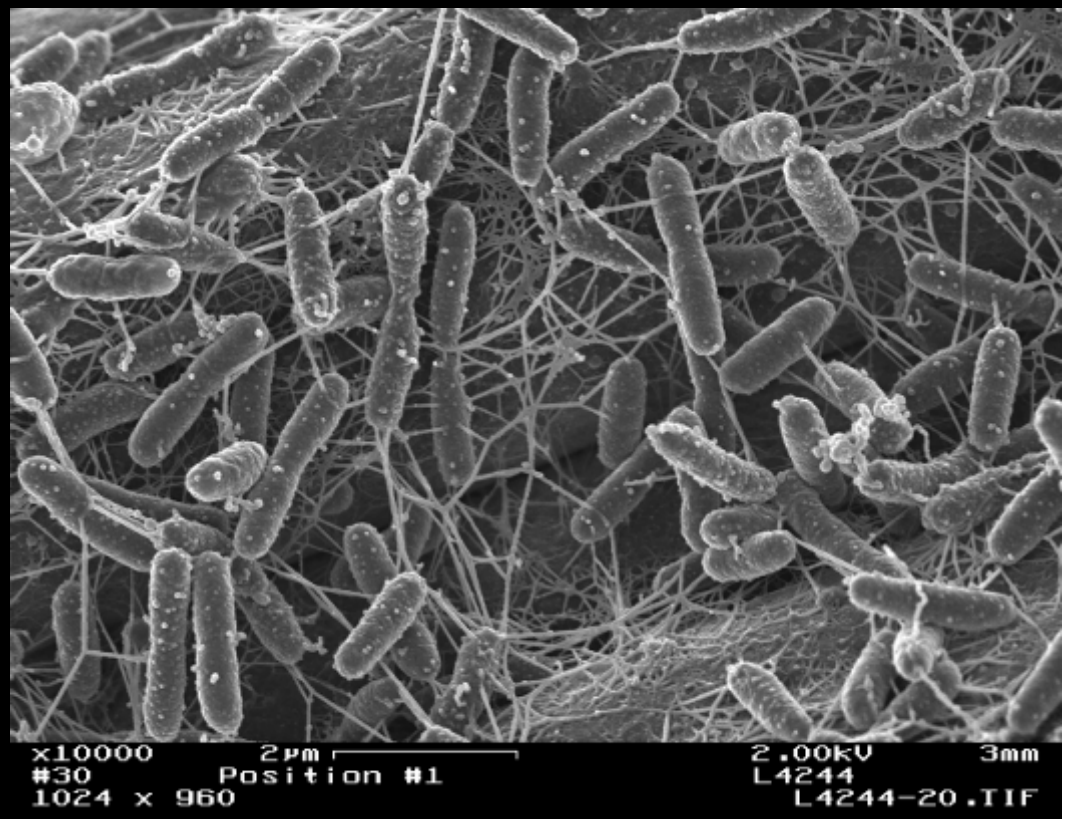
- *Electrogenesis*
  - Generation of electricity
  - Exoelectrogens
  - Microbial fuel cells (MFCs)
- *Electrohydrogenesis*
  - Generation of H_2 gas
  - Exoelectrogens
  - Microbial electrolysis cells (MECs)

Microbial community analysis (DGGE)

Inoculum (substrate)	Community	Reference
River sediment (glucose+glutamic acid)	α-*Proteobacteria* (mainly *Actinobacteria*)	Phung et al. (2004)
River sediment (river water)	β-*Proteobacteria* (related to *Leptothrix* spp.)	Phung et al. (2004)
Marine sediment (cysteine)	γ-*Proteobacteria*, 40% *Shewanella affinis* KMM, then *Vibrio* spp. and *Pseudoalteromonas* sp.	Logan et al. 2005
Wastewater (starch)	36%=unidentified, 25%=β- and 20%=α-*Proteobacteria*, and 19%= *Cytophaga+Flexibacter+Bacterioides*	Kim et al. (2004)
Wastewater (acetate)	24%=α-, 7%=β-, 21%=γ- , 21%= δ-*Proteobacteria;* 27%=others	Lee et al. (2003)

New finding: bacteria use “nanowires”





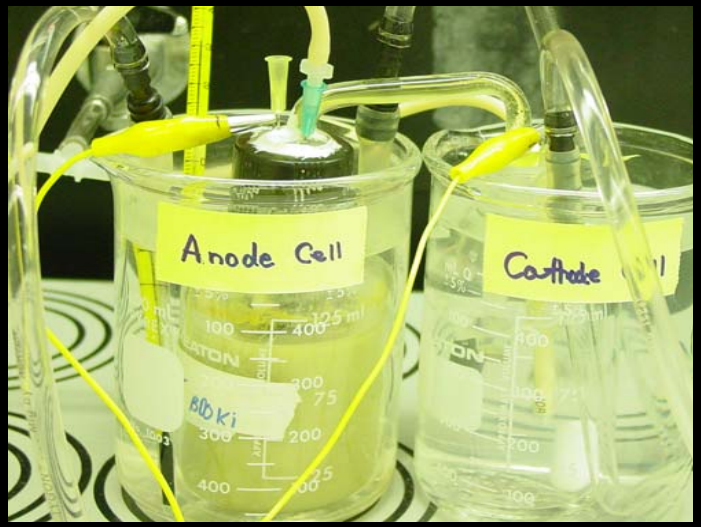
Bacteria that can transfer electrons directly to the electrode:

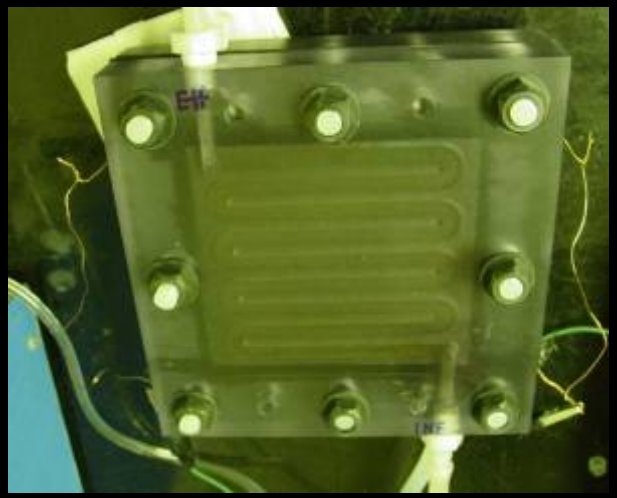
- *Geobacter sulfurreducens*
- *Alteromonas sp.*
- *Shewanella spp.*

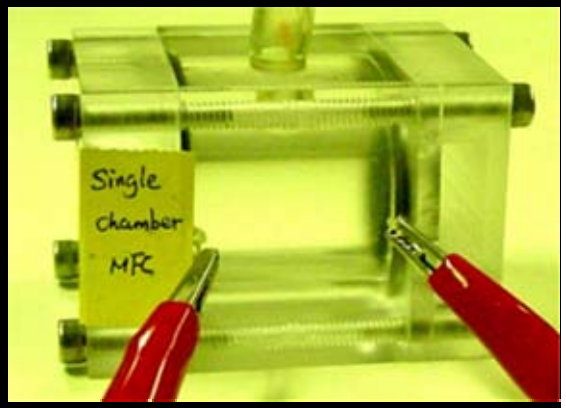
Source: Gorby *et al. PNAS* (2006)

