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**Publisher's version / Version de l'éditeur:**
https://doi.org/10.1016/j.ijhydene.2008.11.003
*International Journal of Hydrogen Energy, 34, 2, pp. 672-677, 2008-12-06*

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# High rate membrane-less microbial electrolysis cell for continuous hydrogen production

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ARTICLE INFO

*Article history:*
Received 12 June 2008
Received in revised form
20 October 2008
Accepted 5 November 2008
Available online 6 December 2008

*Keywords:*
MFC
MEC
Hydrogen
Membrane-less

ABSTRACT

This study demonstrates hydrogen production in a membrane-less continuous flow microbial electrolysis cell (MEC) with a gas-phase cathode. The MEC used a carbon felt anode and a gas diffusion cathode with a Pt loading of 0.5 mg $cm^{-2}$. No proton exchange membrane (PEM) was used in the setup. Instead, the electrodes were separated by a J-cloth. The absence of a PEM as well as a short distance maintained between the electrodes (0.3 mm) resulted in a low internal resistance of 19 Ω. Due to an improved design, the volumetric hydrogen production rate reached 6.3 $L_{STP}\,L_A^{-1}\,d^{-1}$. In spite of the PEM absence, methane concentration in the gas collection chamber was below 2.1% and the presence of hydrogen in the anodic chamber was never observed.


## 1. Introduction

Global energy needs and rising concern about green-house gas emissions have prompted research into alternative sources of fuel and energy. Recently, modification of the microbial fuel cell (MFC) to produce hydrogen has been demonstrated [1–7]. In a microbial electrolysis cell (MEC), organic substrates are converted to hydrogen via a microbially catalyzed process. In this process, anodophilic microorganisms use the anode as an electron acceptor while releasing protons. Then protons are reduced to molecular hydrogen at the cathode providing that additional energy is supplied by an external power supply, which drives the electrons ''uphill'' along the redox ladder. The anodic reaction, therefore, is the same as in the microbial generation of electricity in an MFC, while the cathodic reaction proceeds in the absence of oxygen and requires an additional potential of at least 0.1 V [1,2].

Notably, biological production of hydrogen by fermentation is restricted to a yield of 4 mol $mol^{-1}$ of glucose when acetate is the only fermentation product. In practice, however, other fermentation products are formed decreasing the yield to 1–2 mol $mol^{-1}$ [8]. Microbial electrolysis makes it possible to generate hydrogen from final products of dark fermentation and opens the possibility of using diluted organic matter varying in composition, such as wastewater, for hydrogen production. Therefore a variety of renewable carbon sources can be used.

Initial demonstrations of hydrogen production by microbial electrolysis were carried out under suboptimal conditions, where low volumetric efficiencies of hydrogen production were obtained. For example, a volumetric production rate of 0.01 $L\,L_A^{-1}\,d^{-1}$ (A = anodic chamber) was observed by Liu et al. [2] and a hydrogen production rate of 0.1 $L\,L_A^{-1}\,d^{-1}$ was obtained by Rozendal et al. [1]. These low rates were attributed to large ohmic resistances and electrode overpotentials. Since then volumetric efficiencies were improved to 1 $L\,L_A^{-1}\,d^{-1}$ [3,4]. Recently, a volumetric hydrogen production rate of 3.12 $L\,L_A^{-1}\,d^{-1}$ was achieved in a single

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doi:10.1016/j.ijhydene.2008.11.003

chamber membrane-less MEC operated in batch mode [9]. Yet, this is a relatively low value. For comparison, a high-rate anaerobic digester has a COD removal rate of 15–40 $g\,L_A^{-1}\,d^{-1}$ (R = reactor) with 80–90% removal efficiency and a volumetric methane production rate of 4–10 $L\,L_A^{-1}\,d^{-1}$ [10] and COD removal rates as high as 50–70 $g\,L_A^{-1}\,d^{-1}$ have been reported [11]. Given that 1 mol (22.4 L) of hydrogen can theoretically be produced from 16 g of COD, it can be hypothesized that volumetric rate of hydrogen production as high as 17–45 $L\,L_A^{-1}\,d^{-1}$ can be expected if anodophilic biomass density is similar to that of a high-rate anaerobic reactor. This study presents our recent efforts in the development of a high-rate continuous flow MEC with a liquid-phase anode and a gas-phase cathode.

