Sulfide Effect on Biogas Upgrading with a Bioelectrochemical System

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INTRODUCTION

Biogas from anaerobic digestion consists of carbon dioxide (CO_2), methane (CH_4) and other trace gases (e.g., H_2S). Biogas upgrading is the process of increasing the energy (i.e., CH_4) content of the gas; however, traditional methods separate or sequester CO_2, producing a carbon waste product. Instead, bioelectrochemical systems (BESs) may directly convert CO_2 to CH_4. Methanogenic BESs, which pair an oxidizing bioanode with a CO_2-reducing biocathode, have been successfully demonstrated by feeding pure CO_2 and/or CO_2/N_2 mixtures (Geppert *et al*., 2016). However, the effect of trace gases, such as hydrogen sulfide (H_2S), on BES performance is unknown.

H_2S is a toxic and corrosive gas that is produced by sulfate-reducing bacteria (SRB) during anaerobic digestion (Reiffenstein *et al*., 1992; Peu *et al*., 2012). Biogas H_2S content can be predicted based on the carbon to sulfur (C:S) ratio of the anaerobic digester feedstock; low C:S ratios produce biogas with a higher H_2S content. Anaerobic digestion of municipal and industrial wastewater biological sludge typically produces biogas containing 0.6-1.9% and 0.8-2.0% H_2S v/v, respectively, although alternative feedstocks, such as green seaweed, may produce biogas with 5.5-17.7% H_2S (Peu *et al*., 2012). Thus, the biogas H_2S content is fixed by the anaerobic digester feedstock and downstream H_2S removal is often required. However, sulfide removal in a methanogenic BES biocathode designed for biogas upgrading has not been investigated.

While sulfide is an important sulfur source for methanogens and is beneficial at low concentrations, sulfide (i.e., H_2S_{aq}, HS^-, S^{2-}) is known to affect methanogenesis during anaerobic digestion (Karhadkar *et al*., 1987; Koster *et al*., 1986). Sulfide inhibition is pH-dependent, as only non-ionized, free H_2S can pass through a cell membrane. At pH 7, approximately half of the total sulfide present is free H_2S, with decreasing amounts and, hence, decreasing inhibition, at higher pH values (Koster *et al*., 1986). Although the pH of a typical BES catholyte is circumneutral, the localized pH near the cathode surface is higher due to proton utilization in reduction reactions. Thus, it is not clear whether and at what level H_2S is inhibitory to a methanogenic biocathode community.

Furthermore, gases (e.g., H_2, CO_2, N_2, CH_4) are known to be transported across a BES proton exchange membrane (PEM) in response to a concentration gradient, which may affect BES performance (Dykstra and Pavlostathis, 2017a). Transport of H_2S from the cathode to the anode could result in the oxidation of H_2S at the anode. However, these processes have not previously been investigated. Finally, it is unknown how the presence of H_2S may affect the microbial community in both the cathode and anode, if H_2S is transported across the PEM.

The objective of this study was to: 1) determine the effect of various biocathode H_2S concentrations on BES performance and sulfide removal; 2) assess the potential for H_2S to inhibit biocathode activity; 3) investigate the transport of H_2S across the PEM and the potential for H_2S oxidation in the anode; and 4) assess changes in the anode and cathode biofilm microbial communities following H_2S exposure. By understanding how H_2S affects BES performance, better strategies may be devised for BES-based biogas upgrading.

MATERIALS AND METHODS

An H-type BES, as previously described (Dykstra and Pavlostathis, 2017a), was used in the present study. A potentiostat maintained the cathode potential at -0.8 V (vs. SHE) against an adjacent Ag/AgCl reference electrode, with the anode serving as the counter electrode. The anode and cathode were inoculated with carbon felt clippings from the acetate-fed bioanode and methanogenic biocathode, respectively, of an established BES. Anolyte and catholyte were completely wasted/replaced once per week, for a hydraulic retention time (HRT) of 7 d. At the start of a feeding cycle, sodium acetate was added to the anode at an initial concentration of 2.5 g COD/L and the cathode headspace was flushed with 100% CO_2 and then pressurized to 1.65 atm (absolute pressure). After BES development, at the start of each feeding cycle, H_2S was added to the cathode headspace at various concentrations (0-5% H_2S, v/v). The BES electrochemical and biochemical performance was monitored throughout the cycles and compared. Inhibition was assessed by comparing the BES current capture efficiency [CCE; i.e., fraction of the electron equivalents (eeq) transferred as electric current recovered as CH_4 eeq) and through serum bottle tests at various H_2S concentrations with the biocathode inoculum culture, which is highly enriched in hydrogenotrophic methanogens (Dykstra and Pavlostathis, 2017b). Transport of H_2S was assessed using an abiotic, uninoculated BES. Changes in microbial community were assessed by comparing 16S rRNA gene sequencing of the biocathode and bioanode biofilms prior to the H_2S exposure and at the end of the experiment following sustained H_2S exposure. Electrochemical performance was assessed by monitoring the current, performing cyclic voltammetry (CV) scans and determining the CCE and Coulombic efficiency (CE; i.e., fraction of the eeq produced from the oxidation of the anode electron donor transferred as electric current to the cathode). Biochemical performance was assessed by measuring pH, volatile fatty acids (VFAs), gas production and gas composition in the anode and

cathode, as previously described (Dykstra and Pavlostathis, 2017a). Sulfate was quantified using a Dionex DX-100 Ion chromatography unit (Dionex Corporation, Sunnyvale, CA).

