Bioelectrochemical Conversion of Carbon Dioxide to Methane for Biogas Upgrading

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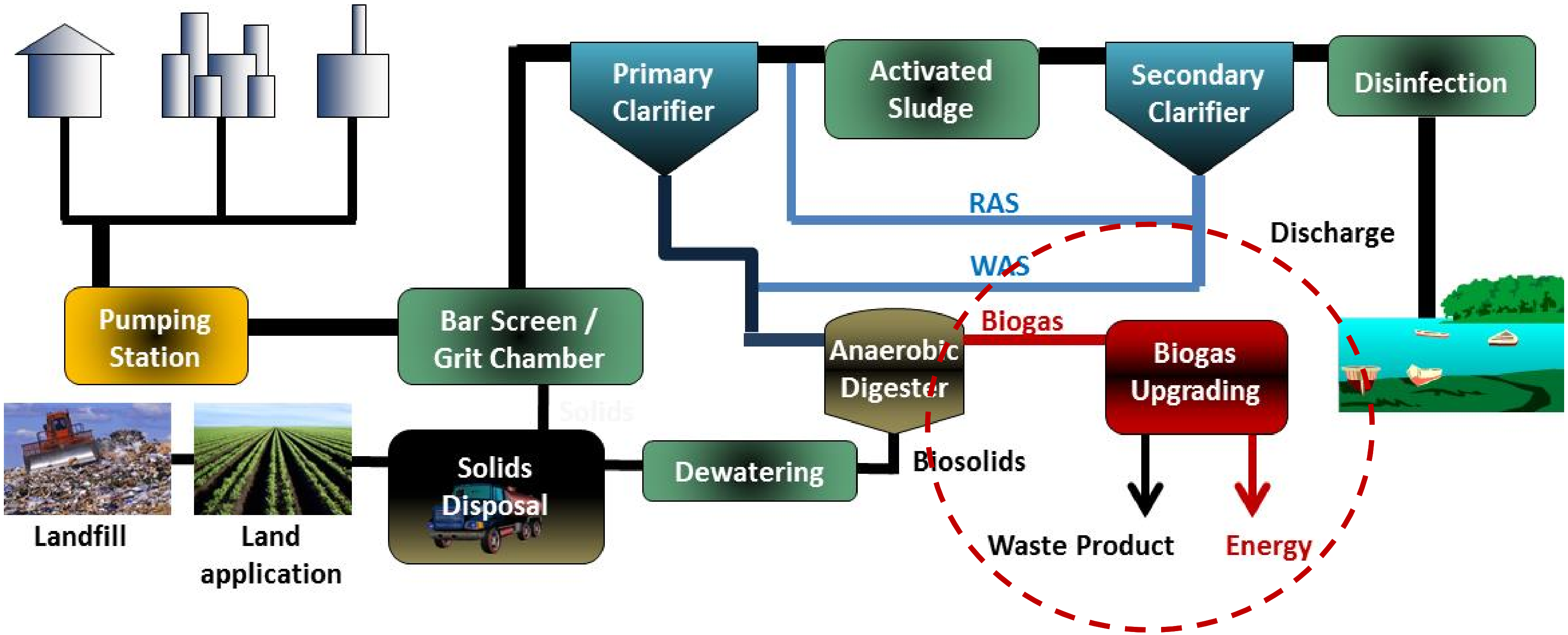
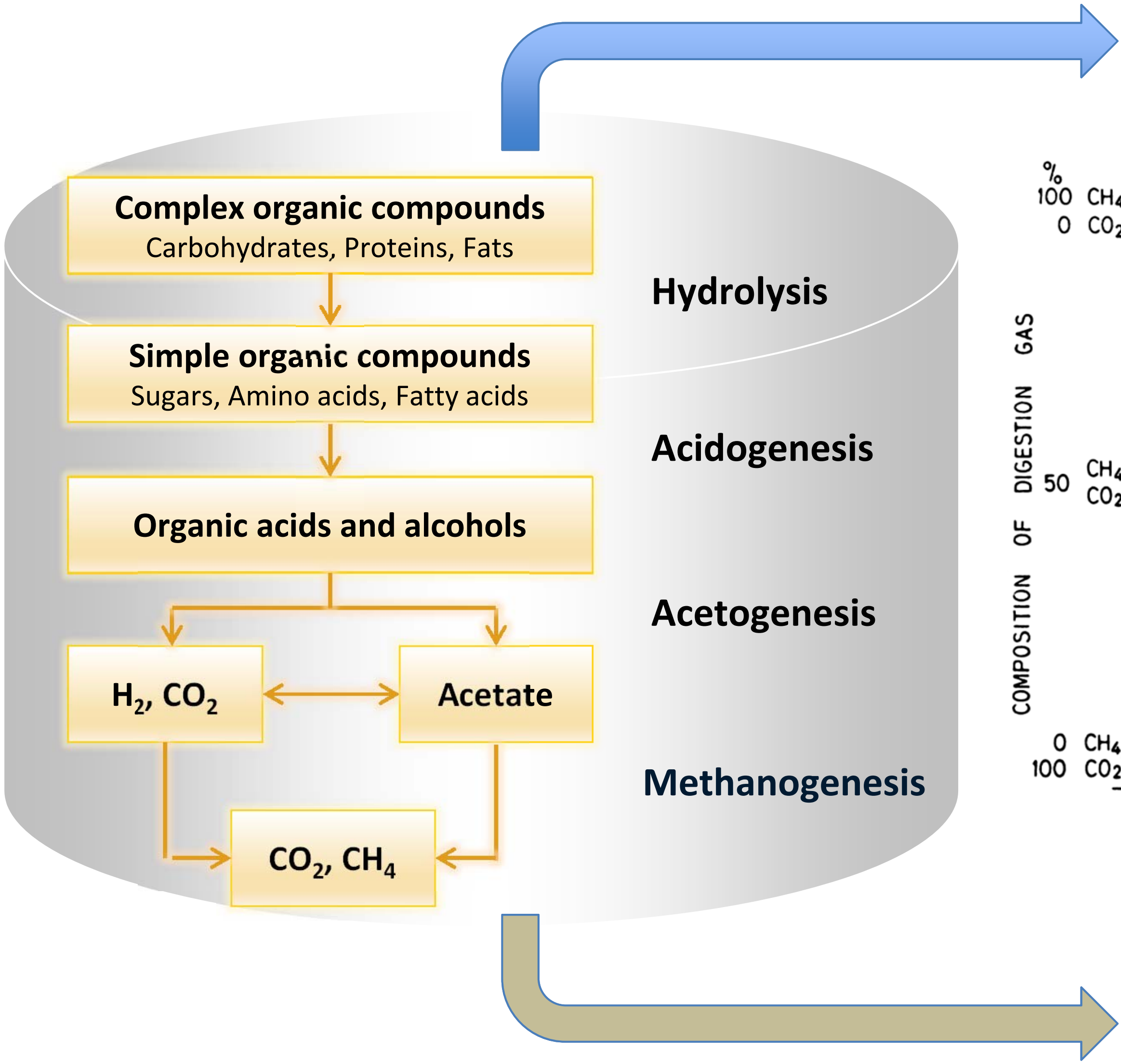
Municipal Wastewater Treatment



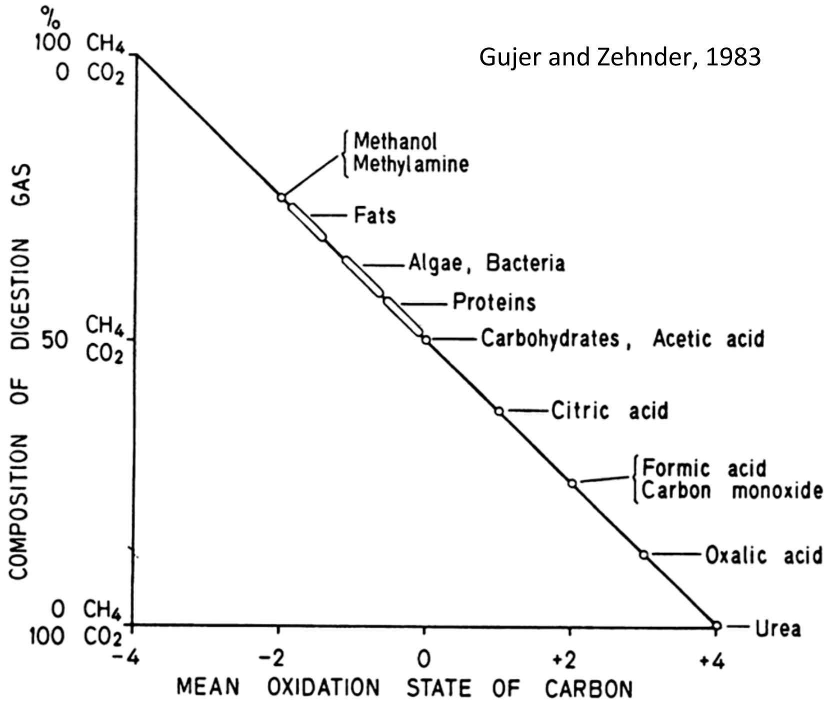
- Opportunities for CO_2 reuse and energy recovery in municipal wastewater treatment plants (WWTP), now referred to as Water Resource Recovery Facilities (WRRF)

Anaerobic Digestion & Biogas Composition



Biogas
(CO_2, CH_4, trace gases)

