PERFORMANCE OF MEMBRANE ELECTRODE ASSEMBLY MICROBIAL FUEL CELLS USING ACTIVATED CARBON CATHODES WITH VARIOUS DIFFUSION LAYERS

A Thesis in
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by
Sarah Hays

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The thesis of Sarah Hays was reviewed and approved* by the following:

Bruce E. Logan  
Kappe Professor of Environmental Engineering  
Thesis Advisor  

John M. Regan  
Associate Professor of Environmental Engineering  

Kamini Singha  
Assistant Professor of Geosciences  

Peggy Johnson  
Professor of Civil Engineering  
Head of the Department of Civil and Environmental Engineering  

*Signatures are on file in the Graduate School
ABSTRACT

A microbial fuel cell (MFC) is a device that uses bacteria to generate electricity through the oxidation of organic matter. MFCs continue to be extensively researched with various chemical feed sources using a conventional setup with widely spaced electrodes, and cathodes containing platinum. However, these specifications make scale-up expensive and difficult to construct. Many anode and cathode materials have been used in different configurations in the past; however, most of these studies chose to use idealized substrates, which is unrealistic for practical applications.

In this study, a membrane electrode assembly (MEA) MFC was constructed using activated carbon (AC) cathodes and either a carbon brush or flat carbon mesh anode, and domestic wastewater as a feed substrate. The use of carbon brush anodes produced consistently higher voltage and power density results than carbon mesh anodes. Over time, the average voltage from the carbon brush anode reactor configurations was $360 \pm 63$ mV, while the carbon mesh anode configuration was $200 \pm 81$ mV. The average decrease in power density over time (89 days) from the carbon brush anode reactor configurations was 15 mW/m², while the carbon mesh anode configuration dropped 190 mW/m² over time. The maximum Coulombic efficiency (CE) for the mesh anode configuration was 22 ± 0.4%, while for the brush anode configuration it was 13 ± 2.9%. The CE for the mesh anode decreased 17% over time and the average CE was only 7.8 ± 7.1%. The average CE for the brush anode configuration was 8.6 ± 2.9% with a 4.6% decrease over time. Brush anodes measured consistently higher average COD removal values per cycle (80 ± 3%) than carbon mesh anodes (58 ± 7%).

To optimize the use of carbon mesh anodes, additional diffusion layers (DLs) were added to the AC cathodes. This hindered oxygen diffusion to the anode, which was expected to be contributing to the decline in performance of reactors using carbon mesh anodes. Increased
voltage and power generation correlated directly to an increase in the number of diffusion layers added. The setup which allowed the least oxygen diffusion used two layers of generic cling wrap (G2-PG), and achieved an average voltage of $310 \pm 52$ mV and a maximum power density of 160 mW/m$^2$. CE values positively correlated with the addition of diffusion layers. However, as seen with the original setups which did not have additional DLs, there was a steady decrease in CE over time. The addition of DLs positively correlated to lower effluent BOD$_5$ values.

These findings showed that the addition of diffusion layers improved the performance of carbon mesh anodes in a MEA reactor configuration. However, the use of brush anodes provided more consistent, reliable results over time than the use of thinner carbon mesh anodes with domestic wastewater.
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1.1 World Energy Needs

It is a well known fact that people use energy. The average annual energy usage for the top eighteen OECD (Organization for Economic Co-operation and Development) countries is 5.0 TOE (tons of oil equivalent) (58 MWh) per person, while the average energy usage in the United States is 8.35 TOE (97 MWh) per person [3]. The problem we are currently facing is how to obtain this energy without negatively impacting the world in which we live. More than 2 billion people around the world do not have access to sufficient sanitation and 1 billion do not have access to clean water. Much of the cause behind these statistics is due to the energy needs associated with these daily needs. The United States consumes nearly 100 quadrillion (one thousand million million or \(10^{15}\) ) BTUs of energy per year [4], and although it contains only 5% of the world’s total population, the U.S. uses 25% of the world’s total energy [4]. Looking to the future, the International Energy Outlook (IEO) estimates a 49% increase in world energy consumption from 2007-2035, equating to a total world energy usage of 739 quadrillion BTUs of energy in 2035 [5]. With these kinds of predictions, it is clear that a reliable, constant source of energy is necessary for the future.

1.2 Nonrenewable Energy

In 2008, 93% of the world’s energy came from nonrenewable energy sources (i.e.: petroleum, natural gas, coal, and nuclear electric power) [6]. The demand for oil is expected to
exceed the amount of known oil reserves in just five to fifteen years (2015-2025) [4]. There are constantly new oil wells being discovered and drilled as well as new technologies for acquiring oil. However, the fact remains that there is a finite amount of oil left on the earth, as is true for the other aforementioned nonrenewable energy sources.

Not only are nonrenewable sources going to eventually be unavailable as a source of energy, their consumption releases harmful gases into our environment, which contributes to potentially detrimental climate changes. The burning of fossil fuels releases stored carbon into the environment, which raises the concentration of carbon dioxide in the environment. This increase has a direct correlation with environmental damages and global climate change [4].

1.3 Renewable Energy

In 2008, of the 7% of the energy used in the world from a renewable source (i.e.: solar, geothermal, wind, hydropower, and biomass), 53% was renewable energy from biomass [6], making it a promising source of future energy needs. One challenge of using renewable energy is the huge capital cost. The estimated cost to replace 70% of fossil fuels with renewable energy sources for 30 years would be between $170 and $200 billion per year [4]. Therefore, additional research and application of renewable energy sources are extremely important for their success in providing our future energy needs.

