Performance of two different types of anodes in membrane electrode assembly microbial fuel cells for power generation from domestic wastewater

Sarah Hays, Fang Zhang, Bruce E. Logan *

Department of Civil & Environmental Engineering, Penn State University, 231Q Sackett Building, University Park, PA 16802, USA

ARTICLE INFO

ABSTRACT

Graphite fiber brush electrodes provide high surface areas for exoelectrogenic bacteria in microbial fuel cells (MFCs), but the cylindrical brush format limits more compact reactor designs. To enable MFC designs with closer electrode spacing, brush anodes were pressed up against a separator (placed between the electrodes) to reduce the volume occupied by the brush. Higher maximum voltages were produced using domestic wastewater (COD = 390 ± 89 mg L^{-1}) with brush anodes (360 ± 63 mV, $1000\,\Omega$) than woven carbon mesh anodes (200 ± 81 mV) with one or two separators. Maximum power densities were similar for brush anode reactors with one or two separators after 30 days (220 ± 1.2 and 240 ± 22 mW m^{-2}), but with one separator the brush anode MFC power decreased to 130 ± 55 mW m^{-2} after 114 days. Power densities in MFCs with mesh anodes were very low (<45 mW m^{-2}). Brush anodes MFCs had higher COD removals ($80 \pm 3\%$) than carbon mesh MFCs ($58 \pm 7\%$), but similar Coulombic efficiencies ($8.6 \pm 2.9\%$ brush; $7.8 \pm 7.1\%$ mesh). These results show that compact (hemispherical) brush anodes can produce higher power and more effective domestic wastewater treatment than flat mesh anodes in MFCs.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Microbial fuel cells (MFCs) are being explored as a new approach to wastewater treatment due to their ability to remove organic matter as well as generate electrical power [1]. The most promising designs use an air cathode in order to avoid the need for non-sustainable reactions at the cathode, as well as to alleviate the need for aerating water [2]. Power production is affected by a number of factors, including solution conductivity, organic matter concentration, electrode materials, and reactor architecture [3]. For low conductivity solutions, such as domestic wastewater, it is important to use MFC designs with little separation between the electrodes in order to minimize ohmic losses [3]. This requires the use of a membrane or separator between the electrodes in order to avoid electrode contact, which would result in short circuiting, as well as to reduce oxygen transfer from the cathode to the anode. It has been found that placing the electrodes within 2 cm or less can result in a reduction of power in the absence of a membrane or separator [4,5].

Reactor designs with the electrodes placed on either side of a membrane or separator are commonly referred to as membrane electrode assembly (MEA) MFCs [6]. The characteristics of the separator are critical to reactor performance. If the pore sizes and porosities are too small proton transfer to the cathode is restricted, reducing current and power densities [7]. If the porosity is too large then oxygen transfer from the cathode to the anode reduces power densities and lowers Coulombic efficiencies due to the bacteria using oxygen rather than transferring electrons to the anode. Cloth and glass fiber separators have been found to be the most effective at maintaining higher power densities and reducing oxygen transfer, although the cloth can be degraded over time [7]. Better performance of an MFC has been obtained using graphite fiber brush anodes instead of flat carbon cloth anodes [6,8]. However, the brush can occupy a large volume of the reactor, limiting the design of reactors with a large number of electrodes. One of the main goals in developing MEA designs is to obtain increased electrode packing (decreased spacing), and therefore more compact reactor designs. The electrode spacing should not be too close, however, as this could potentially lead to reactor plugging with biofilm especially when treating wastewaters containing high concentrations of particulate matter.

In this study we examined a MEA architecture based on placing the anode as close as possible to the cathode by compressing a brush anode against the separator. This resulted in the brush having a hemispherical shape, reducing by half the space needed for the brush electrode. In order to compare the performance of this anode configuration to a completely flat anode design, we also examined the use of a carbon mesh anode similarly placed against the separator (Fig. 1). Carbon mesh is much less expensive than carbon paper or carbon cloth materials designed for fuel

---

* Corresponding author. Tel.: +1 814 863 7908; fax: +1 814 863 7304.
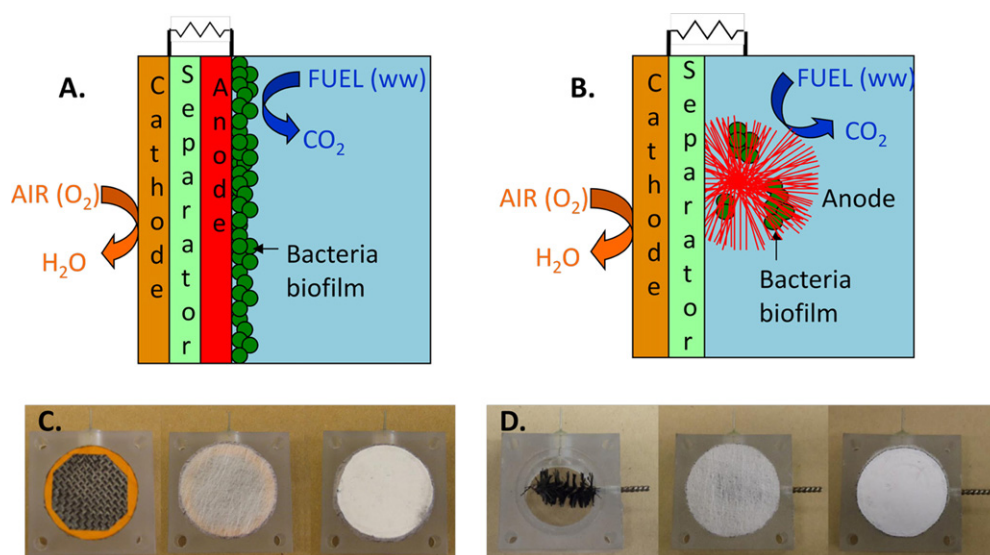E-mail address: blogan@psu.edu (B.E. Logan).

