Enhanced hydrogen generation using a saline catholyte in a two chamber microbial electrolysis cell

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Abstract

High rates of hydrogen gas production were achieved in a two chamber microbial electrolysis cell (MEC) without a catholyte phosphate buffer by using a saline catholyte solution and a cathode constructed around a stainless steel mesh current collector. Using the non-buffered salt solution (68 mM NaCl) produced the highest current density of $131 \pm 12 \ A/m^2$, hydrogen yield of $3.2 \pm 0.3 \ mol \ H_2/mol \ acetate$, and a gas production rate of $1.6 \pm 0.2 \ m^3 \ H_2/m^3 \ d$, compared to MECs with catholytes externally sparged with CO$_2$ or containing a phosphate buffer. The salinity of the catholyte achieved a high solution conductivity, and therefore the electrode spacing did not appreciably affect performance. The coulombic efficiency with the cathode placed near the membrane separating the chambers was $83 \pm 4\%$, similar to that obtained with the cathode placed more distant from the membrane ($84 \pm 4\%$). Using a carbon cloth cathode instead of the stainless steel mesh cathode did not significantly affect performance, with all reactor configurations producing similar performance in terms of total gas volume, COD removal, $r_{cat}$ and overall energy recovery. These results show MEC performance can be improved by using a saline catholyte without pH control.

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1. Introduction

A microbial electrolysis cell (MEC) is a device that can be used to produce hydrogen from renewable biomass, where bacteria on an anode oxidize organic or inorganic compounds and release electrons to a circuit and protons into water. Electrons and protons combine at the anaerobic cathode generating hydrogen gas on the cathode as long as additional energy is applied to the circuit to make hydrogen production thermodynamically favorable. This process was originally developed by modifying a microbial fuel cell (MFC), which produces electrical power, by omitting the oxygen from the cathode [1]. No membrane is needed between the anode and cathode (single chamber MEC), but it is difficult to avoid methane production in a single chamber MEC. In a two chamber MEC with a membrane, the gas evolved at the cathode is nearly pure hydrogen [2,3]. When a membrane is placed between the electrodes in an MFC or MEC, however, the internal resistance of the system increases, resulting in lower current densities than systems lacking a membrane [4]. In addition, charge is balanced by ions other than protons moving between the electrode chambers. This usually results in acidification of the anode and the alkalization of the cathode, producing a pH imbalance between the anode and cathode chambers [5,6]. To minimize pH imbalances in MECs and MFCs, a phosphate buffer is usually used in these bioelectrochemical systems [7,8], although the use of phosphate for this purpose is not sustainable. Even with relatively high phosphate buffer

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concentrations, the catholyte pH will usually increase above a neutral pH range [7,9], and thus the system will operate at less than optimal pH conditions.

One alternative to a phosphate buffer is a bicarbonate/carbonate buffer [10–12]. Power densities were increased by 39% when a phosphate buffer was replaced with a bicarbonate buffer at the same concentration [12]. Total hydrogen gas obtained by cation and anion exchange membranes (CEM and AEM), and thus the use of a saline solution in the cathode chamber was not examined. AEM), and thus the use of a saline solution in the cathode chamber was not examined.

Although the anode pH should be maintained over a relatively neutral pH range to avoid inhibition of current generation by bacteria, there are no such pH limitations for the cathode solution. It was recently reported that high anolyte and low catholyte pHs in MFCs could be used to significantly improve performance [15,16]. While it is expected that a low catholyte pH would improve performance relative to a neutral pH, it was also found that a higher pH range improved performance as well [17]. This suggests that catholyte pH may not need to be controlled with a buffer. Solution conductivity can be more important than the use of any specific buffer, as a high solution conductivity (20 mS/cm) improved MFC performance independent of the type of buffer [7]. It has been shown that an MEC can be operated without a buffer by using salts to increase conductivity [18]. However, in that study three chambers (anode, recovery, and cathode) were separated by cation and anion exchange membranes (CEM and AEM), and thus the use of a saline solution in the cathode chamber was not examined.