1.4 Wastewater Treatment

Wastewater treatment uses 1.5% of the total electricity created in the United States and $25 billion each year [4]. With these values continuing upward in the coming years, alternatives to wastewater treatment technologies are growing more important. A typical wastewater
treatment plant process begins at the pump station, where all water enters the plant. This is followed by screening to remove large debris, and then primary clarification, which allows sediments to settle out and fats to be skimmed from the top of the water. Next is the aeration process, in which air is pumped through the wastewater to aid in the biological degradation of organic materials; the cost of constantly aerating the water accounts for the largest portion of electricity usage at most plants. Flow then goes through secondary clarification where activated sludge settles out and is either recycled back into the clarification tank, land filled, or otherwise recovered. Finally, the remaining water is disinfected to kill any remaining bacteria before the water leaves the plant. The main objectives of a wastewater treatment plant are to remove suspended solids and reduce the BOD and nutrient levels in the effluent water which gets discharged to surrounding natural waters.

The promising science behind wastewater treatment is that wastewater contains energy in the form of biologically degradable organic matter. This degradation occurs through electron transfer using natural bacterial metabolic pathways. At a conventional wastewater treatment plant in Canada there is approximately 9.3 times as much energy in wastewater than is needed to treat the wastewater [4]. Bioelectricity generation captures energy naturally created by the metabolic processes undergone by bacteria and harvests it into a usable energy source, such as electricity. At least, the electricity generated from bacteria would be enough to power a wastewater treatment plant, making it a self sustaining entity. At most, a self-sustaining wastewater treatment plant would have the option of selling excess electricity back to the grid and producing a profit to advance future wastewater infrastructure. The compounds that we are applying energy to remove are the sources behind a promising renewable energy source.
1.5 Microbial Fuel Cell Application

MFCs are devices which use bacteria to generate electricity through the oxidation of organic matter. During oxidation, electrons are produced which travel from the anode, through an external resistor, to the cathode, where they combine with protons and oxygen to form water.

MFCs are growing in popularity as a potential technology for use in wastewater treatment due to their ability to remove organic material as well as generate power. MFCs could potentially be used to replace the aeration and bioreactor processes, which would alleviate aeration costs as well as aid in the removal of organic contaminants through bacterial degradation [7]. One study presented four different ways to use MFCs with present wastewater treatment plant processes [8]. Some of the advantages for using a MFC versus one of the aforementioned conventional methods of wastewater treatment are: production of electricity, minimization of aeration costs, and reduction in solid wastes [4]. There is excess energy in the form of biodegradable organics available in wastewater, which is estimated to be more than enough to treat wastewater if used efficiently. Recovering this energy could help lead to a self sufficient water infrastructure, and thus the potential for providing sanitation and potable water to more areas throughout the world.

1.6 Research Objectives

Some of the troubles behind the realistic use of MFCs are the problems associated with large-scale application. Before MFCs will be used at a wastewater treatment plant, the following must be addressed: maximize power density and efficiency; minimize cost; and create an easily-constructible, durable reactor configuration. Some problems, specific to using MFCs at a
wastewater treatment plant, stem from the low organic strength and low conductivity of the wastewater, which can limit the electricity generation capability.

The motivation behind the research presented in this thesis was to develop a cost effective, easily scalable reactor configuration for application into a wastewater treatment plant. A membrane electrode assembly (MEA) was chosen as the reactor configuration that would best meet this goal and the use of brush and mesh anodes in a MEA reactor configuration were compared. Mesh anodes had been proven to be a less expensive alternative to brush anodes that worked well in MFCs where the anode was kept sufficiently distant from the cathode to prevent oxygen that leaked through the cathode to be used by bacteria on the anode. However, the low conductivity of wastewater requires more closely spaced electrodes in order to minimize internal resistance and maximize power. Therefore, in order to optimize the use of a mesh anode in the MEA, polydimethylsiloxane (PDMS) or generic cling wrap diffusion layers (DLs) were added to the cathode. The purpose of the DLs was to control the amount of oxygen diffusion though the cathode and to establish the most favorable oxygen transfer rate to optimize the mesh anode performance. The goal was to produce a MEA configuration with a carbon mesh anode that could perform comparably to a MEA configuration with a brush anode.
Chapter 2

Literature Review

Various aspects of MFCs are being studied by researchers, many of which focus on the major challenges faced during the scale up of MFCs. These include: reactor cost, material stability/durability, reactor configuration efficiency, power production efficiency, and water treatment capabilities [9]. The literature that is relevant to the research objectives here is reviewed below, on the topics of wastewater treatment processes and the most recent findings on MFCs on substrate and material options for construction, configurations, and data analysis methods.

2.1 Substrate

Substrates in MFCs supply both a carbon and energy source for microbial processes; different substrates change the efficiency of bacterial metabolic processes. There are a wide variety of substrates which have been tested in MFCs. These range from acetate, glucose, and other chemical compounds to synthetic, domestic, brewery, and food-processing wastewaters. The main difference between these two general substrate categories is that the former are simple substrates that can be easily broken down and used by bacteria as a food source. On the other hand, wastewater substrates are much more complex and therefore, more difficult for bacteria to degrade. However, enriching a diverse microbial community can be helpful in degrading these complex organics into simpler substances that can be directly incorporated into cells [10].