Fig. 1. Membrane electrode assembly reactor configurations with carbon mesh anodes M-GFI or M-GF2 (A) and (C) and brush anodes B-GF1 and B-GF2 (B) and (D). (A) and (B) are chemical processes schematics; (C) and (D) are construction progression photographs, with a scale of 1.0:2.5 cm.

cells, and they have been shown to produce higher power densities than carbon cloth in MFCs lacking separators [9]. Most MFC tests with separators have been conducted using highly buffered solutions to minimize ohmic resistances, and using high concentrations of a substrate (usually acetate) to achieve much higher power densities than those typically produced with domestic wastewaters. If a high conductivity solution is used the solution resistance is small even if the electrodes are several centimeters from each other. High current densities can result in greater consumption of the oxygen diffusing into the anode chamber, and thus may not reflect operational conditions that would be encountered when using wastewater. Therefore, we examined performance of these closely spaced anode configurations using domestic wastewater with a relatively low conductivity and concentration of organic matter. Several different types of materials were also added to the outside of the cathode in order to examine if performance of the MFCs treating wastewater could be improved by reducing oxygen transfer to the anode. The performance of brush and mesh designs was also examined using acetate in a buffered solution in order to benchmark results against previously tested designs.

2. Materials and methods

2.1. MFC construction

Cube shaped MFCs with a cylindrical chamber (7 cm^2 cross section, 2 cm long, 14 mL) were constructed as previously described from a single block of Lexan [4]. Carbon mesh anodes (Gaojieshi Graphite Products Co., Ltd., Fujian, China) were cut into circles with a projected surface area of 7 cm^2. Tape was placed around the edges of the mesh before they were cut in order to minimize fraying or unfolding of the loosely woven mesh. Brush anodes (15 mm diameter by 25 mm length) were made from carbon fibers (PANEX 33 160K, ZOLTEK) held between twisted titanium wire [8]. All anodes were heat treated for 30 min at 450 °C before use [10]. Cathodes were made of activated carbon (AC) (VITO, Mol Belgium) as previously described, in order to avoid the need for precious metal catalysts [11]. The outer PTFE diffusion layers had porosities of either 30% or 70% as indicated. Throughout the tests cathodes were cleaned to minimize biofilms on their surface (using a thin razor blade) or replaced with new cathodes in order to minimize any

adverse effects of the cathode on our evaluation of anode and separator performance.

Electrodes were placed on either side of the separator during tests (except as noted during startup) (Fig. 1). Two types of separator materials were used: a glass fiber (GF) mat similar to that previously tested as a separator [7]; and a more durable material pulp laminated glass fiber (PG) mat (Specialty Glass Products, NSG Co., Ltd.). The GF thickness was 1.2 mm (basis weight = 150 g m^{-2}; ρ = 0.13 g cm^{-3}), and either one layer (1.2 mm) or two layers (2.4 mm) were used in tests. The PG separator had a thickness of 2.4 mm (basis weight = 290 g m^{-2}; ρ = 0.24 g cm^{-3}). Separators were replaced during experimentation, as noted, to avoid their deterioration affecting power generation and thus our evaluation of the performance of the anodes. The separator and anode materials used in the MFCs were differentiated by codes with B-GF1 for the brush anode with a single 1.2 mm GF separator (30% porosity AC cathode), and B-GF2 with two separators (total thickness of 2.4 mm) (30% porosity AC cathode). Similarly the mesh anode configurations were M-GF1 and M-GF2 indicating one or two separators (30% porosity AC cathodes).

Additional tests were conducted using materials placed on the outside of the cathode to restrict oxygen transfer and therefore function as diffusion layers. Two materials were used: polydimethylsiloxane (PDMS); and generic plastic wrap. PDMS was made using a 10:1 mixture of SYLGARD 184 silicone elastomer base:elastomer curing agent. This mixture was diluted to various weight percents using toluene to decrease the solution viscosity, which allowed for consistent layers to be applied to each cathode via an airbrush sprayer (Paasche Airbrush Company, VL1007). Two different drying procedures were used. Initially, after applying each layer, the cathodes were air dried for a short time (1 h) and then heated at 80 °C for 30 min to cure the polymer (PS). However, during testing of the cathodes before use in MFCs it was seen that bubbles formed in the multiple PDMS layers which were applied to the cathodes used in the PS setup. It was assumed that this physical change was due to incomplete curing of the PDMS mixture after spraying. Therefore, a longer dry cure time was used (24 h) followed by 30 min heat curing at 80 °C (PL), which resulted in a more stable single layer of PDMS. Additional diffusion layers were also examined by adding one (G1) or two (G2) layers of plastic wrap (distributed by Target Corporation primarily for use in food preservation) on the air side of the cathodes. The plastic wrap diffusion

layers were held between the reactor body and the gasket facing the outer reactor end plate. MFC tests on additional diffusion layers were conducted with the 2.4 mm PG separator and a 70% porosity AC cathode, with designations of PS-PG or PL-PG for the PDMS diffusion layers, and G1-PG or G2-PG for one or two layers of the generic plastic wrap. MFCs tested without additional diffusion layers were indicated solely by the separator as PG and GF2.

2.2. MFC operation

Domestic wastewater collected from the primary clarifier effluent at the Penn State University wastewater treatment plant was used as both an inoculum and feed solution. No additional buffer, vitamins, or minerals were added to the wastewater. Wastewater samples were stored at 4 °C, and new samples were collected approximately every two weeks.

Experiments were conducted in duplicate in a constant temperature room (30 °C). The inoculation procedure consisted of filling the reactor body with wastewater daily until bacteria in the wastewater colonized the electrode and began to produce electricity. The MFC was then operated in fed-batch mode, with the MFC refilled when the voltage dropped below 30 mV (1000 Ω external resistance). MFCs were usually started up in the MEA configuration. However, in initial tests the carbon mesh anode MEAs did not produce current. Therefore, these anodes were first acclimated by placing the anodes on the far side of the chamber in MFCs with a 4 cm electrode spacing [4] produced by using two reactor bodies (each 2 cm long) connected in series with a rubber gasket to prevent leakage. Once stable current was produced, one of the 2 cm pieces was removed, and the anode was moved into the MEA configuration.

