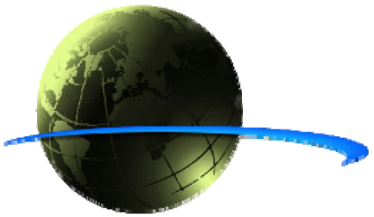
ismet 2015

Consideration of cathode specific surface area and hydrodynamics in scaling up microbial fuel cells

Bruce E. Logan
Penn State University

PENNSTATE

Engineering Energy &
Environmental Institute



What do we need to commercialize MFCs?

- Now have >1 decade of MFC research… why don't we have commercialized MFCs?
- Bacteria: *Geobacter* sp
- Materials: both electrodes < \$100 m^{-2}
  - Anode: many choices; brushes still superior
  - Cathode: activated carbon(s)
- Architecture: Tubular vs plate/frame?
- Manufacturing: Cathode production?
- Secondary processes needed!

PENNSTATE

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

Wastewater Treatment plants:

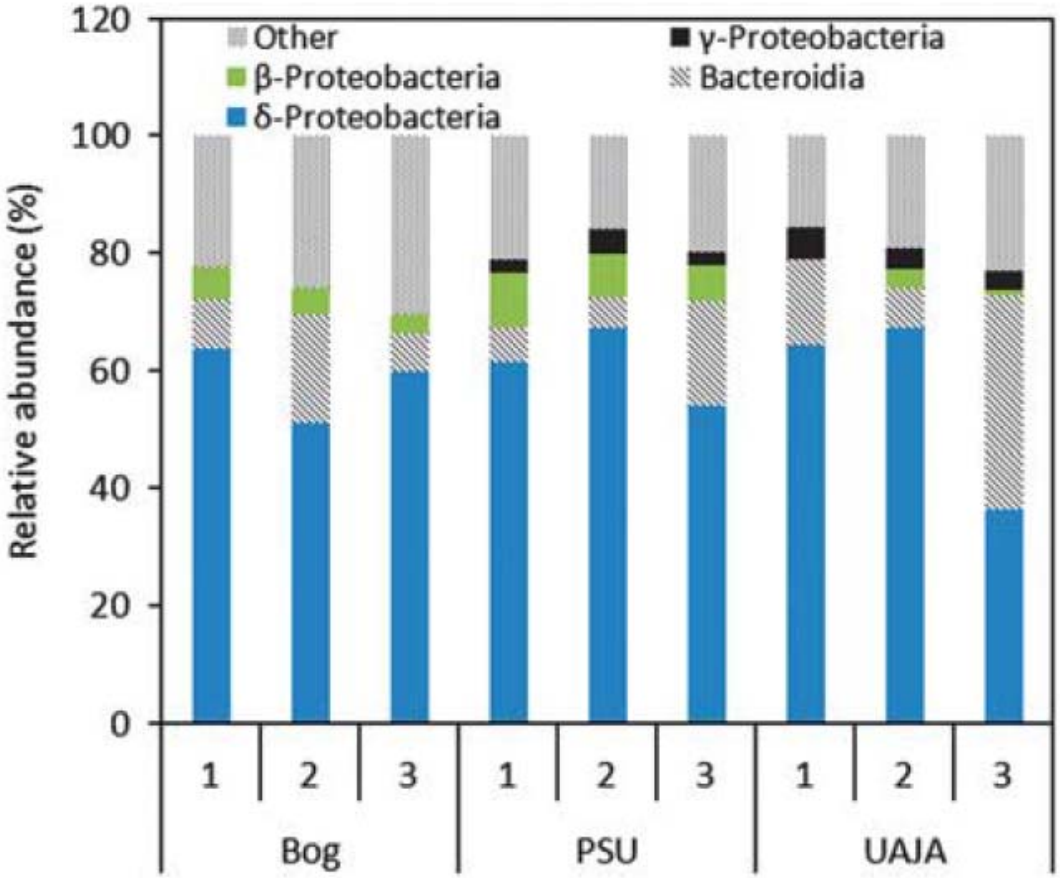
P=PSU, U=UAJA

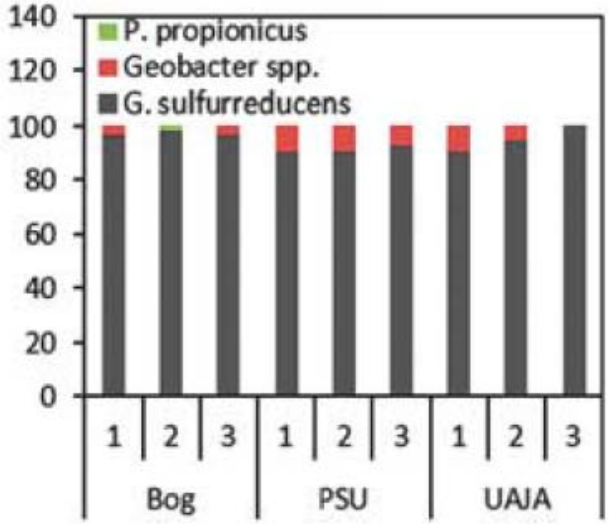
B=Bog

PENNSTATE

Yates, Kiely, Call, Rismani-Yadzi, Bibby, Peccia, Regan, Logan (2012) *ISME J.*

Pyrosequencing: mostly Delta Proteobacteria… and of those, almost all sequences most similar to *Geobacter sulfurreducens*



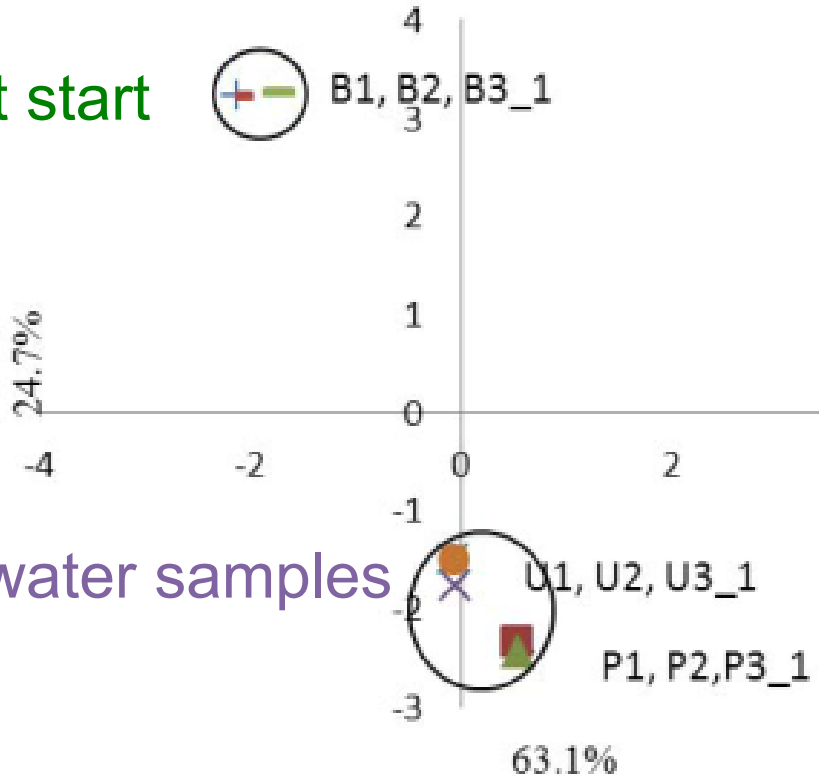


PENNSTATE

Yates et al. (2012) *ISME J.*

DGGE used to show changes in community diversity over time

Bog at start



END: Everything pretty similar

Wastewater samples at start

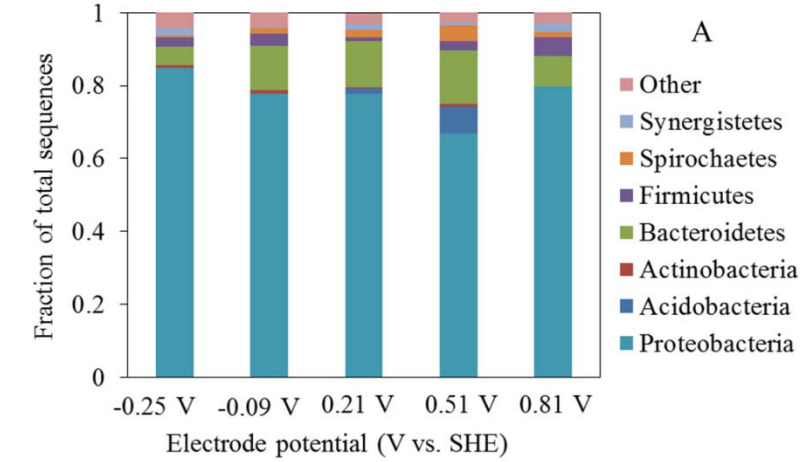
Conclusion:
High power requires *Geobacter* spp.

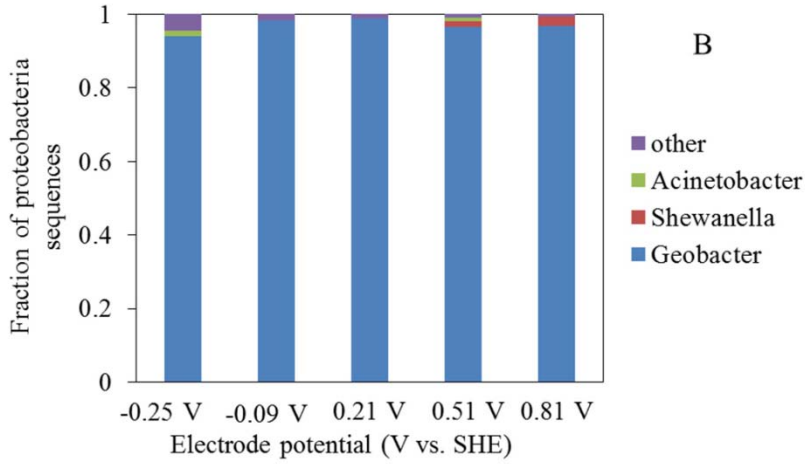
PENNSTATE

B=Bog, P=PSU, U=UAJA

Yates et al. (2012) *ISME J.*

Community composition unchanged at varied set potentials when different reactors used





PENNSTATE

Zhu, Yates, Hatzell, Ananda Rao, Saikaly, & Logan (2014) *ES&T*

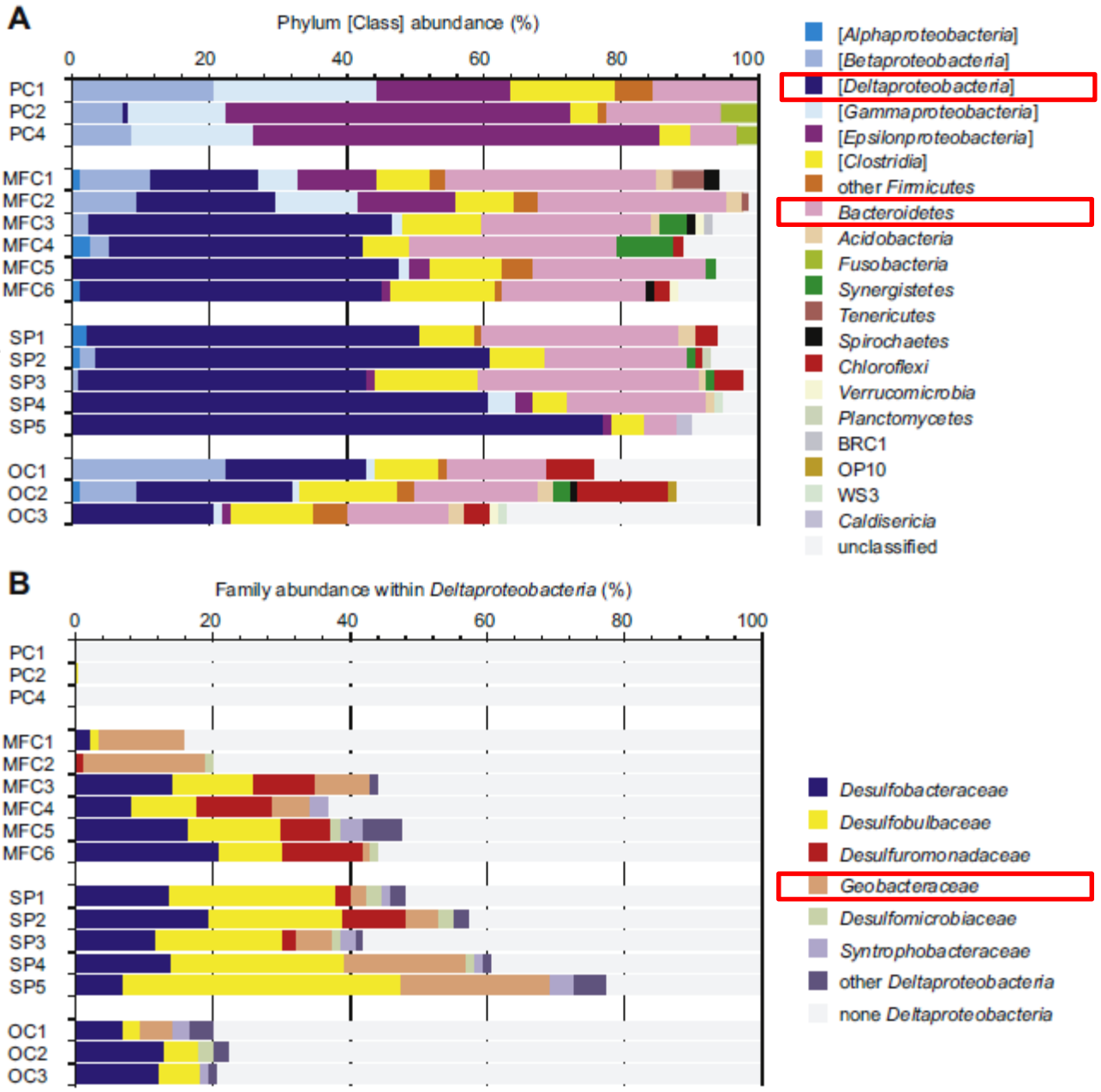
MFCs

Influent

MFCs

Set anode potential

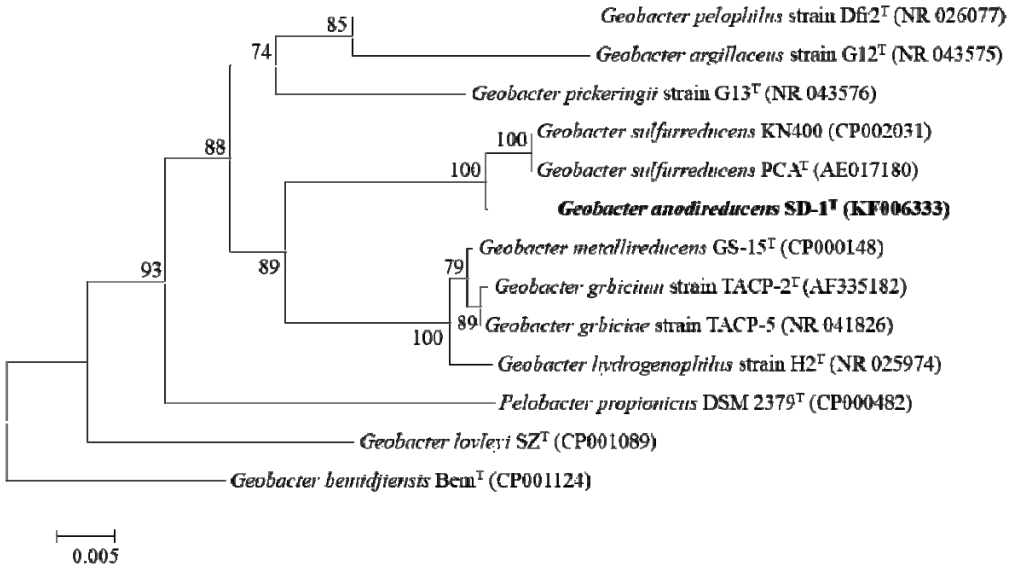
Open circuit



Much greater complexity of bacterial communities with domestic wastewater, but *Geobacter* still quite abundant

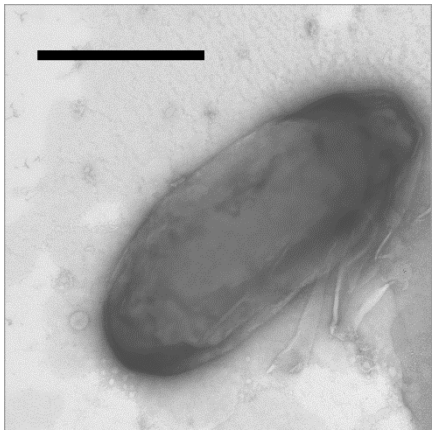
Ishii et al. [J Craig Venter Institute] (2013) *Wat. Res.*

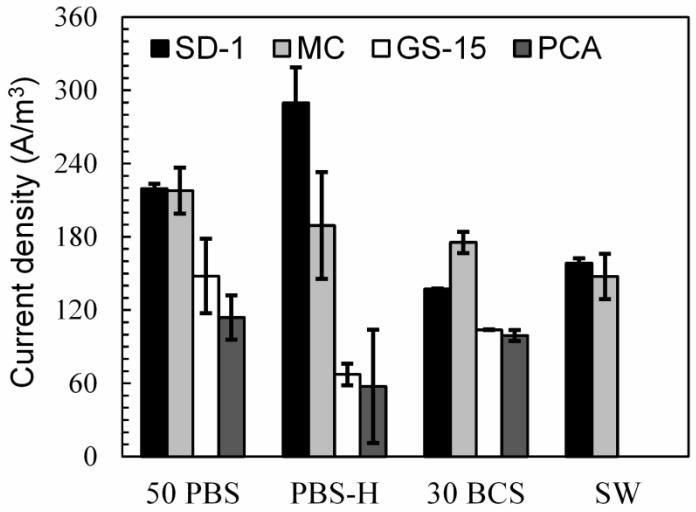
Isolate from MFC: *Geobacter anodireducens SD-1*



Characteristics of *G. anodireducens* SD-1 (*Geobacter sulfurreducens* PCA)

- Isolated from MFC fed formate, 98% similarity to strain PCA
- DNA-DNA hybridizations show a relatedness of 61.6% with PCA (<70%)
- Tolerates up to 3% NaCl (vs 1.7% for PCA)
- Grows well in 200 mM phosphate buffer (PCA does not grow)
- *Cannot grow using fumarate as electron acceptor* (PCA can grow)





