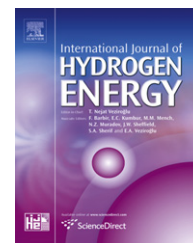




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# Enhanced hydrogen generation using a saline catholyte in a two chamber microbial electrolysis cell

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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  $131 \pm 12 \text{ A/m}^2$ , hydrogen yield of  $3.2 \pm 0.3 \text{ mol H}_2/\text{mol acetate}$ , and gas production rate of  $1.6 \pm 0.2 \text{ m}^3 \text{ H}_2/\text{m}^3 \cdot \text{d}$ , compared to MECs with catholytes externally sparged with  $\text{CO}_2$  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,  $r_{\text{cat}}$  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 generated in the MEC was similar using either a bicarbonate or phosphate buffer. Carbon dioxide (CO<sub>2</sub>) gas addition for pH control has previously been used in MFCs, but not MECs [13,14]. Adding CO<sub>2</sub> directly into the catholyte of MECs at a pH lower than 6.4 ( $pK_{a1} = 6.352$  at 25 °C) should be avoided, as this would reduce the concentration of H<sub>2</sub> gas as a result of dilution with CO<sub>2</sub> in the product gas.

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 sparged with CO<sub>2</sub> and then supplied into the cathode chamber to minimize release of CO<sub>2</sub> into the product gas. Hydrogen generation using this approach was compared to that obtained with different buffering systems: a non-buffered cathode, intermittent addition of CO<sub>2</sub>-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 polycarbonate 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 m<sup>2</sup> 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/cm<sup>2</sup> 10% Pt on Vulcan XC-71 with 33.3 μL/cm<sup>2</sup> of 5 wt% Nafion solution as binder, projected cross sectional area of 7 cm<sup>2</sup>). 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 Ω 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 Na<sub>2</sub>HPO<sub>4</sub>, and 2.45 g/L NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, pH = 7.04), 0.31 g/L NH<sub>4</sub>Cl, 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 CO<sub>2</sub>-sparged liquid into the cathode chamber (MEC\_CO<sub>2</sub>). This liquid in this separate bottle (40 mL) was sparged with CO<sub>2</sub> (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

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