2.3. Calculations and measurements

Voltages were measured every 20 min using a data acquisition system (Model 2700, Keithley Instrument). Current, I [mA], was calculated according to $I = E/R_{ex}$, where E is the voltage [mV] and R_{ex} is the external resistance [Ω]. Power, P [mW], was calculated according to $P = IE/1000$. Current density [mA cm^{-2}] and power density [mW m^{-2}] were determined by normalizing by the cross sectional area of the cathode, A [cm^2] and applying appropriate unit conversions. Polarization curves were initially obtained by the single-cycle method using multiple resistances over a single fed-batch cycle (open circuit to 200 Ω, 20 min per resistor), as previously described [10]. In order to try to minimize power overshoot [10], a multiple cycle method was used in latter tests (as indicated) by running the reactor at a different fixed resistance for a complete fed-batch cycle.

Anode potentials were measured using reference electrodes (RE-5B; BASi, West Lafayette, IN). Cathode potentials were calculated as the difference between the anode and whole cell potentials. All potentials were reported with respect to a Ag/AgCl reference electrode [12].

COD removal (ΔCOD) [%], was calculated based on the initial and final COD. Coulombic efficiency (CE) [%] was based on measured COD removal and four electrons per mole of COD [1]. Chemical oxygen demand (COD) was measured using standard methods [Method 5220, APHA et al., 1995; high range (20–1500 mg L^{-1}) HACH COD system (Hach Co., Loveland, CO)] [5,13]. Biological oxygen demand was determined using a three-day headspace BOD (HBOD$_3$) test [14]. HBOD$_3$ concentrations have been shown for wastewater at the Penn State University treatment plant to be equivalent to five-day biochemical oxygen demand (BOD$_5$) concentrations [15]. Therefore, BOD$_5$ concentrations were estimated assuming a typical COD:BOD$_5$ ratio of 2 [16]. Probes were used to measure pH (Mettler Toledo Seven Multi; Model: pH; S/N: 290843) and conductivity (Mettler Toledo Seven Multi; Model: Cond.; S/N: 291048).
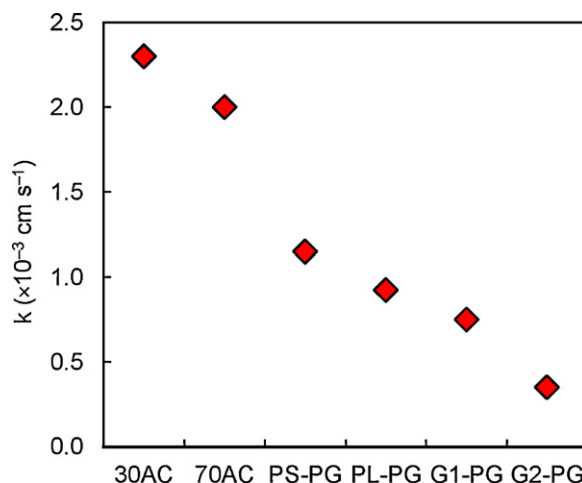

Fig. 2. Oxygen transfer coefficients (k-values) for reactor configurations with additional diffusion layers. AC refers to a VITO activated carbon cathode with no additional diffusion layers and 30 and 70 refer to different cathode porosities.

Oxygen mass transfer coefficients (k) were measured for cathodes prior to their use in MFCs. Dissolved oxygen (DO) measurements were taken in constantly stirred cells (4 cm cube reactors filled with distilled water) using a fiber optic dissolved oxygen probe (FOXY oxygen probe, SF2000, Ocean Optics, Dunedin, FL). Prior to each test the reactor was filled in an anaerobic glove box with degassed water. Tests were conducted for at least 3 h (in duplicate) with oxygen concentrations collected every 1 s. The mass transfer coefficient, k [cm s^{-1}], was calculated [17] using $k = (-v_{an}/At) \ln(C_s - C/C_s)$, where v_{an} is the volume of the anode [28 mL], t the time [s], C_s the saturation oxygen concentration (7.63 mg L^{-1}), and C the measured oxygen concentration [mg L^{-1}]. The corresponding mass transfer coefficient for each cathode setup was measured prior to experiments (Fig. 2).

3. Results

3.1. Performance of anode materials with GF separators

The MFCs with brush anodes maintained stable voltage generation over time, averaging 350 ± 35 mV (B-GF1) and 370 ± 35 mV (B-GF2), or 360 ± 59 mV on average for one or two separators (1000 Ω external resistor). The average voltages achieved by the mesh reactors were 87 ± 63 mV (M-GF1) and 200 ± 82 mV (M-GF2), or 140 ± 91 mV on average. Sudden increases in the voltages of the mesh reactors were attributed to periodic separator and cathode replacement (Fig. 3).

After 30 days of operation, the maximum power densities of the brush reactors were quite similar, averaging 240 ± 22 mW m^{-2} (B-GF2) and 220 ± 1.2 mW m^{-2} (B-GF1). The mesh anode MFC with two separators produced a similar power density at 230 ± 3.3 mW m^{-2} (M-GF2) but the MFC with the thinner separator had a much lower power density of 80 ± 9.6 mW m^{-2} (M-GF1).

After 114 days, the power density of the brush anode MFC with two separators remained constant at 230 ± 9.3 mW m^{-2} (B-GF2), while the MFC with only a single separator decreased to 130 ± 55 mW m^{-2} (B-GF1) (Fig. 4). Both mesh anode MFCs had much lower performance after 114 days of operation, with similarly low power densities of 45 ± 12 mW m^{-2} (M-GF2) and 42 ± 15 mW m^{-2} (M-GF1).