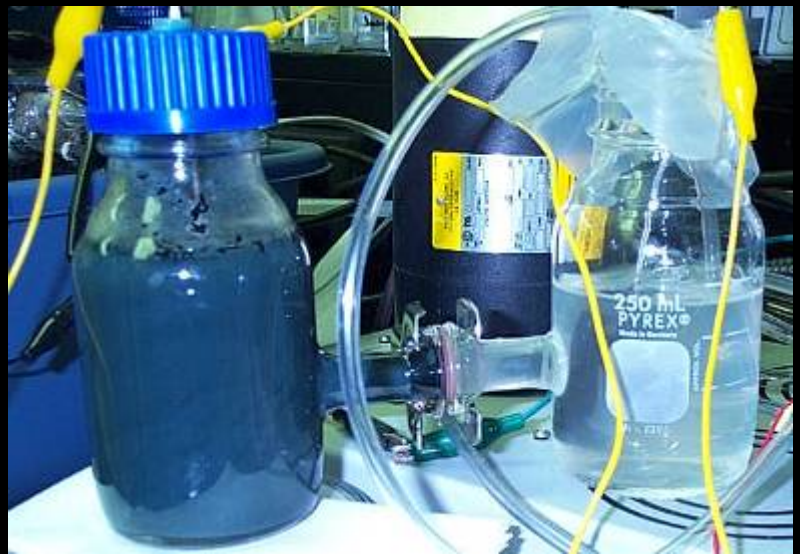
Current level of development:

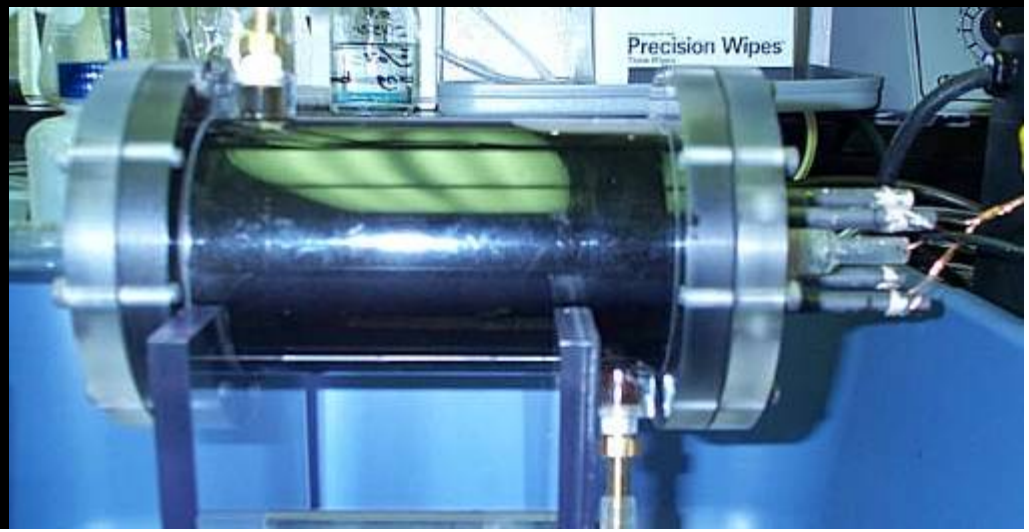
System architecture (not microbiology) limits power





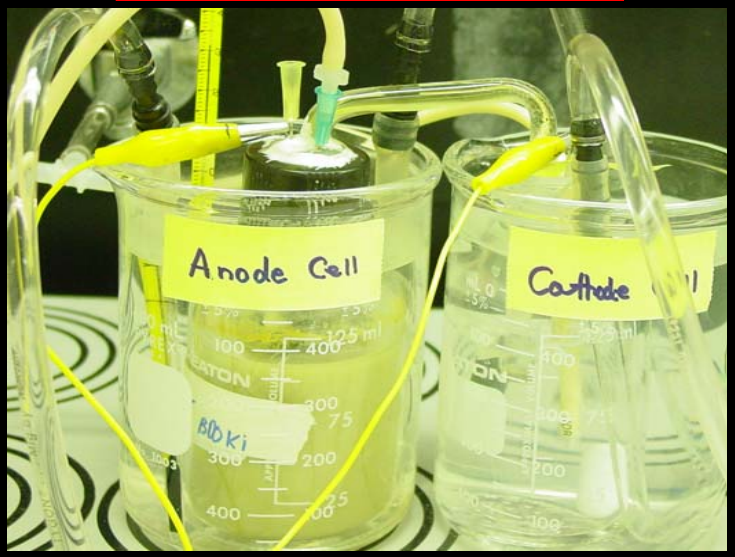






Power density is limited by internal (system) resistance

Power: 0.3-3 mW/m^2



System resistance: 66,920 Ω

Power: 40 mW/m^2

System resistance: 1,756 Ω

$$P = \frac{OCV^2 R_{ex}}{A(R_{int} + R_{ex})^2}$$

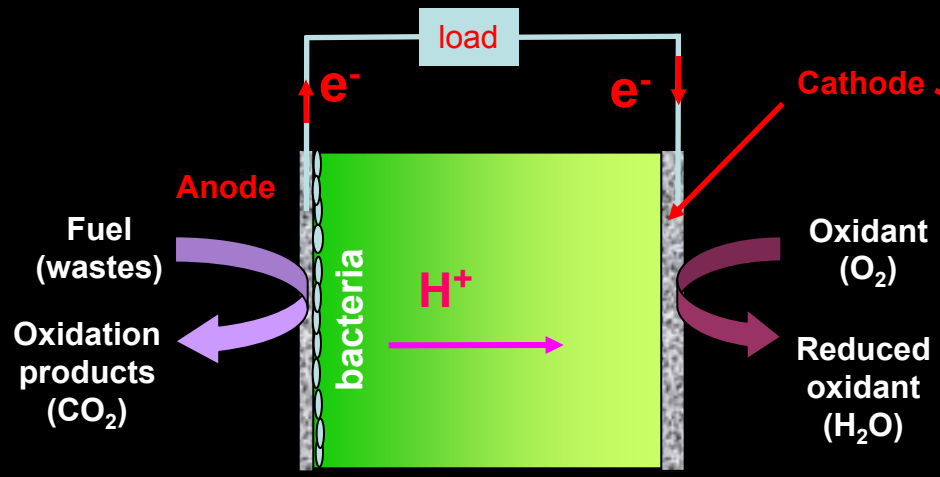
P=	Power normalized surface area
OCV=	Open circuit voltage
R_{ex}=	External resistance
R_{in}=	Internal resistance
A=	Electrode projected surface area