There were several reports in the literature which provided examples of comparable studies where less power production was found with wastewater substrates compared to single chemical substrates. It was also seen in these studies that weaker loadings in substrates resulted in lower Coulombic efficiency (CE) values.
Continuous flow MFCs using either glucose or wastewater as feed sources were compared [9], and the maximum power achieved using glucose was 1540 mW/m², compared to that of wastewater which was 460 mW/m², a 70% decrease. CE values for glucose (60%) and wastewater (27%) were reported. Similarly, the performance of MFCs with and without proton exchange membranes (PEMs) were reported using glucose or wastewater as substrates [11]. Glucose fed reactors with a PEM (260 ± 10 mW/m²) and without a PEM (490 ± 21 mW/m²) outperformed wastewater fed reactors with a PEM (28 ± 3 mW/m²) and without a PEM (150 ± 8 mW/m²). CE values were also higher in the glucose fed reactors (75% without PEM; 55% with PEM) than in the wastewater fed reactors (20% without PEM; 28% with PEM). The maximum power densities of MFCs with similar reactor designs using acetate (510 mW/m²) and domestic wastewater (150 mW/m²) feed sources were also reported [10]. Acetate fed reactors produced a maximum CE of 72%, relative to wastewater whose values were commented to be significantly lower, although no actual CE values were reported.

Single chemical substrate fed reactors consistently produced higher voltage, power, and CE than wastewater fed reactors. These values make it clear that the use of domestic wastewater as a substrate in MFCs lacks efficiency and seeks optimization. More research should be done to idealize the use of low organic content substrates.

Properties of different substrates, such as conductivity and chemical oxygen demand (COD), can partly explain the different performance of MFCs. Increases in conductivity have an inverse relationship with internal resistance (Rint), which corresponds to a higher overall cell performance. A conductivity of 1 mS/cm for domestic wastewater was reported [12], which was expected to show a more amplified drop in cell performance relating to the low conductivity property values and therefore high Rint. Brewery wastewater had a conductivity of 6 mS/cm and produced a maximum power density of 450 mW/m² in an MFC [13]. Anaerobic digester sludge had a conductivity of 3.4 mS/cm – 3.7 mS/cm, more than three times higher than most domestic
wastewaters and still saw a decrease in cell performance attributed to low conductivity and high 
$R_{\text{int}}$ [14]. The effect of wastewater media representing different conductivity ranges is shown in 
Table 2-1 [2].

Table 2-1: Voltage and power output from different media (at 30°C) [2]

<table>
<thead>
<tr>
<th>Anodic medium condition</th>
<th>Conductivity (mS/cm)</th>
<th>Voltage$^e$ (mV)</th>
<th>Power density$^e$ (mW/m$^2$)</th>
<th>Max power density (mW/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WW$^a$ + Ac$^b$ (15 mM)</td>
<td>2.89</td>
<td>555 ± 3</td>
<td>70 ± 1</td>
<td>70 (430 Ω)$^f$</td>
</tr>
<tr>
<td>WW + Ac (15 mM) + PBS$^c$ (100 mM)</td>
<td>11.8</td>
<td>656 ± 4</td>
<td>98 ± 1</td>
<td>320 (180 Ω)$^f$</td>
</tr>
<tr>
<td>BA$^d$ medium + Ac (15 mM) + PBS (100 mM)</td>
<td>13.5</td>
<td>687 ± 6</td>
<td>108 ± 6</td>
<td>353 (200 Ω)$^f$</td>
</tr>
</tbody>
</table>

$^a$ Wastewater  
$^b$ Acetate  
$^c$ Phosphate buffer solution  
$^d$ Basic anaerobic  
$^e$ Average ± standard deviation (SD) (at 1,000 Ω)  
$^f$ Resistor where maximum power density was obtained

The COD of a wastewater may affect the maximum achievable power density due to the 
higher organic loading, but it has been reported that ionic strength is more important for 
producing high voltage output than wastewater organic strength [15]. Brewery wastewater was 
reported to have a COD of between 3000 mg/L and 5000 mg/L and a maximum power density of 
530 mW/m$^2$ [10]. Similarly, in a different study, a COD of 2125 mg/L was reported for brewery 
wastewater and a maximum power density of 450 mW/m$^2$ [13]. Domestic wastewaters in the US 
typically have much lower COD values (between 200 mg/L and 400 mg/L) than those used in the 
laboratory when single chemical substrates are added. This may correlate to lower maximum 
power densities due to the lower organic loading; however it is also important to analyze the ionic 
strengths of these solutions and determine its effect on performance.
There are many challenges to overcome because of the non-ideal properties of wastewater when used in MFCs. Understanding that ionic strength is more important than wastewater organic strength for successful MFC performance, as well as the other reasons why single chemical solutions perform more ideally than wastewaters in MFCs, will help optimize the use of wastewater in the future. Enhancing wastewater substrates or otherwise optimizing their use in a MFC will allow for the possibility of removing pollutants (i.e.: nitrates, sulfates, and sulfide) as well as simultaneous energy production and waste stream treatment [10, 16].

2.2 Cathode materials

MFC studies have been done using a variety of cathode materials. Air cathodes, which are exposed to air on one side and water on the other, are the most commonly used cathodes in MFCs [17]. There are many important physical characteristics of cathodes which make them ideal for use in MFCs. High surface area is often a limiting factor in achieving the maximum power density; therefore tubular cathodes are promising as they provide increased surface area compared to flat cathodes [17]. However, depending on the material type, this setup can be expensive because of the large quantity of material needed. Carbon cloth cathodes are commonly used, but are expensive despite the small quantity needed ($1000/m²) [17]. Cathodes were reported to have contributed up to 47% of the MFC capital costs, which presented an opportunity for economic improvement [17].

