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Source of methane and methods to control its formation in single chamber microbial electrolysis cells

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ABSTRACT

Methane production occurs during hydrogen gas generation in microbial electrolysis cells (MECs), particularly when single chamber systems are used which do not keep gases, generated at the cathode, separate from the anode. Few studies have examined the factors contributing to methane gas generation or the main pathway in MECs. It is shown here that methane generation is primarily associated with current generation and hydrogenotrophic methanogenesis and not substrate (acetate). Little methane gas was generated in the initial reaction time (<12 h) in a fed batch MEC when acetate concentrations were high. Most methane was produced at the end of a batch cycle when hydrogen and carbon dioxide gases were present at the greatest concentrations. Increasing the cycle time from 24 to 72 h resulted in complete consumption of hydrogen gas in the headspace (applied voltage of 0.7 V) with methane production. High applied voltages reduced methane production. Little methane (<4%) accumulated in the gas phase at an applied voltage of 0.6–0.9 V over a typical 24 h cycle. However, when the applied voltage was decreased to 0.4 V, there was a greater production of methane than hydrogen gas due to low current densities and long cycle times. The lack of significant hydrogen production from acetate was also supported by Coulombic efficiencies that were all around 90%, indicating electron flow was not altered by changes in methane production. These results demonstrate that methane production in single chamber MECs is primarily associated with current generation and hydrogen gas production, and not acetoclastic methanogenesis. Methane generation will therefore be difficult to control in mixed culture MECs that produce high concentrations of hydrogen gas. By keeping cycle times short, and using higher applied voltages (≥0.6 V), it is possible to reduce methane gas concentrations (<4%) but not eliminate methanogenesis in MECs.

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1. Introduction

Microbial electrolysis process (MEC) is a process for hydrogen production where substrates are converted to current by exoelectrogenic bacteria on the anode [1,2], and the electrons and protons are catalyzed to form hydrogen gas at the cathode [3–6]. This technology was developed by modifying microbial fuel cells (MFCs) so that oxygen was excluded from the system, and adding a small voltage to the circuit to drive the evolution of hydrogen gas [7,8]. MECs have shown advantages of efficient biomass conversion to biohydrogen gas, high Coulombic efficiencies, and high purity hydrogen gases [3,4,9,10]. Single chamber MECs have recently been developed that do not keep the gas produced at the cathode separate from the bacteria on the anode and in the solution [4,12,14,21]. This has the advantage of increased current densities and lower costs due to the omission of the membrane, but it has been found that there can be high concentrations of methane in the product gas under certain conditions.

Methane production in MECs can occur from two routes in the presence of acetate, carbon dioxide and hydrogen gas. The first pathway is by acetoclastic methanogenesis, while the second is from hydrogenotrophic methanogenesis, or

$$C_2H_4O_2 \Rightarrow CH_4 + CO_2 \quad (1)$$

$$4H_2 + CO_2 = CH_4 + 2H_2O \quad (2)$$

In anaerobic digestion, methane is primarily from acetate (70%) and less from H_2 (30%) [13].

The origin of the methane in MECs (i.e. from acetate or hydrogen) is still not well understood, and better methods are needed to limit methane production to recover more hydrogen gas. In one MEC study using a gas cathode, it was found that when the applied voltage was reduced from 1.3 V to 0.5 V there was a rapid decrease in hydrogen concentration in the gas, and a simultaneous increase in methane concentration [14]. When the applied voltage was then changed to >0.7 V, the hydrogen production rate was restored to previous levels. Evidence was also provided that supported hydrogenotrophic methanogens converted up to 50% of the H_2 produced at the cathode into methane in a continuous-flow MEC [14]. Call and Logan (2008) observed that when the applied voltage was reduced to 0.3 V, methane production was substantially increased compared to reactors operated at 0.4 V or larger [4]. While detention time was believed to aid methane gas production, it was not determined whether the methane was generated primarily from hydrogen or acetic acid, or at what portion in the cycle the methane gas was produced. Rozendal et al. [19] determined that hydrogen consumption was aided by high concentrations of bicarbonate in the medium, supporting hydrogenotropic methanogensis. When the bicarbonate was removed, they showed that methanogenesis was more effectively suppressed in a two-chamber MEC. Low pH is known to inhibit methanogens, and it was found that by using selectively enriched mixed consortia that methane production was inhibited at low pH in an MFC [15,16]. Clauwaert et al. have proposed developing a system based on both hydrogen and methane gas [18]. Rather than inhibit methane gas production, they indicated that methane generation could be stimulated up to a ratio of 0.41 mol methane per mole acetate in a two-chamber MEC. Methane was also found to be the main energetic product in an MEC with graphite granule electrodes, despite continuous operation under carbonate-limited and slightly acidified conditions [21].