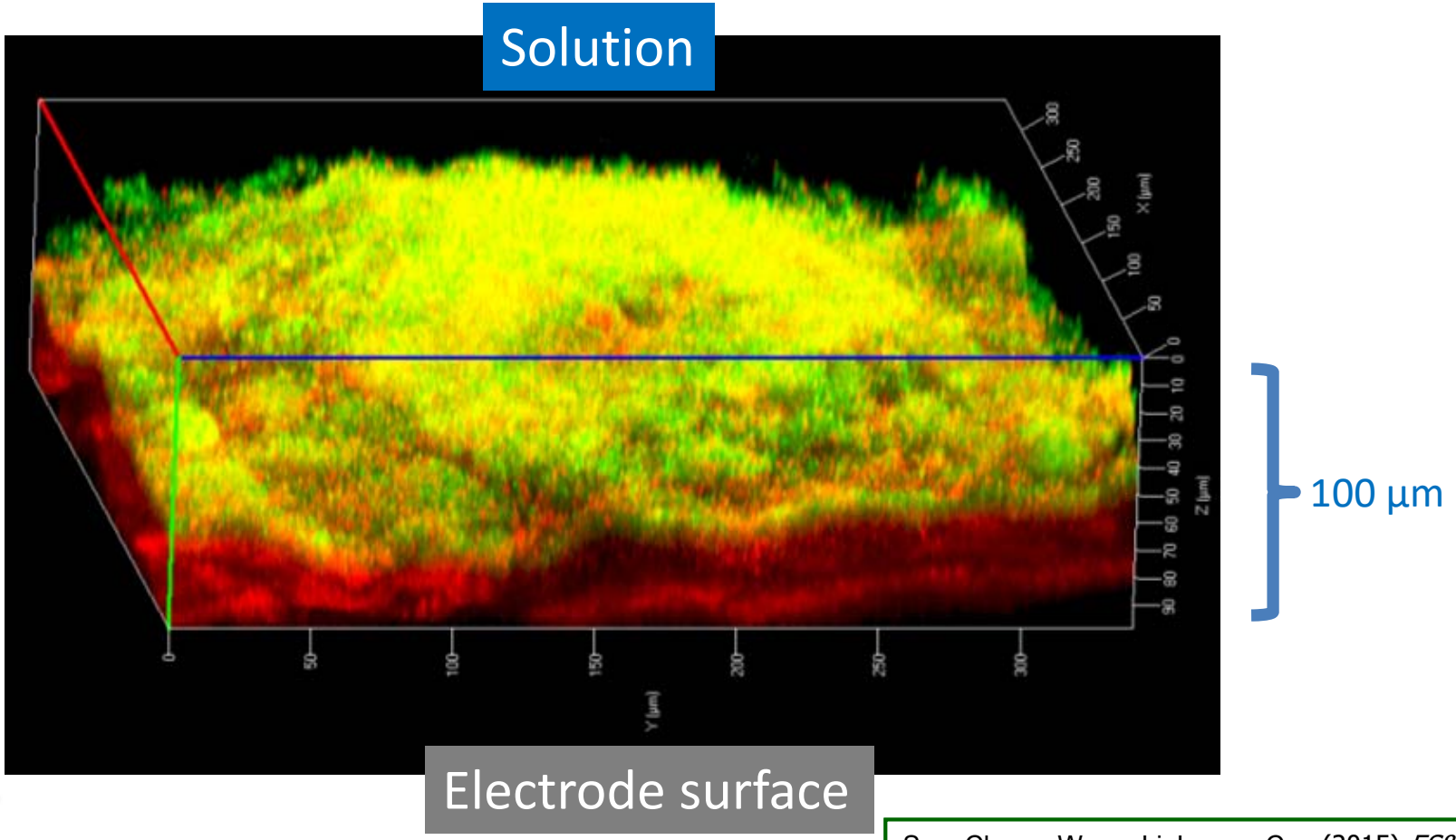
50 PBS: 50 mM phosphate buffer
PBS-H: 200 mM PBS
30 BCS: 30 mM bicarbonate buffer
SW: 3% NaCl (like seawater)

Sun, Wang, Cheng, Yates, Logan (2014) *Int. J. System. Evol. Microbiol.*

Sun, Call, Wang, Cheng, Logan (2014) *Env. Microbiol. Reports*

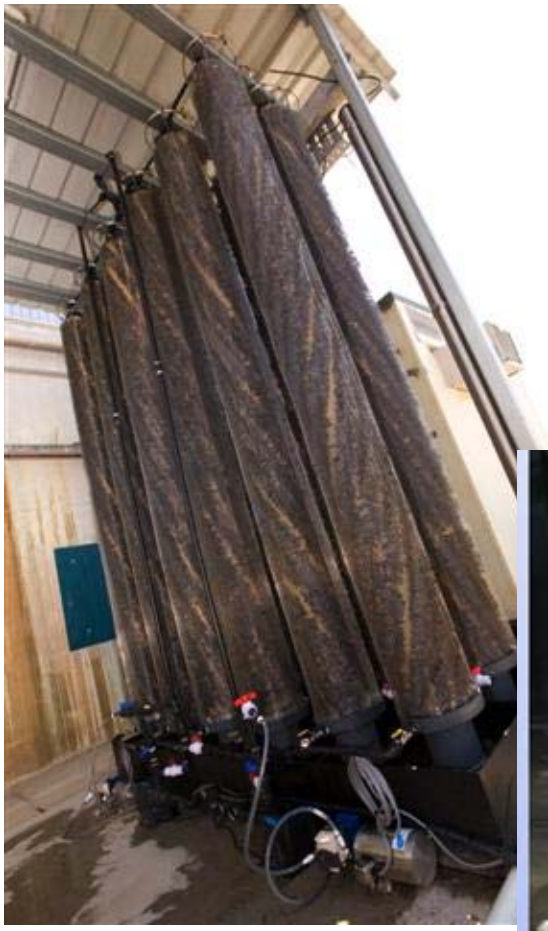
Electrogenic Biofilms

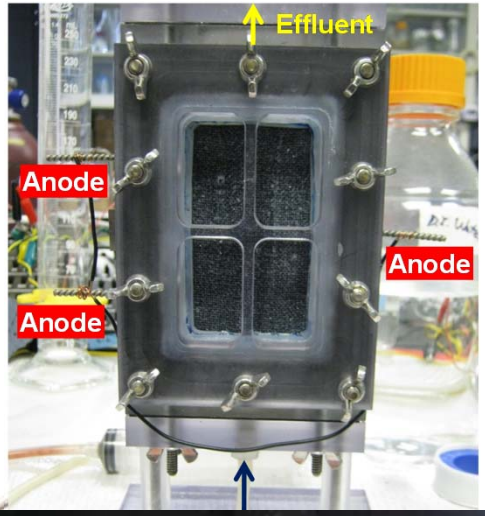
- Dead biofilm (red) remains electrically conductive for active biofilm (yellow/green)

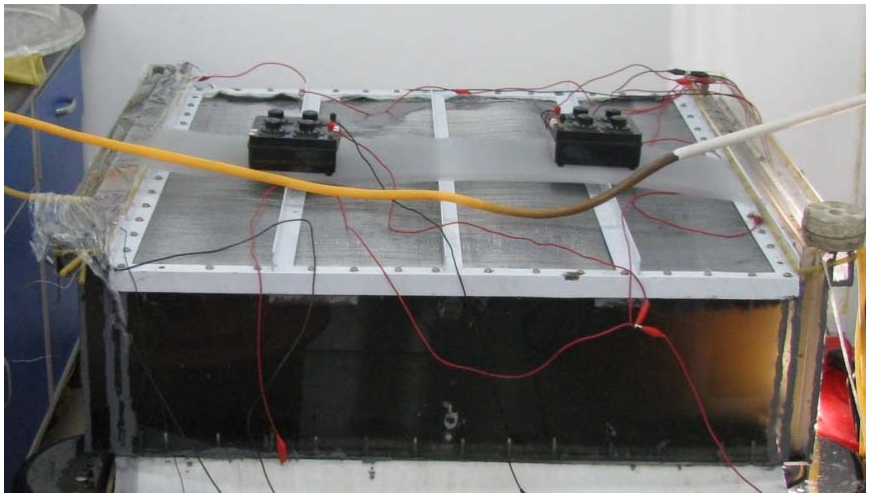


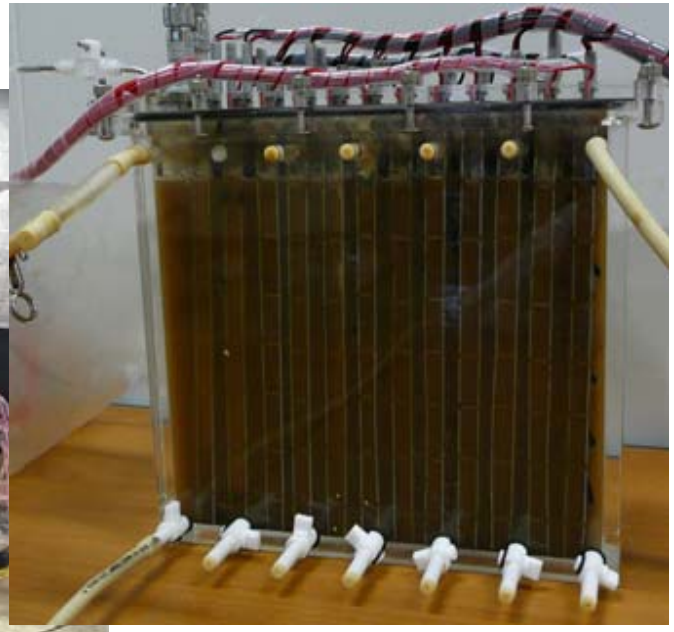
Sun, Cheng, Wang, Li, Logan, Cen (2015) *ES&T*

Scaling up MFCs









PENNSTATE

MFC Architecture

Estimates for MFCs

- **100 € /m² or $130/m²**

Estimates for MECs

- **100 € /m² or $130/m²**

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 $m\Omega m^2$) 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 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

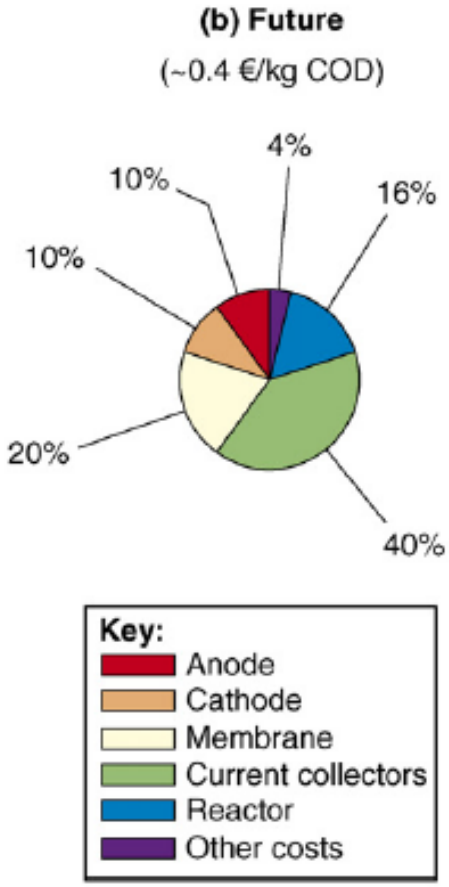
Cell PRESS

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]

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

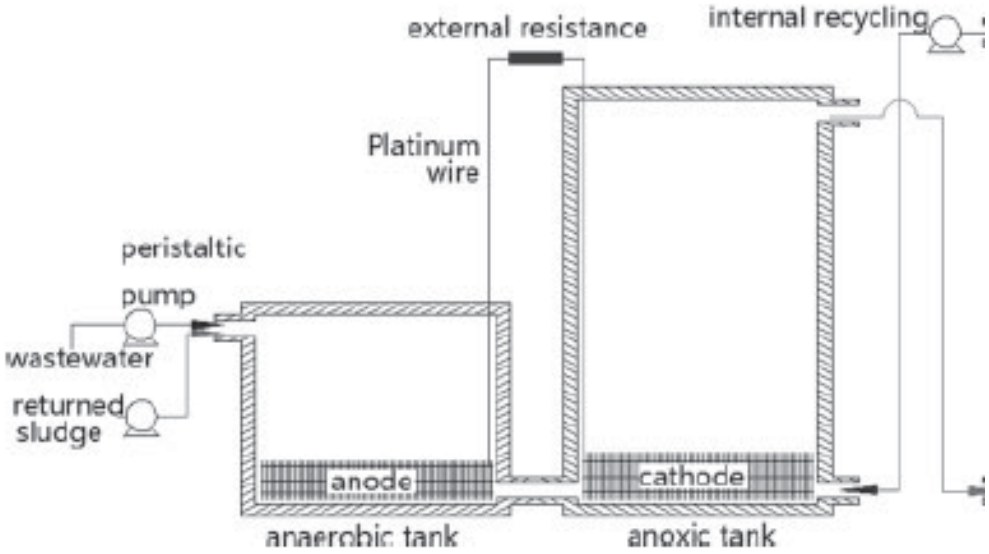
PENNSTATE



Design

- These are bad designs for treatment….Keep the electrodes close (but not too close!)
- You cannot design separate anode and cathode reactors!

Source: B.E. Logan, first MFCs built in 2003



Xie et al. (2013) *J. Chem. Technol. Biotechnol.*

PENNSTATE

ENVIRONMENTAL Science & Technology LETTERS

Review

pubs.acs.org/journal/estlcu

Assessment of Microbial Fuel Cell Configurations and Power Densities

Bruce E. Logan,*[,†] Maxwell J. Wallack,[†] Kyoung-Yeol Kim,[†] Weihua He,[‡] Yujie Feng,[‡] and Pascal E. Saikaly*[,§]

[†]Department of Civil and Environmental Engineering, The Pennsylvania State University, 212 Sackett Building, University Park, Pennsylvania 16802, United States

[‡]State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No. 73 Huanghe Road, Nangang District, Harbin 150090, P. R. China

[§]Water Desalination and Reuse Center, Biological and Environmental Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

Supporting Information

PENNSTATE

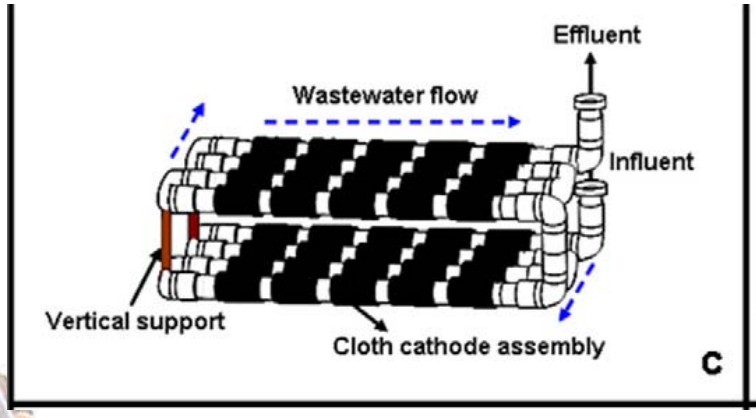
Logan, Wallack, Kim, He, Feng and Saikaly (2015) *Environ. Sci. Technol. Lett.*

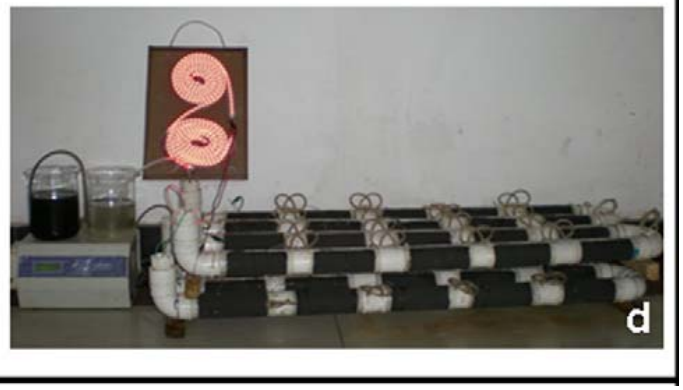
To Design your MFC:

- Materials
  - Anode: Flat (cloth, felt, etc.), brush, granules, or other?
  - Separator: fibrous or ion exchange membrane?
  - Cathode: Activated carbon + binder + diffusion layer
- Architecture:
  - Plate/frame or tubular?
- **Cathode specific surface area:** A_{cat} (m^2/m^3)
  - Defined as cathode area per volume
  - Maximize A_{cat} based on MFC configuration

PENNSTATE

Tubular MFCs





PENNSTATE

Tubular/Cylindrical Designs

- A_{cat} (m^2/m^3) based on a cylinder diameter, *d*
  - Area of the cathode is: A_{cyl}
  - Volume of the MFC is: V_{cyl}
  - $A_{Cat} = \frac{A_{cyl}}{V_{cyl}} = \frac{\pi dL}{\frac{\pi}{4}d^2L} = \frac{4}{d}$
  - If d= *5 cm:* $A_{Cat} = \frac{4}{d} = \frac{4}{(5\ cm)}\frac{100\ cm}{m}$ = 80 m^2/m^3
- Tube designs need air flow around outside cylinder, so *d* = tube diameter + air space
  - If d= *5 cm + 2 cm,* A_{Cat} = 57 m^2/m^3

PENNSTATE

The Largest Tubular MFC

- A_{cat} = 22 m^2/m^3 based *d* = 18 cm (volume around tubes not included)
- Performance not published in peer reviewed literature, but:
  - Tested brewery wastewater
  - Produced 330 mW/m^2 (8 W/m^2)
  - HRT= unknown

PENNSTATE

Sources: www.microbialfuelcell.org accessed in 2010; Logan (2010) *Appl. Microbiol. Biotechnol.*; and Rabaey personal communication.

Small tube MFC

- Two tubes, each 2 L in volume (4 L total)
- A_{cat} = 80 m^2/m^3 (*d*=5 cm, just the tube; each 100 cm long)
- HRT = 11 h
- Power = 10-50 mW/m^2
- Final COD= 80–100 mg/L
- CE=11%

PENNSTATE

Zhang et al. (2013). Long-Term Performance of Liter-Scale Microbial Fuel Cells Treating Primary Effluent Installed in a Municipal Wastewater Treatment. *Environ. Sci. Technol.* 47:4941−4948
Personal communication: Prof. Zhen He

Racks of many smaller tube MFCs

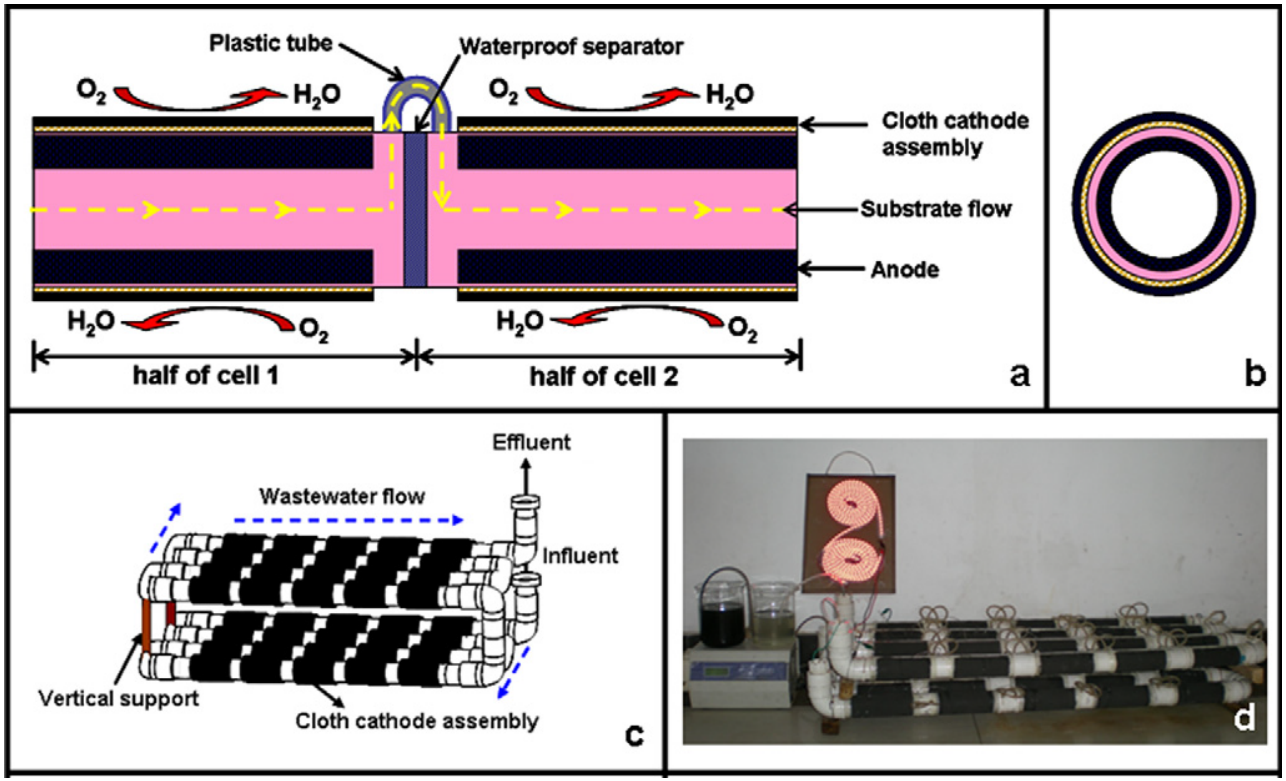
- 200 L based on 96 tubes, each ~2 L in volume
- A_{cat} = 80 m^2/m^3 (*d*=5 cm, just the tube; each 100 cm long)
- 6 – 9 mW/m^2 (84 - 130 mW, 15 m^2 cathode)
- HRT = 12 h
- Final COD= 33 mg/L