In this study, we examined the use of a saline catholyte solution as an alternative to a phosphate buffered solution (PBS). To examine whether minimizing pH increases in the cathode chamber would affect performance, the catholyte was externally spiked with CO2 and then supplied into the cathode chamber to minimize release of CO2 into the product gas. Hydrogen generation using this approach was compared to that obtained with different buffering systems: a non-buffered catholyte, intermittent addition of CO2-sparged liquid, and a phosphate buffer. The use of a saline catholyte should also effectively remove solution resistances in the cathode chamber, allowing greater flexibility in the location of the cathode in the cathode chamber. We therefore examined whether changing the cathode location relative to the membrane would affect gas production and reactor performance. The cathode used here, which was constructed around a stainless steel mesh, was also compared to more commonly used carbon cloth.

2. Material and methods

2.1. Reactor set up

Two chamber MECs were constructed from two cubes of poly-carbonate drilled to contain a cylindrical chamber 3 cm in diameter and 4 cm long [19,20]. The anode and cathode chambers were separated by an AEM (AMI-7001, Membranes International Inc.), with working volumes of the 28 mL for the anode, and 30 mL for the cathode. A cylindrical glass tube for gas collection was attached on the center of the cathode chamber top, and the tube was sealed using a butyl rubber stopper and an aluminum crimp cap. The anode was heat-treated graphite brush (25 mm diameter × 25 mm length; 0.22 m2 surface area; fiber type; PANEX 33 160 K, ZOLTEK). Two different cathodes were used, stainless steel (SS) mesh and carbon cloth (CC), with both types of cathodes containing a Pt catalyst (50 mg/cm² 10% Pt on Vulcan XC-71 with 33.3 µL/cm² of 5 wt% Nafion solution as binder, projected cross sectional area of 7 cm²). The catalyst was placed on the side of the cathode facing away from the AEM and toward middle of the chamber where the glass tube was located (except as noted) so that the gas could bubble up into the glass collection tube. The SS mesh was type 304 (#60 mesh size, wire diameter 0.019 cm, pore size 0.0023 cm; McMaster-Carr) and the CC was 30% wet-proofed carbon cloth (Type B, E-TEK). Because gas can evolve from both sides of the SS mesh, a section at the top of the mesh was cut and folded back to allow gas bubbles produced to release freely to the solution and headspace to avoid gas accumulation between the mesh cathode and the AEM.

2.2. Experiments and measurements

Anodes were pre-acclimated in MFCs and then transferred to MECs [20]. The MEC was operated by adding 0.9 V using a power supply (model 3645A; Circuit Specialists, Inc.), by connecting the negative lead of the power source in series to a 10 Ø resistor for current measurements and the cathode, with the positive lead on the anode. Voltage across the resistor was measured using a multimeter (Model 2700; Keithley Instruments, Inc.). All reactors were operated in fed-batch mode in duplicate (MEC1 and MEC2) at 30 °C in a constant temperature room.

The anode chambers were fed a solution containing 1.5 g/L sodium acetate and a buffered nutrient medium consisting of a 50 mM PBS (4.58 g/L Na2HPO4 and 2.45 g/L NaH2PO4·H2O, pH = 7.04), 0.31 g/L NH4Cl, 0.13 g/L KCl, trace vitamins and minerals [7]. The initial pH of the anode solution was ~7, and the conductivity 8.1 mS/cm. Three different catholyte solutions were examined with an SS mesh cathode (electrode spacing = 2 cm). The four MECs were initially all operated with 50 mM PBS (MEC_PBS). After obtaining stable performance with this PBS buffer, the catholyte of two of the MECs was shifted to a solution lacking PBS but having a similar conductivity (7.3 mS/cm) due to the addition of 68 mM NaCl (MEC_NaCl). The catholyte of the other two reactors also contained 68 mM NaCl and no PBS but a separate bottle was added to supply CO2-sparged liquid into the cathode chamber (MEC_CO2). This liquid in this separate bottle (40 mL) was sparged with CO2 (pH 4.1) and then recirculated through the cathode chamber at a rate of 0.5 mL/h.

