Bioelectrochemical Upgrading of Anaerobic Digestion Biogas
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Synopsis
The objective of this presentation is to review the potential of bioelectrochemical systems (BES) to increase the anaerobic digestion biogas methane (CH\textsubscript{4}) content in a process termed “biogas upgrading”. The presentation includes the following: a) brief introduction to anaerobic digestion with focus on biogas composition; b) technologies for carbon dioxide (CO\textsubscript{2}) capture, conversion and valorization; c) brief review of BES with focus on factors affecting BES performance; d) brief review of two current studies highlighting the effect of pre-enriched biocathode inoculum and hydrogen sulfide (H\textsubscript{2}S) on biocathodic conversion of CO\textsubscript{2} to CH\textsubscript{4}; and e) summary of observed methanogenic BES performance and remaining challenges needed to be addressed before such systems are considered for industrial applications.

Anaerobic Digestion – Gas Composition & Biogas Upgrading
Anaerobic digestion, as a well-established process of converting organic waste into biogas (Angenent et al., 2018; Pavlostathis, 2011; Tezel et al., 2011), is an excellent choice for high-strength waste treatment, especially in the pursuit of sustainable, carbon neutral, net zero energy water resource recovery facilities (WEF, 2014). Anaerobic co-digestion of municipal sludge and high-strength waste streams (e.g., food waste, agricultural residue, etc.) is gaining interest because of the potential for electricity production along with heat energy recovery via combined heat and power (CHP). Biogas produced by anaerobic digestion contains a mixture of CO\textsubscript{2} and CH\textsubscript{4}, along with other trace gases (N\textsubscript{2}, H\textsubscript{2}S, NH\textsubscript{3}). The typical range of biogas CH\textsubscript{4} and CO\textsubscript{2} content is 55-75% and 25-45% (v/v), respectively (Rittmann and McCarty, 2001). The biogas CH\textsubscript{4} and CO\textsubscript{2} content is primarily determined by the mean oxidation state of the carbon in the organic matter fed to the digester (Gujer and Zehnder, 1983; Pavlostathis, 2011), which is related to the chemical composition of the feed, in particular its carbohydrate, protein, and lipid content. Anaerobic digester biogas often limits energy recovery by CHP units. As a result, CO\textsubscript{2} is often removed to increase the biogas energy (i.e., CH\textsubscript{4}) content. Biogas upgrading to high-quality CH\textsubscript{4} (≥95% CH\textsubscript{4} v/v) would allow biogas to be used in a far wider range of applications in addition to CHP, or to be added to natural gas pipelines.

CO\textsubscript{2} Capture, Conversion and Valorization
Physical/chemical methods, which are used to separate or sequester CO\textsubscript{2}, include absorption, adsorption, cryogenics, and membrane separation. Some of the above-mentioned methods have been tested for anaerobic digestion biogas upgrading. However, expensive material, high energy and chemical input, as well as capital cost have been the major concerns for these types of biogas upgrading processes (Muñoz et al., 2015). Following CO\textsubscript{2} capture, a large number of valorization technologies have been developed, such as (Pan et al., 2018): a) supercritical CO\textsubscript{2} to be used as a reactive solvent; b) mineralization of CO\textsubscript{2} to inorganic carbonates; c) catalytic reduction of CO\textsubscript{2} to organic transportation fuels; d) transformation of CO\textsubscript{2} to value-added chemicals; and e) biological CO\textsubscript{2} fixation and utilization.
Bioelectrochemical Systems (BES)
Bioelectrochemical systems typically consist of an anode compartment where oxidation takes place and a cathode compartment where reduction occurs; usually the two compartments are separated by a proton exchange membrane (PEM). Protons and electrons generated in the anode are transported to the cathode through the PEM and an external electric circuit, respectively. Depending on the specific goal, BES are classified as:
- Microbial fuel cells (MFC), producing electric current through an external resistor
- Microbial electrolysis cells (MEC), producing hydrogen (H₂) in the cathode
- Microbial electromethanogenesis cells (MEMC), producing CH₄ in the cathode
- Microbial electrosynthesis cells (MESC), producing 1+ carbon compounds in the cathode
With the exception of MFC, all other BES types require an external applied potential to overcome thermodynamic limitations for the intended cathodic reactions. A methanogenic BES is capable of converting CO₂ to CH₄, improving both biogas energy content and CH₄ yield (Villano et al., 2010; Muñoz et al., 2015; Geppert et al., 2016). In a methanogenic BES, a low applied cathode potential (<1 V) drives an oxidation reaction in the bioanode and the reduction of CO₂ to CH₄ in the biocathode (Cheng et al., 2009). While direct electron transfer from the cathode to methanogens may occur (Eq. 1), H₂ may also be produced at the cathode from the reduction of protons (Eq. 2), and utilized by hydrogenotrophic methanogens to reduce CO₂ to CH₄ (Eq. 3). Alternately, mediators may accept electrons from the cathode and, in turn, act as electron donors for the reduction of CO₂.