The key components necessary for an air cathode are: diffusion layers to hinder oxygen intrusion, a catalyst for oxygen reduction, and a current collector. Below, I discuss alternate materials for cathode construction and their corresponding results.
2.2.1 Catalyst

Improved cathode performance could be achieved by making the following changes: optimizing the use of a platinum (Pt) catalyst at room temperature (by minimizing the amount of Pt needed to optimize the oxygen reduction reaction), lowering the internal resistance, and using better oxidants (i.e.: ferricyanide) [18]. Lowering the overpotential of the oxygen reduction reaction through the use of a catalyst lowers the activation energy needed and thus improves cathode performance [19]. Pt is a commonly used catalyst on air cathodes and achieved higher power densities in MFCs than non-catalyzed electrodes [9, 17, 19]. Pt is an ideal catalyst because of its low activation energy for oxygen reduction and high affinity for oxygen, but it is expensive and rare [19, 20]. Other materials have been tested which may replace this costly, precious metal catalyst. Co-tetramethylphenylporphyrin (CoT-MPP), iron (II) phthalocyanine (FePc), and manganese/lead dioxides were tested and seen to effectively reduce oxygen and perform similarly to platinum catalysts [9, 13, 18, 20-22]. Activated carbon is also an alternative for a cheaper cathode because of its high surface area, which can be idealized using specific regeneration processes which increase the material porosity [19, 23]. Vulcan XC-72R was used as a catalyst and produced comparable power densities and CEs to Pt catalysts by using HNO₃ treatment to increase the surface area [19]. Increasing the area available for reaction lowered the cathodic overpotential [20].

2.2.1.1 Binder

Polymers are used to bind catalysts and carbon to the electrode surface; the two most common binders that are used in MFCs are perfluorosulfonic acid (Nafion) and polytetrafluoroethylene (PTFE). Nafion is much more expensive than PTFE. However, a 0.5 mg
cm² Pt loading with a Nafion binder produced a maximum power of 480 mW/m², which was 14% higher than that achieved with the same Pt loading using a PTFE binder [18, 20]. Another study confirmed that increasing the percentage of Nafion in the catalyst binder increased power generation [24]. Increasing the PTFE loading in the binder was thought to increase the pore space which allowed excess oxygen diffusion and therefore resulted in a decrease in power and CE.

2.2.2 Current collector

While flat carbon materials (i.e.: mesh, cloth) were commonly used as cathodes, the lack of rigidity and high electrode ohmic losses provide room for improved efficiency and performance. Metal mesh is beneficial for use in cathode construction as a structural support as well as a current collector. The use of stainless steel (SS) and nickel (Ni) metal mesh as current collectors were evaluated and comparable performances were produced from both [23]. This suggested that SS mesh was a cost-effective alternative for a current collector and that metal mesh current collectors were consistent, reliable materials for MFCs. Metal-based conductive paints have also been tested for use as a current collector. A Ni-based paint was applied to GORE-TEX cloth cathodes and produced a cost effective MFC with high power production and low charge transfer ($R_{ct}$) and internal ($R_{in}$) resistances [20]. Differing properties of metal current collectors can influence the oxygen transfer, proton transfer, and conductivity (due to variations in contact between surfaces), which lead to overall reactor performance changes [25].

2.2.3 Electron acceptors

Electron acceptors in MFCs are reduced using the electrons created from the oxidation of organics by bacteria at the anode [21]. Oxygen is the most ideal electron acceptor to date because
of its availability, sustainability, high redox potential and thoroughly studied and applied process [16]. Although alternatives have been tested, an oxidant that is more ideal than air is yet to be determined. Ferricyanide, hexacyanoferrate, permanganate, and H₂O₂ can all produce much higher power densities than oxygen due to their low cathodic overpotentials, but are unrealistic as alternative oxidants due to their constant replacement need after reduction [16, 26]. In the absence of oxygen, nitrates became an alternate electron acceptor and continued electricity production [21]. However, the limitation to using nitrates as the oxidant is that, depending on the relative amount of nitrates available, they could potentially be entirely depleted before the organic matter is entirely removed. They also select for a different type of bacteria, thus changing the community and effecting the power production and CE.

2.2.4 Oxygen hindrance

2.2.4.1 Diffusion layers

Diffusion layers (DLs) are an important component of the cathode because they control the amount of oxygen leakage through to the solution side of the cathode as well as preventing water leakage out of the reactor. Important physical properties of the oxygen diffusion layer are a hydrophobic and microporous surface. Water permeation into DLs slows the diffusion of O₂ from the gas phase to the liquid phase. The mass transfer coefficient, k, of O₂ through water (at 30°C) is 2.26 × 10⁻⁵ cm²/sec; compared to k-O₂ through air (at 30°C) of 2.33 × 10⁻¹ cm²/sec [27]. Thus, this decrease in oxygen flow through liquid leads to both lower current production and overall reactor performance [28].

It is important to find the correct balance of oxygen diffusion through the cathode; excess oxygen can lead to aerobic anode conditions, but too little oxygen can limit the oxygen reduction
reaction in the cathode, both of which result in poor reactor performance [26]. Excess oxygen diffusion through the cathode during start up periods of MFCs can elongate the acclimation period of the bacteria to the anode [9, 22]. A surplus of oxygen in solution is also harmful to the anode because it creates an aerobic environment, which allows the bacteria to preferentially use oxygen in solution rather than reduce the anode, and therefore decreases electricity generation and CE.

