



Short Communication

High hydrogen production rate of microbial electrolysis cell (MEC) with reduced electrode spacing

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ABSTRACT

Practical applications of microbial electrolysis cells (MECs) require high hydrogen production rates and a compact reactor. These goals can be achieved by reducing electrode spacing but high surface area anodes are needed. The brush anode MEC with electrode spacing of 2 cm had a higher hydrogen production rate and energy efficiency than an MEC with a flat cathode and a 1-cm electrode spacing. The maximum hydrogen production rate with a 2 cm electrode spacing was 17.8 m³/m³d at an applied voltage of $E_{ap} = 1$ V. Reducing electrode spacing increased hydrogen production rates at the lower applied voltages, but not at the higher (>0.6 V) applied voltages. These results demonstrate that reducing electrode spacing can increase hydrogen production rate, but that the closest electrode spacing do not necessarily produce the highest possible hydrogen production rates.

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1. Introduction

Hydrogen is considered as an environmentally acceptable, alternative energy carrier that can be used in vehicles (Service, 2004). Biological processes are an environmental friendly technology for producing hydrogen, but dark fermentation has a low energy recovery and low yield (4 mol H₂ per mol of glucose, compared to a stoichiometric potential of 12 mol H₂/mol). Higher yields can be achieved using photobiological processes or pure enzymes, but neither of these methods so far shown sufficient promise for economical production of hydrogen (Miyake et al., 1999; Woodward et al., 2000).

A new technology called a microbial electrolysis cell (MEC) can achieve sustainable hydrogen production from various types of biomass (Cheng and Logan, 2007; Liu et al., 2005; Rozendal et al., 2006). In an MEC, organic materials are degraded by microbes at the anode and hydrogen is evolved at cathode from protons in solution and electrons released to the anode. This process has several advantages over other biohydrogen processes, such as high hydrogen yields and the ability to use many different types of substrates including fermentable and non-fermentable organics (Cheng and Logan, 2007; Ditzig et al., 2007). MEC hydrogen production rates have ranged from 0.01 to 6.3 m³/m³d (Liu et al., 2005; Tartakovsky et al., 2009), which is lower than that using dark fermentation (up to 64.5 m³/m³d) (Li and Fang, 2007). Hydrogen

production rates therefore need to be increased for practical applications of MECs.

Several factors can affect hydrogen production rate of MEC, including reactor architecture (Call and Logan, 2008; Hu et al., 2008; Lee et al., 2009; Tartakovsky et al., 2009), electrode materials (Cheng and Logan, 2007; Lee and Rittmann, 2010; Selembo et al., 2009), solution chemistry (Merrill and Logan, 2009) and operation in fed-batch or continuous flow modes (Lee and Rittmann, 2010; Selembo et al., 2009; Tartakovsky et al., 2009). Initial tests with two-chamber MECs had low hydrogen production rates (0.01–0.1 m³/m³d) (Liu et al., 2005; Rozendal et al., 2006). By increasing anode surface area and by using an anionic exchange membrane, hydrogen production increased to 1.1 m³/m³d (Cheng and Logan, 2007). Removing the ion exchange membrane (single-chamber MEC) increased the production rate to 3.12 m³/m³d (292 A/m²) at an applied voltage of $E_{ap} = 0.8$ V (Call and Logan, 2008). Hydrogen production rates are reduced if the electrode density is low. For example, Hu et al. obtained only 0.53 m³/m³d at $E_{ap} = 0.6$ V with an electrode area of 18 m²/m³ (Hu et al., 2008). In a continuous flow system, a hydrogen production rate of 4.3 m³/m³d was obtained due to a high current density (1600 A/m²) (Lee et al., 2009). Changing the architecture by isolating the cathode from the anode using a cloth separator produced 6.3 m³/m³d (Tartakovsky et al., 2009).

These results show that high hydrogen production rates require a high volumetric current density. In microbial fuel cells (MFCs), it has been shown that current densities are mainly limited by internal resistance (Cheng et al., 2006). Many factors affect internal resistance, but reducing the electrode spacing important if oxygen cross over from the cathode can be controlled. Reducing the electrode

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spacing from 3 to 2 cm decreased internal resistance from 56 to 35 Ω , and increased power of the MFC by 22%. Further decreases in electrode spacing decreased power due to oxygen cross over despite a decrease internal resistance from 35 to 16 Ω (Cheng et al., 2006). In an MEC, however, there is no oxygen in the system to prevent close electrode spacing. In previous tests when electrode spacing was reduced a separator was added to the system (Fan et al., 2007), but a separator can increase solution resistance (Zhang et al., 2009). In order to determine the most optimal electrode spacing, we examined a range of applied voltages in reactors where we systematically reduced electrode spacing while at the same time we decreased the reactor volume to optimize volumetric current density.

