ABSTRACT

Title of Document: ELECTRICITY GENERATION USING SEDIMENT MICROBIAL FUEL CELLS WITH A MANGANESE DIOXIDE CATHODE CATALYST

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Wastewater treatment plants employ an energetically costly aerobic unit process to remove organic matter from municipal wastewater; this process is known as activated sludge. Microbial fuel cells (MFCs) present an anaerobic, energy-saving approach to wastewater treatment that results in electricity generation. However, MFCs are often limited by internal resistance from membrane fouling and slow cathodic oxygen reduction.

This work examined an option to overcome these limitations-- adapting membrane-less sediment microbial fuel cells (SMFCs) for use with wastewater as an organic substrate by using floating carbon cloth air cathodes coated with an oxygen reduction reaction (ORR) catalyst. The performance of a platinum ORR catalyst at the cathode was compared to a manganese dioxide ORR catalyst and several additional cathode materials and reactor configurations were tested to optimize SMFC

performance. The MnO_2 catalyst, though significantly cheaper than platinum, was unable to sustain consistent high cathode potentials in wastewater over time.

ELECTRICITY GENERATION USING SEDIMENT MICROBIAL FUEL CELLS WITH A MANGANESE DIOXIDE CATHODE CATALYST

By

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1.1 Literature Review

1.1.1 The water crisis in developing countries

In the developing world, more children under five years old die from water-borne illnesses than by other diseases. Over 2.5 billion people live without adequate sanitation, and 1.5 million children die annually as a result of poor sanitation (Anon 2014c). The absence of proper sanitation can directly result in the contamination of drinking water sources with wastewaters carrying fecal-borne diseases.

Because of this global public health crisis, international development organizations, including the United Nations and the World Health Organization (WHO), have made access to clean water and sanitation major priorities. The lack of adequate (or complete absence of) sanitation is most strongly felt in sub-Saharan Africa where 64% of the population is without improved sanitation. Here, diarrheal-related deaths are more common than any other part of the world and the need for low-cost, effective sanitation is most pronounced (Montgomery & Elimelech 2007).

Offering improved sanitation even without changing the quality of the drinking water supply is likely to lower the spread of fecal-borne diseases (Hutton & Haller 2004). This would entail providing people with proper sewage disposal to reduce the contamination of food and drinking water sources. Installing decentralized systems (e.g. pit latrines) is significantly cheaper than connecting rural households to even the most basic centralized wastewater treatment systems. A WHO report estimates that significant financial benefits in productivity and avoided deaths would result from improving sanitation globally (Hutton & Haller 2004). However, many rural communities have little to no access to reliable electricity that would be necessary to power the conveyance and basic treatment of wastes.

1.1.2 Sanitation and energy consumption in the United States

The United States enjoys a high standard of water quality due to its extensive network of drinking water and wastewater treatment systems. Over 54,000 community water systems provide safe drinking water to over 250 million Americans, which have virtually eliminated the spread of disease by waterborne pathogens (WIN, 2000). Many of these water and sanitation systems were built several decades ago however and need updating due to aging infrastructure, increases in population served, and new mandates from the Clean Water and Safe Drinking Water Acts. According to the American Society of Civil Engineers' 2013 report card on America's infrastructure, the United States' water and wastewater infrastructure is in poor condition and will need $84 billion in addition to the estimated funding that is has been assigned by 2020 (Anon 2013). This additional support is needed for infrastructure repairs and maintenance and to meet the continued rise in operating costs.

Examining wastewater treatment alone, publicly owned treatment works (POTW) in the United States treat over 32 billion gallons of domestic wastewater each day (Anon 2014a). The transport and treatment of this wastewater consumes 100 billion kWh at a cost of over $25 billion annually (Goldstein & Smith 2002; Menendez 2009). The average energy consumption of American wastewater treatment plants (WWTP) is 1,200 kWh per million gallons of wastewater treated;

however, this number varies greatly depending on the size of the treatment operation. POTWs with flows on the order of millions of gallons per day (MGD) are much more efficient (100s of kWh per MG), while those with low flow rates can use several thousand kWh per million gallons treated. Energy accounts for 30-80% of WWTP operating costs and 4% of all electricity used in the United States (Goldstein & Smith 2002; Menendez 2009). WWTPs can be the largest electricity consumers within their communities and a breakdown of each process's electricity consumption is given in Figure 1-1.

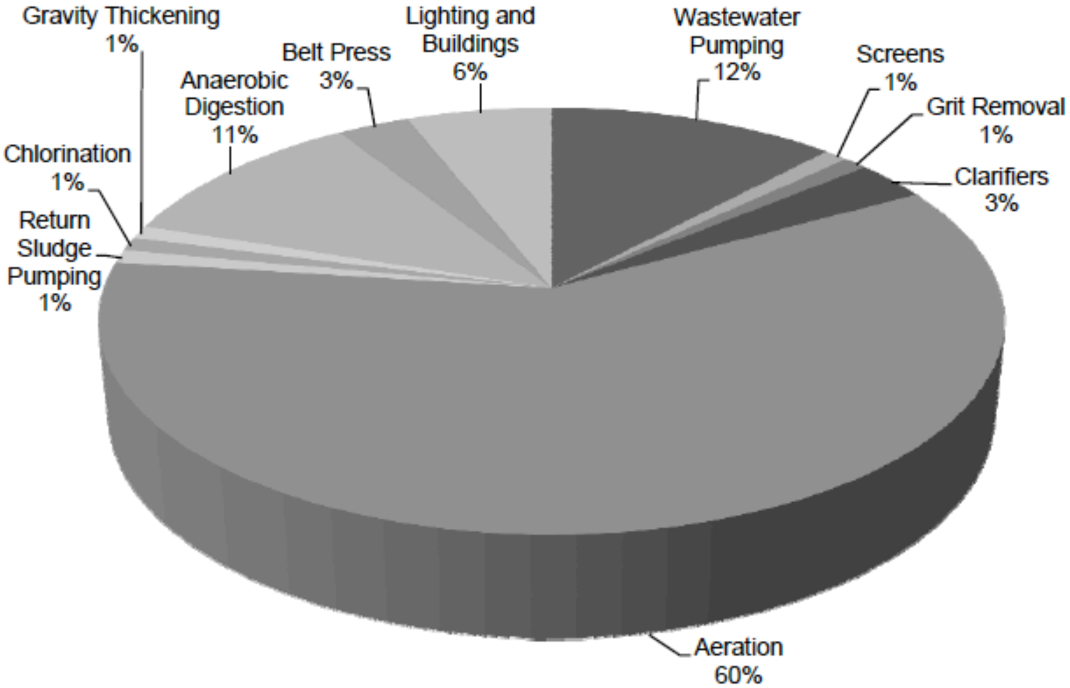

Figure 1-1: Typical POTW percentage of energy consumption by unit process. Note: Aeration includes activated sludge and dissolved air flotation thickening. (Menendez 2009)

1.1.3 Wastewater Treatment

Wastewater treatment techniques vary from plant to plant depending on the size of the community served and the area available for the WWTP itself. Generally speaking, a plant that treats a flow on the order of several MGD follows a fairly standard process: the influent passes through screens that remove large debris to the primary clarifiers where solids are settled out for processing and treatment. Next, the supernatant [resulting wastewater] flows to the secondary reactors where it is continuously aerated to allow aerobic bacteria to consume the remaining organic matter. After secondary treatment, also known as activated sludge, it undergoes more settling in order to remove biomass produced during activated sludge, and then either to tertiary treatment or straight to disinfection before being discharged. The process used by DC Water at Blue Plains Advanced WWTP in Washington, DC is illustrated in figure 1-2.

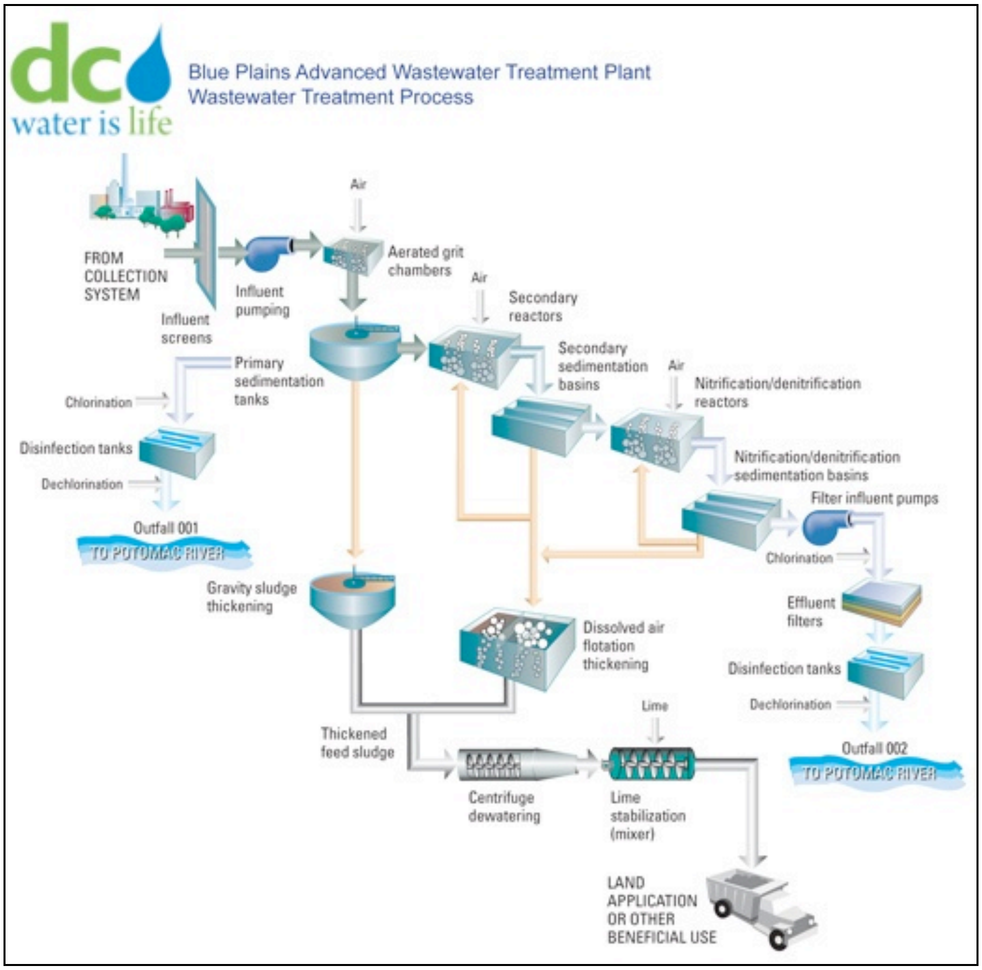

Figure 1-2: Blue Plains advanced WWTP schematic

1.1.4 Low-energy wastewater treatment

Energy-saving wastewater treatment methods, such as lagoons, currently exist but are not often practical at municipal scale. Lagoons are essentially large holding ponds that allow for natural aerobic or anaerobic processes to break down organic matter over time. Once wastewater is pumped into a lagoon, little-to-no external energy is necessary for treatment. However, they require relatively long retention times- anywhere from three to 50 days depending on their depth, aeration, and temperature (Anon 1997)- and are only appropriate for small communities with enough available land to build sufficiently large holding ponds to handle their flow of wastewater. Facultative lagoons, which contain both aerobic and anaerobic zones, generally require an acre of space for every 200 people served. Aerated lagoons need only a fraction (one-tenth to one-third) of the space of a facultative lagoon and less detention time, but they require an energy input for their aeration.

A similar wastewater treatment technique is the septic tank, which is applicable on an individual household level and works very much like an anaerobic lagoon (Anon 1997). Again, space becomes a limiting factor in more densely populated communities and contamination of groundwater from ammonia and phosphates can also be a concern.

1.1.5 Energy recovery from wastewater

Wastewater is mostly composed of water and a variety of organic compounds including carbohydrates, volatile fatty acids, and aromatics, and large amounts of chemical energy is contained in these molecules. Some estimate that raw wastewater can contain up to nine times the amount of energy used in treatment (Shizas & Bagley 2004) in the form of organic matter (usually represented by chemical oxygen demand (COD [mg/L]). Approximately 66% of this energy is removed during primary sedimentation and sent for solids treatment, leaving 34% in wastewater that proceeds to secondary treatment. Anaerobic digestion (AD), whereby the digestion of biosolids from anaerobic bacteria results in the production of biogas, is currently employed by wastewater treatment operations of all sizes. Efficient digesters can eliminate 85% of COD and yield 96% methane from COD eliminated (methane produced = $0.85*0.96*COD_{in}$). The biogas produced by anaerobic digesters is generally 60-70% methane, which can be used as a fuel (Lettinga 1995).

While AD provides an energy-producing technique for the treatment of biosolids, a viable, energy-positive treatment method for the wastewater separated from solids in conventional WWTPs has yet to be developed. The latter is needed because the treatment of this remaining wastewater through activated sludge is an extremely energy-intensive unit process.

Activated sludge utilizes mechanical aeration of wastewater to facilitate break down of organic matter by aerobic bacteria (Oh et al. 2010). This process forgoes capturing the energy liberated by the reaction, which is dissipated as heat. As much as 60% of energy consumed by a WWTP is due to aeration (Menendez 2009), which accounts for 21 billion kWh/y in the US alone (Goldstein & Smith 2002) and is by far the most costly step in conventional wastewater treatment. For example, Blue Plains utilizes sixteen 1-MW fans to aerate approximately 320 million gallons of waste per day. Developing less energy-intensive wastewater treatment strategies would not only reduce cost and carbon emissions associated with power generation, but could allow for better sanitation in developing countries where operational costs of conventional treatment methods are prohibitive.

Blue Plains WWTP in Washington, DC serves 2.2 million people and consumes 20 megawatts (MW) of power on average to mechanically aerate 1.2 billion liters of wastewater per day. In contrast, this amount of wastewater contains 40 MW assuming an energy content of wastewater organic matter of 14.7 kJ/g-COD and an influent to secondary treatment containing 200 mg/L-COD (Shizas & Bagley 2004). More recent estimates, which attempt to include energy content of volatile organic compounds (VOCs) not previously accounted for, put the energy of domestic wastewater even higher (Heidrich et al. 2011). Using a freeze-drying method to measure the energy in wastewater organic matter, it was estimated that domestic wastewater contains 17.8 kJ/g-COD (Heidrich et al. 2011). Using this estimate and the conditions described above, the daily flow of wastewater at Blue Plains contains over 49 MW of power. Harnessing any of that power while reducing the amount of aeration needed for secondary treatment would greatly improve Blue Plains' operational efficiency and overall carbon footprint.

1.1.6 Microbial Fuel Cells

Microbial fuel cells (MFCs) are electrochemical devices that, like anaerobic digesters, use anaerobic bacteria as the catalysts to oxidize organic matter (OM) and ultimately generate power (Logan et al. 2006). In a MFC however, a unique consortium of bacteria, called anode-respiring bacteria (ARB), are selected for because they can perform extracellular electron transfer and form a biofilm, usually several cells thick, that covers the anode. The growth of this biofilm on carbon cloth over time is illustrated in figure 1-3 with the specie *Geobacter sulfurreducens* and a consortium of ARB. To generate electricity, the net MFC reaction is separated into two half reactions, oxidation of OM at the anode and reduction of an electron acceptor (typically oxygen) at the cathode. ARB in the anode biofilm degrade simple OM through oxidation and transfer the electrons to the anode. The digestion of OM occurs in an anoxic environment so that oxygen or other electron acceptors do not consume the electrons. Protons are created at the anode as a byproduct of this microbial oxidation. As the electrons flow through the external circuit to the cathode, the protons diffuse/migrate through the MFC to the cathode where they recombine with the electrons under the influence of a catalyst (usually a metal, such as platinum) in the presence of oxygen and form water. Electrical current is harnessed by physically separating the reactants (OM and oxygen) and allowing the electrons to travel through an external circuit connecting the electrodes. As electrons are liberated by the oxidation reaction at the anode, they can have higher potential energy (more negative potential) than when they are subsequently consumed by the reduction reaction at the cathode. The difference in potential energies (voltage) results in energy that can be imparted to the external circuit connecting the anode to the cathode. A common MFC utilizes acetate as the fuel, either added to water or as found in wastewater, and oxygen as the oxidant. The net MFC reaction is described by the following chemical equation (when acetate is used as the substrate):

Anodic half-reaction: $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-$

Cathodic half-reaction: $2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$

Net Reaction: $CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$, $\Delta G^0 = - 875$ kJ/mole of acetate reacted

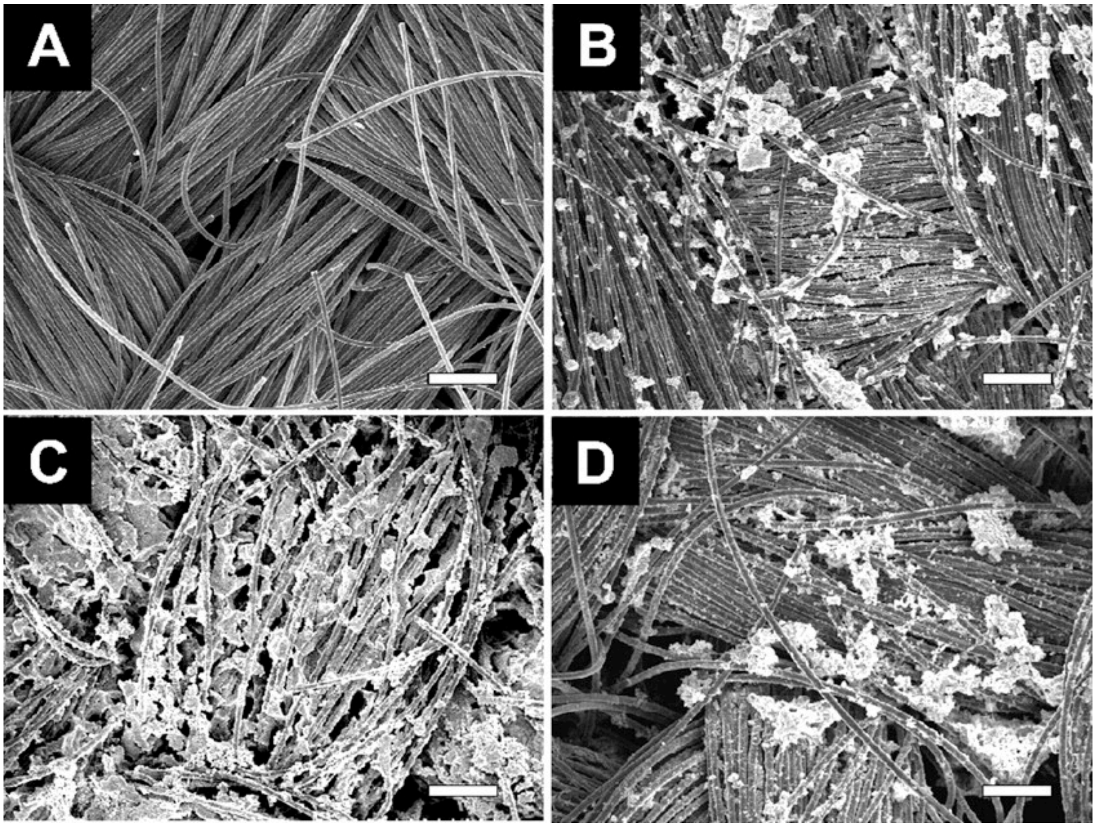

Figure 1-3: SEM images of (A) plain carbon cloth, (B) a biofilm of *Geobacter sulfurreducens* cells after 11 days, (C) after 216 days, (D) consortium biofilm after 28 days. Bars, 100 µm (Ishii et al. 2008)

1.1.7 Overview of MFC materials and designs

Microbial fuel cells are typically constructed either as single-chamber or double-chamber devices. The two-chamber configuration utilizes an ion-exchange membrane separating the anode and cathode chambers to maintain the anode in an anaerobic, substrate-rich environment while providing the cathode access to dissolved oxygen in water (Figure 1-4). The ion-exchange membrane enables a net concomitant flow of positively charged ions from the anodic half-cell to the cathodic half-cell to compensate for charge accumulation in each half-cell due to electron flow through the external circuit. For this configuration, it is best to minimize anode and cathode separation thereby reducing the distance protons must travel through the MFC (Logan

2010). The greater the electrode separation, the slower the proton transport and the greater the internal resistance; however contact between anode and cathode will result in short-circuiting and is prevented through the use of a membrane. Lacking alternatives, MFCs use the same ion exchange membranes, such as Nafion (Dupont Co., USA) (Logan et al. 2006), used in conventional fuel cells. The performance of these membranes is dramatically lower in MFCs however, owing to the complex nature of MFC anolytes (e.g., wastewater) which contain trace metals that irreversibly bind into ion exchange membranes (Sleutels et al. 2009). As consequence, ion exchange membranes have been shown to be a factor significantly limiting MFC power output (Rozendal et al. 2006). Current research efforts are searching for a better, cheaper material.