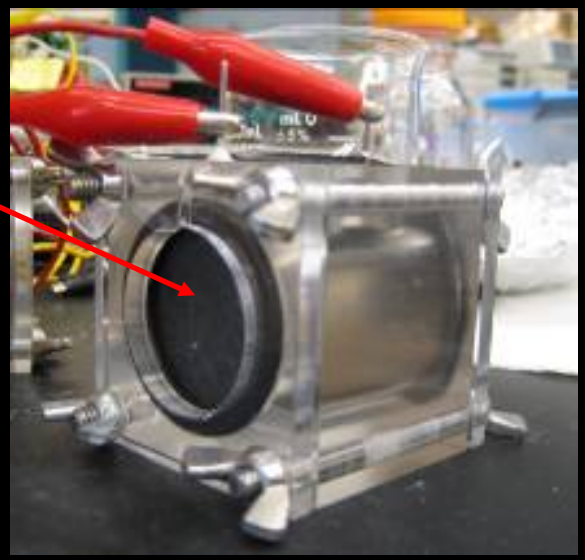
Source: Min et al., *Wat. Res (2005)*

Air Cathode MFC

- Bacteria oxidize organic matter

- Generate electricity from any form of biodegradable organic matter



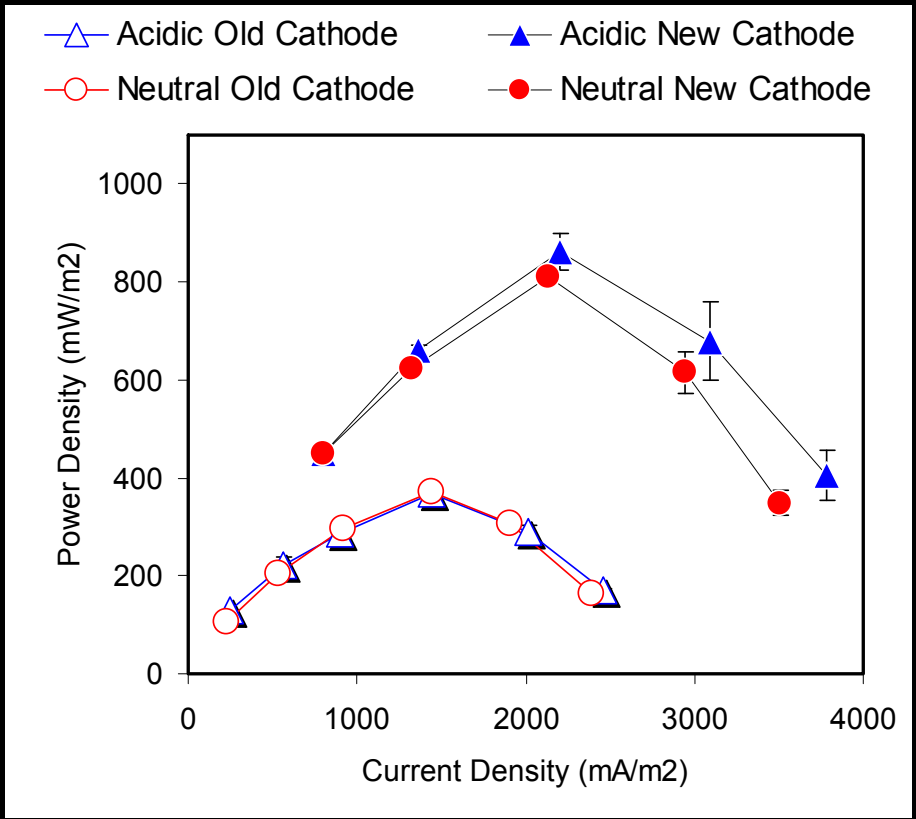


Power production (early studies)

Substrate	Power (mW/m^2)
Glucose	494
Acetate	506
Butryate	309
Protein	269
Domestic wastewater	146

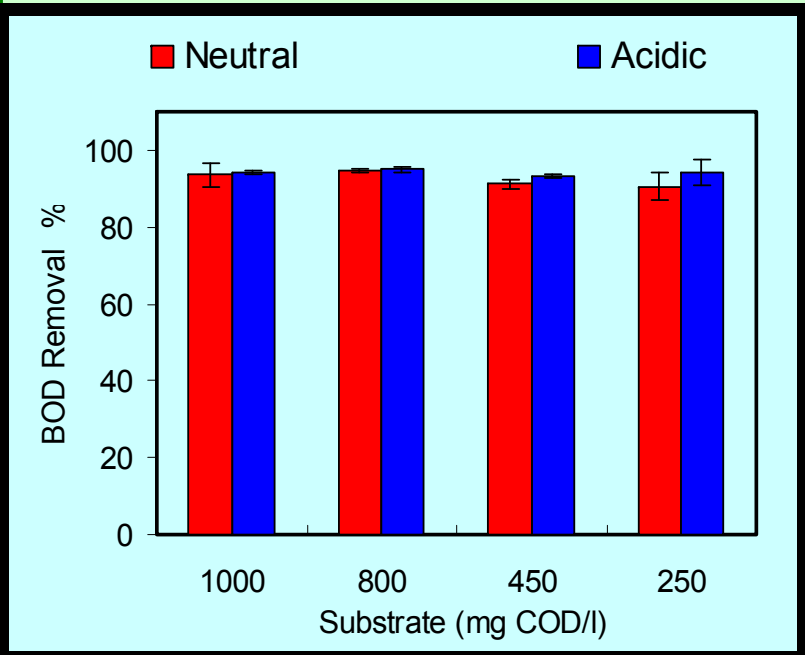
Electricity from corn stover hydrolysates

Corn stover: 90% of 250 million tons remains unused in fields (largest source of solid waste biomass in USA)



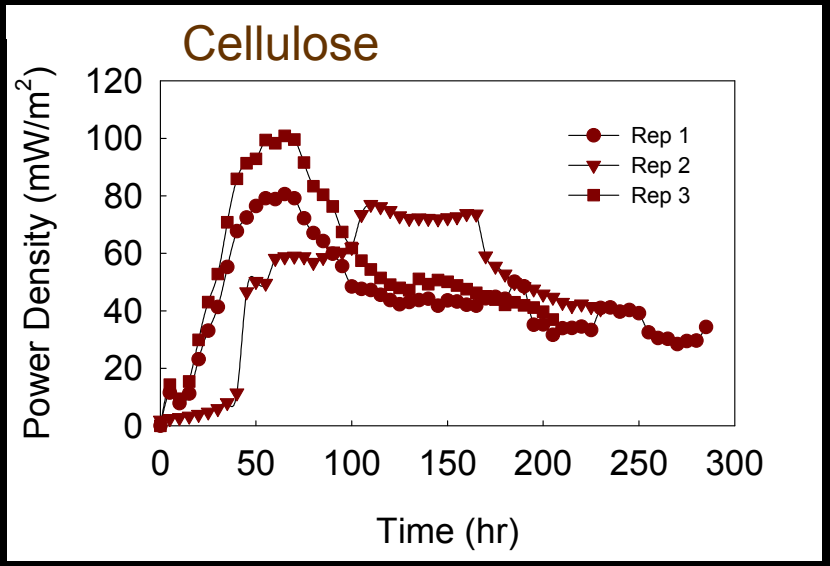
Maximum Power= 860 mW/m^2

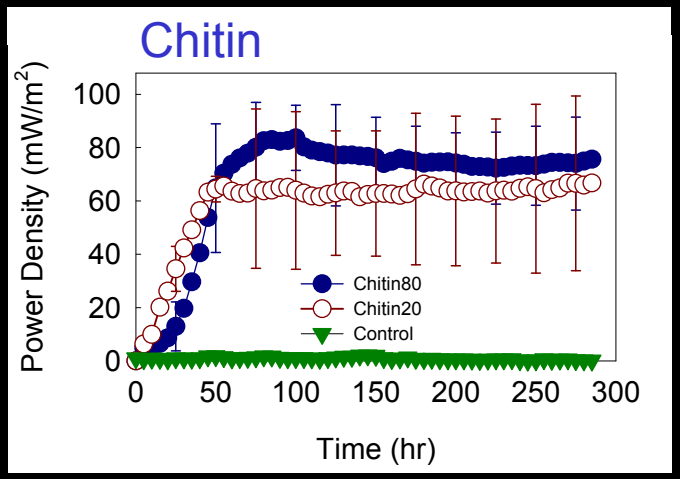
~93% removal of biodegradable organic matter