PENNSTATE

Ge et al. (2015) Energy extraction from a large-scale microbial fuel cell system treating municipal wastewater. *J. Power Sources.* 297:260-264
Personal communication: Prof. Zhen He

Serpentine MFC design

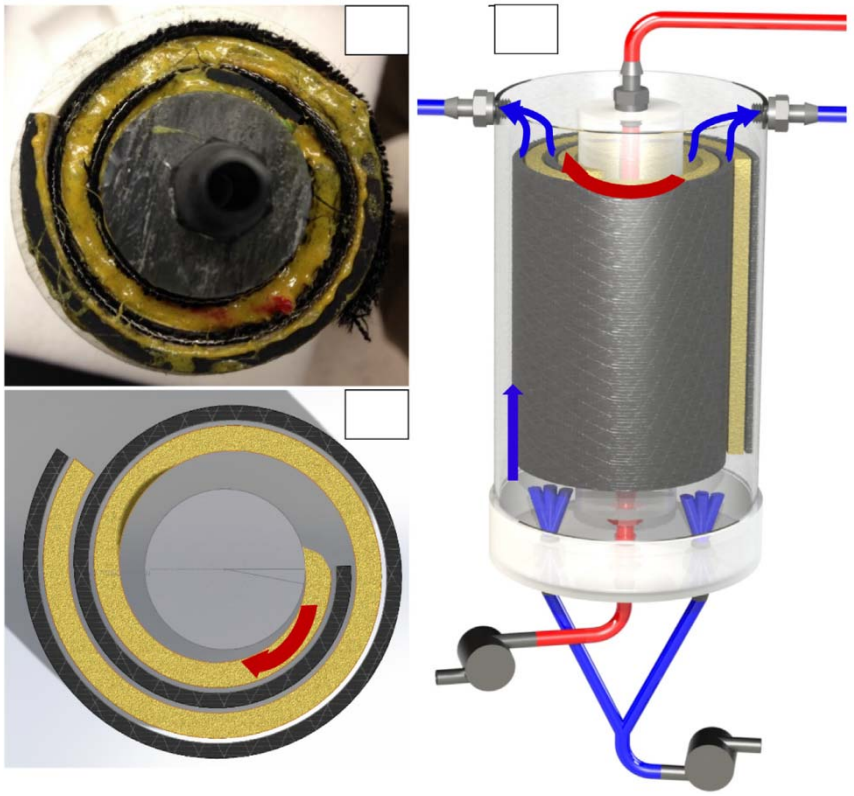
- A_{cat} = 86 m^2/m^3 based estimated *d*=4.6; no volume around tubes
- A_{cat} = 62 m^2/m^3 based on given summed electrode areas
- Produced 66 mW/m^2; HRT= ???; connector tube could clog



Zhuang et al. (2012). Long-term evaluation of a 10-liter serpentine-type microbial fuel cell stack treating brewery wastewater. *Biores. Technol.* 123:406–412.

Wound stack electrodes

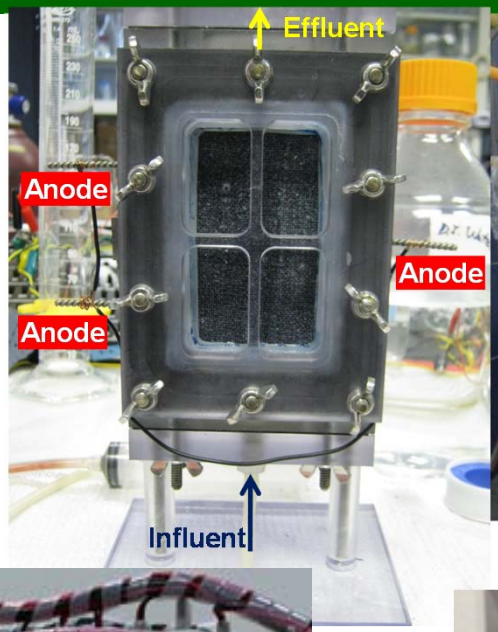
- Cylinder, but more similar to a plate design: more of a "wound plate"
- Not ww or air:
  - Acetate
  - Percarbamate cathode (O_2 release compound)
- 2 Designs (HRT=20 min)
  - 350 m^2/m^3; 94 mW/m^2
  - 700 m^2/m^3; 73 mW/m^2

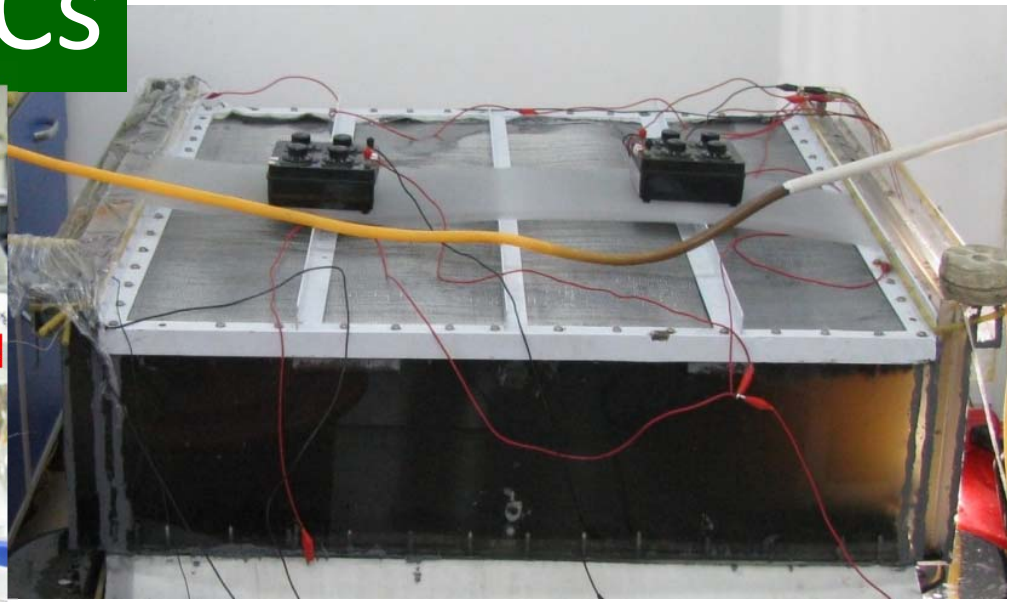


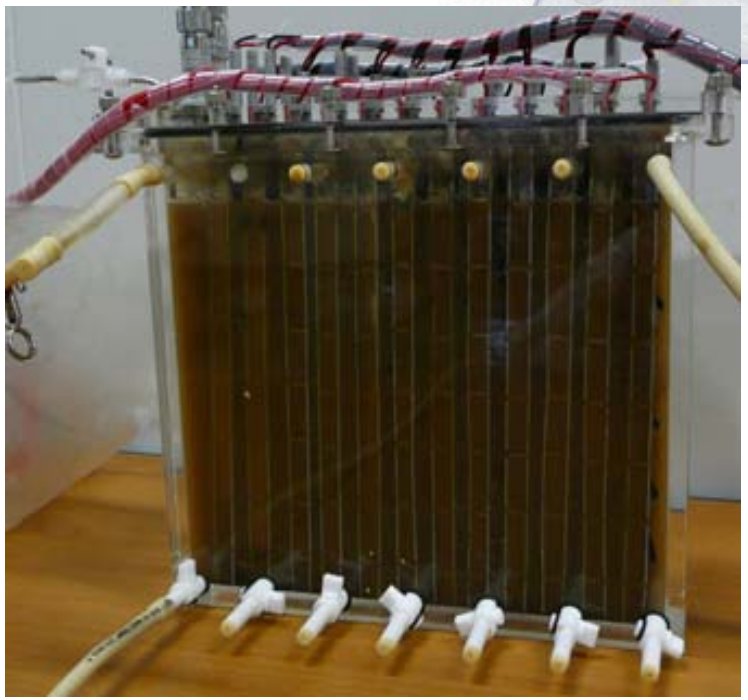
PENNSTATE

Haeger et al. (2014) High performance spiral wound microbial fuel cell with hydraulic characterization. *Biores. Technol.* 174:287-293

Plate/Frame MFCs

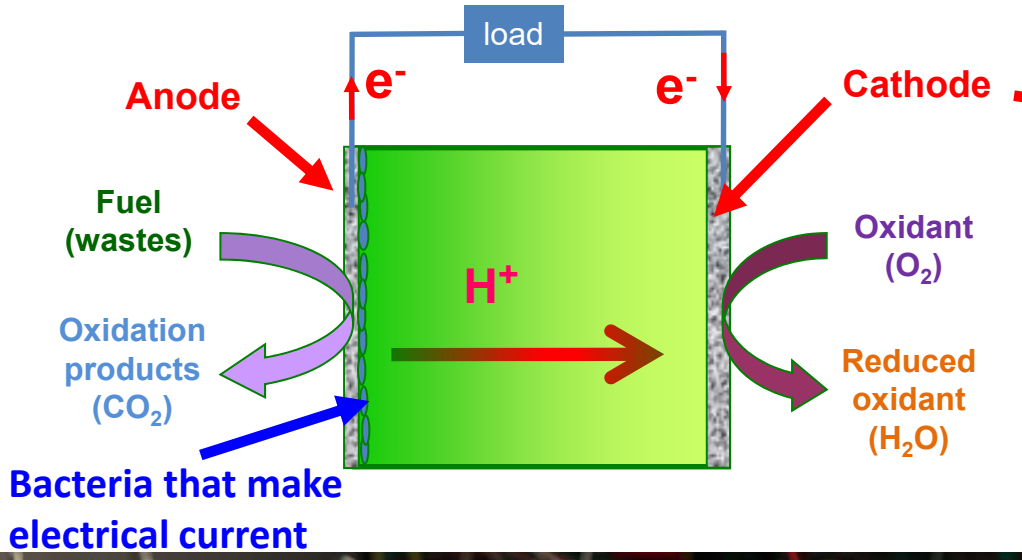


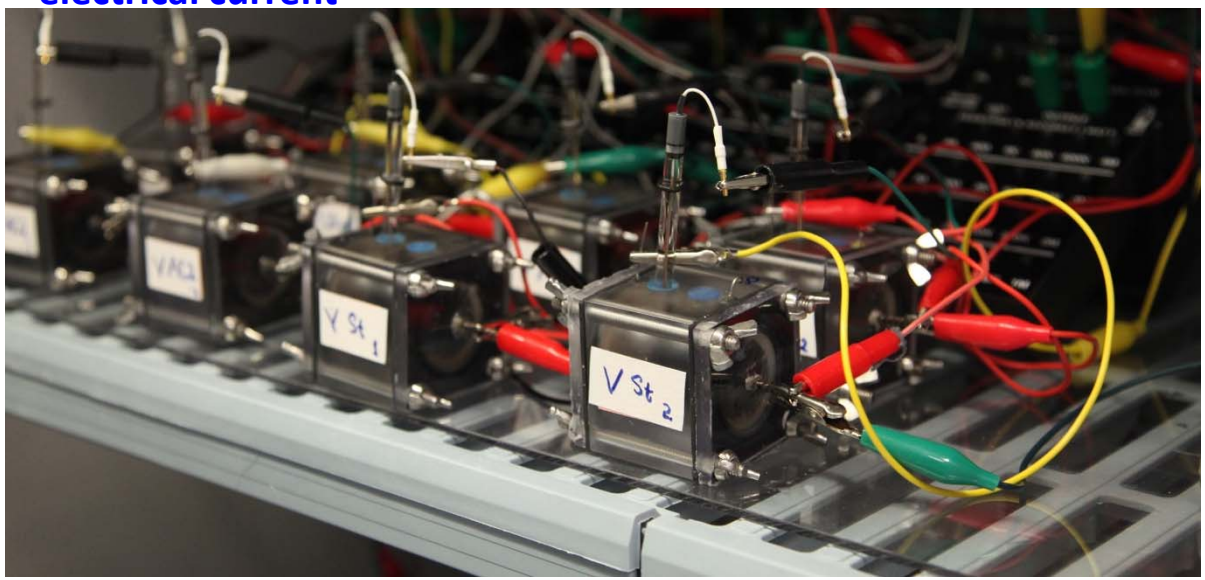


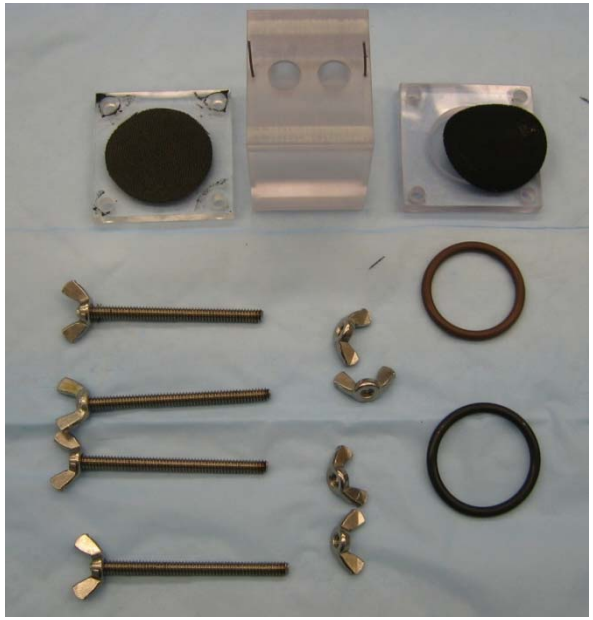


MFCs

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

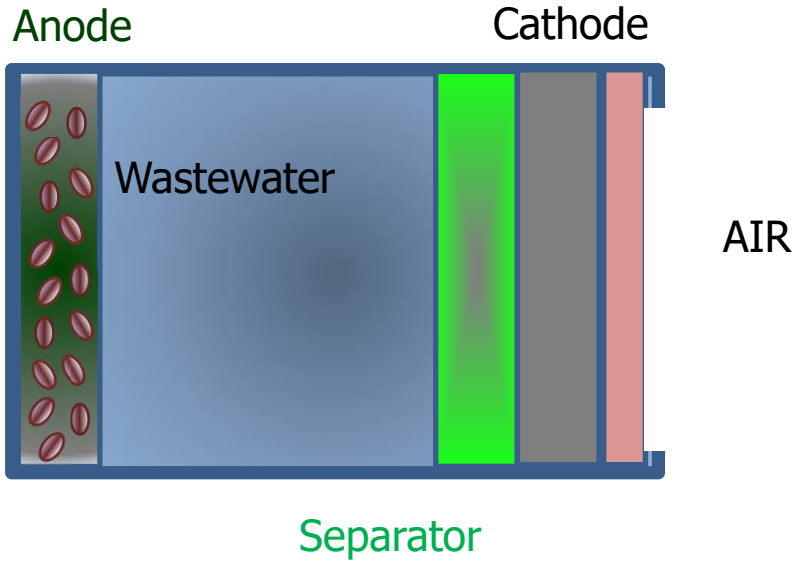






Liu et al. (2004) *Environ. Sci. Technol.*

MFC Materials



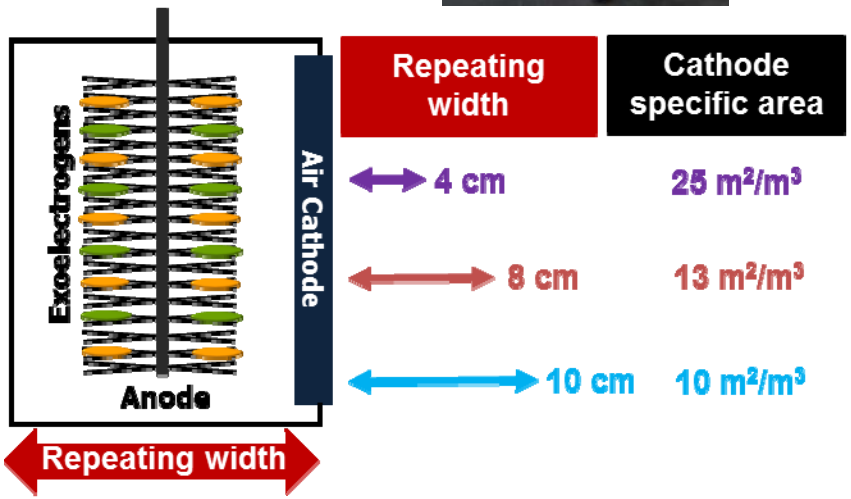
Low cost	$/m^2 (US)
• **Anode (brushes)**	$20
• Separator (cloth)	$ 1
• **Cathode**	$15
- SS mesh	
- AC + PVDF Binder	
• **TOTAL**	**$36**

PENNSTATE

Key to cathode specific surface area is the "unit width"!

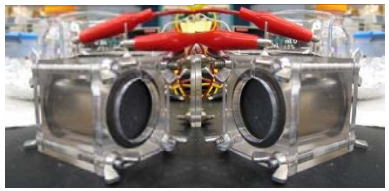
- Cathode specific surface area: A_{cat} (m^2/m^3)
  - Defined as cathode area per volume
  - Maximize based on MFC configuration
- Plate/Frame:
  - Width of anode chamber is: W_{An}
  - Width of cathode chamber is: W_{Cat}
  - $A_{Cat} = \frac{1}{W_{An}+W_{Cat}}$
  - If $W_{an} = 3$ cm, $W_{Cat} = 1$ cm

    $A_{cat} = 25\ m^2/m^3$



Logan, Wallack, Kim, He, Feng and Saikaly (2015) *Environ. Sci. Technol. Lett.*

MFC Architecture



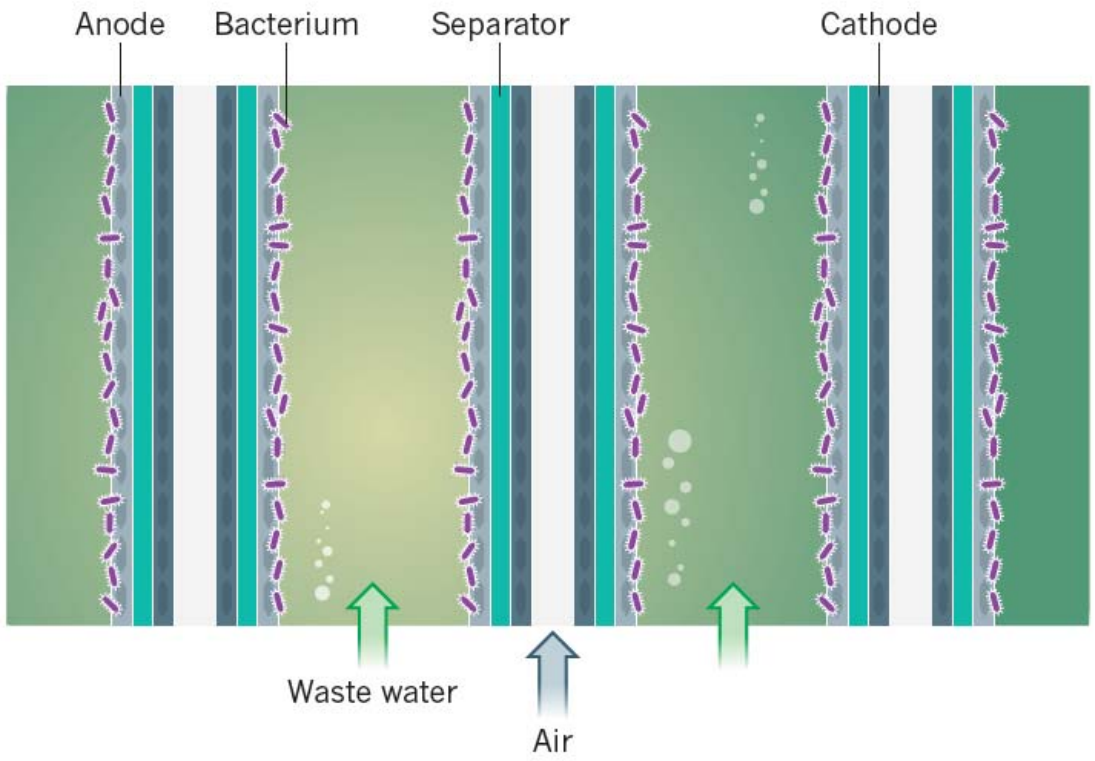
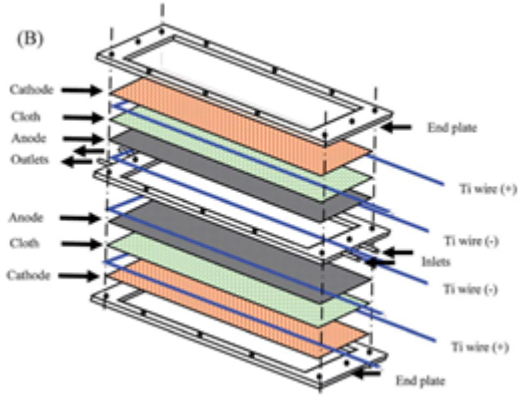


Figure 3 | An MFC stack. MFCs are arranged close together to reduce internal resistance and form compact reactors. Within the stack the electrodes consist of repeating units of an anode coated in a mat of bacteria, or biofilm, an insulating separator and a cathode. Waste water flows over the anodes and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

Logan & Elimelech (2012) *Nature*

How close can electrodes be?

