Microbial Electrotechnologies for Converting CO₂ into Natural Gas and Chemicals



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Daily Energy Use and Carbon Emissions

Fundamentals and Applications for Students and Professionals



Gas (CH₄) is 16% of Energy use by Denmark



Electroactive microorganisms for Bioelectrochemical Systems

- Exoelectrogenic microorganisms
 - Generate electricity using inorganic (H₂) and simple organic molecules (e.g. acetate)
- Electro<u>trophic</u> microorganisms
 - Accept electrons and reduce CO₂ to chemical products such as methane (CH₄) and simple organic molecules
- Interspecies electron transfer
 - Electron transfer between two microorganisms of different species
- Bioelectrochemical systems (BES)
 - Use electroactive (electrogenic or electrotrophic) microorganisms in systems with electrodes.





3

Exoelectrogenic microorganisms span all 3 domains of life!

- Bacteria
- Archaea
- Eukarya





Exoelectro<u>trophic</u> microorganisms span 2 domains of life

- Bacteria
- Archaea (no Eukarya)



Bioelectrochemical Sysems (BES)

BES: Any reactor with microbes and electrical current MET: Microbial Electrochemical Technologies (MFC, MEC, etc.)

Anode

- Exoelectrogenic **Microbes (Bioanode)**
- or
- Abiotic (no microbes)



Cathode

- Electrotrophic **Microbes (Biocathode)**
- or
- Abiotic (no microbes)

Power

- Generated (P) = Microbial fuel cell (MFC) -
- Added (PS) \rightarrow Microbial electrolysis cells (MEC) for H₂ or CH₄ generation at the cathode

Membrane

None



1 or more

Many different chemicals can be used by electrotrophs to finally accept electrons from the cathode

Electron acceptors

- Oxygen (makes electricity)
- Nitrate (denitrification)
- Metals (Copper plating)
- CO₂: reduction to produce organic compounds such as acetate
- CO₂: reduction by methanogens to make methane (CH₄)





3 Main METs: MFCs, MECs, MMCs (MES)

Bacteria that generate electricity



Microorganisms that consume electricity (or H₂)





MES: Microbial ElectroSynthsis of chemicals

- BES \rightarrow MES: Microbial electrosynthesis
- MET → MMC: microbial methanogensis cells



H₂ can be used to enhance methane concentrations and performance of anaerobic digesters (AD)

MMCs can make methane from renewable electricity





How can we move the MES technology forward?

- 1. Need to understand and optimize components
 - a. Most effective <u>microorganisms</u>?
 - b. <u>How</u> do methanogens get electrons?
 - c. What are the best <u>cathode materials</u>?
- 2. How do we construct the reactor?
 - a. MET: Different configurations
 - b. MMC: New designs for methane generation
 - c. Operation
 - d. Materials
- 3. What next?

- BES \rightarrow MES: Electromethanogensis
- MET \rightarrow MMC: microbial methanogensis cells





1a. What microbes are on the cathodes to make methane?

- Seek out diverse but rich sources of microorganisms
 - Anaerobic Digesters (AD), from the Penn State WWTP
 - Freshwater bog sediments (Bog)
- Examine in small reactors
 - Methane production with biotic anodes and cathodes
 - Amount of current
 - Microbial community



Call & Logan Biosens & Bioelectr 2011









Cathode Communities (Archaea) are mostly Methanobacterim



PennState Siegert, Li, Yates, Logan (2015) Frontiers Microbiol.

Methanobacterium predominant (except with Pt)



¹ Electrophic Methanogens: facilitate current







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

1b. How do electrons get to methanogens?

Key: Bacterium H_2 [•]H₂ H₂

H₂ released by bacteria

Methanogen

Electrons released by outer membrane enzymes

Electrons released by bacterial nanowires



Hydrogenase from methanogen moves



Nanowires produced by methanogens?



1c. Best cathode materials for methane production in MMCs?