Source: Zuo et al. (2006) Energy & Fuels

Electricity from cellulose and chitin in a sediment MFC



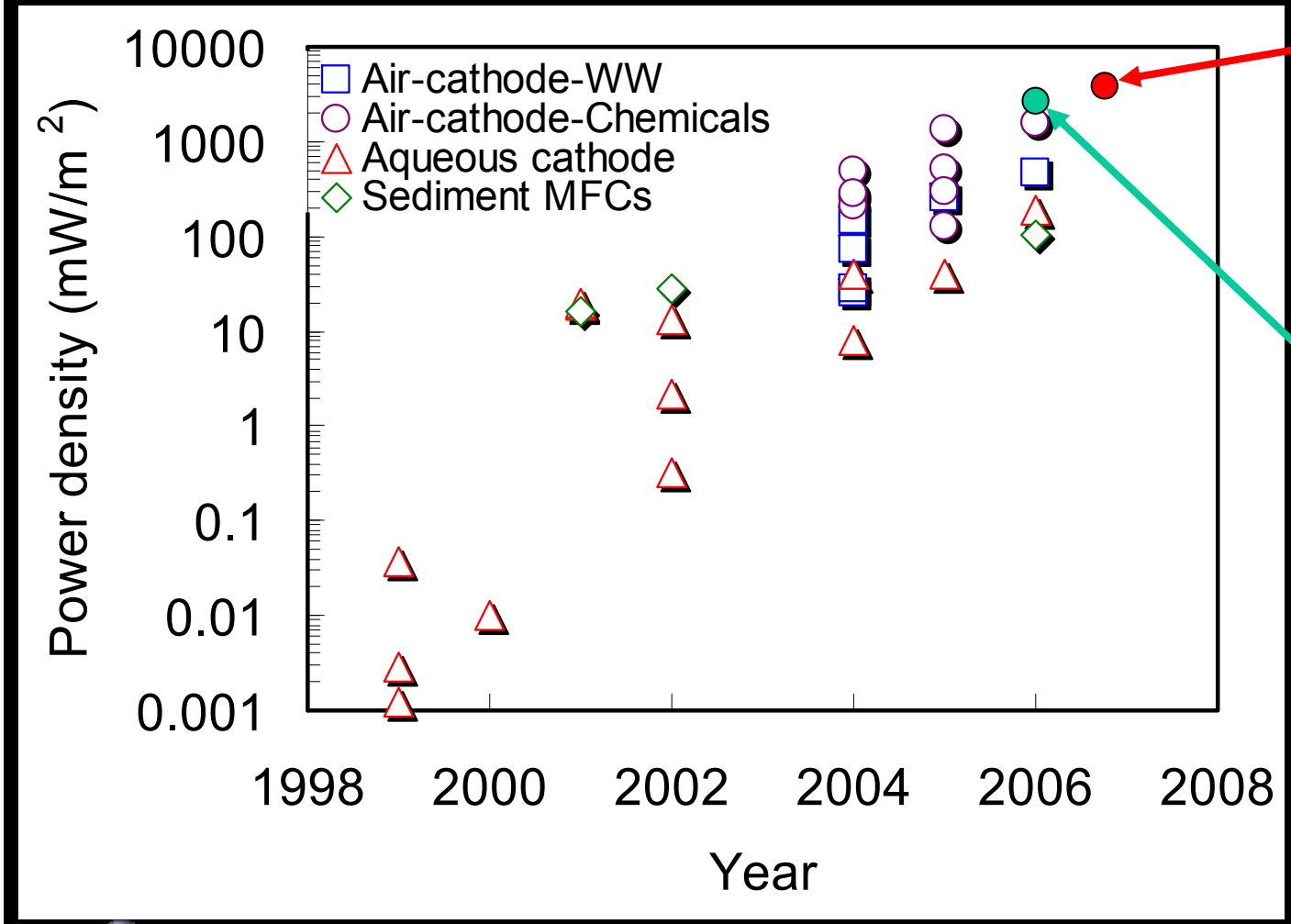


Rezai, Richard, Brennan and Logan, *ES&T* (2007)

Advances in operating conditions and materials selection

- Factors affecting performance
  - Solution conductivity
  - Electrode spacing
  - Continuous flow
- Cathode materials
  - Non-precious metal cathode catalyst
  - Diffusion layers for water control
- Anode materials
  - Treatment technique for rapid power generation (high-temperature ammonia gas)

Power production in MFCs is improving



Start of 2007:
2400 mW/m^2
76 W/m^3

End of 2006:
1970 mW/m^2
115 W/m^3

System Scale
(Wastewater Treatment)

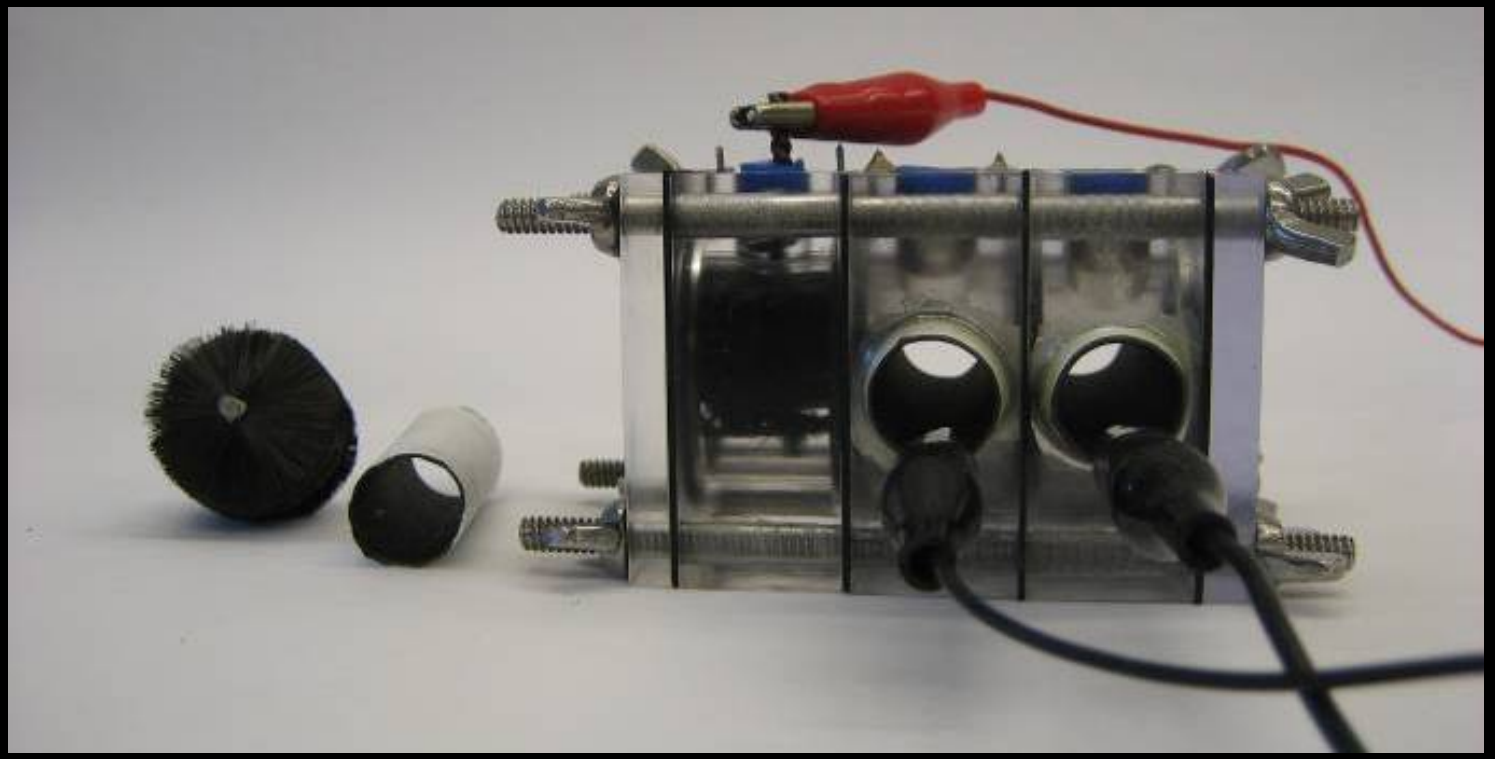
What will a large scale MFC system of the future look like?