In order to further examine the origin of methane in an MEC, and to better understand the effect of the applied voltage on methane production, several experiments were conducted with single chamber MECs using acetate as a substrate. The evolution of both hydrogen and methane gases was examined during a single fed-batch cycle, and the amounts of these gases were determined as a function of applied voltage and cycle length over multiple cycles. These results provide additional evidence that methane gas production is associated with current generation and hydrogen gas production in MECs, and not acetoclastic methanogenesis.

2. Materials and methods

2.1. Reactor setup

Experiments were conducted using single chamber MECs made of polycarbonate as previously described [4]. The total empty volume was 43 mL, consisting of a 28.5 ml chamber (3 cm inner diameter and 4 cm long) and a tube attached to the top of the reactor (1.6 cm inner diameter and 7.5 cm length; 14.5 mL capacity). The anode was an ammonia treated graphite brush (25 mm diameter × 25 mm length; 0.22 m^2 surface area; fiber type: PANEX 33 160 K, ZOLTEK), with a specific surface area of 18,200 m^2/m^3 and a porosity of 95%. The cathode was made from carbon cloth with 30% PTFE wet-proofing (type B; E-TEK); the surface area was 7 cm^2 with a Pt catalyst layer (0.5 mg/cm^2) in one side and PTFE diffusion layers in the other side [17]. The cathode was placed opposite to anode brush while it was glued and sealed completely on the diffusion layers side from the beginning for MEC operation.

2.2. Operation and measurement

A series of reactors were inoculated using a 50:50 mixture of medium and wastewater. The medium was prepared in a buffer (50 mM phosphate buffer, PBS, pH 7.0) and nutrient solution (NH_4Cl, 310 mg l^{-1}; KCl, 130 mg l^{-1}; trace nutrient medium, [11]) with sodium acetate (1500 mg l^{-1}). During startup and except as noted, a fixed voltage of 0.7 V was applied to all reactors (model 3645A; Circuit Specialists, Inc.). The medium was replaced when current decreased below 0.2 mA before each cycle, the chamber was purged using high purity nitrogen gas (99.998%) for 20 min to remove oxygen. A control reactor (C0) was operated in the same way except it was kept in open-circuit mode following inoculation through the end of the experiment. A second control test reactor (C1) was operated at 0.7 V until methane production was observed and was steady over several cycles. Then, the reactor was operated for the next

cycle in open-circuit mode, and the composition of the gas produced over the next cycle was measured to determine gas production from an acclimated reactor in the absence of an applied voltage. All batch tests were conducted in a constant temperature room (30 °C).

Gas was collected in gas bags (0.1 L capacity; Cali-5-Bond, Calibrated Instruments Inc.). Voltages were measured using a multimeter (model 2700; Keithley Instruments, Inc.) and current calculated as previously described [4]. Reactors were equipped with an Ag/AgCl reference electrode (RE-5B; BASi) for measuring anode potentials. The chemical oxygen demand (COD) was measured at the beginning and end of each cycle according to standard methods (TNT plus COD Reagent; HACH Company). The gas in the reactor headspace and gas bag (H_2, N_2, CO_2 and CH_4) was analyzed by gas chromatography [4] with samples taken using a gastight syringe (250 μL, Hamilton Sample-lock Syringe).

Coulombic efficiency (CE) is calculated as $CE = C_{current}/C_{substrate}$; where $C_{current}$ is the coulomb of current through the circuit, calculated as $\int i\,dt$, and dt (s) is the interval (20 min) over which data were collected; $C_{substrate}$ is the coulomb of substrate (acetate) oxidized to CO_2, calculated on COD removal [4]. Conversion of hydrogen (CH) is calculated as $CH = C_{H_2}/C_{substrate}$; where C_{H_2} is the coulomb of hydrogen collected finally.