MEC performance was also examined as a function of the cathode distance from the AEM. Except as noted, the SS mesh current collector was always placed 2 cm far from the end of the anode brush with the Pt loading facing away the membrane (MEC_SS2). In some experiments the SS (MEC_SS6) or carbon cloth (MEC_CC6) cathodes were placed at the far end of the cathode chamber (6 cm from the anode brush end), with the Pt catalyst facing toward the membrane to allow the evolved gas
bubbles to flow into the gas collection tube. The 68 mM NaCl solution was used to evaluate MEC performance with different electrode materials and electrode distances.

Gas from the gas collection tube was collected for analysis in gas bags (0.1 L capacity; Cali-5-Bond, Calibrated Instruments Inc.) with the gas volume measured using a respirometer (AER-200; Challenge Environmental). Gas chromatographs (GCs; SRI Instruments) were used to analyze the gas composition in the reactor headspace as well as in the gas bags for H₂, N₂, CO₂ and CH₄ as previously described[8]. Total chemical oxygen demand (COD) of both anolyte and catholyte was measured at the beginning and end of each batch (TNT plus COD Reagent; HACH Company).

2.3. Calculations

The performance of the MECs was evaluated as previously described [21] in terms of: coulombic efficiency (CE, %), based on total coulombs recovered compared to the initial mass of substrate; cathode hydrogen recovery (r_cat, %); and volumetric hydrogen production rate (Q, m³ H₂/m³/d), normalized to the anode working volume. Hydrogen yields (Y, mole H₂/mole acetate) were the moles of hydrogen produced divided by the moles of acetate consumed. The volumetric current density (I_v, A/m³) was an average of the maximum current production over a 2 h period divided by the liquid volume. Energy efficiencies were calculated relative to electrical input (η_e, %) as the ratio of energy content of hydrogen produced to the electrical energy added; and as an overall recovery based on both electric and substrate input (η_e+η_s, %), taking into account both electric and substrate energy input.

3. Results and discussion

3.1. Comparison of different catholytes in two chamber MECs

3.1.1. Current and gas generation

Using PBS in the cathode chamber solution (MEC_PBS) resulted in a peak current of 3.4 ± 0.5 mA (Fig. 1). When the catholyte was changed to a non-buffered salt solution (MEC_NaCl), the current increased to 4.0 ± 0.4 mA (Fig. 1). When an AEM is used in an MEC, negatively charged ions in the cathode will move into the anode chamber through the ion selective membrane to balance charge [22]. As a result of using a high concentration of NaCl in the cathode chamber, Cl⁻ anions moved through the AEM to balance charge. Due to the favorable and high concentration gradient, the rate of charge transfer with Cl⁻ was more efficient than that achieved with phosphate ions, resulting in improved performance of the NaCl catholyte despite the lack of pH control. It was previously reported that high Cl⁻ concentration in the anode chamber could limit anode performance in microbial desalination cells [3]. However, it was found here that higher peak current could be obtained when using a NaCl solution, so Cl⁻ inhibition was not an issue here. Using a CO₂-sparged liquid (recirculated through the cathode chamber; MEC_CO₂) resulted in a current of 3.7 ± 0.4 mA. The maximum volumetric current densities for these different conditions were: I_v = 131 ± 12 A/m³ (MEC_NaCl), 111 ± 16 A/m³ (MEC_PBS), and 113 ± 20 A/m³ (MEC_CO₂). Although the CO₂ addition resulted in a 152% increase in steady state power density compared to PBS in a previous MFC study [13], current generation here using CO₂ (MEC_CO₂) in MECs was similar to that obtained using PBS (MEC_PBS).