## 2. Material and methods

### 2.1. Media composition

The stock solution of carbon source was composed of (in $g\,L^{-1}$): sodium acetate (90.7), yeast extract (6.7), $NH_4Cl$ (18.7), KCl (148.1), $K_2HPO_4$ (64.0), and $KH_2PO_4$ (40.7). Yeast extract had a COD of 0.96 $g\,L^{-1}$. The stock solution of trace metals was prepared according to Rozendal et al. [3] and contained (in $mg\,L^{-1}$) $FeCl_24H_2O$ (2000), $H_3BO_3$ (50), $ZnCl_2$ (50), $CuCl_2$ (30), $MnCl_24H_2O$ (500), $(NH_4)_6Mo_7O_{24}4H_2O$ (50), $AlCl_3$ (50), $CoCl_26H_2O$ (50), $NiCl_2$ (50), EDTA (500), and HCl (1 mL). All solutions were filter sterilized and maintained at 4 °C until use. Distilled water was used for solution preparation, and all chemicals and reagents used were of analytical grade.

### 2.2. Analytical measurements

Acetic acid was analyzed on an Agilent 6890 gas chromatograph (Wilmington, DE) equipped with a flame ionization detector and a 1 × 2-mm 60/80 mesh Carbopack C column (Supelco, Bellafonte, PA, USA) coated with 0.3% Carbowax 20 M and 0.1% $H_3PO_4$. The carrier gas was nitrogen, which had a flow rate of 20 mL $min^{-1}$. The injector and the detector were maintained at 200 °C. Samples (0.5 μL) were fortified at a ratio of 1:1 (V/V) using an internal standard of iso-butyric acid dissolved in 6% formic acid.

Gas production in the MEC was measured on-line by means of bubble counters connected to glass U-tubes containing a dye and interfaced with a data acquisition system. The measurements were converted to standard conditions for temperature and pressure (STP). Gas composition was measured using a gas chromatograph (6890 Series, Hewlett Packard, Wilmington, DE) equipped with an 11m × 3.2-mm 60/80 mesh Chromosorb 102 column (Supelco, Bellefonte, PA, USA) and a flame ionization detector. Carrier gas was argon.

### 2.3. MEC design, instrumentation, and operation

All experimentation was carried out in continuously fed MECs. Two cells were constructed, each with a series of polycarbonate plates arranged to form an anodic chamber and a gas collection chamber. Each chamber had a volume of 50 mL. The cells were equipped with lines for influent, effluent, liquid recirculation and gas exits (Fig. 1). Temperature and pH were controlled at 25 °C and pH 7, respectively. More details on MEC design can be found elsewhere [12].

The liquid filled (anodic) chambers contained a 5-mm thick carbon felt measuring 10 × 5 cm (Speer Canada, Kitchener, ON, Canada). In one of the cells (MEC-1), an E-TEK gas diffusion electrode (GDE) with a Pt load of 0.5 $mg\,cm^{-2}$ (GDE LT 120EW, E-TEK Division, PEMEAS Fuel Cell Technologies, Somerset, NJ, USA) was used as a cathode. This cell contained no proton exchange membrane. Another cell (MEC-2) contained the same GDE cathode, however, a Nafion 117 proton exchange membrane (PEM) was hot-pressed onto it. In both cells the cathodes were separated from the anodes by a piece of J-cloth so that the estimated distance between the electrodes was 0.3 mm. The second chamber of each MEC contained no liquid and was used for gas collection (Fig. 1). The MECs were inoculated with 5 mL of homogenized anaerobic sludge (Rougemont, QC, Canada).