The variations in performance of the MFCs with the different anodes was due to the anode potentials. The two brush MFCs had the most negative anode potentials (B-GF1: −360 mV, B-GF2: −410 mV), resulting in the largest whole cell potentials (Fig. 5).
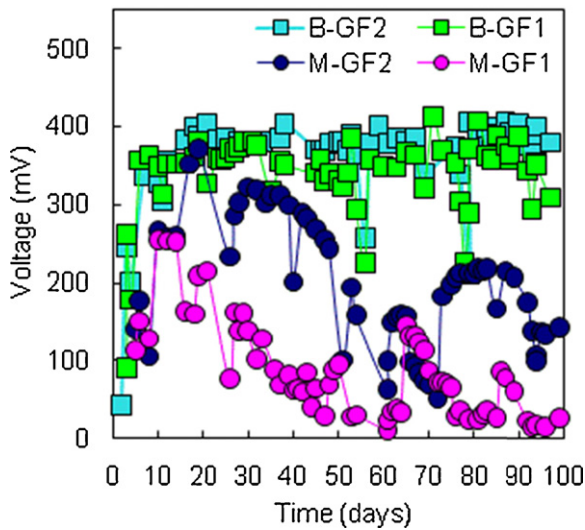
Fig. 3. Voltage profile for membrane electrode assembly reactor configurations, where "voltage" refers to the maximum voltage achieved during each feed cycle.

The anode potentials of both brush MFCs improved over time and became slightly more negative. In contrast, the mesh anode potentials were much more positive, with +60 mV for the mesh anode with a single separator on day 54 (M-GF1), and −85 mV on day 86. The anode potential of the mesh MFC with two separators (M-GF2) was more negative (−340 mV) after 54 days, but it became slightly
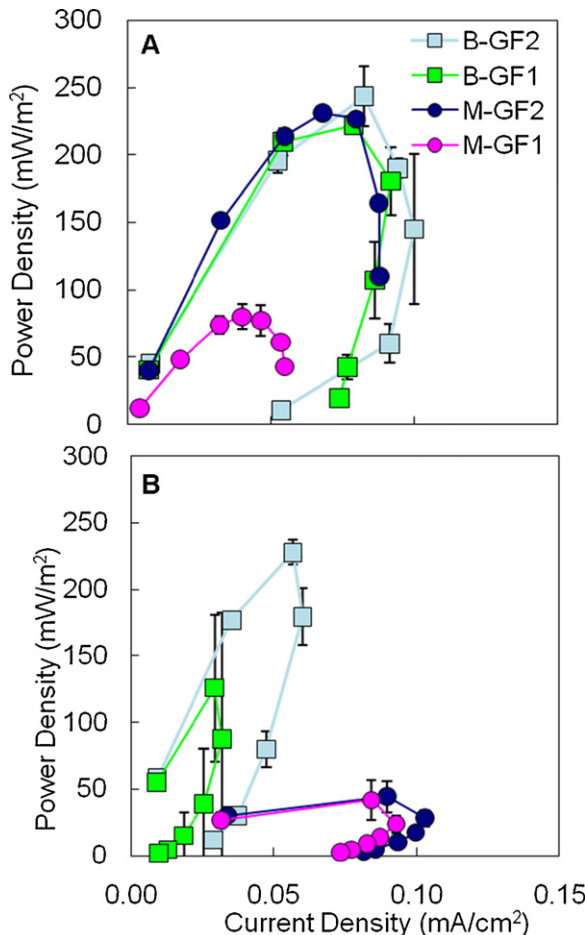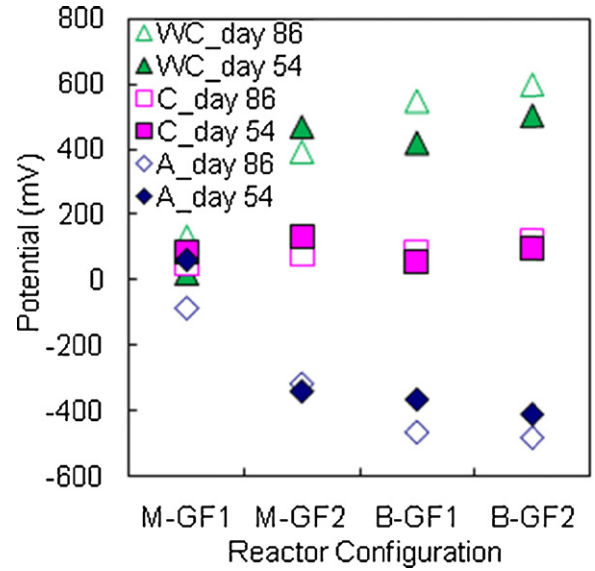

Fig. 5. Electrode potentials for membrane electrode assembly reactor configurations at two time points, where WC represents "Whole Cell", C represents "Cathode", and A represents "Anode" potentials.

more positive over time resulting in a decrease in the whole cell potential.

3.2. Performance of mesh anode MFCs with additional cathode diffusion layers

Additional experiments were conducted with the mesh anode MFCs with a different separator and with different diffusion layers, in order to try to achieve performance similar to that obtained with the brush anode MFCs. In all cases, adding diffusion layers to the MFCs improved performance relative to controls lacking these additional materials. The control (PG) produced an average voltage of 180 ± 65 mV, similar to that of the control with the two glass fiber separators (GF2: 170 ± 52 mV). The MFC with the two layers of plastic wrap produced the highest average voltage of 310 ± 52 mV (G2-PG) (Fig. 6). Maximum voltages decreased for the other reac-

Fig. 4. Power density curves for membrane electrode assembly reactor configurations at day (13) (A) and at day 102 (B).
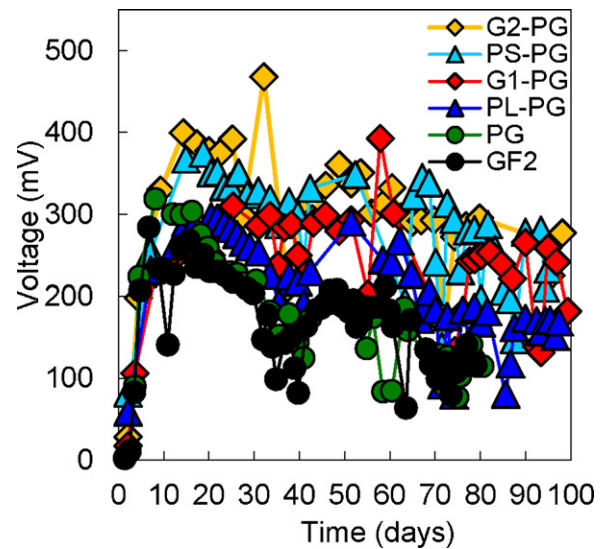