Liquid digestate,
Biosolids

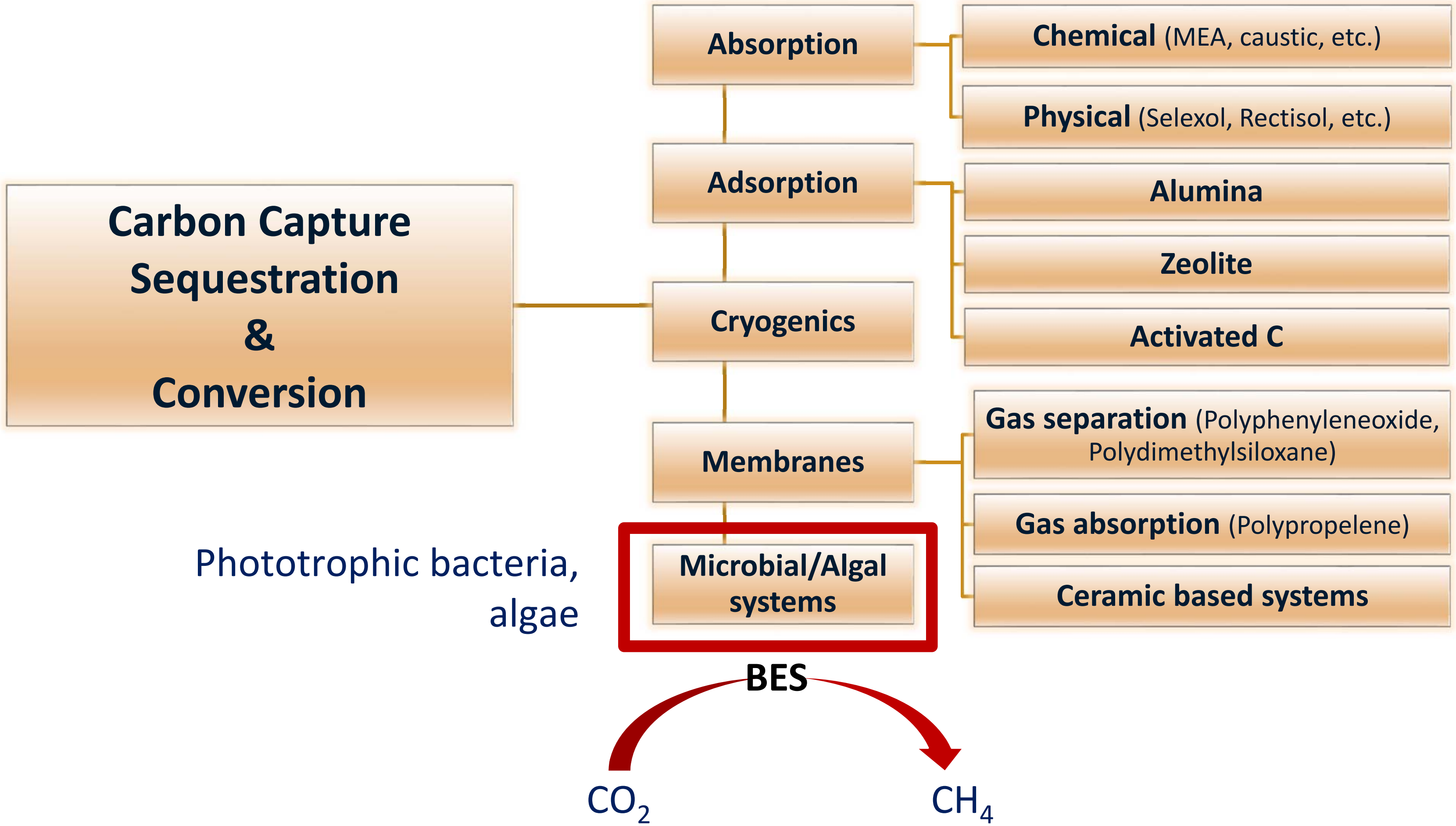


Gujer and Zehnder, 1983

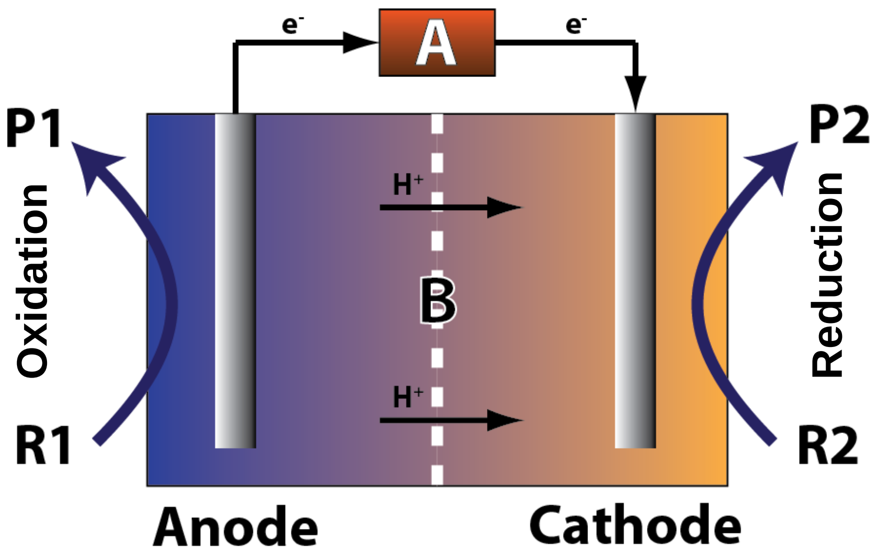
$OS = 4 - 1.5\ (COD/TOC)$

$CH_4\ (\%) = 100 - 12.5\ (OS + 4)$

CO_2 Capture & Conversion



Bioelectrochemical Systems (BES)



A, Resistor (MFC) or applied potential (MEC)
B, Proton exchange membrane
R1, Reactant in the anode (oxidation half reaction)
P1, Product in the anode
R2, Reactant in the cathode (reduction half reaction)
P2: Product in the cathode

Microbial Fuel Cell (MFC)
Produces electrical current

Microbial Electrolysis Cell (MEC)
Produces hydrogen (H_2)

Microbial Electromethanogenesis
Produces methane (CH_4)

Microbial Electrosynthesis (MES)
Produces 2+ carbon compounds
(e.g., acetate, methanol, etc.)

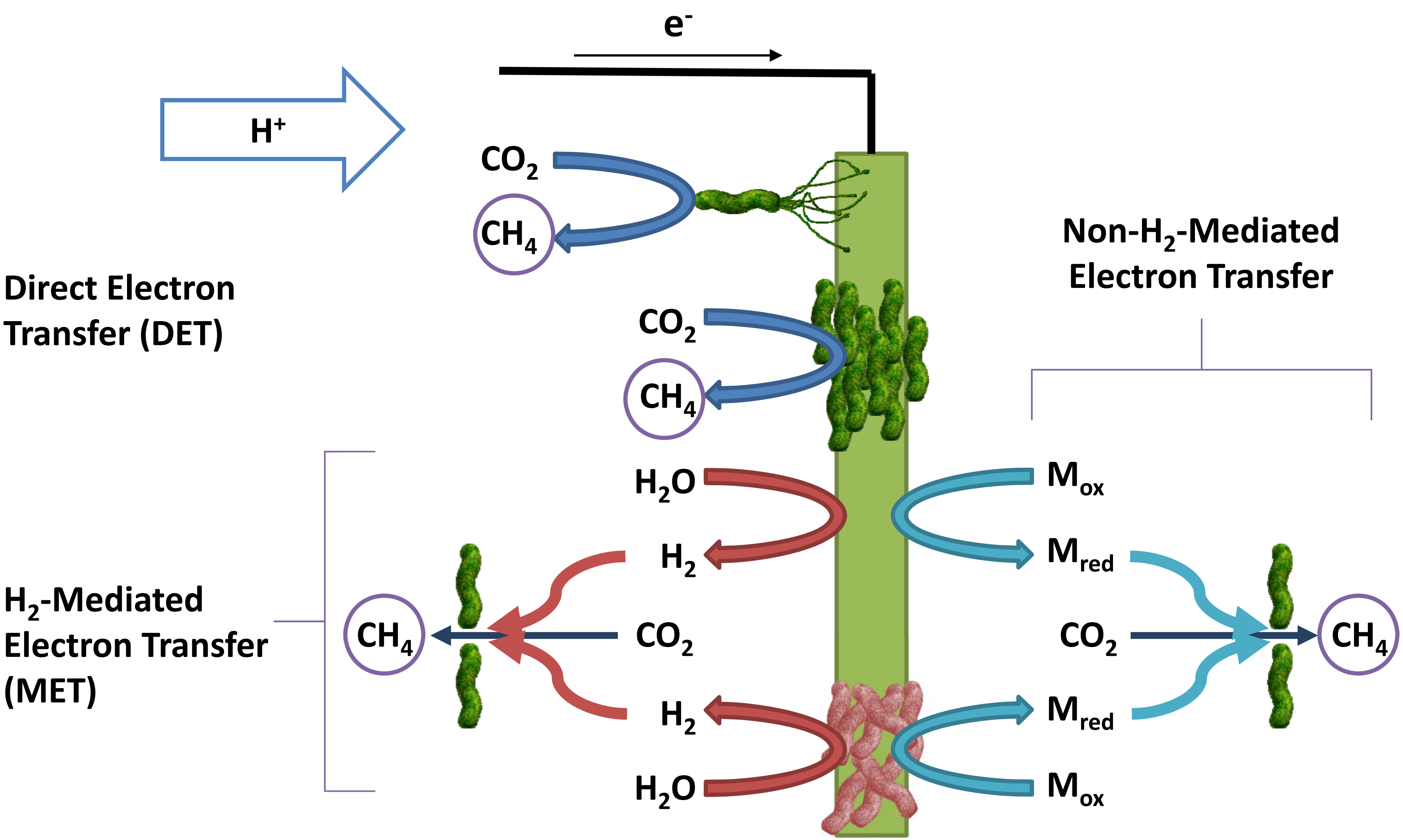
$2H^+ + 2e^- \rightarrow H_2$
$E_H°' = -0.414$ V

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$
$E_H°' = -0.244$ V

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
$\Delta E°' = 0.170$ V

At 25 °C, 1 atm, pH 7.

Electron Transfer Mechanisms in BES



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Overall Objective

To develop and test bioelectrochemical systems (BESs) to directly convert CO_2 to CH_4 for anaerobic digester biogas upgrading

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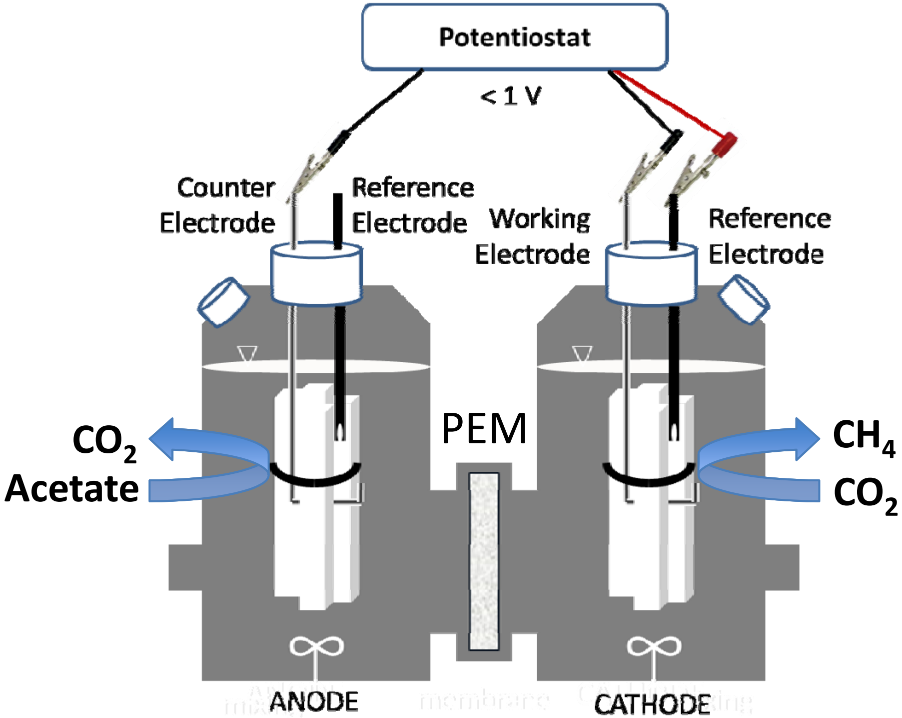
Materials & Methods

Batch-fed systems at 22±2°C
Hydraulic retention time, 7 days

ANODE
- Carbon felt electrode/SS collector
- Acetate-fed (1.5 g COD/L)
- N_2-flushed headspace
- Potential allowed to fluctuate; measured against an adjacent Ag/AgCl reference electrode
- 300 mL total volume
- 250 mL liquid anolyte (phosphate buffer, pH 7.0; trace minerals; vitamins)
- Inoculated with biofilm-attached carbon felt from an active MFC