System Scale up

- Scale up covered by two Penn State patents
  - "Materials and configuration for scalable microbial fuel cells." Provisional patent.
  - "A bioelectrochemically assisted microbial reactor (BEAMR) that generates hydrogen gas." (60/588,022)

System Scale up

Brush anodes and tube cathode reactors



Sources: Logan et al. (2007) and Zuo et al. (2007) both in: *Environ. Sci. Technol.* (2005)

Energy Production using MFC technologies

- Electricity production using microbial fuel cells (MFCs)
- H_2 Production from biomass using the MEC/BEAMR process: overcoming the "fermentation barrier"
- A path to renewable energy

Essentials of the MEC Process

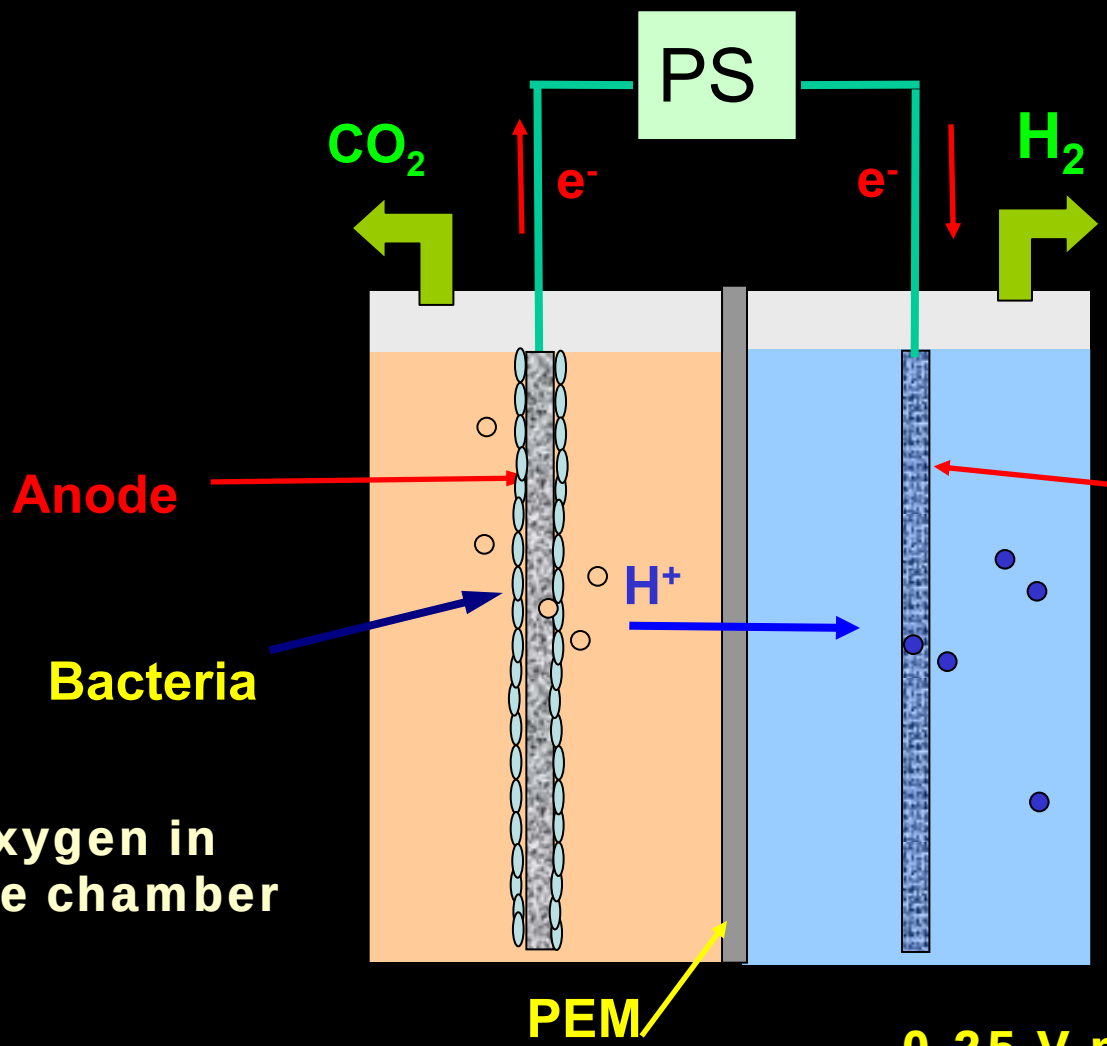
- Conventional MFC: oxygen at the cathode
  - Anode potential= -300 mV
  - Cathode Potential= +200 mV (+804 mV theory)
  - Circuit working voltage= 200 - (-300) = 500 mV

Anode: $C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 8\ e^- + 8\ H^+$
Cathode: $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

- *MEC: (no oxygen)*
  - Anode potential= -300 mV
  - Cathode potential: 0 mV
  - Needed to make H_2= 410 mV (theory)
  - Circuit (~300 mV) augmented with >110 mV= >410 mV

Anode: $C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 8\ e^- + 8\ H^+$
Cathode: $8\ H^+ + 8\ e^- \rightarrow 4\ H_2$

Biomass H_2- from any biomass using MECs



0.25 V needed
(vs 1.8 V for water electrolysis)

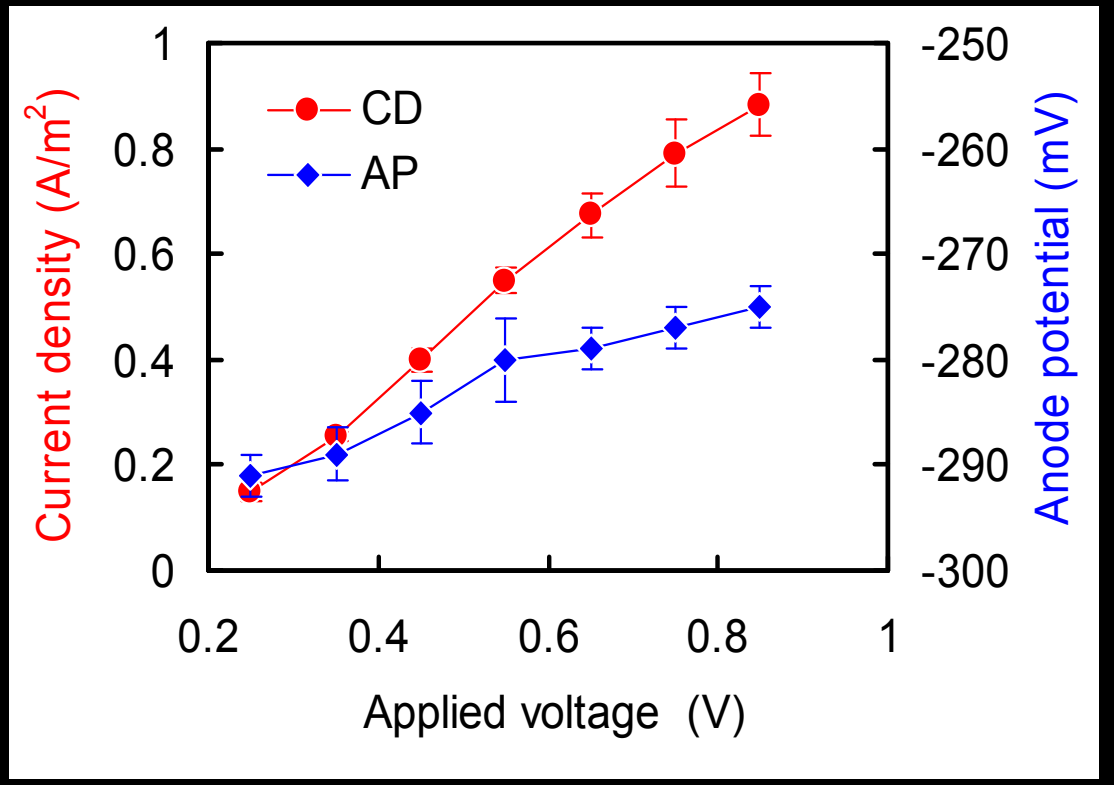
Ref: Liu et al. *Environ. Sci. Technol.* (2005)