2. Experimental

2.1. MEC construction and operation

Single-chamber MECs were constructed using a previously described design (Call and Logan, 2008) modified to allow the length of the cylindrical anode chamber to be 1, 2, 3 or 4 cm. Cathodes (7 cm²) were made of a carbon cloth containing a Pt catalyst (0.5 mg/cm²). Anodes for the 2, 3 and 4 cm long MECs were ammonia gas treated graphite fiber brushes originally 14 mm in diameter and 25 mm in length (fiber type PANEX 33 160K, ZOLTEK) (Logan et al., 2008). Brush anodes could not be used in the 1 cm reactor without short circuiting the electrodes. Therefore, the anodes for the 1 cm long MECs were ammonia gas treated carbon cloth (Type A, non wet-proofed, E-TEK; projected surface area of 7 cm²). Brush anode MECs had the length of the wire perpendicular to the cathode while the flat anode was placed on the opposite side of the chamber. The edge of the brush anodes were trimmed flat to avoid short circuiting. The average electrode spacing (from anode center to cathode) and liquid volumes were 1 (6 mL), 2 (10 mL), 3 (17 mL) and 3.5 cm (26 mL), with \sim 1 cm between the edge of the brush and the cathode. The final electrode specific areas for the anodes were 117 m²/m³ (1 cm), \sim 6500 m²/m³ (2 cm), \sim 4100 m²/m³ (3 cm), and \sim 3700 m²/m³ (3.5 cm), and for the cathodes were 117 m²/m³ (1 cm), 70 m²/m³ (2 cm), \sim 41 m²/m³ (3 cm), and \sim 27 m²/m³ (3.5 cm).

The MECs were inoculated with suspended bacteria obtained from the anode biofilm of an acetate-fed MFC reactor operating for three years that was initially inoculated with primary clarifier effluent (Cheng and Logan, 2007). Reactors were fed 100 mM phosphate buffer (PBS) containing a trace nutrient medium (Cheng et al., 2006) and 1 g/L of sodium acetate. Voltage was applied to the circuit (-0.6 V except as noted) using a potentiostat (Wontech, Korea) by connecting the working electrode to cathode, and connecting the reference and the counter electrode to anode. The bacterial inoculum was omitted once a reactor produced >1 mA. When a reproducible maximum current was obtained for at least three successive batch cycles, the anode was considered fully acclimated and tests were conducted at different applied voltages. The reactor liquid was sparged with ultra high purity (UHP) nitrogen (99.998%) for 20 min before voltage was applied. The tests were conducted in duplicate in a constant temperature room (30 $^{\circ}$ C).

2.2. Measurements

Gas production was continuously recorded using a respirometer (AER-200; Challenge Environmental) (Cheng and Logan, 2007) and collected in a gas bag (0.1 L capacity; Cali-5-Bond, Calibrated Instruments Inc.). Prior to each test, respirometer flow cells were sparged with UHP N₂ gas to remove any remaining gas from a pre-

vious cycle. Gas bags were filled with UHP N₂ gas and emptied by vacuum before being used.

The gas composition of the anaerobic tube headspace and gas bag was analyzed by two gas chromatographs (models 8610B and 310, SRI Instruments, CA) equipped with Alltech Molesieve 5A 80/100 stainless steel-tubing columns and thermal conductivity detectors (TCDs). Argon was used as carrier gas for H₂, O₂, N₂ and CH₄ analysis, and helium was used as the carrier gas for CO₂ analysis.

Total chemical oxygen demand (COD) analysis of the solution was performed at the beginning and end of each batch cycle using standard methods (TNTplus COD Reagent; HACH Company).

2.3. Calculations

MEC performance was evaluated in terms of volumetric hydrogen production rate (Q_{H_2}), volumetric current density (I) based on the total volume of MEC, hydrogen recovery (R_{H_2}) and electrical energy recovery (η_E) based on electricity input, and overall energy recovery (η_T) based on both electricity input and substrate removed. All parameters were calculated as previously described (Cheng and Logan, 2007; Logan et al., 2008). Current density for each cycle was obtained by averaging the top 10 current densities at the beginning of each cycle.

