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Preface

This study was conducted for the US Department of Defense under the Strategic Environmental Research and Development Program (SERDP), "Evaluating a Multi-Panel Air Cathode Through Electrochemical and Biotic Tests."

The work was performed by the US Army Engineer Research and Development Center–Construction Engineering Research Laboratory (ERDC-CERL). At the time of publication, Sean Wallace was acting branch chief; and Tim Shelton was acting division chief. The deputy director of ERDC-CERL was Michelle Hanson, and the director was Dr. Andy Nelson.

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COL Christian Patterson was commander of ERDC, and Dr. David W. Pittman was the director.

Evaluating a multi-panel air cathode through electrochemical and biotic tests

ABSTRACT

To scale up microbial fuel cells (MFCs), larger cathodes need to be developed that can use air directly, rather than dissolved oxygen, and have good electrochemical performance. A new type of cathode design was examined here that uses a "window-pane" approach with fifteen smaller cathodes welded to a single conductive metal sheet to maintain good electrical conductivity across the cathode with an increase in total area. Abiotic electrochemical tests were conducted to evaluate the impact of the cathode size (exposed areas of 7 cm^2, 33 cm^2, and 6200 cm^2) on performance for all cathodes having the same active catalyst material. Increasing the size of the exposed area of the electrodes to the electrolyte from 7 cm^2 to 33 cm^2 (a single cathode panel) decreased the cathode potential by 5%, and a further increase in size to 6200 cm^2 using the multi-panel cathode reduced the electrode potential by 55% (at 0.6 A m^{-2}), in a 50 mM phosphate buffer solution (PBS). In 85 L MFC tests with the largest cathode using wastewater as a fuel, the maximum power density based on polarization data was 0.083 ± 0.006 W m^{-2} using 22 brush anodes to fully cover the cathode, and 0.061 ± 0.003 W m^{-2} with 8 brush anodes (40% of cathode projected area) compared to 0.304 ± 0.009 W m^{-2} obtained in the 28 mL MFC. Recovering power from large MFCs will therefore be challenging, but several approaches identified in this study can be pursued to maintain performance when increasing the size of the electrodes.

1. Introduction

Microbial fuel cells (MFCs) have been intensively studied for achieving energy neutral wastewater treatment, or even generating net power production during treatment (Logan and Rabaey, 2012; Logan et al., 2015; Lovley, 2006). Recent advances in MFC reactor architecture and electrode materials have increased energy efficiencies in laboratory scale reactors, and simultaneously lowered material costs (Santoro et al., 2017; Sleutels et al., 2012; Zhang et al., 2014b). However, most MFC studies have used acetate as a substrate rather than actual wastewaters as the fuel, or well-buffered solutions with higher conductivities than those of typical wastewaters, and reactor volumes <1 L (Zhang et al., 2013). Small electrode sizes and more favourable test conditions relative to wastewaters, including high substrate concentrations, more conductive solutions, and elevated temperatures (~30 °C), can result in performance levels that are much better than those possible using low-strength wastewaters typical at municipal wastewater treatment facilities (He et al., 2016b; Zhang et al., 2013). Although power densities have reached 4.7 ± 0.2 W m^{-2} for small MFCs (0.028 L) fed phosphate buffer solutions (PBS 200 mM) amended with sodium acetate (Yang and Logan, 2016), and 0.8 ± 0.03 W m^{-2} using domestic wastewater from a primary clarifier (Yang and Logan, 2016), few systems have been examined at reactor sizes of 10 L or more.

The main challenges for scaling up MFCs are improving power densities with low-conductivity wastewaters (Fornero et al., 2010;

Lanas et al., 2014; Stager et al., 2017), having direct air cathodes rather than dissolved oxygen cathodes, and using inexpensive materials and simple designs for their manufacture (Li et al., 2013). Most of the large-scale MFCs (volume > 10 L) to date had two-chamber configurations that use an aqueous catholyte (Dekker et al., 2009; Lu et al., 2017; Vilajeliu-Pons et al., 2017; Wu et al., 2016). One disadvantage of this two-chamber design is that oxygen must be dissolved in the catholyte, which can consume more energy than produced by the MFC in these systems. With air cathodes, oxygen transfer is passive and thus it consumes no energy (Dekker et al., 2009). Another disadvantage is that having a second liquid chamber adds additional ohmic resistance to the system, which will increase the internal resistance and thus lower power production (Liu and Logan, 2004). Power densities for larger-scale MFCs with aerated catholyte systems are low, and in the range of 0.002–0.72 W m^{-2} [0.002 W m^{-2} (Lu et al., 2017); 0.67 W m^{-2} (Vilajeliu-Pons et al., 2017); and 0.72 W m^{-2} (Dekker et al., 2009), using an acidified catholyte, pH = 4]. Although a high power density of 7.58 W m^{-2} (125 W m^{-3}) was recently reported for a two-chamber MFC design (Liang et al., 2018), the values were at least an order of magnitude too large based on conventional methods to report power densities. If the power was normalized by the total of 5 membranes (5 separate circuits) in the module, rather than one membrane area, the maximum power from polarization tests would be 1.52 W m^{-2}. If the total reactor volume was used, rather than a single net anolyte volume, the power density would be 15 W m^{-3}. However, power densities were produced under steady conditions were only 0.085 W m^{-2} (0.98 W m^{-3}). Air cathodes have only been used in a few larger-scale MFCs. In one study, a power density of 0.18 W m^{-2} was obtained with a 90 L MFC treating a brewery wastewater, but individual cathodes had surface areas of only 600 cm^2 (Dong et al., 2015). In another study where a 10000 cm^2 cathode was used, the maximum power density was only 0.058 W m^{-2}, and the design required a thin horizontal flow (flow rate 42 L d^{-1}) to minimize hydrostatic pressure and prevent water leakage (Feng et al., 2014).