Fig. 6. Voltage profile for membrane electrode assembly reactor configurations with additional diffusion layers, where "voltage" refers to the maximum voltage achieved during each feed cycle. A pulp laminated glass fiber (PG) separator was used with generic plastic wrap (G) or PDMS (P) diffusion layers.
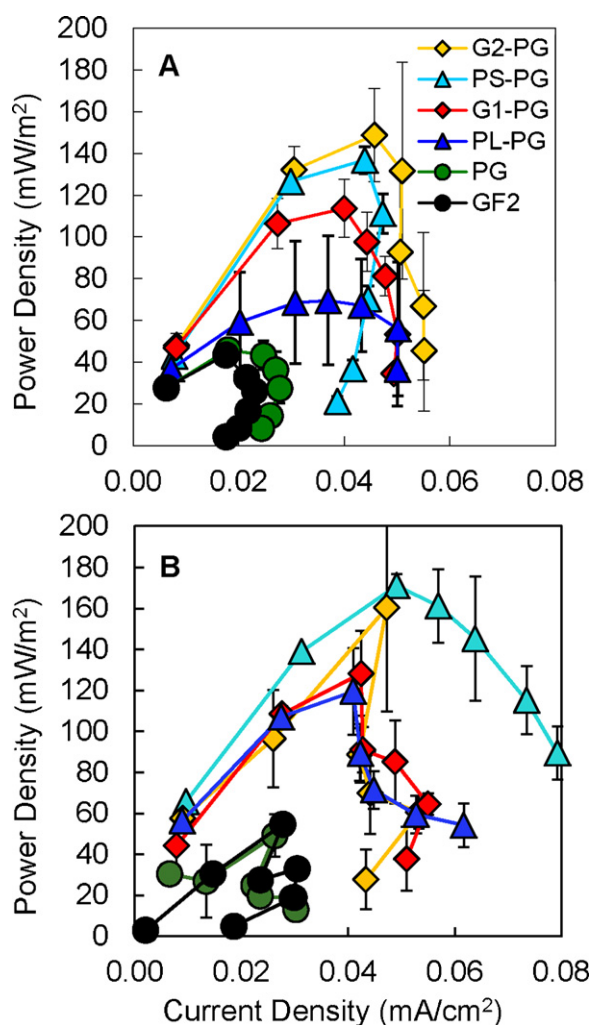
Fig. 7. Power density curves for membrane electrode assembly reactor configurations with additional diffusion layers using (A) single-cycle and (B) multiple-cycle polarization methods.

tors in the order 280 ± 62 mV (PS-PG), 250 ± 53 mV (G1-PG), and 210 ± 59 mV (PL-PG).

Maximum power densities followed the same trend as voltage, with the highest power density from the MFC with two layers of plastic wrap of 150 ± 22 mW m^{-2} (G2-PG). The maximum power densities for the other MFCs decreased in the order 140 ± 6.4 mW m^{-2} (PS-PG), 110 ± 14 mW m^{-2} (G1-PG), and 70 ± 31 mW m^{-2} (PL-PG). The maximum power densities were similar and much lower for the MFCs lacking the additional diffusion layers (PG: 46 ± 2.4 mW m^{-2}, GF2: 44 mW m^{-2}). Substantial power overshoot was observed in the power density curves obtained using the single-cycle method, as seen by a doubling back of the power density curve at lower resistances (Fig. 7A). Performing multiple-cycle polarization tests delayed the onset of power overshoot, but it did not entirely prevent it (Fig. 7B). Maximum power densities in all of these tests were lower than originally obtained with the best performing mesh MFC (M-GF2: 230 mW m^{-2}). This could have been due to changes in the wastewater composition over time, but more likely it reflected the continued difficulty of starting up and achieving good performance with mesh anode MFCs.

One operational problem encountered with using plastic wrap as a diffusion layer was that in some (but not all) reactors there was a buildup of liquid between the cathode and the plastic wrap. The inconsistency of the liquid accumulation in different reactor configurations was probably due to a poor seal between the plastic wrap and cathode, allowing fluid to leak out rather than accumu-

late. This accumulation of water could be avoided in future designs by using rigid plastic mesh to press the electrodes together, avoiding the possibility of liquid accumulation. The presence of a water film would likely have reduced oxygen mass transfer through the cathode from gas to liquid phase. The oxygen mass transfer through liquid is four orders of magnitude slower than that through gas, and therefore the liquid accumulation may have accounted for some of the dissimilar results found using plastic wrap diffusion layers (G1-PG and G2-PG).

The anode and whole cell potentials were measured for the two best performing MEA reactors with additional diffusion layers (G2-PG and PS-PG) during each external resistance (R_{ex}) of the multiple-cycle power density curve. The brush control anode potentials remained relatively constant (-400 ± 60 mV) for all resistances examined (data not shown). However, the average anode potentials of the reactors with additional DLs were more positive than the brush controls, especially during tests with lower resistances, averaging -200 ± 140 mV (G2-PG) and -120 ± 140 mV (PS-PG). This suggests that the more positive anode potentials contributed to the resulting power overshoot.

3.3. Coulombic efficiencies

From days 62–93 of operation the CEs for the brush anode MFCs were slightly higher (B-GF1: 5.6%, B-GF2: 7.2%) and in general more consistent than MFCs with mesh anodes (M-GF1: 1.8%, M-GF2: 4.6%) (Fig. 8A). This trend of higher CEs for the brush anodes was generally observed for the remainder of the tests.

Adding diffusion layers increased CEs. For example, on day 34 the CEs were $15 \pm 2.6\%$ (G2-PG), $12 \pm 2.6\%$ (PS-PG), $11 \pm 1.3\%$ (G1-PG), and $11 \pm 1.3\%$ (PL-PG) (Fig. 8B). The plastic wrap DLs produced higher average CEs ($12 \pm 4.3\%$, G2-PG; $9.1 \pm 2.0\%$, G1-PG) than reactors with PDMS DLs ($7.6 \pm 4.9\%$, PS-PG; $7.3 \pm 4.5\%$, PL-PG).