CATHODE
- Carbon felt electrode/SS collector
- CO_2-fed (1.6 atm, absolute)
- CO_2-flushed headspace
- Potential fixed at -0.8 V (vs. SHE) using an adjacent Ag/AgCl reference electrode
- 300 mL total volume
- 250 mL liquid catholyte (phosphate buffer, pH 7.0; trace minerals; vitamins)
- Inoculated with a suspended-growth, enriched hydrogenotrophic culture



Materials & Methods

Gases

Pressure transducer

GC-TCD for gas composition

Liquids

GC-FID for acetate measurement

Dissolved CO_2 measured by sample acidification (6 N H_2SO_4) followed by composition analysis of evolved gas (conditional calibration)

Solids and Biomass

TSS/VSS for suspended biomass

Protein analysis of biofilm and suspended biomass

Molecular Analysis

DNA extraction using UltraClean Soil DNA Kit and PowerSoil DNA Isolation Kit (Mo Bio Laboratories, Carlsbad, CA)

16S rRNA gene sequencing (Illumina MiSeq)

Phylogenetic analysis using Mega 7.0 software

Diversity analyses performed with QIIME 1.9.0 and R

Results

Biocathode performance with respect to:

- ❑ Methanogenic inoculum
- ❑ Hydrogen sulfide (H_2S) gas feed contaminant
- ❑ Anaerobic digester biogas feed (upgrading)

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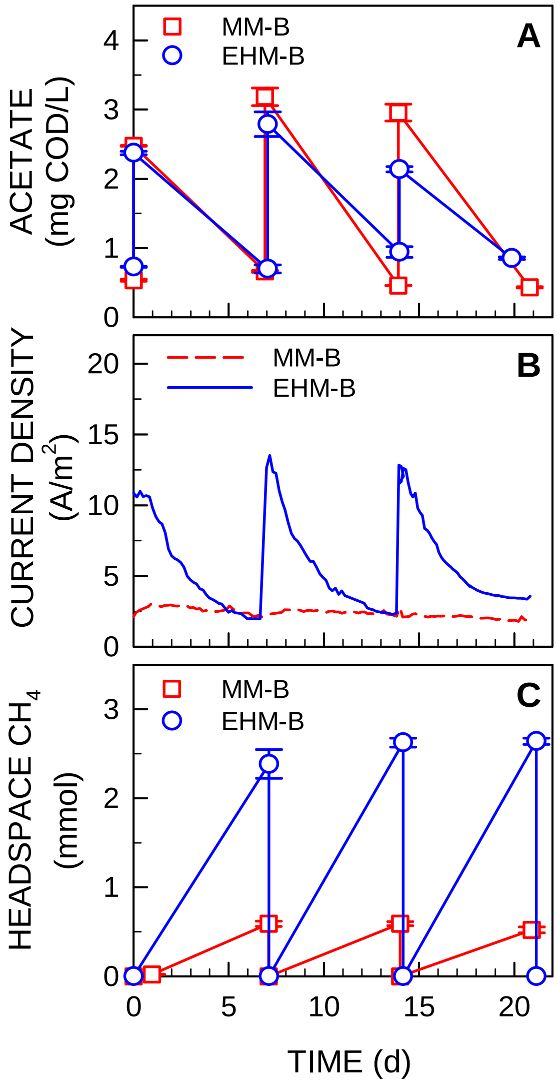
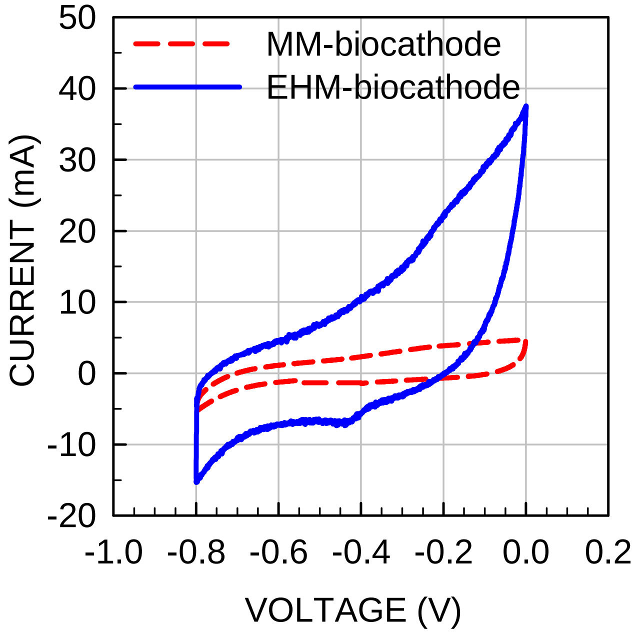
Biocathode Performance – Effect of Inoculum

Biocathode methanogenic inocula: MM, mixed; EHM, pre-enriched hydrogenotrophic





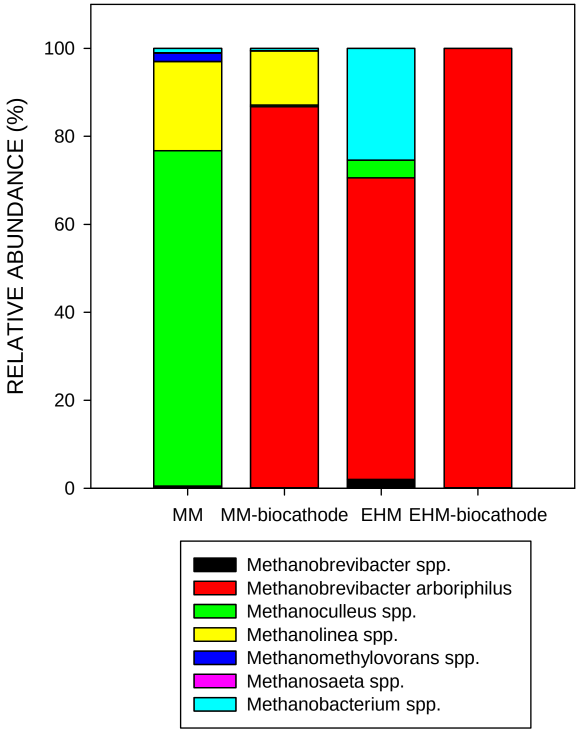
Biocathode	Final Biofilm Biomass (mg)	Mean CH_4 Production (mmol CH_4/mg biomass-day)
MM-inoculated	0.54 ± 0.07	0.15 ± 0.01
EHM-inoculated	0.64 ± 0.19	0.59 ± 0.03

Dykstra, C.M.; Pavlostathis, S.G. 2017. Methanogenic biocathode microbial community development and the role of Bacteria. Environ. Sci. Technol. 51(9) 5306-5316.

Biocathode Performance – Effect of Inoculum

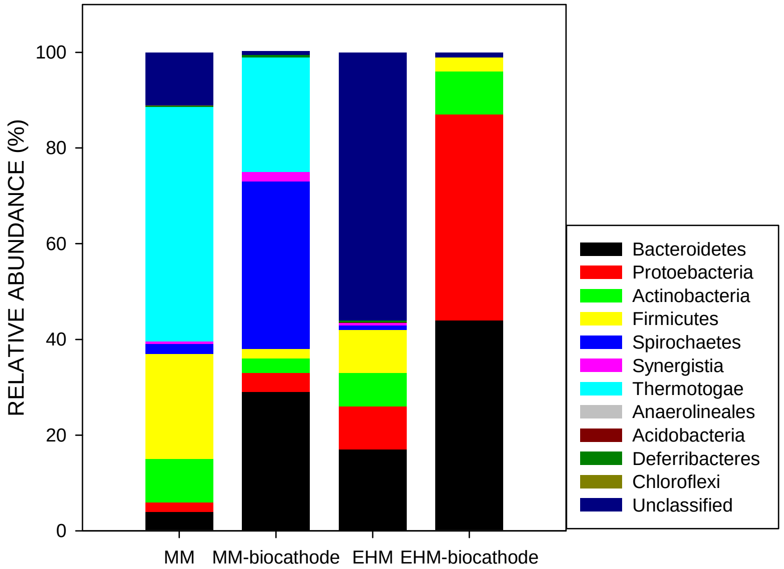
Biocathode methanogenic inocula: MM, mixed; EHM, pre-enriched hydrogenotrophic

Archaea

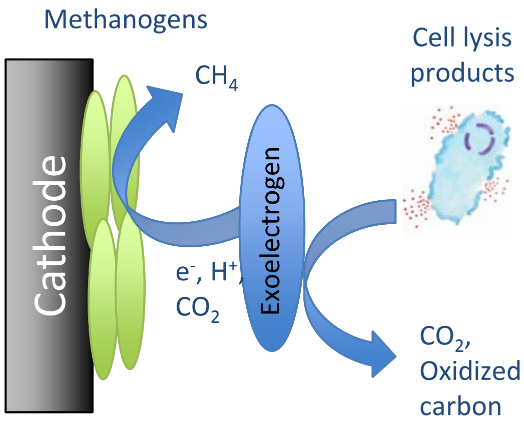


- Biocathode archaeal communities converged on the same phylotypes, *Methanobrevibacter arboriphilus*
- Inoculum pre-enrichment with H_2/CO_2 selects for methanogens that are also selected for by biocathode conditions (faster biocathode start-up)

Bacteria



- MM-biocathode enriched in *Spirochaetes* and other non-exoelectrogenic, fermentative Bacteria
- EHM-biocathode enriched in *Proteobacteria*, exoelectrogens and putative producers of electron shuttle mediators