Low applied voltages used for H_2 production

Minimum voltage needed is >0.25 V

(=0.11 V theory)

BEAMR voltage much less than that needed for water electrolysis (1.8 V)



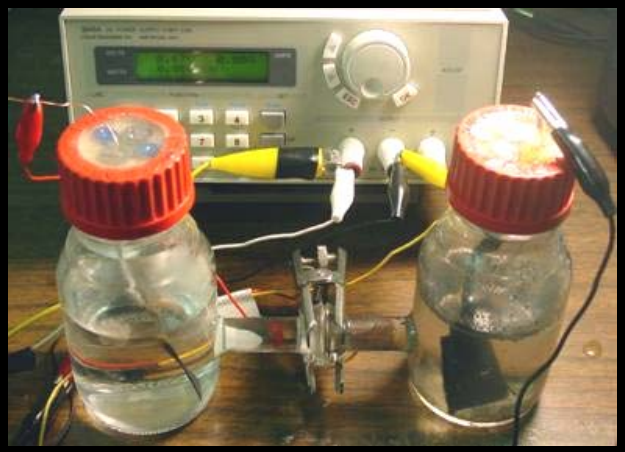
Source: Liu et al. *Environ. Sci. Technol.* (2005)

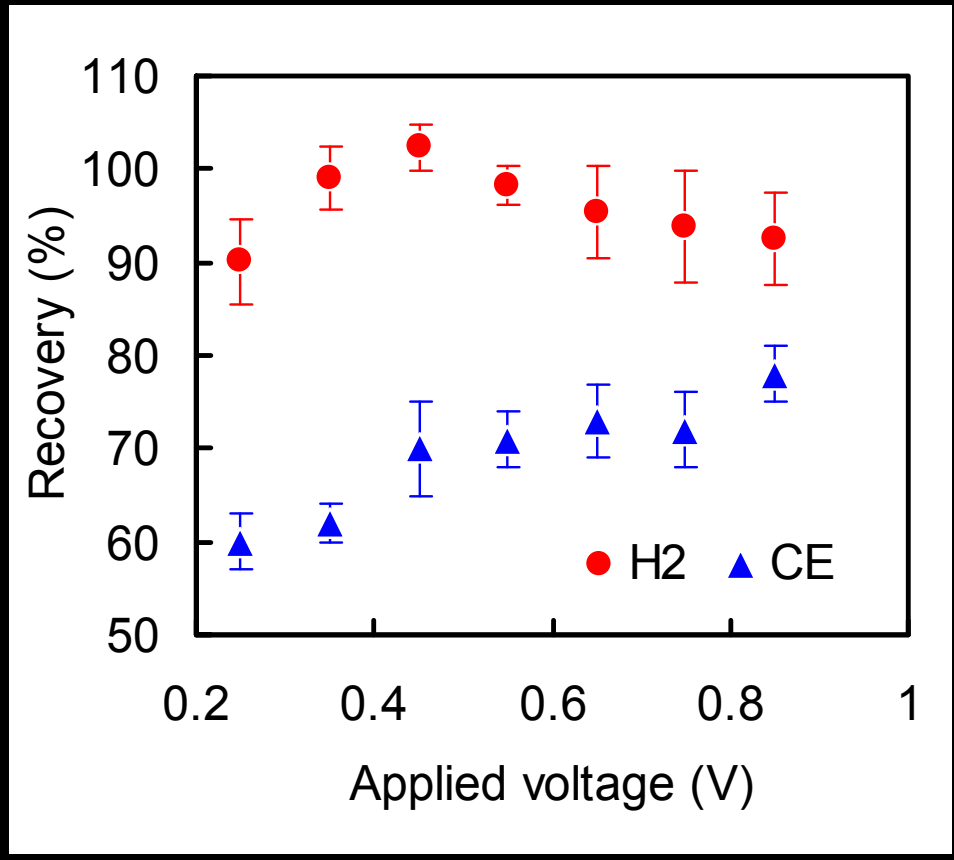
H_2 Recovery

R_{CE}= 60%-78%
(electrons from substrate)

R_{Cat}=90-100%
(H_2 from electrons)

-**Overall:**
R_{H2}= >70% (>0.5 V)
(=2.9 mol-H_2/mol-acetate
vs maximum of 4 mol/mol)





Source: Liu *et al. Environ. Sci. Technol.* (2005)

Breakthrough in H_2 production rates and energy efficiencies

PNAS PNAS PNAS PNAS

Sustainable and efficient biohydrogen production via electrohydrogenesis

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Edited by James M. Tiedje, Michigan State University, East Lansing, MI, and approved September 17, 2007 (received for review July 9, 2007)

Hydrogen gas has tremendous potential as an environmentally acceptable energy carrier for vehicles, but most hydrogen is generated from nonrenewable fossil fuels such as natural gas. Here, we show that efficient and sustainable hydrogen production is possible from any type of biodegradable organic matter by electrohydrogenesis. In this process, protons and electrons released by exoelectrogenic bacteria in specially designed reactors (based on modifying microbial fuel cells) are catalyzed to form hydrogen gas through the addition of a small voltage to the circuit. By improving the materials and reactor architecture, hydrogen gas was produced at yields of 2.01–3.95 mol/mol (50–99% of the theoretical maximum) at applied voltages of 0.2 to 0.8 V using acetic acid, a typical dead-end product of glucose or cellulose fermentation. At an applied voltage of 0.6 V, the overall energy efficiency of the process was 288% based solely on electricity applied, and 82% when the heat of combustion of acetic acid was included in the energy balance, at a gas production rate of 1.1 m^3 of H_2 per cubic meter of reactor per day. Direct high-yield hydrogen gas production was further demonstrated by using glucose, several volatile acids (acetic, butyric, lactic, propionic, and valeric), and cellulose at maximum stoichiometric yields of 54–91% and overall energy efficiencies of 64–82%. This electrohydrogenic process thus provides a highly efficient route for producing hydrogen gas from renewable and carbon-neutral biomass resources.

biofilms | cellulose | electron transport | hydrogen | microbial fuel cells

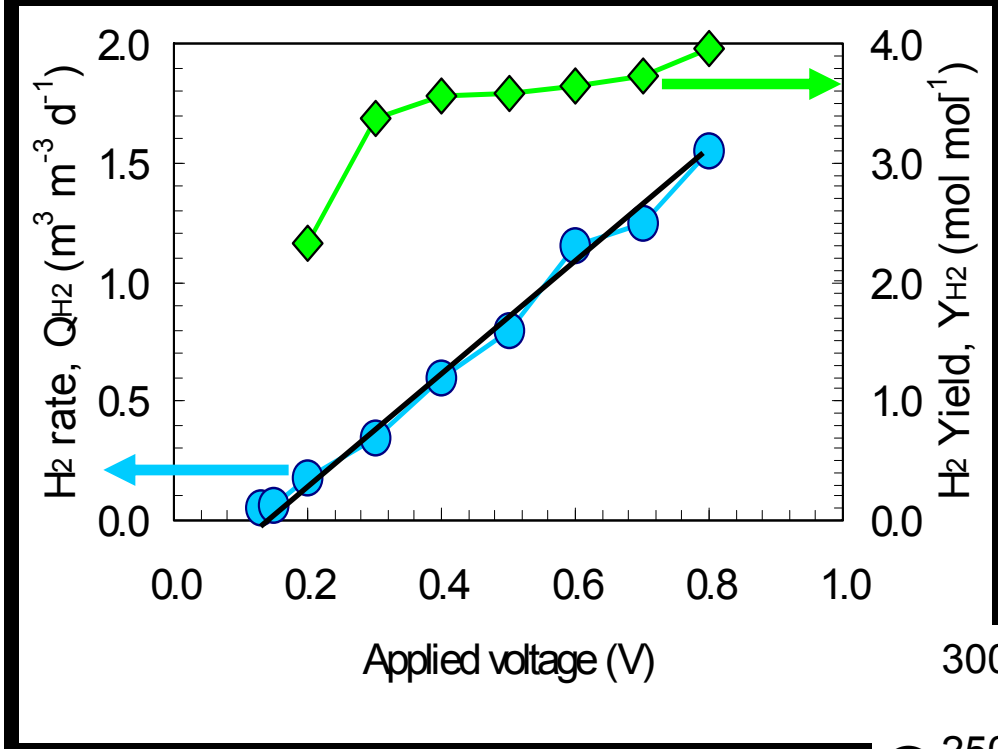
posed by the microbial formation of fermentation dead-end products, such as acetic acid. However, overall process efficiencies and hydrogen production rates have previously been low.