When scaling up MFCs, the electrode design should be reasonably compact, and allow for easy installation and maintenance (He et al., 2016b; Logan et al., 2015). For a flat plate-and-frame type MFC, the electrode packing density is calculated from the spacing between repeating cathode and anode units. For example, for an anode chamber width of 2 cm (filled with graphite fiber brush anodes) and a cathode chamber width of 2 cm (a 4 cm wide anode-cathode unit), the electrode specific surface area is 25 m^2 m^{-3} (area of the cathode per volume of the reactor) (Logan et al., 2015). Very high electrode packing densities should be avoided to minimize clogging or short circuiting between the electrodes (Li et al., 2013), and the design should allow easy access for maintenance or replacement. One plate-and-frame configuration, called a "cassette" MFC, was made by bolting the anode and cathode together as part of the same cassette (Miyahara et al., 2013; Zhuang et al., 2012). While this allows for good installation and cassette removal, a single electrode cannot be extracted without removing and disassembling the whole cassette. In addition, this design provided only one cathode per anode. More recently, a modular design was developed that used repeating anode and cathode modules, so that anode or cathode modules could be manufactured, installed, and removed without removing the counter electrodes (He et al., 2016a, 2016b). For this specific modular architecture, the anode module was constructed from an array of anode brushes wired together, while a cathode module was formed from two cathodes joined together with an air space between them (He et al., 2016a, 2016b; Logan et al., 2015). These modules were wired so that each anode was connected to two cathodes (one on each side), to improve power production and reduce treatment times.

Anode brushes have been frequently used in large scale systems (Cusick et al., 2011; Logan, 2010) but not air cathodes. Two challenges for building large air cathodes are the impact of water pressure on cathode performance (Ahn et al., 2014; Cheng et al., 2014a), and increased electrode overpotentials due to reduced electrical conductivities (Cheng et al., 2014b). As the hydraulic pressure on the cathode is increased with the height of the water in the reactor, even if the cathode does not leak, its performance could be reduced due to the high water pressure that reduces the area of the catalyst exposed to the air (Yang et al., 2015). For example, an electrochemical impedance spectroscopy (EIS) analysis of air cathodes showed that the charge transfer resistance increased from 23 Ω to 44 Ω when the water pressure increased from 0.1 m to 2 m against the electrode (Cheng et al., 2014a). Electrical conductivities are a major concern during scale up, as electrode dimension gets larger, ohmic resistance increases, because the distance between where electrons are generated and the leading-out terminal where current flows out of anode increases (Cheng et al., 2014b). Even though cathodes are made with relatively conductive carbon materials, there can be substantial power losses due to the electrode overpotentials with the increased size of the electrodes. For example, it was estimated that the electrical power loss could be as much as 47% by increasing the size of a carbon mesh anode from 10 cm^2 to 1 m^2 (current density of 3 A m^{-2}), based on only one connection to the electrode (Cheng et al., 2014b).

In order to obtain large cathodes with good electrical conductivity and performance, we designed and tested a new multi-panel cathode that contained many smaller cathodes welded into a single metal sheet, much like windows are made of many panes of glass (Fig. 1) (Patent application no EP17194627). Using a metal sheet provided good electrical connections for all individual cathode panes to the circuit. For the individual panels, we used commercially available cathodes with a size of 18 by 18 cm (324 cm^2) (Pant et al., 2010; Zhang et al., 2011, 2014a). To evaluate the impact of this design on performance, we constructed a cathode containing 15 individual cathode panes (3 cathodes high, 5 cathodes wide, 6800 cm^2 total projected area, 6200 cm^2 exposed area). Performance was examined in an 85 L tank under abiotic conditions using chronoamperometry, and in biotic MFC fed with domestic wastewater. We compared the electrochemical performance of this larger cathode with two smaller cathodes made from a portion of a single cathode pane: 11.3 cm^2 total projected area square cathodes (7 cm^2 exposed area) typically used in 0.028 L MFCs (Yang et al., 2017a); and larger 52 cm^2 (33 cm^2 exposed area) cathodes in a specially designed reactor (0.22 L). Following electrochemical tests, the large multi-paned cathode was examined for power production in an MFC using an anode module with 8 or 22 brush anodes, in multiple fed batch tests using domestic wastewater.

2. Materials and methods

2.1. Electrode materials

The cathodes used in electrochemical tests and MFCs were all prepared using sheets (18 by 18 cm, 324 cm^2, 0.45 mm thick) that were manufactured by VITO (Mol, Belgium) using a proprietary process (VITO CORE®) based on pressing together a mixture of activated carbon (AC) (70–90 wt%; Norit SX plus, Norit Americas Inc., TX) and polytetrafluoroethylene (PTFE) binder, onto a stainless steel mesh current collector. A PTFE diffusion layer (70% porosity) was then added on top of the catalyst layer which became the air-side of the cathode (Pant et al., 2010). The cathodes for the small (11.3 cm^2) and medium (52 cm^2) chambers were made from portions cut from these cathode sheets. A circular cathode 3.8 cm in diameter (11.3 cm^2) was used for the smallest reactor (0.028 L), and

