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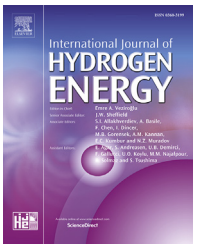

Hydrogen production rates with closely-spaced felt anodes and cathodes compared to brush anodes in two-chamber microbial electrolysis cells

Emily Zikmund, Kyoung-Yeol Kim, Bruce E. Logan *

Department of Civil and Environmental Engineering, The Pennsylvania State University, 231Q Sackett Building, University Park, PA, 16802, USA

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ABSTRACT

Flat anodes placed close to the cathode or membrane to reduce distances between electrodes in microbial electrolysis cells (MECs) could be used to develop compact reactors, in contrast to microbial fuel cells (MFCs) where electrodes cannot be too close due to oxygen crossover from the cathode to the anode that reduces performance. Graphite fiber brush anodes are often used in MECs due to their proven performance in MFCs. However, brush anodes have not been directly compared to flat anodes in MECs, which are completely anaerobic, and therefore oxygen crossover is not a factor for felt or brush anodes. MEC performance was compared using flat felt or brush anodes in two-chamber, cubic type MECs operated in fed-batch mode, using acetate in a 50 mM phosphate buffer. Despite placement of felt anodes next to the membrane, MECs with felt anodes had a lower hydrogen gas production rate of 0.32 ± 0.02 m^3-H_2/m^3-d than brush anodes (0.38 ± 0.02 m^3-H_2/m^3-d). The main reason for the reduced performance was substrate-limited mass transfer to the felt anodes. To reduce mass transfer limitations, the felt anode electrolyte was stirred, which increased the hydrogen gas production rate to 0.41 ± 0.04 m^3-H_2/m^3-d. These results demonstrate brush electrodes can improve performance of bio-electrochemical reactors even under fully anaerobic conditions.

Introduction

Microbial electrolysis cells (MECs) are being investigated as a method of renewable hydrogen gas production using waste biomass [1–7]. Exoelectrogenic bacteria on the anode of an MEC use biodegradable organic matter, for example in wastewaters or fermentation effluents, as the fuel for current generation, with hydrogen gas produced electrochemically at the cathode [8,9]. The voltage produced by the bacteria is not sufficient to generate hydrogen gas at the cathode, and thus voltage must be added to the circuit to drive electrochemical hydrogen production [5,8,10]. MECs are therefore a green method for hydrogen gas production as long as the additional energy required for MEC operation is supplied by a renewable energy source such as solar, wind, salinity gradient energy, or by waste biomass powered microbial fuel cells (MFCs) [11,12]. Electrical power is generated in MFCs using the same type of anode and reactor structure as an MEC, with an exoelectrogenic biofilm on the anode, but oxygen is used as the final

* *Corresponding author.*
E-mail address: blogan@psu.edu (B.E. Logan).

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electron acceptor at the cathode in an MFC producing a spontaneous reaction [13].

To maximize hydrogen gas production rates per volume of reactor in MECs, or current generation in MFCs, thin electrode chambers should be used in order to provide a high specific electrode surface area of the electrodes (area of electrodes per volume of reactor) [14–17]. Placing the electrodes close to each other not only produces a more compact reactor design, the close electrode spacing also reduces the internal resistance of the system by minimizing the solution resistance. However, when flat electrodes were used in MFCs with an electrode spacing of <2 cm, power was decreased despite the reduction in solution resistance, due to oxygen crossover from the cathode to the anode [18,19]. In the presence of dissolved oxygen, the anode potential becomes more positive which reduces the voltage and therefore power production. With cylindrical-shaped graphite fiber brush anodes, however, a more negative anode potential is maintained even when the brush is very close to the air-cathode (<0.5 cm), resulting in high power generation [20,21]. Thus, power densities in MFCs with brush anodes placed close to the cathode (1.36 ± 0.20 W/m^2 for studies in our laboratory at Penn State, or 1.11 ± 0.45 W/m^2 at many different locations [22]) are higher than those with flat carbon cloth or felt anodes (1.05 W/m^2 in our laboratory using carbon felt [23], compared to 0.79 ± 0.19 W/m^2 using carbon felt and 0.51 ± 0.00 W/m^2 using carbon cloth at different locations) [22]. The impact of flat anode size and electrode spacing has been extensively tested in MFCs [23–29] but not in MECs. In one study where the thickness of the anode was examined in an MEC with a cloth separator between the electrodes, the current increased by using a thicker anode, but net hydrogen gas production did not improve [24]. The main reason for a lack of improved hydrogen recovery was likely hydrogen gas crossover to the anode, as this can enhance current production but not increase hydrogen gas recovery (hydrogen gas is consumed by anodic bacteria or loss of hydrogen to methane production) [30–33]. While the use of an ion exchange membrane can reduce hydrogen losses [34,35], flat and brush anodes have not been compared in two chamber MECs with closely-spaced electrodes and an ion exchange membrane as the separator.