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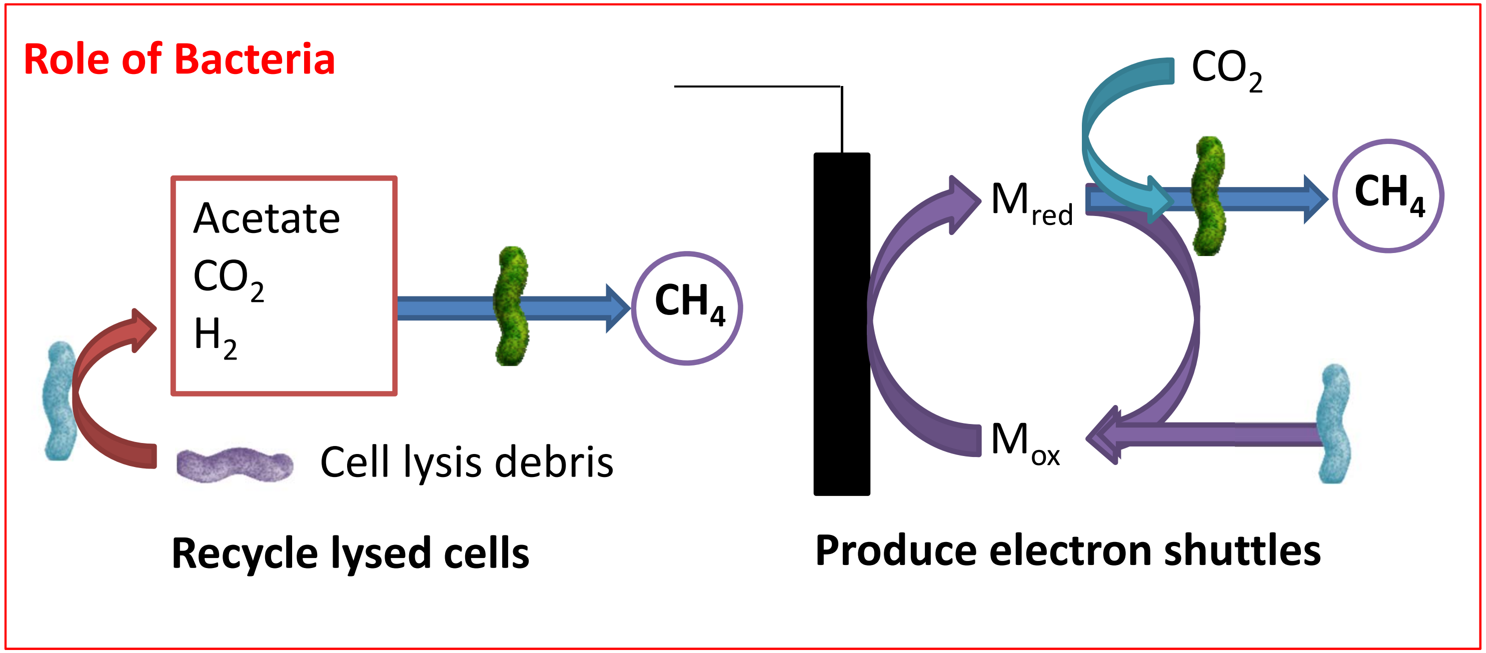
Dykstra, C.M.; Pavlostathis, S.G. 2017. Methanogenic biocathode microbial community development and the role of Bacteria. Environ. Sci. Technol. 51(9) 5306-5316.

Biocathode Performance – Effect of Inoculum

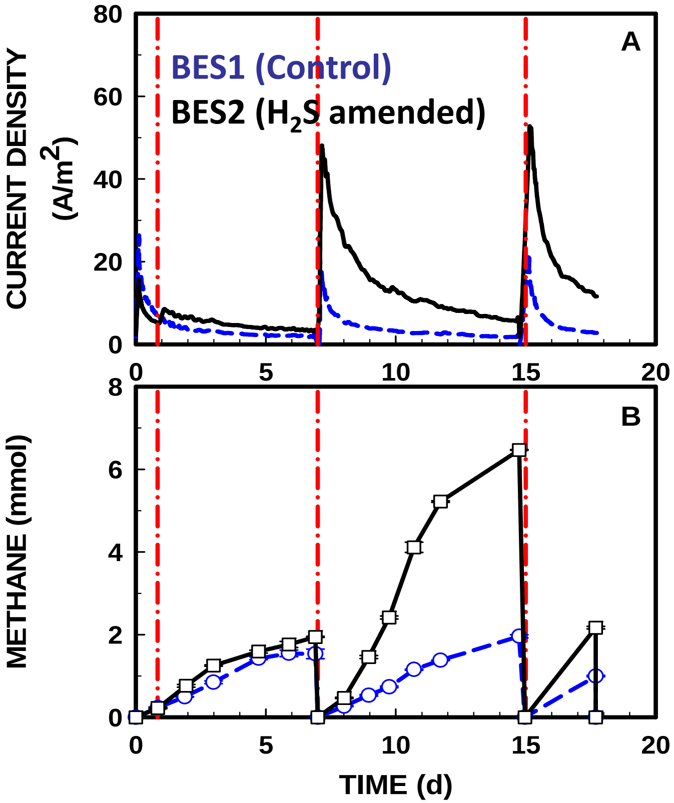
- The bacterial community of a biocathode has a significant effect on archaeal CH_4 production
- Increased biocathode CH_4 production occurs with a bacterial community enriched in:
  - Putative producers of electron shuttles/mediators
  - *Proteobacteria*
  - Exoelectrogens

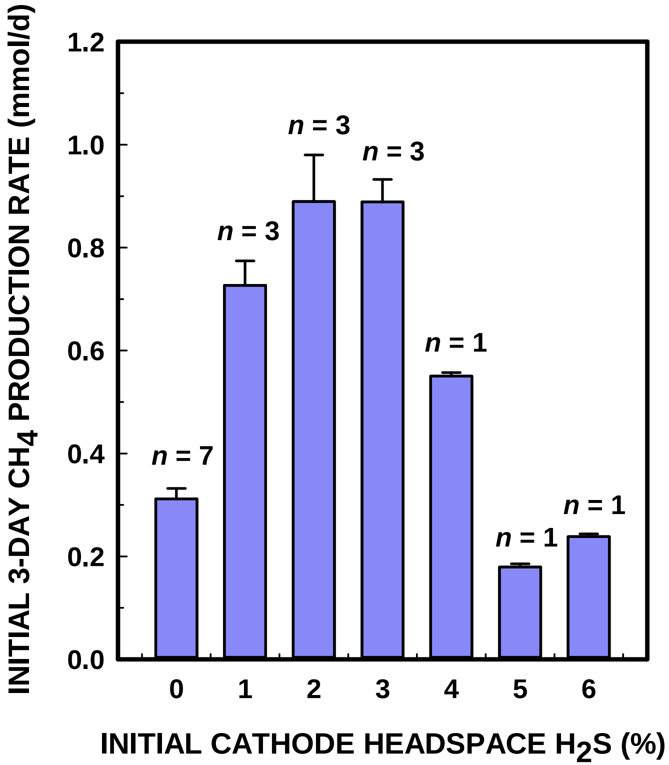


Dykstra, C.M.; Pavlostathis, S.G. 2017. Methanogenic biocathode microbial community development and the role of Bacteria. Environ. Sci. Technol. 51(9) 5306-5316.

Biocathode Performance – Effect of H_2S

Biocathode Headspace H_2S (1% v/v)





Headspace H_2S (% v/v)	CE (%)	CCE (%)
0	11	100
4	19	99
5	58	13
6	58	15

CE, Coulombic efficiency
CCE, cathode capture efficiency

Two competing effects:

- **Depression of CH_4 production (≥4% H_2S):** Inhibition of methanogens?
- **Enhancement of CH_4 production (≤3% H_2S):** What is/are the process(es) involved?

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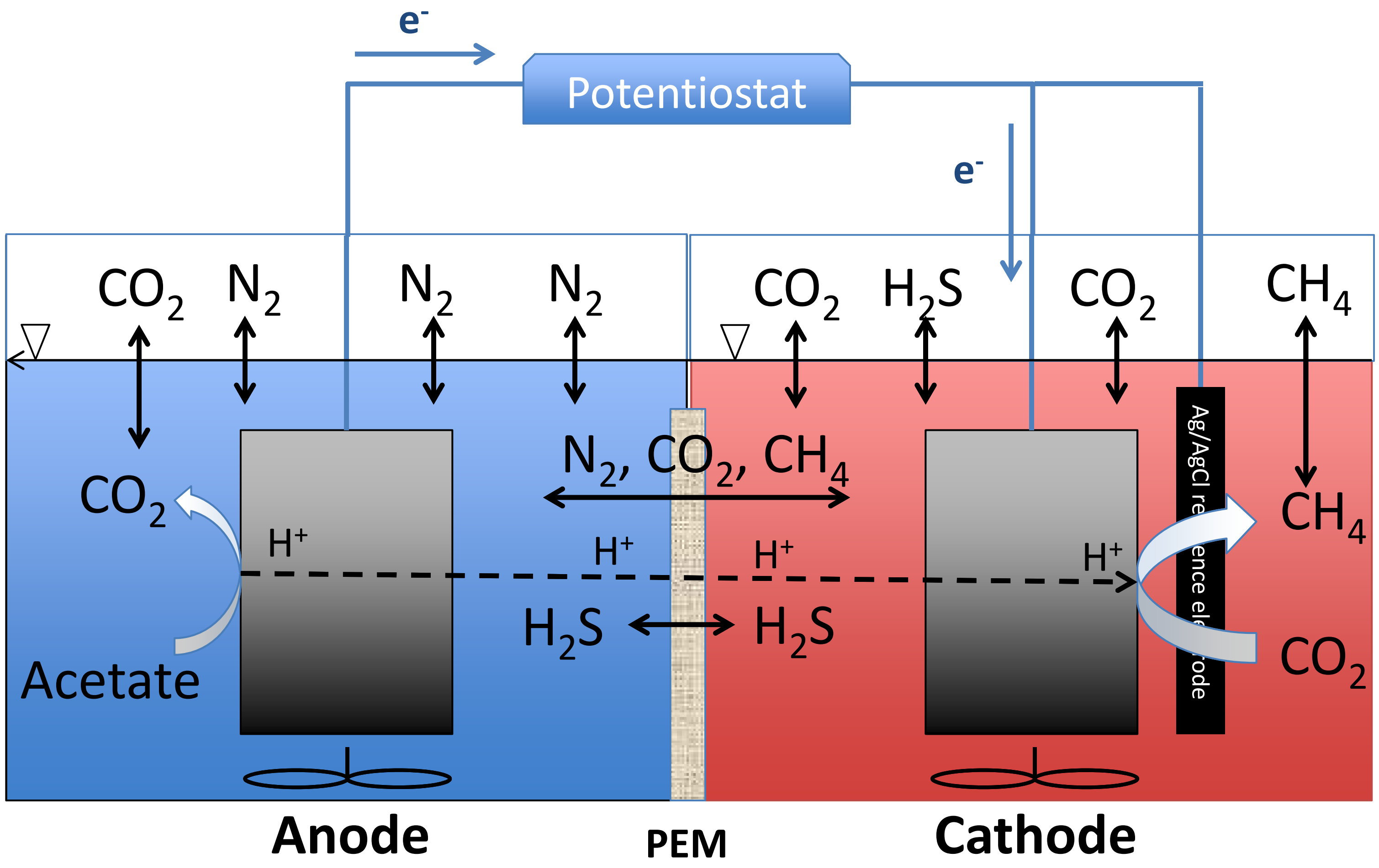
Biocathode Performance – Effect of H_2S

Gas transport between biocathode and bioanode



Dykstra, C., Pavlostathis, S.G. (2017), "Evaluation of gas and carbon transport in a methanogenic bioelectrochemical system (BES)", *Biotechnology & Bioengineering*, 114(5), 961-969.