Many different types of materials have been used as DLs, including PTFE, carbon (Vulcan XC-72R and Acetylene Black), and PDMS [17, 29]. The thickness of the DL influenced the reactor performance more than the percentage of PTFE in the DL [29]. To achieve maximum power densities, an ideal thickness of 50 µm balanced the reduction in electrical resistance and the length of oxygen diffusion [29]. Similar trends were reported using PDMS, where the maximum voltage and power generation was achieved using 2 DLs (each with a loading of 6.25 mg/cm²). While PDMS is oxygen permeable, applying multiple layers of PDMS decreased the amount of oxygen flux through the cathode and lowered the oxygen mass transfer coefficient. PTFE and PDMS diffusion layers were compared and it was concluded that PDMS was more ideal as a DL in MFCs because it was highly hydrophobic, available, easy to apply to cathodes, and less expensive than PTFE (<$1.00/kg-PDMS; $1-2/kg-PTFE) [17].

In addition to diffusion layers, MFCs which utilize continuous flow through the anode chamber towards the cathode are useful for limiting the amount of oxygen diffusion through the cathode. This MFC design increases power generation due to both the minimization of oxygen diffusion through to the anode chamber and the increased proton transfer with flow towards the cathode [16].
2.2.5 Cathodic biofilm effects

The presence of a bacterial biofilm on the cathode led to lower reactor performance by creating a physical barrier. The barrier blocked proton and oxygen transport, and led to lower power production and increased CE over time in direct correlation with the thickness of the biofilm [30]. Cathodic biofilms were reported to negatively impact reactor performance by blocking proton transfer, decreasing the amount of oxygen available for the oxygen reduction reaction at the cathode due to oxygen consumption by aerobic bacteria, and deactivating the catalyst due to bacterial activity [31].

2.3 Anode materials

The characteristics which are of importance for anode materials are conductivity, biocompatibility, chemical stability, high porosity, and high surface area [16]. The ability for bacteria to attach to the surface is a significant characteristic, as it controls the electron transfer and power generation capabilities of the bacteria [12]. High porosity is important to prevent clogging at the anode which can lead to decreased ion transport [16]. Low anodic overpotential, which corresponds to a fast oxidation reaction, is needed in conjunction with a low cathodic overpotential to improve voltage generation in MFCs.

The most common anode materials that have been tested for use in MFCs are carbon and graphite anodes. There are a variety of forms of carbon anodes used in MFCs, including: cloth, mesh, felt, paper, granules, plates, and rods [16]. In addition, graphite fiber brushes comprised of a titanium rod are commonly used in MFCs [17, 32, 33]. A maximum power generation of 2400 mW/m² (normalized to cathode surface area) was achieved using graphite fiber brushes and an air cathode in phosphate buffer solution (PBS) [34]. Conductive polymers were used in the
construction of anodes, which increased the achievable current density [26]. However, one downfall to the use of conductive polymers is rapid degradation of the polymer coating by the bacteria.

Granular activated carbon (GAC) is a possible anode material candidate because of its high surface area, durability, and low cost. The high surface area of GAC allowed more bacterial adhesion onto the anode surface, which resulted in increased electron transfer (CE) and power generation [12]. The comparison of different anode materials shows that higher current ($I$) directly correlates to the internal surface area of the anode material (carbon felt > carbon foam > graphite) [16]. However, in large scale MFCs, increased surface area does not necessarily have a large effect on power density. Increasing the anode surface area by a factor of 56, using graphite brushes instead of carbon cloth, only increased the power density by 4% [31].

### 2.4 Reactor configurations

Many different reactor configurations and reactor-body materials have been used in single-chamber and two-chamber MFCs. Commonly used reactor-body materials are Plexiglas, beakers, and glass bottles. Two-chamber reactors typically contain a PEM between chambers, ideally, to allow proton transfer but prevent substrate and oxygen transfer [16]. Single-chamber reactors may contain a separator to provide a physical barrier between the anode and cathode electrodes. Advances in MFCs were reviewed and reactor designs were divided into four main categories: two-chamber where anode and cathode are separated by ion exchange membrane; single-chamber air-breathing with anode and cathode placed at opposite ends of reactor (with or without separator); single-chamber with anode, cathode, and separator in a single MEA; and cassette-electrode where two MEAs share a common aerated chamber and anolyte [26]. Further research was suggested that focused on the optimization of these reactor designs to overcome
limiting factors in each of the designs [26]. Each one provided a viable option for the configuration of a system that could eventually be integrated into a wastewater treatment plant.

### 2.4.1 Separator materials

Separators are an integral part of many MFC setups, and several different materials have been used including PEMs, or cation exchange membranes (CEMs), anion exchange membranes (AEMs), J-cloth, nylon, cellulose, and glass fiber [30]. The characteristics which make a material ideal for use as a separator are non-conductive, durable/non-biodegradable, inexpensive, high proton transfer coefficient, and low oxygen transfer coefficient [28, 30]. Previously reported oxygen transfer coefficients ($k$-values) for materials used in MFCs are presented in Table 2-2.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$-value ($\times 10^{-5}$ cm/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM (membrane)</td>
<td>9.4</td>
<td>[30]</td>
</tr>
<tr>
<td>Nafion (membrane)</td>
<td>13</td>
<td>[35]</td>
</tr>
<tr>
<td>Zirfon (separator)</td>
<td>19</td>
<td>[20]</td>
</tr>
<tr>
<td>J-cloth (separator)</td>
<td>29</td>
<td>[30]</td>
</tr>
<tr>
<td>Glass fiber 1.0 mm (separator)</td>
<td>5.0</td>
<td>[30]</td>
</tr>
<tr>
<td>SS cathode with 4 PDMS diffusion layers</td>
<td>20</td>
<td>[17]</td>
</tr>
</tbody>
</table>