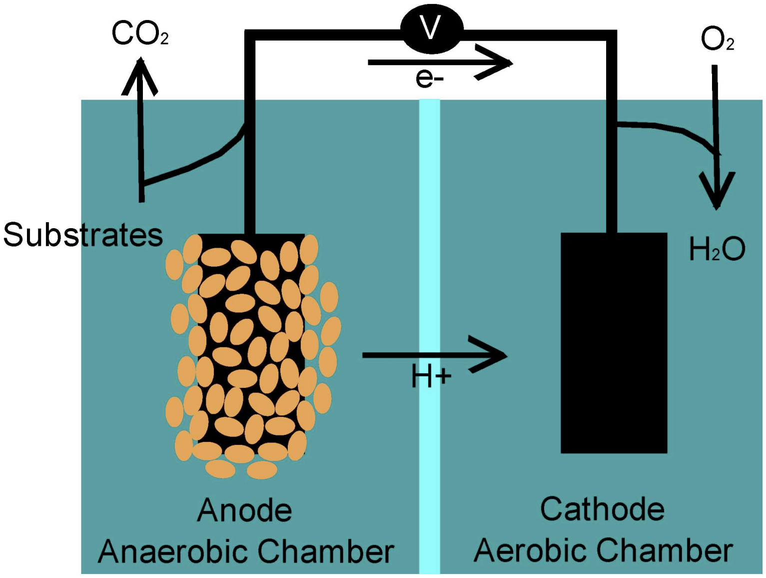

Figure 1-4: Two-chamber MFC

In the case of a single-chamber MFC, a permeable cathode (e.g., carbon cloth) is used to seal a chamber containing the anode (like the head of drum; figure 1-5). The cathode uses oxygen in air contacting its outer side as the oxidant. This is advantageous since unlike a liquid catholyte containing dissolved oxygen that requires constant energy-intensive aeration, the air cathode relies on passive oxygen diffusion. The outer side of the cathode must be sealed in such a way that oxygen can diffuse through the sealant to the cathode, but fluid containing fuel inside the chamber does not leak through. Such MFCs have their own limitations depending on whether or not they employ a membrane. While omitting a membrane can enhance proton transport reducing internal resistance, its absence can allow excess oxygen to enter through the cathode and reach the anode thereby killing the anaerobic bacteria on the anodic biofilm.

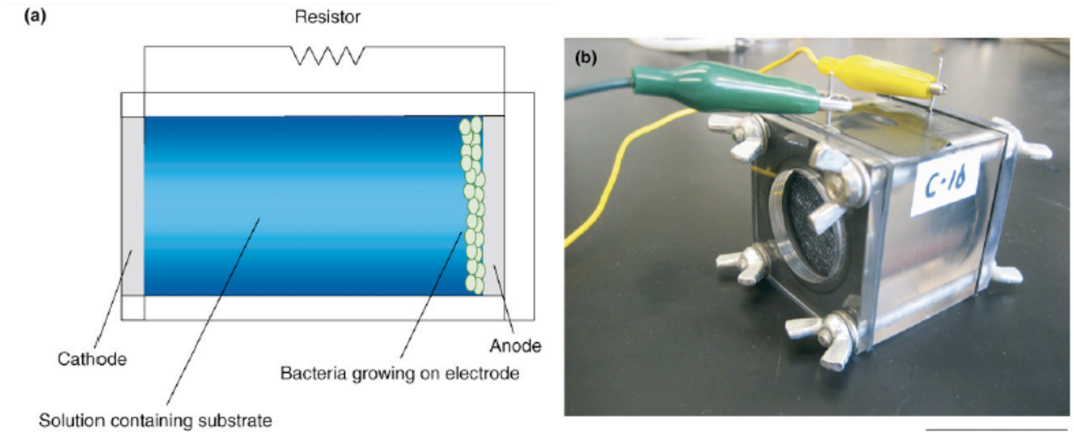

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Figure 1-5: (a) Schematic of single-chamber MFC, (b) photo of single-chamber MFC (Logan & Regan 2006)

The anode must be conductive and biocompatible (e.g., copper is toxic to bacteria, other metals corrode) to allow the biofilm to grow and thrive while remaining chemically stable in the solution. The most versatile electrode material is carbon, which is available in many forms. The simplest materials for anode electrodes are graphite plates or rods because they are relatively inexpensive, easy to handle, and have a defined surface area (Logan et al. 2006). Another option is a graphite fiber brush anode where a core made of a non-corrosive metal, such as titanium, and graphite fibers that extend away from the core, provide a very high surface area for the biofilm to attach (Logan 2010). While much work has gone into increasing anode surface area to maximize the ARB in a system, the anode reaction is rarely what limits MFC performance.

The cathode is often the limiting aspect of an MFC's electricity production due to the slow nature of the oxygen reduction reaction (ORR) and its need for a catalyst. Air cathodes (for a single-chamber MFC) must have an ORR catalyst on a conductive material that is exposed to both air and water, which makes their engineering difficult (Logan 2008). One common air cathode configuration is that of carbon paper or cloth that is coated on one side with platinum, which acts as the catalyst (Logan 2008). Recently, progress has been made in replacing the platinum catalyst used for oxygen reduction with non-precious metals and metal-organic compounds based on cobalt and iron (Logan 2010). Ferricyanide is popular as an experimental electron acceptor in microbial fuel cells (Logan et al. 2006), but must be continuously replenished to the cathode chamber and creates hazardous waste. Cathodes using only bacteria (biocathodes) show great promise, but so far, these systems have required the use of dissolved oxygen rather than air and would require regular aeration in a wastewater treatment system which would increase energy costs. Some work has gone into developing cathodes that can use nitrate as an electron acceptor that would be very applicable to ammonia-rich wastewater (Clauwaert et al. 2007; Logan 2010). Nitrogen removal is important to wastewater treatment, since WWTPs are subject to EPA standards that dictate maximum levels of nitrogen allowed in wastewater effluent before it can be discharged into a natural waterway.

Once ammonia is oxidized to nitrate through wastewater aeration, it can be fed into a cathode chamber and used as an electron acceptor by denitrifying bacteria on the cathode. Thus far, studies have only found denitrifying cathodes able to remove significant amounts of nitrate when operated at potentials of less than 0.0V vs. SHE, therefore limiting the reactor's performance as a fuel cell (Clauwaert et al. 2007).

1.1.8 Wastewater Microbial Fuel Cells

Over the last decade, researchers have been evaluating the possibility of using MFCs to process wastewater and potentially generate net positive electricity for a wastewater treatment facility (Rozendal et al. 2008; Oh et al. 2010; Ahn & Logan 2010; Lefebvre et al. 2011). Since MFCs use an anaerobic process to oxidize organic matter, their application in a wastewater treatment plant would significantly decrease a facility's electricity consumption by eliminating the need for aeration during secondary treatment. This role of COD removal alone would save energy and reduce operating costs. As MFCs continue to be enhanced to produce increasing amounts of power in addition to COD removal, they could decrease the need for WWTPs to use any energy from outside power grids. Most testing so far has been small-scale and laboratory-based using very low volumes of wastewater. However, a few researchers have attempted scaling-up their experiments to see the potential applications of MFCs in WWTPs (Logan 2010; Jiang et al. 2011) and the large-scale production and sale of MFCs is being explored by private enterprise (Anon 2014).

A review of the literature showing a range of results from wastewater MFCs using a variety of substrates and two-chamber vs. single-chamber MFCs is summarized in tables 1-1 and 1-2. SCMFCs operated with municipal wastewater as their organic substrate typically produced maximum power densities during polarization of approximately 300 mW/m^2.

Table 1-1: Wastewater MFCs and their power outputs from Fornero review (Fornero et al. 2010)**. Power densities are presented either as power per unit anode surface area or power per unit anode volume.**

Substrate	Anode Vol. (mL)	COD (mg/L)	Maximum Power
Acetate	560	458	48 W/m^2
Hospital WW	390	332	25 W/m^3
Municipal WW	390	429	10 W/m^3
Soluble Swine Waste	28	8320	261 mW/m^2
Municipal WW	22	379	72 mW/m^2
Slaughterhouse WW	28	1420	80 mW/m^2
Brewery WW	5400	1168	5 W/m^3

Table 1-2: Single-chamber wastewater MFCs and their power outputs

Substrate	Anode Vol. (mL)	COD (mg/L)	Max. power	Citation
Primary influent	130	303	328 mW/m2	(Ahn et al. 2014)
Primary influent	130	303	282 mW/m2	(Ahn et al. 2014)
primary effluent	28	not given	300 mW/m2	(Ahn & Logan 2010)
brewery wastewater	28	2250	170 mW/m2	(Feng et al. 2008)
brewery wastewater	100	430	18 W/m3	(Katuri & Scott 2010)

1.1.9 Single-chamber microbial fuel cells for wastewater treatment

Single-chamber MFCs (SCMFC) typically employ an air cathode that utilizes atmospheric oxygen for the cathodic oxygen reduction reaction. In this configuration, there is no longer a need for mechanical aeration of a cathode chamber and the use of a proton exchange membrane may also be eliminated. These advantages have increased the use of SCMFCs in recent wastewater MFC studies.

One experiment used a SCMFC that contained eight graphite electrodes (anodes) and a single air cathode. The system was operated under continuous flow conditions with primary clarifier effluent obtained from a local wastewater treatment plant. This SCMFC generated a maximum power density of 26 mW/m^2, while removing up to 80% of the wastewater's COD. Power output was proportional to the concentration of COD in the substrate (ranging from 50 to 220 mg/L of COD) and inversely proportional to the hydraulic retention time (HRT- ranging from 3 to 33 hours). The coulombic efficiency of the system, based on COD removal and current generation, was <12% indicating a substantial fraction of the organic matter was lost without current generation (Liu, Ramnarayanan et al. 2004). This signifies that much more electricity could be generated if coulombic efficiency is improved. However, it is important to note that the high percentage of COD removal indicates that the MFC was effective in terms of treating the wastewater.

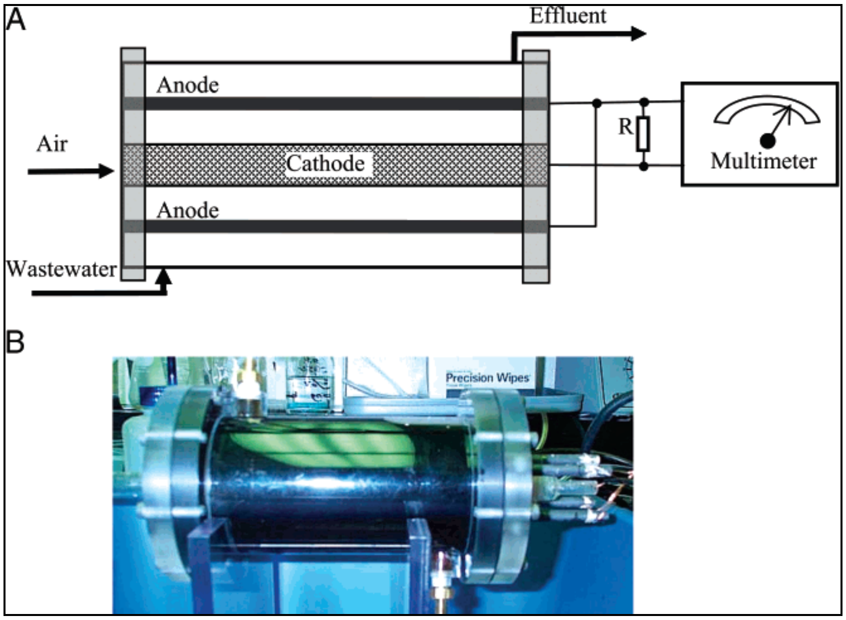


Figure 1-6: SCMFC of one cylindrical plexiglass chamber (vol. 388 mL) with 8 graphite rods (anode) placed about one air cathode of carbon/Pt catalyst/PEM layer (Liu et al. 2004)**.**

1.1.10 Benthic Microbial Fuel Cells

Benthic MFCs (BMFC, also referred to as sediment MFCs) are unique because they do not require the use of a synthetic membrane and have a simple design in that they are not contained in the same way as single- and double-chamber MFCs. Because ocean sediment redox conditions transition from being oxidizing to reducing over the top few centimeters, this area acts as a natural proton exchange membrane between the anode (under the sediment) and the cathode (in the overlying water) (Reimers et al. 2001; Tender et al. 2002). BMFCs sit in sediment, which provides fuel to the anode. Power generation of a BMFC is mainly limited by the mass transport of fuel to the anode, which is attributed both to diffusion, and to advection driven by the movement of sediment pore water coupled with the motion of the overlying water due to current and tidal activity.

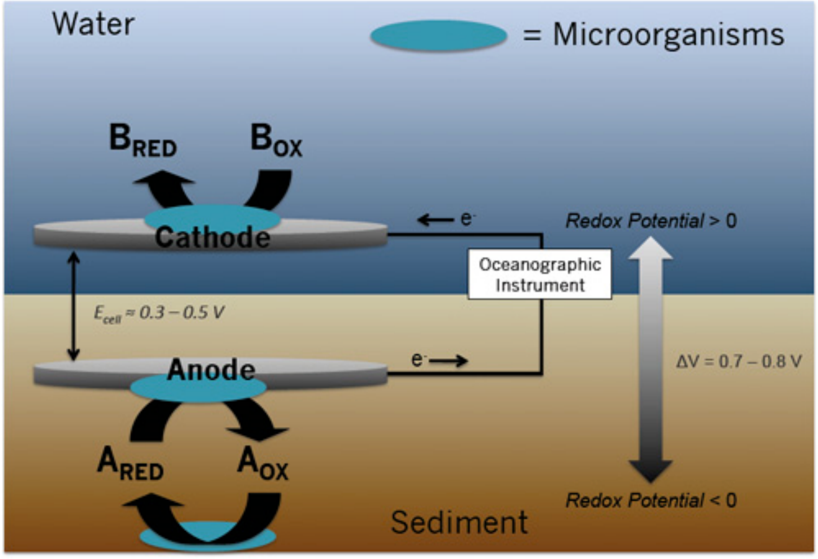


Figure 1-7: Schematic depiction of typical benthic MFC configuration

Initial lab-scale tests where BMFCs were constructed in small aquariums meant to simulate the ocean floor and used platinum mesh electrodes showed sustained power densities of 1.0 mW/m^2 (Reimers et al. 2001). Several models of BMCFs have been tested in the field over the last 10 years with emphases on facilitating deployment, increasing mass transport of fuel to the anode, and maximizing power production. BMFCs have provided demonstrations of successful power production by an MFC and practical applications by powering environmental monitoring devices over several months. Because BMFCs serve the specific purpose of powering devices, their study has focused on maximizing power production and little attention has been paid to maximizing their COD removal. One study using BMFCs looked at sediment organic matter (SOM) and its decomposition. SOM is broken down during the operation of BMFCs, with the simplest particles having the highest rate of oxidation while complex molecules have lower rates of oxidation. The breakdown efficiency of SOM was higher under closed circuit conditions than under open circuit conditions (Hong, Kim et al. 2010).

One version of a BMFC was deployed in the Potomac River in Washington, DC and had a mass of 230 kg, a volume of 1.3 m^3, and sustained 24 mW (Tender et al. 2008). This BMFC was comprised of seven subunits (each consisting of two graphite plates) connected in a row. The subunits were affixed to the top and bottom of an enclosure that was deployed on the bottom of the Potomac River. The bottom electrodes (anodes) were covered by 5 cm of sediment and the top electrodes (cathodes) were exposed to overlying water (water depth ranged between 1 and 3 m) (Tender et al. 2008).

Another version of a BMFC had a mass of 16 kg, a volume of $0.03m^3$, and sustained 36mW. This smaller version was much easier to deploy (Tender et al. 2008). The anode of this BMFC consisted of 12 graphite plates arranged in a vertical array and were affixed to the underside of a fiberglass top plate. The cathode consisted of a meter-long graphite bottle brush electrode positioned in overlying water. The BMFC was deployed in August 2006 to power a buoy in a boat basin carved into a salt marsh near Tuckerton, NJ, USA. It sustained 36 mW in the salt-water environment, which represents a power density of 16 mW/m^2 (Tender et al. 2008).

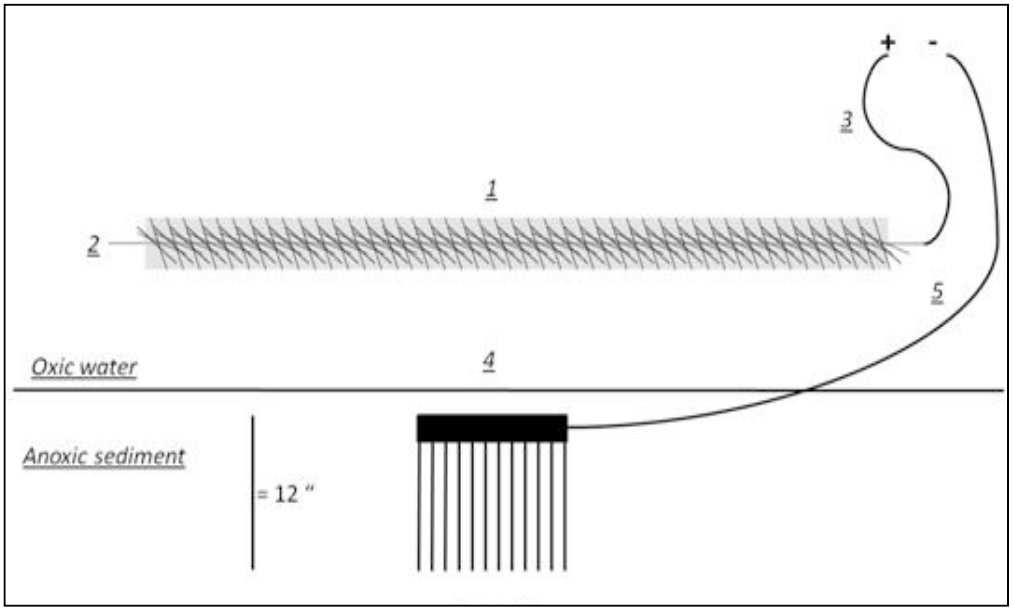


Figure 1-8: Schematic depiction of the cube anode based BMFC. 1: graphite bottle-brush cathode, 2: twisted core wire current collector, 3: cathode electrical lead, 4: benthic (sediment/water) marine interface

One way to improve mass transport to BMFC anodes, and therefore power output, is by decreasing the volume of the anode while increasing its surface area. This was accomplished by utilizing a graphite-fiber bottlebrush electrode for the anode as well as the cathode. Using a cylindrical anode, it was possible to benefit from radial diffusion of organic matter to the anode. In order to provide necessary rigidity to the anode and prevent compaction of carbon fiber strands by direct contact with sediment, the anode carbon fiber electrode was inserted into a small diameter slotted PVC tube (e.g., 1 in). One such model deployed in San Diego Bay during a 2010 experiment was equipped with a 5 ft long x 2 in diameter graphite bottle brush anode housed in 5 ft long x 1 in diameter slotted PVC tube embedded inches below and parallel to the anode surface. This BMFC sustained 15 mW with a power density of 120 mW/m^2 (Tender 2011) when power is normalized by anode footprint area.