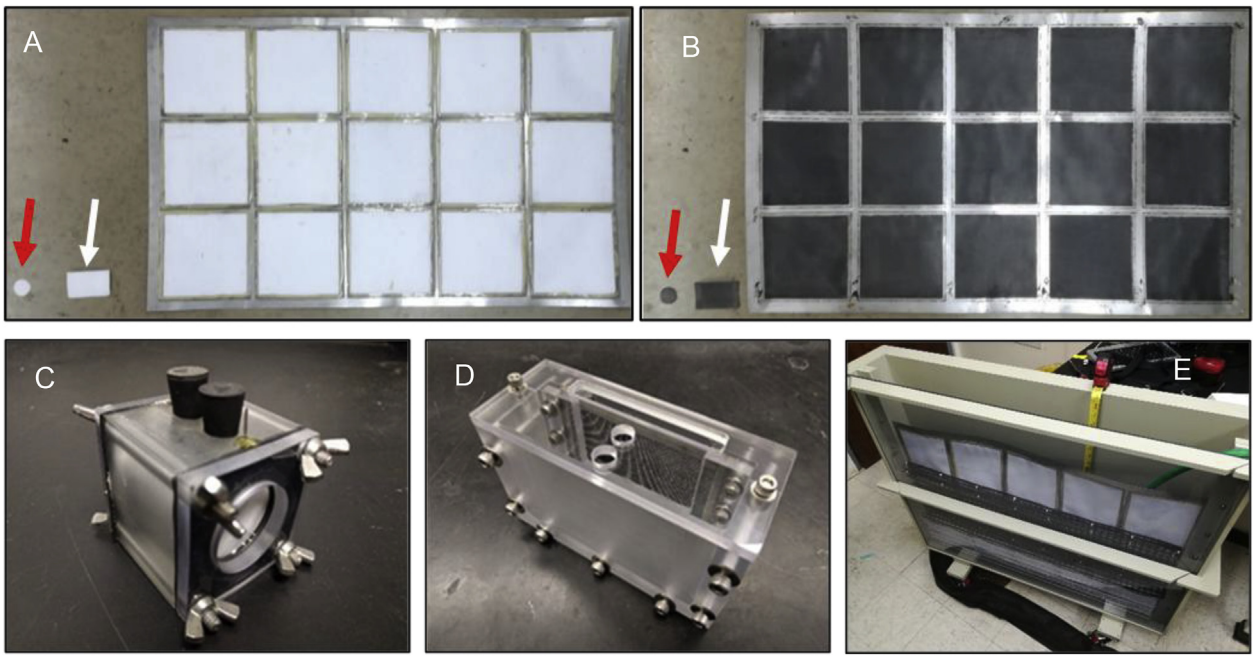

Fig. 1. Photos of the (A) air and (B) solution side of the three cathodes, with sizes (total areas - from left to right) of: 11.3 cm^2 (red arrow), 52 cm^2 (white arrow) and 6800 cm^2. (C) Small, (D) medium and (E) large cells used for the electrochemical tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

a rectangular cathode of 9.2 cm by 5.6 cm (52 cm^2) was used in the middle-sized reactor (0.22 L). The large cathode (107 cm long by 0.64 cm in height, 6800 cm^2) was manufactured by VITO based on a specified overall electrode size, and contained 15 cathode sheets that were welded into laser cut holes ("window panes") in the stainless steel frame to allow the cathode sheets to be exposed to water on one side, and air on the other side (Fig. 1). The use of a single metal panel enabled a low resistance of $\leq$0.2 Ω between the center of any cathode panel and any part of the external stainless steel panel.

Brush anodes were made with two different sizes for the various sized-chamber MFC tests. For the smaller reactor, brushes were 2.5 cm in diameter, and 2.5 cm long, and made from graphite fiber (PANEX 35 50K, Zoltek) wound between two titanium wires (Mill-Rose, Mentor, OH) (Logan et al., 2007; Yang et al., 2017a). The brushes used in the larger reactor were 5.1 cm in diameter and 61 cm long, made from the same materials as the smaller brushes (Gordon Brush, CA, USA) (Cusick et al., 2011). All anodes were heat treated at 450 °C in air for 30 min prior to use in MFCs (Feng et al., 2010).

2.2. Bench and pilot-scale reactors

Three different electrochemical cells were constructed to evaluate the impact of scaling up the cathode size on the electrochemical performance (Fig. 1). The small cell (SC) was a single chamber, cube-shaped reactor constructed from a polycarbonate block 4 cm in length (5 cm × 5 cm), with an inside cylindrical chamber having a diameter of 3 cm (0.028 L total volume), and an exposed cathode area of 7 cm^2 that has been used in many previous MFC laboratory studies (Fig. 1C) (Yang et al., 2017a). The cathode specific surface area was 25 m^2 m^{-3} anolyte volume.

The medium-sized cell (MC) was a polycarbonate rectangular-shaped reactor, with an anolyte chamber 10.9 cm long, 3.5 cm wide, and 6.2 cm high, filled with 0.22 L of electrolyte (Fig. 1D, Fig. S1). The cell had a bracket slot 3.5 cm from the wall of the water side, where the cathode was attached separating the anolyte chamber from the air cathode chamber. The cathodes were secured to the frame with 10 screws using a plastic U-shape fastener and a gasket (butyl rubber). The air chamber was 6.8 cm long, 1.0 cm wide and 4.4 cm high. The cathode specific surface area was 15 m^2 m^{-3} anolyte volume.

The large cell (LC) was a custom rectangular tank (1.1 m long, 0.15 m wide and 0.85 m height) that was used to examine the physical properties of the cathodes, such as mechanical strength (deformation when filled) and the resistance to water pressure (based on leaking), as well as to evaluate the electrochemical characteristics of the cathodes (Fig. 1E). The tank had a bracket slot 10 cm from the wall of the water side, where the cathode was attached to form the anolyte chamber. The cathodes were secured to the frame with 25 screws using a plastic U-shape fastener and a gasket (closed cell PVC vinyl foam). The anolyte tank was filled with 85 L of water, and examined by eye for deformation and water leakage when filled. The cathode specific surface area was 7.3 m^2 m^{-3} anolyte volume. This lower specific area of the cathode was used here in order to accommodate the larger diameter anode brushes and to enable easy inspection of the condition of the electrodes. The cathode air chamber was formed by sliding a sheet of PVC into a slotted groove 5 cm from the cathode. To reduce the cathode deformation due to the pressure of the water on the cathode, the space between the clear PVC sheet and the cathode was filled with 19 spacers, constructed by rolling polypropylene mesh (XN3110-48P, Industrial Netting, USA) into tubes (4 cm diameter by 1 m long), with the rolled tubes held together using zip ties (Fig. S2).

To examine actual power generation in the LC, an anode module made of polyvinyl chloride (PVC) was constructed using a linear array of graphite fiber brushes. The PVC module held either 8 or 22 brushes (as indicated), with the ends of the brushes secured at the top and bottom of the module (Fig. S3). The brush module was placed parallel to the cathode, in the middle of the anode chamber, producing a distance of 3.5 cm between the edge of the anode

brushes and the cathode surface in initial tests (Lanas et al., 2014). The anodes were connected in parallel to the circuit by an external single titanium wire. At the top of the anode module, a clip was used to reduce the bending of the cathode sheet and to secure it in position while improving its electrical connection (Fig. S4). For the smaller chamber, the anodes were placed horizontally in the middle of MFC chambers (perpendicular to the cathode) with a distance of 1.4 cm between the edge of the brush and the cathode (Vargas et al., 2013; Yang et al., 2017b).