A stock solution of carbon source was fed using an infusion pump (model PHD 2000, Harvard Apparatus, Canada) at a rate of 5 $mL\,d^{-1}$, which corresponded to an acetate load of 4 $g\,L_A^{-1}\,d^{-1}$. One milliliter of trace metals stock solution was added to 1 L of the dilution water. The dilution water was fed at a rate of 146 $mL\,d^{-1}$ using a peristaltic pump (Cole-Parmer, Chicago, IL, USA) providing a retention time of 10 h. During electricity production mode, MECs were routinely operated at an external resistance of 400 Ω and the gas collection chambers were exposed to atmosphere by opening gas lines located at the top and the bottom of the chamber. To avoid the influence of microbial growth and adaptation on MEC performance in hydrogen production tests, applied voltage was changed in the following sequence: 0.74; 1.15; 0.85; 0.7;

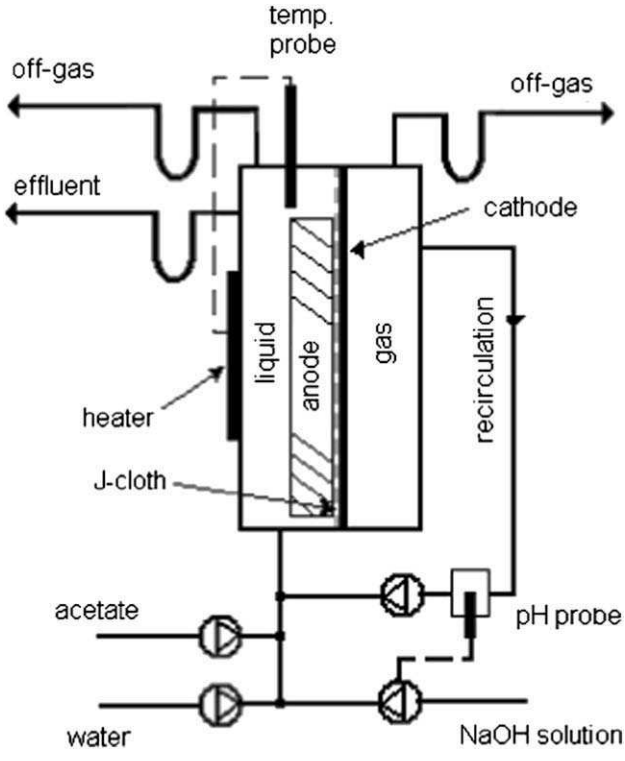


**Fig. 1 – Diagram of a continuous flow MEC setup.**

0.55; 0.4; 0.55; and 1.0 V (MEC-1) and 1.0; 1.15; 0.85; 0.7; 0.55; 0.4; 0.85; and 0.55 V (MEC-2). Each voltage setting was maintained for 1–5 days. Hydrogen production measured during the last 12 h of each test was used for all calculations.

### 2.4. MEC characterization and calculations

Voltage was measured on-line at 10 min intervals using a data acquisition system (Labjack U12, Labjack Corp, Lakewood, CO, USA). In electrically-assisted (MEC) mode, a 15-Ω resistor was added to the circuit for current measurements, which were also conducted at 10 min intervals. To account for power losses at the resistor, applied voltage was measured directly at the MEC. An adjustable DC power supply (IF40GU Kenwood, Japan) was used to maintain voltage at the preset setpoint.

In MEC mode, voltage scans were performed by changing applied voltage between 0 and 1.2 V and measuring the resulting current. A 10-min interval was allowed after each voltage change. Internal resistance was calculated as a slope of the voltage vs current curve.

Hydrogen yield (mol of hydrogen produced per mol of acetate consumed) was estimated over the time interval $\Delta t = t - t_0$ as follows:

$$Y_{H_2} = \frac{\left(\frac{p \times F_{H_2} \Delta t}{R \times T}\right)}{\frac{W}{M}} \quad (1)$$

where $p$ is the pressure ($p = 1$ atm); $F_{H_2}$ is the hydrogen production rate ($L_{STP}\,d^{-1}$); $R$ is the ideal gas constant; $T$ is the temperature ($T = 273$ K); $M$ is the substrate molecular weight (60 g mol$^{-1}$ for acetate); and $W$ is the amount of substrate consumed for hydrogen production (g). The latter was estimated as $W = (S_0 - S_t)V_a + (S_{in} - S_{out})F_{in}\Delta t$, where $S_0$, and $S_t$, are the acetate concentrations in the anodic chamber at the beginning and at the end of the interval $\Delta t$ (g L$^{-1}$); $S_{in}$ and $S_{out}$ are the concentrations of acetate in the influent and in the effluent (average during $\Delta t$), respectively (g L$^{-1}$); $V_a$ is the anode chamber volume (L); and $F_{in}$ is the influent flow rate (L d$^{-1}$).