In a series of experiments led by Clare Reimers at Oregon State University in 2004, a BMFC comprised of graphite bottlebrush cathode and graphite spike anode was deployed on a cold seep in the Monterey Canyon on the coast of California in which a remotely operated vehicle was used to insert the anode spike directly into the seep. This demonstrated a maximal sustained power density of 34 mW/m^2 of anode SA corresponding to 1.1 W/m^2 of seafloor area (Reimers et al. 2006). The power density based on the footprint area of the spike (1.1 m^2 FPA) is the highest of any recorded to date for a BMFC and is attributed to the high flux of fuel infused pore water flowing out of the seep onto the anode. However, wastewater MFCs have consistently achieved power densities on an order of magnitude greater than this BMFC as noted in Tables 1-1 and 1-2. The results from Monterey Canyon were later corroborated by a second experiment in which a chambered BMFC was placed overtop the seep (Nielsen et al. 2008). This shows that as the amount of fuel provided to the anode of a BMFC increases, so does its power output. Since these BFMCs have been limited by mass transport in almost all experiments to date, one can infer that the maximum power generation of BMFCs has not yet been realized.

1.1.11 Cathodic limitations of wastewater MFCs

Researchers at Ohio State University lay out general cathode limitations (Rismani-Yazdi et al. 2008) and emphasize cathodic overpotentials resulting from activation, ohmic, and mass transport losses. It appears that the greatest limitation in a MFC cathode is the sluggish nature of the oxygen reduction reaction (ORR) at neutral pH and low temperatures. Oxygen is often used as the electron acceptor in the cathode chamber because of its abundance and high positive redox potential (Oh et al. 2004; Roche & Scott 2009; Zhang et al. 2009). A fuel cell's performance is limited by the slow kinetics of the ORR at neutral pHs, which results in a large cathodic overpotential; a catalyst is typically used to overcome this limitation (Zhang et al. 2009). Platinum is commonly used as an ORR catalyst in hydrogen fuel cells and batteries and has also been tested in MFCs. In pure substrate MFCs (e.g. acetate-fed), a platinum catalyst applied to the cathode surface has been used successfully to improve MFC performance. However, platinum appears to foul over time in the presence of a variety of common compounds, and it is prohibitively expensive for use at a large scale (Zhang et al. 2009). Common contaminants that adsorb to platinum and block active sites for oxygen reduction include various sulfur compounds such as H_2S and SO_2, COS, ammonia, and chloride ions (Baturina & Garsany, 2011) all present in wastewater. Exposure to these compounds can poison Pt electrocatalysts within a matter of hours, observable through resulting voltage drops over time at constant current densities (Nagahara et al. 2008). The complexity of raw wastewater as a fuel source for MFCs and its high concentrations of ammonia, hydrogen sulfide, and other compounds increase the likelihood of rapid fouling of a Pt catalyst at the cathode. It has been shown that the fouling of platinum-coated cathodes in wastewater-fed MFCs reduced cathode performance over time (Dong et al. 2013).

Alternative catalysts and MFC configurations are being explored for their use in wastewater treatment and electricity generation. An ideal catalyst would overcome the activation losses associated with ORR, have longevity in wastewater, and be inexpensive and easily applied. Studies that have explored other transition metal ORR catalysts found that manganese-based compounds, MnO and MnO_2, are promising catalysts as they are more affordable than platinum and relatively easy to synthesize (Roche & Scott 2009; Li et al. 2010; Zhang et al. 2009). When applied as an ORR catalyst at the cathode, MnO_x was found to perform almost as well in synthetic wastewater-fed batch MFCs as platinum. MFCs with MnO_x cathodes achieved 161 mW/m^2 while those with Pt cathodes achieved 193 mW/m^2 (Roche et al. 2009). Certain MnO_x cathode catalysts used in MFCs under continuous flow out-performed MFCs with Pt cathodes in both electricity generation and treatment efficiency when MFCs were inoculated with wastewater influent and then fed synthetic wastewater (Li, Hu, Suib, Lei, & Li, 2011). Maximum power densities measured during polarization differed most between MnO_x and Pt MFCs at lower hydraulic retention times (i.e., at HRT= 10 h, MnO_x MFCs achieved 75 mW/m^2, while Pt MFCs only reached approximately 50 mW/m^2). At the longest HRT, 40 h, all MFCs achieved comparable maximum power densities during polarization of approximately 200 mW/m^2. Lastly, COD removal efficiencies were 15-19% higher for MnO_x MFCs than

Pt MFCs (Li et al. 2011). The authors emphasize that not only did MFCs with MnOx cathodes outperform those with platinum cathodes under continuous flow conditions; they did so at 5% of the cost of platinum cathodes MFCs.

1.2 Study objectives and design

1.2.1 Study Aim

The aim of this work was to evaluate the potential of adapting the sediment MFC (SMFC) for use in a wastewater treatment plant's primary sedimentation tanks. SMFCs have been used in marine or freshwater environments relying on diffusion of SOM to the anode aided by tidal and storm events for substrate replenishment (Tender et al. 2008). Because of the slow nature of this diffusion mechanism, SMFCs had previously been considered anode-limited. Because a wastewater treatment plant has a constant stream of organic-rich substrate [primary influent], it was assumed that a wastewater SMFC would be cathode-limited due to the slow nature of oxygen reduction at neutral pHs as noted in the literature (Logan 2010; Rismani-Yazdi et al. 2008). To date, many studies on wastewater MFCs employ some form of a platinum catalyst at the cathode that effectively boosts MFC performance but fouls over time (Baturina & Garsany 2011; Liu & Logan 2004). In addition to the need for an effective ORR catalyst, it was necessary to overcome the obstacle posed by the anoxic nature of wastewater if a membrane-less MFC was to be used. Previous studies have successfully employed a carbon cloth air cathode (Middaugh et al. 2008) to use atmospheric oxygen at the cathode of a single-chamber MFC (Feng et al. 2008;

Liu & Logan 2004; Liu et al. 2004). This study aimed to develop an appropriate air cathode for a wastewater SMFC that tested an alternative ORR catalyst to platinum.

1.2.2 Study Objectives

The objectives of this work were threefold:

1. Develop an air cathode that can be deployed in an open system.

   It was necessary to identify the best cathode material that would meet certain requirements for successful use in a wastewater SMFC; float at the wastewater-air interface, maintain conductivity, and have a high surface area. Once these parameters were met, a protocol for the fabrication of a floating air cathode could be created and followed for all subsequent tests.

2. Identify an alternative to platinum for use as a cathode catalyst that is less costly and does not foul in wastewater.

   Cathodes using a MnO_x catalyst and those using a platinum catalyst were used in identical MFCs to evaluate and compare their performances. Additionally, loss of cathode potential was measured along with loss of catalyst over time.

3. Perform a bench scale electrochemical analysis of a wastewater SMFC.

   A standard electrochemical protocol was followed in all tests to evaluate biofilm growth over time in a wastewater SMFC when using a 3-electrode configuration where a potential is applied to the anode versus a reference electrode. Cyclic voltammetry was performed on the anode to evaluate its change in current output over time depending on substrate depletion. Changes in electrode potentials at different points in the study (at open circuit vs.

discharging current) were recorded and analyzed. Maximum power outputs of wastewater SMFCs under various conditions were recorded.

Chapter 2: ELECTRICITY GENERATION USING SEDIMENT MICROBIAL FUEL CELLS WITH A MANGANESE DIOXIDE CATHODE CATALYST

Abstract

Microbial fuel cells present an energy-saving process for wastewater treatment that results in electricity generation. In this study, sediment microbial fuel cells (SMFCs) were adapted for use with wastewater as an organic substrate by using floating carbon cloth air cathodes coated with an oxygen reduction reaction (ORR) catalyst. The performance of a platinum ORR catalyst at the cathode was compared to a manganese dioxide ORR catalyst.

Open circuit voltages of SMFCs with MnO_2 cathodes dropped over time while those with Pt cathodes remained stable. Over 90% loss of MnO_2 from the cathode surface occurred within the first two weeks of SMFC operation. After 55 days, Pt-SMFCs had a slightly higher average maximum power density during polarization than MnO_2 SMFCs, 65.35 mW/m^2 ± 4.59 and 48.32 mW/m^2 ± 10.13 respectively. Based on power densities recorded throughout the study, the better ORR catalyst could not be conclusively determined.

2.1 Introduction

Wastewater treatment plants (WWTPs) are often the largest consumers of power in their communities. As much as 30% of a WWTP’s operating costs are from energy consumption which accounts for 4% of all electricity used in the US and other developed countries (Network 2000; Goldstein & Smith 2002; Menendez 2009). The most widely used wastewater treatment technology in the US is the activated sludge process which utilizes mechanical aeration of wastewater to facilitate break down of organic matter by aerobic bacteria (Oh et al. 2010). This process forgoes capturing the energy liberated by the reaction, which is dissipated as heat. As much as 60% of energy consumed by a WWTP is due to aeration (Menendez 2009), which accounts for 21 billion kWh/y in the US alone (Goldstein & Smith 2002). In contrast, wastewater contains significant amounts of organic matter that some estimate could provide 14.7 kJ/g-COD if energy liberated by its oxidation with oxygen were captured (Shizas & Bagley 2004). For Blue Plains Advanced WWTP in Washington, DC, this would equate to 38.7 MW per day (assuming organic content of 200 mg/L of wastewater and a flow of 300 MGD). The ability to harvest this energy could transform wastewater from a community's costly problem to a sustainable fuel and many researchers are currently exploring possible technologies to do so (Graham-Rowe 2012; Shizas & Bagley 2004; Regan & Logan 2006; Rozendal et al. 2008).

Microbial fuel cells (MFCs) are electrochemical systems that produce electricity from the oxidation [breakdown] of organic matter (OM) under anaerobic conditions and are often touted as a potential waste-to-energy technology. They use specialized anaerobic bacteria, known as anode-respiring bacteria (ARB) as the catalysts to oxidize OM and ultimately generate power (Logan, Hamelers et al. 2006). The ARB biofilm oxidizes OM at the anode, liberating electrons that flow through an external circuit to the cathode where they reduce oxygen and form water.

In a two chamber MFC, an ion exchange membrane separates the chambers in which each half reaction occur. The two-chamber configuration utilizes an ion-exchange membrane to separate the anode and cathode chambers in order to maintain the anode in an anaerobic, substrate-rich environment while providing the cathode access to dissolved oxygen in water. Nafion © [Dupont] membranes, typically used in conventional fuel cells, do not perform as well in MFCs owing to the complex nature of MFC anolytes (e.g., wastewater) which contain trace metals that irreversibly bind into ion exchange membranes (Sleutels et al. 2009). These membranes have been shown to significantly limit MFC power output and increase their internal resistance (Rozendal et al. 2006).

Most MFCs use oxygen as the electron acceptor (Logan et al. 2006), owing to its abundance and high positive redox potential (Oh et al. 2004; Roche & Scott 2009; Zhang et al. 2009), in which oxygen combines with protons generated by the anode and electrons form the cathode forming water. MFC performance is severely limited however by slow kinetics of the oxygen reduction reaction (ORR) at neutral pHs inherent to MFCs to maintain viability of ARB and a catalyst is typically used to partially overcome this limitation (Zhang et al. 2009). While platinum is commonly used as a catalyst in MFCs, its high cost prohibits its use at a larger/commercial scale (Zhang et al. 2009). Additionally, fouling of platinum-coated cathodes in wastewater-fed MFCs results in reduced cathode performance over time (Dong et al. 2013). Common contaminants that adsorb to platinum and block active sites for oxygen reduction included sulfur compounds such as H_2S and SO_2, COS, ammonia, and chloride ions (Baturina & Garsany, 2011). Exposure to these compounds can poison Pt catalysts within a matter of hours, observable through resulting voltage drops over time at constant current densities (Nagahara et al. 2008). Studies that have explored other transition metal ORR catalysts found that manganese-based compounds, MnO_x, are promising catalysts as they are more affordable than platinum and relatively easy to synthesize (Roche & Scott 2009; Li et al. 2010; Zhang et al. 2009). Since they have yet to be tested in wastewater, their tendency to foul in a complex substrate is still unknown.

Microbial fuel cells can also be assembled in a single-chamber configuration in which the cathode and membrane are combined. Here, an air-permeable, water-impermeable cathode (typically comprised of a carbon cloth) is used to cover the open end of the anodic chamber which allows the ORR at the cathode to use atmospheric oxygen instead of dissolve oxygen. The design of air cathodes is very challenging wherein in order for each surface element of the cathode to be catalytically active it must simultaneously be exposed to protons and water molecules originating from inside the MFC and oxygen originating from outside the MFC. In the case of wastewater-fed MFC, direct exposure of the air cathode to the wastewater anolyte leads to cathode fouling, further limiting MFC performance.

One MFC variation that circumvents the need for a membrane while physically isolating the anode from the oxidant and the cathode from the anolyte is the “benthic” or sediment microbial fuel cell (SMFC) that generates electrical power to operate oceanographic sensors by oxidizing organic matter residing in marine sediments using oxygen in overlying water (Tender et al. 2008). To do so, the SMFC exploits the naturally occurring redox gradient between reducing conditions in anaerobic sediment at the bottom of many marine environments to oxidizing conditions in overlying water. Because of its need for large volumes of oxygenated water and the anoxic nature of wastewater, it has been said that the SMFC could not be adapted for wastewater treatment (Liu et al. 2004). However, a similar redox gradient exits between anoxic wastewater in primary settling tanks of WWTP and overlying atmospheric oxygen, which could allow adaptation of SMFCs for wastewater treatment.

The study reported here assessed the feasibility of adapting SMFCs for the treatment of domestic wastewater in order to reduce a treatment plant's energy consumption and produce useful power. An air cathode was developed that floated on the surface of wastewater in laboratory open top reactors containing wastewater collected from a WWTP primary settling tank. Owing to oxygen intrusion from overlying water and waste settlement, the top millimeters of wastewater in these reactors tend to be partially oxygenated and low in organic matter content, minimizing direct exposure of the cathode. Additionally, the performance of MnO_2 as an ORR catalyst was evaluated in comparison with previously tested platinum. While MnO_x catalysts have shown promise in previous studies, they have not yet been tested in domestic wastewater. Because of the low specific surface area (electrode SA: reactor volume) of the SMFC tested and its open configuration, COD depletion due to oxidation by ARB could not be distinguished from aerobic oxidation. Therefore, COD readings are not reported. The results indicate that benthic MFCs using wastewater as the primary substrate are able to achieve power densities higher than those achieved by benthic MFCs immersed in sediments. MFCs with MnO_2-coated cathodes performed comparably to those with Pt-coated cathodes, yet the platinum cathodes maintained a higher electrode potential.

2.2 Materials and Methods

2.2.1 Manganese Oxide Catalyst preparation

To synthesize the MnO_2 ORR catalyst for the cathode, a procedure previously reported by Roche and Scott was followed (Roche & Scott 2009). In brief, 4 grams of Vulcan Carbon (VC) XC-72 [Cabot, Boston, MA] were suspended in 100 mL of a 10 mM $MnSO_4$ [Sigma-Aldrich, St Louis, MO] aqueous solution in a 500mL one-neck flask. The VC was sonicated for 15 minutes at room temperature to assure that it was evenly coated with $MnSO_4$. A magnetic stir bar and reflux condenser were added prior to heating the slurry at 80°C for 30 min. An aqueous 114 mM solution of $KMnO_4$ [Sigma-Aldrich] was added through the reflux condenser over a five-minute period with heating. After the addition the reaction was refluxed for 30 minutes and filtered hot through a GV 0.2 μm filter [Pyrex, Tewksbury, MA] and washed with warm water. The resulting solid was dried in vacuum at 100°C for 12 hrs. The final yield was 3.9g (99%) and the loading of MnO_2 to carbon was approximately 20% (wt. percent) maximum.

2.2.2 Electrode Construction

The anode was constructed of a flat, circular graphite plate [Mersen ® G10] with a surface area of 15.4 cm^2 that was sonicated in deionized water for 15 minutes, three times. A press fit electrical connection was made using a nylon screw, nut, washer and titanium wire [McMaster-Carr ®, Princeton, NJ] connected to the potentiostat.

The cathode was constructed by applying oxygen diffusion layers to Panex 30 High Purity Carbon Cloth [Zoltek, St Louis, MO] as described by the first section of the protocol “How to make an air cathode with single diffusion layers for single-chambered MFCs,” (Middaugh et al. 2008). For this study, the carbon cloth used was not preliminarily wet-proofed and only 2 layers of 60% PTFE [Sigma-Aldrich] were applied instead of the recommended 4. This was done to reduce the internal resistance created by the PTFE layers, as two wet-proof layers were determined adequate to allow the carbon cloth to float at the surface of a liquid without any intrusion through the fibers. The edges of the PTFE-coated carbon cloth were then folded up and affixed using superglue to give the air cathode a boat-like shape with the diffusion layer facing the air and the carbon cloth serving as the base. These cathodes floated on the wastewater surface with a wetted surface area of 21 cm^2. Next, the carbon cloth side was coated with a catalyst layer. The catalytic layer of 0.5 mg MnO_2/cm^2 or 0.5 mg Pt/cm^2 was prepared by using 3.33 mg 20% MnO_2/vulcan carbon powder [see above for synthesis] or 15% Pt/VC [FuelCell Earth©, Stoneham, MA] per cm^2 of cathode surface area. The MnO_2/VC powder was mixed with 0.83 uL DI water, 10 uL liquion solution [Ion Power, New Castle, DE], and 3.33 uL isopropanol per mg of MnO_2/VC powder used. The mixture of these ingredients was sonicated with glass beads for one hour and the resulting catalyst ink was magnetically stirred for 4-6 hours to ensure a homogenous composition. Finally, the catalyst ink was evenly applied to the wetted cathode surface area using a paint brush (procedure adapted from “How to make an air cathode…”). A press fit electrical connection was made using a nylon screw, nut, washer and a plastic-coated titanium wire (same as the anode: see above) at the edge of the cathode and connected to the potentiostat.