To avoid any short circuiting and reduce biofilm growth on the cathode, all reactors were operated during the biotic tests with a separator placed on the cathode (PZ-1212, Contec, USA) (Wei et al., 2013; Yang et al., 2017b). For the SC, a separator with the same area of the cathode was cut from a 30 cm by 30 cm wipe separator. In the LC, 12 separators were sewn together and cut to the final area, same as the cathode (6800 cm^2).

2.3. Electrochemical cell (abiotic) tests

Electrochemical tests were performed using a potentiostat (VMP3, BioLogic, Knoxville, TN) with the cathode as the working electrode (WE), and a steel mesh as the counter electrode (CE) in the medium and large chamber reactors and Pt mesh as the CE in the small chamber. Electrochemical performance of the cathodes was evaluated using chronopotentiometry (CP) tests in a 50 mM phosphate buffer solution (PBS; Na_2HPO_4, 4.58 g L^{-1}; $NaH_2PO_4 \cdot H_2O$, 2.45 g L^{-1}; NH_4Cl, 0.31 g L^{-1}; KCl, 0.13 g L^{-1}; pH 7.0; conductivity of $\kappa = 6.25$ mS cm^{-1}) or sodium chloride amended tap water ($\kappa = 1.45 \pm 0.05$ mS cm^{-1}) in the presence or absence of the separator. Current was fixed for 20 min over a range of 0 to − 4 mA in the SC, 0 to − 10 mA in the MC, and 0 to − 0.4 A in the LC. An Ag/AgCl reference electrode (RE - 5B, BASi, West Lafayette, IN; + 0.209 V vs. SHE) was used in the SC and MC electrochemical tests, and placed 1.2 cm from the cathode. The ohmic losses due to the distance between the RE and the WE were corrected based on the conductivity of the solution (see information in SI and Fig. S5) (Logan et al., 2018). An immersion reference electrode (AGG, Electrochemical Devices Inc., OH; + 0.199 V vs. SHE) was used in the large chamber and kept attached to the cathode, in the same position for all the tests. All potentials are reported versus SHE.

2.4. Microbial fuel cell (biotic) tests

Only the small (SC) and the large cells (LC) were used for biotic tests. The anodes in the SC were fully acclimated to wastewater in MFCs for over four months at a fixed external resistance of 1000 Ω, at a constant temperature (30 °C). Domestic wastewater was collected once a week from the effluent of the primary clarifier at the Pennsylvania State University Wastewater Treatment Plant, and stored at 4 °C prior to use. Total and soluble COD were measured using method 5220 (Hach COD system, Hach Company, Loveland, Colorado). Single cycle polarization tests were conducted by varying the external resistance from 1000, 500, 200, 100 and 75 Ω at a 20 min interval after open circuiting for 2 h with a total test duration of 3.7 h, in a constant temperature room (30 °C).

The LC was operated at room temperature in a laboratory at the Pennsylvania State University Wastewater Treatment Plant in order to feed it directly with fresh primary effluent wastewater (WW). During acclimation of the anodes for the first week of operation, the feed solution was 35 L of primary effluent wastewater mixed with 40 L of 0.5 g L^{-1} sodium acetate in 50 mM PBS, and 10 L effluent collected over several weeks from MFCs fed acetate and wastewater. The external resistance was 1000 Ω for the first two days and then was decreased daily to 100 Ω, 25 Ω, 10 Ω and 5 Ω over the following four days. For the second week of acclimation, the solution was 55 L of wastewater, 20 L of 50 mM PBS containing 0.5 g L^{-1} sodium acetate, and 10 L of MFC effluent. Thereafter, the LC was operated using only primary effluent wastewater. After a stable potential production for three successive fed-batch cycles, single cycle polarization tests were conducted on the LC by feeding the reactor with fresh wastewater and holding the system at open circuit conditions for 2 h, and then varying the external resistance from 100, 25, 10, 5, 2, 1 to 0.4 Ω at 20 min intervals.

The current was calculated based on the voltage drop (U) across the external resistor, and recorded using a computer based data acquisition system (2700, Keithley Instrument, OH). Current densities (i) and power densities (P) were normalized to the total exposed cathode area (large chamber area, $A_{LC} = 6200$ cm^2, and power P_{LC}; small chamber area, $A_{SC} = 7$ cm^2, and power P_{SC}), and calculated as $i = U/RA$ and $P = iU$, where R is the external resistance and A is the cathode projected area. During each polarization test, anode and cathode potentials were also recorded using a reference electrode. An Ag/AgCl reference electrode (RE-5B, BASi, West Lafayette, IN; + 0.209 V vs. SHE) was used to measure the anode potential (E_{An}) in the SC biotic tests at a distance of 1.2 cm from the cathode. The cathode potential (E_{Ct}) was calculated from the anode potential and the cell potential as $E_{Ct} = U + E_{An}$, and then corrected based on the conductivity of the solution and the distance from the RE (Logan et al., 2018) (SI and Fig. S5). An immersion reference electrode (AGG, Electrochemical Devices Inc., OH; + 0.199 V vs. SHE) was used in the LC biotic tests to measure the anode potential (E_{An}), and it was kept close to the cathode, and in the same position for all the tests. The anode potential was corrected based on the conductivity of the solution and the distance from the RE. The cathode potential (E_{Ct}) was estimated using the cell potential as $E_{Ct} = U + E_{An}$ (see information in SI and Fig. S5). All potentials are reported versus SHE.

