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Hydrogen production from continuous flow, microbial reverse-electrodialysis electrolysis cells treating fermentation wastewater

Valerie J. Watson [a], Marta Hatzell [a,b], Bruce E. Logan [a,*]

[a] Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

HIGHLIGHTS

- Fermentation effluent fed MREC produced hydrogen without grid energy consumption.
- Doubling RED stack from 5 to 10 cell pair doubled the maximum current produced.
- At high stack potentials anode potentials were stabilized by decreasing anolyte HRT.
- Hydrogen production reached 0.9 ± 0.1 L $H_2/L_{reactor}/d$ (yield = 1.1 ± 0.1 L H_2/g COD).
- COD removal increased, but hydrogen production rates decreased at higher HRT.

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ABSTRACT

A microbial reverse-electrodialysis electrolysis cell (MREC) was used to produce hydrogen gas from fermentation wastewater without the need for additional electrical energy. Increasing the number of cell pairs in the reverse electrodialysis stack from 5 to 10 doubled the maximum current produced from 60 A/m^3 to 120 A/m^3 using acetate. However, more rapid COD removal required a decrease in the anolyte hydraulic retention time (HRT) from 24 to 12 h to stabilize anode potentials. Hydrogen production using a fermentation wastewater (10 cell pairs, HRT = 8 h) reached 0.9 ± 0.1 L $H_2/L_{reactor}/d$ (1.1 ± 0.1 L H_2/g-COD), with 58 ± 5% COD removal and a coulombic efficiency of 74 ± 5%. These results demonstrated that consistent rates of hydrogen gas production could be achieved using an MREC if effluent anolyte COD concentrations are sufficient to produce stable anode potentials.

1. Introduction

Achieving sustainable biological hydrogen gas production from renewable resources is important for avoiding environmental impacts associated with its production using fossil fuels (Ho et al., 2012). Dark fermentation can be used for conversion of waste biomass into hydrogen gas at high rates, but the process effluent contains high concentrations of organic acids and other end products that cannot be further converted to hydrogen in that process (Levin et al., 2006; Magnusson et al., 2008; Show et al., 2010). Microbial electrolysis cells (MECs) have been used as a secondary stage to produce additional hydrogen, but they require additional electrical energy to produce the potential required for hydrogen evolution at the cathode (Escapa et al., 2013; Lalaurette et al., 2009; Lee and Rittmann, 2010; Nam et al., 2014).

Reverse-electrodialysis (RED) stacks have been proposed as a method to provide the electrical energy needed to drive hydrogen production in an MEC. By placing an RED stack in between the anode and cathode chambers of an MEC, hydrogen gas can be produced without the need for electrical grid energy (Kim and Logan, 2011). In these RED-based MEC systems, called microbial reverse-electrodialysis electrolysis cells (MRECs), high and low concentrate (HC and LC) salt solutions flow through chambers formed using a stack of alternating pairs of anion (AEM) and cation (CEM) exchange membranes. The difference in ion concentration across each cell produces an electrical potential that is needed to drive cathodic hydrogen gas evolution. Thermolytic salt solutions, such as ammonium bicarbonate (Cusick et al., 2012; Elimelech and

* Corresponding author. Tel.: +1 814 863 7908; fax: +1 814 863 7304.
E-mail address: blogan@psu.edu (B.E. Logan).

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Phillip, 2011; Luo et al., 2012; Nam et al., 2012), can be used in the stack to provide salinity gradient energy. These thermolytic solutions can be used to regenerate HC and LC solutions in closed-loop systems using low grade waste heat and conventional distillation systems.

There have been few studies on the impact of RED stack architecture on MECs or the impacts of operational conditions on MREC performance. Previous work with RED stacks in microbial fuel cells (MFCs) have shown that using only a few cell pairs (one or two) increases MFC performance, but the incremental impact on power is diminished using additional cell pairs (Cusick et al., 2013). In an MREC study under fed-batch conditions using an acetate anolyte (30 mL), it was shown that adding cell pairs increased performance up to 5 cell pairs, but that the use of additional cell pairs (up to 7) did not further improve performance (Luo et al., 2013). This lack of an increase in performance with more cell pairs was attributed to the relatively high internal resistance of the stack, and the observation that adding more cell pairs produced only a minimal increase in current. A maximum hydrogen gas production rate of 1.5 L $H_2/L_{anolyte}$-d was achieved at the beginning of a fed-batch cycle in the MREC (7 cell pairs) when the acetate concentration in the anolyte was high (initially 0.78 g COD/L), but the rate decreased over the fed-batch cycle. There have been no previous MREC studies, and only a few MEC studies, under continuous flow conditions (Escapa et al., 2013; Gil-Carrera et al., 2013; Nam et al., 2014). The effect of hydraulic retention time (HRT) and applied potentials on the performance of larger (210–302 mL liquid volume) continuous flow MECs treating real and synthetic fermentation effluent has been studied (Escapa et al., 2013; Nam et al., 2014). The system used by Escapa et al. produced up to 1.42 L H_2/L_{anode}/d with an organic loading rate of 6.4 g-COD/L_{anode}/d and an applied voltage of 1.0 V.