RESULTS AND DISCUSSION

Similar biocathode CH_4 production was observed at 0-4% H_2S, but at 5% H_2S, the CH_4 production declined by 68% compared to the H_2S-free control, with similar performance at 6% H_2S (Figure 1). Low CE and high CCE were observed at H_2S concentrations of 0-4% (Table 1), indicating that the bioanode was active but relatively inefficient and the biocathode was not inhibited at H_2S concentrations up to 4%. Serum bottle tests with the biocathode inoculum culture confirmed no inhibition at up to 4% H_2S, suggesting that hydrogenotrophic methanogens are more resilient to H_2S than acetoclastic methanogens, which could explain why H_2S has a larger effect on anaerobic digestion methanogenesis, which is by large mediated by acetoclastic methanogens. However, as the initial cathode headspace H_2S concentration increased, the CCE decreased but the CE increased, indicating that initial biocathode headspace H_2S concentrations greater than 4% inhibited the biocathode but the bioanode electron transfer efficiency was substantially improved.

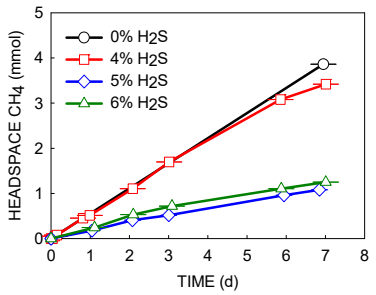

Figure 1. Biocathode CH_4 production over a feeding cycle with 0, 4, 5 and 6% (v/v) initial H_2S gas concentration.

Cyclic voltammograms conducted at the end of a feeding cycle show a slightly improved current with 4% H_2S, as compared to the H_2S-free control (Figure 2). However, at 5% and 6% H_2S, the catalytic activity of the biofilm was substantially reduced (Figure 2). Dissolved H_2S transport to the anode occurred, which was confirmed by abiotic tests and from the detection of increasing sulfate in the anolyte. At the end of the feeding cycles, 18-24% of the sulfide initially added to the cathode was recovered as sulfate in the anode. These results indicate that dissolved sulfide passed through the PEM into the anode chamber, where it was oxidized at the anode, contributing to the observed enhanced CE. At high H_2S concentrations, which resulted in increased H_2S transport into the anode, sulfate accumulated in the anode to a level that SRB were able to divert acetate electron equivalents away from exoelectrogenic Bacteria at the anode. However, the H_2S produced by SRB was oxidized at the anode, thus cycling sulfur. This result explains the observed increase of the CE at higher headspace H_2S concentrations. A microbial community analysis of the bioanode and biocathode is currently being conducted to determine how exposure of the BES biofilm to H_2S affected the community structure.

Table 1. Comparison of Coulombic efficiency (CE) and current capture efficiency (CCE) at various initial biocathode H_2S concentrations (v/v).

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

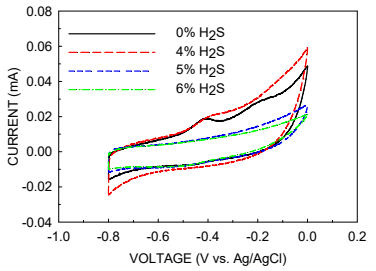

Figure 2. Cyclic voltammograms at the end of a feeding cycle for BESs with 0, 4, 5 and 6% initial H_2S biocathode headspace concentration.

CONCLUSIONS

BES-based biogas upgrading technology is highly promising for use with typical anaerobic digestion processes as biocathode CH_4 production was maintained up to 4% H_2S, which is higher than the 2% maximum typically encountered with municipal or industrial anaerobic digesters. However, to use BES-based biogas upgrading technology with anaerobic digesters that process higher sulfur content-bearing feedstocks leading to the production of high-sulfide biogas (>4% H_2S), H_2S removal technologies should be employed or new PEM materials should be developed to reduce H_2S gas transport and its effect on BES performance.

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REFERENCES

Dykstra CM, Pavlostathis SG. 2017a. *Biotechnol Bioeng* DOI: 10.1002/bit.26230

Dykstra CM, Pavlostathis SG. 2017b. *Environ. Sci. Technol.* (under review)

Geppert F, Liu D, van Eerten-Jansen M, Weidner E, Buisman C, ter Heijne A. 2016. *Trends Biotechnol.* 34:879-894.

Karhadkar PP, Audic JM, Faup GM, Khanna P. 1987. *Water Res.* 21:1061-1066.

Koster IW, Rinzema A, deVegt AL, Lettinga G. 1986. *Water Res* 20:1561-1567.

Peu P, Picard S, Diara A, Girault R, Béline F, Bridoux G, Dabert P. 2012. *Biores Technol* 121:419-424.

Reiffenstein, R.J.; Hulbert, W.C.; Roth, S.H. 1992. *Ann. Review Pharmacol. Toxicol.* 32:109-134.