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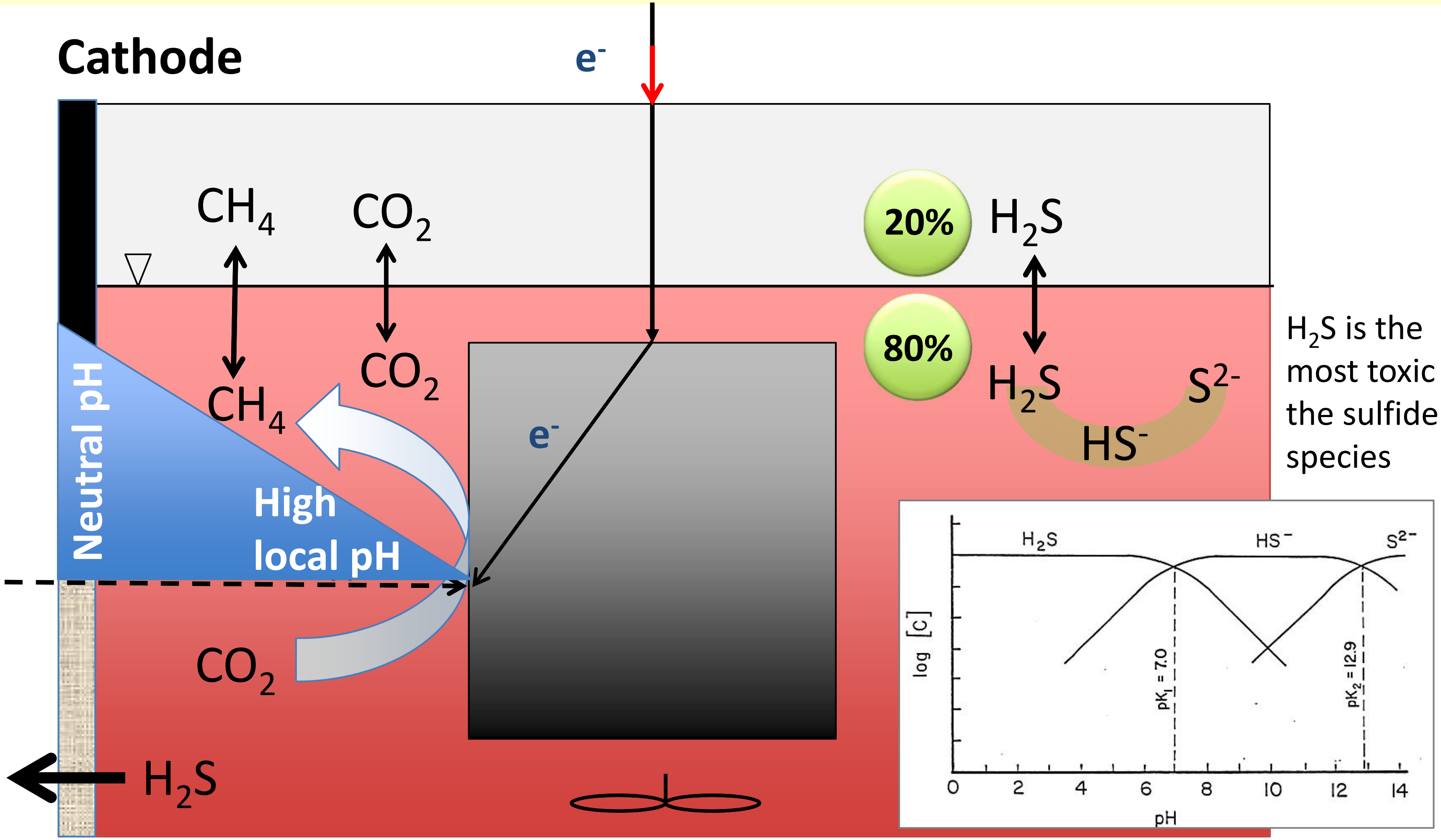
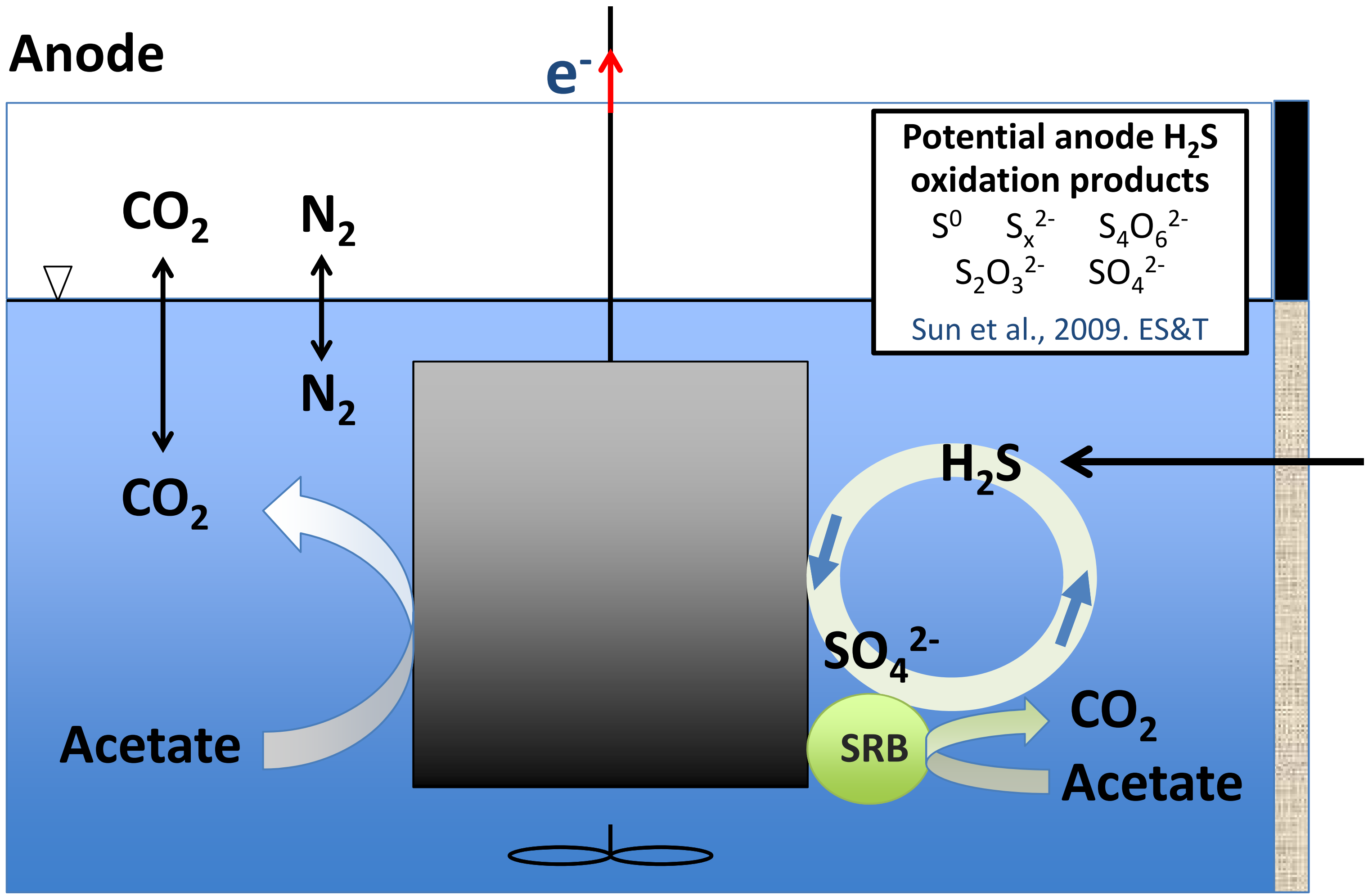
Biocathode Performance – Effect of H_2S



H_2S is the most toxic of the sulfide species

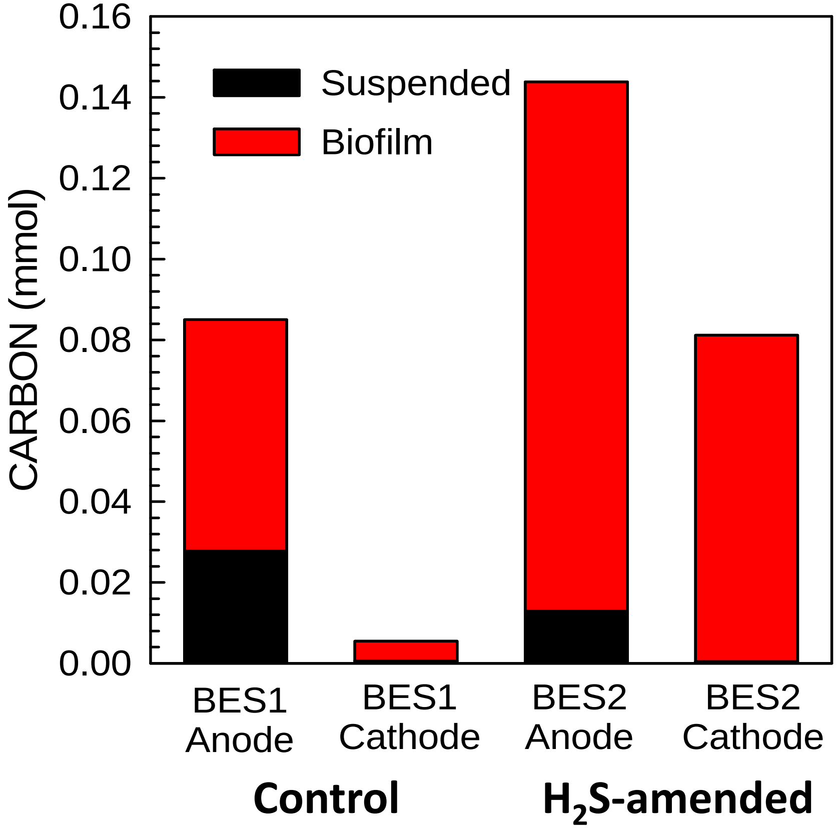
The methanogenic biocathode is protected from sulfide inhibition by **biofilm formation** and a **local high pH** at the cathode surface.