As a result of the use of a membrane, the anolyte pH decreased and the catholyte pH increased. The final anolyte pHs ranged from 6.3 ± 0.1 to 6.7 ± 0.1, and two of the catholyte solutions had final pHs of 10.7 ± 0.6 (MEC_PBS) and 10.8 ± 0.7 (MEC_NaCl). The pH of the catholyte in the MEC that was fed a CO₂-sparged solution (MEC_CO₂) was maintained at 8.4 ± 0.8 (range of 7.7–9.1). Because the CO₂-sparged liquid in the storage bottle was recirculated through the cathode, the pH of the liquid in the bottle increased from 4.0 ± 0.1 to 6.6 ± 0.2 after a cycle. These results show that the use of a CO₂-sparged liquid did not improve performance relative to current densities with PBS (MEC_PBS) or only NaCl (MEC_NaCl) despite the lower catholyte pH produced by with CO₂ sparging.

Total gas generation (39 ± 3 mL) was significantly larger (p < 0.03) using the saline cathode (MEC_NaCl) than with the other two catholytes, with nearly pure hydrogen gas produced (Fig. 2), demonstrating that addition of the salt without a buffer improved MEC performance. In contrast, the addition of a phosphate buffer produced 30 ± 6 mL, similar to that obtained with the CO₂-sparged liquid (31 ± 5 mL). The hydrogen...
production rate for MEC NaCl was 1.6 ± 0.2 m$^3$/H$_2$/m$^3$·d, which was also greater than that produced with the PBS or CO$_2$-sparged catholyte (Fig. 2). The hydrogen yield (3.2 ± 0.3 mol H$_2$/mol acetate) was also higher with the saline catholyte than with the other two conditions (2.8 ± 0.6 mol H$_2$/mol acetate, MEC PBS; 2.5 ± 0.4 mol H$_2$/mol acetate, MEC CO$_2$). These results show that it is possible to achieve higher gas production rates and yields when no buffer is added to the cathode chamber if a high catholyte conductivity is used.

### 3.1.2. Efficiencies and energy recovery

Reactor performance was similar in terms of CEs and COD removals for all cathode types, with CEs ranging from 74 ± 11% to 80 ± 8%, and COD removals of 82 ± 7% to 90 ± 4% (Fig. 3). The cathodic hydrogen recoveries were the largest in high salinity MEC, with $r_{cat} = 117 ± 23%$, followed by $r_{cat} = 93 ± 19%$ (MEC PBS) and $r_{cat} = 87 ± 22%$ (MEC CO$_2$). In single chamber MECs, $r_{cat}$ is typically <100% due to hydrogenotrophic methanogens consuming H$_2$ [23]. In the two chamber system used here, the microorganisms growing in the anode chamber were completely separated from the cathode, resulting in high cathodic hydrogen recoveries. The highest overall energy recovery ($\eta_E = 67 ± 6%$) was achieved with high salinity MEC, which had an electrical energy efficiency of $\eta_E = 197 ± 38%$. This overall energy recovery was slightly lower than that previously produced with a single chamber MEC with a plain SS mesh (no Pt catalyst, $\eta_E = 74%$, 0.9 V applied) or a carbon cloth cathode with Pt ($\eta_E = 86%$, 0.8 V applied) [4,19]. Energy recoveries were $\eta_E = 59 ± 12%$ and $\eta_E = 167 ± 46%$ using the phosphate buffer, and $\eta_E = 51 ± 7%$ and $\eta_E = 141 ± 33%$ with the CO$_2$-sparged catholyte.