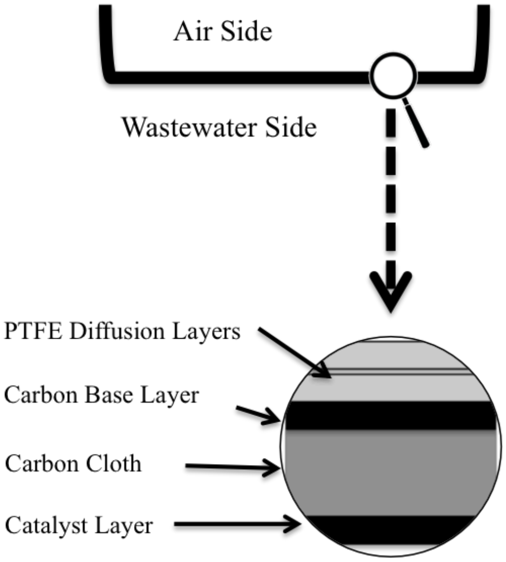


Figure 2-1: Cross-section of floating air cathode with close-up of cathode layers

2.2.3 Sampling and Experimental Setup

Six sediment microbial fuel cells, referred to as Mn1, Mn2, Mn3, Pt1, Pt2, Pt3 (3 with MnO_2/VC and 3 with Pt/VC cathodes) were built using two-liter glass beakers filled with wastewater and containing an anode suspended 6 cm below the wastewater surface where an air cathode floated. These batch reactors were operated in parallel at room temperature under a chemical hood for odor control and deionized water was periodically added to compensate for evaporation. Electrodes were connected to a Solartron® potentiostat [Ametek], which measured current density over time and performed various electrochemical tests. Wastewater was collected from Blue Plains Advanced Wastewater Treatment Plant (AWWTP) in Washington, DC. Samples were taken from the center of the primary clarifier and the primary settled solids tank and stored in plastic 1-gallon jugs at 4C. Storage did not exceed 2 days before fuel cells were started.

Previous trials [results not shown] had determined that the organic content of primary clarifier effluent was rapidly depleted under batch conditions. In order to maximize the anodic biofilm growth and lengthen each batch cycle, additional organic matter in the form of primary solids was added to primary clarifier wastewater at a 1:4 ratio. Organic matter was replenished at the completion of each batch run (after 3-4 weeks) through the addition of 200-300 mL of primary clarifier effluent or a primary effluent-primary solids mixture. The ratios of primary effluent-to-primary solids were selected based on the performance of the SMFC in the previous batch in order to maximize power production.

2.2.4 Data Collection and Analysis

A standard electrochemical protocol was followed for each replication of SMFC. The SMFCs were initially allowed 48 hours at open circuit voltage and switched to a 3-electrode configuration where the working electrode [anode] was poised at -0.2V vs. Ag/AgCl [BASi, West Lafayette, IN] (-0.397V vs. SHE) and the cathode served as a counter electrode. The poising of the anode at this low potential selects for anode-respiring bacteria (ARB), specifically *Geobacter sulfurreducens* and those which are genetically similar to it (Torres et al. 2009) that promote power generation. Current was recorded over time and once a plateau in current was observed the SMFCs were switched to 24 hours at open circuit voltage before performing a polarization test (gradual change in cell voltage from open circuit to closed circuit). Upon completion of polarization, SMFCs were allowed 3 hours of open circuit before being switched to 2-electrode configuration where the fuel cell voltage was set at that which achieved the highest power density during polarization. Current density, power density, and fuel cell voltage data were collected over time, generally periods of 3-14 days without interruption, using a potentiostat. Cyclic voltammagrams of the anode were taken at various points during the experiment and electrode potentials vs. Ag/AgCl monitored using a voltmeter.

The anode served as the working electrode in all tests conducted using a 3-electrode configuration and subsequent data were normalized by anode geometric surface area. Because previous studies have shown that the ORR at the cathode is usually the limiting reaction in a microbial fuel cell (Ahn & Logan 2010; Rismani-Yazdi et al. 2008), all data from tests conducted using a 2-electrode [fuel cell] configuration were normalized by cathode geometric surface area. Due to the small sample size, data for each replicate are presented.

2.2.5 Determination of Mn-leaching from cathodes

Based on the initial loading of the cathodes (0.5 mg 20% w/w MnO_2/VC per cm^2 of cathode surface area), it was determined that each cathode (SA = 21 cm^2) contained 2.41×10^{-5} moles Mn or 1.33 mg. Wastewater samples were analyzed at the start of the experiment and after 17 days to measure the change, if any, in total Mn concentration. Two hundred mL samples were taken for determination of total Mn concentration using the EPA 200.8 method.

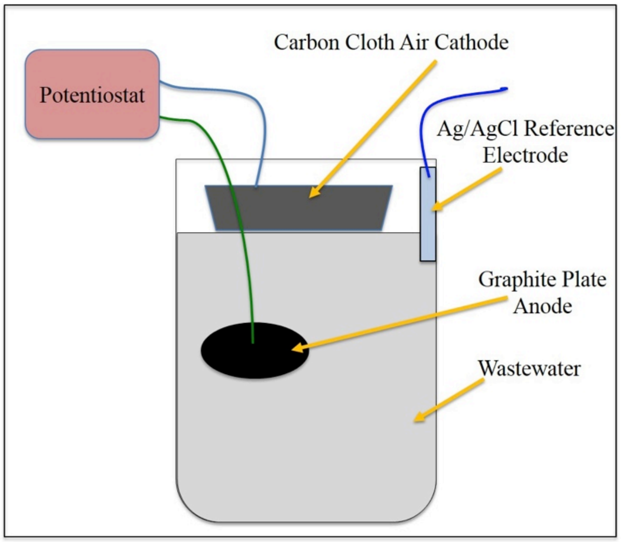


Figure 2-2: Lab-scale wastewater sediment MFC

Figure 2-3: SMFCs in 3-electrode configuration

2.3 Results and Discussion

2.3.1 Three-electrode configuration of MFCs

The onset of current and its subsequent steady increase indicated the gradual colonization of the anode by ARB. The eventual plateau in current density, or steady state anodic current, was indicative of a mature biofilm. Theoretically, each SMFC should have reached identical steady state current densities since anode surface area was the same for all replicates, however the data showed some dissimilarities between replicates. Variability in anode surface area at the microscopic level as well as variability in wastewater composition of each SMFC may have been responsible for these discrepancies. The data do demonstrate that the maximum attainable current density with this SMFC configuration, assuming a non-limiting cathode, should be between 250 and 500 mA/m^2 of anode surface area, 5-fold greater than observed for sediment microbial fuel cells using marine sediment and seawater.

For the second batch, 200 mL of the same 1:4 (primary settled solids: primary effluent from Blue Plains WWTP) mixture was added to each SMFC. After 24 hours of open circuit and then poising the anodes at -0.2V vs. Ag/AgCl in 3-electrode configuration for nearly 4 days, the MFCs were unable to attain original current densities with the exception of Mn3 as shown in figure 2-4. These data suggest that the fuel cells were either anode or substrate-limited. Because there was no change to the anodes or operating conditions (pH, DO levels, and temperature remained constant), the most likely cause for failure to achieve original current densities is depletion of available organic matter. The third segment of figure 2-4 depicts current density after adding primary clarifier effluent, which is much lower in COD than the original mixture (~150 mg/L vs. ~1500 mg/L). Current densities did not come close to the original levels consistent with organic matter limitation. The last segment shows all MFCs reaching comparable current densities in 3-electrode configuration after the addition of 300 mL of a 1:1 mixture of the wastewaters. Wastewater with high organic matter content was used to overcome the substrate limitation observed in the previous two batch cycles. This segment shows steady-state current densities of just over 300 mA/m^2 of anode SA, comparable to current densities achieved at the start of the study, when organic matter is in excess in the system.

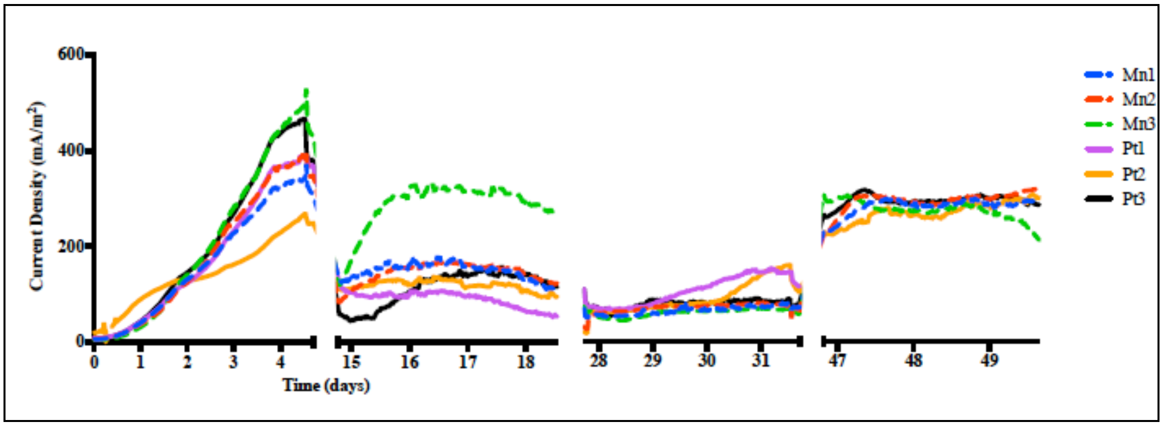


Figure 2-4: Current density when SMFCs were operated in 3-electrode configuration with the anode as the working electrode, cathode as counter electrode, and a Ag/AgCl reference electrode. Anodes were poised at -0.2 V versus reference. Normalized by anode SA

2.3.2 Polarization and maximum power densities

Initial polarization tests indicated that SMFCs with manganese-based cathodes produced higher maximum power densities at higher current densities than those with platinum-based cathodes. The average maximum power from the manganese MFCs was 40.12 ± 3.72 mW/m^2 (normalized by cathode surface area) while the average for the platinum MFCs was 30.06 ± 0.47 mW/m^2. Previous tests with catalyst-free air cathodes show that the addition of either platinum or manganese increased the maximum power of the MFC by at least 4-fold (results not shown).

The subsequent polarization tests, after new wastewaters were added and the experiment repeated, show a shift of maximum power production between both MFCs with platinum-based cathodes, and those with manganese-based cathodes. Those with platinum cathodes eventually achieved higher average maximum power densities at higher current densities than the MFCs with manganese cathodes. Figure 2-5 shows the power curves for each MFC after 9, 37, and 55 days, and the average maximum power densities of the three replicates for both types of cathodes at those times are displayed in figure 2-6. Interestingly, both average maximum power densities and the current densities at which they occurred increased over the multiple cycles MFCs were run. While these average values increased over time, so did their variability, and the maximum power density values for Mn-cathode SMFCs after 9 days were within one standard deviation from those obtained after 55 days.

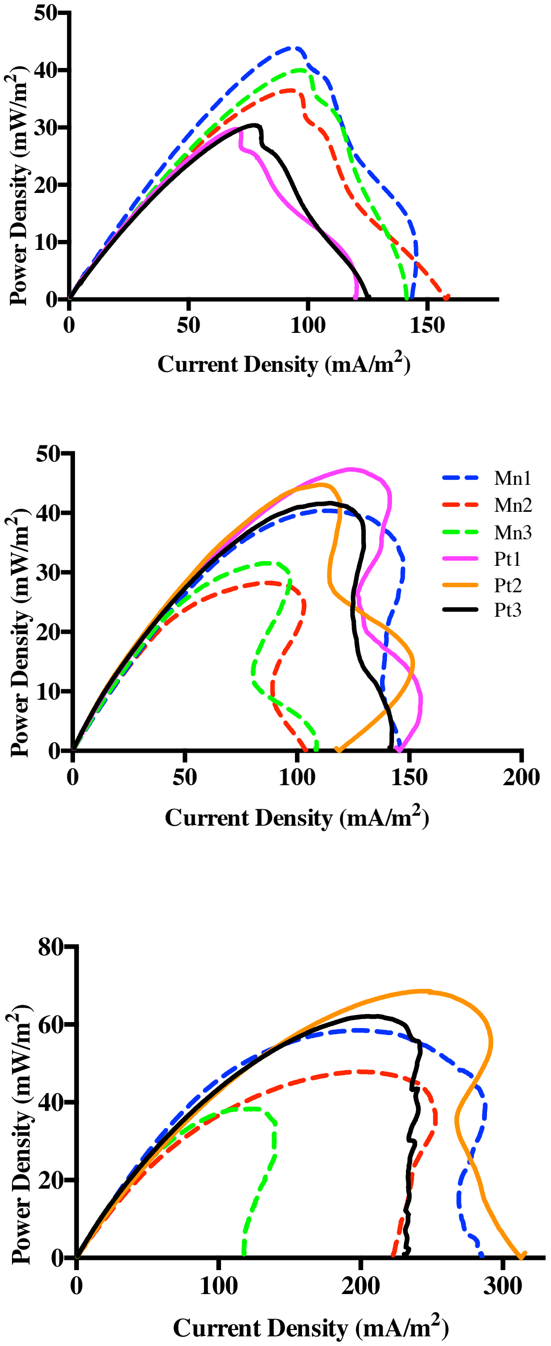


Figure 2-5: Power curves determined during polarization. Power normalized by cathode SA. From top to bottom: Polarization #1 after 9 days, polarization #2 after 37 days, polarization #3 after 55 days.
Note: Pt2 and Pt1 omitted from #1 & #3 respectively due to instrument error at the time of polarization.

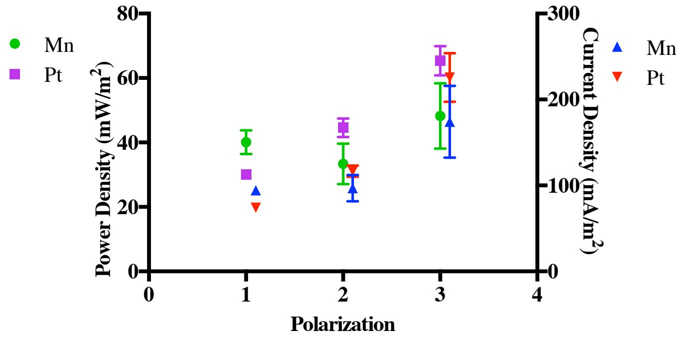


Figure 2-6: Ave. max. power and current densities at which they were reached for both types of cathode (error bars of one standard deviation)

2.3.3 Cyclic voltammetry

Cyclic voltammetry (CV) was performed on the anode of each SMFC periodically throughout the experiment to evaluate the development of the biofilm over time. No significant differences were observed between the two types of MFCs. All CVs performed on anodes with established biofilms exhibited half-wave oxidation potentials of -0.35V vs. Ag/AgCl, which is typical of *Geobacter sulfurreducens* (Strycharz-Glaven & Tender 2012) and consistent with anodes colonized by ARB. As illustrated in figure 2-7, the highest current densities were achieved after the initial growth in 3-electrode configuration. After 6 days of MFC operation (2-electrode configuration), there was a substantial decrease in current production at the oxidation peak likely due to the depletion of organic matter. Once organic matter was replenished with the addition of primary clarifier wastewater and settled solids, an increase in current density was observed, but most SMFCs did not recover to their initial maximum current densities consistent with the second segment of figure 2-4.

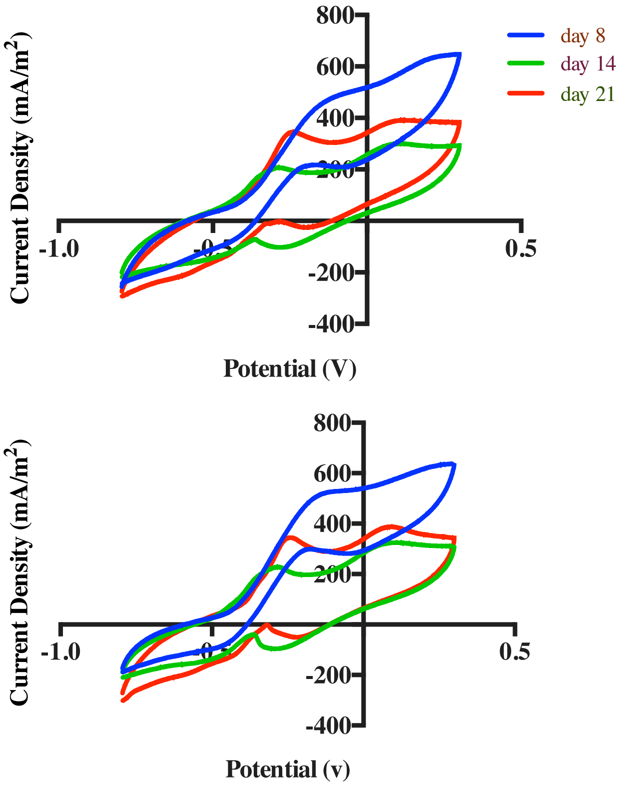


Figure 2-7: Cyclic voltammagrams of 2 SMFCs (each representative of their group) where day 8 = after operation in 3-electrode config., day 14 = after 6 days operation in 2-electrode config., day 21 = after second operation in 3-electrode config. Top: Mn1, Bottom: Pt3

2.3.4 Power density of microbial fuel cells

SMFCs were poised in 2-electrode [fuel cell] configuration based on their performance during polarization: manganese-based cathodes at 0.5V cell voltage and platinum-based cathodes at 0.45V cell voltage (vs. Ag/AgCl reference) in the first segment and all SMFCs at 0.4V cell voltage for the subsequent 3 segments. Power density over time, shown in figure 2-8, indicates a large variability in the SMFCs' power production. After approximately one week of operation, SMFCs experienced either gradual or steep drops in power density, most likely due to the depletion of available organic matter reaching the anode. Because the SMFCs remained unstirred, the substrate availability was diffusion-limited. Additionally, leaching of manganese from the MnO_2-coated cathodes (see below) also may have contributed to the rapid loss of power density observed in those SMFCs.

Interestingly, the data presented in figure 2-8, though more variable than those presented in figure 2-5 [polarization], would indicate that SMFCs with platinum-based cathodes produced slightly higher average power densities than SMFCs with manganese-based cathodes. All SMFCs produced lower power densities when operated in a 2-electrode configuration than the initial polarization test indicated possible with the exception of Pt1 during the first two segments and Mn3 during the third. Additionally, a significant drop in cathode potential was observed when SMFCs were switched from open circuit voltage to a set cell voltage for power generation. This drop in cathode potential and lower power density (versus what was seen during polarization) indicate that the systems were still cathode-limited despite the presence of ORR catalysts.