Biocathode Performance – Effect of H_2S

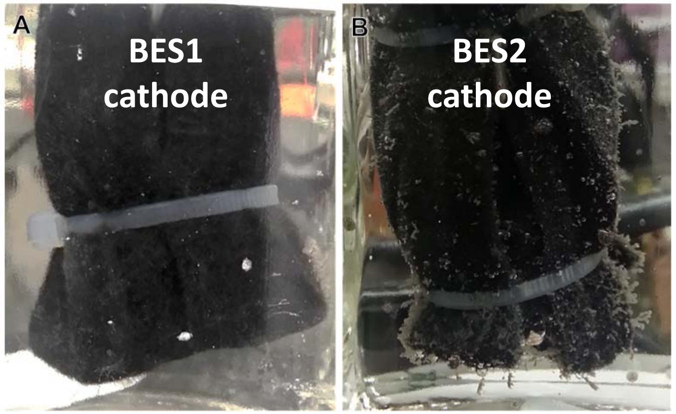


- **Low H_2S** → more electrons donated to the anode → higher biocathode CH_4 production
- **High H_2S** → stimulate sulfur cycling → divert acetate eeq from the anode → lower biocathode CH_4 production

Biocathode Performance – Effect of H_2S



- H_2S stimulated total biomass growth in both anode and cathode
- H_2S stimulated SRB growth in the anode biofilm



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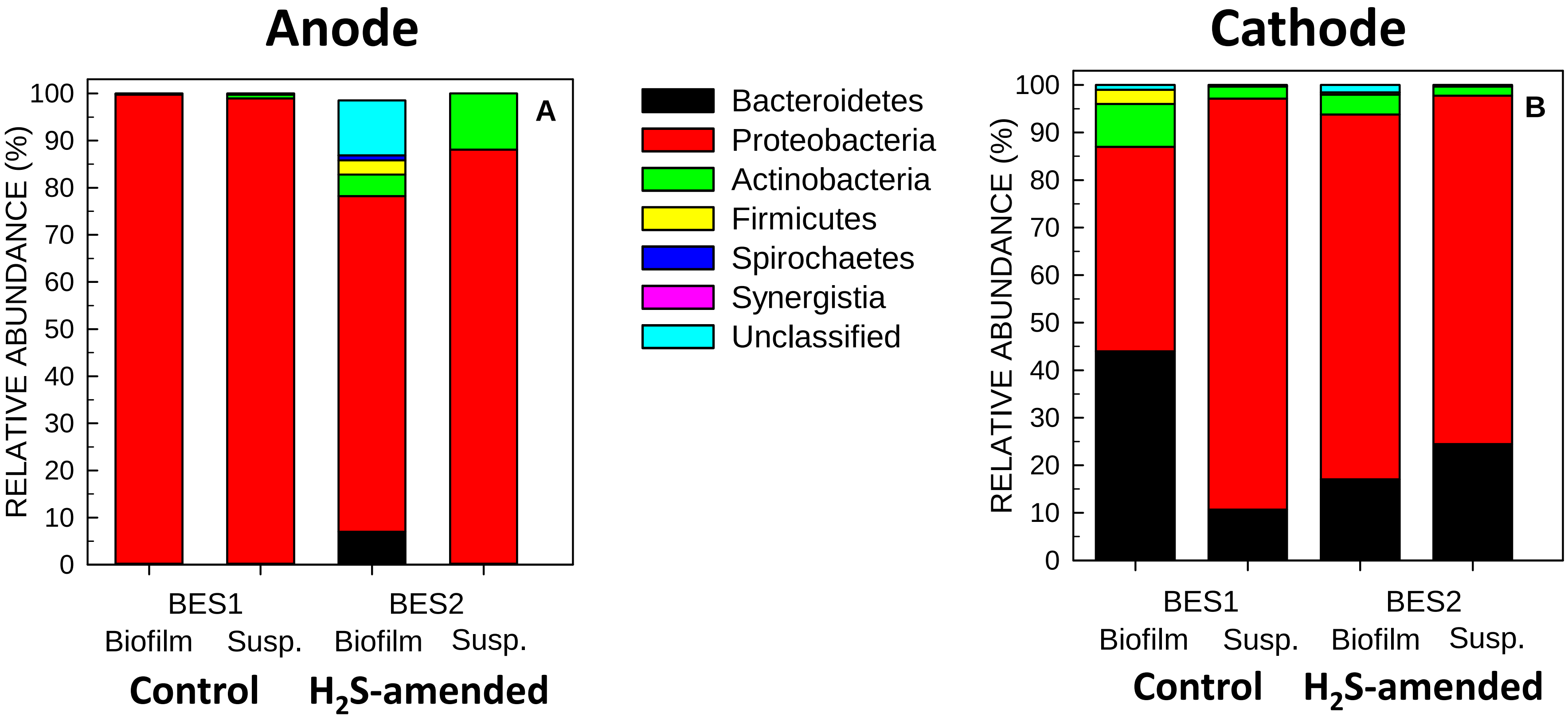
Biocathode Performance – Effect of H_2S



- *Deltaproteobacteria* were not detected in any anode or cathode biofilm or suspended growth samples, **except in the BES2 anode biofilm.**
- SRB phylotypes in the BES2 anode biofilm represented 32% of *Deltaproteobacteria* and 1% of total Bacteria.
- Identified SRB phylotypes include *Desulfobulbus propionicus*, *Desulfovibrio* sp. and *Syntrophobacterales* spp.

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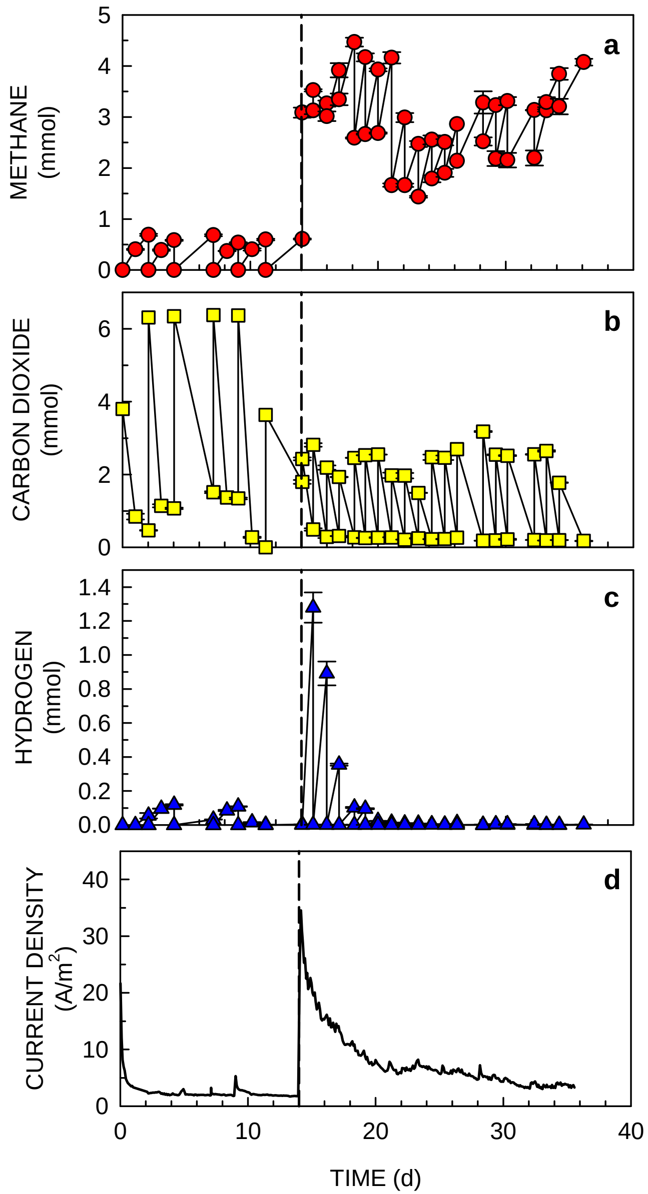
Biocathode Performance – AD Biogas Feed



- Day 14: Switched from feeding the biocathode 100% CO_2 to feeding anaerobic digester biogas (53-66% CH_4 and 34-47% CO_2).
- No CH_4 production for the first 2 biogas feedings. However, after the 2 days, the biocathode CH_4 production rate increased substantially.
- Although less total CO_2 was removed during biogas-fed cycles than during CO_2-fed cycles, the remaining CO_2 was consistently lower at the end of biogas-fed cycles.
- Hydrogen production occurred after switching to biogas, likely due to the increase in current density and slowed methanogenesis.

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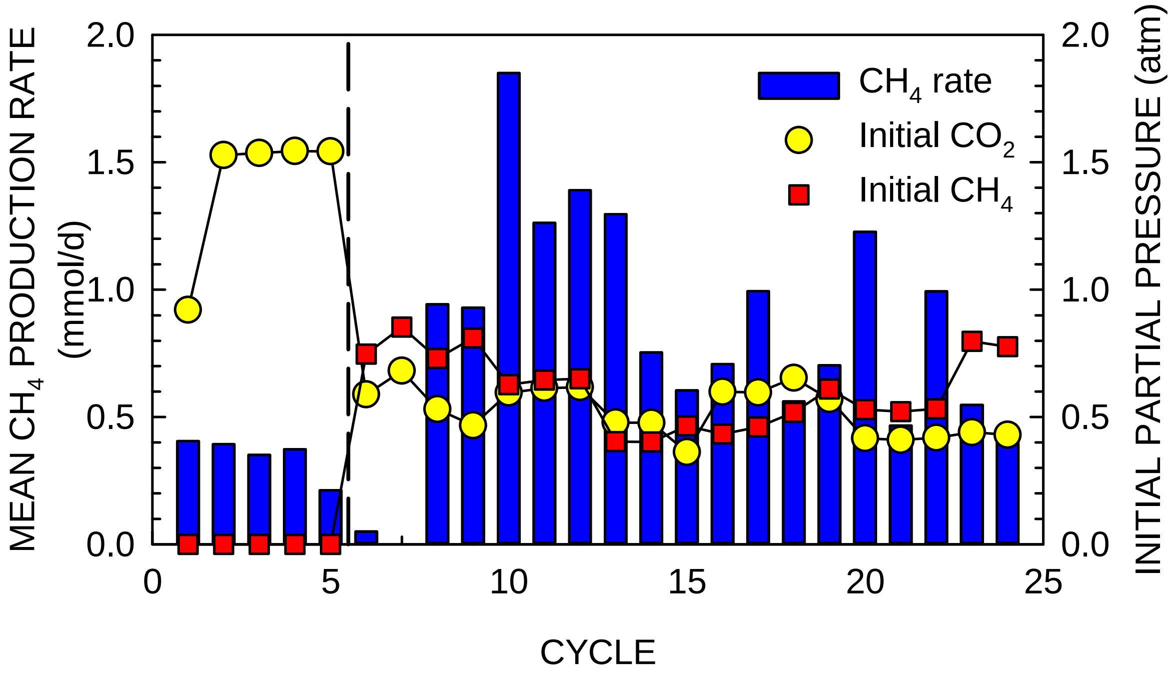
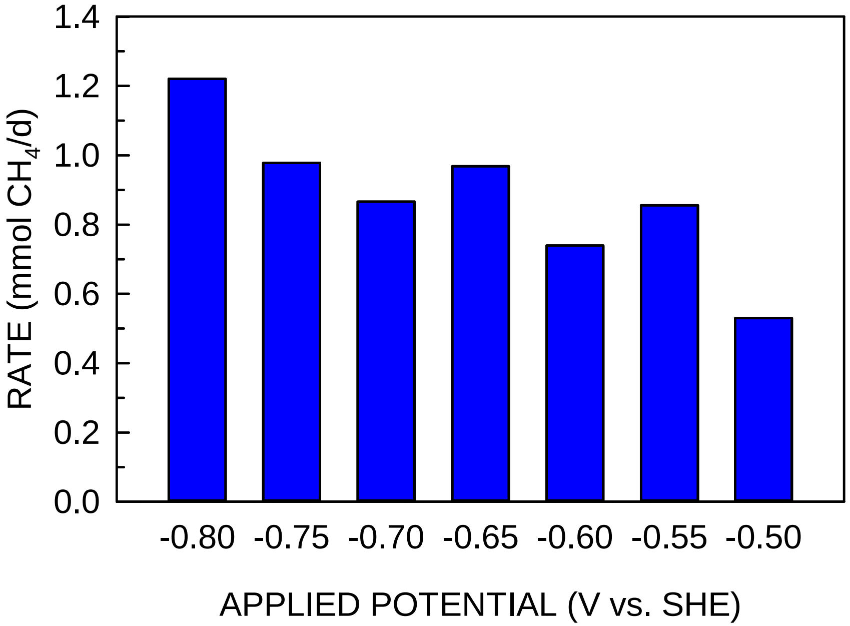
Biocathode Performance – AD Biogas Feed



- Maximum CH_4 production rate occurred during a biogas-fed cycle (1.85 mmol/d), which was 350% higher than the maximum CH_4 production rate during a CO_2-fed cycle (0.41 mmol/d).
- No significant correlation between the CH_4 production rate and the initial CO_2 or CH_4 partial pressure.