In this study, we compared the performance of flat felt anodes to commonly used brush anodes in MECs using typical fuel (acetate), electrolyte (50 mM phosphate buffer), and reactor conditions (3 cm diameter, cube shaped reactors) [22]. Both the felt and brush anodes were placed adjacent to the ion exchange membrane to minimize ohmic resistances. MEC performance was compared by measuring the current densities, total hydrogen production rates and chemical oxygen demand (COD) removals based on a complete fed-batch cycle, and energy recoveries relative to the electrical energy consumed by the systems.

Materials and methods

Anodes and their acclimation in MFCs

Two types of anodes were examined for performance in MFCs and MECs, cylinder-shaped graphite fiber brush anodes, and flat disc-shaped felt anodes. Brush anodes (2.5 cm length, 1.5 cm diameter, encased volume of 4.4 cm^3) were made from carbon fibers twisted between two titanium wires (PANEX 33 160K, ZOLTEK) [21,36]. Carbon felt anodes (0.64 cm thick, Alfa Aesar, Ward Hill, MA) were cut into circles with a 7 cm^2 cross sectional surface area (encased volume of 4.5 cm^3) [23]. Both types of anodes were acclimated for stable current generation in single chamber MFCs prior to their use in MECs. Brush anodes were placed across the middle of the 2 cm wide anode chamber (14 mL volume), so that the stem was parallel to the cathode reactor, with only a small gap (calculated to be 0.25 cm, but in effect only <0.3 cm based on variations in brush fiber lengths) between the brush outer surface and the cathode (Fig. S1a). While this configuration resulted in a brush that did not fully cover the cathode, which can lower power production relative to complete surface coverage [25,37], this placement enabled the use of a 2.5 cm long brush in a 2 cm wide chamber due to its 1.5 cm diameter. To minimize the impact of oxygen intrusion on felt anode acclimation in MFCs, the felt anodes were placed on the opposite side of the chamber from the cathode in 4 cm long reactors with a volume of 28 mL, instead of the 2 cm long chambers [37]. All anodes were heat treated for 30 min at 450 °C in a muffle furnace before being placed into the MFCs [36]. The cathodes for the MFCs were activated carbon cathodes produced by VITO (Mo, Belgium) [38–40].

MEC reactor configuration

Two chamber MECs were constructed that had 3 cm diameter chambers formed in cubes of polycarbonate, with 2 cm long anode chambers and 4 cm long cathode chambers (28 mL of liquid with 7 mL in headspace) (Fig. 1) [34]. The anode and cathode chambers were separated by an AEM (anion exchange membrane, Selemion AMV, AGC Engineering Co. Ltd., JP). The anode chambers for the brush anodes were the same as those used in the MFCs. The lengths of the anode chambers for the MFCs with felt anodes were changed to 2 cm. The felt anodes were removed from the MFCs and placed against the AEM, with a ring of titanium foil pressed against the felt to function as a current collector. The working volumes of the anode chambers were 16 mL for the brush anode (with minimal water displacement by the electrode), and 14 mL for the felt anode (2 mL water displacement). The smaller volume of water for the felt anode was due to the water displacement for the lower porosity felt anode, the volume displaced by the gasket to hold it in place, and the curvature (bowing out) of the felt that trapped some water between the felt and the membrane so that it was not replaced when the fluid in the MEC was changed (Fig. 1). For the brush anode MEC, the brush anode spanned a distance of 0.25–1.75 cm of the 2 cm thick chamber (although it did not fully cover the AEM), while the felt anode extended only 0.64 cm into the fluid but completely covered the AEM.

The cathodes for all reactors were discs of stainless steel mesh (7 cm^2) containing a platinum catalyst and carbon black (0.5 mg/cm^2, 10% Pt and Vulcan XC-72), with a Nafion binder (5 wt% solution, Aldrich Nafion® perfluorinated ion-exchange resin) as previously described [34]. Cathodes were placed 1 cm from the AEM to avoid trapping hydrogen gas between the

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