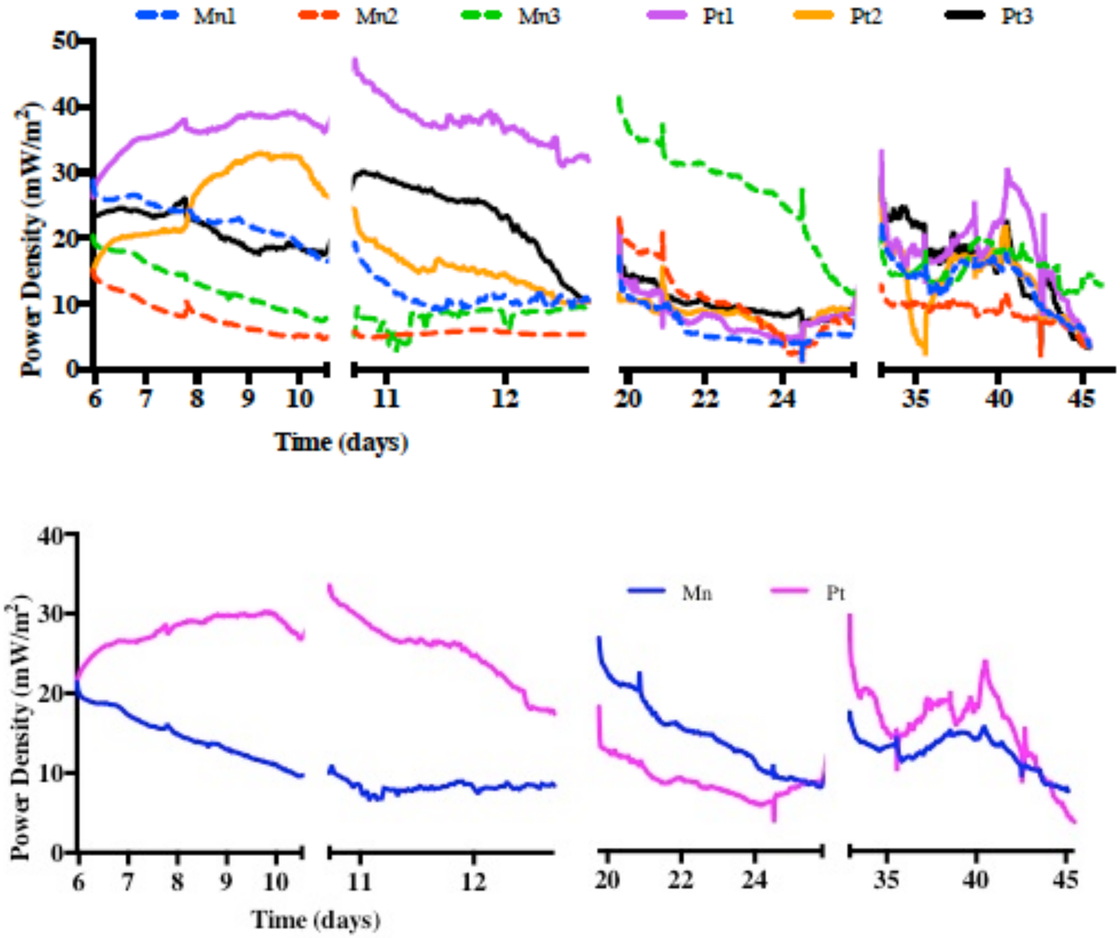


Figure 2-8: Power density of MFCs. After the first break, cyclic voltammetry was run on anodes, subsequent breaks in data correspond with replenishment of substrate and operation of SMFCs in 3-electrode config. for 3-5 days. Normalized by cathode SA.
Top: all MFCs, Bottom: average power density for each set of 3 replicates

The average values for manganese and platinum cathode SMFCs appear to both converge and decrease over time. This could be explained by the rapid dissolution of the MnO_2 early on (see below), followed by the fouling of the Pt so that all SMFCs experienced a decrease in power production over time due to reduced cathode performance. However, worth noting is that the addition of significant levels of organic matter resulted in a bump in power production on every occasion. Therefore, it is possible that repeating this study under continuous flow conditions could better illustrate how these ORR catalysts perform over time as well as how they compare to one another.

2.3.5 Electrode potentials

Cathode potentials when SMFCs were allowed to reach open circuit at different points throughout the experiment are reported in Table 2-1. While there exists significant variability in the cathode potentials from day to day, the Pt-based cathodes remained consistently higher than MnO_2-based cathodes. Additionally, a decrease in manganese cathode potentials over time was observed while platinum cathode potentials were able to reach original values after 31 days in wastewater. This could be due to the rapid solubilization of manganese observed by measuring the total manganese present in the wastewater before and after the cathodes were introduced. The initial concentration of manganese in wastewater was 0.38 mg/L. After 17 days of operation with only the addition of deionized water, Pt SMFCs showed no change in total Mn levels, while the Mn SMFCs now had concentrations of Mn ranging from 1-1.9 mg/L. A mass balance of total Mn in the system using the initial concentration in the wastewater and the 0.5 mg/cm^2 of 20% w/w MnO_2/VC loading of the cathode indicates that, on average, over 90% of the Mn was lost from the cathode surface. While the gradual drop in Mn-coated cathode potentials could indicate some loss of catalyst over time, the cathodes still maintained higher potentials than a plain carbon cloth cathode (results not shown).

Table 2-1: Cathode open circuit potentials at various points throughout the study. Values are presented in milivolts (mV) versus reference (Ag/AgCl) *Day 22 values are of initial OCP, all others are after at least 24 hrs at open circuit

SMFC	Day 0	Day 6	Day 14	Day 18*	Day 27	Day 46
Mn1	245	193	203	79	208	170
Mn2	238	150	143	45	215	167
Mn3	229	135	131	21	172	50
Mn_Ave	237	159	159	48	198	129
Pt1	233	158	211	286	294	221
Pt2	261	133	269	194	260	203
Pt3	386	143	245	219	279	210
Pt_Ave	293	145	242	233	278	211

2.4 Conclusions

While certain electrochemical analyses showed SMFCs with MnO_2-coated cathodes performing best, others showed better performance with Pt-coated cathodes. When considering all the data collected, no consistent significant difference in performance between the two types SMFCs tested could be determined. The limitations of Pt-based catalysts have already been explored and published. Most problematic are the high cost of platinum, which would be prohibitive at a large scale, and its tendency to foul over time in complex substrates. While manganese oxides are much cheaper than platinum, this study shows that they also have their limitations regarding their use in wastewater. The rapid dissolution of Mn into the water could have been due to its reduction into the soluble form by ARB. Once the Mn is solubilized, it could leach from the cathode surface and no longer serve as an ORR catalyst. If this issue could be overcome by the use of higher concentrations of ion-binders or another method, it is possible MnO_x's could serve as affordable alternatives to Pt for the reduction of oxygen in wastewater MFCs.

Sediment microbial fuel cells do show improved performance with wastewater due to its high concentration of organic matter. Because this study used a batch set-up, it was largely substrate-limited and it is expected that power densities would improve if repeated under continuous flow conditions. Additionally, increasing the electrode surface area-to-volume ratio of the reactor would help determine whether SMFCs could attain significant COD removal under typical WWTP retention times.

The adaptation of the air cathode of single-chamber MFCs to a floating air cathode is a first and crucial step toward the use of SMFCs in existing wastewater treatment plant clarifiers for wastewater treatment and electricity generation. Further research in the crossover from ocean sediment to wastewater as SMFC substrate could yield a practical wastewater MFC design.

Chapter 3: Additional Results and Discussion

3.1 Summary

Along with the findings presented in chapter 2, several studies were conducted as part of this graduate work that provided additional insight into the workings of wastewater SMFCs with MnO_2 ORR catalysts. These preliminary results not only contributed to the design of the chapter 2 study, but could also serve as starting points for future work regarding SMFCs for wastewater treatment and electricity generation. First, the performances of SMFCs using plain carbon cloth air cathodes compared with those using MnO_2-coated air cathodes are presented and indicate a significant improvement in wastewater SMFC performance when an ORR catalyst is applied to the air cathode. Secondly, the need for a floating air cathode in the presence of the MnO_2 ORR catalyst is evaluated by comparing the performance of SMFCs with floating cathodes with that of SMFCs with cathodes placed just below the surface of the wastewater where minute amounts of dissolved oxygen exist. This trial indicated that without ample oxygen at the cathode, a SMFC would not function, even with MnO_2 present. Moreover, the results indicated that MnO_2 on the cathode does behave as an ORR catalyst instead of a sacrificial electron acceptor. Next, a variation on the original reactor configuration that increased the electrode surface area-to-reactor volume ratio was examined. While only one new reactor was constructed, its performance indicated that increasing the total electrode surface area in a given volume of wastewater would significantly increase the amount of energy that can be harnessed from that volume. Lastly, the use of three carbon foams of varying porosities as cathodes was examined with the intent of developing a MnO_2-coated air cathode with a high surface area. These results showed initial high cell voltages at open circuit, but the SMFCs failed to function after just a few hours or days of operation. The preliminary results of these four investigations are presented below.

3.2 Comparison of plain carbon cloth air cathode with MnO_2-coated air cathode

The first trial with MnO_2 catalyst in wastewater used the boat-shaped floating air cathodes described earlier and compared two MFCs with plain carbon cloth air cathodes to two with MnO_2-coated air cathodes. Section 2.2 describes construction and assembly of electrodes and MFC reactors as well as the synthesis and application of the MnO_2/VC ORR catalyst. A similar electrochemical protocol was followed, though with fewer repetitions. MFCs were initially filled with wastewater sampled from primary clarifiers at Blue Plains AWWTP in Washington, DC, and 100 mL of primary settled solids was added to each after 48 hours at open circuit conditions.

After approximately 115 hours of operation in 3-electrode configuration where the anode was poised at -0.2V vs Ag/AgCl, maximum current levels were reached between 280 and 325 mA/m^2 of anode surface area. As figure 3-1 illustrates, no significant difference was observed between MFCs with an ORR catalyst on the cathode and those without as was expected of MFCs with identical anodes and substrates operated in 3-electrode configuration.

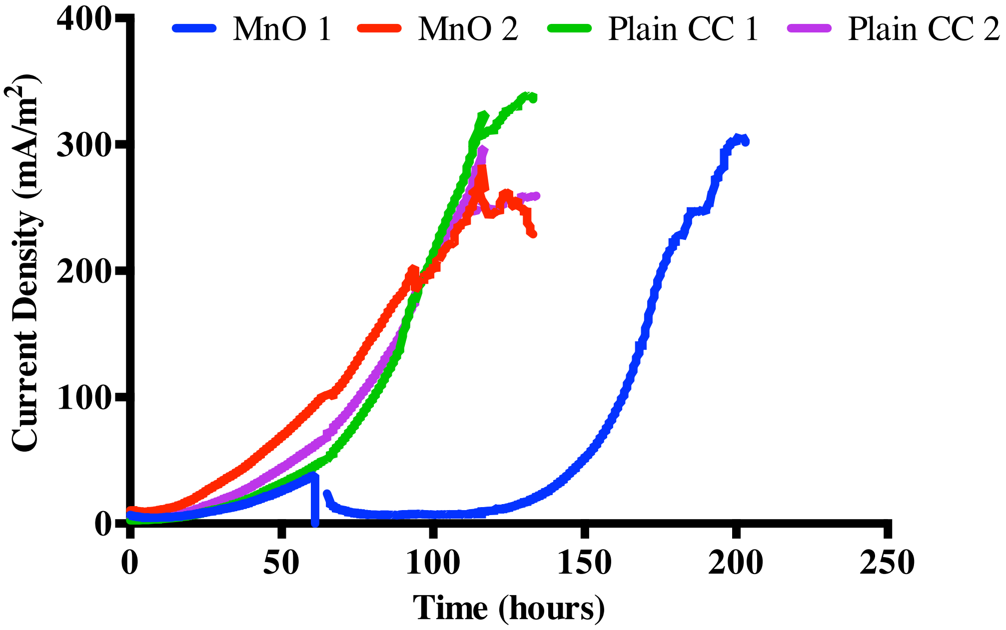


Figure 3-1: Current density (normalized by anode SA) in 3-electrode configuration. Note: MnO 1 had to be restarted due to a technical problem with the instrument

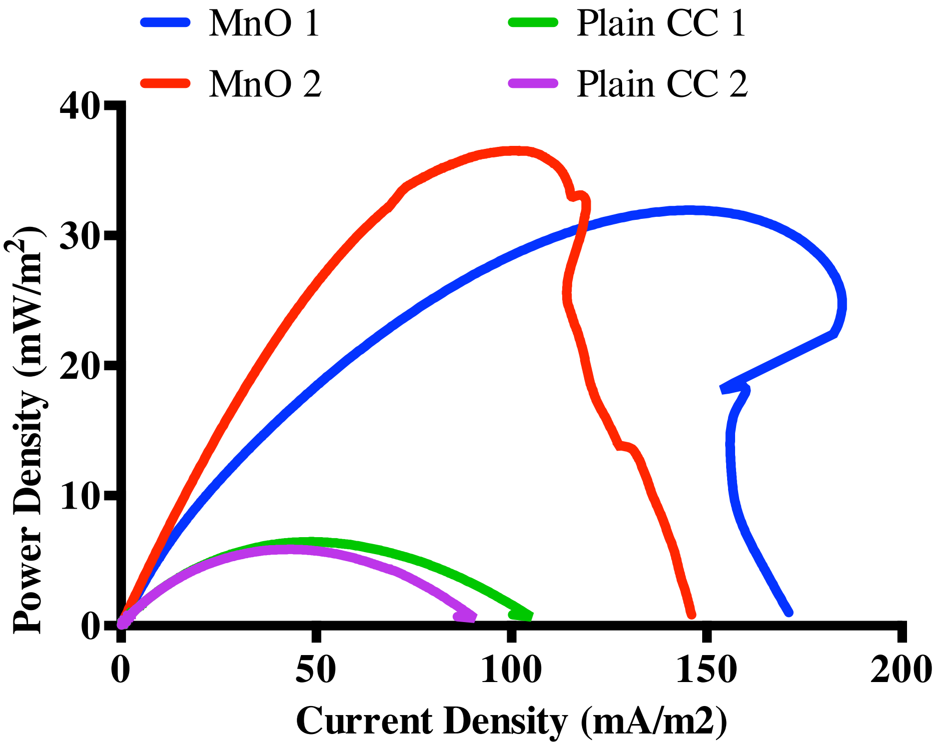


Figure 3-2: Power curves from polarization (normalized by cathode SA)

After more than 4 days in 3-electrode configuration, the fuel cells were allowed to reach open circuit voltage for 24 hours before polarization was conducted on each. SMFCs with MnO_2 cathodes achieved significantly higher open circuit voltages than those without an ORR catalyst (0.66 and 0.58V vs. 0.42 and 0.43V), shown in appendix B. This resulted in much greater maximum power and current densities in the MnO_2 SMFCs as opposed to the plain carbon cloth SMFCs [figure 3.2]. The average maximum power and current density at which they occurred for MnO_2-cathode SMFCs were 32.24 mW/m^2 and 124.39 mA/m^2 respectively. Conversely, plain carbon cloth-cathode SMFCs achieved an average maximum power of 6.17 mW/m^2 at the average current density of 46.40 mA/m^2.

In order to maximize power production, SMFCs were poised at the following cell voltages: MnO1- 0.25V, MnO2- 0.35V, Plain CC1 and Plain CC2- 0.1V. These cell voltages for operation in 2-electrode [power-generating] configuration were determined by identifying the cell voltage at which maximum power occurred during polarization [appendix B]. As shown in figures 3-2 and 3-3, MFCs with MnO_2 cathodes clearly out-performed those without an ORR catalyst at the cathode. At day 16, wastewater from primary clarifiers was added to all MFCs and an increase in power density was observed in each. Interestingly, while they still produced higher power densities than their uncatalyzed counterparts, MnO_2 MFCs experienced steeper drops in power output over time than those without an ORR catalyst. Even when subsequent additions of fresh wastewater were made (indicated by spikes in power output at days 31, 35, and 40), power densities dropped quickly and MnO_2-cathodes were unable to regain their initial open circuit voltages indicating a decrease in ORR catalyst performance. It was later seen that MnO_2 leaves the cathode surface and dissolves into the wastewater [section 2.3.5], which likely explains the decrease in cathode potential over time.

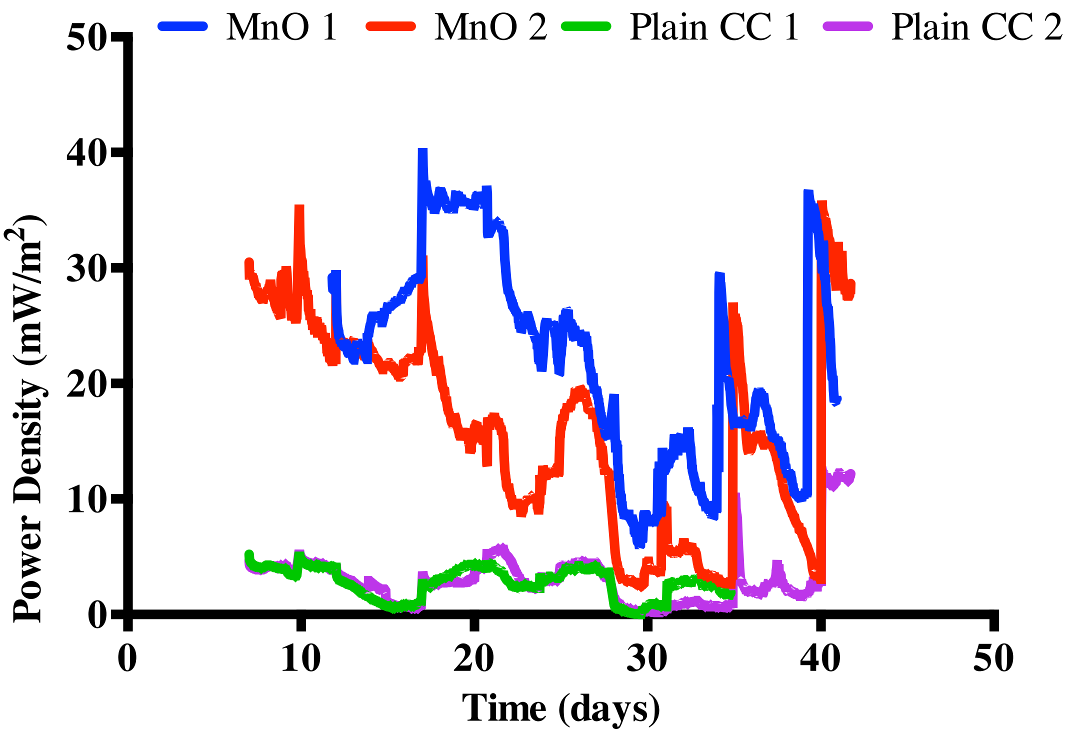


Figure 3-3: Power density in 2-electrode configuration (normalized by cathode SA)

This preliminary study examining the use of MnO_2 as an ORR catalyst at a wastewater SMFC cathode showed an increase in SMFC performance, if only in the short term, due to the presence of this catalyst. It ultimately led to the comparison of MnO_2 as an ORR catalyst to platinum in wastewater SMFCs.

3.3 Performance of MnO_2 air cathode vs. MnO_2 submerged cathode

It was hypothesized that manganese itself was being used as the terminal electron acceptor in the SMFCs instead of acting as an ORR catalyst. To test this hypothesis, the performance of SMFCs with MnO_2-coated air cathodes were compared to those with MnO_2-coated cathodes not exposed to atmospheric oxygen. If, in fact, manganese was acting as the terminal electron acceptor in the cathodic reaction, both configurations of SMFCs should have produced power regardless of whether or not the cathodes were exposed to oxygen. Three floating air cathodes of 21 cm^2 (referred to as “boats” in this preliminary study) were assembled and coated with MnO_2/VC, as described in section 2.2. Three “nonboat” cathodes were constructed using rectangular pieces of plain carbon cloth (no wet-proofing with PTFE) coated with MnO_2/VC on one side so that they had the same catalyst surface area as the boats. These were laid flat on a titanium wire that was press-fit connected to the carbon cloth [using a nylon screw as previously described] and the entire cathode was suspended evenly 2 cm below the surface of the wastewater. All anodes were graphite discs [as described in section 2.2] with 15.4 cm^2 suspended 6 cm below the surface of 2 L of wastewater; half primary settled solids, half primary clarifier wastewater. Wastewater with extremely high organic content (due to the large volume of primary settled solids) was used to ensure the systems would not be substrate-limited.

