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

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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^2 to 120 A/m^2 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/Lreactor/d (yield = 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.

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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 (Escala et al., 2013; Lalauvette 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 a 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
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 H₂/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 (315 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 H₂/L_anolyte-d with an organic loading rate of 6.4 g-COD/L_anolyte-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 MECs (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 cm² 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 m² 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 cm² cross section) was made from stainless steel mesh (type 304 SS, #60 mesh, McMaster-Carr, USA) and coated with Pt (0.5 mg Pt/cm² each side), carbon black (Vulcan XC-72) and a Nafion binder (33.3 mL/cm², 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 H₂, N₂, CO₂, and CH₄. The volume
of hydrogen produced was determined using a method based on gas concentrations relative to initial nitrogen gas concentration in the gas collection bag compared to concentrations after an addition of 10 mL of nitrogen was added to the gas bag, as previously described (Ambler and Logan, 2011; Ullery and Logan, 2014). Hydrogen production rate \( Q \, (\text{L} \, \text{H}_2 / \text{L}_{\text{reactor}} / \text{d}) \) was normalized to the reactor volume of the anode and cathode chambers. Chemical oxygen demand was measured in the anode influent and effluent streams during periods of stable continuous operation (COD Reagent, HACH Co.).  

Coulombic efficiency (CE, %) was calculated as the ratio of the total charge accumulated over a period of time to the total coulombs available based on the COD removed during the same period of time. The pH and conductivity of solutions were monitored using conductivity and pH meters (SevenMulti, Mettler-Toledo International Inc.).

### 3. Results and discussion

#### 3.1. Influence of cell pairs and anolyte HRT on current generation

Current generation in the MREC under continuous flow conditions at an HRT of 24 h using acetate (organic loading rate, OLR = 0.77 g-COD/L/d) varied between 40 and 60 A/m\(^3\) (2.0–3.0 A/m\(^2\)) with a 5 cell pair RED stack fed (Fig. 2A). This current production is similar to the maximum current obtained in previous tests \( (100 \, \text{A/m}^3, 4.0 \, \text{A/m}^2) \) at the start of a fed-batch tests using a smaller (60 mL, 7 cm\(^2\)) MREC that also contained 5 cell pairs, but different membranes (Selemion AMV and CMV, Asahi glass, Japan) (Luo et al., 2013). The electrode potentials were relatively constant, with \(-0.402 \pm 0.009 \, \text{V} \) for the anode, and \(-0.726 \pm 0.002 \, \text{V} \) for the cathode. Because the electrode potentials were stable for these conditions, variations in current densities were due to changes in stack potential (0.44–0.52 V). Current production demonstrated that these stack potentials provided enough added energy to make up for the unfavorable anode and cathode potentials to enable hydrogen gas production from the cathode (Kim and Logan, 2011). Over time, energy extraction from the LC and HC solutions reduced the salinity ratio between these recycled solutions, which decreased the stack voltages. Each spike shown in Fig. 2 (indicated with blue arrows) reflects replacement of the stack solutions with fresh HC and LC solutions. The COD of the anolyte averaged 0.15 ± 0.01 g/L \( (n = 3) \).