Apparent Coulombic efficiency (CE) of hydrogen production was estimated as [13]:

$$CE = \frac{I \times \Delta t \times M}{F \times n \times W} \quad (2)$$

where $I$ is the average current (A); $\Delta t$ is the time interval during which current was measured (s); $F$ is Faraday's constant, 96485 (C mol$^{-1}$); and $n$ is the number of electrons transferred per mol of the substrate oxidized into $CO_2$ ($n = 8$ for acetate).

COD recovery ($R_{COD}$) was calculated by comparing estimated and measured effluent substrate fluxes using the following equation [12]:

$$R_{COD} = \left(\frac{Q_{out} + Q_{H_2} + Q_{CH_4}}{Q_{in}}\right) \times 100\%, \quad (3)$$

where $Q_{in}$ and $Q_{out}$ are the influent and effluent substrate fluxes, respectively (g d$^{-1}$); $Q_{H_2}$ is the substrate consumed by the anodophilic microorganisms for hydrogen production (g d$^{-1}$); and $Q_{CH_4}$ is the substrate used by the methanogenic microorganisms for methane production (g d$^{-1}$). The substrate utilization for methane and hydrogen production was estimated using the theoretical methane and hydrogen yields on acetic acid, $Y_{CH_4} = 0.37\ L_{STP}\,g^{-1}$, and $Y_{H_2} = 1.49\ L_{STP}\,g^{-1}$, respectively. Therefore, $Q_{CH_4} = F_{CH_4}/Y_{CH_4}$ and $Q_{H_2} = F_{H_2}/Y_{H_2}$, where $F_{CH_4}$ is the experimentally measured methane production rate ($L_{STP}\,d^{-1}$).

## 3. Results and discussion

MEC-1 (without PEM) and MEC-2 (with PEM) were simultaneously operated under identical operational conditions, i.e. an acetate load of 4 g $L_A^{-1}$ d$^{-1}$ (equivalent acetate load of 4.4 g $L_A^{-1}$ d$^{-1}$ with respect to yeast extract content in the stock solution), a temperature of 25 °C, and an HRT of 8–10 h. After inoculation, both MECs were initially operated in electricity production mode. Accordingly, gas collection chambers were open to air and electrodes were connected to external resistances. Once power production stabilized, open circuit potential (OCP) was measured after disconnecting the external resistance. These measurements yielded similar OCP values of 650–670 mV for both cells.

The mode of operation was changed to hydrogen production by connecting an external power source to each MEC. Routinely, both MECs were operated at an applied voltage of 1.0 V. Once stable hydrogen production was observed, voltage scans were carried out. Analysis of these scans (Fig. 2) suggested that the PEM, when present, led to significantly higher internal resistance. From voltage scans, internal resistances ($R_{int}$) of 19 and 27 Ω were estimated for MEC-1 (without PEM) and MEC-2 (with PEM), respectively. Both in MEC-1 and in MEC-2 relatively high background currents were observed and were possibly attributed to non-biological (i.e. electrochemical) reactions.

While voltage scans confirmed activity of anodophilic microorganisms, small volumes of hydrogen produced at each voltage setting did not allow for accurate measurements of hydrogen production. Therefore, measurements of hydrogen production were carried out in a range of applied voltages from 0.2 to 1.2 V, where MECs were operated for at least 24 h at each applied voltage. These tests clearly demonstrated improved hydrogen production in the PEM-less setup (Fig. 3A).