- Materials can affect MES through changing:
 - H_2 evolution rates: Adding catalysts impacts how fast H_2 can be released from the surface
 - How methanogens take in electrons or their enzymes interact with the surface
- Materials Tested:
 - Platinum: the best catalyst for H₂ evolution
 - Metals & Minerals that are good catalysts and inexpensive:
 Stainless Steel, Ni, MoS₂; ferrihydrite, magnetite, FeS
 - Carbon: not good catalyst, very cheap: carbon fiber brushes have very high surface area!





Effect of cathode materials on CH₄ production

- If current forms H₂, that is the blue bar
 - 4 moles hydrogen needed to form 1 mole of methane
- Platinum (Pt) is the best
 - Noble metal, expensive
 - Agreement of blue and green bars indicates H₂ gas produced that was then used to make methane
- Carbon brushes
 - Next best material
 - High surface area of carbon brushes likely facilitates direct electron transfer







2a. Scaling up METs:



2a. Scaling up METs: Pilot-scale MFCs for electricity



Scaling up MECs for H₂ gas: from 5 mL to 1000 L



Single-Chamber MECs: $H_2 \rightarrow CH_4$ Thus, methane not H_2 is the product

gas

5 mL mini-MEC



28 mL MEC



2.5 L MEC







MECs can produce methane from organic matter in dilute wastewaters



CH₄ was produced from wastewater with small energy input

- Elec. Energy in = 6 W/m^3
- Energy Out $(CH_4) = 99 W/m^3$

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



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

2c. Scaling up MES: Methane Generation from <u>Water Splitting</u>

1 Chamber: Generate O₂ at the anode

2 Chamber Bottle reactors: not suitable for scaling up

2 Chamber Brush electrodes: Need too much space (need compact reactors)





2 C: keeps O₂ in separate chamber





Cathode 🔮 Anode

Challenge 1 C system: O₂ kills methanogens

The Challenges of these 2 C systems

- Wide (or separate) chambers = large energy losses
- The electrode with methanogens gets a high pH

Compact MMC for water splitting & biocathodes

The process

- Anode: H⁺ produced with O₂ generated by water splitting anode (electrochemical)
- Membrane: CEM (cation exchange membrane) transports only H⁺ to cathode
- Cathode: H+ combines with OH- released from anode
- Methane is biologically produced by methanogens on the cathode





Water-splitting MMCs have not been scaled up ...





There can be many of these cell pairs in a stack. Just one cell pair shown here



2d. What have we achieved in MMCs?

- New compact (slab) systems
 - Most energy efficient MMC ever designed:
 ohmic resistance was 2.4 ± 0.5 mΩ m²
 - Improved gas production: 2.9 L/L-d (17 A/m²)
- Previous (bottle) systems
 - Very <u>energy intensive</u> due to high ohmic resistance: $20-25 \text{ m}\Omega \text{ m}^2$ ($10 \times \text{ higher}$)
 - 1000 × lower gas production (0.0062 L/L-d)







Costs to produce CH₄: Only electricity

Conditions	Euro	Danish krone
Electricity cost	0.35 €/kWh	2.6 kr/kWh
Natural gas cost (home)- volume	<mark>2.3 €/m³</mark>	<mark>17 kr/m³</mark>
- energy	0.19 €/kWh	1.4 kr/kWh
Renewable biomethane – volume	<mark>2.5 €/m³</mark>	<mark>19 kr/m³</mark>
- energy	0.23 €/kWh	1.7 kr/kWh

- Energy in 1 m³ of natural gas = 12.2 kWh
 - Same energy in 1.3 L of petrol
 - More energy needed than energy in the gas (thermodynamics)
- Efficiency of changing electricity \rightarrow CH₄?
 - Currently 17% \rightarrow This can be improved!
- For comparison: reverse process of $CH_4 \rightarrow$ electricity
 - Currently 33-65% efficiency based on energy

2e. Future Directions in Electrosynthesis of Methane

- Generate Hydrogen first?
 - Use and MEC? But that requires a source of <u>organic matter</u> for the anode.
 - Rates of MEC > MMC
- Cheap, efficient cathode catalysts
 - Brush and carbon electrodes lack a cathode catalyst.
 - Could we use non-precious metal Nibased catalysts developed for MECs in MMCs?