3.4. COD and BOD removals

Wastewater samples tested on the day they were acquired had average conditions of pH = 7.5 ± 0.37, conductivity = 1.5 ± 0.15 mS cm^{-1}, and an influent COD = 390 ± 89 mg L^{-1}. The average HBOD$_3$ was 200 ± 40 mg L^{-1}, resulting in a COD:HBOD$_3$ ratio of 2.0 ± 0.2. A typical ratio of COD:BOD$_5$ is 2 [15], supporting our assumption that the HBOD$_3$ was approximately equal to the BOD$_5$.

COD removals using brush anodes were substantially larger than those with mesh anodes (Fig. 9A). After 21 days, COD removals for the brush anodes were $83 \pm 0.1\%$ (B-GF1: ΔCOD = 360 ± 0.35 mg L^{-1}) and $82 \pm 6.8\%$ (B-GF2: ΔCOD = 360 ± 29 mg L^{-1}), compared to $58 \pm 0.3\%$ (M-GF1: ΔCOD = 290 ± 1.4 mg L^{-1}) and $59 \pm 3.1\%$ (M-GF2: ΔCOD = 290 ± 15 mg L^{-1}) for the mesh anodes. The brush anode MFCs maintained good COD removals from days 21 to 93 (B-GF1: $83 \pm 5.1\%$, B-GF2: $80 \pm 5.0\%$) compared to mesh anode MFCs (M-GF1: $60 \pm 5.9\%$, M-GF2: $58 \pm 6.9\%$). After 144 days, the COD removals seemed to improve for the mesh anode MFCs (M-GF1: 89%, M-GF2: 91%) but COD values were not obtained for the brush reactors on these days making it difficult to know if this was due to better performance of the mesh reactors or changes in wastewater biodegradability.

Adding diffusion layers increased COD removal, although there was no apparent correlation between measured oxygen mass transfer coefficients and COD removal (Fig. 9B). MFCs with two layers of plastic wrap had the highest COD removal (99%, G2-PG). The average COD removals for these setups were $87 \pm 9.1\%$ (G2-PG), $85 \pm 7.2\%$ (PS-PG), $85 \pm 9.0\%$ (PG), $82 \pm 5.7\%$ (GF2), $82 \pm 7.8\%$ (G1-PG), and $80 \pm 6.8\%$ (PL-PG). The final BOD$_5$ was estimated for each COD removal by assuming a COD:BOD$_5$ ratio of 2, resulting in BOD$_5$ values of 24 mg L^{-1} (G2-PG), 28 mg L^{-1} (PS-PG), 29 mg L^{-1} (PG),
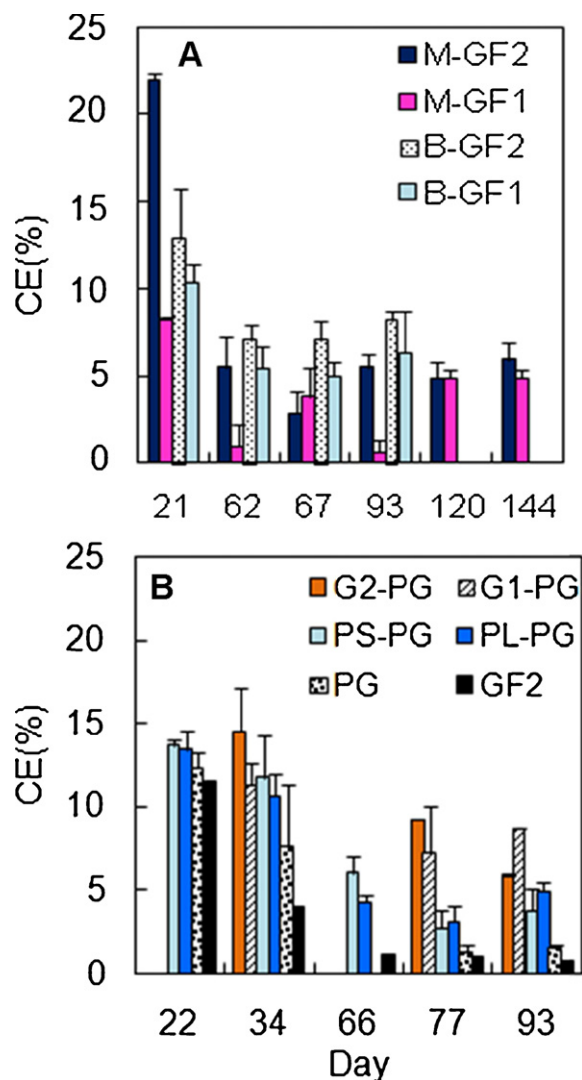
Fig. 8. Coulombic efficiencies at different times for membrane electrode assembly reactor configurations (A) without additional diffusion layers, and (B) with additional diffusion layers.

Fig. 9. COD removals at different times for membrane electrode assembly reactor configurations (A) without additional diffusion layers, and (B) with additional diffusion layers.

33 mg L^{-1} (B-GF1), 34 mg L^{-1} (GF2), 35 mg L^{-1} (G1-PG), 38 mg L^{-1} (B-GF2), 39 mg L^{-1} (PL-PG), 57 mg L^{-1} (M-GF1), and 80 mg L^{-1} (M-GF2).

3.5. Performance of acetate-fed reactors

The MEA reactors were also tested with glass fiber separators using acetate (1 g L^{-1}, COD = 780 mg L^{-1}) in a well buffered higher conductivity solution (6.9 mS cm^{-1}). The maximum power densities obtained using the single-cycle method with brush anodes (0.9 mm GF separator) was 1300 mW m^{-2} (Fig. 10). This power density was larger than that obtained with mesh anodes (960 mW m^{-2}, 1.2 mm GF separator) consistent with wastewater results.