To substantially increase hydrogen generation rates and efficiencies, we developed a compact reactor system using chemically modified three-dimensional graphite granule anode and an anion exchange membrane. Graphite granules were treated by a high-temperature ammonia gas process to increase bacterial adhesion and overall power generation (10). Hydrogen fuel cells, and most other reactors previously examined, use a cation exchange membrane (e.g., Nafion) to keep reactor chambers separated. The membrane reduces the diffusion of hydrogen evolved at the cathode into the anode solution where it can be lost to bacterial oxidation. Cation exchange membranes preferentially transfer cations present at high concentration in solution rather than protons (e.g., Na^+ and K^+) (11, 12), resulting in an elevated pH at the cathode that limits the hydrogen evolution reaction and a reduced pH at the anode that limits bacterial growth. Low pH cannot be used at the anode because exoelectrogenic bacteria require near-neutral pH conditions, resulting in low proton concentrations (i.e., 10^{-7} M) which can limit the overall reaction rate. By using an anion exchange membrane, proton conduction was enhanced by protons being carried by negatively charged phosphate anions through the membrane.

Results and Discussion

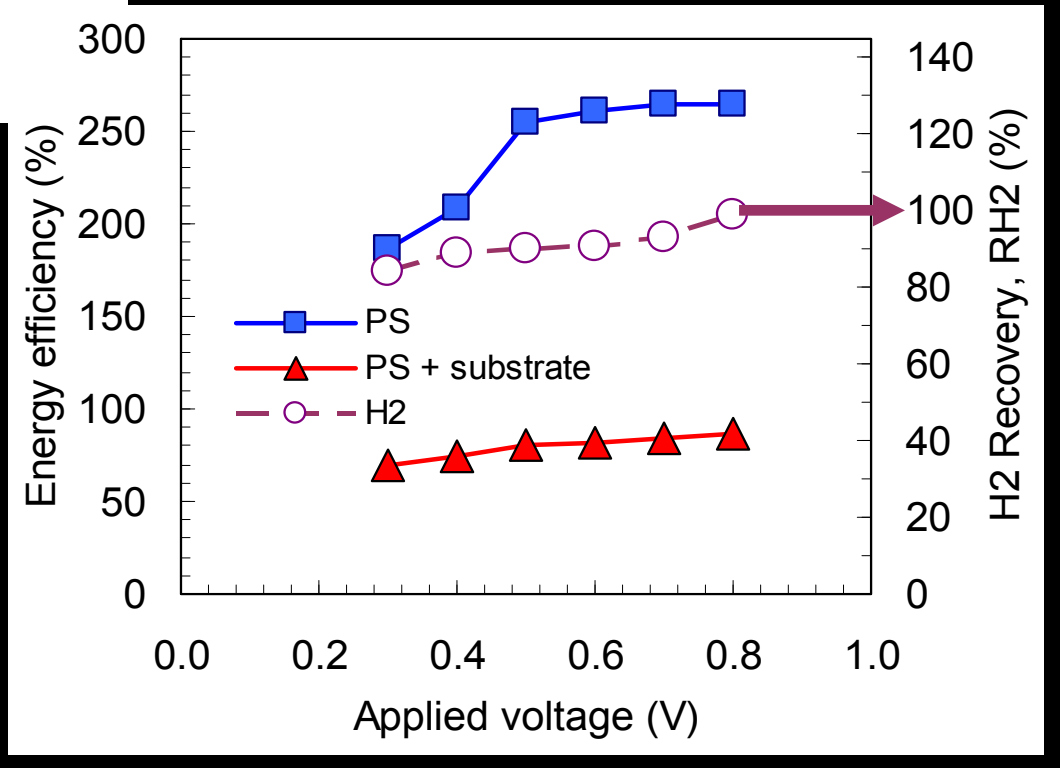
Hydrogen gas production from acetic acid, the predominant

Cheng & Logan, *PNAS* (2007)



High hydrogen yields except at 0.2 V

H_2 production increases with applied voltage



Source: Cheng & Logan, *PNAS* (2007)

H_2 production from various substrates

Substrate	Y_{H2} (mol-H_2 mol- substrate^{-1})	R_{H2} (%)	**Production rate** (m^3 m^{-3} d^{-1})	η_w (%)	η_{W+S} (%)
Glucose	8.55	71	1.23	266	64
Cellulose	8.20[a]	68	0.11	268	63
Acetic acid	3.65	91	1.10	261	82
Butyric acid	8.01	80	0.45	285	77
Lactic acid	5.45	91	1.04	283	82
Propionic acid	6.25	89	0.72	248	79
Valeric acid	8.77	67	0.14	263	66

Source: Cheng & Logan, *PNAS* (2007)

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Energy Utilization in the USA

US energy use:	97 quad
US electricity generation:	13 quad
Energy used for water infrastructure (water and wastewater)	0.6 quad (5%)

97 quad [quadrillion BTUs] = 28,400 TWh (terawatt hours)

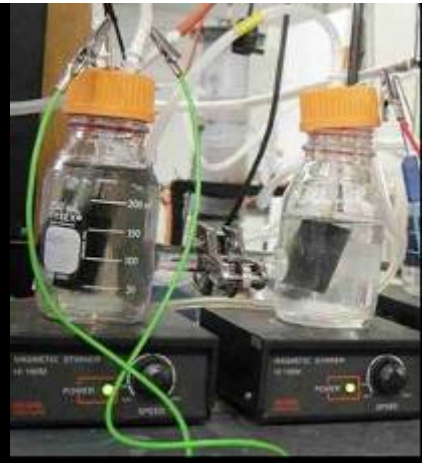
Energy value of wastewater

- Electricity used for water infrastructure= 0.6 quad (~5% of all electricity)
- Energy in wastewater= 0.5 quad
  - 0.1 quad of energy in domestic wastewater
  - 0.1 quad in food processing wastewater
  - 0.3 quad in animal wastes

Wastewater has 9.3× more energy than treatment consumes

(Toronto WWTP, Shizas & Bagley (2003)

CONCLUSIONS



- MFCs represent a viable technology for simultaneous electricity generation and wastewater treatment
- The MEC/BEAMR process can overcome the "fermentation barrier" and result in high yields of hydrogen from any source of biomass
- The technology now exists for system scaleup– pilot testing is needed.