The oxygen permeability of a Zirfon separator was reported to be comparable to that of a four-diffusion layer coated cathode [20]. The cost of using Nafion and Zirfon were also compared and Nafion was determined to be ten times more expensive than Zirfon, making Zirfon a promising material for future use in MFCs [20]. J-cloth and glass fiber separators were used to reduce the amount of oxygen transfer to the anode and to provide a physical barrier between electrodes; however, both of these materials were shown to degrade over time, and therefore were impractical for use in MFCs [30]. The negatives to using a PEM as a separator were oxygen
permeability, expense, and pH gradient production. The accumulation of protons in the anode
chamber due to the transport of other cations (i.e.: Ca^{2+}, Na^{2+}, Mg^{2+}) through the PEM caused a
pH gradient which led to a decline in bacteria activity [20]. These numerous requirements make it
difficult to find a separator material which meets all the needs for use in a MFC and additional
separator research is necessary.

A review of ion exchange membranes, size selective separators, course pore filters, and
salt bridge materials determined that separators were important for advancing power generation in
MFCs, but that they caused problems that need addressed [35]. All of the reviewed materials
were promising, but had at least one downfall: cost, pH gradient, or oxygen permeability. It was
concluded that additional research needs to be done to find an ideal, inexpensive, more efficient
separator and its discovery would be an important improvement towards optimizing the
performance of MFCs [35].

2.4.2 Electrode spacing

The distance between electrodes proportionally relates to the internal resistance in a
reactor configuration, and thus overall reactor performance. The use of a double-cloth electrode
anode (CEA) assembly (using a J-cloth separator) allowed a small electrode spacing (1.7 cm) to
be used, and produced a high power density (1010 W/m³) under continuous flow conditions [28].
Reduced electrode spacing improved reactor performance by lowering the internal resistance
[14]. As the electrode spacing decreased from 4 cm to 2 cm, the internal resistance decreased
from 161 Ω to 77 Ω, and the power density increased from 720 to 1210 mW/m². Decreasing the
distance between electrodes to 2 cm lowered the internal resistance, and benefitted the overall
performance of a glucose-fed batch reactor (811 mW/m³) [9]. When the electrodes were moved
closer together, both CE and energy recovery increased [9]. However, moving the anode and
cathode too close (1 cm) decreased power production (423 mW/m²), which was observed through a drop in open circuit potentials as well as a decline in bacterial activity. It was concluded that the drop in anode potential was likely due to excess oxygen diffusion through the cathode to the anode with such a small distance between electrodes [9].

Minimizing electrode spacing is important in systems using wastewater substrate because of its high solution resistance and low conductivity. However, the effect of electrode spacing is also dependent on the MFC configuration and the significance of other resistances within the system. Limiting the internal resistance by reducing electrode spacing has the potential to increase power generation, but quantification and comparison of resistances within the reactor will determine the effect of electrode spacing on performance.

### 2.5 Polarization methods

Power was calculated using Equations 1 and 2.

\[ P = IV \]  
\[ I = \frac{V}{R} \]  

Using measured voltage and fixed external resistance, power values were determined using Equation 3.

\[ P = \frac{V^2}{R} \]

A polarization curve is a graphical representation of voltage as a function of the current, which is used to calculate power density. A power density curve is a graphical representation of power as a function of current and is usually normalized to a sizing of the reactor (i.e.: anode volume or anode/cathode surface area) in order to allow comparison over different sized systems. However, there are many different methods used by laboratories and researchers to determine
polarization curves and it is important to understand the differences between these methods and the corresponding effects on the results.

2.5.1 Single-cycle curves

Single-cycle polarization curves were reported using a range of external resistances from 5000 – 5 Ω with 15 minutes at each resistance [13] and using a range from open circuit voltage (OCV) to 25 Ω with 20 minute intervals [36]. The appearance of power overshoot phenomenon was reported in the latter study at resistances lower than 250 Ω, at which time the acetate-fed system could not respond to the high current demand, and therefore showed a doubling back of the power density curve [36]. The former study did not show power overshoot in the power density curves produced from brewery wastewater fed reactors [13]. However, the curves did not extend through the entirety of the lower resistances, and therefore it was assumed that power overshoot occurred and was not shown. The different curve shapes could also be a result of a number of different factors, including different cathode assemblies and materials used. In addition, the brewery wastewater substrate (as previously described) [13] had nearly three times the COD (mg/L) and half the conductivity (mS/cm) of 100 mM phosphate buffer solution (PBS) with 1 g/L sodium acetate [36]. The extent to which these different feed solutions affected the power density curves is unknown. A similar result was reported in another study, where a substrate with a COD concentration of 2500 mg/L (comparable to brewery wastewater) was used during a single-cycle polarization curve [37]. The results show a drop off of power at lower resistances, but no distinct power overshoot.
2.5.2 Electrochemical curves

A potentiostat can be used to produce electrochemical polarization curves. A scan rate of 1 mV/s was suggested, which was thought to be sufficiently slow enough for these electrochemical tests [16]. It was also reported that the scans should be performed both forward and backward at steady-state conditions to ensure results [16]. Electrochemical polarization curves are also reported in the literature. Linear sweep voltammetry (LSV) was performed at a scan rate of 1 mV/s from OCV to 0.5 V and determined that LSV methods overestimated the maximum power density, even when 1 hour intervals or slower scan rates were used [36]. The overestimation of power by LSV polarization curves was also recorded in a study where both 0.1 mV/s and 1 mV/s scan rates were used from OCV to 100 mV [37]. The results showed an overestimation in power output, relative to the results using single and multiple-cycle polarization methods, for a scan rate of 1 mV/s. Since the complete cycle of the curve created using the 1 mV/s scan rate only took 30 minutes, it was assumed that the bacteria did not have adequate time to adjust to the environmental changes they underwent [37]. It was concluded that using a scan rate of 0.1 mV/s was accurate for producing electrochemical polarization curves comparable with those produced using the single-cycle and multiple-cycle methods [37].