H₂ production rates by MECs are higher than CH₄ in MMC





Other chemicals can be produced in MES

- MMC indicates methane is primary product, but MES = other products
- Using mixed cultures (many microbes) and applying a high voltage can also release
 - H2 abiotically from the cathode
 - Organics or "VFAs" (acetate, formate, etc.) appear in later cycles at higher applied voltages
- Adding a fluidized bed bioreactor (FBR) could further convert these to more methane
 - Advantage is higher current density, so more methane per MES reactor







2e. Future Directions in Electrosynthesis of Methane

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What are suitable materials and catalysts for MMCs?

- Need inexpensive catalysts
 - Carbon electrodes is not good catalysts.
- Materials previously tested
 - Non-precious metals like stainless steel
 (SS) or Ni-based catalysts such as Ni particles and Ni₂P used
- Better materials being developed





Stainless Steel wool cathodes



Nickel particles, pNi on activated carbon



Nickel Phosphide Ni₂P

•Ni₂P Nanoparticles Carbon Black



New, more effective Pt Catalyst: NiMo

MMO Anode

- Method 1: Hydrothermal method (Ht) (shown on right)
 - Many steps
 - High energy use
- **Method 2**: Electrochemical method (Elec)
 - Simple procedure: Electrochemical deposition of catalyst is very desirable
 - Well controlled conditions
 - But... lower performance than Ht method (so far)





3. Scaling Up Compact Reactors

- MFCs and MECs have reached 1000 Liter scale
- Engineering 1000 L **MMC** will be a fun engineering challenge!
- Stay tuned...!

What will the MMC look like?



Active area = 7 cm² (1 electrode) Active area = 0.42 m^2 (4200 cm²) x 6 electrodes



Final Note: Avoid Methane Emissions!

- Methane is a potent greenhouse gas, with a global warming potential (GWP) of:
 - $-25 \times CO_2$ over 100 yr
 - 85× CO₂ over 20 yr (more appropriate)
- Almost no difference in atmospheric impact from fossil or renewable CH₄
- Redefining the GWP of methane (from 25 to 85) increases GHG emissions by 25% in the USA

A WORRYING TREND

Atmospheric methane levels have been rising since the Industrial Revolution. Growth slowed between 1999 and 2006, but methane levels have increased sharply since 2007. Neither trend is well understood.





CONCLUSIONS: Green Methane Makes Sense!

- Advances in MET designs have made it possible to develop thin and energy-efficient reactors for CH₄ and H₂ production.
- Achieved 3 L/L-d of CH₄ in preliminary (nonoptimized) tests.
- Should be able to substantially increase CH₄ production rates due to 89 L/L-d of H₂, equivalent to 18 L/L-d of CH₄.

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Challenges for Energy in Denmark

• High amount of <u>Petroleum Use</u>

PennState

- 28% of all energy is renewable
- If you electrify 8.8 D_e replaces 26.3 D_{ff} (assuming 33% fuel to electricity), total = 19.1 D
- Energy embedded in the food system
 - Much of the energy consumption is externally consumed (food grown elsewhere)





Examples of Volumetric Current Densities

Technology	A _{cat} (m²/m³)	l _A (A/m²)	l _v (A/m³)	Rate (kg/d-m ³)
MEC- Reports	62	6.5	400	0.36 (H ₂)
- Max	50	50	2500	2.25 (H ₂)
MMC- Reports	5	0.11	0.55	1.6 (CH ₄)
- Max	50	50	2500	4.5 (CH ₄)
MES- Reports	0.5	200	100?	0.54 (acetate)
- Max	100	50	5000	34 (acetate)

 $1100 \text{ A/m}^3 = 1 \text{ kg H}_2/\text{d-m}^3$ $1 \text{ kg H}_2 = 2 \text{ kg CH}_4 = 7.5 \text{ kg CH}_3\text{COOH}$



Examples of Scaling up METs

Technology	Challenges / Opportunities
MFC	 Can recover electrical power for particle-free solutions Wastewater: Maximize current (throw away power)
MEC	Electrical power input but H ₂ gas is a valuable product
MES/MMC	The "power to gas" technology has great potential and opportunities to inject C-neutral CH ₄ fit into gas pipelines