In this study, the impact of cell pair number and HRT was examined on hydrogen gas production using a relatively large (315 mL) MREC reactor under continuous flow conditions. An ammonia bicarbonate HC solution was used in the stack in order to examine hydrogen gas production using a thermolytic solution that could be regenerated using waste heat. The RED stack had thin channels, and therefore improved power production, relative to those previously examined for hydrogen gas production in MRECs (Luo et al., 2013; Nam et al., 2012). Tests were initially conducted on stack performance using acetate, and a synthetic dark fermentation effluent, to better control the impact of feed solutions on system performance. Following these optimization tests, the effluent from dark fermentation of synthetic cellulose (Avicel) was used in continuous flow tests. MREC performance was evaluated by measuring current production when for the acetate solution, and additionally in terms of hydrogen production, yield, coulombic efficiency (CE) and COD removal when treating the synthetic or actual fermentation effluent.

2. Methods

2.1. Reactor setup

A continuous flow MREC (Fig. 1) was constructed by modification of a commercially available electrodialysis cell (PCcell, Heusweiler, Germany). The anode chamber was enlarged to 150 mL (64 cm^2 cross section) by routing out the endplate to increase the depth of the chamber to be equal the diameter of the anodes. An inlet was drilled in the bottom corner diagonally opposite the top outlet to allow for continuous flow in the chamber. Eight carbon fiber brush anodes (titanium wire core, 2.5 cm diameter, 2.5 cm length, and 0.22 m^2 surface area) were heat treated at 450 °C (Feng et al., 2010) before being connected by titanium wire and placed in the anode chamber behind a plastic grid (modified tube rack, 1.5 × 1.5 cm openings) that provided membrane support. The cathode chamber (165 mL) was also modified in the same fashion, but the top of the chamber was tapered to join with a cylindrical glass tube which was connected to tubing to enable continuous flow of catholyte and product gas from the cathode. The cathode (64 cm^2 cross section) was made from stainless steel mesh (type 304 SS, #60 mesh, McMaster-Carr, USA) and coated with Pt (0.5 mg Pt/cm^2 each side), carbon black (Vulcan XC-72) and a Nafion binder (33.3 mL/cm^2, 5 wt% solution). Each chamber contained an Ag/AgCl reference electrode (RE-5B, BASI) to measure electrode potentials.

The RED stack, situated between the anode and cathode chambers, contained 5 or 10 cell pairs (11 or 21 membranes) each 0.5 mm thick, with a total volume of 32 mL (from the cross section and membrane spacing for 10 cells) or 64 mL (20 cells). CEMs were used as the last membrane on each side of the stack, in order to ensure a low concentrate chamber was adjacent to the anode chamber to avoid ammonia crossover that could negatively affect the anode biofilm. Both AEMs and CEMs were standard ion exchange membranes (PC–SA and PC–SK, PCA GmbH) provided with the electrodialysis cell. HC (1.4 M ammonium bicarbonate) and LC (distilled water) solutions (10 L each) flowed in parallel through the stack and were recycled at 300 mL/min in a closed loop (Nam et al., 2012). The LC solution entered into the channel next to the anode chamber to help reduce ammonia crossover into the anode chamber, and HC entering next to the cathode chamber. A gas collection bag (1 L capacity, Cali-5-Bond, Calibrated Instruments Inc.) was connected to the top of the catholyte storage container. All tests were conducted at room temperature ~25 ± 3 °C.

Anodes were first pre-acclimated on acetate in microbial fuel cells (MFCs) using inocula from existing acetate-fed MFCs. The anolyte was continuously fed into the anode chamber of the MREC at HRTs of 8, 12, or 24 h, as noted. The acetate medium contained 100 mM sodium bicarbonate buffer amended with vitamins and minerals and 1.0 g/L of sodium acetate (0.77 g-COD/L, pH 8.4, conductivity = 9.5 mS/cm). Prior to tests using the fermentation effluent, the anodes were acclimated to a synthetic fermentation wastewater with a COD of 1.2 g/L that was 24% acetate (0.29 g-COD/L), 20% ethanol (0.24 g-COD/L), 13% glucose (0.16 g-COD/L), and 7% lactate (0.08 g-COD/L) in a buffered medium (100 mM sodium bicarbonate buffer amended with vitamins and minerals, pH 8.4, conductivity = 9.5 mS/cm). The synthetic fermentation effluent also contained bovine serum albumin (0.43 g-COD/L, 36% of the total COD) as previous tests showed that this lignocellulosic fermentation effluent contained a high proportion of protein (Nam et al., 2014). The actual fermentation wastewater provided by NREL (produced by a dark fermentation process utilizing synthetic cellulose, 5 g/L Avicel) had an initial COD of 5.8–6.6 g/L (pH 7, conductivity = 8 mS/cm), and was diluted (with 100 mM sodium bicarbonate buffer) to obtain an influent COD of 1.2 g/L (pH 8.4, conductivity = 8.2 mS/cm). The catholyte (1 M sodium bicarbonate, 515 mL) was recycled at 8 mL/min (HRT = 20 min) in all tests.

2.2. Experimental measurements and calculations

Electrode potentials and stack potential (vs. Ag/AgCl reference electrodes), as well as the cell voltage across a 10 Ω resistor, were recorded every 30 min using a multimeter (model 2700 Keithley Instruments, Cleveland, OH) and data acquisition system. Current density was calculated from the cell potential across the 10 Ω resistor and normalized to the total volume of the anode and cathode chambers (315 mL).

Gas produced at the cathode was collected and analyzed using gas chromatographs (GCs, SRI Instruments) to measure volume produced and concentration of H_2, N_2, CO_2, and CH_4. The volume