Cyclic voltammetry (CV) was used to produce a polarization curve over a range of 1 to 3M Ω [19]. No conclusion can be made about the effectiveness of this method for producing a polarization curve because multiple methods were not compared. However, CV is a continuation of LSV that reverses the potential scan back towards the start potential. It can be assumed that this method of producing an electrochemical polarization curve may have also overestimated maximum power densities.
2.5.3 Multiple-cycle curves

The most accurate method for measuring power density production in MFCs is likely the multiple-cycle method. There are a multitude of papers in the literature which report appropriate results from the use of this method, which introduces a different external resistance for each new feed cycle [14, 17, 23, 28, 30, 36]. The multiple-cycle method ensures that the bacteria have sufficient time (approximately 1-2 days) to acclimate to the new resistance, and thus eliminates the appearance of power overshoot [36]. The same range of resistances used in the single-cycle method (OCV – 25 mV) was repeated, but instead each external resistance was fixed to its own cycle [36]. At 100 Ω resistance, where the single-cycle method began to show overshoot, the multiple-cycle curve continued outward and there was no recorded increase in anode potential, which was the cause for the drop in the single-cycle method curve. A range of resistances from 1000 - 20 Ω [30] and 1000 – 50 Ω [17, 23] were reported, where each resistance was used for a single fed batch cycle. Similarly, a range from 1000 – 25 Ω was used and each resistance was set for two batch cycles to ensure accurate bacterial acclimation to the given condition [28]. However, it was shown in another that one full cycle at each fixed external resistance was adequate for producing accurate polarization curves [36].

One downfall to using the multiple-cycle method is that it is system dependent, and since it requires a longer time to complete, there is a risk of shifts in the bacterial community over time that may change the measured power results. This is especially of concern in systems using complex substrates (i.e.: wastewaters), as there is a possibility for changes in bacteria with each new introduction of a wastewater sample. In these instances, single-cycle polarization curves should be used if they can be produced without power overshoot present. Otherwise, multiple-cycle polarization curves should be used, paying special attention to the overall cell performance.
and electrode potentials to identify any changes. Further research should be done to identify a method for producing accurate, reliable polarization curves using complex substrates.
Chapter 3

Materials and Methods

3.1 MFC construction and operation

MFCs were constructed from a solid block of Lexan drilled to contain a cylindrical chamber, 2 cm in length and 3 cm in diameter (14 mL empty bed volume). Two types of reactor configurations were used in these experiments. The standard setup referred to the anode and cathode placed on opposite ends of the reactor, while the membrane electrode assembly referred to the anode and cathode placed on the same end of the reactor with a separator material between them. The anode materials used were carbon mesh (projected surface area 7 cm$^2$; Gaojieshi Graphite Products Co. Ltd., Fujian, China) and graphite fiber brushes (15 mm diameter by 25 mm length; fiber type PANEX 33 160K, ZOLTEK). Each anode was heat treated for 30 minutes at 450°C before use [36]. In order to minimize fraying, tape was placed around the exterior of the carbon mesh anodes before they were cut out for use in MFC reactors.

Two types of separator materials were used in the MEA: glass fiber mat (GF) and pulp separator laminated with glass fiber mat (pg) (Specialty Glass Products, NSG Co., Ltd.). NSG Co. provided various manufactured thicknesses of glass fiber mat (gf), ranging from 0.6 mm (basis weight= 84 g/m$^2$; $\rho$=0.14 g/cm$^3$) to 1.2 mm (basis weight= 150 g/m$^2$; $\rho$=0.13 g/cm$^3$). The PG separator had a thickness of 2.4 mm (basis weight = 290 g/m$^2$; $\rho$=0.24 g/cm$^3$). In certain tests, multiple layers of separator materials were used. Separator materials were replaced during experimentation, as noted, when it was anticipated that their deterioration was contributing to decreased power and voltage generation.

Startup procedures varied based on the reactor configuration. Both standard and MEA setups used domestic wastewater as an inoculum. However, a biofilm would not form on the 2 cm
mesh anodes when started up in the MEA configuration. When this was observed, reactors were started up with the standard 4 cm MFC electrode spacing. To accomplish this, 2-2 cm reactor bodies were connected in the middle using a rubber gasket to prevent leakage; and, the anode and cathode were placed on opposite ends of the reactor. This method was used to minimize disruption of the anode biofilm during the transformation into a 2 cm MEA setup. Once stable bacterial activity was detected, the 2 cm reactor body was removed and a separator and cathode were placed on the outside of the existing anode to produce a 2 cm reactor MEA configuration.

3.1.1 Reactor Configuration Abbreviations

The reactor configurations used for experimentation use 2 cm reactor bodies and activated carbon cathodes and will be referred to by the abbreviations defined in Table 3-1. Figure 3-1 and Figure 3-2 show schematics and photographs of these setups.