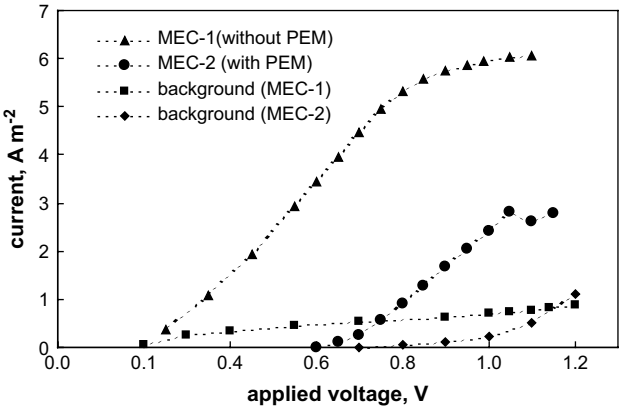


**Fig. 2 – Current densities (per cathode area) obtained in voltage scans with 5 min intervals between voltage changes. Background values were obtained by excluding acetate from the stock solution.**

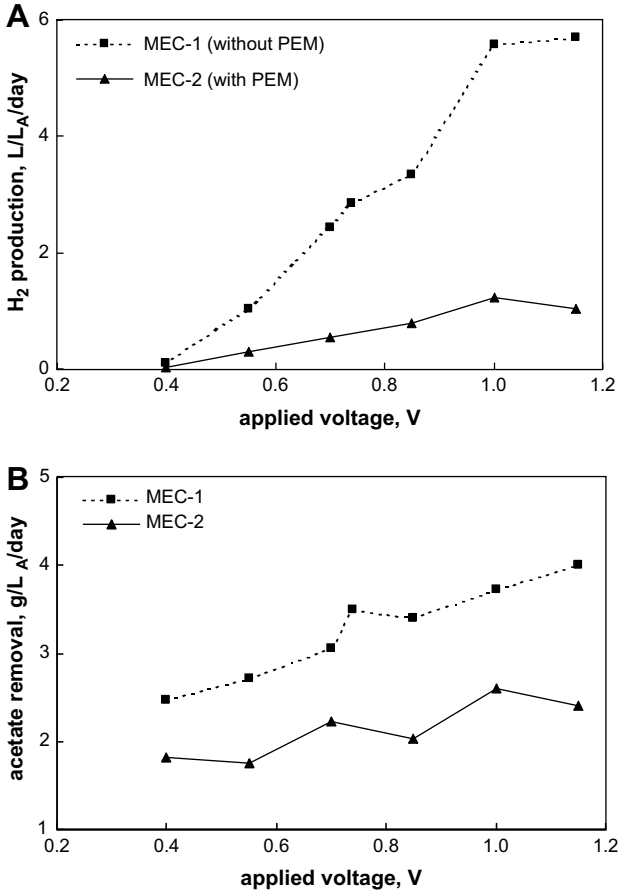


**Fig. 3 – (A) Volumetric rates of hydrogen production and (B) acetate removal in MEC-1 (without PEM) and MEC-2 (with PEM) at different applied voltages and an acetate load of 4 g $L_A^{-1}$ $d^{-1}$. Standard deviation was estimated at 0.14 $L_{STP}$ $L_A^{-1}$ $d^{-1}$ and 0.6 g $L_A^{-1}$ $d^{-1}$ for $H_2$ production and acetate removal measurements, respectively.**

In MFC-1 hydrogen production was measurable starting from an applied voltage of 0.4 V. Overall, at applied voltages between 0.4 and 1.0 V volumetric rates of hydrogen production increased in response to increases in voltage. Consequently, in both MECs highest hydrogen production was achieved at 1.0 V. Under substrate non-limiting conditions (acetate concentration above 400 mg $L^{-1}$), hydrogen production rates of 6.1–6.5 $L_{STP}$ $L_A^{-1}$ $d^{-1}$, and 1.0–1.3 $L_{STP}$ $L_A^{-1}$ $d^{-1}$ were obtained in MEC-1 and MEC-2, respectively (Fig. 3A). These values are comparable with hydrogen production rates previously observed, i.e. a hydrogen production rate of 3 L $L_A^{-1}$ $d^{-1}$ observed at 30 °C in a single chamber membraneless MEC [9] and a rate of 1 L $L_A^{-1}$ $d^{-1}$ observed in a MEC equipped with a PEM [3].