When the number of membrane pairs in the stack was increased from 5 to 10 (same HRT of 24 h), cathode potentials remained constant but there were large changes in the anode potentials. Following addition of fresh LC and HC solutions to the stack, the anode potentials immediately increased to \(-0 \, \text{V} \), and then they declined to \(-0.4 \, \text{V} \) over a period of 11 ± 1 h. This rise in anode potential decreased the amount of energy that could be extracted from the salinity differences in the RED stack. Initially, the stack potential was 1.0 V, or about twice that obtained using the 5 cell pair stack, which is expected when doubling the number of membrane pairs (Długołęcki et al., 2009; Kim and Logan, 2011). However, the total stack potential decreased over time to 0.44 V as the salinity ratio between the HC and LC was reduced due to recycling the stack effluents. The resulting current production varied from 84 to 40 A/m\(^3\) (4.0–2.0 A/m\(^2\)) (Fig. 2B). When the stack potential decreased to potentials equivalent to those observed with the 5 cell pair stack, the anode potential again stabilized at around \(-0.4 \, \text{V} \). The instability of the anode potentials was likely due to the low and highly variable effluent COD concentration of 0.070 ± 0.040 g/L. It has been shown in MFC tests that there is a rapid decline in current generation when acetate concentrations decreased to less than \(-0.1 \, \text{g-COD/L} \) (Ren et al., 2014b; Zhang et al., 2015). This is around the same substrate concentration that has been reported to impact microbial kinetics based on a monod-type relationship between power generation and substrate concentrations in other bio-electrochemical systems. Liu et al. (2005) estimated the half saturation coefficient for acetate to be 141 mg/L at maximum power production, while Lee et al. (2009) found the half-maximum-rate concentration to be 119 mg COD/L when taking into account the impact of substrate diffusion and anode potential limitations (Lee et al., 2009; Liu et al., 2005; Marcus et al., 2010).
In order to increase the effluent COD, the anolyte HRT was decreased to 12 h (OLR = 1.5 g-COD/L/d), which increased the effluent COD to 0.27 ± 0.03 g/L (n = 3). Under these conditions, the anode potential once again stabilized at -0.4 V over time. While the initial stack potential was not as high as that expected based on tests using 5 cell pairs, it was initially 0.74 V, and it gradually decreased to 0.44 V as the salinity gradient of the LC and HC solutions decreased over time (Fig. 2C). The decrease in anolyte HRT provided the substrate to the anode at an increased/non-limiting rate. This decreased the anodic overpotential resulting in a higher whole cell current. The increased electrical current created a corresponding increase in ionic current within the stack, which consequently decreased the stack potential through increased mixing of the high and low concentrate solutions. Thus, the anode overpotential, dictated by the rate of substrate delivery, limits the RED stack performance through providing an additional resistance. The more consistent anode performance resulted in a 40% increase in initial current production with a slower decline in the current produced, which ranged from 120 to 50 A/m³ (6.0–2.5 A/m²) before fresh LC and HC solutions were provided. The maximum current produced at this HRT of 12 h was 40% higher than that obtained with a 24 h HRT, even though the maximum stack potential was 30% lower. When the effluent COD becomes too low, anodes connected to each other at the influent and effluent sides of the reactor can be driven to different potentials, resulting in a more positive anode potential (Ren et al., 2014b). Therefore, it is important when changing the HRT to avoid very low COD concentrations (Zhang et al., 2015) or large changes in COD in the same reactor (Ren et al., 2014b).

3.2. Current generation using synthetic fermentation wastewater

As soon as the COD composition in the anolyte feed was changed from acetate only to the synthetic wastewater, the anode potentials at an HRT of 12 h became highly variable over the cycle, suggesting substrate limitations similar to those observed using acetate at the longer HRTs (Fig. 3A). While a higher COD concentration was used for the synthetic fermentation effluent (1.2 g-COD/L) than the acetate medium (0.77 g-COD/L), the concentration of acetate in the synthetic fermentation effluent was only 0.29 g-COD/L. Thus, we hypothesized that the large change in the anode...
potential (0.2 V to –0.35 V over 26 ± 1 h during each cycle, observed over 3 cycles or 3.7 d) was due to either large changes in COD composition (i.e., decrease in acetate concentration) in the reactor or low effluent COD concentrations. Therefore, the HRT was decreased to 8 h (OLR = 3.6 g-COD/L or 0.87 g-CODacetate/L), which stabilized anode potentials again and produced a negative potential of around –0.4 V. Under these conditions, the stack potentials with the synthetic fermentation effluent ranged from 0.75 to 0.5 V, with current varying from 130 to 60 A/m³ (6.4–3.0 A/m²) (Fig. 3B).

3.3. Current generation and hydrogen production using fermentation wastewater

After 32 days of continuous operation on the synthetic fermentation effluent, the MREC anolyte feed was switched to the actual fermentation wastewater at an HRT of 24 h. The anode potential again became unstable as previously observed. In an attempt to stabilize the anode potential by further acclimation of the biofilm to the fermentation effluent, the MREC was run at an HRT of 24 h for 21 more days, but the anode performance did not stabilize over that time (data not shown). The HRT was then switched back to 8 h, and the anode and cathode potentials became stable and similar to those obtained using the synthetic wastewaters, and thus the stack voltages (0.75–0.6 V) and volumetric current densities (80–110 A/m³) were also very similar (0.6–0.75 V) (Fig. 3C). Performance of the MREC using the fermentation wastewater (Fig. 4A) was then examined in terms of hydrogen gas production, COD removal, and coulombic efficiency at three different HRTs of 8, 12, and 24 h.