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\begin{align*}
\text{CO}_2 + 8\text{H}^+ + 8e^- & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} & \Delta E_{H^0}^e &= \text{0.170 V vs. SHE} \\
2\text{H}^+ + 2e^- & \rightleftharpoons \text{H}_2 & \Delta E_{H^0}^e &= \text{0.421 V vs. SHE} \\
\text{CO}_2 + 4\text{H}_2 & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} & \Delta E_{H^0}^e &= \text{0.244 V vs. SHE}
\end{align*}
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The BES performance depends of many factors, such as (Geppert et al., 2016):
- Electron donor (anode)
- Cathode potential
- System design (e.g., PEM surface area, electrode type and surface area)
- Inoculum type
- Reactor type (One- vs. two-chamber systems; batch vs. continuous flow)
- Operational parameters (e.g., pH, temperature)

For methanogenic BES, the methane production rate depends on (Geppert et al., 2016):
- Cathode potential (V)
- Current density (A/m²)
- Current-to-methane efficiency (%)

**Effect of Biocathode Inoculum on the Performance of a Methanogenic BES**
A recent study by Dykstra and Pavlostathis (2017) compared the performance and microbial community composition of a biocathode inoculated with a mixed methanogenic (MM) culture to a biocathode inoculated with an enriched hydrogenotrophic methanogenic (EHM) culture, developed from the MM culture following pre-enrichment with H₂ and CO₂ as the only externally supplied electron donor and carbon source, respectively. The biocathode potential was poised at -0.8 V (vs. SHE) using a potentiostat, with the bioanode acting as the counter electrode. The methane production in the MM- and EHM-biocathode was 0.153±0.010 and 0.586±0.029 mmol CH₄/mg biomass-d, respectively. Thus, the H₂/CO₂ pre-enriched inoculum enhanced biocathode CH₄ production, although the archaeal communities
in both biocathodes converged primarily (86-100%) on a phylotype closely related to *Methanobrevibacter arboriphilus*. The bacterial community of the MM-biocathode was similar to that of the MM inoculum but was enriched in *Spirochaetes* and other non-exoelectrogenic, fermentative Bacteria. In contrast, the EHM-biocathode bacterial community was enriched in *Proteobacteria*, exoelectrogens and putative producers of electron shuttle mediators. Thus, although the archaenal communities were similar in the two biocathodes, the difference in bacterial community composition was likely responsible for the 3.8-fold larger CH₄ production rate observed in the EHM-biocathode.

**Effect of Hydrogen Sulfide on the Performance of a Methanogenic BES**

A current study by Dykstra and Pavlostathis (unpublished data) has assessed the effect of cathode H₂S on the biocathodic conversion of CO₂ to CH₄ at a range of initial gas-phase H₂S concentrations (0-6% v/v), as well as its effect on the anode and cathode microbial communities. As initial cathode headspace H₂S increased from 0% to 2 and 3% (v/v), biocathodic CH₄ production increased two-fold to 3.56 ± 0.36 and 3.55 ± 0.17 mmol/L-d, respectively, due to dissolved H₂S transport from the cathode to the anode and subsequent oxidation. Above 3% initial cathode headspace H₂S, CH₄ production declined due to biocathode inhibition. Sulfate and elemental sulfur were detected H₂S oxidation products in the anode. A phylotype most closely related to *Methanobrevibacter arboriphilus* dominated the cathode archaenal communities. In the sulfide-amended BES, a phylotype similar to the exoelectrogen *Ochrobactrum anthropi* was enriched in both the anode and cathode, whereas phylotypes related to sulfate-reducing and sulfur oxidizing Bacteria were detected in the bioanode. Thus, sulfide transport and anode sulfur cycling play an important role in methanogenic BESs treating sulfide-bearing biogas in a process that may be used to both upgrade anaerobic digestion biogas and remove H₂S.

**Methanogenic BES Performance**

Based on recently published reports (Geppert et al., 2016) and current studies by Dykstra and Pavlostathis (unpublished data), the methanogenic BES performance is summarized as follows:

- Methane production rate: 0.01 to 0.4 L CH₄/L reactor/day (compared to 1.4 to 9.8 L CH₄/L reactor/day in high-rate anaerobic digesters)
- Typical cell voltage: from -0.7 to -1.5 V
- Current-to-methane efficiency: 23 to 99% (>100% microbially induced cathode corrosion)
- Energy (electrical) input: for water anode electron donor, 19 to 97 Wh/L CH₄

Methanogenic BES have a great potential for anaerobic digestion biogas upgrading. However, before such systems are considered for industrial applications, several challenges remain to be addressed, such as:

- Choice of anode electron donor
- Reduction of energy losses (internal resistance; cathode overpotential; new materials)
- Reduction of gas transport through the membrane
- Scale-up
REFERENCES