Analysis of anodic chamber acetate concentrations suggested that at high-applied voltages hydrogen production rate in MEC-1 was substrate-limited. Indeed, in MEC-2, acetate concentration in the anodic chamber was always above 400 mg $L^{-1}$ suggesting no substrate limitation in this cell. In MEC-1 acetate accumulation was observed at 0.4 and 0.55 V (1000–1200 mg $L^{-1}$ at 0.55 V). When voltage was changed from 0.55 to 1.0 V, acetate concentration gradually decreased, while hydrogen production reached 6.3 $L_{STP}$ $L_A^{-1}$ $d^{-1}$ (12 h average at an acetate concentration of 450 mg $L^{-1}$). Then hydrogen production decreased and stabilized at 5.57 $L_{STP}$ $L_A^{-1}$ $d^{-1}$ with an acetate concentration decreasing to 57 mg $L^{-1}$, i.e. hydrogen production was substrate-limited. Further voltage increase to 1.15 V did not significantly improve hydrogen production as acetate load remained unchanged. Overall, the difference in $R_{int}$ observed in voltage scan tests for MEC-1 and MEC-2 (Fig. 2) agreed with the difference in hydrogen production rates thus demonstrating the advantage of a membrane-less design. Throughout the tests acetate removal rate was proportional to applied voltage (Fig. 3B), confirming that acetate was consumed by anodophilic microorganisms.

Importantly, gas composition measurements in the gas collection (cathodic) chamber showed a methane content of only 1.2–2.1% in both MECs. Anodic chamber headspaces contained up to 9% methane, although methane production rate in the anodic chambers of both MECs was low (Table 1). Notably, methane can be produced from acetate by acetoclastic methanogenic microorganisms and from hydrogen diffused to the anodic chamber by hydrogenotrophic methanogenic microorganisms. The observed low rate of methane production suggested low activity of both populations.

Calculations of acetate recovery using material balance Eq. (3) showed a recovery of 40–90% (Table 1). Notably, the material balance was least accurate at an applied voltage of 0.4 V, which corresponded to low hydrogen production rates leading to large errors in gas flow measurements. Apparently, at low hydrogen production rates, the accuracy of the material balance was affected by hydrogen losses through the tubing connecting the gas collection chamber with the gas counter. Significant hydrogen losses through tubing at low production rates were observed by Ditzig et al. [5]. Also, theoretical yields used to calculate acetate equivalents based on hydrogen and methane production did not take into account acetate consumption for biomass growth thus resulting in underestimation of acetate consumption for hydrogen and methane production. Hydrogen yield calculations were also affected by hydrogen losses. While at high production rates corresponding to MEC-1 operation at 1.0 and 1.15 V the yield approached 3.7–3.8 mol $mol^{-1}$ (Table 1), much lower values were estimated for applied voltages below 1.0 V and for MEC-2 where hydrogen production was lower. A comparison of Coulombic efficiencies suggested that the presence of Nafion membrane resulted in somewhat decreased efficiency at applied voltages above 0.8 V, i.e. when overpotentials were the largest (Fig. 4). Coulombic efficiencies in a range of 80–100% were reported for a membrane-less MEC [9], while a Coulombic efficiency of 23% was reported for a single chamber PEM setup [3].

The absence of a PEM was expected to increase power requirements and lead to hydrogen losses as part of hydrogen can diffuse to the anodic chamber and be consumed both by methanogenic microorganisms for methane formation and anodophilic microorganisms (electron recycling). However, these losses were not observed. It was hypothesized that biofilm formation at the cathode surface as well as a stagnant layer at the gas–liquid interface of the cathode-limited hydrogen diffusion into anodic chamber. Indeed, effective diffusivity of hydrogen in the stagnant layer adjacent to the