4. Discussion

4.1. Performance of the MFCs with wastewater

Brush anodes consistently showed better performance than the mesh anodes when placed against the separator in an MEA type of configuration. The best performance with brush anodes was obtained using two glass fiber separators (B-GF2), resulting in sim-
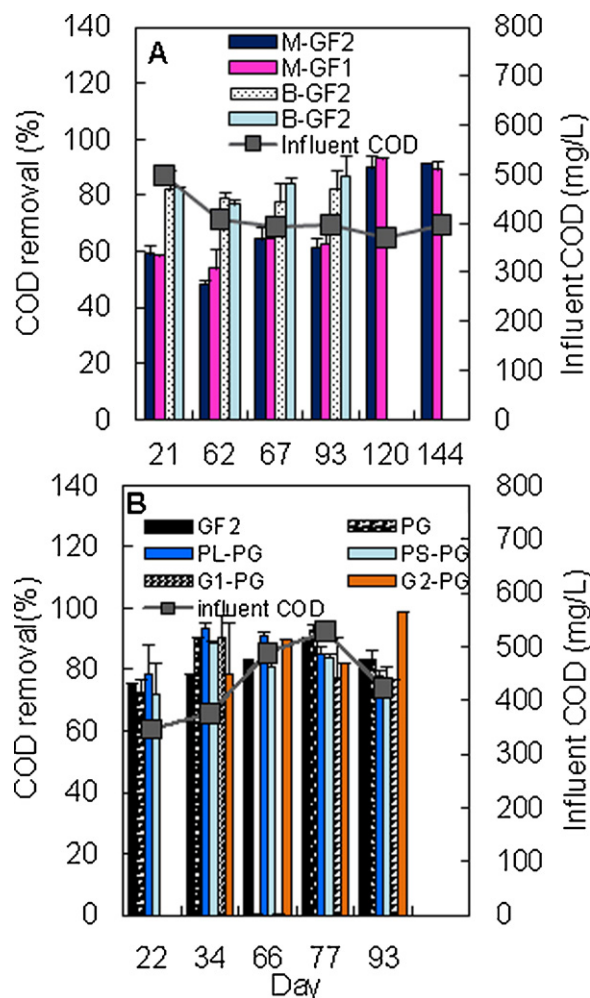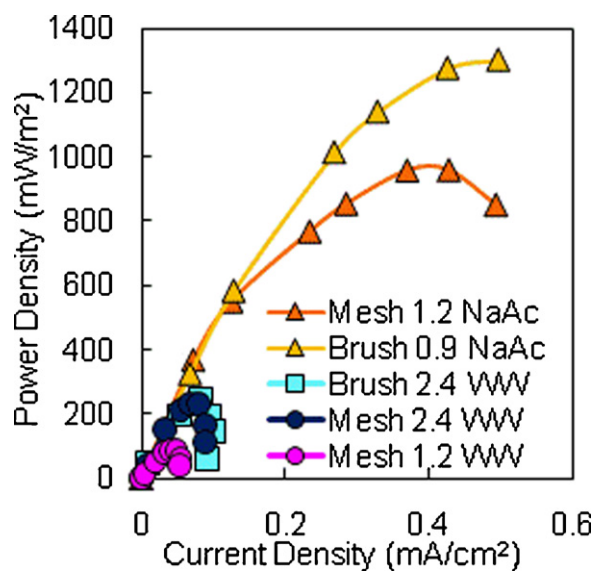

Fig. 10. Power density curves for membrane electrode assembly reactor configurations with activated carbon cathodes, and either carbon mesh or brush anodes with glass fiber separators (0.9, 1.2 or 2.4 mm, as specified in legend), fed sodium acetate (NaAc) or domestic wastewater (WW).

ilar maximum power densities of 240 ± 22 mW m^{-2} after 13 days and 230 ± 9.3 mW m^{-2} after 102 days (Fig. 4). The MFCs with a single separator produced similar values after 13 days, but declined to 130 ± 55 mW m^{-2} after 102 days. This indicates that the thicker separator was needed to achieve stable performance, consistent with our expectations that reducing oxygen crossover by using thicker separators can increase power production. However, if the separator is too thick power can decrease due to inhibition of proton transfer from solution to the cathode [7]. These power densities are larger than values previously obtained using domestic wastewater in MFCs (4 cm long by 3 cm diameter, 28 mL empty bed volume) with carbon paper anodes lacking proton exchange membranes (146 ± 8 mW m^{-2}) [4].

The CE values were largest for the brush anode MFC with two separators (B-GF2, 7.2%) compared to the single separator or mesh anode MFCs. These values indicate that only a small percent of the organic matter could be captured as current. Our results, however, are consistent with previous reports showing low CEs (9–12%) when using domestic wastewater in MFCs lacking a proton exchange membrane [4]. COD removals were very good despite low CE values. The brush electrodes with different numbers of separators produced similar COD removals, with 80 ± 5.0% with two separators (days 21–93) and 83 ± 5.1% with one separator.

Carbon mesh anodes have previously performed well in tests compared to carbon cloth, but under conditions where the electrodes were well separated. Here, the MFCs with carbon mesh did not acclimate well and MFCs failed to start up in the MEA configuration with close electrode spacing due to oxygen contamination of the anode. This was shown to be the reason because start up problems were avoided by first acclimating the mesh anodes separated from the cathode so that a thick biofilm could develop on the anode. This biofilm would consume oxygen allowing other bacteria on the anode to produce power. This procedure of separating the electrodes during startup, however, would not be practical in real applications. The mesh electrode MFC with two separators initially produced good power densities when moved next to the cathode after startup (230 ± 3.3 mW m^{-2}, M-GF2) but the MFC with the single separator produced a much lower power density (M-GF1: 80 ± 9.6 mW m^{-2}). Longer term operation (after 102 days) resulted in poor performance from both mesh reactors (<45 mW m^{-2}). This degradation in performance was due to oxygen transfer to the mesh anodes that prevented stable power generation. The mesh anode potentials became more positive over time, indicating that the anode was responsible for the poor performance and not the cathode. The very low COD concentration of the wastewater, compared to previous tests with much higher concentrations of acetate, was likely a contributing factor to the poor anode performance. Less oxygen is consumed to degrade wastewater than acetate, and thus oxygen cross over becomes more problematic with the lower COD wastewater than the higher COD acetate solutions typically used.