3. Results and discussion

3.1. Hydrogen production

Hydrogen production rate was increased as the electrode spacing decreased from 3.5 to 1 cm at all applied voltages except for 1 cm MECs at $E_{ap} > 0.5$ V (Fig. 1A). The highest hydrogen production rate was 17.8 m³/m³d using the 2 cm MEC at $E_{ap} = 1$ V. Hydrogen production rate increased linearly with applied voltage for all the MECs except for the 1-cm MEC at $E_{ap} > 0.5$ V, with slopes of 25 m³/m³dV (1 cm, $E_{ap} < 0.5$ V), 22 m³/m³dV (2 cm), 15 m³/m³dV (3 cm), and 9 m³/m³dV (3.5 cm). The maximum H₂ production rate obtained here is 179 \times higher than that previously obtained with

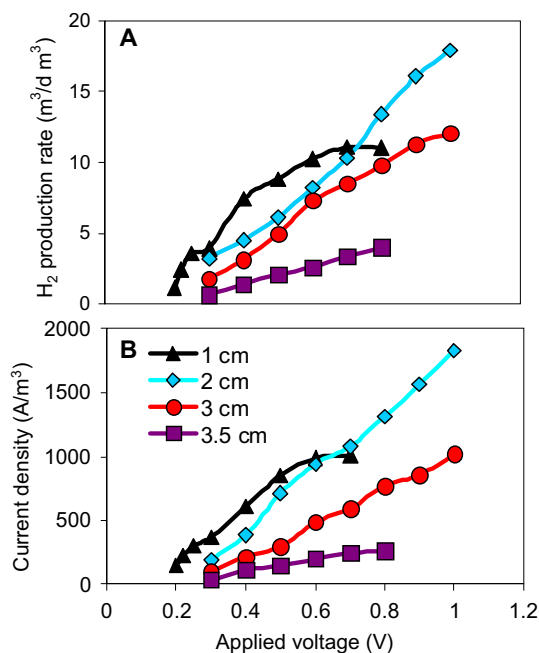


Fig. 1. Hydrogen production rate (A) and current density (B) with the function of the applied voltage at different electrode spacings.

two-chamber MEC (Rozendal et al., 2006), and 3–6 × higher than that obtained with single-chamber MECs (Call and Logan, 2008; Lee and Rittmann, 2010; Tartakovsky et al., 2009).

For the 1-cm MEC, the hydrogen production rate did not increase for $E_{ap} > 0.5$ V. The reason for that was likely insufficient surface area on the anode for bacteria. In order to reduce the electrode spacing to 1 cm a flat electrode had to be used to avoid short circuiting. For purely electrochemical reactions, reducing the electrode spacing should reduce ohmic resistance and increase current. The fact that current decreased shows that reducing the electrode spacing was not as important in an MEC as maintaining high anode surface area for bacteria. This effect of anode surface area is consistent with other MFC studies where the electrodes are more than 1 cm from the cathode (Cheng et al., 2006). Another possible factor limiting MEC performance could be hydrogen consumption by microorganisms on the anode (Lee et al., 2009). However hydrogen recoveries were all high, suggesting that hydrogen losses to the anode microbes were low. In addition, there was little methane production likely due to short cycle times of 3–15 h compared to 30–70 h by others (Hu et al., 2008; Lee et al., 2009).

The hydrogen production rate increased in proportion to current density (Fig. 1B). For example, at $E_{ap} = 0.4$ V, the current density was 103 A/m^3 at the electrode spacing of 3.5 cm, with a H_2 production rate of $1.41 \text{ m}^3/\text{m}^3\text{d}$. Decreasing electrode spacing to 2 cm increased the current density by 3.7× to 385 A/m^3 , and the hydrogen production rate 3.2× to $4.5 \text{ m}^3/\text{m}^3\text{d}$. At this same applied voltage, the MEC with a 1 cm electrode spacing produced 5.9× more current (607 A/m^3) and 5.2× more hydrogen ($7.4 \text{ m}^3/\text{m}^3\text{d}$). Decreasing the electrode spacing increased the current density, but the reduction in volume produced a greater proportional change in volumetric current density. For example, a decrease in electrode spacing from 3.5 to 2 cm increased the current $1.4\times(2.69\text{--}3.85 \text{ mA})$ but the volumetric current density increased by 3.7×.