3. Results and discussion

3.1. Electrochemical tests

Chronopotentiometry tests on cathodes of different sizes showed differences in performance, with the smaller cathodes producing the lowest overpotentials at the different set current densities (Fig. 2A, Fig. S5). For example, at 0.61 ± 0.00 A m^{-2} the smaller cathode produced 0.35 ± 0.00 V, which was only 5% higher than the potential produced by the middle-sized cathode (0.33 ± 0.00 V at 0.62 ± 0.01 A m^{-2}) but 121% higher than that obtained with the large cathode (0.16 ± 0.03 V at 0.64 ± 0.00 A m^{-2}). The adverse impact of the increased size of an electrode on performance was consistent with previous studies that showed a loss in power as cathode sizes were increased (Cheng et al., 2014b; Dewan et al., 2008).

Chronopotentiometry tests were conducted on the different size cathodes in tap water amended with sodium chloride ($\kappa = 1.45 \pm 0.05$ mS cm^{-1}), to evaluate performance in an unbuffered solution with a conductivity similar to that of domestic wastewater (Fig. 2B). The overpotentials of all cathodes were larger in the less conductive solution, with the large cathode having much higher overpotentials with respect to the other two cathodes at a given current density. For example, at a current density of 0.64 ± 0.00 A m^{-2} the potential of largest cathode was 0.09 ± 0.01 V, which was much lower than that of 0.23 ± 0.00 V of the medium size cathode (0.63 ± 0.00 A m^{-2}) and 0.26 ± 0.01 V (0.62 ± 0.00 A m^{-2}) for the smallest cathode.

Additional chronoamperometry tests were conducted using the large cell to evaluate the impact of the presence of the separator on the electrochemical performance of the cathode over a current density range relevant to operation of the large MFC using

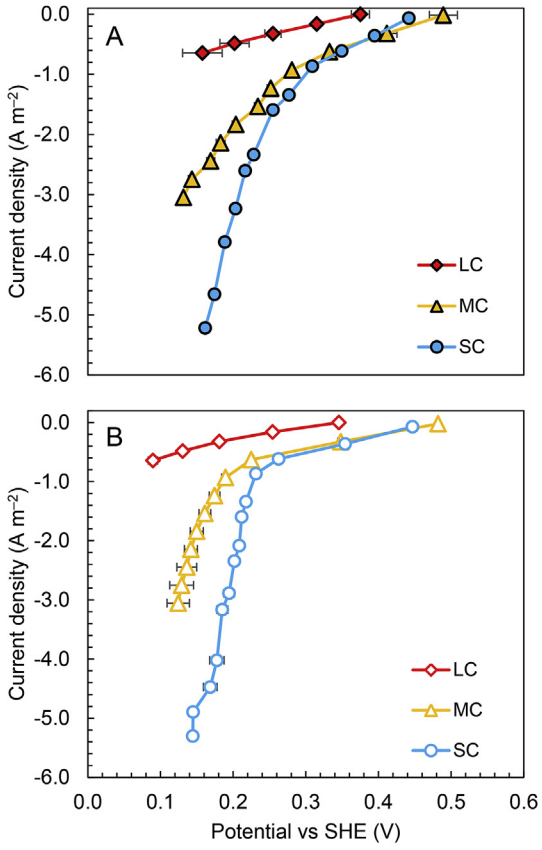

Fig. 2. Cathode potential as a function of current density in the abiotic electrochemical cell for the cathodes in the small (SC), medium (MC) and large cells (LC) in (A) 50 mM PBS (6.25 mS cm^{-1}) and (B) tap water amended with NaCl (1.45 ± 0.05 mS cm^{-1}).

wastewater (Fig. S6A). The presence of the extra layer of the separator reduced the potential output at 0.64 A m^{-2} from 0.16 ± 0.03 V to 0.13 ± 0.01 V in PBS, and from 0.09 ± 0.01 V to 0.06 ± 0.00 V in a low conductivity solution. Insufficient airflow in the cathode chamber could reduce oxygen availability and, thus, cathode performance (Yang et al., 2012). Therefore, an additional electrochemical test was conducted by blowing air into the bottom of the air chamber at 0.5 L min^{-1} (Fig. S6B). This airflow across the cathode did not impact the cathode performance, indicating that the size of the air chamber was sufficient to passively provide oxygen transfer to the cathode and that the spacers did not impede passive air flow.

3.2. Power production of the 85 L MFC fed domestic wastewater (22 anodes)

Following acclimation of the 85 L MFC with the anode module (Fig. S3) over three fed-batch cycles, polarization tests were conducted using domestic wastewater (Fig. 3). The maximum power density was 0.083 ± 0.006 W m^{-2}, which was 73% lower than that obtained in the small chamber MFC (0.304 ± 0.009 W m^{-2} in wastewater). The cathode potentials were similar in the abiotic and biotic tests in the 85 L and in the 28 mL reactors (Fig. 3A and B). There was a significant difference between the open circuit potential (OCP) of the biotic (0.32 ± 0.00 V) and abiotic (0.44 ± 0.00 V) tests for the small chamber, but the cathode potentials matched well over the current density range relevant to operation of wastewater fed MFCs. The anode performance was a factor in the reduced power production by the 85 L MFC compared to the 28 mL MFC. For example, after correction for the solution resistance, the slope of the trendline from the linearization of the anode potential was 0.29 Ω m^2 in LC biotic test, 3.6× higher than the 0.08 Ω m^2 from the SC biotic tests (Fig. 3D, Fig. S7). However, there was a much larger reduction in the cathode performance (change of |0.30 V|, from 0.37 ± 0.04 V at OCP to 0.07 ± 0.02 V at 0.46 ± 0.03 A m^{-2}) compared to that of the anodes (change of |0.13 V|, from − 0.31 ± 0.01 V at OCP to − 0.18 ± 0.02 V at 0.46 ± 0.03 A m^{-2}). This larger difference for the cathode indicated that in this system the cathode was primarily limiting power production. The decrease in the anode performance was likely a result of both increased size of the anodes and the cathode performance. The anodes in the 85 L MFC were much longer, and had a larger diameter, than those in the small MFC, which both could have contributed to higher overpotentials (Cheng et al., 2014b; Dewan et al., 2008). The increase in water pressure could also have decreased the performance of the cathodes, particularly at the bottom of the MFC where the water pressure was the highest, relative to those at the top of the reactor (Cheng et al., 2014a). This change in the cathode performance could have impacted performance of the anodes opposite to the cathode in the bottom of the large reactor. The reduced active area of the cathode due to the metal frame could also have been a factor in reducing electrode performance, as the metal frame accounted for 23% of the exposed projected area of the cathode (Fig. 1). Normalizing the power produced by only the active cathode area results in a power density of 0.10 W m^{-2}.