New MMC Design: Thin, compact reactors





Electrotrophic Methanogens

Mixed culture (Methanobacterium palustre)





- Water splitting at the anode. Using Pt. Two phases:
 - 1-2: Carbon cloth (degraded)
 - 3-6: Titanium
- Increased applied voltages
 - -2.0-3.1 V
 - H2 measured at 3.1 V
 - Returning to 2.5 V showed lower H₂; likely biocathode damage
- Methane recovery: highest with 2.8 V
 - ~ 10 A m²
 - ~ 2 L/L-d CH₄

	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6
Duration (cycles)	1–7	8–11	12–16	17–19	20–22	23-25
Anode material	CC/Pt	CC/Pt (new)	Ti/Pt	Ti/Pt	Ti/Pt	Ti/Pt
E _{ap} (V)	2.0	2.0	2.5	2.8	3.1	2.8



25

0

20

15

0

5

10

Cycle

10

Cycle

5

15

20

25



The zero-gap configuration maintains pH

- Need to avoid alkaline catholyte pH
- 1-24 cycles: catholyte switched each cycle (~1-2 d)
 - 6.6 <pH < 7.2
- 25th cycle: extended for 6 days
 - No change in pH

	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6
Duration (cycles)	1–7	8–11	12–16	17–19	20–22	23-25
Anode material	CC/Pt	CC/Pt (new)	Ti/Pt	Ti/Pt	Ti/Pt	Ti/Pt
E _{ap} (V)	2.0	2.0	2.5	2.8	3.1	2.8



VFAs produced in addition to methane



Methanobacteriaceae and Firmicutes

ΟΤυ	Phylum	Family	Genus	MES1 (%)	MES2 (%)	AVG (%)
OTU 1	Euryarchaeota	Methanobacteriaceae	Methanobrevibacter	32.5	38.8	35.7
OTU 2	Firmicutes	Clostridiaceae 1	Clostridium sensu stricto 1	12.4	9.4	10.9
OTU 3	Firmicutes	Eubacteriaceae	Eubacterium	12.7	3.6	8.2
OTU 4	Bacteroidetes	Rikenellaceae	-	7.0	9.3	8.1
OTU 5	Proteobacteria	Rhodocyclaceae	Azospira	4.0	12.1	8.0
OTU 6	Proteobacteria	Pseudomonadaceae	Pseudomonas	6.5	3.5	5.0
OTU 7	Proteobacteria	Burkholderiaceae	Alcaligenes	4.1	3.6	3.8
OTU 8	Actinobacteria	Nocardiaceae	Gordonia	1.6	2.6	2.1
OTU 9	Firmicutes	Lachnospiraceae	Tyzzerella	1.8	1.7	1.7
OTU 10	Euryarchaeota	Methanobacteriaceae	Methanobrevibacter	2.0	1.0	1.5

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MES: Methane Generation by Water Splitting & Biocathodes



- Water splitting at the anode. Using Pt. Two phases:
 - 1-2: Carbon cloth (degraded)
 - 3-6: Titanium
- Increased applied voltages
 - -2.0-3.1 V
 - 3.1 V too high (H₂ measured)
- Methane recovery:
 - Highest at 2.8 V
 - 2 L/L-d CH₄ (10 A m²)

	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6
Duration (cycles)	1–7	8–11	12–16	17–19	20–22	23-25
Anode material	CC/Pt	CC/Pt (new)	Ti/Pt	Ti/Pt	Ti/Pt	Ti/Pt
E _{ap} (V)	2.0	2.0	2.5	2.8	3.1	2.8
(p 5.0 (p −1/1) a, 4.0 • Meth	nane prod	uction rate				80 (p-1/1) 60 - 60





Does adding electrodes into AD work?