Figure 3-4 shows the initial establishment of anodic biofilms in each SMFC when they were operated in a 3-electrode configuration (anode poised at -0.2 V vs Ag/AgCl). The variability in peak current densities reached may be due to differences in the initial presence of bacteria between subsamples. Wastewater for this experiment was collected in December when the water temperature of primary clarifiers had remained just above freezing for several weeks likely inhibiting microbial activity. This may also explain why SMFCs reached lower-than-expected current densities after 4 days of operation in 3-electrode configuration.

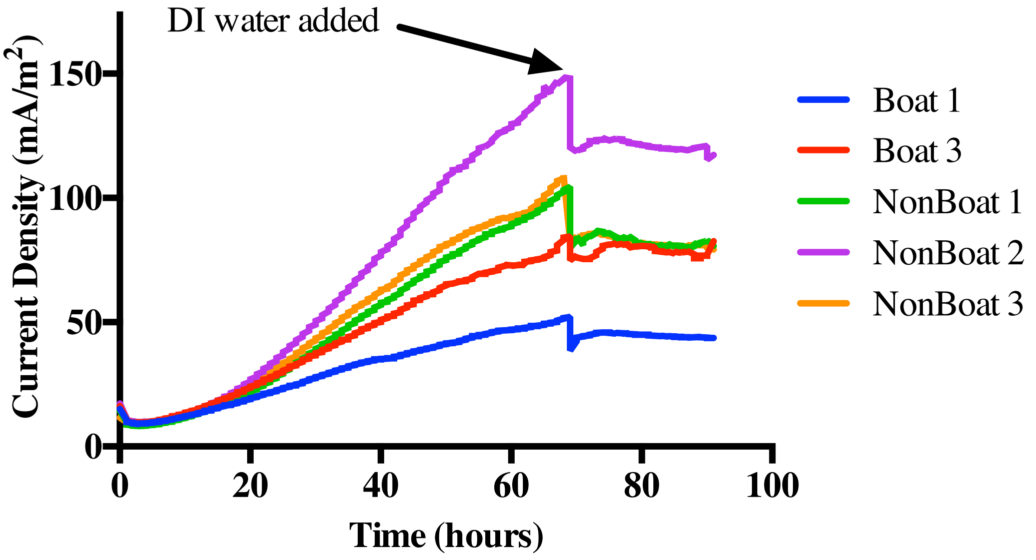


Figure 3-4: Current density in 3-electrode configuration (normalized by anode SA). Note: Boat 2 was omitted due to an instrument malfunction

Nonboat SMFCs achieved an average open circuit cell voltage of -0.082 V. This indicated that non-boat cathodes achieved more negative open circuit potentials than the anodes, and during polarization no appreciable power or current was produced. Because these SMFCs did not function as fuel cells, data on maximum power density during polarization and power density over time for non-boat cathode SMFCs are not presented. Nonboat SMFCs were dismantled at this time, but the operation of boat SMFCs continued for several weeks.

Boat-cathode SMFCs performed as expected [consistent with previous tests] and achieved an average open circuit voltage of 0.669 V after 24 hours at open circuit prior to polarization. Their average maximum power density was 20.70 mW/m^2, which was lower than previous trials. Power and polarization curves are presented in appendix D. Again, the slightly lower maximum power values could be due to the cold conditions under which the wastewater was collected. Following polarization, boat SMFCs were poised at a fixed cell voltage of 0.3V and continuously stirred during operation in 2-electrode configuration. Deionized water was periodically added to maintain the water level of SMFCs at 2 liters.

Because organic matter was present in excess and the SMFCs were continuously stirred, the only limitation to the system was thought to be the diffusion of oxygen to the cathode. In order to test whether the slow diffusion of oxygen through the cathode was limiting SMFC performance, reactors were loosely covered with parafilm to decrease the cathodes' exposure to air. At this time, approximately 100 mL of primary settled solids were added to each SMFC to ensure any observed decrease in power output would be due entirely to oxygen limitation. Interestingly, covering the SMFCs led to a pronounced increase in power density as seen in figure 3-5. Because the new power densities reached were much higher than those observed initially, this increase in power production was attributed to the change in reactor configuration, not the addition of substrate. After 2 days of remaining covered, SMFCs were uncovered causing a steep drop in power density. While these results were not expected, if the air flow due to ventilation in the chemical hood is considered forced, they are consistent with findings of a previous study that evaluated the effect of forced air flow into a tubular air cathode on MFC performance (Liu & Logan 2004). When air was blown through the air cathode of the single chamber MFC in the Liu and Logan study (previously described in section 1.1.9), a drop in cell voltage was observed. The cell voltage later recovered after the airflow was shut off and oxygen was allowed to passively diffuse through the air cathode. Because the SMFCs in this preliminary study were not completely sealed by the parafilm, it is likely that it merely acted as a shield against the ventilation from the chemical hood. These results indicate that oxygen diffusion does not appear to be a limiting factor in SMFC performance.

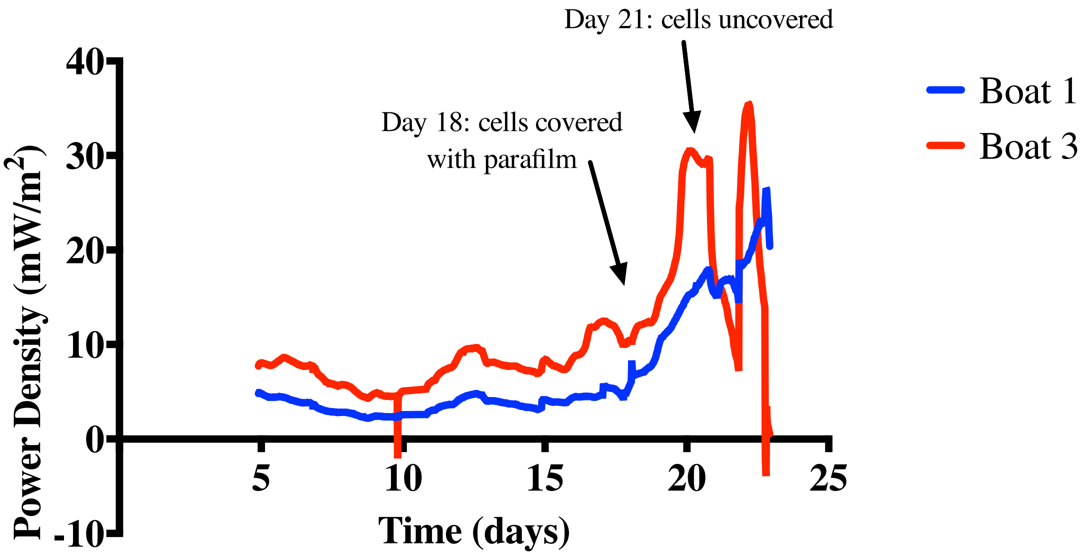


Figure 3-5: Power density (normalized by cathode SA) of SMFCs with "boat" cathodes

In summary, this experiment illustrated two key points: First that the placement of the air cathode must be at the wastewater-air interface in order for the ORR to occur and the SMFC to function. And secondly, it confirmed the conclusion of Liu et al. that passive oxygen diffusion maximizes energy output of MFCs using air cathodes. These results are important for the future improvement of floating air cathodes for wastewater SMFCs.

3.4 Effects of increasing the ratio of electrode SA to reactor volume

As stated in chapter 2, the air cathode floated at the wastewater surface, therefore limiting the maximum possible cathode surface area by the reactor's shape; specifically by the surface area of wastewater exposed to air. Because the cathodic reduction reaction is coupled with the anodic oxidation reaction, scale-up of both electrode surface areas must be done together. In order to be able to increase the anode surface area and therefore increase the amount of ARB present in the system to breakdown organic matter and generate current, the cathode surface area had to be increased. This was done in two ways; first, a shallow rectangular reactor with dimensions of approximately 21 x 21 x 5 cm^3 was used instead of a standard, cylindrical 2-liter beaker (dimensions: 154 cm^2 x 13 cm). This reactor provided 400 cm^2 of wastewater exposed to air where a floating air cathode could operate. Secondly, to further increase cathode surface area, the teflonated carbon cloth was made in a fan-shaped mold (see figure 3-6) with the expectation that while only some of it would be touching the wastewater directly, water would be drawn up to the rest of its surface through capillary action [wicking]. Besides this modified shape, the floating air cathode was prepared in the same fashion as the boat-shaped cathodes using the same loading [see section 2.2] of MnO_2/VC ORR catalyst for a total surface area of 176 cm^2. The anode was constructed of plain carbon cloth weighted with a small graphite frame (to prevent its movement or flotation) with a press fit electrical connection of titanium wire and nylon screw. The total anode surface area was 200 cm^2.

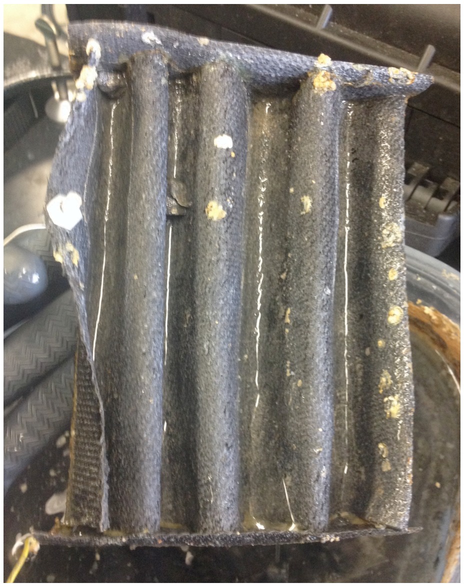


Figure 3-6: Fan air cathode as viewed from above

The same electrochemical protocol as described in chapter 2 was followed and under a 3-electrode configuration [anode poised at -0.2V vs Ag/AgCl] a maximum current density of 213 mA/m^2 was achieved. This current density is consistent with current densities previously observed, though on the lower end of the spectrum. When the SMFC was returned to 3-electrode configuration after several weeks of operation and regular substrate additions, approximately the same current density was observed as illustrated in figure 3-7.

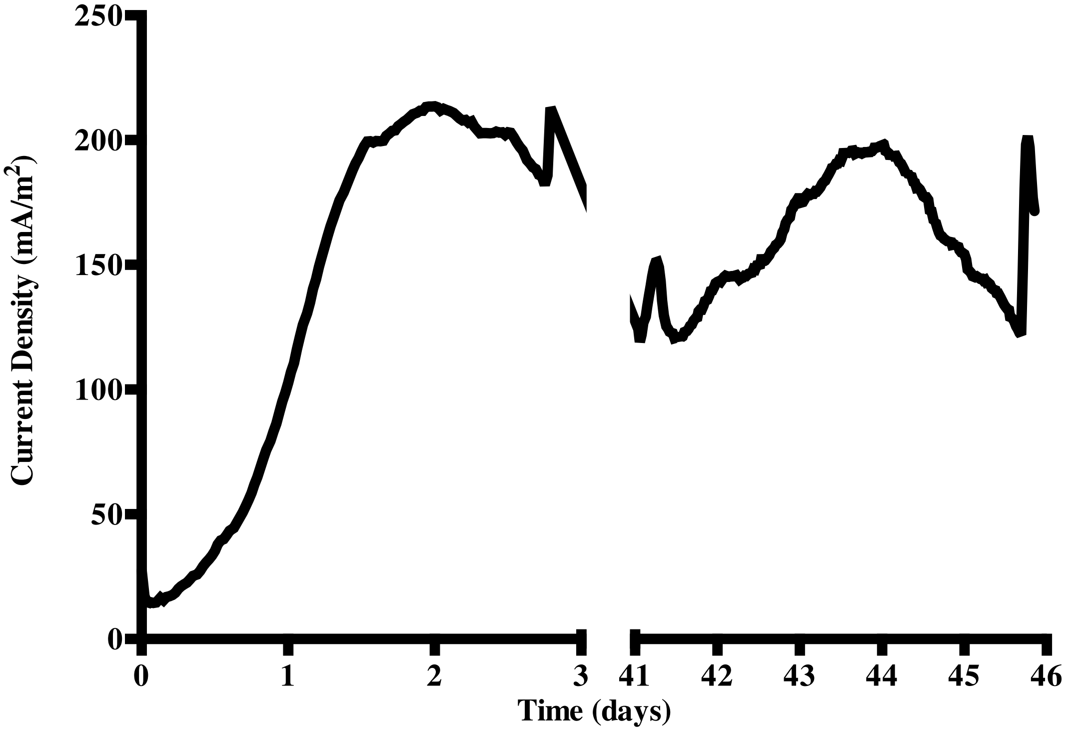


Figure 3-7: Current density (normalized by anode SA) of the fan air cathode SMFC operated in 3-electrode configuration

Figure 3-8 shows the fan air cathode SMFC in two-electrode configuration over almost 60 days. The first two sections show power density over time when the SMFC was poised at a 0.6V cell voltage and the second two when it was kept at a 0.5V cell voltage. Power density decreased over time, presumably as substrate was depleted and also due to the dissolution of cathode catalyst. Interestingly, power densities appeared to recover after each addition of wastewater and maintained a relatively consistent steady-state power output compared with other trials that used smaller electrodes.

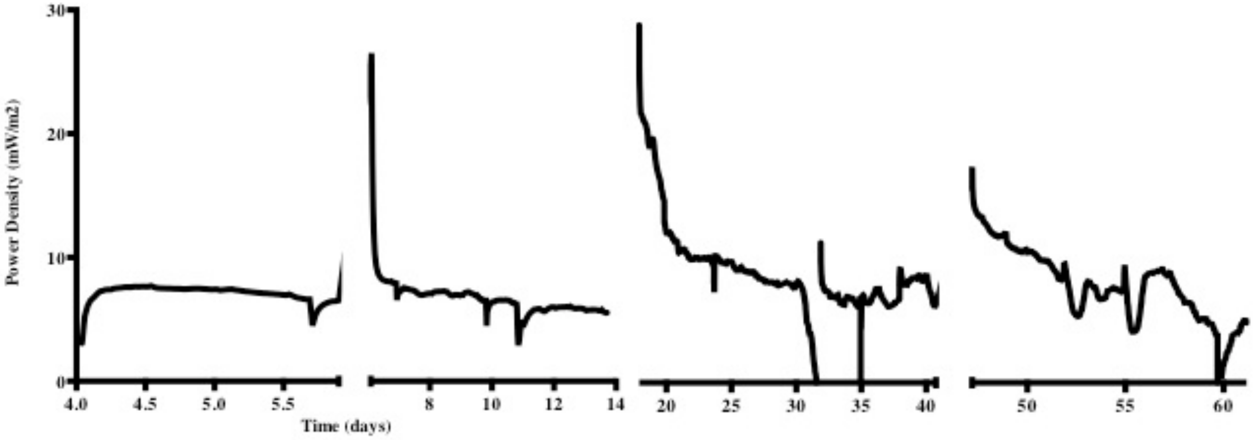


Figure 3-8: Power density (normalized by cathode SA) of fan air cathode SMFC in 2-electrode configuration

The initial polarization test [figure 3-9] showed maximum power production at a high cell voltage of 0.5V, and was used to determine the cell voltage of the SMFC in 2-electrode configuration. Polarization was repeated after 47 days of operation and the SMFC obtained significantly higher maximum power and current densities than the initial polarization test performed after 3 days of biofilm growth in 3-electrode configuration, though at a lower cell voltage of 0.3V. Interestingly, the open circuit voltage of the SMFC obtained after 24 hours at open circuit before each polarization dropped from 0.684 V to 0.623 V, most likely due to some loss of ORR catalyst and the resulting drop in cathode potential. Despite this drop in cell voltage, the maximum power density increased to 80.44 mW/m^2 during the second polarization from 53.99 mW/m^2 initially.

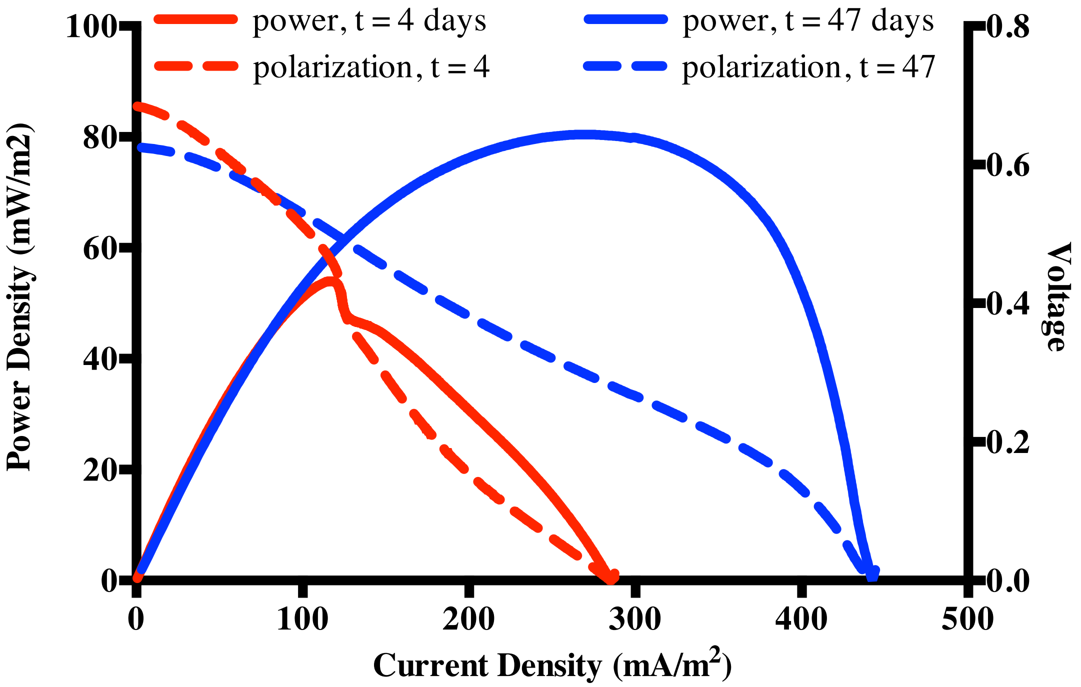


Figure 3-9: Fan air cathode SMFC power (normalized by cathode SA) and polarization curves after 4 and 47 days of operation

This increase in maximum power and current densities is not consistent with results observed using the 2-liter beaker reactors and "boat" air cathodes. This could be due to the larger anode that may have needed more time and several additions of substrate to become saturated with ARB. Both polarizations yielded slightly higher maximum power densities than other studies, but the values observed were still within less than an order of magnitude of expected values.

In order to determine whether the change in reactor design proved an effective method of extracting more power from a given volume of wastewater, power and current densities achieved during polarization were normalized by reactor volume instead of cathode surface area [figure 3-10]. When this power density was compared with that of the 2-liter beaker, an increase of an order of magnitude was observed (approximately 500 mW/m^3 as opposed to 50 mW/m^3). As expected, increasing the ratio of electrode surface area to reactor volume significantly increased the amount of energy produced from a given volume of wastewater. Additionally, a greater electrode surface area in two liters of wastewater may allow for the measurement of organic matter breakdown due to oxidation by ARB though COD was not measured in this instance. This finding has practical implications for future wastewater SMFC studies and possible scale-up of reactors, and suggests that the configuration of an SMFC greatly affects its performance. Since wastewater SMFCs are constrained by the surface area of the reactor due to the cathode's need for passive oxygen diffusion, a shallow reactor with high electrode surface area-to-volume ratio would be best for wastewater treatment and electricity generation.