3. Results and discussion

3.1. *Methane and hydrogen production in MEC tests*

After 3 days of operation, H_2 gas was detected by the end of the first cycle. The reactors were then run over multiple batch cycles over the next month to ensure stable and consistent operation before conducting hydrogen production tests (Fig. 1). During the last six cycles, the Coulombic efficiency averaged 88.8 ± 1.6% while the overall conversion efficiency acetate into hydrogen averaged 77.1 ± 2.3%. The percent of methane gas produced increased over the 12 cycles, stabilizing in the last four cycles at 3.1 ± 0.2%. As a result of the small concentration of methane gas and the high CE values, it was not possible at this point to determine if the methane gas evolved primarily from acetate or hydrogen gas, or from both. The origin of this methane gas was therefore further examined in further tests.

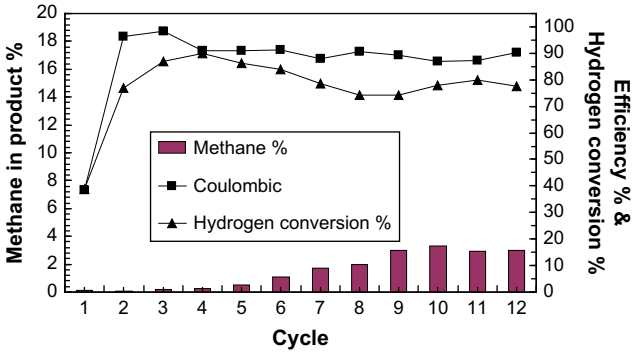

Fig. 1 – Methane production and hydrogen conversion efficiency in a single chamber MEC at 0.7 V applied voltage.

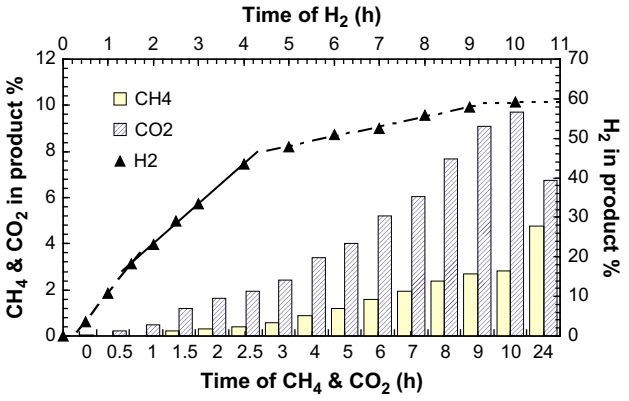

Fig. 2 – Gas concentrations in an MEC over a complete cycle (0.7 V applied voltage). The data show all gases produced during a cycle. (Nitrogen gas initially present in the reactor headspace is not included.)

In a typical batch cycle, H_2 was detected after only 20 min, while CH_4 was not detected until 1.5 h (Fig. 2). Note that in the last hours (from 10 to 24 h) the carbon dioxide gas concentration decreased while that of the methane increased, suggesting the conversion of hydrogen gas to methane required carbon dioxide fixation via hydrogenotrophic methanogenesis. Little gas was produced in the two control reactors operated under open-circuit conditions even after 50 h, and there was only a net production of CO_2 gas as no methane or hydrogen was measured in the headspace (Fig. 3). A comparison of the rates of CO_2 production in the MECs and control reactors (no applied voltage) shows that CO_2 produced in the initial 10 h in the MEC was a result of current generation (Fig. 4). This shows that there was little methanogenesis in the presence of acetate, and that methane production required current and hydrogen gas production.