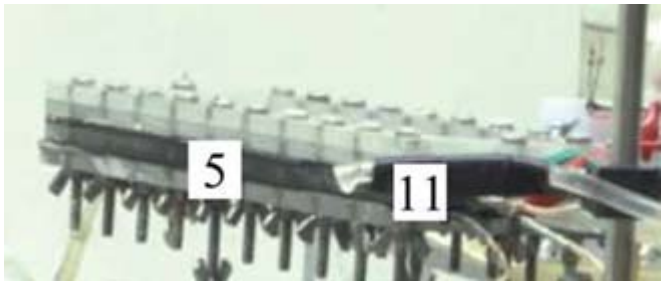
- Need room for electrodes, wastewater, air
- Acetate = no particles like real ww
- Too little space for ww→ clogging



25 m^2/m^3 (25 mL reactor)

Acetate: 2.8 W/m^2 (2.1 kW/m^3)

WW: 0.5 W/m^2



680 m^2/m^3 (30 mL reactor)

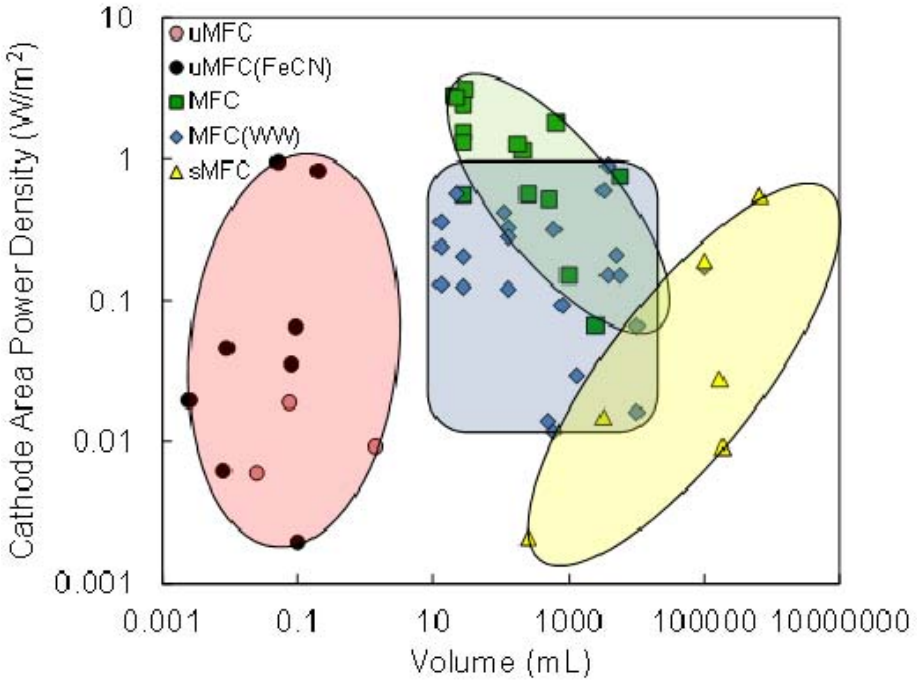
Acetate: 3.1 W/m^2 (2.1 kW/m^3)

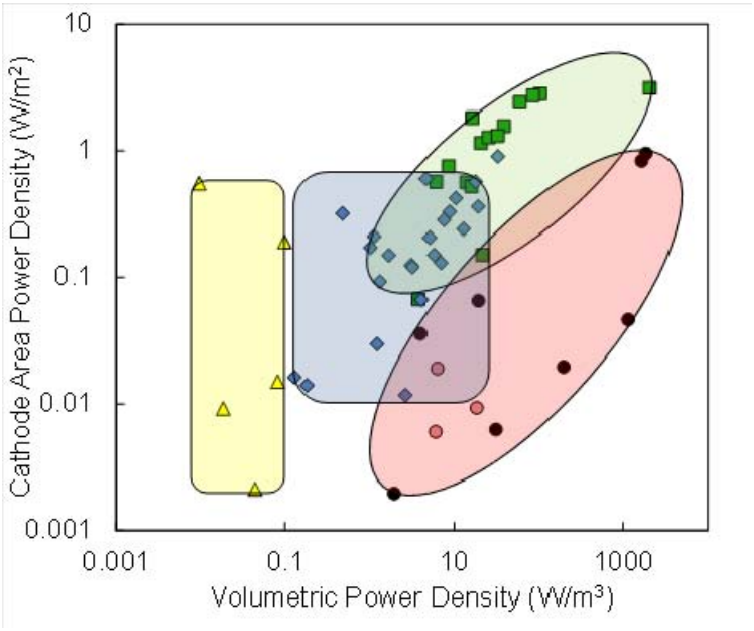
WW: (not tested)

Fan et al. (2013) *Energy Env. Sci.*

Range of power densities

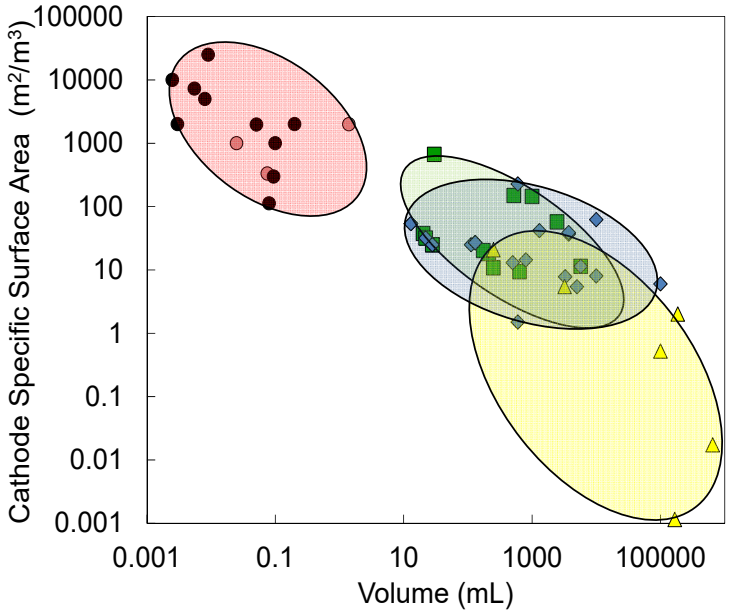
- For MFCs treating single substrates, ■ area power density:
  - decreases with larger size reactors (left figure)
  - Shows an increase with volumetric density
- For MFCs treating wastewater, no trends!

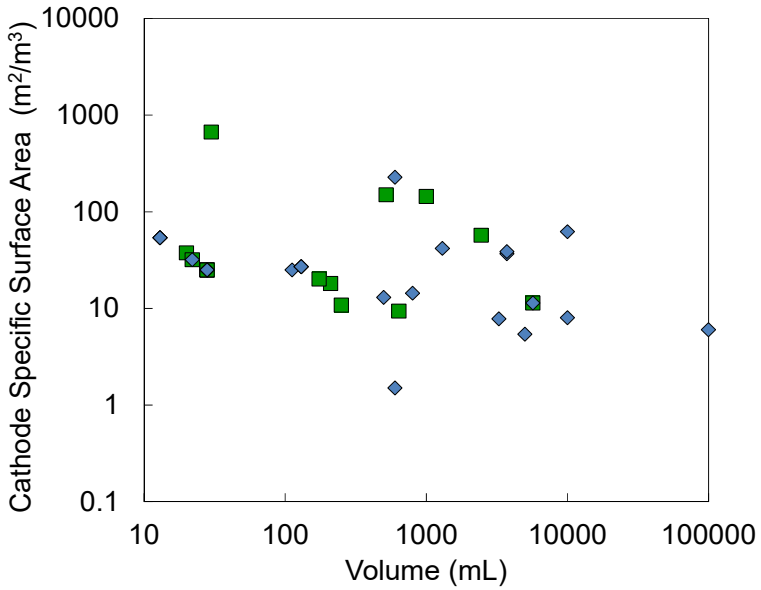




Logan, Wallack, Kim, He, Feng and Saikaly (2015) *Environ. Sci. Technol. Lett.*

Cathode specific surface area decreases with reactor size



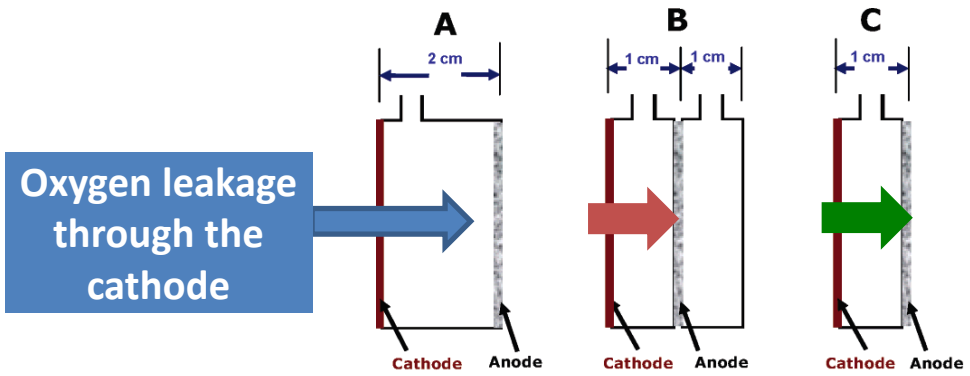


PENNSTATE

Logan, Wallack, Kim, He, Feng and Saikaly (2015) *Environ. Sci. Technol. Lett.*

Electrode spacing?

- Flat electrodes: ≥ 2 cm
- Brush electrodes:
  Is closer is OK?



Environ. Sci. Technol. **2006**, *40*, 2426–2432

Increased Power Generation in a Continuous Flow MFC with Advective Flow through the Porous Anode and Reduced Electrode Spacing

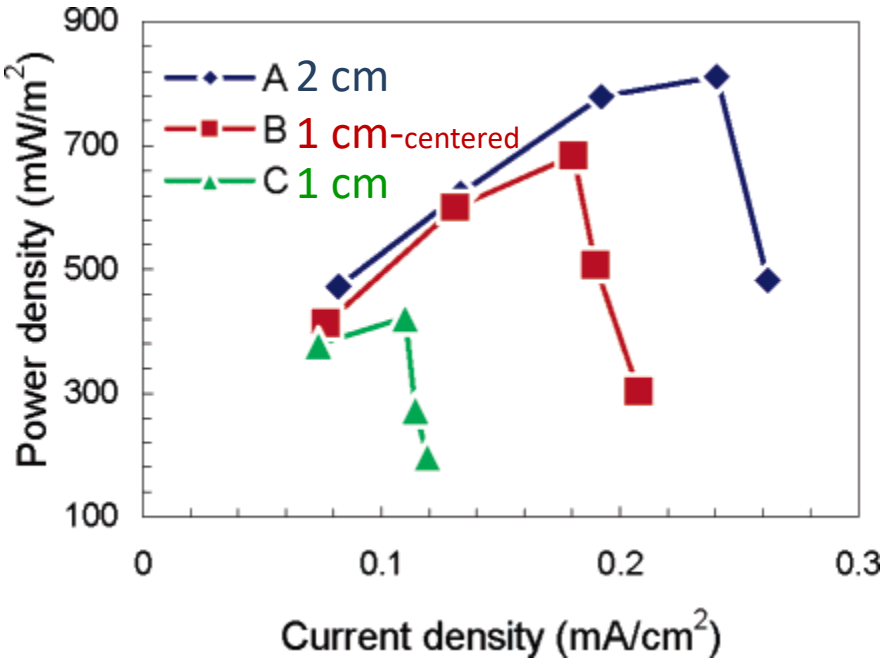
SHAOAN CHENG,† HONG LIU,† AND BRUCE E. LOGAN*,†,‡

Department of Civil and Environmental Engineering and The Penn State Hydrogen Energy (H_2E) Center, The Pennsylvania State University, University Park, Pennsylvania 16802

The maximum power generated in a single-chamber air-cathode microbial fuel cell (MFC) has previously been shown to increase when the spacing between the electrodes is decreased from 4 to 2 cm. However, the maximum power from a MFC with glucose (500 mg/L) decreased from 811 mW/m^2 (R_{ex} = 200 Ω, Coulombic efficiency of CE = 28%) to 423 mW/m^2 (R_{ex} = 500 Ω, CE = 18%) when the electrode spacing was decreased from 2 to 1 cm (batch mode operation, power normalized by cathode projected area)

with both electrode
One of the main
wastewater treatmer
generate electricity
Power densities pro
larger than those ob
differences in powe
tration and form (so
kinetics, and the co
the biofilm that is ne
(*9*).

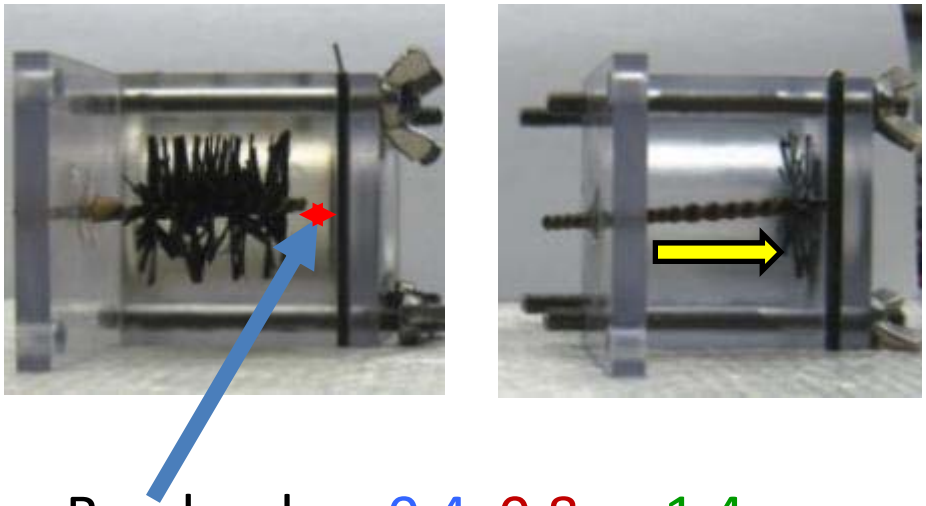
Power densities
modifying the anc
performance using
produce high concer
the PEM in systems
et al. (*14*) achieved
mediator-producing
However, ferricyani
for wastewater treatr
An advantage of us
reaction is self-susta
on cathodes, and al
be reduced to as littl
generation (*16*). P
alternatives such as
MPP) or iron(II) ph



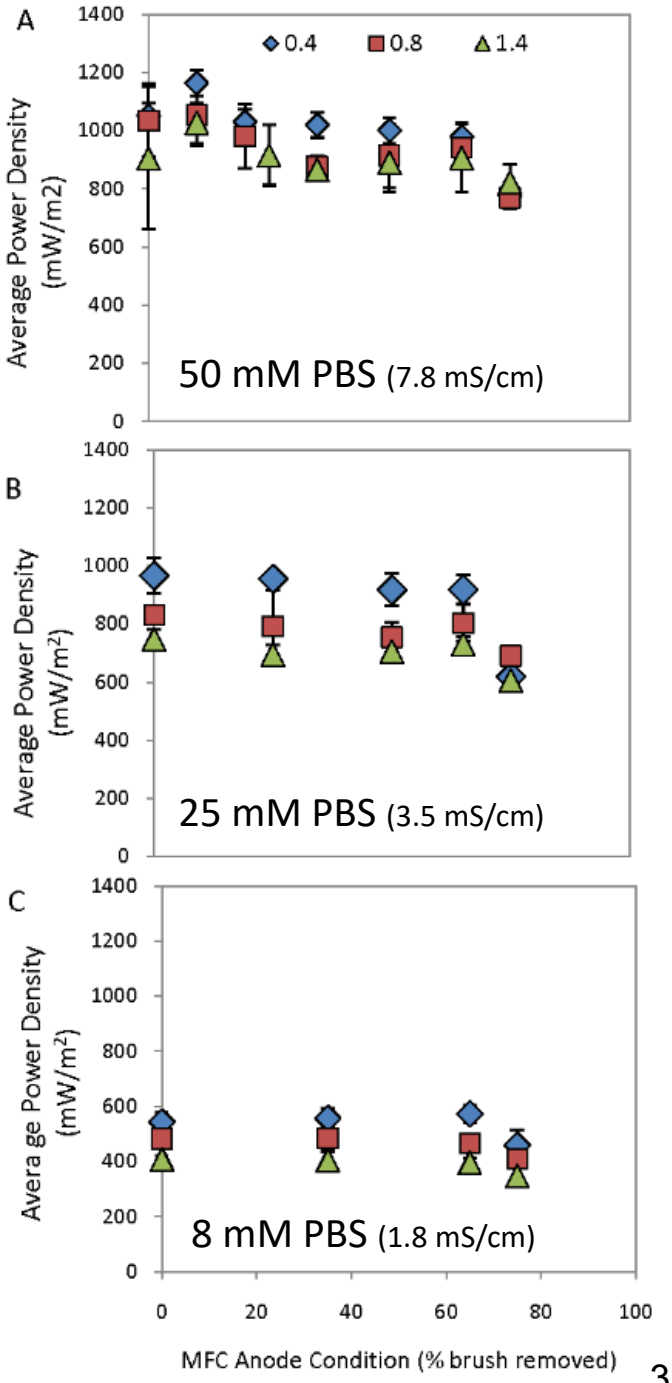
Cheng, Liu, Logan (2006) *Environ. Sci. Technol.*

B

Brush to cathode distance



- Brush edge: 0.4, 0.8 or 1.4 cm
  - Closer brush works better, even up to 0.4 cm!
- 30-80% of brush removed from most distant side of the brush
  - No decrease in power until 80% of the brush removed. **Brushes near the cathode are okay!**