The highest current density was 1830 A/m^3 , which was obtained for a 2 cm electrode spacing and $E_{ap} = 1$ V. This maximum current density is 6.3× higher than that previously reported by Call and Logan (2008) (292 A/m^3), with 5.7× the hydrogen production rate ($3.12 \text{ m}^3/\text{m}^3\text{d}$). A continuous flow MEC with a smaller electrode spacing (<1 mm) produced 1630 A/m^3 , but had a lower H_2 production rate of $4.3 \text{ m}^3/\text{m}^3\text{d}$ relative to that possible at their current density $18.2 \text{ m}^3/\text{m}^3\text{d}$ (Lee and Rittmann, 2010). The low hydrogen recovery was due to hydrogen oxidation by bacteria and a low cathodic conversion efficiency. Thus, an efficient cathode catalyst is needed to achieve high hydrogen production rates and recoveries.

The maximum hydrogen production rate achieved here was higher than the $10 \text{ m}^3/\text{m}^3\text{d}$ estimated to be required for a full-scale MEC system (Rozendal et al., 2007). However, the highest current density obtained here is three times lower than that achieved in an MFC (5600 A/m^3) (Fan et al., 2007). If this current density obtained in the MFC could be achieved in the MEC, then the hydrogen production rate could reach to 51–54 $\text{m}^3/\text{m}^3\text{d}$, a value that is similar to the highest hydrogen production rates achieved in dark fermentation biohydrogen production (Li and Fang, 2007).

3.2. Hydrogen recovery

Generally, hydrogen recovery increased as the electrode spacing decreased (Fig. 2). The lowest hydrogen recovery (64%) was obtained at 3.5-cm electrode spacing at $E_{ap} = 0.3$ V, and highest hydrogen recovery (98%) was obtained with a 2-cm electrode spacing at $E_{ap} = 0.9$ V. In general, hydrogen recovery increased inversely with electrode spacing, except at the closest electrode spacing of 1 cm. For example, decreasing the electrode spacing from 3.5 to 3 cm increased hydrogen recovery by 34% (from 64% to 84%), but

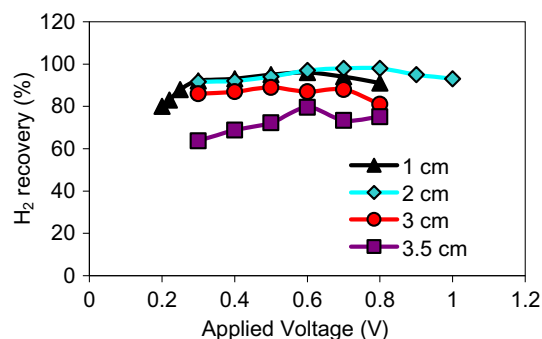


Fig. 2. Hydrogen recovery with the function of the applied voltage at different electrode spacings.

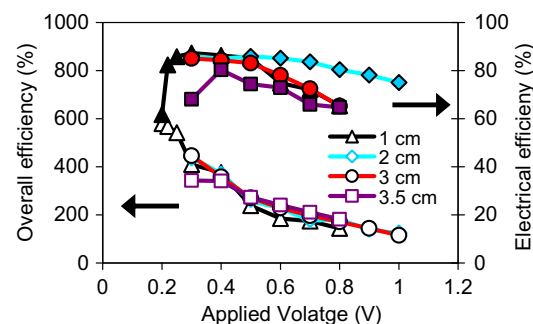


Fig. 3. Electrical energy efficiency (A) and Overall energy efficiency (B) with the function of the applied voltage at different electrode spacings.

when the electrode spacing was reduced from 2 to 1 cm the hydrogen recovery was unchanged (92%) ($E_{ap} = 0.3$ V). Hydrogen recovery varied with applied voltages and therefore hydrogen production rates. Hydrogen recoveries increased with applied voltage for the lower applied voltages, but then decreased for the highest applied voltages. For example, hydrogen recovery increased from 92% to 98% as E_{ap} increased from 0.3 to 0.8 V, but it decreased to 93% at $E_{ap} = 1$ V. The change in hydrogen recovery was largest for the 3.5-cm MEC (64–80%).

3.3. Energy efficiencies

The energy efficiency based on the electricity input decreased from $\eta_E = 580\%$ at 0.2 V to $\eta_E = 115\%$ at 1 V (Fig. 3). A decrease in values of η_E are expected based on the larger proportion of electrical energy input into the system at higher applied voltages (Logan et al., 2008). Overall energy efficiency (η_T), based on both substrate energy and input electrical energy was influenced by both applied voltage and electrode spacing (Fig. 3). Overall energy efficiencies decreased as the applied voltage increased except for the MECs with 4-cm and 1-cm electrode spacing at 0.3 V. The highest η_T of 87% was obtained at electrode spacing of 1 cm and a voltage of 0.3 V.