Biocathode Performance – AD Biogas Feed



- At a more positive applied cathode potential, the cell potential (driving force for electron transport) decreased and the anode potential decreased.
- At lower anode potentials, the transfer of electrons from a substrate to the anode is less energetically favorable.
- However, anode acetate removal did not reflect the biocathode CH_4 production rate, likely due to microbial acetate uptake and storage.

Cathode Potential (V vs. SHE)	Mean CH_4 Production Rate[a] (mmol/d)	Final Biocathode CH_4 [a] (%)	Final Biocathode CO_2 [a] (%)	Anode Acetate Removal[a] (%)	Anode Potential (V vs. Ag/AgCl)	Cell Potential (V)
-0.80	1.22 ± 0.07	79.9 ± 1.4	3.7 ± 0.1	21.2 ± 0.3	1.14-1.17	2.28-2.33
-0.75	0.98 ± 0.04	76.1 ± 0.9	4.1 ± 0.1	9.3 ± 1.1	1.09-1.10	2.14-2.17
-0.70	0.87 ± 0.12	78.3 ± 2.5	4.8 ± 0.1	NR[b]	1.04-1.07	2.05-2.08
-0.65	0.97 ± 0.05	78.4 ± 1.0	5.4 ± 0.1	9.1 ± 5.3	1.03-1.04	1.98-2.01
-0.60	0.74 ± 0.04	72.4 ± 0.9	6.2 ± 0.2	13.4 ± 0.4	1.02-1.04	1.93-1.94
-0.55	0.86 ± 0.14	70.7 ± 2.7	6.4 ± 0.1	NR	1.02-1.05	1.88-1.90
-0.50	0.53 ± 0.08	76.7 ± 1.7	8.3 ± 0.1	4.0 ± 0.1	0.16-0.36	1.15-1.34

[a] Mean ± standard deviation; *n* = 3; [b] No removal.

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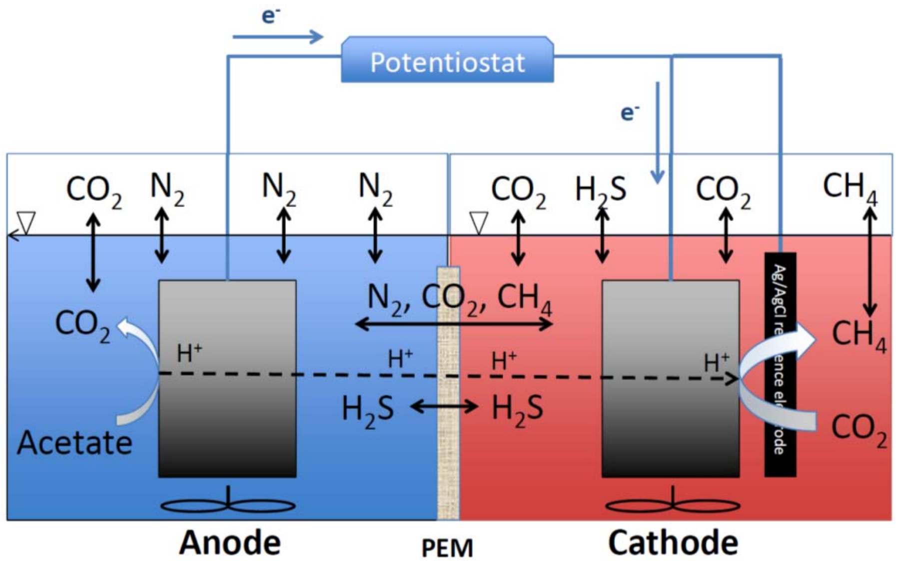
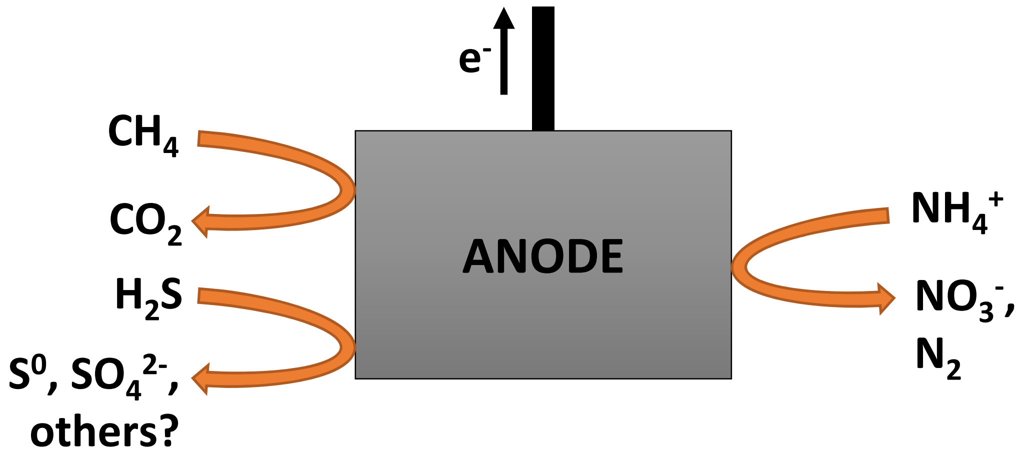
Biocathode Performance – AD Biogas Feed

Do biogas components contribute to BES current?

- Other biogas components (CH_4, H_2S and NH_3) may contribute to increasing current and CH_4 production.
- CO_2, CH_4, N_2, H_2 and H_2S can be transported as dissolved gases across a Nafion 117 proton exchange membrane when there is a concentration gradient.[1]
- As reduced species, CH_4, H_2S and NH_3 could become oxidized at the bioanode, donating electrons to the electrode and contributing to current production.

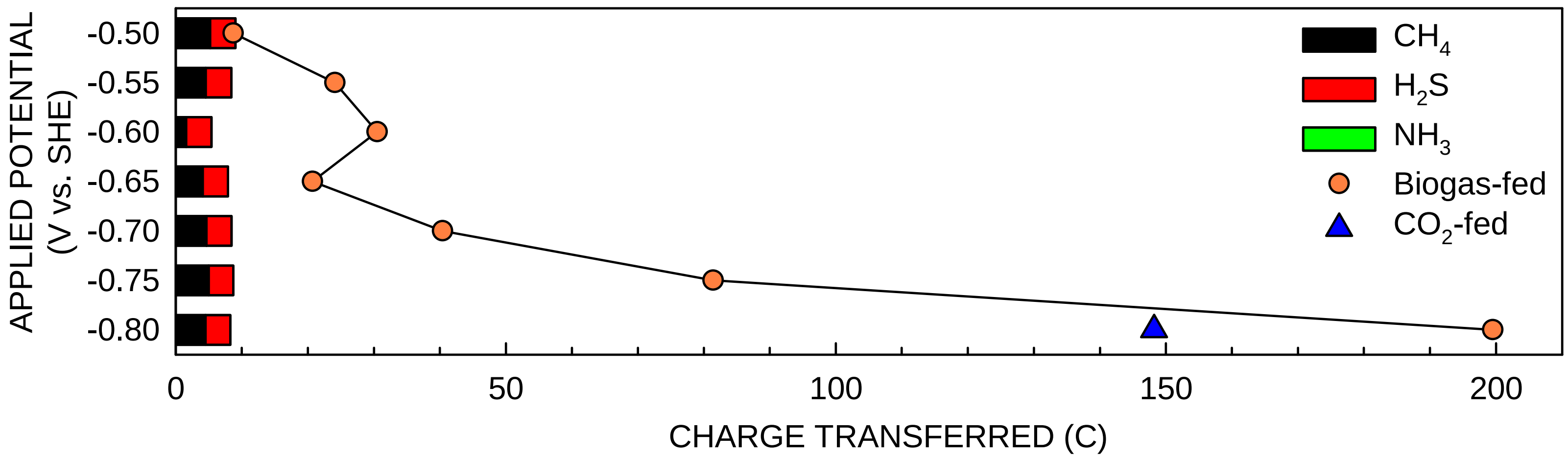




[1]Dykstra, C., Pavlostathis, S.G. (2017), "Evaluation of gas and carbon transport in a methanogenic bioelectrochemical system (BES)", *Biotechnology & Bioengineering*, 114(5), 961-969.

Biocathode Performance – AD Biogas Feed

Do biogas components contribute to BES current?



- At more negative applied cathode potentials, the maximum possible contribution of CH_4, H_2S and NH_3 to the charge transferred during a 1-d feeding cycle was minimal.
- NH_3 was not an important contributor to charge due to its low abundance in biogas.
- At -0.80 V cathode potential, the difference in the amount of charge transferred in the biogas-fed cycle and the CO_2-fed cycle cannot be completely explained by the oxidation of biogas CH_4, H_2S and NH_3 at the anode.
- Changes in microbial community and/or gene expression? (Under investigation)

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Conclusions

- The biocathode bacterial community significantly affects archaeal CH_4 production. Exoelectrogenic heterotrophs may promote biocathode CH_4 production within a biofilm fed only with CO_2.
- H_2S, a common biogas contaminant, is transported across the proton exchange membrane from cathode to anode, where it is oxidized and contributes electrons to the anode.
- At low H_2S concentrations (≤ 3%, v/v), H_2S increases biocathode CH_4 production due to increased current. At high H_2S concentrations (≥ 4%, v/v), H_2S may be inhibitory to the methanogenic biofilm and reduce overall biocathode CH_4 production.
- Anaerobic digester biogas was successfully upgraded using a methanogenic bioelectrochemical system.

Acknowledgement

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Extra Slides

MATERIALS AND METHODS

Efficiency Calculations

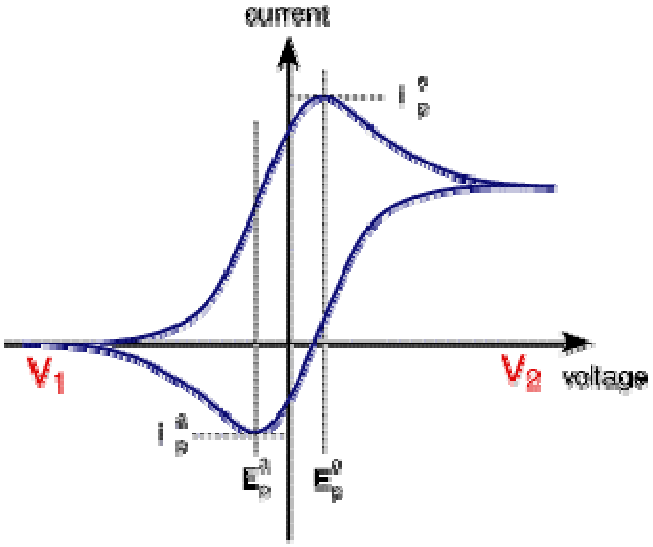
CE, Coulombic Efficiency: The ratio of total Coulombs actually transferred to the anode from the substrate, to maximum possible Coulombs if all substrate removal produced current. [1]

CCE, Cathode Capture Efficiency: The ratio of total Coulombs actually transferred to the CH_4 from the cathode, to maximum possible Coulombs if all current produced CH_4. [2]

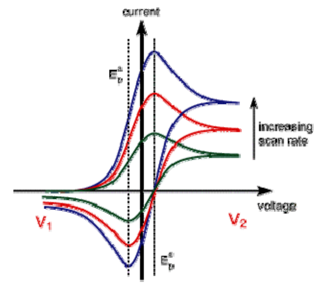
Electrochemical Analyses

Ohm's Law: I = V/R where I is the current, V is the voltage between the anode and cathode and R is the sum of all resistances within the circuit.