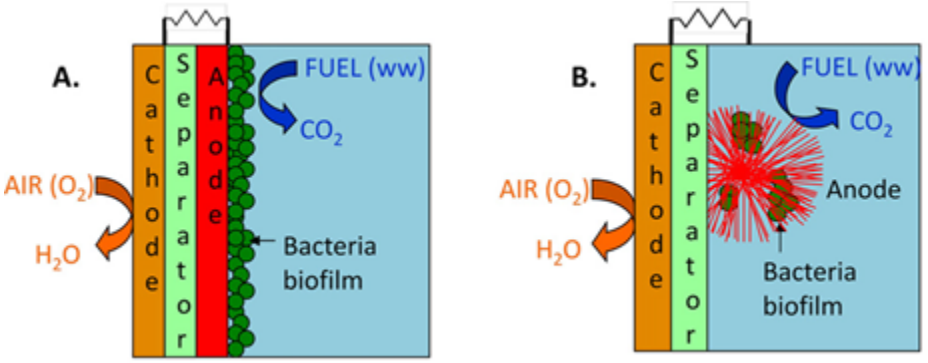


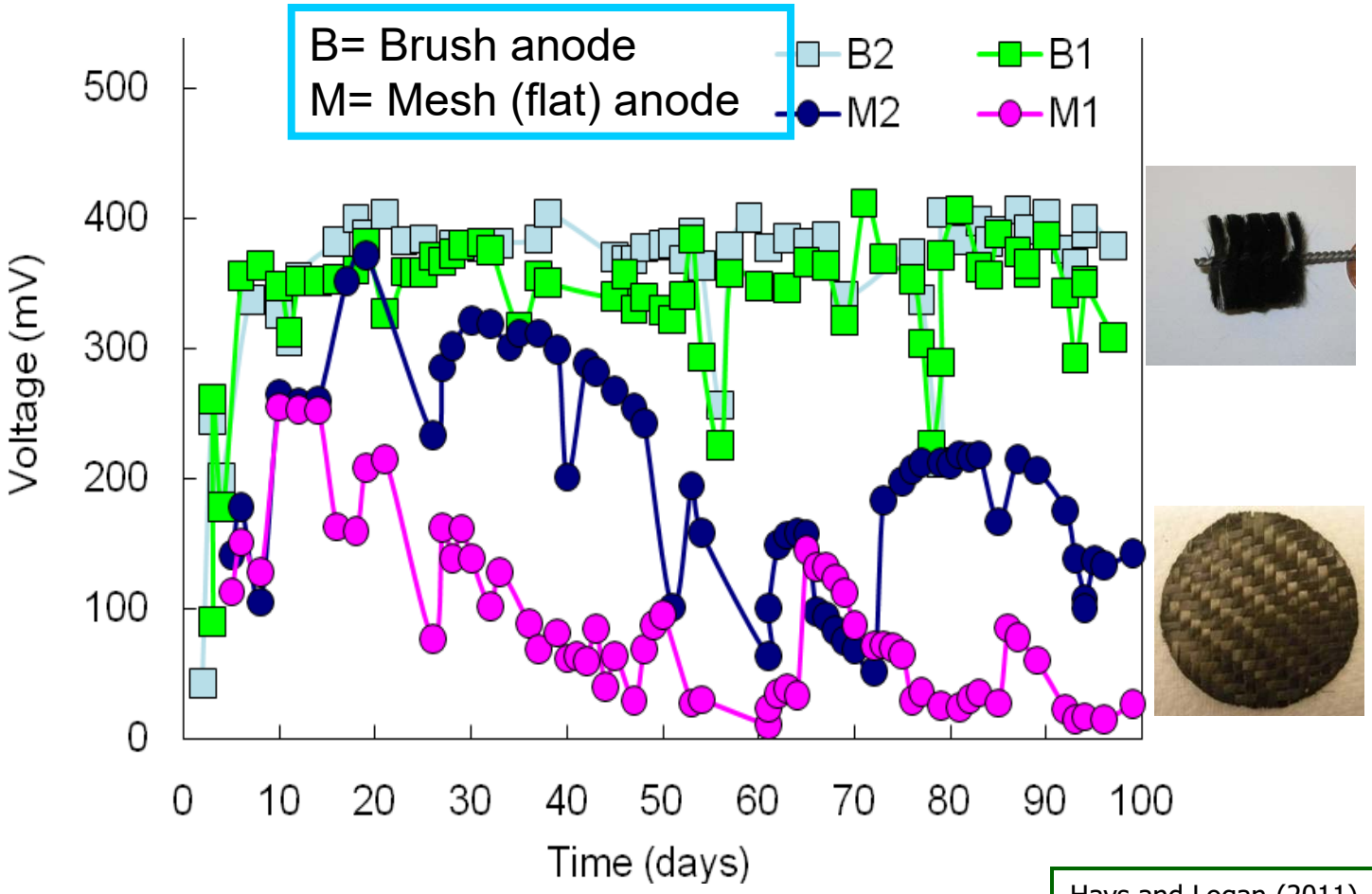
PENNSTATE

Hutchinson, Tokash, Logan (2011) *J. Power Sources*

Voltage Production:

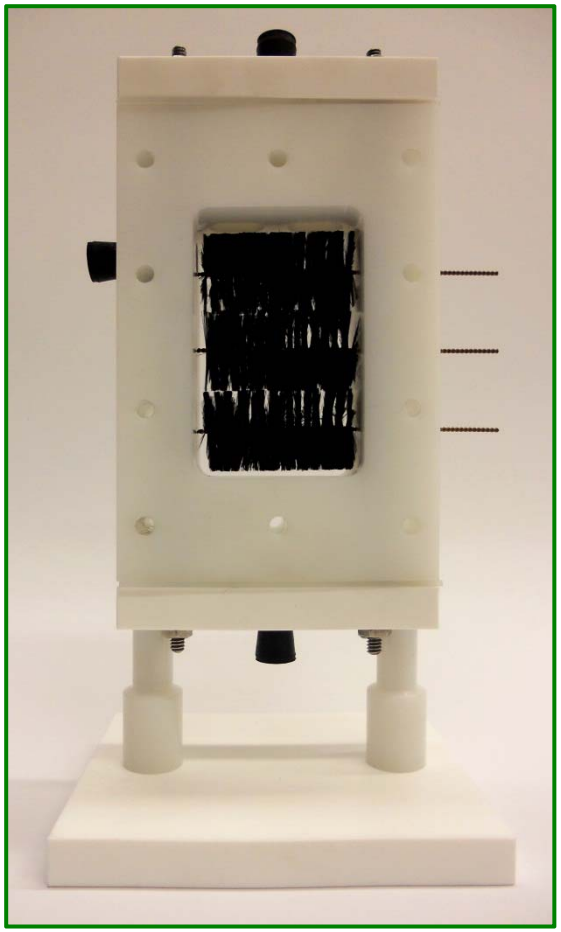
Mesh vs Brushes (domestic ww)



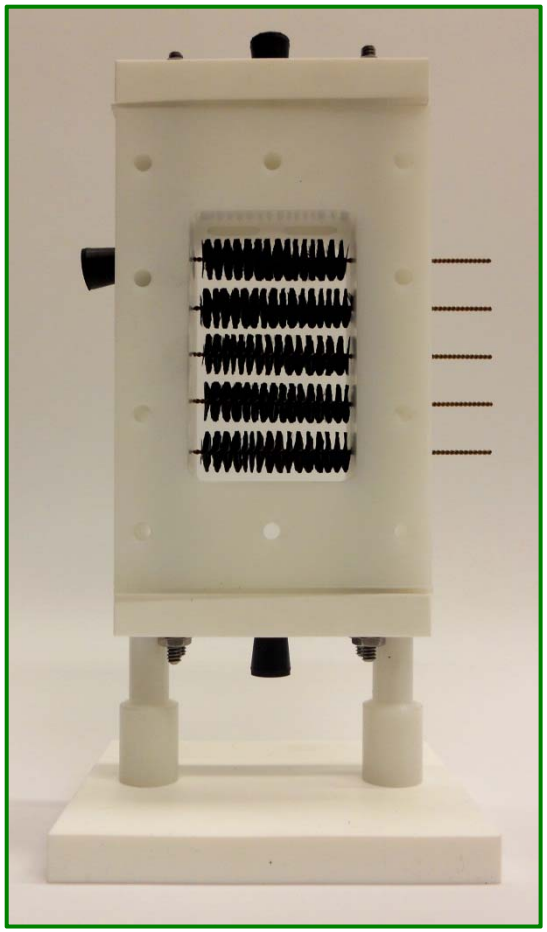


Hays and Logan (2011) *J. Power Sources*

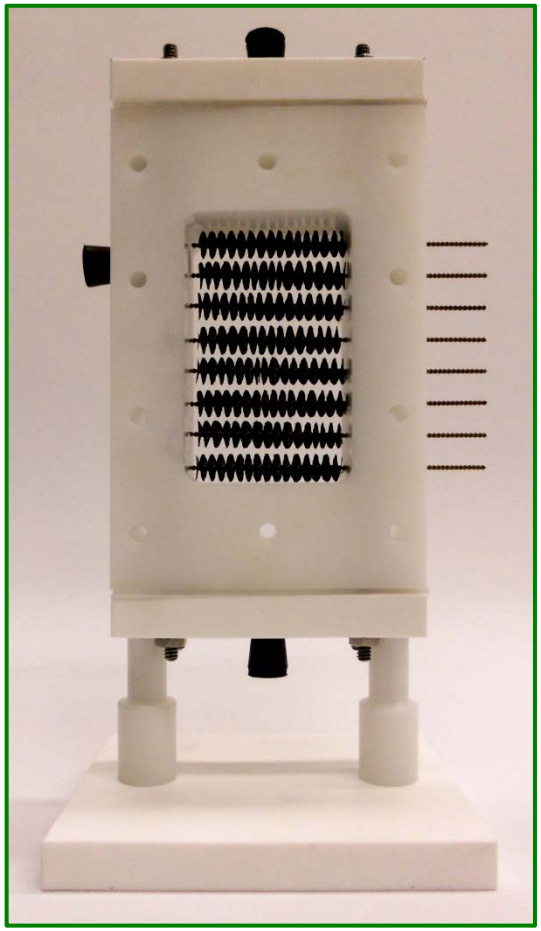
Multi-electrode MFCs



3 brushes (**R3**)
3500 m^2/m^3



5 brushes (**R5**)
2800 m^2/m^3



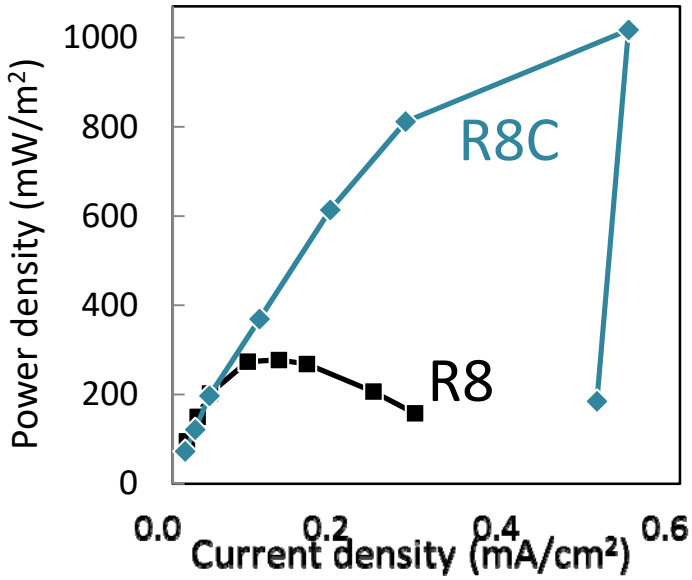
8 brushes (**R8**)
2900 m^2/m^3

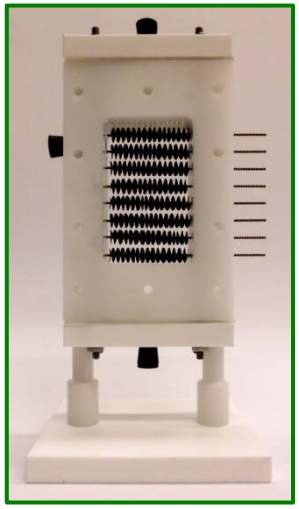
Electrode area (2.5 cm diameter brush/chamber width = 40 m^2/m^3

Lanas & Logan (2013) *J. Power Sources*

Smaller, closer brushes work best.. with acetate

(Continuous flow, acetate in buffer)





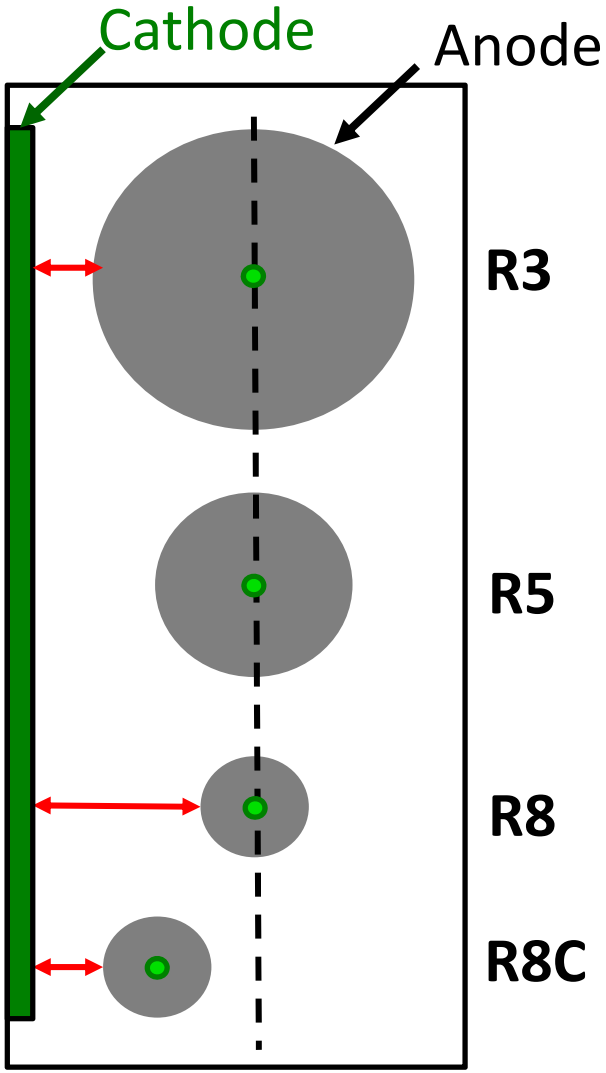
Maximum power densities

R8C= 1020 mW/m²

R8= 280 mW/m²

(R3= 560 mW/m²)

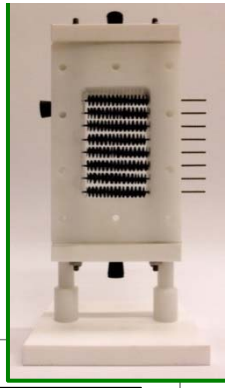
(not shown)

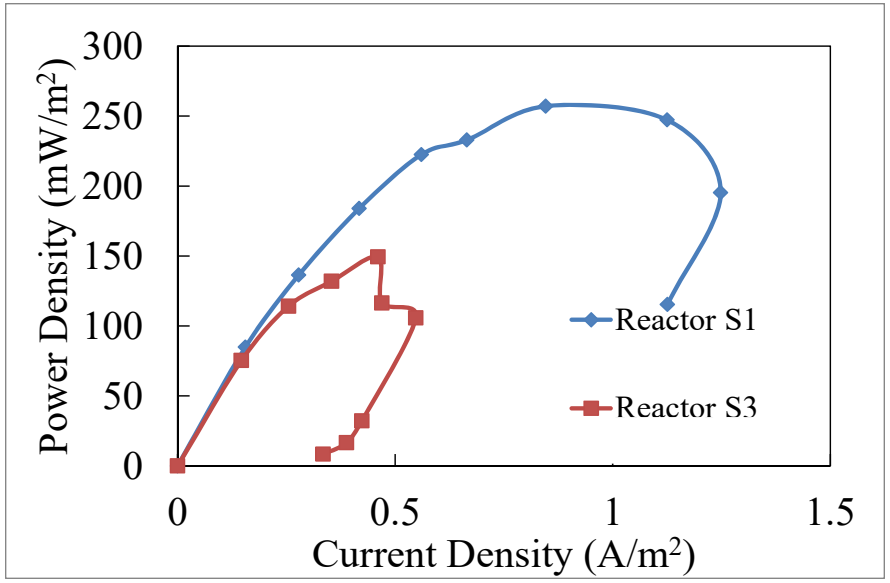


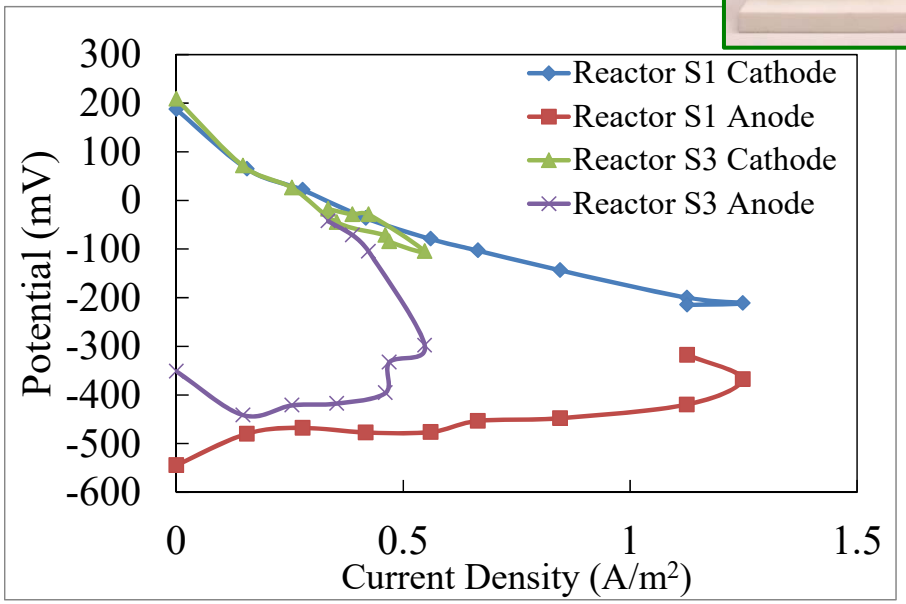
Lanas & Logan (2013) *J. Power Sources*

Reactor instability smaller brushes: wastewater

Continuous flow, 4 h HRT, domestic ww







Maximum power quite different:

260 mW/m² vs **150 mW/m²**

Not possible to get true "duplicates"

- Cathode performance similar
- Anodes performance unstable (S3)

Conclusion: Avoid the use of very thin brushes

(it produces conditions similar to "flat anodes")