4. Conclusions

Reducing the electrode spacing can increase hydrogen production, but the highest hydrogen production rate ($17.8 \text{ m}^3/\text{m}^3\text{d}$, $E_{ap} = 1$ V) was achieved with a 2-cm electrode spacing and not a 1-cm spacing. The larger electrode spacing allowed the use of brush anodes which supported sufficient bacteria to produce high current density of 1830 A/m^3 . This hydrogen production rate is a

notable achievement because it is higher than the $10 \text{ m}^3/\text{m}^3\text{d}$ estimated to be required for a full-scale MEC system (Rozendal et al., 2007).

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References

- Call, D., Logan, B.E., 2008. Hydrogen production in a single chamber microbial electrolysis cell (MEC) lacking a membrane. *Environ. Sci. Technol.* 42, 3401–3406.
- Cheng, S., Liu, H., Logan, B.E., 2006. Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing. *Environ. Sci. Technol.* 40, 2426–2432.
- Cheng, S., Logan, B.E., 2007. Sustainable and efficient biohydrogen production via electrohydrogenesis. *PNAS* 104, 18871–18873.
- Ditzig, J., Liu, H., Logan, B.E., 2007. Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR). *Int. J. Hydrogen Energy* 32, 2296–2304.
- Fan, Y., Hu, H., Liu, H., 2007. Sustainable power generation in microbial fuel cells using bicarbonate buffer and proton transfer mechanisms. *Environ. Sci. Technol.* 41, 8154–8158.
- Hu, H., Fan, Y., Liu, H., 2008. Hydrogen production using single-chamber membrane-free microbial electrolysis cells. *Water Res.* 42, 4172–4178.
- Lee, H.-S., Torres, C.S.I., Parameswaran, P., Rittmann, B.E., 2009. Fate of H_2 in an upflow single-chamber microbial electrolysis cell using a metal-catalyst-free cathode. *Environ. Sci. Technol.* 43, 7971–7976.
- Lee, H.S., Rittmann, B.E., 2010. Significance of biological hydrogen oxidation in a continuous single-chamber microbial electrolysis cell. *Environ. Sci. Technol.* 44, 948–954.
- Li, C., Fang, H.H.P., 2007. Fermentative hydrogen production from wastewater and solid wastes by mixed cultures. *Critical Rev., Environ. Sci. Technol.* 37, 1–39.
- Liu, H., Grot, S., Logan, B.E., 2005. Electrochemically assisted microbial production of hydrogen from acetate. *Environ. Sci. Technol.* 39, 4317–4320.
- Logan, B.E., Call, D., Cheng, S., Hamelers, H.V.M., Sleutels, T.H.J.A., Jeremiasse, A.W., Rozendal, R.A., 2008. Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environ. Sci. Technol.* 42, 8630–8640.
- Merrill, M.D., Logan, B.E., 2009. Electrolyte effects on hydrogen evolution and solution resistance in microbial electrolysis cells. *J. Power Sources* 191, 203–208.
- Miyake, J., Miyake, M., Asada, Y., 1999. Biotechnological hydrogen production: research for efficient light energy conversion. *J. Biotechnol.* 70, 89–101.
- Rozendal, R., Hamelers, H.V.M., Molenkamp, R.J., Buisman, C.J.N., 2007. Performance of single chamber biocatalyzed electrolysis with different types of ion exchange membranes. *Water Res.* 41, 1984–1994.
- Rozendal, R.A., Hamelers, H.V.M., Euverink, G.J.W., Metz, S.J., Buisman, C.J.N., 2006. Principle and perspectives of hydrogen production through biocatalyzed electrolysis. *Int. J. Hydrogen Energy* 31, 1632–1640.
- Selembro, P.A., Merrill, M.D., Logan, B.E., 2009. The use of stainless steel and nickel alloys as low-cost cathodes in microbial electrolysis cells. *J. Power Sources* 190, 271–278.
- Service, R.F., 2004. The hydrogen backlash. *Science* 305, 958–961.
- Tartakovsky, B., Manuel, M.F., Wang, H., Guiot, S.R., 2009. High rate membrane-less microbial electrolysis cell for continuous hydrogen production. *Int. J. Hydrogen Energy* 34, 672–677.
- Woodward, J., Orr, M., Cordray, K., Greenbaum, E., 2000. Biotechnology – enzymatic production of biohydrogen. *Nature* 405, 1014–1015.
- Zhang, X., Cheng, S., Wang, X., Huang, X., Logan, B.E., 2009. Separator characteristics for increasing performance of microbial fuel cells. *Environ. Sci. Technol.* 43, 8456–8461.