Analysis of the rate of hydrogen gas concentration versus time shows that H_2 was produced at the greatest rate during the first 1.5 h of a batch cycle (14.6%/h; Table 1) before methane was detected. The rates of CH_4 production and CO_2 consumption were much slower in the initial time period (t = 0–4 h), with 0.28%/h for CH_4 and 0.92%/h for CO_2 (Fig. 2, Table 1). During the next time period (t = 5–9 h), the rate of

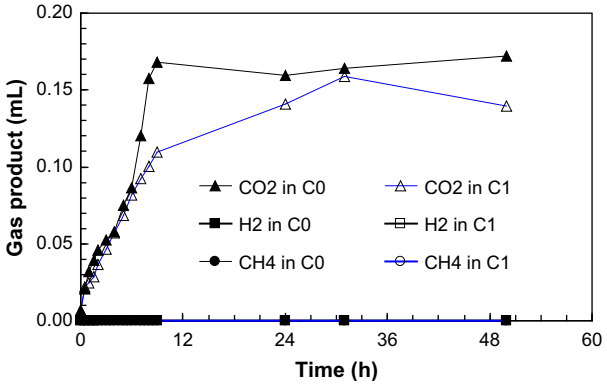

Fig. 3 – Gas concentrations in the headspace of the control reactors (open-circuit conditions).

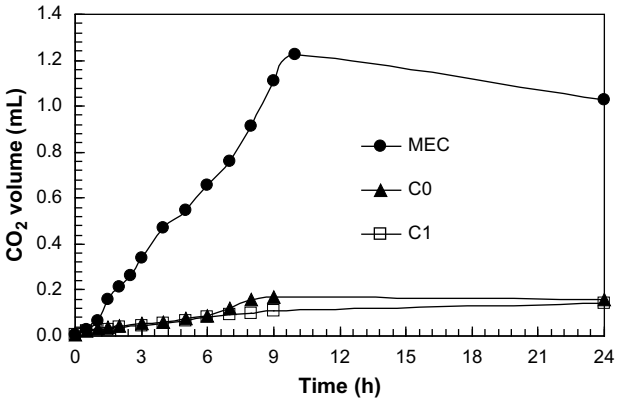

Fig. 4 – CO_2 production in the headspace of the MEC and control reactors.

methane generation increased reaching 0.37%/h, and production of CO_2 also increased to 1.26%/h, with the net rate of hydrogen gas production decreasing to 2.5%/h. At the end of the cycle (t = 10–24 h), hydrogen gas rate was low (0.19%/h) and the methane rate was only 0.14%/h. In this last period, there was a net consumption of CO_2 (−0.21%/h). The initial high rate of H_2 production, combined with a lack of an initial high rate of CH_4 production (and CO_2 consumption), and an increase in methane generation when hydrogen gas was produced, supports methanogenesis primarily from hydrogen gas and not from acetate.

The mass balance for hydrogen was checked in the last four cycles (Fig. 1) when methane generation was stable. The total H_2 from electrons was 281.3 ± 8.0 C (calculated by Coulomb of COD × Coulombic efficiency); the electrons for CH_4 that makes H_2 lose was 33.7 ± 1.8 C; the remaining H_2 converted from electrons of 248.3 ± 8.4 C. According to electrons balance for hydrogen in the reactor: (moles for H_2 produced totally from electrons: 281.3 C) – (moles used for CH_4 formation: 33.7 C) = moles of remaining H_2 measured: 247.6 C. The result was fit well to 248.3 C which was measured actually in the reactor. Moreover, there was little methane production in the control reactors which were operated under open-circuit conditions, and did not have any hydrogen gas production. In 24-h, the control test reactor (C1) produced 0.1 ml CO_2 for a reduction in COD of 8.6%, which is less than that produced in the MEC (1.22 ml CO_2; 88.5% COD consumption) (Fig. 4). The lack of methane production in the control reactors suggests that there was little selection over time for acetoclastic methanogens. As the solution was replaced after each batch cycle, only microbes growing on the electrodes or the walls of the reactor could have been responsible for hydrogenotrophic methanogenesis [18,19]. It was observed that over time a biofilm developed on the cathode. However, the origin of the methane gas was not a result of methanogens growing on the cathode. When we replaced the cathode with a new cathode lacking microorganisms, there was no change in the composition of the gas produced (data not shown). Thus, methane production was not a result of a biocathode and was likely due to the growth of microorganisms on the high surface area anode.