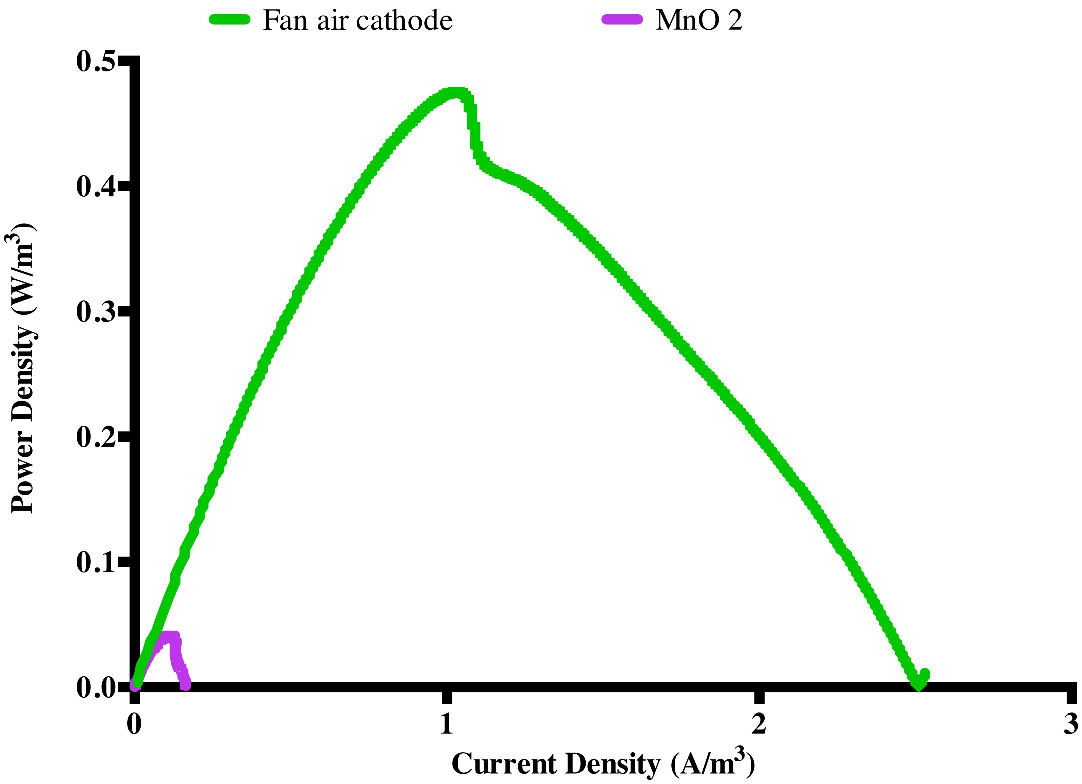


Figure 3-10: Power densities during polarization (normalized by reactor volume) of the fan air cathode SMFC and SMFC MnO2 from section 3.2

3.5 Evaluation of carbon foams as floating air cathodes

Another approach to further increasing anode surface area and the specific surface area of the reactor (electrode surface area-to-volume ratio), involved the exploration of cathode materials with higher surface areas than carbon cloth. A flat, carbon cloth floating air cathode was limited by the reactor surface area, thus making another, more porous material that could still be used as an air cathode desirable. Samples of reticulated vitreous carbon foam [Duocel © ERG Aerospace Corporation] of various porosities [table 3.1] were obtained and coated directly with MnO_2 using the previously described protocol used to coat Vulcan carbon. Each sample had a relative density of 3 percent. The same graphite discs previously described in section 2.2 were used as anodes.

Table 3-1: Carbon foam cathode characteristics

	Porosity (PPI*)	Volume (cm^3)	Specific SA (ft^2/ft^3)	Specific SA (cm^2/cm^3)	Surface Area (cm^2)
Foam 1	45	7.44	960	31.5	234.36
Foam 2	45	7.44	960	31.5	234.36
Foam 3	80	7.44	1550	50.9	378.70
Foam 4	80	7.44	1550	50.9	378.70
Foam 5	100	7.44	2000	65.6	488.06
Foam 6	100	7.44	2000	65.6	488.06

*PPI stands for pores per inch of foam

Reactors were filled with 1.5L of wastewater (1L from primary clarifier, and 0.5L of primary settled solids from Blue Plains AWWTP). Previously used carbon cloth air cathodes were used as counter electrodes during the initial 48 hours at open circuit and subsequent poising of the anode at -0.2V vs Ag/AgCl in 3-electrode configuration. This was done in order to minimize the amount of MnO_2 lost from the foam cathodes while the ARB biofilm was established. Once a mature biofilm was present, indicated by a plateau in current after 3.5 days in 3-electrode configuration [figure 3-11], cyclic voltammetry was run on the anodes following which the carbon cloth air cathodes serving as counter electrodes were replaced with the MnO_2-coated foams. The SMFCs were then allowed 24 hours of OC before polarization to determine their maximum power densities.

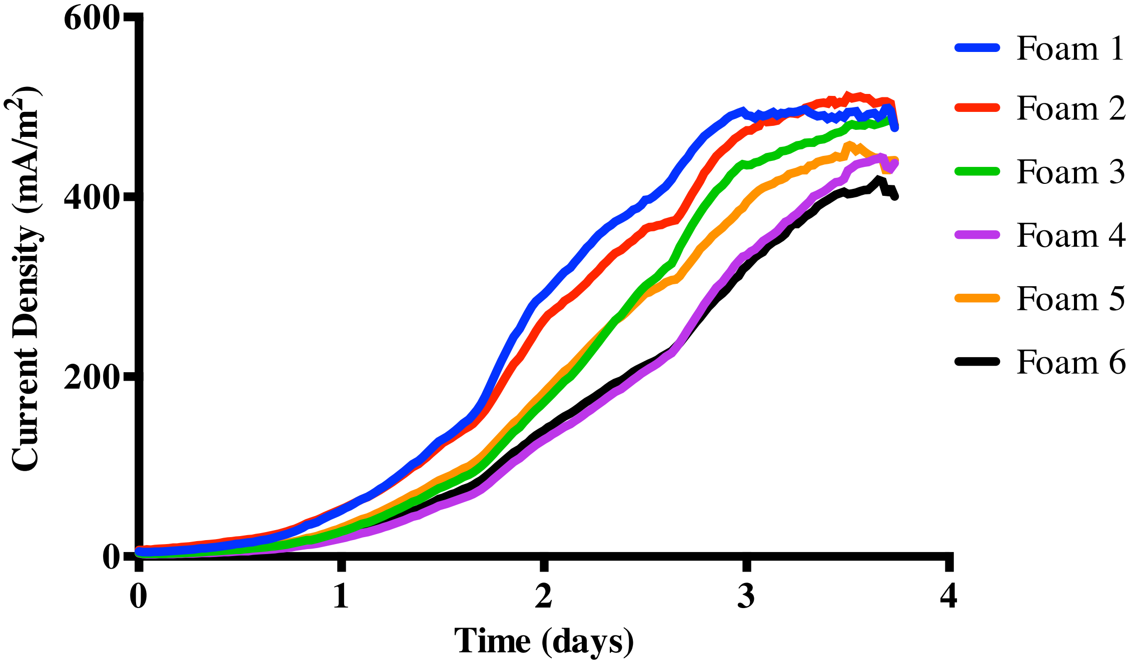


Figure 3-11: Current density (normalized by anode SA) of foam SMFCs in 3-electrode configuration

Initial polarization showed no significant increase in maximum power density when power was normalized by anode surface area [figure 3-12] as compared with previous trials using MnO_2-cathodes. In fact, the maximum power densities achieved by these SMFCs were slightly lower than those achieved using MnO_2-coated carbon cloth air cathodes when both are normalized by anode surface area, and significantly lower when normalized by cathode surface area. While the increase in cathode surface area provided by the porous carbon foam cathodes allowed these SMFCs to reach greater open circuit voltages than previously observed, it did not increase the attainable maximum power.

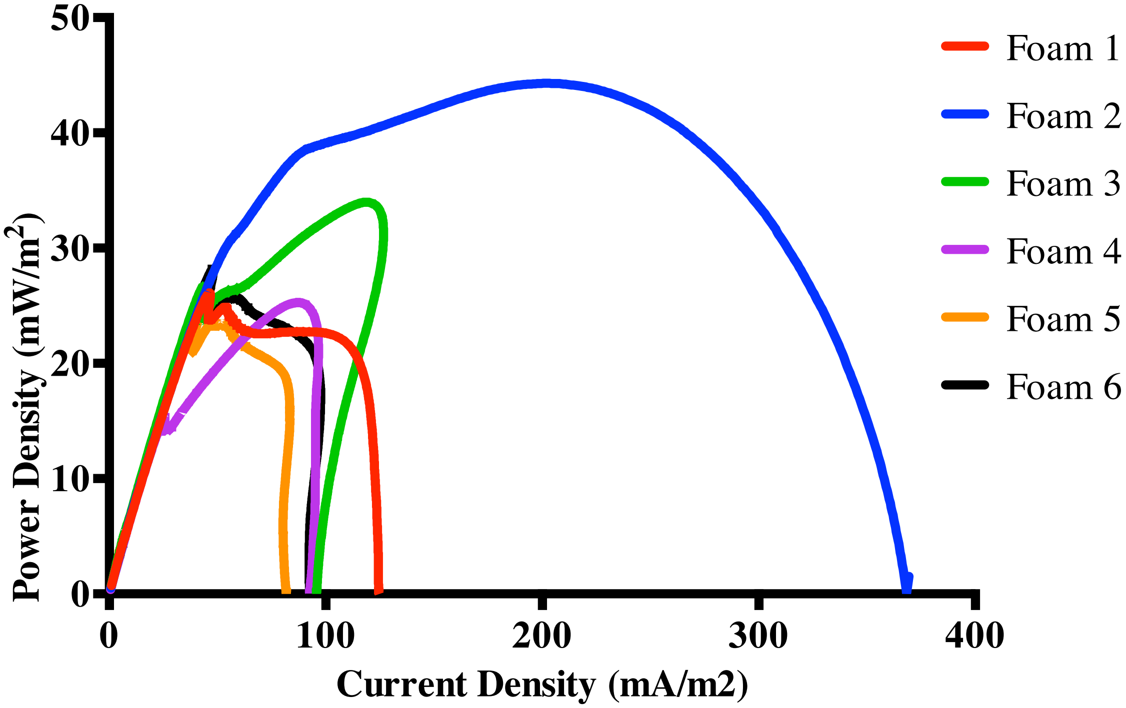


Figure 3-12: Power densities during polarization (normalized by anode SA)

When the SMFCs were poised at a cell voltage of 0.5V in 2-electrode configuration, they quickly stopped producing anodic current and ceased to function as fuel cells. Power density over time of three of the six foam cathode SMFCs (the three not shown never produced positive power in 2-electrode configuration) is illustrated in Figure 3-13, and quickly goes to zero. Adding primary clarifier wastewater did not improve power outputs, but lifting the cathodes out of the electrolyte for approximately 30 seconds and replacing them did result in a spike in power at day 7.

It is likely that the MnO_2-coated carbon foam cathodes experienced rapid loss of catalyst in the wastewater as occurred in the study described in chapter 2 especially considering that the catalyst was deposited directly onto the carbon foam without the use of an ion-binder such as liquion. However, it also appears that limited mass transport of oxygen to these cathodes also interfered with the MFCs' performance. These cathodes were suspended right at the wastewater surface, but were not impermeable to water in the same manner as the PTFE-coated air cathodes. It is possible that anoxic wastewater saturated the cathode pores, preventing oxygen from reaching the electrode surface and therefore interrupting the overall MFC reaction. As stated earlier and previously shown in section 3.3, despite the presence of an ORR catalyst, the amount of dissolved oxygen in the upper few centimeters of wastewater is insufficient for a successful cathode reaction.

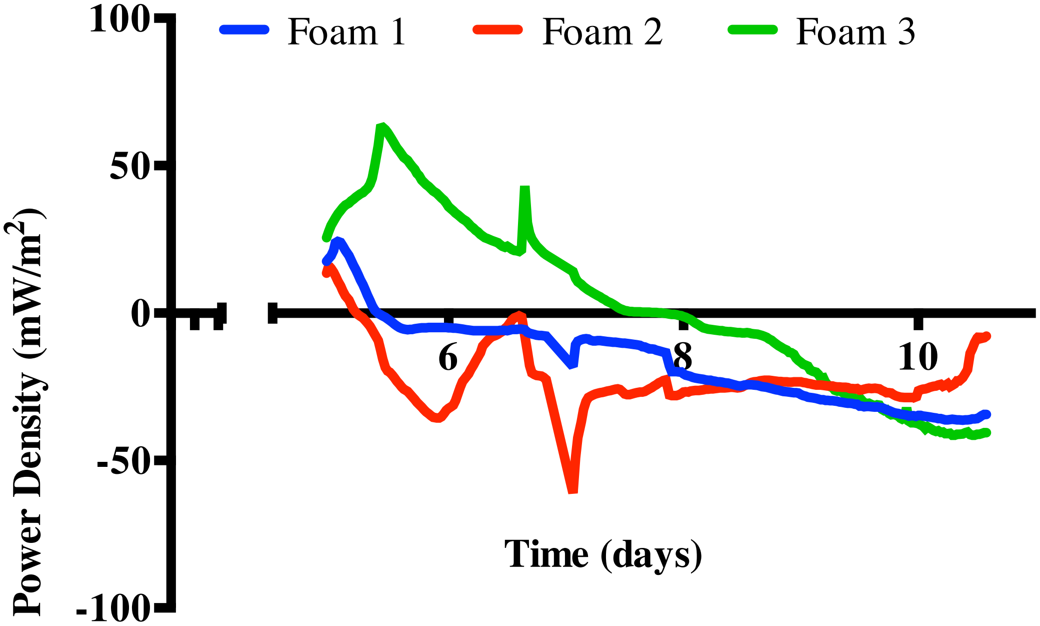


Figure 3-13: Power density (normalized by anode SA) when the cell voltage was set at 0.5 V

Chapter 4: Conclusions and Future Work

4.1 Conclusions

The results presented in chapter 2 demonstrate that sediment microbial fuel cells can be adapted to oxidize organic matter present in wastewater in addition to that found in sediments. While the continuous supply of organic-rich wastewater may have resolved the anodic limitation seen previously in benthic MFC studies (Lowy et al. 2006; Tender et al. 2008), the absence of dissolved oxygen became an obstacle in the operation of wastewater SMFCs. The design and fabrication of a floating air cathode presented a viable solution to this difficulty, though the reactor surface area exposed to air limited its size and therefore the surface area of the anode that could be employed.

The batch wastewater SMFCs sustained much higher power densities than previously found with SMFCs, with the exception of one deployed in a Pacific cold seep (Nielsen et al. 2008) that attained slightly higher sustained power densities than those reported here (39 mW/m^2 versus ~21 mW/m^2 [of anode SA] in wastewater SMFCs). Maximum power densities obtained during polarization tests were nearly an order of magnitude lower than those reported in previous wastewater MFC studies (Ahn et al. 2014; Ahn & Logan 2010). It appears that the open configuration of the SMFCs tested provides a less efficient reactor design than a sealed single-chamber MFC. Moreover, a large volume of wastewater was used in these lab trials in comparison with many batch experiments performed using municipal wastewater reported in the literature (Ahn & Logan 2010; Ahn et al. 2014; Fornero et al. 2010) which could be an indication of the difficulties that accompany scaling-up MFCs. Re-designing wastewater SMFCs to increase the electrode SA-to-reactor volume ratio allowed for a significant increase in the amount of power extracted from a given volume of wastewater. Additionally, the exploration of cathode designs and materials demonstrated the importance of maximizing cathode surface area while maintaining its ability to float at the wastewater surface.

The evaluation of manganese oxides (MnO_x) as an ORR cathode catalyst in wastewater SMFCs had not been done previously. The adaptation of a common protocol used to coat air cathodes in a platinum-based catalyst (Pt/VC) (Middaugh et al. 2008) was not adequate for binding the MnO_x nanoparticles to the cathode surface. While MnO_x-coated cathodes showed high initial potentials and corresponding maximum power densities, they appeared to lose their effectiveness faster than Pt-coated cathodes. This was due to the dissolution of manganese into the wastewater. Because of this finding, MnO_x did not provide a solution to the fouling of Pt in wastewater over time, though manganese is a much cheaper catalyst material.

4.2 Future Work

This proof of concept study provides a good foundation for future studies at larger scales of the treatment efficiency of wastewater SMFCs. The findings reported in section 3.4 suggest a large, shallow reactor would be best in order to maximize anode and cathode surface areas. Additionally, this reactor configuration using a floating air cathode has not yet been tested under flow conditions. Previous wastewater MFC studies have shown that current density usually increases with shorter HRTs, but at the expense of COD removal. This work has led to the conceptualization of a shallow 30-liter rectangular reactor that will be installed on-site at Blue Plains AWWTP to treat secondary influent wastewater. A similar electrochemical protocol will be used to evaluate its performance as a fuel cell.

There is still much work to be done in order to develop a viable ORR catalyst that can be used in wastewater without fouling or reduced performance over time. MnO_x, like platinum, showed great promise in pure substrate conditions, but quickly lost its effectiveness in a complex substrate. Other catalysts continue to be explored, and activated carbon may be a promising material to test in a wastewater SMFC (Zhang et al. 2013).

4.3 Practical implications

One advantage of the SMFC design is the ability to use it in existing WWTP infrastructure with few costly modifications. As stated in the first chapter, finding an energy-saving alternative to activated sludge for wastewater treatment could halve a WWTP's power consumption. In the United States where POTWs consume 2-4% of the country's electricity, such a reduction would be quite significant both in lowering the cost of wastewater treatment and in decreasing carbon emissions. The real value of MFCs (sediment or otherwise) appears to lie in their potential to save energy and less in their ability to generate electricity. Because of the low observed efficiencies, and resulting low power outputs, the benefits derived from saving energy are much greater than those derived from producing it.

In the developing world, the story, and potential application of wastewater MFCs, is completely different. While producing a few watts of power may not be very relevant in the U.S., it could be life changing in communities that currently lack reliable access to electricity. The ability to power a light bulb by which to study or charge a cell phone battery would have great impacts on families in remote areas where homes are not connected to a power grid. Since there is a general absence of wastewater conveyance and treatment infrastructure, demonstrating the health and practical benefits of installing decentralized systems [pit latrines] could help encourage their adoption.

Microbial fuel cells are not ready for large-scale implementation as an energy-saving step at municipal WWTPs or as a power-source in developing world homes. However, they continue to show promise as an innovative tool to addressing key concerns of the water-energy nexus.