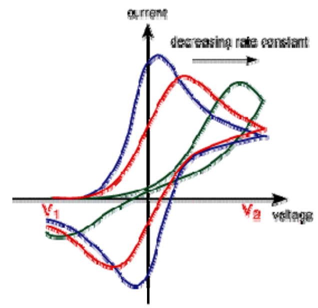
Cyclic Voltammetry: [3]



Biofilm development on the cathode may catalyze the cathodic reaction and reduce the total resistance in the circuit, thereby increasing the current at a particular applied voltage.



Reversible rxn



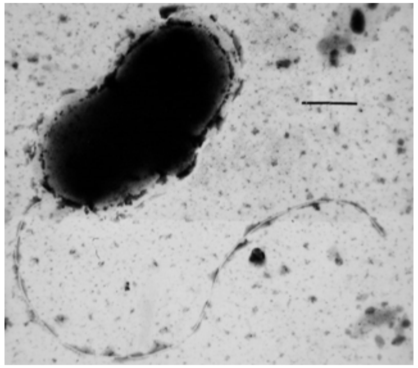
Non-reversible rxn

[1] Logan et al., 2006. ES&T; [2] Villano et al., 2013. Bioresource Technol.; [3] http://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/linear-sweep-and-cyclic-voltametry-the-principles

EFFECT OF CATHODE H_2S ON BES PERFORMANCE

- Corrosive, toxic (NIOSH, IDLH = 100 ppm)
- Produced by sulfate-reducing bacteria during anaerobic digestion and by the breakdown of HS-containing compounds (e.g., cysteine)
- Inhibitory to methanogenesis during anaerobic digestion [1]
- Feedstock C:S ratio predicts biogas H_2S [2]

Feedstock	C/S (g/g)	Theoretical Biogas H_2S (%, range)
Grease trap waste	798	0.0 – 0.1
Biological sludge	59	0.6 – 1.9
Industrial WW biological sludge	46	0.8 – 2.0
Pig bristles	19	2.0 – 4.9
Harvested green seaweed	7	5.5 – 17.7

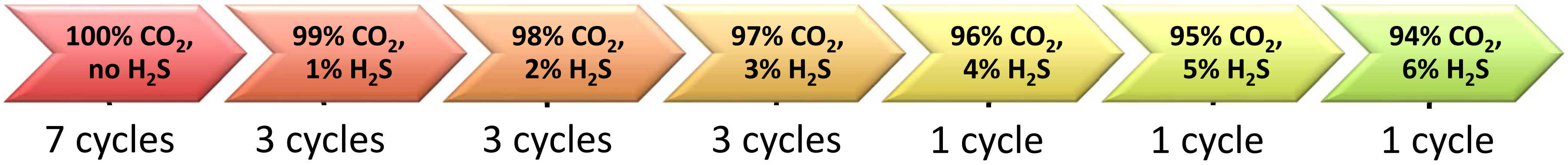


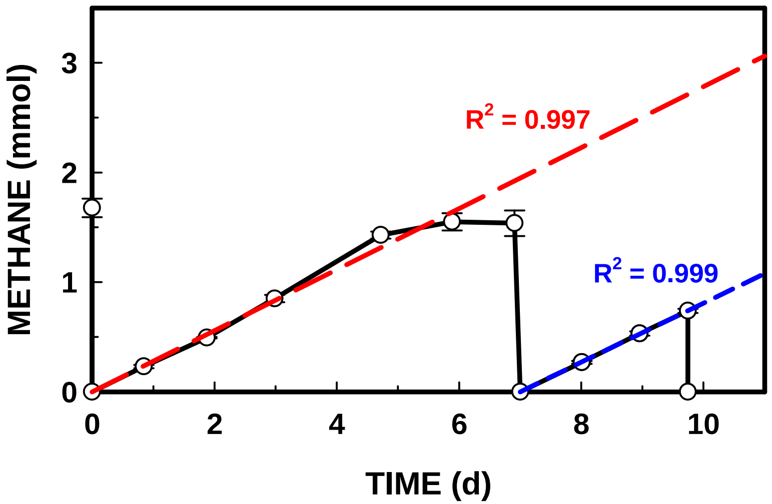
Desulfovibrio vulgaris

[1] Chen, Y., et al., 2008. Biores. Technol. 99(10), 4044-4064.

[2] Peu, P., et al., 2012. Bioresource Technol. 121, 419-424.

EFFECT OF CATHODE H_2S ON BES PERFORMANCE



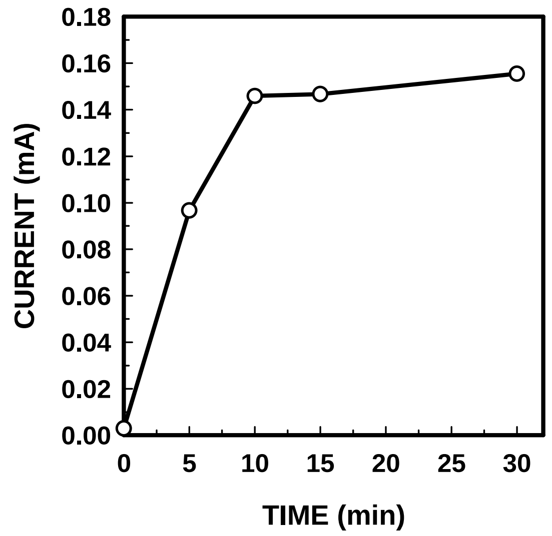


Linear biocathode CH_4 production during the first 3 days of a feeding cycle

Abiotic H_2S Transport within a BES

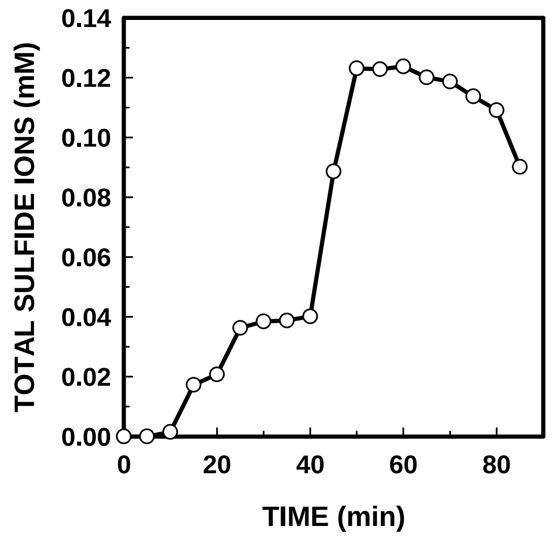
H_2S Dissolution in the Cathode

- Abiotic BES with Pt-coated carbon cloth cathode and carbon felt anode
- Open circuit conditions
- Magnetically mixed
- 3% H_2S added to the headspace of the cathode
- Cyclic voltammetry from -1.2 V to 0.2 V (vs. Ag/AgCl) at 100 mV/s; Measured current at 0.2 V.

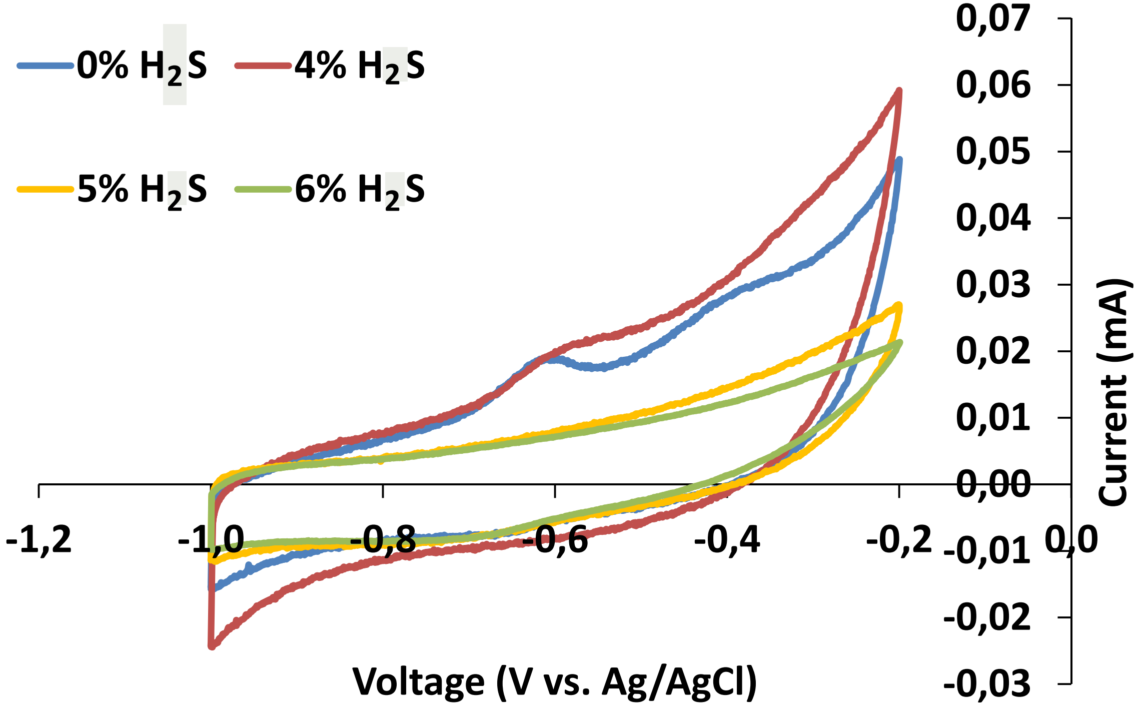


H_2S Transport Across the Membrane

- Abiotic BES with Pt-coated carbon cloth anode and carbon felt cathode
- Open circuit conditions
- Magnetically mixed
- 3% H_2S added to the headspace of the cathode
- Cyclic voltammetry from -1.2 V to 0.2 V (vs. Ag/AgCl) at 100 mV/s
- Sodium sulfide calibration curve constructed to convert current at 0.2 V vs. Ag/AgCl to sulfide ions



EFFECT OF CATHODE H_2S ON BES PERFORMANCE



H_2S (%)	CE (%)	CCE (%)
0	11	100
4	19	99
5	58	13
6	58	15

Above 4% H_2S v/v, the cathode biofilm is significantly inhibited.

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