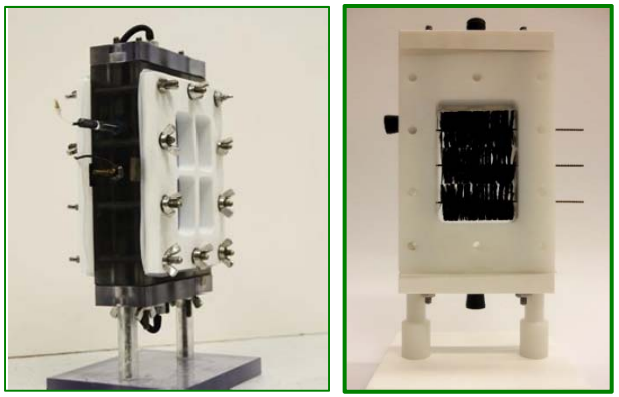
PENNSTATE

Stager & Logan, *Unpublished*

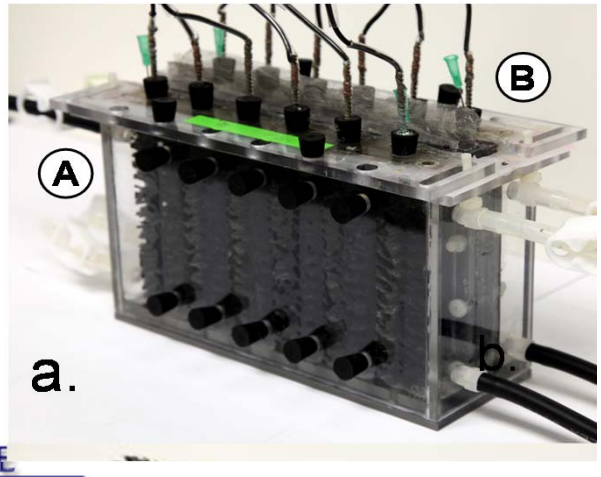
Reactor Designs

Gen 0: 0.025 L, 25 m^2/m^3

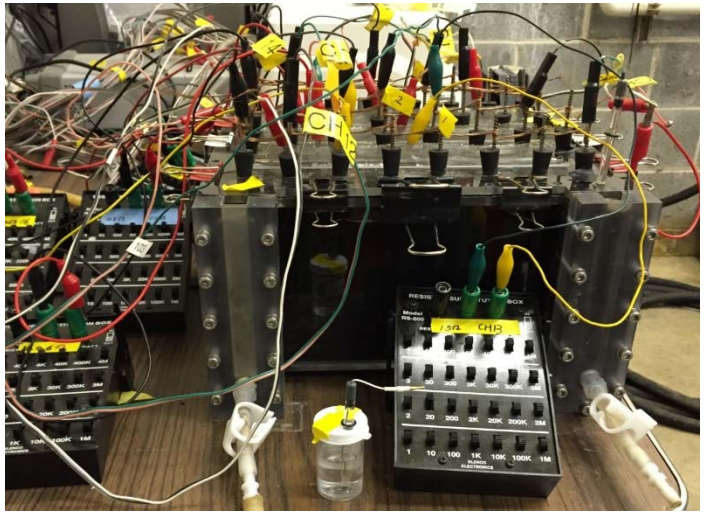
Gen 1: ~0.13 L, 25 m^2/m^3



Gen 2: 2 L, 2 chambers, 25 m^2/m^3



Gen 3: 5.7 L, 4 chambers

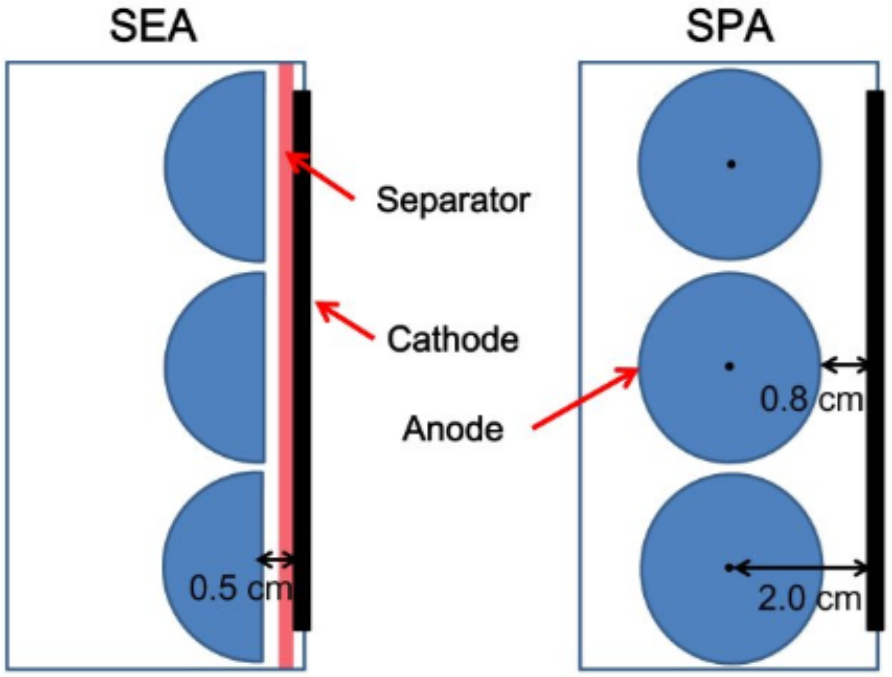


PENNSTATE

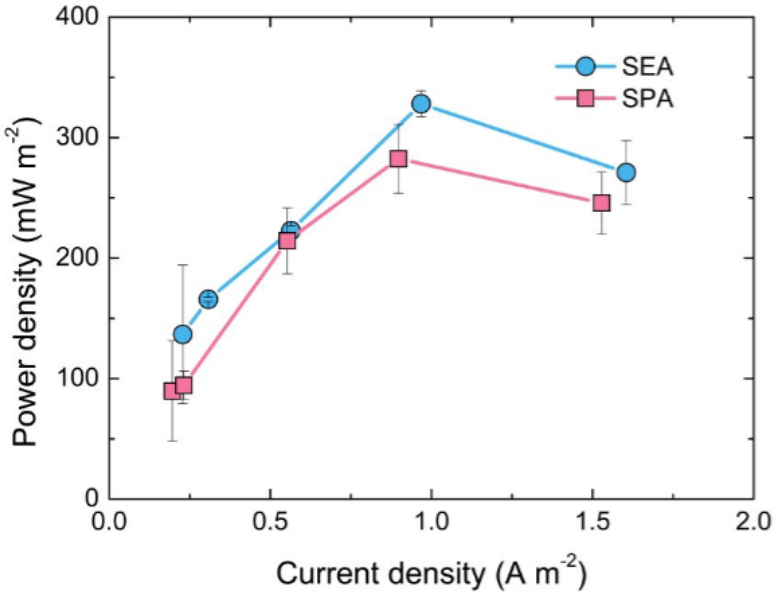
Gen 1 MFCs: Separator or no separator?

Separator
(Separator Electrode Assembly, **SEA**)

No-separator
(Spaced electrode assembly, **SPA**)



Tests using domestic wastewater

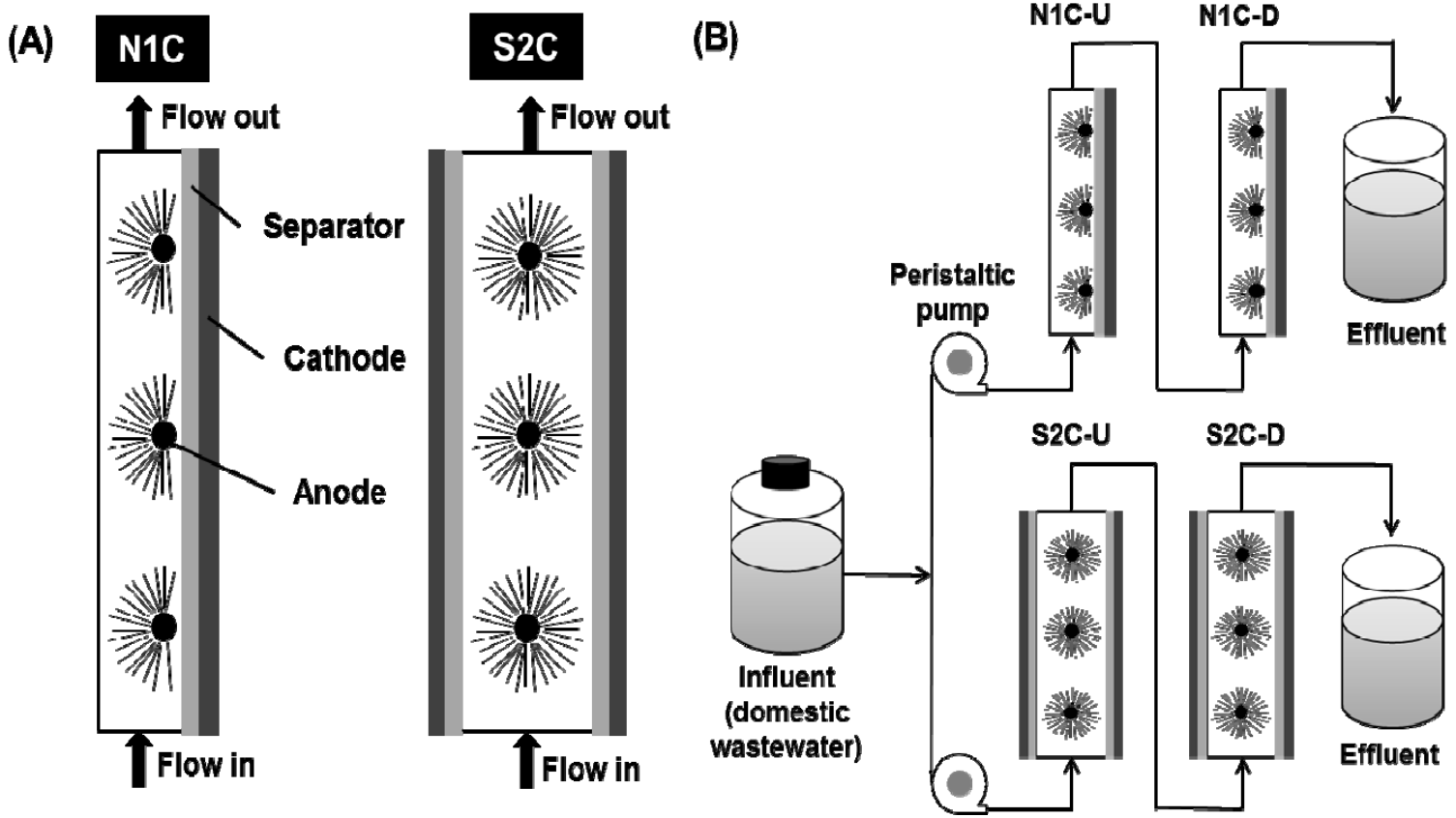


Maximum power densities similar for SEA & SPA

Ahn, Hatzell, Zhang, Logan (2014) *J. Power Sources*

Gen 1 MFCs: 1 or 2 Cathodes

1 cathode 2 cathodes



N1C=SEA (previous terminology)

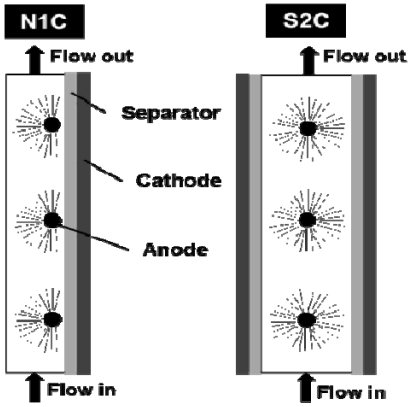
PENNSTATE

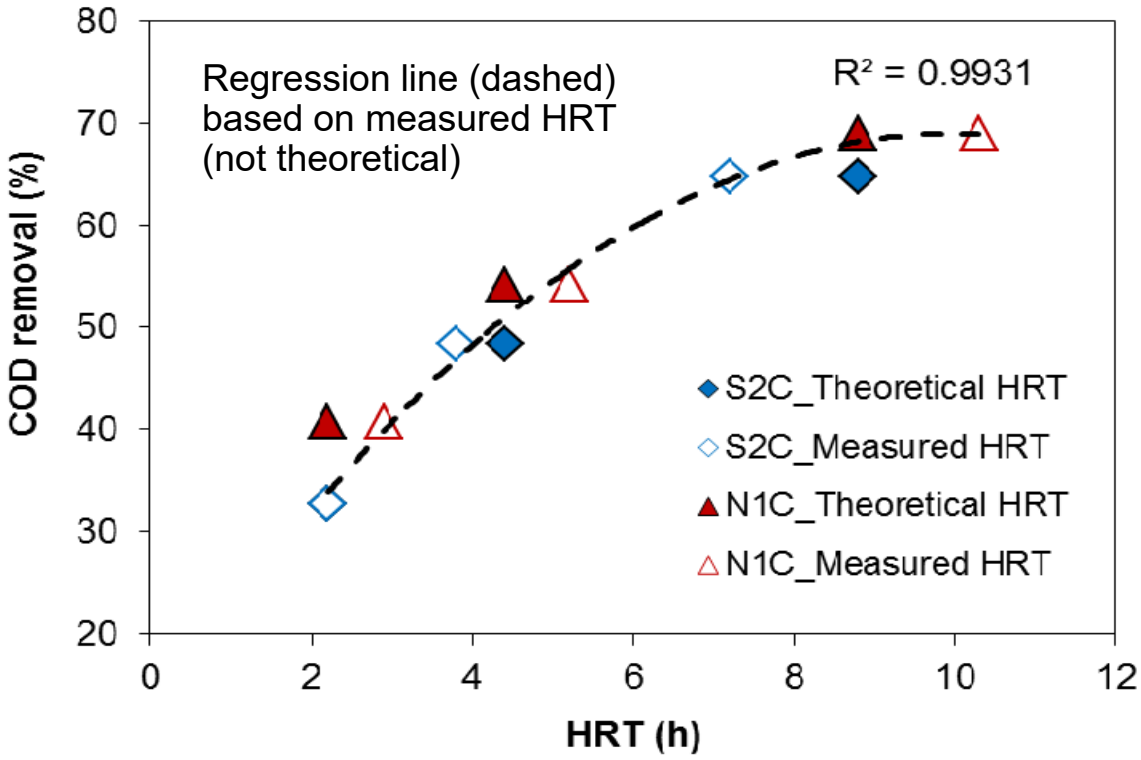
Kim, Yang and Logan (2015) *Water. Res.*

COD Removals vs actual HRTs

HRTs: N1C > S2C

- Same theoretical HRT set for reactor comparisons
- N1C > S2C



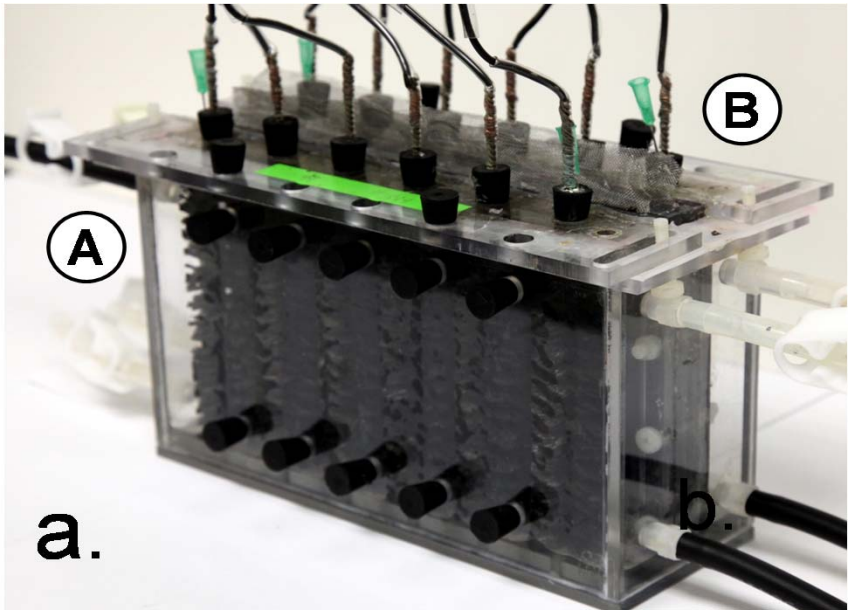


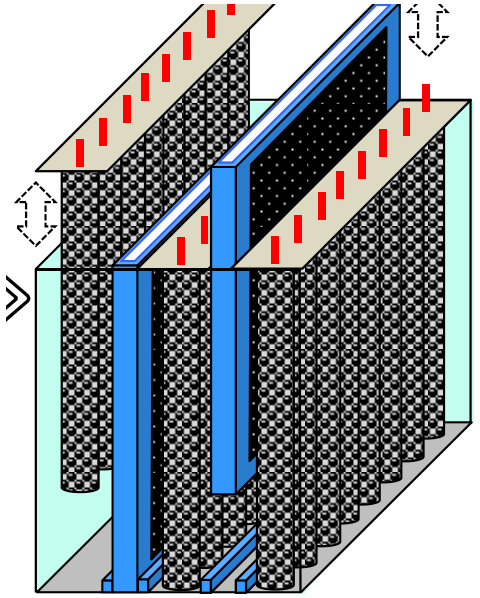
It is important to *measure* actual HRTs

PENNSTATE

Kim, Yang and Logan (2015) *Water. Res.*

Gen 2 MFCs: Design



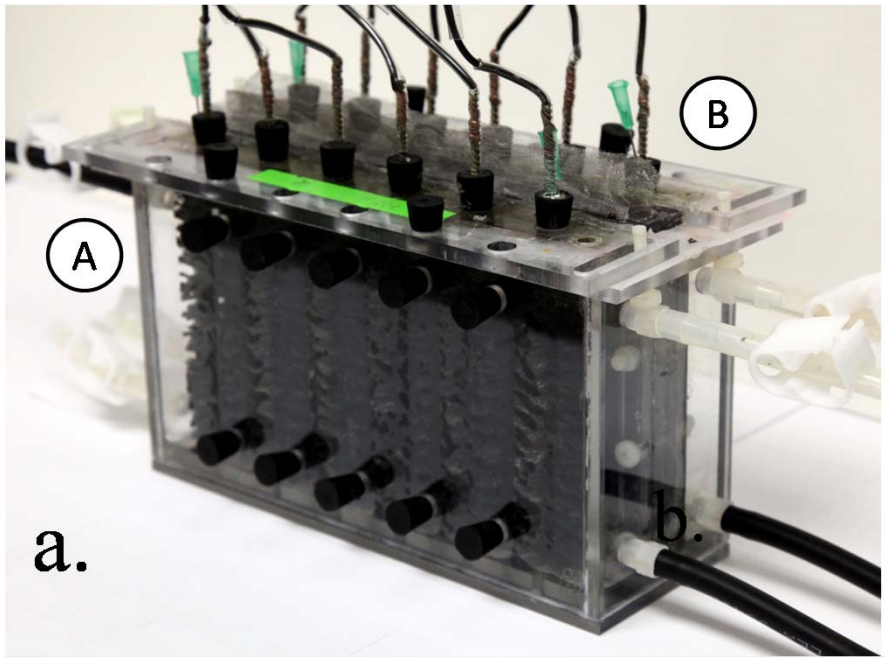


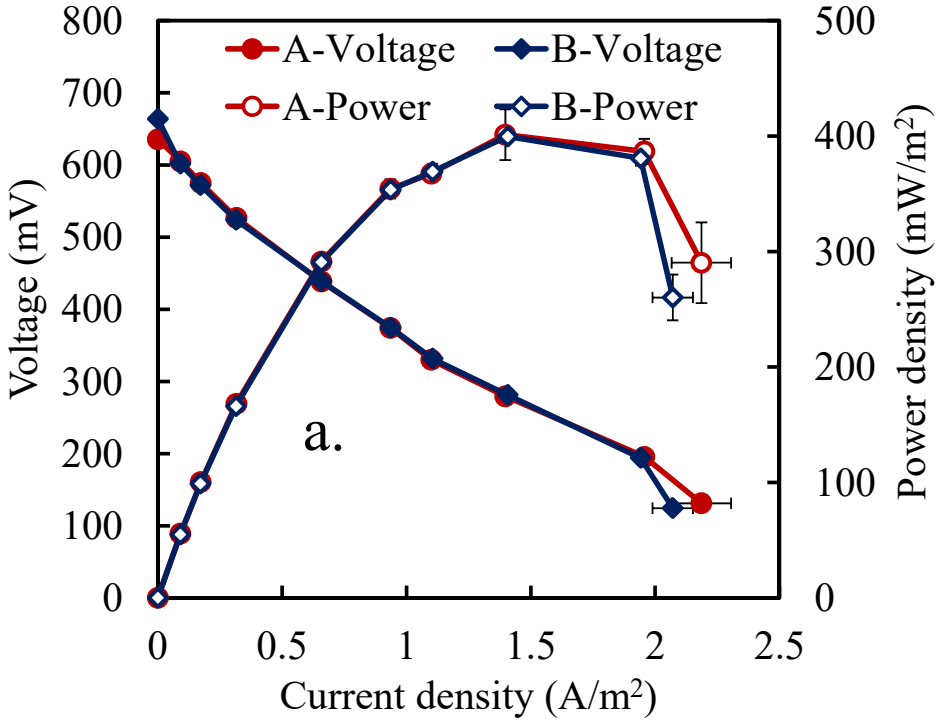
- **Modular MFC**
  - Gen II reactor has 2 banks of 8 anodes; 2 cathodes
  - Cathode specific surface area: 29 m^2 m^{-3} based on total liquid volume (1.4 L), or 20 m^2 m^{-3} based on total reactor volume (2 L).
  - Not a "cassette" (anode+cathode) but separate anode and cathode modules.