3.2. *Controlling methane production by limiting fed-batch cycle time*

The time of the overall batch cycle affected the final H_2 yield (Table 2). Under typical conditions, the fed-batch cycle time was 24 h and there was an average production of hydrogen as of 32.3 ± 0.6 mL. If the cycle was stopped after 12 h, the gas yield was essentially unchanged 33.1 ± 1.2 mL, suggesting that any further hydrogen gas produced in the reactor between 12 and 24 h was consumed. However, when the cycle time was increased to 72 h, there was no detectable concentration of H_2 gas detected in the headspace at the end of the cycle, and the overall production of hydrogen gas produced was reduced to 8.3 mL. In these 12, 24 and 72 h cycle time tests, methane was 3.0%, 2.8% and 4.0% of the product gas. Examples of current generation over typical 12, 24 and 72 h cycles are shown in Fig. 5. These results further demonstrate that hydrogen gas was consumed for methane production, and that decreased cycle times increase hydrogen recovery and decrease overall methane production. However, methane decreased little when cycle time reduced from 24 to 12 h. Methane generated after hydrogen arrived at some level around 1.5 h in Fig. 2. Short cycle could reduce the reaction time that methane generation from H_2, but methane could not eliminate by reducing cycle time too short or even in continuous flow because substrate utilization would be less as the cycle time was shorter, and the methane problem was till significant [14]. However, system would be different assuming cycle time was short enough or even in continuous-flow operation in this single chamber MEC reactor.

Table 1 – Slope values of gas concentration according in the batch cycle in Fig. 2.

Testing time (h)	0.5–1.5	1.5–4	5–9	10–24
H_2 Slope (%/h)	14.6	10.1	2.5	0.19
CO_2 Slope (%/h)	0.95	0.90	1.26	−0.21
CH_4 Slope (%/h)	0.48	0.31	0.37	0.14

The phases were divided according to the slope of H_2, which R^2 for all slopes was not less than 0.99. Then slopes of other gases were calculated accordingly in each interval. For CH_4, it started to be detected at 1.5 h and the slope was only calculated by two points in the first phase.

Table 2 – Gas products in different cycle operational times (Fig. 5).

Time (h)	H_2 (%)	CH_4 (%)	CO_2 (%)	Volume (ml)	CE (%)	CH (%)
12	92.0 ± 1.3	3.0 ± 0.04	5.0 ± 1.3	36.0 ± 0.9	88.8 ± 2.0	78.8 ± 1.6
24	88.4 ± 1.0	2.8 ± 0.7	8.8 ± 0.5	36.5 ± 0.6	89.0 ± 2.0	75.5 ± 2.1
72	37.08	4.0	3.76	22.41	90.7	50.0

The experiment was done at 0.7 V. Gas concentrations in product are shown as H_2%, CH_4% and CO_2%, excluding N_2. CE is Coulombic efficiency and CH is conversion of hydrogen from acetate.

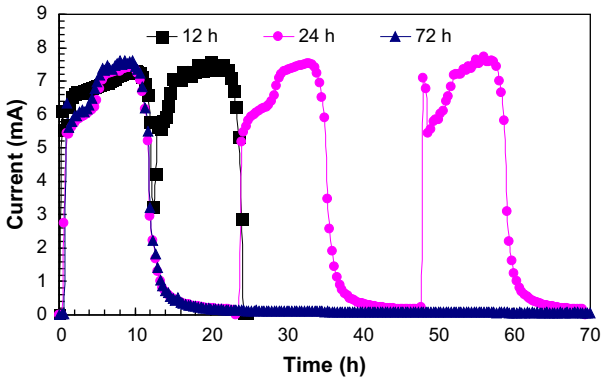

Fig. 5 – Effect of operation time on current generation in MECs over 70 h.

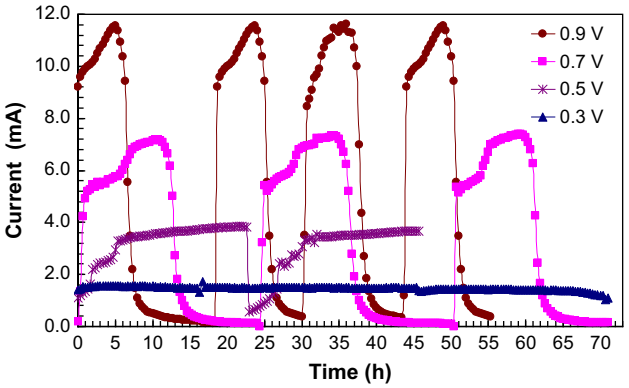

Fig. 7 – Current generation in MECs at different applied voltages showing changes in maximum current densities.