**Table 1 – MEC performance during hydrogen production tests at a 4 g $L_A^{-1}$ $d^{-1}$ (equivalent acetate load of 4.4 g $L_A^{-1}$ $d^{-1}$ considering yeast extract).**

| MEC | Voltage, V | $H_2$ production, $L_{STP}$ $L_A^{-1}$ $d^{-1}$ | $CH_4$ production, $L_{STP}$ $L_A^{-1}$ $d^{-1}$ | Current density, A $m^{-2}$ | Power input, Wh $L^{-1}$ | $H_2$ yield, mol/$mol^{-1}$ | COD recovery, % |
|---|---|---|---|---|---|---|---|
| MEC-1 (without PEM) | 0.40 | 0.09 | 0.008 | 0.6 | 6.4 | 0.1 | 40.3 |
| | 0.55 | 1.03 | 0.039 | 1.4 | 1.8 | 1.0 | 51.2 |
| | 0.70 | 2.85 | 0.044 | 2.5 | 1.5 | 2.1 | 65.0 |
| | 0.74 | 3.34 | 0.064 | 3.2 | 1.7 | 2.2 | 61.1 |
| | 0.85 | 3.35 | 0.061 | 3.2 | 1.9 | 2.6 | 71.9 |
| | 1.00 | 5.57[a] | 0.099 | 4.3 | 1.9 | 3.7 | 82.3 |
| | 1.00 | 6.32[b] | 0.083 | 4.7 | 1.8 | 3.9 | 90.6 |
| | 1.15 | 5.70[a] | 0.0 | 4.2 | 2.0 | 3.8 | 89.6 |
| MEC-2 (with PEM) | 0.40 | 0.0 | 0.0 | 0.4 | – | – | 61.9 |
| | 0.55 | 0.30 | 0.01 | 1.2 | 5.3 | 0.6 | 68.5 |
| | 0.70 | 0.54 | 0.0 | 1.4 | 4.4 | 0.7 | 59.1 |
| | 0.85 | 0.78 | 0.02 | 1.6 | 4.2 | 1.3 | 68.3 |
| | 1.00 | 1.22 | 0.02 | 1.8 | 3.5 | 1.4 | 60.0 |
| | 1.15 | 1.04 | 0.01 | 1.8 | 4.8 | 1.3 | 62.4 |

Standard deviation was estimated at 0.05 and 0.14 $L_{STP}$ $L_A^{-1}$ $d^{-1}$ for $CH_4$ and $H_2$ measurements, respectively. COD recovery was calculated according to Eq. (3) and using yields of $Y_{CH_4} = 0.37$ $L_{STP}$ $g^{-1}$ and $Y_{H_2} = 1.49$ $L_{STP}$ $g^{-1}$ for methane and hydrogen, respectively.
a At acetate concentrations of 57 mg $L^{-1}$ (1.0 V) and 15 mg $L^{-1}$ (1.15 V).
b At an acetate concentration of 448 mg $L^{-1}$ (substrate non-limiting conditions).

cathode surface might be several orders of magnitude higher than that expected in the porous material of the gas diffusion electrode. As well, the formation of biofilm on the cathode surface and J-cloth was observed after several days of MEC operation and this biofilm might create an additional diffusion barrier. The existence of substrate and ion gradients in the biofilm due to diffusion limitations has been previously demonstrated [14]. Furthermore, unrestricted transport of ions helped to maintain near neutral pH at the cathode, as opposed to high pH values observed in a MEC where Nafion membrane was used [3,15].

A comparison of the two setups showed a higher power consumption in MEC-2 (Table 1). This observation was attributed to additional ohmic resistance created by the Nafion membrane. The high proton selectivity of Nafion may be compromised by high concentrations of other cations contained in the growth media. Negatively charged sulfonated groups of the Nafion were shown to react with these other cations rather than protons and as a consequence less protons are conducted to the cathodic chamber [16]. Overall, power input required for hydrogen production in MEC-2 was somewhat higher than 2.2 Wh $L^{-1}$ reported by Rozendal et al. [3] using similar inoculum. Hydrogen production in MEC-1 required 2 Wh $L^{-1}$ at a voltage of 1.0 V and 1.5 Wh $L^{-1}$ at 0.7 V.

