

# Bioelectrochemical reduction of CO<sub>2</sub> to alternative fuels

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## Outline

- Introduction
- Biofilm on electrodes
- Results
- Summary and Outlook



#### Introduction

# **Bioelectrochemical systems**



Microbial electrochemical technologies (METs) link a microbial metabolism to an electrochemical system

- Interaction between biocatalysts and electrodes
- Microorganisms are attached on electrode surface "catalysts" for reactions on electrodes



http://www.is-met.org

# METs for CO<sub>2</sub> conversion



- Methanogenic cultures
  - Methane as product
  - First report on MEC use for  $CO_2$  reduction in 2009 by Cheng<sup>1</sup> et al.
  - Literature reports claim coulombic efficiencies between 60 100% [1,2,3,4]
- Acetogenic cultures
  - Products are organic acids, ethanol, butanol, acetone,...
  - Literature reports claim coulombic efficiencies of around 86% [5,6,7]

1 Cheng S., Xing D., Call D.F., Logan B.E., 2009;Environ. Sci. Technol. 43, 3953-3958

2 M. Villano, G. Monacor, F. Aulenta,, M. Majone, 2011, Journal of Power Sources, 196, 9467-9472

3 Y. Jiang, M. Su, Y. Zhang, G. Zhan, Y. Toa, D. Li, 2013, Int. J. of Hydrogen Energy Volume 38, Issue 8, Pages 3497–3502

4 M.C.A.A. Van Eerten-Jansen, A.T. Heinjne, C. J.N. Buisman, H. V.M. Hamelers, 2011, Int. J. Energy Res., 2011

5 K. P. Nevin, T. L. Woodard, A. E. Franks, Z. M. Summers, D. R. Lovley, mBio, 1(2), 2010, doi:10.1128/mBio.00103-10

6 T. Zhang, H. Nie, Ti. S. Bain, H. Lu, Mengmeng Cui, O. L. Snoeyenbos-West, A. E. Franks, K. P. Nevin, T. P. Russelland D. R. Lovley, *Energy Environ. Sci., 6,2013,217* 7 P. Nevin, S. A. Hensley, A. E. Franks, Z. M. Summers, J. Ou, T. L. Woodard, O. L. Snoeyenbos-West, D. R. Lovley, *Appl Environ Mircobiol, 77(9), 2011, 2882-2886*  CO<sub>2</sub> reduction with methanogens



- Microorganism metabolism:  $CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O$
- Adaption of microorganisms to electrode  $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2 H_2O$

# CO<sub>2</sub> reduction in a microbial electrolysis cell (MEC)







#### **Biofilm on electrodes**



# Two-Chamber MEC with mixed cultures

#### Setup

- Cation-exchange membrane (CEM): Nafior 324
- Working electrode (WE):
   Carbon or stainless steel material
- Counter electrode (CE):
   Dimensionally stable anode (DSA)
- Reference electrode (RE): Ag/AgCI
- const. temp., stirred, anaerobic
- Anode chamber
  - Phosphate buffer
- Cathode chamber
  - Nutrient medium enriched with vitamins, trace elements and 5 g/l NaHCO<sub>3</sub>

#### Inoculum: sewage sludge



# **Biofilm on Electrodes**



three different carbon materials were investigated

Carbon felt



Carbon rod



Carbon plate





#### Results

# **Biofilm on Electrodes**



- · Best results with carbon felt as electrode material
- -800mV vs Ag/AgCI
- Methane was detected



biocathode

### Carbon felt- SEM analysis





regular structure of single stranded fibers with superficial longitudinal side groove structure (along its entire length)

SEM analysis was done by S. Weiss ESEM Quanta FEG 250

### **Biocathode - SEM analysis**





Microorganisms (rods) were found on biocathode

SEM analysis was done by S. Weiss ESEM Quanta FEG 250



#### Comparison biocathode/abiotic cathode



electrolysis (24 hours)

Long-term experiment MEC





## Long-term experiment MEC



Coulombic Efficiency (CE)

$$\eta_{CE} = \frac{V_{CH_4} \cdot F \cdot n}{V_m \cdot \int\limits_{t=0}^{t} I dt}$$

V<sub>CH4</sub>: cumulative gas production (m<sup>3</sup> CH<sub>4</sub>)
F: Faradays constant (96485 C/mole e<sup>-</sup>)
n: mol of electrons per mole of methane (8 moles e-/mol CH<sub>4</sub>)
V<sub>m</sub>: molar volume (0,02447 m<sup>3</sup>/mole)
I: current (A)
t: time (s)



# Experiments with pure cultures

- -900 mV vs. Ag/AgCI
- 30°C/37°C depending on the MO
- 70 rpm
- 2-bromoethanosulfonic acid (to prevent methane production)
- 2 phases
  - Glucose-feeding

- CO<sub>2</sub>



Microbial electrolysis cell



### Results with pure cultures





# Summary and Outlook



- Adaption of mixed and pure cultures to e<sup>-</sup> successful
- Coulombic efficiency depends on applied potential
- H<sub>2</sub> may be a key pathway for methane formation
- Longterm MEC operation successful (nearly three years)
- Pure cultures in MEC reduce CO<sub>2</sub> to acetate and butyrate

# MECs are a promising tool for the reduction of CO<sub>2</sub> to liquid and gaseous energy carriers

Optimization of operating conditions (flow, pH control,...)





#### Thank you for your attention!

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