3.3. Power production of the 85 L MFC fed domestic wastewater using 8 anodes

To further examine the impact of the anodes on performance, we conducted tests using 8 anodes instead of 22 anodes. Reducing the number of anodes decreased the anodic projected area by 58% (from 6000 cm^2 to 2500 cm^2), but this decreased the maximum power density by only 27%, from 0.083 ± 0.006 W m^{-2} to 0.061 ± 0.003 W m^{-2} based on the cathode projected area (Fig. 4). Power normalized to the projected anode area was 0.152 ± 0.009 W m^{-2}, which is consistent with previous results showing that using two electrodes with different projected areas improves the relative performance of the smaller electrode (He et al., 2016a; Oh and Logan, 2006). Reducing the number of anodes resulted in slightly increased anode overpotentials. For example, the anode potential at the maximum power density was − 0.177 ± 0.002 V at 0.206 ± 0.006 A m^{-2} (normalized to the projected cathode area) compared to − 0.23 ± 0.01 V at the highest current density of 0.250 ± 0.006 A m^{-2} with 22 anodes. Thus, maximizing full coverage of the cathodes by the anodes is needed to improve power production (Lanas and Logan, 2013).

3.4. Impact of the operation time on the MFC performance

Following polarization tests with the 8 anodes, the impact of cathode fouling was examined by comparing the maximum power densities with the existing cathode, which had been operated for 1 month, to the same cathode that was cleaned to remove the surface biofilm, and to a new cathode. The maximum power density increased to 0.057 W m^{-2} after removing the biofilm, which was 36% higher than that obtained prior to biofilm cleaning (0.042 W m^{-2}) (Fig. 5). When a new cathode was used, the maximum power density was 0.064 W m^{-2}, which was essentially the same as that originally obtained at the start of the experiments with 8 anodes.

The maximum power density decreased by 34% after one month of operation, with 23% due to biofilm formation on the solution side of the cathode, and the remaining 11% due to a combination of the

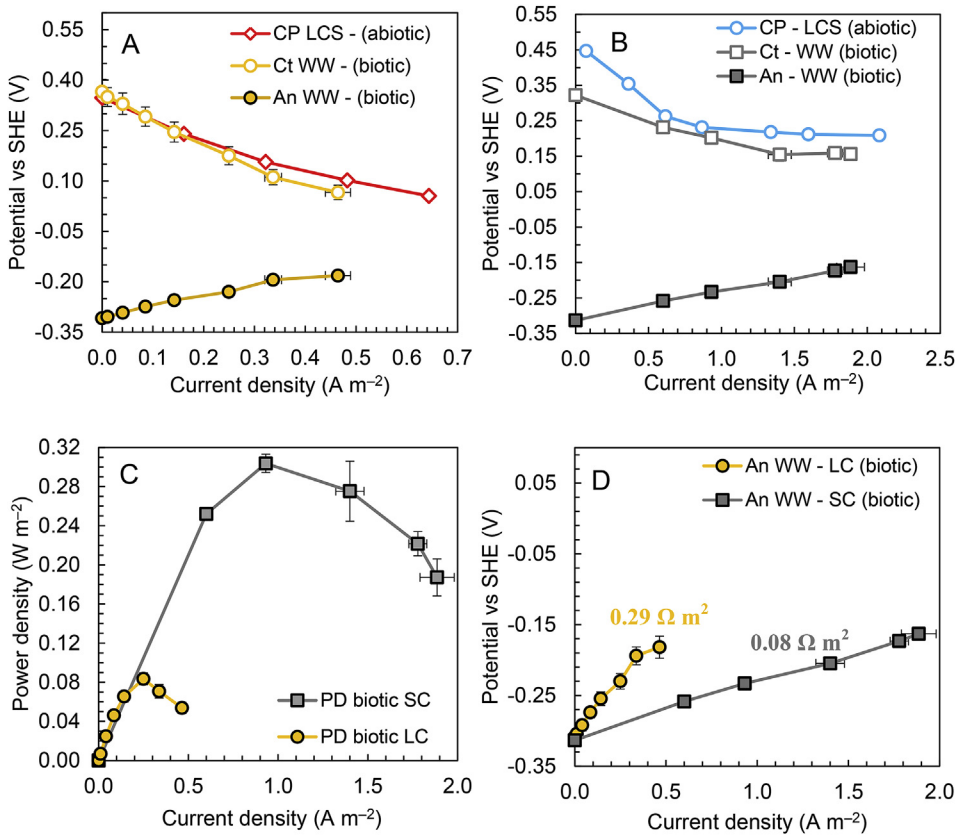

Fig. 3. Cathode (Ct) potentials from the biotic polarization tests and the abiotic chronopotentiometry (CP) in low conductivity solution (LCS) and anode (An) potentials from the biotic polarization tests in the (A) large and (B) small chamber in wastewater (WW). (C) Biotic power density curves in the small chamber (SC) and large chamber (LC) MFC. (D) Comparison of corrected anode potentials in LC and SC.

precipitation of salts (An et al., 2017) and the adsorption of organic matter in the wastewater such as humic acids (Yang et al., 2016) and metabolic by-products such as extracellular polymers (Liu et al., 2018). This decrease is only slightly lower than the 39% decrease in the performance previously reported for small chamber MFCs (28 mL volume, 7 cm^2 exposed cathode area) after one month of operation (Rossi et al., 2018). This fouled smaller cathode was shown to be successfully cleaned by soaking in a weakly acidic solution for several hours (Rossi et al., 2017; Zhang et al., 2014a), but this approach might not be practical for larger cathodes. We are currently investigating easier ways to clean fouled cathodes. No corrosion of the stainless steel structure was observed after one month of operation.