### 3.2. Effect of electrode spacing and cathode materials

In general, the placement of the cathode (2 or 6 cm) or the type of cathode (SS or CC) did not affect many aspects of MEC performance except for the maximum current density and hydrogen production rate. With the standard SS cathode with a 2 cm electrode spacing, the maximum peak current was 3.7 ± 0.7 mA (MEC SS2), compared to 2.8 ± 0.3 mA for the longer electrode spacing (MEC SS6), and 2.9 ± 0.1 mA when using CC and a larger electrode spacing (MEC CC6) (Fig. 4). The highest volumetric current density ($I_v = 127 ± 22$ A/m$^3$) produced by the MEC SS2 configuration (Table 1) is consistent with higher current production and hydrogen production rates. The highest hydrogen production rate (6.9 ± 0.8 m$^3$ H$_2$/m$^3$·d) was obtained with MEC SS2, which was 1.4 times higher than with MEC SS6, and 1.2 times higher than with MEC CC6. Electrode spacing was therefore important for maximizing current generation and hydrogen production rates despite the
Energy recoveries (and cathodic hydrogen recovery) compared to a phosphate buffered or CO₂-sparged catholyte, with non-buffered, saline solution in the cathode chamber, electrode distance and current collector materials. Results obtained for oxygen reduction in an MFC [24]. Hydrogen production. This result was consistent with previous rates the current collector, performs as well as the CC for less expensive SS type of cathode, which inherently incorporates in the design of two chamber MECs [4,19]. Thus, the use of a saline solution that had high solution conductivity, which minimized solution resistance.

The total volume of gas produced was not affected by the type of cathode or its position in the cathode chamber (33 ± 2–36 ± 1 mL), and nearly pure hydrogen was produced in all cases (Table 1). COD removal efficiency (88%) was the same in all experiments and CEs were similar, ranging from 79 ± 3% to 84 ± 4% (Fig. 5). Hydrogen recovery and energy efficiencies were similar for all reactors, indicating that the electrode distance didn’t affect loss of H₂ through the AEM (Table 1). Energy recovery based on electrical input ranged from 147 ± 9% to 152 ± 2%, with overall energy recoveries of 56 ± 2% to 59 ± 3%. These values are slightly lower than those obtained using single chamber MECs due to larger internal resistance inherent in the design of two chamber MECs [4,19]. Thus, the less expensive SS type of cathode, which inherently incorporates the current collector, performs as well as the CC for hydrogen production. This result was consistent with previous results obtained for oxygen reduction in an MFC [24].

4. Conclusions

The highest hydrogen yield (Y = 3.2 ± 0.3 mol H₂/mol acetate) and production rates (Q = 1.6 ± 0.2 m³ H₂/m³ d) were obtained with non-buffered, saline solution in the cathode chamber, compared to a phosphate buffered or CO₂-sparged catholyte, even though the pH of the non-buffered solution substantially increased from 7.0 to 10.8 ± 0.7. This system also had the highest energy efficiency relative based on only electrical energy input (ŋₑ = 197 ± 38%) or substrate and electrical energy (ŋₑ+S = 67 ± 6%) relative to the two other catholyte solutions. A reduced electrode distance between the anode and the cathode increased the peak current density and hydrogen gas production rate, but otherwise did not significantly affect overall performance. COD removal efficiencies (88%), CEs (83–84%), and cathodic hydrogen recoveries (ŋₑ+S = 87–90%), and overall energy recoveries (ŋₑ+S = 57–59%) were not affected by electrode distances. A comparison of the SS cathode with a carbon cloth cathode demonstrated that the two types of electrodes coated with Pt produced similar results. Thus, the SS mesh (ca. $50/m²) based cathode is a more economical alternative to the carbon cloth (ca. $1000/m²) for hydrogen production in MECs as well as in MFCs, and using saline catholytes is an inexpensive method of improving MEC performance. These results suggest that using non-sustainable phosphate buffer is not needed, and that a saline solution such as NaCl or seawater can be used just as effectively in the cathode chamber. Examination of different salinities and feasibility tests of other saline solutions such as seawater are needed in future MEC tests under continuous flow conditions.

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References

[12] Fan YZ, Hu HQ, Liu H. Sustainable power generation in microbial fuel cells using bicarbonate buffer and proton...