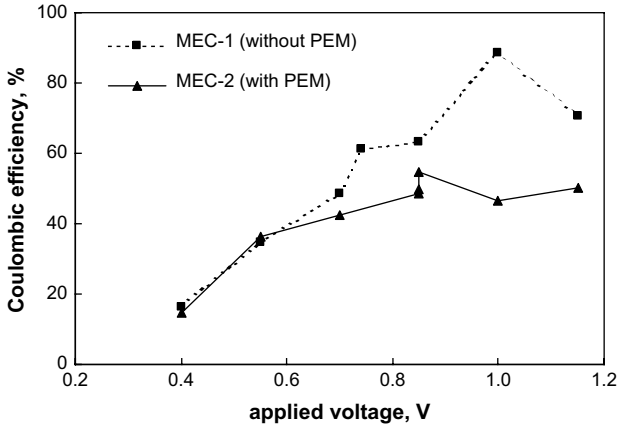


**Fig. 4 – Calculated Coulombic efficiencies in MEC-1 and MEC-2 at different applied voltages and an acetate load of 4 g $L_A^{-1}$ $d^{-1}$.**

Higher power density and decreased internal resistance in a membrane-less MECs have previously been demonstrated for electricity generation [17,18]. Also, electrode separation by a J-cloth was shown to enhance Coulombic efficiency and power density of an air-cathode MFC [18]. Thus far, almost all demonstrations of hydrogen production in a MEC have used a PEM [1–4,12]. It has been argued that the membrane is required to prevent diffusion of methane to the cathodic chamber as well as limit hydrogen diffusion to the anodic chamber [1]. Nevertheless, even in a hydrogen producing MEC equipped with a PEM, methane has been observed in the cathodic chamber [3]. Also, methane production was observed in a single chamber MEC lacking a membrane [9]. This MEC was operated in a batch mode and anode was periodically exposed to air in order to reduce methanogenic activity. The presence of methane in the gas collection chamber has also been observed in our previous study [12], when a PEM was used. Methane production was attributed to microbial contamination of this chamber and cathode fouling. Notably, high humidity of the gas collection chamber combined with the presence of carbon dioxide and hydrogen created conditions suitable for proliferation of hydrogenotrophic methanogens. As a result, the net hydrogen yield was decreased considerably. Similar results were obtained by Rozendal et al. [3], who also used an anaerobic inoculum.

Low internal resistance of membrane-less MEC provided conditions favorable for proliferation of anodophilic microorganisms, which were able to compete with methanogenic populations. In our previous study [12] a significant amount of

acetate was diverged to methanogenic populations of the anodic chamber. While this study used the same type of inoculum, no significant biogas production was observed in the anodic chamber. It can be hypothesized that anodophilic microorganisms proliferated at the anode surface and consumed most of the available carbon source (acetate) thus restricting growth of methanogenic microorganisms, which were present in the inoculum. In general, conditions in the anodic chamber are favorable for the growth of anaerobic methanogenic microorganisms and it might be difficult to avoid proliferation of the methanogens when operating MEC under non-sterile conditions over long periods of time. Therefore, long-term operation of MEC with non-sterilized influents, such as wastewater, requires operational conditions, which will limit proliferation of methanogenic populations. Although this can be achieved by using pure cultures of anodophilic microorganisms, population control aimed at creating growth advantages for the anodophilic microorganisms by MEC operation under optimal conditions (such as applied voltages and substrate loads) might lead to increased density of the anodophilic microorganisms in the biofilm.

## 4. Conclusion

This study demonstrated high rate of hydrogen production in a membrane-less MEC. The absence of a PEM resulted in decreased internal resistance. Electrode separation by a J-cloth allowed for reduced distance between the electrodes, which further minimized ohmic losses and increased volumetric power production. A volumetric hydrogen production rate of 6.3 $L_{STP}\,L_A^{-1}\,d^{-1}$ was achieved under substrate non-limiting conditions at an applied voltage of 1 V, a power input of 2 Wh $L^{-1}$–$H_2$, a hydrogen yield of 3.9 mol $mol^{-1}$–acetic acid, and a current density of 6 A $m^{-2}$. Further increase in volumetric hydrogen production rate and decrease in power input might be expected through optimization of electrode materials, operational conditions, and the use of a biocathode [19–21].

## Acknowledgment

The assistance of Dr. K. Fatih (IFCI–NRC) in the manufacturing of partial MEA is greatly appreciated. This is NRC publication no 49956.

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