ABSTRACT: Conductive materials (CM) have been extensively reported to enhance methane production in anaerobic

digestion processes. The occurrence of direct interspecies

electron transfer (DIET) in microbial communities, as an

alternative or complementary to indirect electron transfer (via

hydrogen or formate), is the main explanation given to justify

the improvement of methane production. Not disregarding

that DIET can be promoted in the presence of certain CM, it

surely does not explain all the reported observations. In fact, in

methanogenic environments DIET was only unequivocally

demonstrated in cocultures of Geobacter metallireducens with

Methanosaeta harundinacea or Methanosarcina barkeri and

frequently Geobacter sp. are not detected in improved methane

production driven systems. Furthermore, conductive carbon

conclusions in reported experiments, are critically revised and discussed.

Supporting Information

Cite This: Environ. Sci. Technol. 2018, 52, 10241–10253

Conductive

materials

Anaerobic digester

Methane Production and Conductive Materials: A Critical Review

nanotubes were shown to accelerate the activity of methanogens growing in pure cultures, where DIET is not expected to occur,

and hydrogenotrophic activity is ubiquitous in full-scale anaerobic digesters treating for example brewery wastewaters, indicating

that interspecies hydrogen transfer is an important electron transfer mechanism in those systems. This paper presents an

overview of the effect of several iron-based and carbon-based CM in bioengineered systems, focusing on the improvement in

methane production and in microbial communities' changes. Control assays, as fundamental elements to support major

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Critical Review pubs.acs.org/est

CH_a production

OIR

lag phases

redox potential

electrical conductivity

microbial communities

electron transfer mechanisms

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Interfacing anaerobic digestion with (bio)electrochemical systems: Potentials and challenges



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ABSTRACT

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For over a century, anaerobic digestion has been a key technology in stabilizing organic waste streams, while at the same time enabling the recovery of energy. The anticipated transition to a bio-based economy will only increase the quantity and diversity of organic waste streams to be treated, and, at the same time, increase the demand for additional and effective resource recovery schemes for nutrients and organic matter. The performance of anaerobic digestion can be supported and enhanced by (bio) electrochemical systems in a wide variety of hybrid technologies. Here, the possible benefits of combining anaerobic digestion with (bio)electrochemical systems were reviewed in terms of (1) process monitoring, control, and stabilization, (2) nutrient recovery, (3) effluent polishing, and (4) biogas upgrading. The interaction between microorganisms and electrodes with respect to niche creation is discussed, and the potential impact of this interaction on process performance is evaluated. The strength of combining anaerobic digestion with (bio)electrochemical technologies resides in the complementary character of both technologies, and this perspective was used to distinguish transient trends from schemes with potential for full-scale application. This is supported by an operational costs assessment, showing that the economic potential of combining anaerobic digestion with a (bio)electrochemical system is highly case-specific, and strongly depends on engineering challenges with respect to full-scale applications.

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Using MECs for Enhanced Anaerobic Digestion?



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

I	1			
<u>Iran</u>	0.001			
Algeria	0.003			
Belarus	0.005			
Argentina	0.007			
Russia	0 .009			
Bangladesh	<mark>0</mark> .011			
Turkey	<mark>0</mark> .011			
Bahrain	0.013			
Azerbaijan	0.014			
<u>Tunisia</u>	0.0 <mark>19</mark>			
Malaysia	0.025			
<u>Ukraine</u>	0.026			
Hungary	0.026			
Taiwan	0.028			
<u>Serbia</u>	0.031			
Canada	0.035			
Colombia	0.042			
South Korea	0.044			
USA	0.046			
Slovakia	0.057			
New Zealand	0.058			
Mexico	0.070			
Australia	0.072	_		
Ireland	0.082			
Bulgaria	0.088			
Poland	0.089			
Barbados	0.090			
Portugal	0.093			
Switzerland	0.100			
Chile	0.101			
United Kingdom	0.104			
Japan -	0.107			
France	0.117			
Greece	0.122			
Hong Kong	0.139			
Czech Republic	0.140			
Belgium	0.150			
Singapore	0.154			
Austria	0.163			
<u>Italy</u>	0.164			
<u>Spain</u>	0.176			
<u>Denmark</u>	0.194			
Brazil	0.199			
<u>Germany</u>	0.215			
Sweden	0.245			



Water-splitting MMCs have not been scaled up ...