The decline in the cathode potentials further demonstrated that the main reason for the reduced performance of the MFC after one month of operation was the cathode performance. For example, at the maximum power density the potential of the new cathode was 0.19 V (at 0.212 A m^{-2}), compared to 0.07 V (at 0.171 A m^{-2}) for the used cathode. After scraping off the biofilm from the solution side of the fouled cathode, the electrode potential reached 0.16 V (0.200 A m^{-2}) at the maximum power density, which was an overall decrease of 11% compared to the new cathode.

3.5. Treatment performance based on COD removal

The MFC with 8 or 22 anodes achieved similar COD removal efficiencies of 75–80%. The presence of a higher number of anodes therefore did not increase the rate of COD removal, although the number of anodes did impact the amount of COD converted to electricity. The total COD decreased from 428 ± 12 mg L^{-1} to 88 ± 4 mg L^{-1} after 9 days in the 8 anode configuration. With 22 anodes, the COD decreased from 376 ± 4 mg L^{-1} to 90 ± 5 mg L^{-1} in 11 days. The longer time needed to reduce the COD with 22 anodes was likely due to the higher oxygen content in the 8 anode configuration that might have increased the COD removal rate. The coulombic efficiency (Logan et al., 2006) (CE) was 27% when using 22 anodes, but it decreased to 13% with 8 anodes. The CE obtained here is essentially the same as the 22% previously achieved in small chamber MFC for domestic wastewater at low external resistance (100 Ω) (Zhang et al., 2015).

3.6. Approaches to improve electrochemical performance

Increasing the sizes of the anodes and cathodes resulted in a decrease in the electrode performance despite maintaining the same catalyst and reactor configuration. The greatest impact on performance was due to the cathode. The power density of the large MFC was about one order of magnitude lower than that obtained in the small MFC (0.083 ± 0.006 W m^{-2} vs 0.304 ± 0.009 W m^{-2}). Fortunately, there are a number of changes in the reactor or electrode design which could be made to improve performance.

It should be possible to further improve performance in the large MFC by connecting the anode arrays to two cathodes rather than one cathode, as done in this study. The test chamber used here was designed primarily to test hydraulic stability and electrochemical performance of an abiotic cathode, and thus it was only possible to connect an array of anodes to a single cathode. However, we have previously demonstrated that connecting an anode array

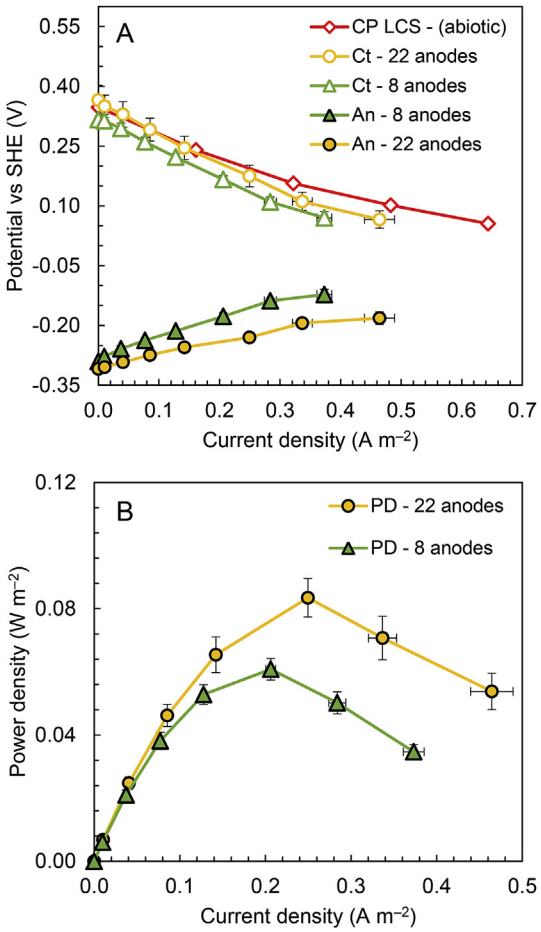

Fig. 4. (A) Cathode potentials (Ct) and anode potentials (An) with an anode module with 8 (projected area = 2500 cm^2) and 22 anode brushes (projected area = 6000 cm^2) compared with the abiotic chronopotentiometry data (CP) and (B) correspondent power density curves.

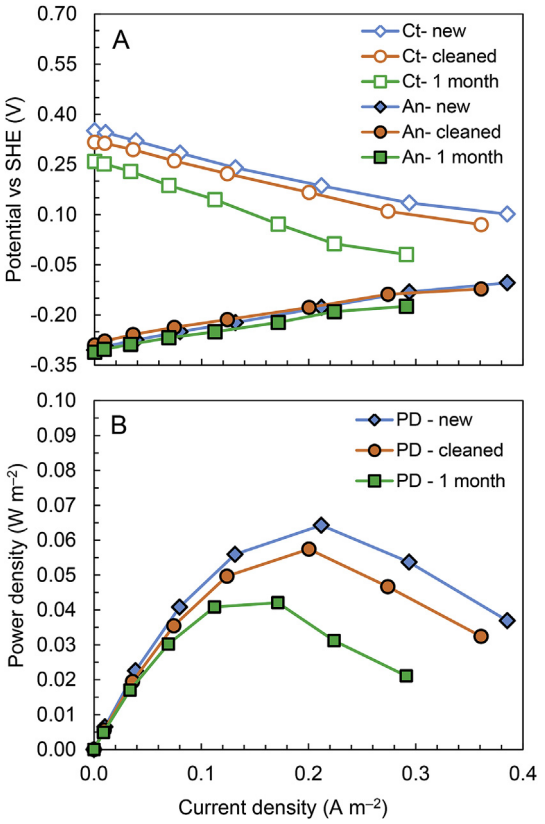

Fig. 5. (A) Cathode potentials (Ct) and anode potentials (An) of the new, cleaned and used (1 month) cathode and (B) correspondent power density curves.

with two cathodes, one on either side of the anode array, increased the maximum power density by 62% in fed-batch MFCs (Cheng and Logan, 2011), and by 39–53% for MFCs operated in continuous flow with a feed of domestic wastewater (Kim et al., 2015).