PENNSTATE

He, Zhang, Logan (2014) *Submitted*

Gen 2 MFCs: Power production



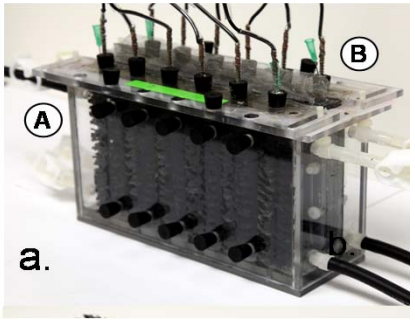


- Modular MFC
  - Shown with 2 anodes, 2 cathodes; 20 m^2 m^{-3} (total volume)
  - Produced ~ **400 mW/m^2** with domestic wastewater, highest to date for this source

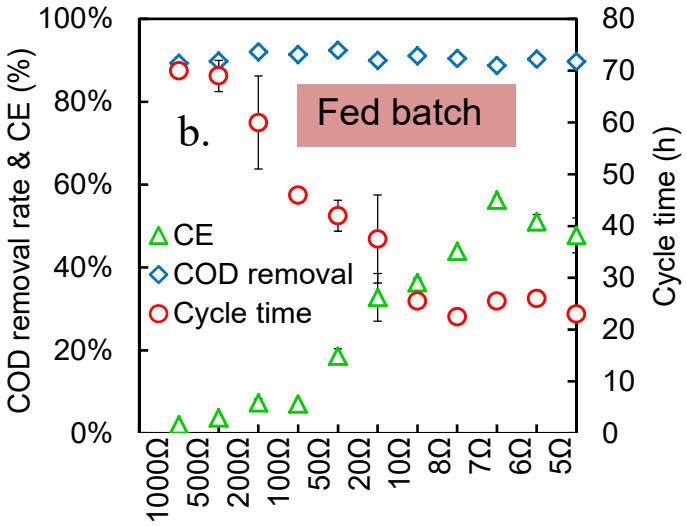
PENNSTATE

He, Zhang, Logan (2014) *Submitted*

Gen 2 MFCs: Performance



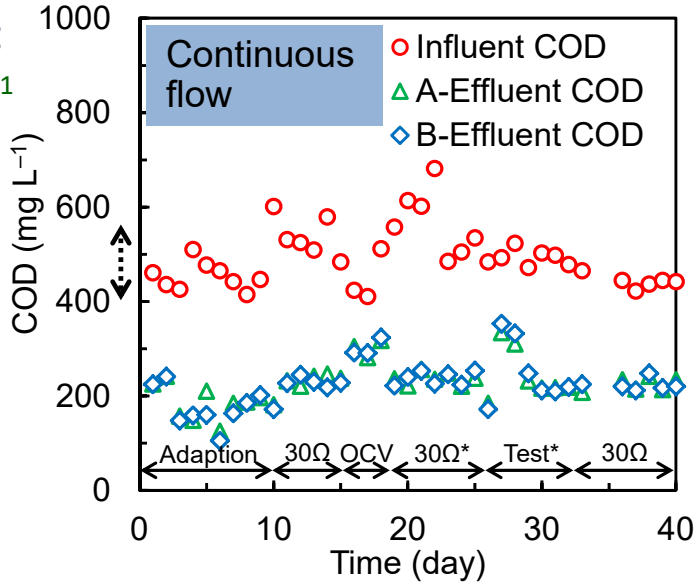
Fed batch: Long cycle times, high COD removal

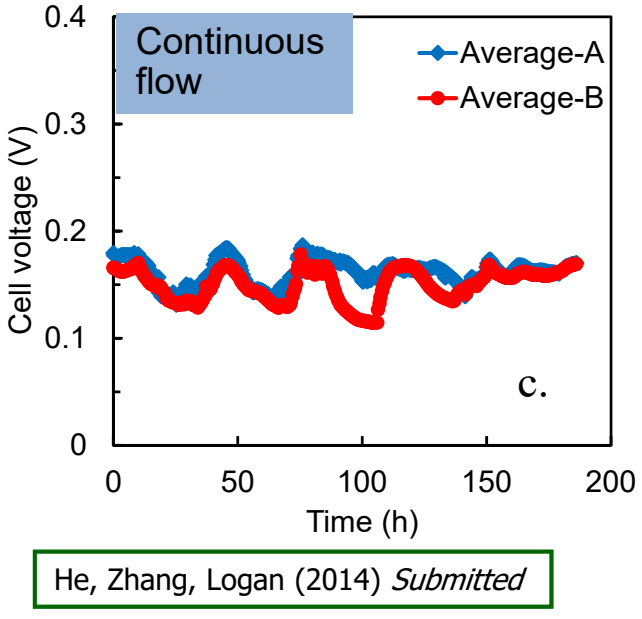


Continuous flow (8 h HRT):

Influent: 480 ±25 mg L^{-1}

COD removal: 57 ±5%





He, Zhang, Logan (2014) *Submitted*

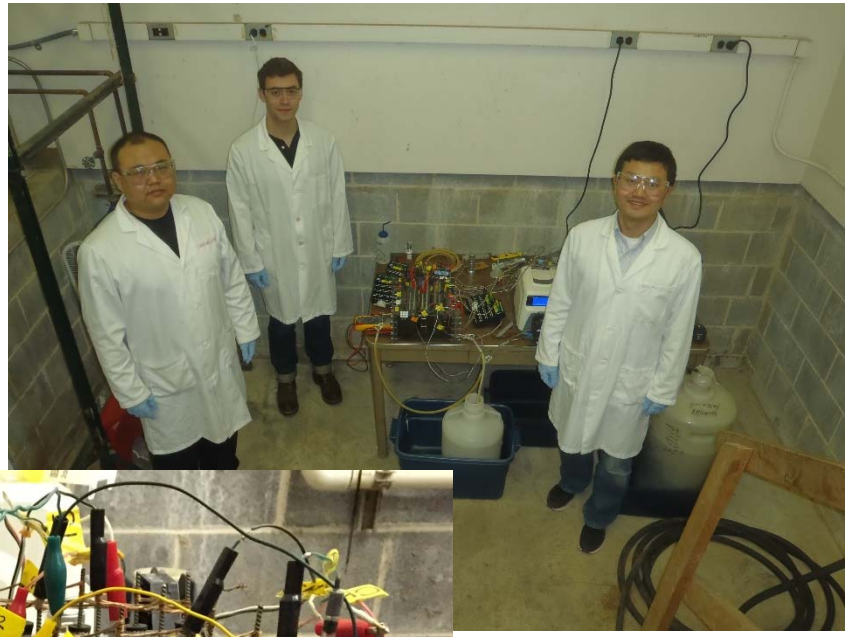
PENNSTATE

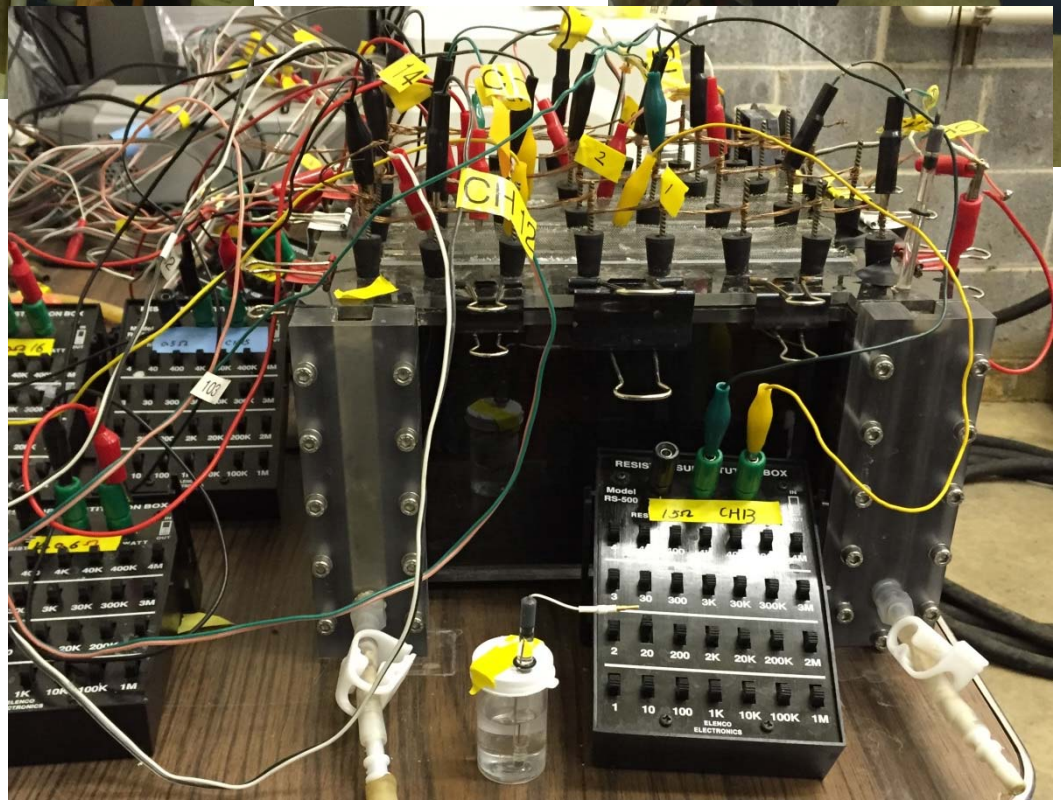
Power density comparisons: WW

Substrate	Notes	Power (mW/m^2)	Reference
Domestic WW + Ac	Batch	1100	This study
Domestic WW	Batch	400	This study
Domestic WW	Cont. flow, 8 h HRT	250	This study
Domestic WW	25 mL, batch	332	Cheng&Logan
Domestic WW	25 mL, batch	130-240	Hays&Logan(2013)
Domestic WW	180 mL, Cont flow	280-330	Ahn et al (2014)
Domestic WW	180 mL, Batch	230	Yang et al. (2015)
Domestic WW	Cassette	100	Morio et al. (2013)
Domestic WW	Cassette	150	Yu et al. (2012)

PENNSTATE

Gen 3 MFCs (in progress)





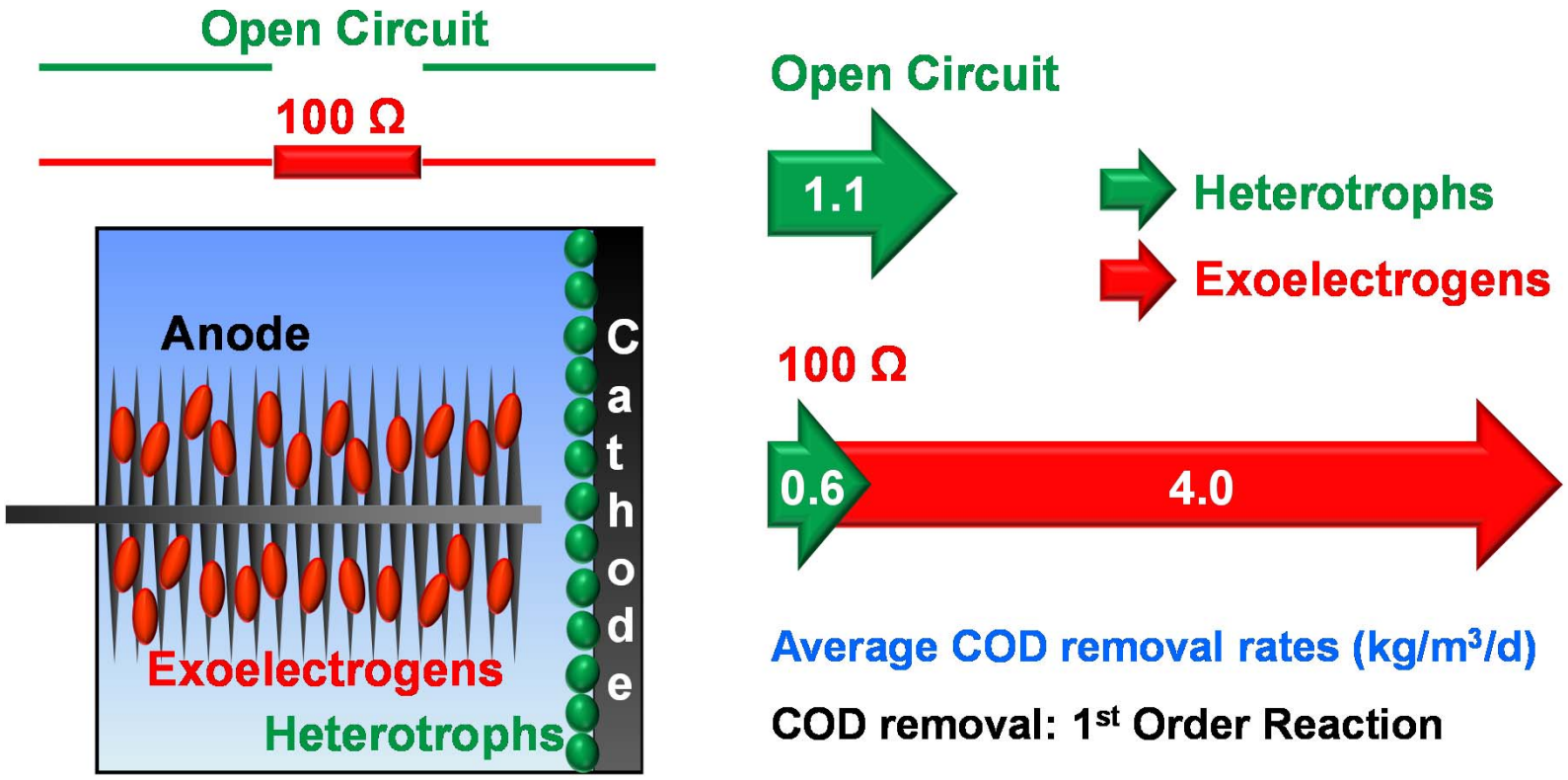
PENNSTATE

Final thoughts on using MFCs for Domestic Wastewater Treatment

- COD cannot be removed to < 30 mg/L with electricity generation
- A second process must be added after the MFC to further reduce COD
- Nutrient removal of anaerobic effluents is a research frontier (not just MFCs)

PENNSTATE

Current generation shifts more substrate to electricity generation in MFCs (acetate)

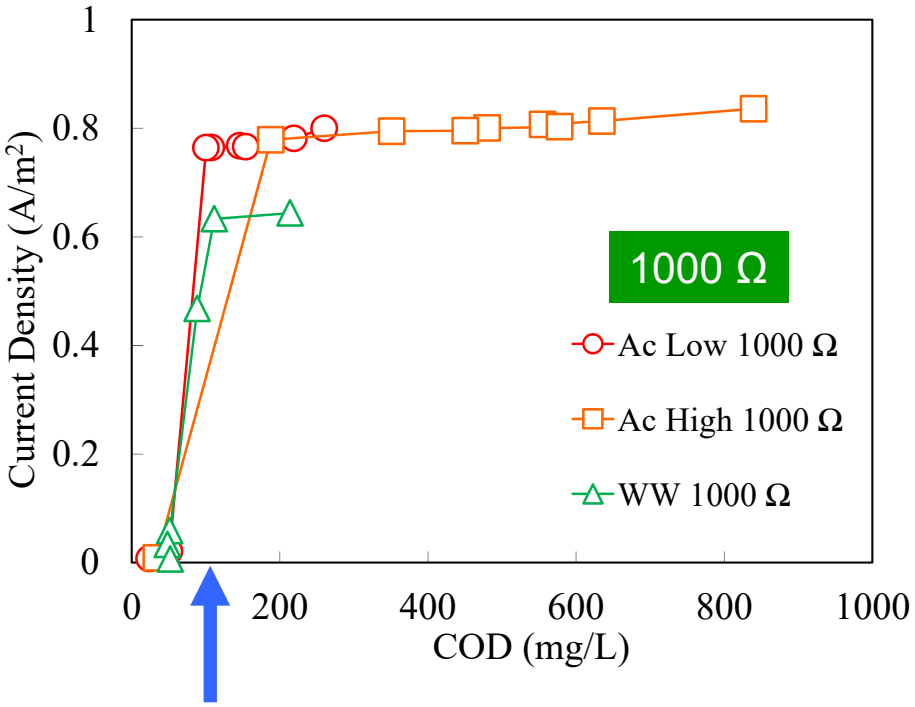


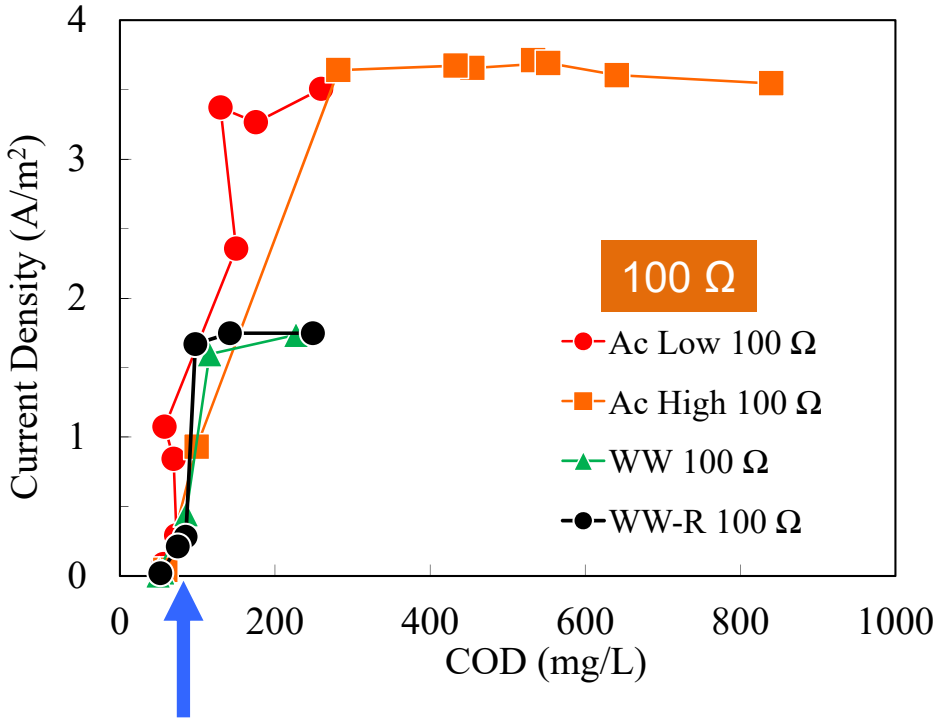
PENNSTATE

Zhang, He, Ren, Evans, Logan (2015) *Biores. Technol.*

Current density vs soluble COD (sCOD)