The use of GF separators was a problem for routine operation of the system as they tended to unravel and had to be replaced with new separators. There may have also been some short circuiting of the mesh fibers through the separator to the cathode as replacement of the separator produced temporary improvement in performance. However, these changes in voltage generation were not large, indicating short circuiting was not the primary reason for poor performance with the mesh anodes. The periodic replacement of separators in practice would not be possible, and thus better and more stable separators need to be found than the ones used here.

Diffusion barriers added to the outside of the cathodes successfully improved MFC performance relative to controls lacking these additional oxygen barriers. The best performance was obtained with two layers of plastic wrap, resulting in a maximum power density of 150 ± 22 mW m^{-2} (G2-PG). However, this power density with a mesh anode is still lower than that obtained with a brush anode, and therefore optimized materials were not able to be obtained for these mesh electrodes in this MEA format using wastewater. The use of plastic wrap was also problematic due to water accumulation between the cathode and wrap. If plastic wrap is used for these systems, a method will need to be found to bond the plastic wrap to the outside of the activated carbon cathodes.

4.2. Performance of acetate-fed reactors

Acetate-fed reactors produced higher power densities than wastewater-fed reactors for both brush and mesh anode MFCs. The maximum power densities achieved with acetate-fed MEA reactors with mesh or brush anodes were 4 times higher than those of the wastewater-fed reactors (Fig. 10). The low conductivity of wastewater (1.5 mS cm^{-1}) resulted in higher solution resistances than with the acetate solution (6.9 mS cm^{-1}), even though we used an MEA configuration to minimize adverse effects of low solution conductivity. The improvement in current and power densities in MFCs by the use of higher ionic strength solutions is well known, and thus the low ionic strength of typical wastewater solutions is a continuing challenge.

The acetate fed reactors had nearly double (1.93×) the organic loading of the wastewater fed reactors. The higher COD with acetate was chosen here (rather than one comparable to wastewater) in order to benchmark the performance of the materials used here with previous systems tested with acetate. The use of inexpensive carbon mesh anodes here produced 960 mW m^{-2} (30% porosity AC cathode, 1.2 mm GF separator) with acetate. This power density is only 20% lower compared that that previously obtained (1195 mW m^{-2}) using more expensive plain carbon cloth anodes and Pt-catalyzed carbon cloth cathodes (1.0 mm GF separator) [7]. Power was increased here to 1300 mW m^{-2} (76 W m^{-3}) by using a brush anode pressed against the thinner GF separator (0.9 mm) with an AC cathode (70% porosity), due to the better performance of the brush than mesh anode. This power production with the brush anode was similar to that previously obtained of 74 W m^{-3} (without a plastic mesh supporter) or 75 W m^{-3} (with a supporter) with a brush anode kept 1 cm from the separator (1.0 mm-thick glass fiber) using a carbon cloth cathode and a Pt catalyst [6]. This shows that by using a high conductivity phosphate buffer solution, additional electrode spacing with a brush anode will not appreciably affect power production. However, the electrode spacing is important in low conductivity solutions [3].

5. Conclusions

MFCs with brush anodes consistently generated higher voltages, power densities, COD removal rates and CEs than the mesh anodes. Adding diffusion layers to reduce oxygen transfer to the cathode improved performance of the mesh anode MFCs, but the power densities were never equal to those produced in the original tests with brush anodes. The best diffusion layer performance was obtained by adding two layers of a plastic wrap to the air-side of the cathode. While this improved performance, the accumulation of water between the plastic wrap was a problem. Methods will need to be developed to avoid this in future designs, perhaps by bonding the wrap to the cathode surface. In general there was a good correlation between CE and number of diffusion layers, reinforcing the finding that oxygen diffusion through the cathode was the main limitation for higher power production. These results show that for long term use, brush anodes offered more consistent and dependable results for use in the MEA configuration than carbon mesh anodes, and that improved separators are needed to ensure stable and long term performance when treating wastewater in these systems.

Acknowledgement

References

[1] B.E. Logan, P. Aelterman, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguiac, W. Verstraete, K. Rabaey, Environmental Science & Technology 40 (2006) 5181–5192.
[2] Y. Fan, H. Hu, H. Liu, Journal of Power Sources 171 (2007) 348–354.
[3] H. Liu, S. Cheng, B.E. Logan, Environmental Science & Technology 39 (2005) 5488–5493.
[4] H. Liu, B.E. Logan, Environmental Science & Technology 38 (2004) 4040–4046.
[5] S. Cheng, H. Liu, B.E. Logan, Environmental Science & Technology 40 (2006) 2426–2432.
[6] X. Zhang, S. Cheng, P. Liang, X. Huang, B.E. Logan, Bioresource Technology 102 (2011) 372–375.
[7] X. Zhang, S. Cheng, X. Wang, X. Huang, B.E. Logan, Environmental Science & Technology 43 (2009) 8456–8461.
[8] B.E. Logan, S. Cheng, V. Watson, G. Estadt, Environmental Science & Technology 41 (2007) 3341–3346.
[9] X. Wang, S. Cheng, Y. Feng, M.D. Merrill, T. Saito, B.E. Logan, Environmental Science & Technology 43 (2009) 6870–6874.
[10] V.J. Watson, B.E. Logan, Electrochemistry Communications 13 (2011) 54–56.
[11] F. Zhang, S. Cheng, D. Pant, G.V. Bogaert, B.E. Logan, Electrochemistry Communications 11 (2009) 2177–2179.
[12] F. Zhang, M.D. Merrill, J.C. Tokash, T. Saito, S. Cheng, M.A. Hickner, B.E. Logan, Journal of Power Sources 196 (2011) 1097–1102.
[13] D. Jiang, B. Li, Biochemical Engineering Journal 47 (2009) 31–37.
[14] B.E. Logan, R. Patnaik, Water Environment Research 69 (1997) 206–214.
[15] B. Min, D. Kohler, B.E. Logan, Water Environment Research 76 (2004) 39–47.
[16] D. Mara, Handbook of Water and Wastewater Microbiology, Elsevier, 2003.
[17] S. Cheng, H. Liu, B.E. Logan, Electrochemistry Communications 8 (2006) 489–494.