Acknowledgements

Current research sponsors

NSF (BES Program): 2003-2007

WERF (Busch Award): 2004

AFOSR: 2006-2009

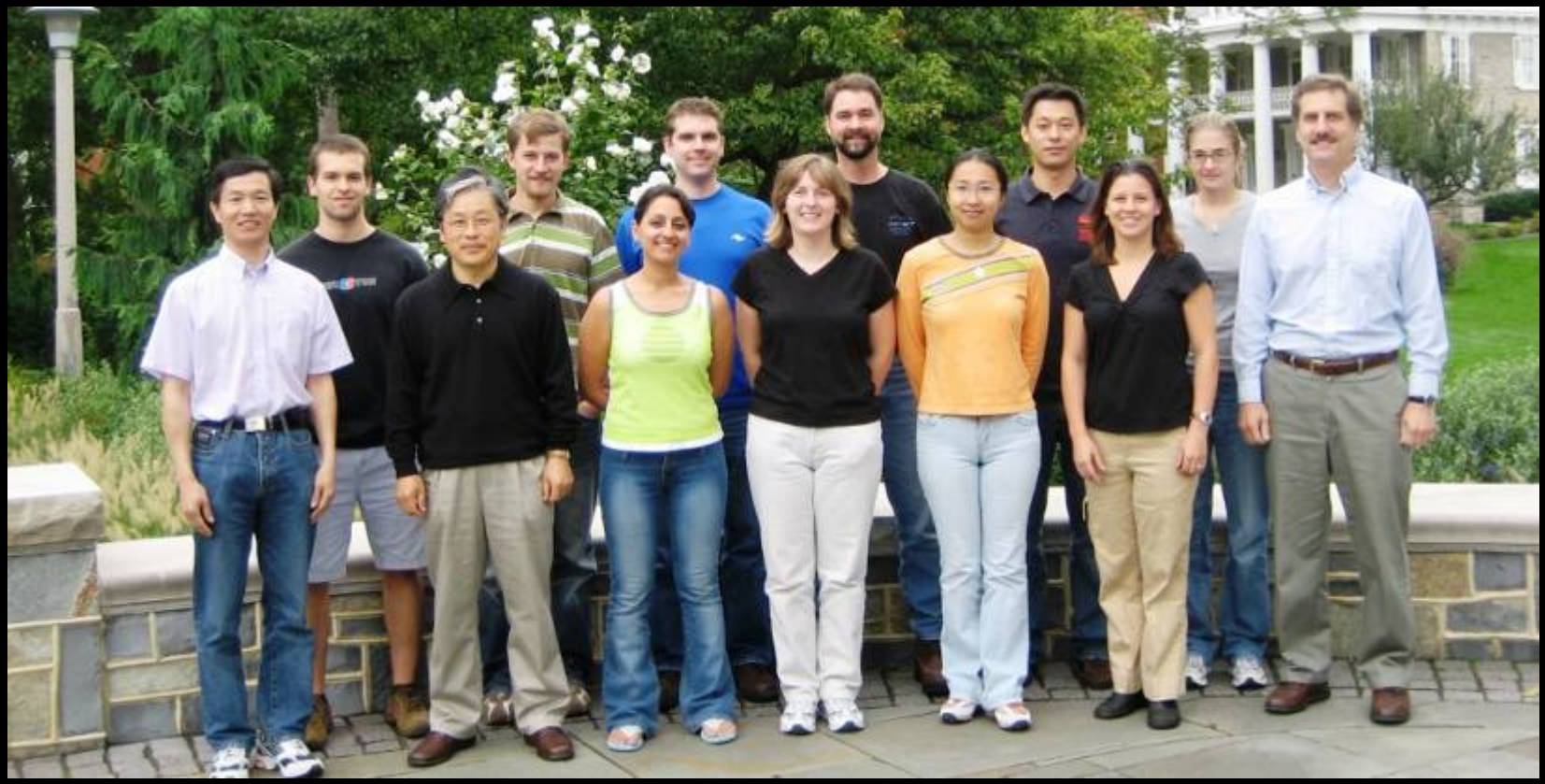
Air Products: 2006-2008

Previous sponsors:

NSF & EPA TSE (CTS Program)

USDA-DOE

Thanks to students and researchers in my laboratory at Penn State!

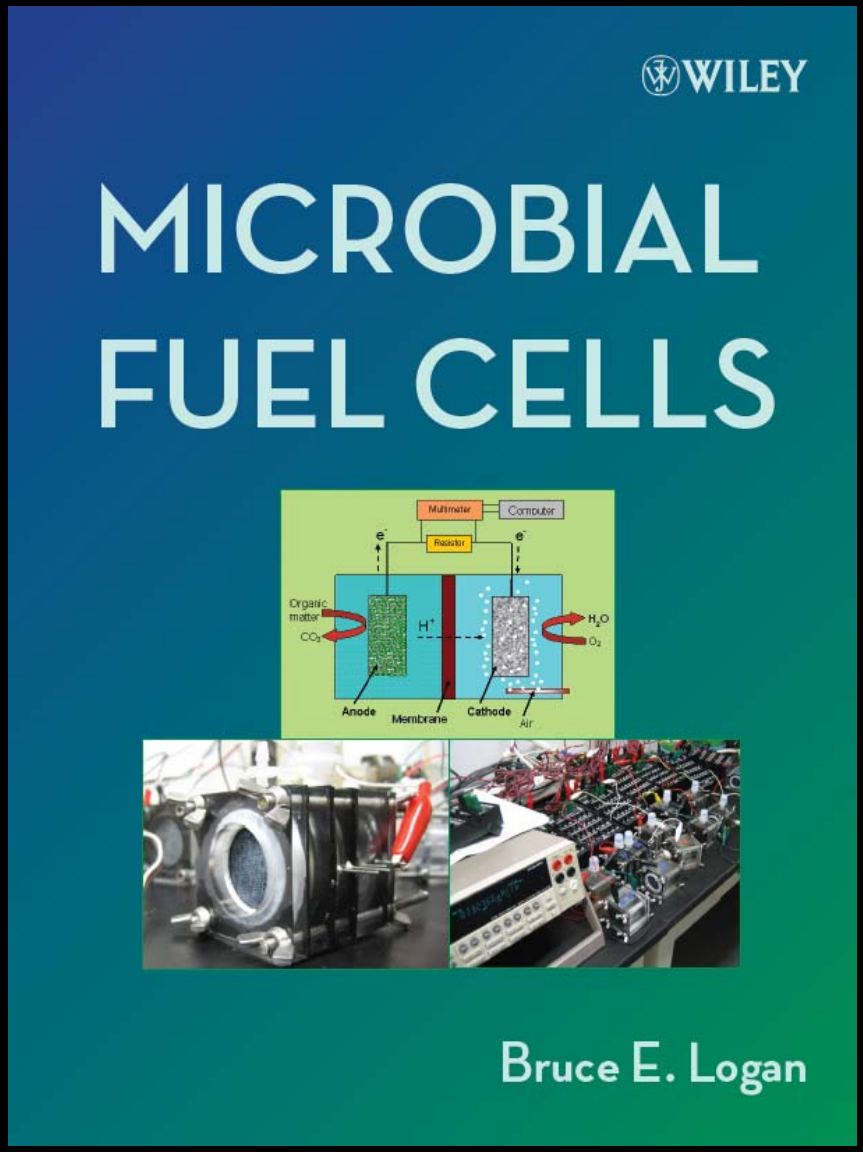


Left to right: Shaoan Cheng, Doug Call, KyeongHo Lim (visiting Prof), Markus Coenen (visitor), Farzaneh Rezai (PhD Ag&BioEng), Charles Winslow, Valerie Watson, David Jones (technician), Yi Zuo, Defeng Xing, Priscilla Selembo (PhD ChE), Rachel Wagner, [Bruce Logan]

Missing: Yujie Fang and YoungHo Ahn (visiting Profs), Jooyoun Nam (visiting student)

Further information?

- New book on MFCs (published by John Wiley, 2008)
- Microbial Fuel Cell Symposium, May 27-29, 2008, Penn State University



Links

Email: blogan@psu.edu

Web page:
www.engr.psu.edu/ce/enve/logan.htm

Logan MFC webpage:
www.engr.psu.edu/ce/enve/mfc-Logan_files/mfc-Logan.htm

International MFC site:
www.microbialfuelcell.org

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

www.engr.psu.edu/mfccam