3.3. *Controlling methane production by increasing the applied voltage*

It was previously observed that methane production was limited in MEC tests, except at a low applied voltage of 0.3 V using the same type of single chamber MEC reactor [4]. To further investigate this effect of applied voltage on methane and hydrogen gas production, we varied the applied voltages over a range of 0.3–0.9 V. Low voltages resulted in long cycle times (up to 70 h) before the current decreased to 0.2 mA. At applied voltages of >0.6 V, the product gas was consistently $87.7 \pm 3.5\%$ hydrogen gas, and <4% methane gas (Fig. 6). At 0.5 V methane gas concentration further increased, and when 0.4 V was applied the methane gas concentration reached 68% with only 22% H_2. At the lowest applied voltage of 0.3 V, there was a low current and little hydrogen produced, with H_2 reaching a concentration of 2% at 24 h (data not shown) and no H_2 gas remaining at the end of the cycle (70 h) but methane (79.2%) and CO_2 (20.7%) were present. Coulombic efficiency was relatively unaffected by the applied voltage ($89.9 \pm 3.1\%$ for 0.4–0.9 V). In all cases, the peak current increased with applied voltage as expected (Fig. 7). The increase in this current density resulted in a shorter cycle time as shown in Fig. 6.

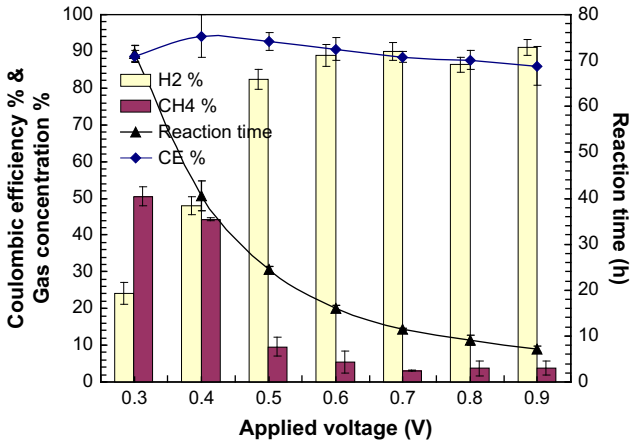

Fig. 6 – Coulombic efficiency, gas concentrations (H_2 and CH_4) and time needed for one full cycle as a function of different applied voltages.

These results suggest that substantial methane production can be avoided by increasing the applied voltage and operating the reactor under short cycle times. In tests using reactors acclimated for more than 26 cycles over several months, we found that ≥0.6 V was needed to reduce CH_4 concentrations below 4%. However, in previous tests it was observed that CH_4 concentrations in the product gas were minimal except at 0.3 V. The difference in the voltage needed to avoid substantial methane production is likely a result of the operation history of the different reactors. The longer operation times examined here than in previous studies likely resulted in a more established methanogen community in the biofilms in the systems. However, further work on the microbial communities in these systems will be needed to verify this. To date, there is little community analysis has been performed on MECs compared to MFCs [20].

4. Conclusions

Methane production in single chamber MECs can be substantial, depending on the operation time and applied voltage. It was shown here that the origin of the methane recovered is primarily associated with hydrogen gas and not acetoclastic methanogenesis. This is different than that typically observed in anaerobic digesters where most of the methane is derived from volatile fatty acids. Methane production primarily occurred in the latter part of the reaction cycle when hydrogen gas concentrations were high, and not in the beginning of the cycle when acetate concentrations were highest. No methane was produced in control reactors in the absence of current generation and hydrogen gas production. When the reactor was operated at an applied voltage of 0.7 V, methane production stabilized at only 3.1 ± 0.2 % during a typical 24-test reaction cycle, with an average Coulombic efficiency of $89 \pm 1.6\%$. Decreasing the applied voltage, and increasing the reaction time, increased methane production. Methane production was higher than hydrogen gas production at an applied voltage of 0.4 V, but at ≥0.6 V, methane production was always <4%. These results demonstrate that methane production can be reduced, but not eliminated, in single chamber MECs using mixed cultures through the use of short operation cycles and higher applied voltages.

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