Appendix A: Total Manganese in SMFCs at start and after 16 days- values and calculations

Sample	Date	Total Mn (mg/L)	Date	Total Mn (mg/L)
Mn1	3/11/14	0.38	3/27/14	1.9
Mn2	3/11/14	0.38	3/27/14	1
Mn3	3/11/14	0.38	3/27/14	1.2
Pt1	3/11/14	0.38	3/27/14	0.23
Pt2	3/11/14	0.38	3/27/14	0.22
Pt3	3/11/14	0.38	3/27/14	0.23

Original mass of Mn introduced to SMFCs through application to the cathode:

0.5 mg/cm^2 [MnO_2/VC] x 21 cm^2 [cathode SA] = 10.5 mg MnO_2/VC

20% w/w loading → 0.2 x 10.5 mg = 2.1 mg MnO_2

MW MnO_2 = 86.94 g/mol = 86940 mg/mol

$$\frac{2.1\ mg}{86940\ {}^{mg}/_{mol}} = 2.415\ x\ 10^{-5}\ mols$$

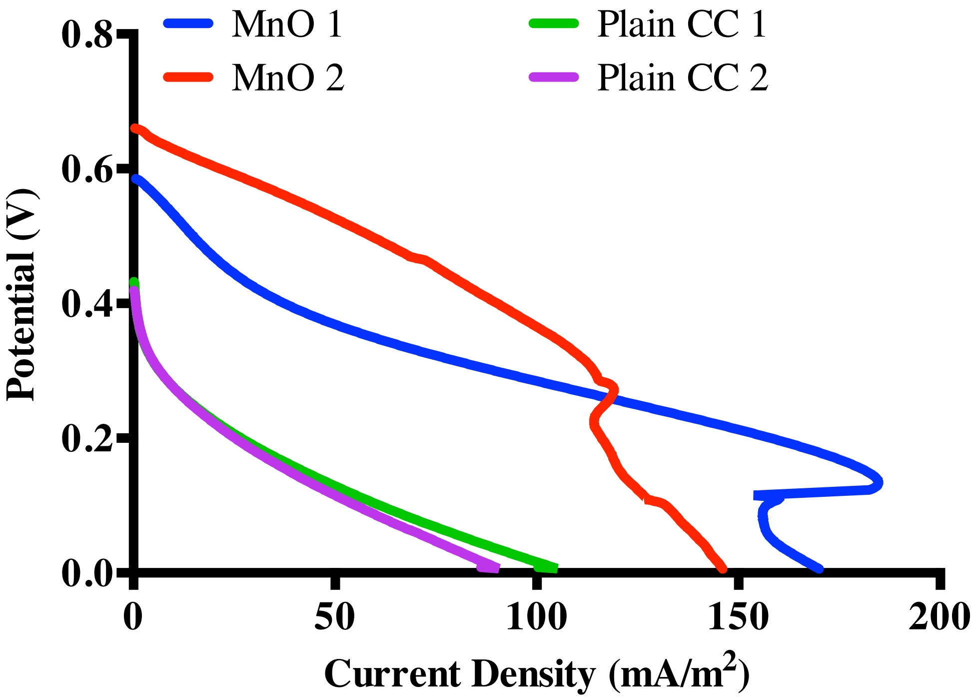
MW Mn = 54.94 g/mol = 54940 mg/mol

54940 mg/mol x $2.415\ x\ 10^{-5}\ mols$ = **1.33 mg Mn**

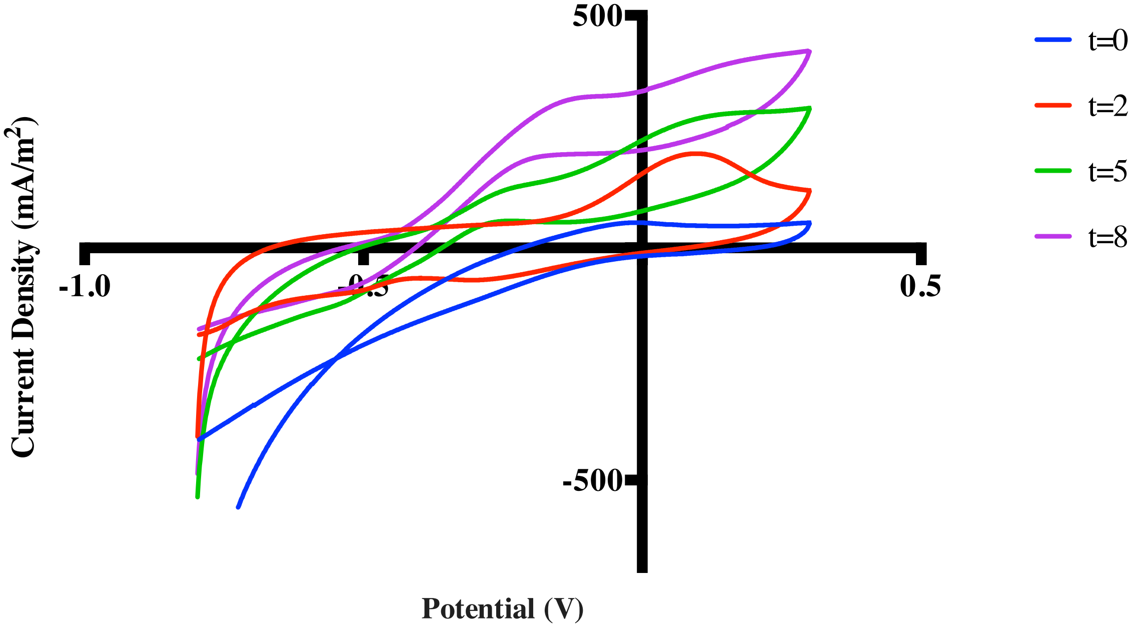
Initial and final mg Mn/reactor- average

	Initial Conc. (mg/L)	Initial Total Mass (mg)	Final Conc. (mg/L)	Final Total Mass (mg)	Actual total mass (mg)
Pt_ave	0.38	0.76	0.23	0.45	-0.31
Mn_ave	0.38	0.76	1.37	2.73	1.97

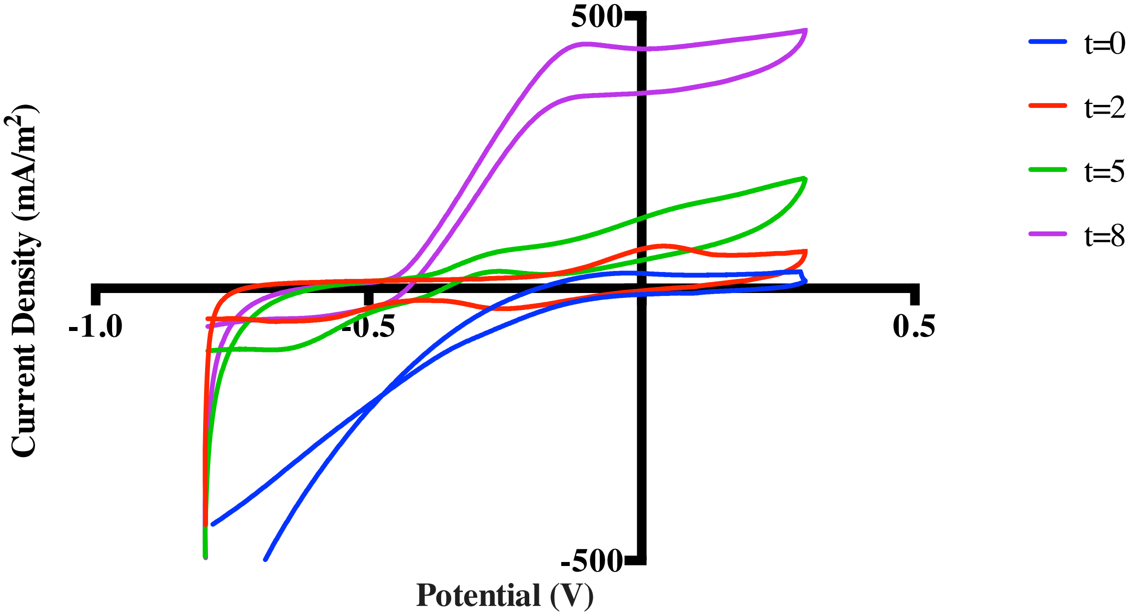
Appendix B: Polarization curves for MnO2-cathode SMFCs versus plain CC-cathode SMFCs



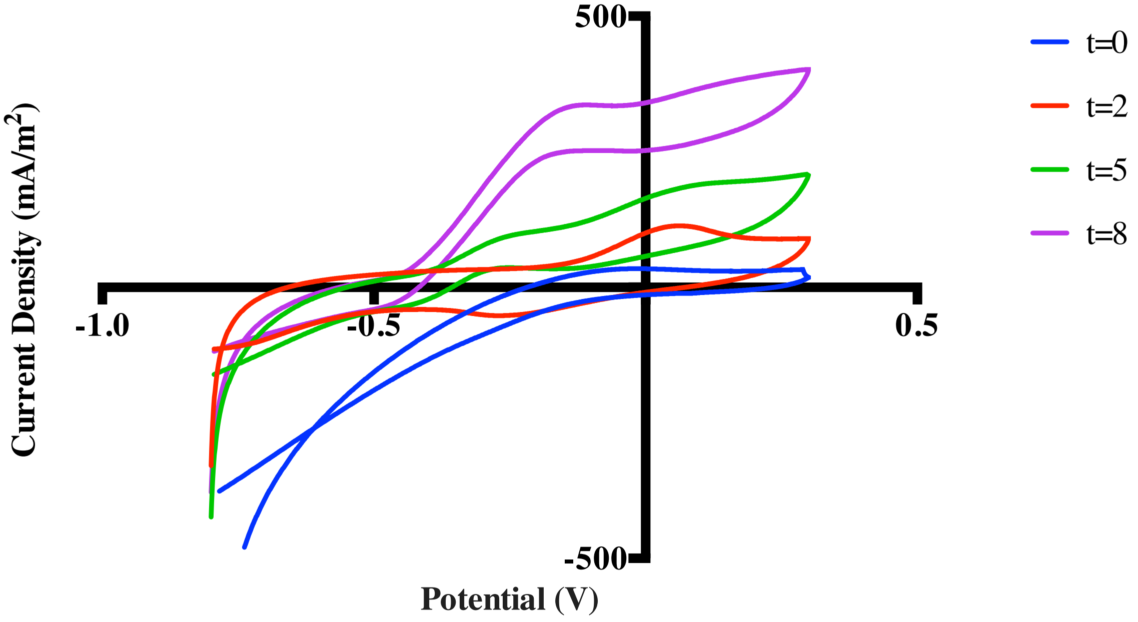
Appendix C: Electrode cyclic voltammagrams for MnO versus plain CC cathode- SMFCs



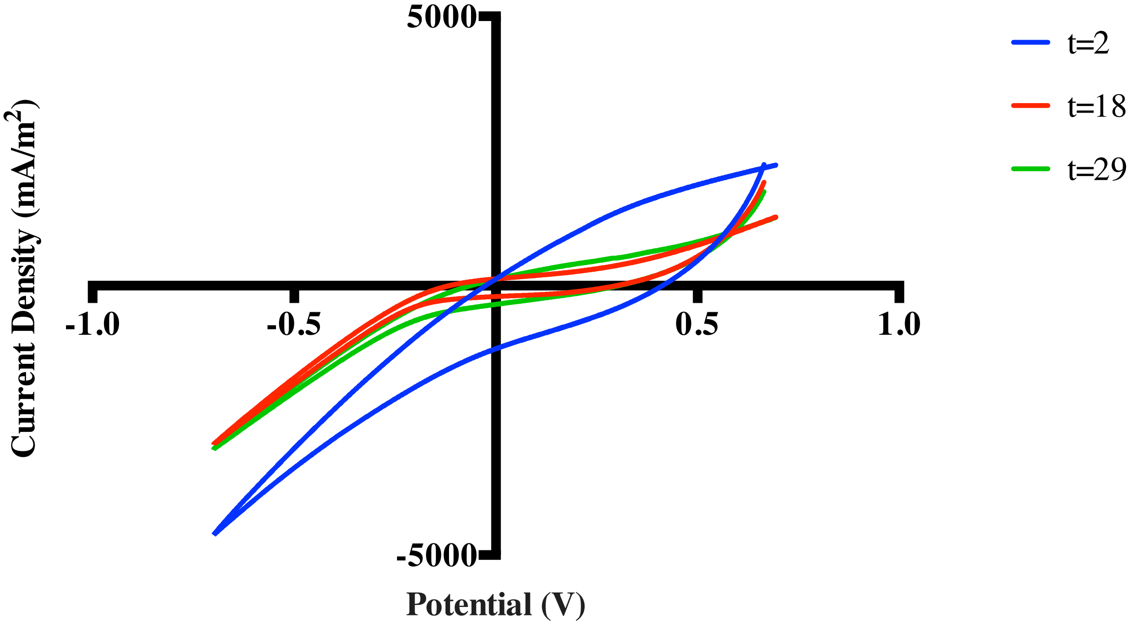
MnO 2 anode CVs



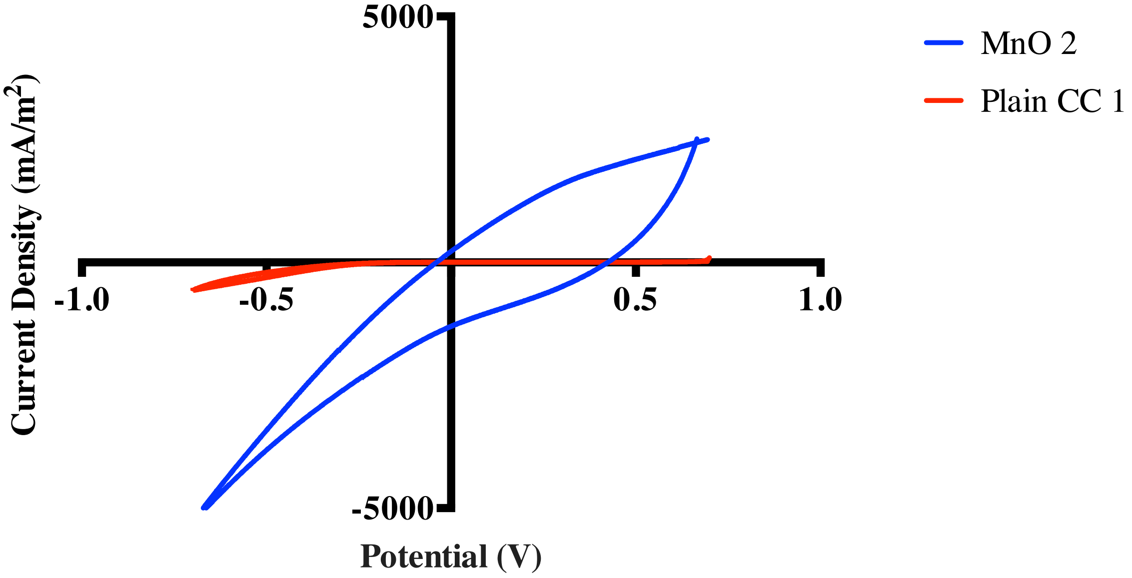
Plain CC 1 anode CVs



Plain CC 2 anode CVs

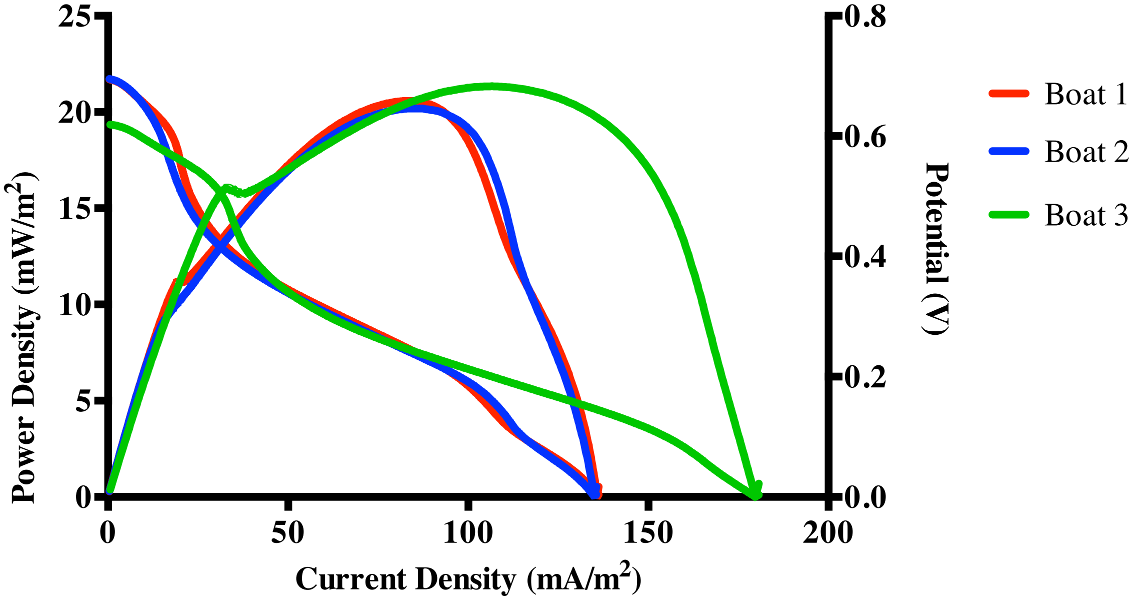


MnO 1 cathode CVs

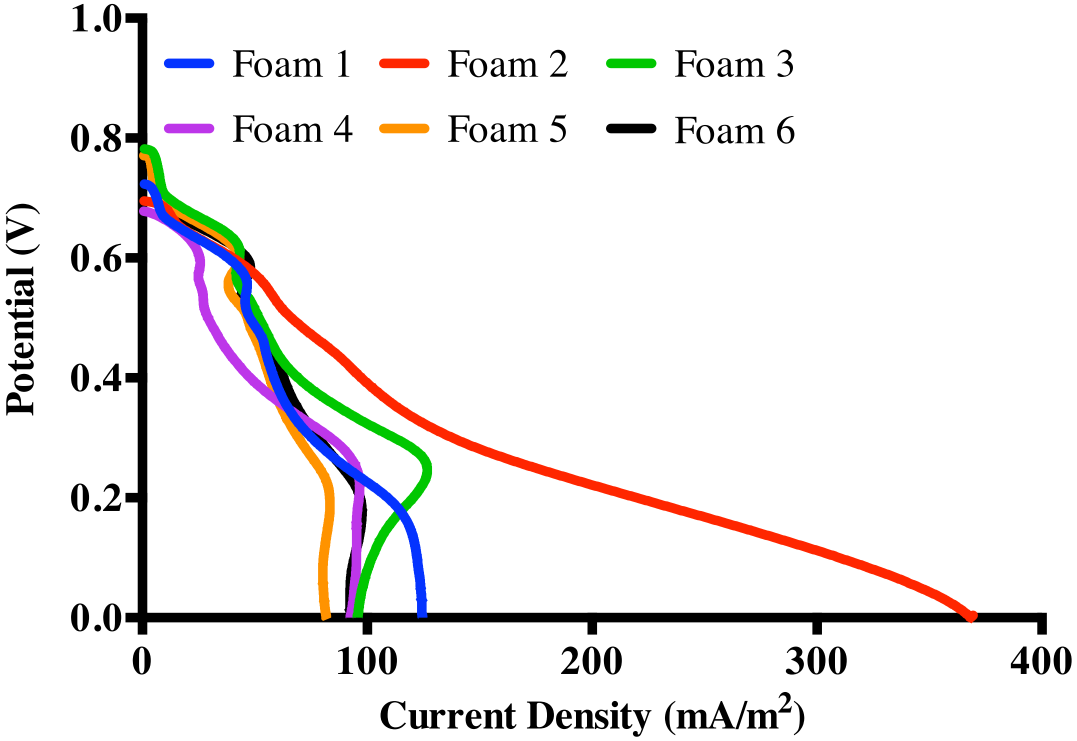


Comparison of cathode CVs at t=2 days

Appendix D: Polarization and power curves of boat SMFCs



Appendix E: Polarization curves of foam cathode SMFCs



Curves from initial polarization

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