Current rapidly drops off at ~100 mg/L sCOD





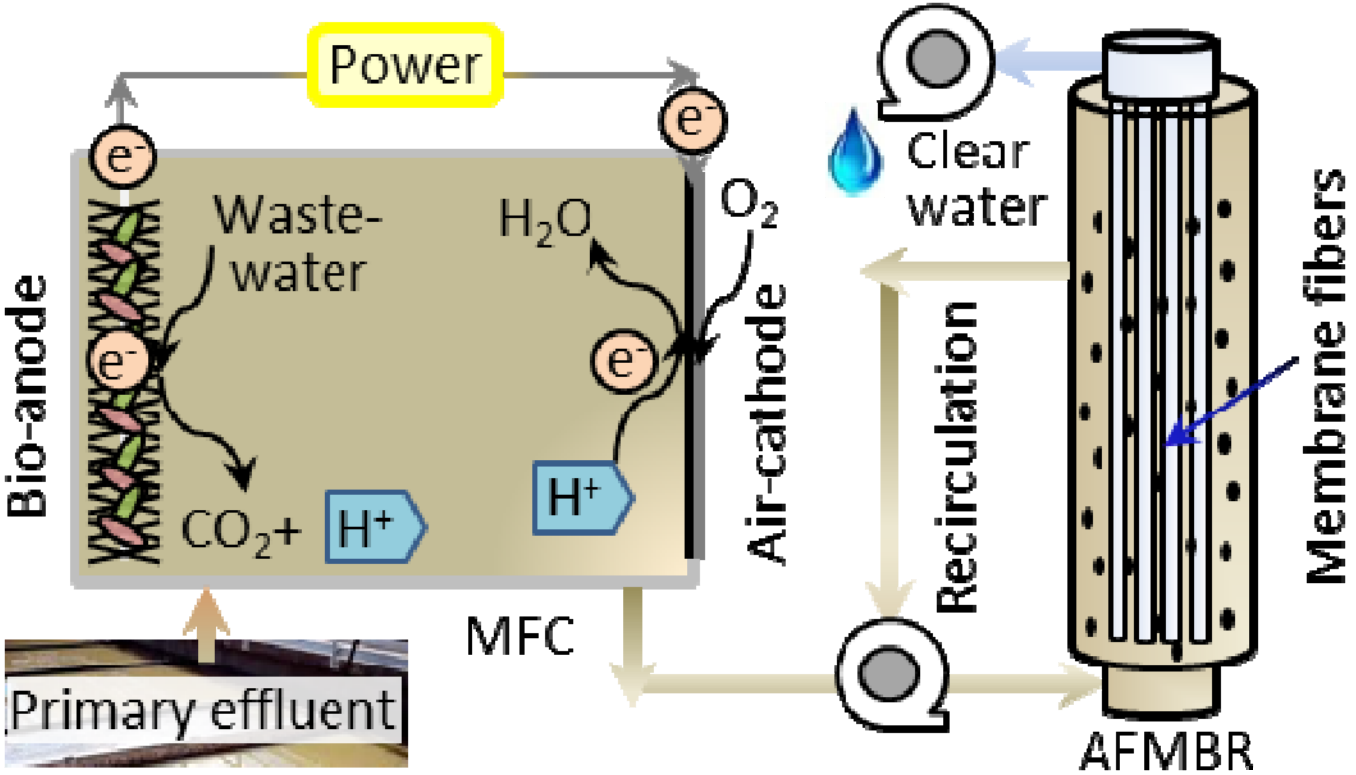
In both cases, current rapidly decreases when sCOD is still high (~100 mg/L)

PENNSTATE

Zhang, He, Ren, Evans, Logan (2015) *Biores. Technol.*

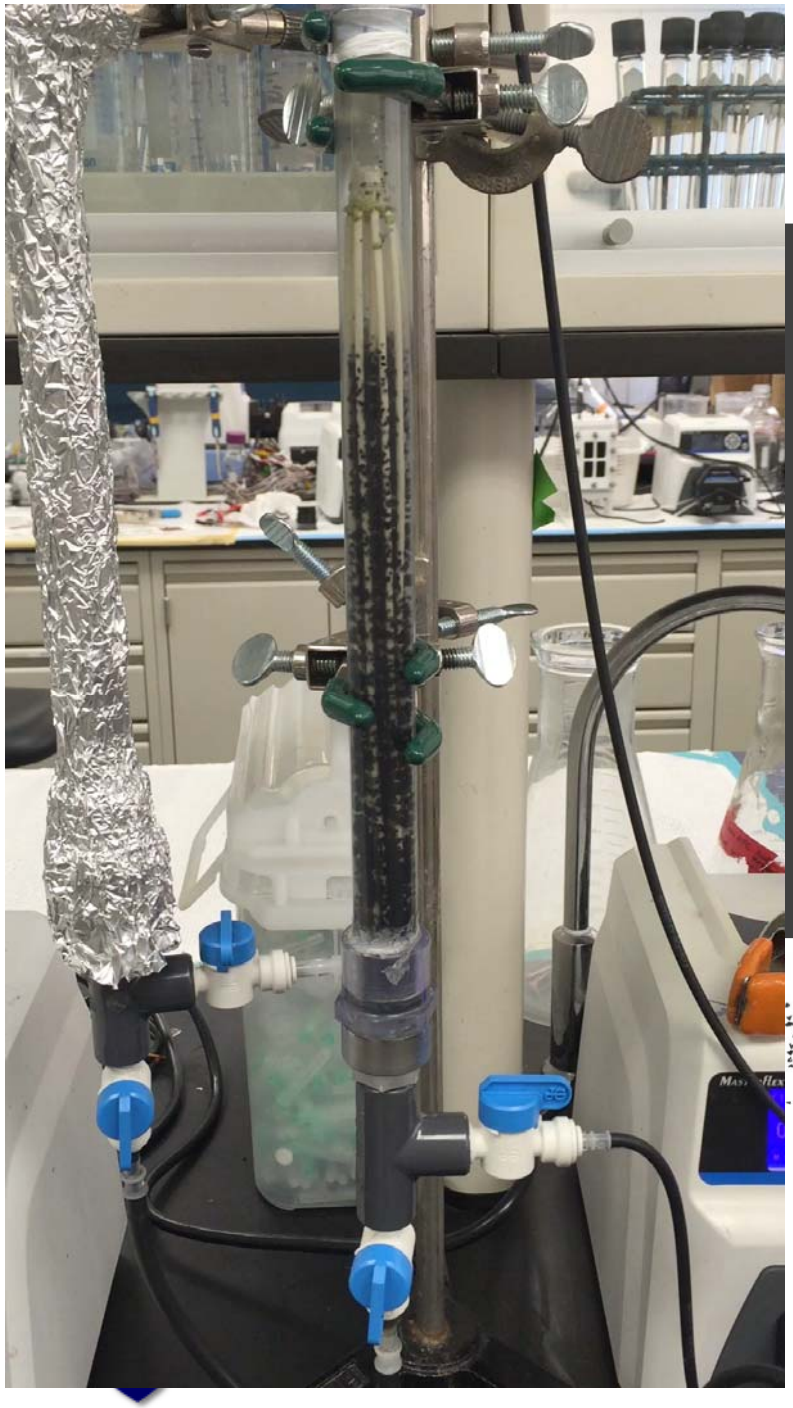
MFC + AFMBR

(Anaerobic Fluidized Bed Membrane Bioreactor)



PENNSTATE

Ren, Ahn & Logan (2014) *Environ. Sci. Technol.*



AFMBR Construction

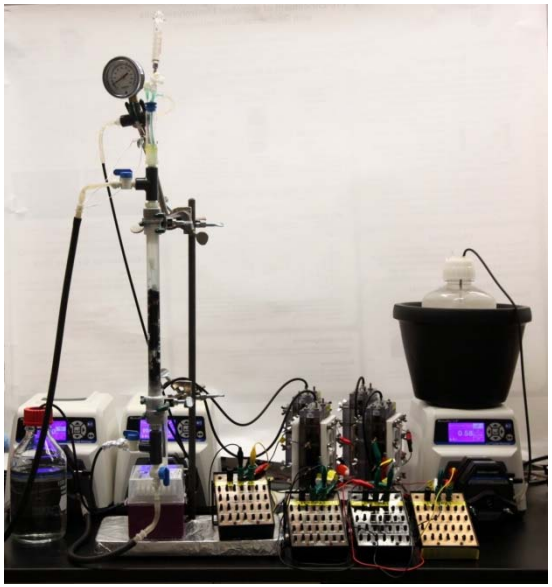
- Idea of AFMBR first published by Chae et al. (ES&T). Used as a second stage to granular fluidized bed anerobic digester
- AFMBR consists of a reactor body + ultrafiltration membrane + granular activated carbon (GAC)
- GAC fluidized by recirculation
- In tests here, used with a hydraulic retention time of 1 hour

Ren, Ahn & Logan (2014) *Environ. Sci. Technol.*

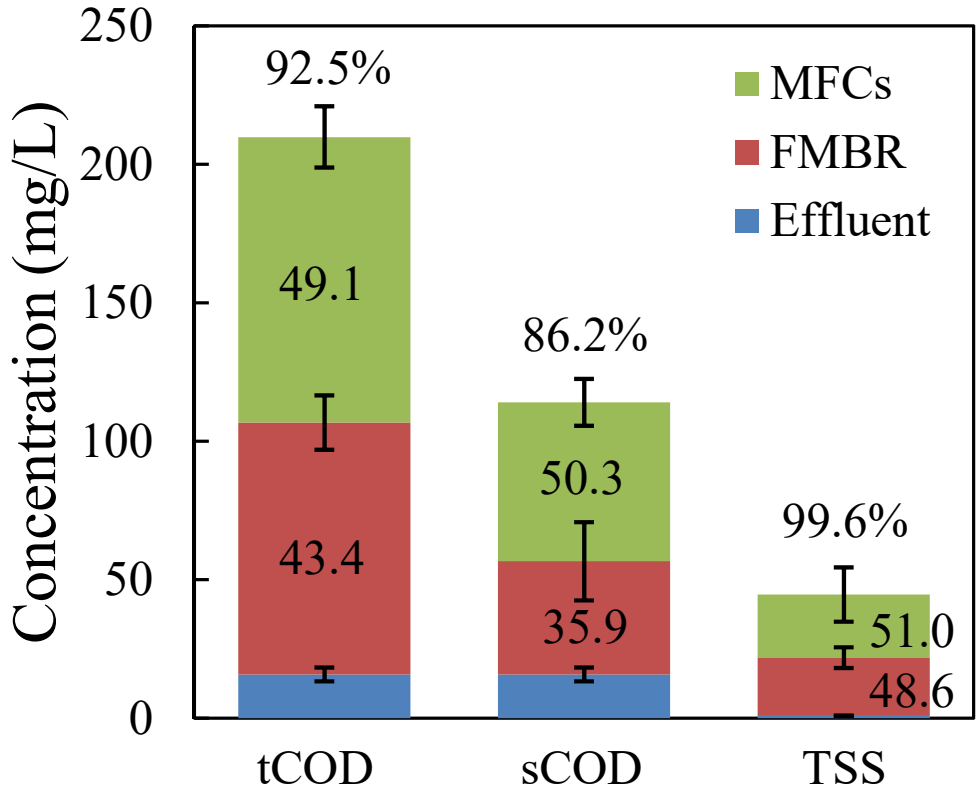
Effluent reduced to 16 mg/L tCOD

- Two trains of MFC (HRT = 4 h) to AFMBR (HRT = 1 h)
- Membrane flux 16 L/m^2/h
- 50 days performance
- Energy balanced

  (MFC produced = AFMBR used)



WW in AFMBR Permeate



- Effluent COD = 16 mg/L
- Effluent TSS <1 mg/L

Ren, Ahn & Logan (2014) *Environ. Sci. Technol.*

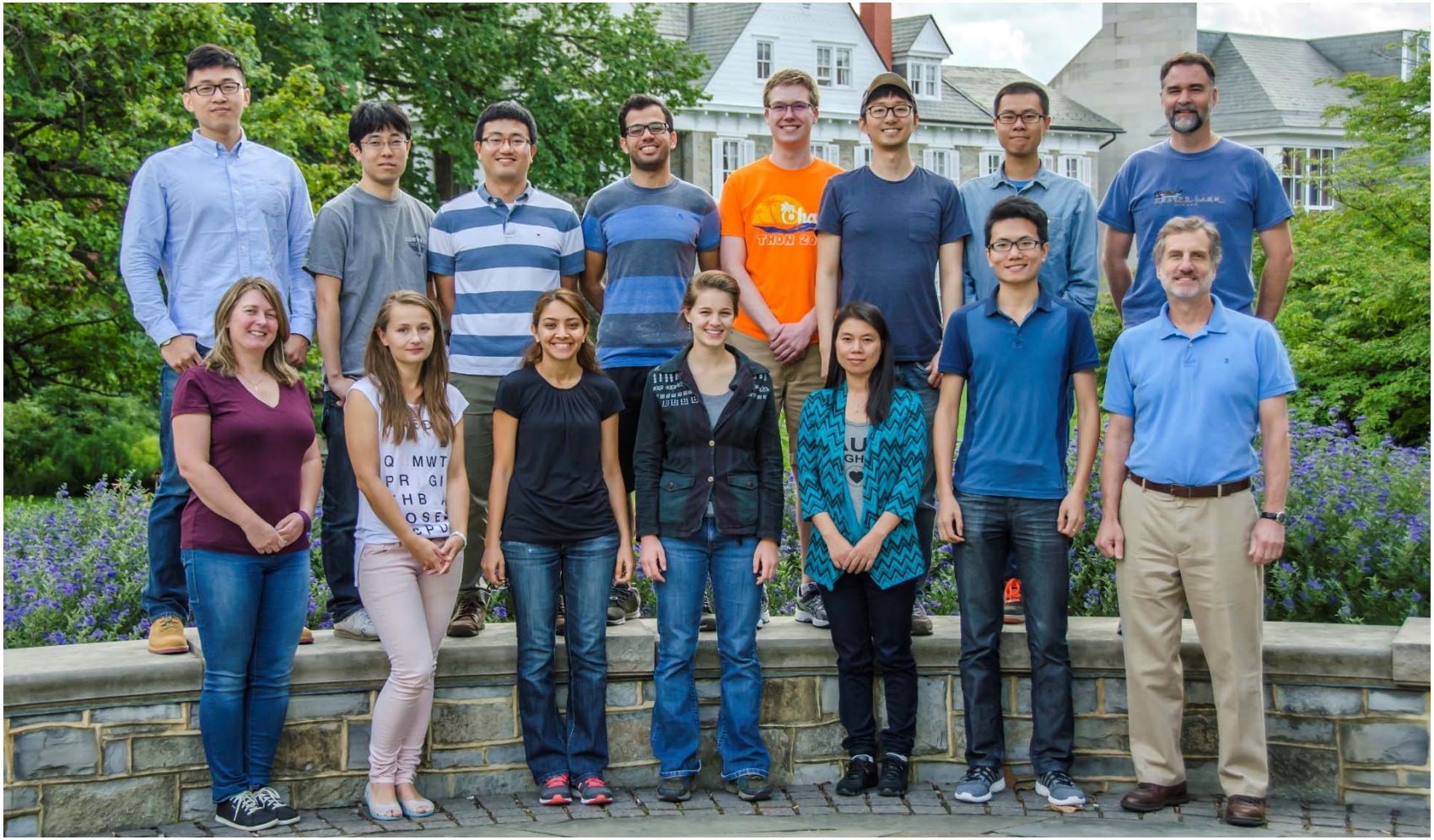
Conclusions

- MFCs can be used for domestic wastewater treatment
  - Cost of electrodes reduce: to < \$40 m^{-2}
  - High performance for brush anodes and activated carbon cathodes
  - Cathode specific surface area must be maintained as reactor sizes are increased

- A second process is needed for COD removal
  - Adding an AFMBR increased COD removal to achieve <20 mg/L
  - TSS < 1 mg/L, so no secondary clarifier needed
  - Nutrients need to be solved.

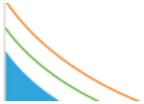
PENNSTATE

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

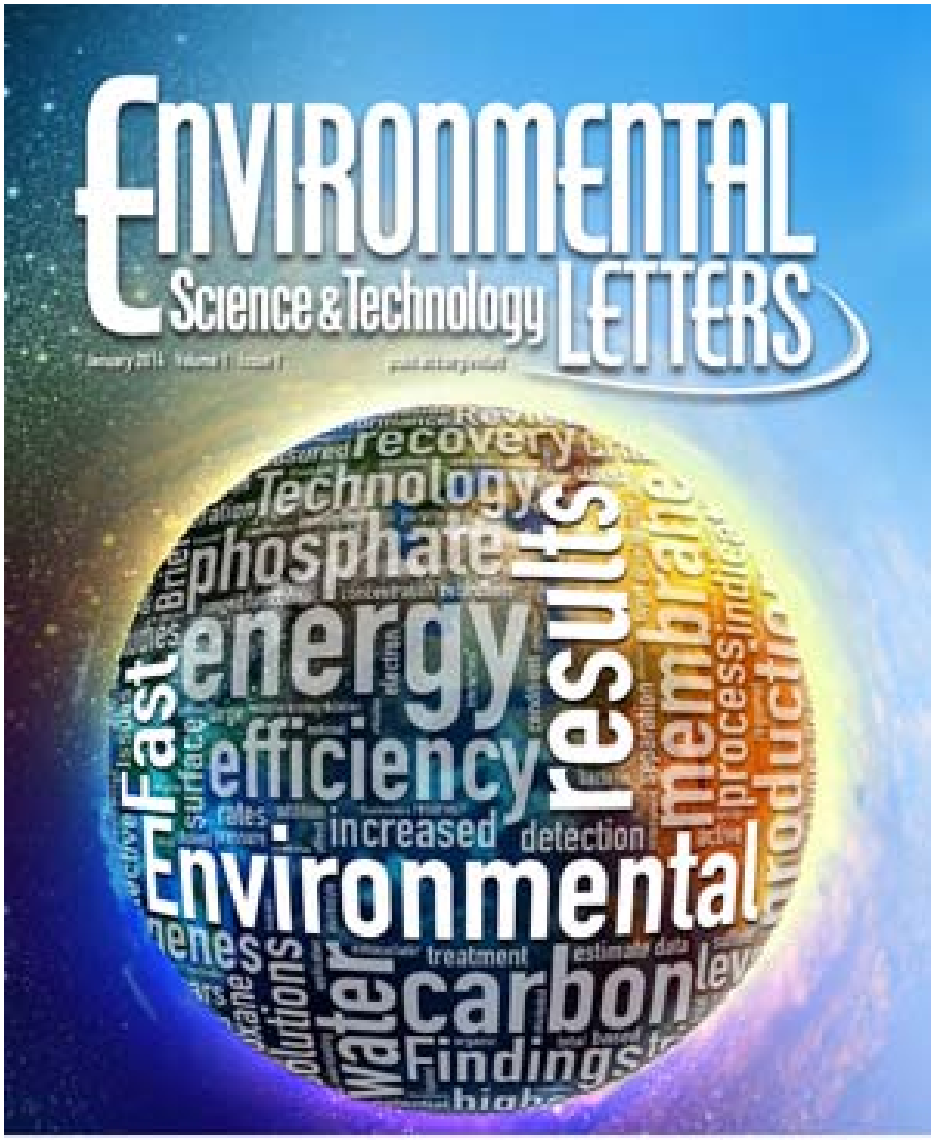


Current research sponsors
SERDP/DOD (2012-2015); GCEP/Stanford (2012-2015); NREL/DOE (2014-2017); NSF SusChem-EAGER (2015-2016)

International Collaborations



DeTao Masters Academy



ACS Publications
Most Trusted. Most Cited. Most Read.

The New Environmental Forum for Rapid Communications »»

Environmental Science & Technology Letters is a forum for letters (3000 words) reporting on novel results with significant findings and brief reviews (5000 words) on emerging environmental science & technology topics.

TOPICS COVERED INCLUDE:

- ✓ **Characterization of Natural and Affected Environments**
- ✓ **Environmental Processes**
- ✓ **Environmental Measurement Methods**
- ✓ **Environmental Aspects of Nanotechnology**
- ✓ **Novel Remediation and Control Technologies**
- ✓ **Energy and the Environment**

Submit your manuscript at
pubs.acs.org/estlett

Publication Timeframe of 4-6 weeks