Hydrogen production increased inversely with the set HRT (Fig. 4B and C). At an HRT of 8 h, hydrogen gas was produced at a rate of 0.9 ± 0.1 L H₂/Lreactor/d (overall yield of 1.1 ± 0.1 L H₂/g-COD), which was similar to rates produced in MEC studies treating complex substrates (Gil-Carrera et al., 2013; Montpart et al., 2015). The gas collected at all HRTs was predominantly hydrogen (95 ± 1%), with the remainder CO₂ that was stripped from the bicarbonate medium. Hydrogen gas production was highly variable at the longer HRTs as shown by the large standard deviations in Fig. 4B. The rate of hydrogen gas production of 0.3 ± 0.1 L H₂/Lreactor/d at the longest HRT (24 h) in the MREC was less than that measured in a previous study using an MEC (0.49 ± 0.05 m³/m³/d) (Nam et al., 2014), but the effect of using different HRTs was not investigated. The inverse relationship between hydrogen production rate and HRT observed here is different from a previous MEC study by Escapa et al. (2013), as they reported that hydrogen production increased when the HRT was changed from 8 to 12 h. The organic loading rate used in their study was almost twice as high as the one used here, and they used a different substrate and a higher applied voltage of 1.0 V, which may preclude direct comparisons of the studies on the effect of HRT on gas production. However, in this MREC study the rates of degradation of the complex organic matter in the fermentation effluent used as the MREC substrate were likely slower than that of acetate, so at long HRTs there were relatively lower concentrations of the more easily degradable components (such as acetate) in the anode chamber, resulting in lower hydrogen production at longer HRTs.

The rate of COD removal was found here to increase with a shorter HRT, in agreement with the observed rate of hydrogen gas production. At an HRT of 24 h, the COD removal rate was 0.8 ± 0.1 g/L/d, and it increased to 1.9 ± 0.1 g/L/d at an HRT of 8 h (Fig. 5), which is also evident in the increased current and stabilized anode potential at the lower HRT. When the HRT was decreased, both the coulombic efficiency (93 ± 3% at a 24 h HRT, and 74 ± 5% at an 8 h HRT) and percent of COD removal (74 ± 1% at a 24 h HRT, 58 ± 5% at an 8 h HRT) decreased. The reduction in coulombic efficiency with HRT was unexpected as typically it increases with current density (Ren et al., 2014b) in microbial fuel cells. The coulombic efficiency obtained here at an 24 h HRT was
still 27% higher than that obtained using an MEC (66 ± 11%), even though the COD removal was similar to that in the MEC (76 ± 6%) (Nam et al., 2014). The measured hydrogen yields were lower than expected when compared to the theoretical hydrogen production based on the observed coulombic efficiency. This difference is most likely due to loss of hydrogen due to its diffusion through the membrane into the stack, tubing, and other connections in the cathode chamber during catholyte recycling.

The decrease in the COD removal efficiency with shorter HRTs resulted in greater residual CODs in the MREC effluent, consistent with more stable anode potentials, as observed with acetate and the synthetic fermentation wastewater. At a 24 h HRT, the effluent COD of the fermentation wastewater was 0.21 ± 0.001 g/L but anode potentials were highly variable. This COD concentration is higher than that found to greatly reduce current generation using acetate or domestic wastewater (~0.1 g/L) in fed-batch tests (Zhang et al., 2015). However, the use of multiple brush anodes here under continuous flow conditions could have resulted in COD concentration changes that affected the potentials between the different anodes (Ren et al., 2014b). Also, the complex nature of the fermentation wastewater, which contained multiple possible substrates, might have affected anode potentials as the relative concentrations of substrates, such as acetate, could have changed with flow through the reactor similar to COD composition changes observed in batch fed MECs (Lu et al., 2012). At an 8 h HRT the effluent COD was much higher (0.51 ± 0.03 g/L) than at the 8 h HRT, but this HRT resulted in relatively stable and consistently negative anode potentials.

If lower COD concentrations are desired in the MREC effluent, the process would likely have to be operated in two stages, with the first reactor optimized for hydrogen production, and the second for COD removal. A secondary process, such as an anaerobic fluidized bed membrane bioreactor (AFMBR) was recently shown to effectively reduce the effluent COD from an MFC to <0.020 g/L (Ren et al., 2014a). Higher hydrogen gas production rates could possibly be obtained by using higher MREC influent COD concentrations, as this should increase COD removal rate and stabilize anode potentials. The fermentation wastewater examined here was diluted to a concentration to be similar to those previously used in MECs (Lalaurie et al., 2009; Nam et al., 2012; Nam and Logan, 2011; Nam et al., 2011, 2014; Ullery and Logan, 2014), so the use of higher influent COD concentrations could easily be achieved. The effect of organic loading on the MREC performance, in terms of anode potentials and hydrogen gas production rates, should therefore be examined in future studies.

4. Conclusions

Hydrogen was produced from an MREC treating fermentation wastewater. Increasing the number of cell pairs increased current production, but a decreased anolyte HRT was needed to stabilize anode potentials. With 10 cell pairs, hydrogen production reached 0.9 ± 0.1 L H2/Leactored/d (yield = 1.1 ± 0.1 L H2/g COD) and 74 ± 5% coulombic efficiency, with 58 ± 5% COD removal. Increased COD removal and lower COD levels in MREC effluent can be achieved, but at the expense of hydrogen production and COD removal rates.

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References