It might be possible to improve performance by changing the diameter or the fiber density of the brush anodes. For the tests conducted here, we used anodes with a diameter of 5.1 cm due to their availability from a previous MEC reactor design (Cusick et al., 2011). This larger diameter could have resulted in reduced power due to the average distance of the anode (from the wire core) to the cathode. It was previously shown that reducing 2.5 cm diameter anodes to 0.8 cm improved power, as long as the anode-cathode spacing was not changed. This reduction in size resulted in a 49% increase of the maximum power density (from 0.690 W m^{-2} to 1.030 W m^{-2}) using acetate as a substrate in continuous flow MFCs (Stager et al., 2017). However, additional tests with the very small brushes (0.8 cm) with a wastewater feed resulted in unstable MFC performance, while the use of 2.5 cm diameter brushes did not (Stager et al., 2017). Thus, a decrease in brush size from 5.1 cm to 2.5 cm might improve MFC performance without adversely impacting stable power generation, but only if the anode resistance is a substantial part of the overall internal resistance.

Reducing the spacing between two deployed electrodes will reduce the ohmic drop and could increase power output, and thus a further reduction in electrode spacing could also improve the performance if the ohmic losses are a main factor in power production (Li et al., 2013). For example, the solution resistance in the large chamber with a 3.5 cm electrode spacing was 0.47 Ω, which was 21% of the internal resistance of the reactor (2.19 Ω). Reducing the spacing from 3.5 cm to 1.4 cm could further decrease the solution resistance by 60%, to 0.19 Ω, and raise the maximum power density.

Increasing the active area of the cathode, and operating with lower hydraulic pressure, could also improve its performance. The stainless steel frame used here reduced the active area of the cathode by 23%, and thus reducing the size of the frame relative to the cathode panels could help improve performance. The hydraulic pressure against the cathode has been shown to reduce the performance of some cathodes, likely due to the increased catalyst flooding with water (Ahn et al., 2014; Cheng et al., 2014a). Further experiments should be conducted on the impact of hydraulic pressure on large scale cathodes by carrying out abiotic tests with different volumes of electrolyte in the chamber. It might be possible to improve the cathode performance by making them more hydrophobic by varying binder content or diffusion layer porosities, or by using a different type of diffusion layer (Yang et al., 2015). It might also be possible to use different cathodes in the bottom of the chamber where the water pressure is greatest, compared to cathodes at the top where water pressure is lower.

As previously noted, a critical factor in scaling up MFCs is maintaining sufficient cathode surface area per volume (cathode specific surface area) as the reactor size is increased in order to achieve rapid COD removal and maintain a good volumetric power density (Logan et al., 2015). The cathode specific surface area of the large chamber used in this study was only 7.3 m^2 m^{-3}, due to the original design factors for evaluating abiotic cathode performance. This is much lower than the 25 m^2 m^{-3} previously used in many

MFC tests (He et al., 2016b; Logan et al., 2015). Thus, the overall performance in terms of COD removal rate as well as power density will be increased in planned larger scale designs based on closer electrode spacing, and connecting an anode array to two cathodes.

4. Conclusions

A 6200 cm^2 air-cathode made of fifteen smaller cathodes welded to a single conductive metal sheet was examined in abiotic and biotic tests. Overall, the performance of the large cathode (6200 cm^2) decreased relative to the smaller cathodes (7 cm^2, 33 cm^2). However, the maximum power density of $0.083 \pm 0.006\ W\ m^{-2}$ was comparable to that obtained in other larger-scale aqueous catholyte MFCs, but there was no catholyte or water aeration needed for our system. Thus, the design provided an energy-positive system due to passive oxygen transfer to the air cathode. Full coverage of the cathode by the brush anodes was needed, as reducing the anode projected area from 6000 cm^2 to 2500 cm^2 decreased the maximum power density by 27% to $0.061 \pm 0.003\ W\ m^{-2}$. These tests showed the first time that an air cathode could function in a large-scale MFC at a high hydrostatic water pressure (85 cm water height). Several design factors were discussed that could lead to further improvements in overall power production, such as closer electrode spacing and a more hydrophobic diffusion layer with increased water pressures.

Notes

In the event of Vito's fabrication method of the large electrode being commercialised, two authors (Deepak Pant and Yolanda Alvarez Gallego) declare a competing financial interest due to employment at VITO. The other authors have no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2018.10.022.

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14. ABSTRACT

To scale up microbial fuel cells (MFCs), larger cathodes need to be developed that can use air directly, rather than dissolved oxygen, and have good electrochemical performance. A new type of cathode design was examined here that uses a "window-pane" approach with fifteen smaller cathodes welded to a single conductive metal sheet to maintain good electrical conductivity across the cathode with an increase in total area. Abiotic electrochemical tests were conducted to evaluate the impact of the cathode size (exposed areas of 7 cm^2, 33cm^2, and 6200 cm^2) on performance for all cathodes having the same active catalyst material. Increasing the size of the exposed area of the electrodes to the electrolyte from 7 cm^2 to 33 cm^2 (a single cathode panel) decreased the cathode potential by 5%, and a further increase in size to 6200 cm^2 using the multi-panel cathode reduced the electrode potential by 55% (at 0.6 A m^{-2}), in a 50 mM phosphate buffer solution (PBS). In 85 L MFC tests with the largest cathode using wastewater as a fuel, the maximum power density based on polarization data was $0.083 \pm 0.006 Wm^{-2}$ using 22 brush anodes to fully cover the cathode, and $0.061 \pm 0.003 Wm^{-2}$ with 8 brush anodes (40% of cathode projected area) compared to $0.304 \pm 0.009 Wm^{-2}$ obtained in the 28 mL MFC. Recovering power from large MFCs will therefore be challenging, but several approaches identified in this study can be pursued to maintain performance when increasing the size of the electrodes.

15. SUBJECT TERMS

Microbial fuel cells; Scaling up; Wastewater; Chronopotentiometry; Air cathode

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