Table 3-1: Reactor configuration abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Anode</th>
<th>Separator</th>
<th>Additional Diffusion Layer(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-GF1</td>
<td>brush</td>
<td>1.2 mm glass fiber (GF)</td>
<td>none</td>
</tr>
<tr>
<td>B-GF2</td>
<td>brush</td>
<td>2.4 mm glass fiber</td>
<td>none</td>
</tr>
<tr>
<td>M-GF1</td>
<td>mesh</td>
<td>1.2 mm glass fiber</td>
<td>none</td>
</tr>
<tr>
<td>M-GF2</td>
<td>mesh</td>
<td>2.4 mm glass fiber</td>
<td>none</td>
</tr>
<tr>
<td>GF2</td>
<td>mesh</td>
<td>2.4 mm glass fiber</td>
<td>none</td>
</tr>
<tr>
<td>PG</td>
<td>mesh</td>
<td>2.4 mm pulp laminated glass fiber (PG)</td>
<td>none</td>
</tr>
<tr>
<td>PS-PG</td>
<td>mesh</td>
<td>2.4 mm pulp laminated glass fiber</td>
<td>1 PDMS</td>
</tr>
<tr>
<td>PL-PG</td>
<td>mesh</td>
<td>2.4 mm pulp laminated glass fiber</td>
<td>Multiple PDMS</td>
</tr>
<tr>
<td>G1-PG</td>
<td>mesh</td>
<td>2.4 mm pulp laminated glass fiber</td>
<td>1 generic cling wrap</td>
</tr>
<tr>
<td>G2-PG</td>
<td>mesh</td>
<td>2.4 mm pulp laminated glass fiber</td>
<td>2 generic cling wrap</td>
</tr>
<tr>
<td>B-PG</td>
<td>brush</td>
<td>2.4 mm pulp laminated glass fiber</td>
<td>none</td>
</tr>
</tbody>
</table>
Figure 3-1: Membrane electrode assembly reactor configurations with carbon mesh anodes: M-GF1 or M-GF2 (A, C) and brush anodes: B-GF1 or B-GF2 (B, D). (A) and (B) are chemical processes schematics; (C) and (D) are construction progression photographs, with a scale of 1.0:2.5 cm.
Figure 3-2: Membrane electrode assembly reactor configurations with PDMS diffusion layers: PL-PG or PS-PG (A) and with generic cling wrap diffusion layers: G1-PG or G2-PG (B, C). (A) and (B) are chemical processes schematics; (C) is a construction progression photograph, with a scale of 1.0:1.8 cm.

3.2 Cathodes

Activated carbon (AC) air cathodes were made by VITO, a company in Mol, Belgium. The cathodes were built around a nickel (Ni) mesh current collector (#53 mesh, 330 μm opening, 150 μm wire diameter, 7 cm² projected surface area) with a 70-90 weight% activated carbon mixture with a PTFE binder pressed onto the solution side. The air side of the AC cathode had a PTFE diffusion layer loading of 1 kg/m² and 70% porosity, unless otherwise noted, with a final
cathode thickness of 0.45 mm [23]. Cathodes were replaced and the biofilm on the cathode was removed, using a razor blade and rinsing, randomly during experimentation, as it was anticipated that the biofilm was causing a decrease in power and voltage generation.

Two different diffusion layers, PDMS or generic cling wrap, were added to the AC cathodes, as noted. PDMS was made using a 10:1 mixture of SYLGARD 184 silicone elastomer base and SYLGARD 184 silicone elastomer curing agent. This mixture was diluted to various weight percents (wt%) using toluene to decrease the solution viscosity, which allowed for consistent layers to be applied to each cathode via an airbrush sprayer (Paasche Airbrush Company, VL1007). After applying each layer, cathodes were air dried. Initially, the cathodes were dried for 1 hour and then heated at 80°C for 30 minutes to cure the polymer. However, during testing of the cathodes before use in MFCs it was seen that bubbles formed in the multiple PDMS layers which were applied to the cathodes used in the PS-PG setup. It was assumed that this physical change was due to incomplete curing of the PDMS mixture after spraying. Therefore, a longer dry cure time was allotted (24 hours) followed by 30 minutes heat curing at 80°C, which resolved the issue and provided stable PDMS layer properties. This procedure was used for the cathodes in the PL-PG setup, which had only 1 applied layer of PDMS. Alternately, generic cling wrap (distributed by Target Corporation, which is comparable to Glad® Cling Wrap), was placed on the exterior of the air side of the AC cathodes to act as an additional oxygen diffusion layer. The cling wrap diffusion layers were attached between the reactor body and the gasket which lies inside the reactor end plate.

3.3 Inoculation and feed solution

Domestic wastewater collected from the primary clarifier effluent at the Pennsylvania State University wastewater treatment plant was used as both an inoculum and feed solution for
the duration of the reactor lifetime. No additional buffer, vitamins, or minerals were added to the wastewater. The wastewater samples were kept in a 4°C constant temperature, and a new sample was collected approximately every 2 weeks. A pH probe (Mettler Toledo Seven Multi; Model: pH; S/N: 290843) and conductivity probe (Mettler Toledo Seven Multi; Model: Cond.; S/N: 291048) were used to record wastewater properties.

COD readings were obtained using standard methods for examining wastewater [Method 5220, APHA et al. 1995; High range (0-1500 mg/L) HACH COD system (Hach Co., Loveland, CO)] [9, 12].

The three-day headspace BOD (HBOD₃) test was chosen as the BOD testing measure for the wastewater samples [22]. It was conducted by placing 10 mL of wastewater in 28 mL test tubes (triplicate samples) and with air sample controls in the same 28 mL test tubes (duplicate). The tubes were sealed with crimp tops to prevent gas leakage and incubated at 20°C in a constant temperature room. On day 3 of the HBOD₃ test, a gastight syringe (250_1; Hamilton Samplelock Syringe) was used to sample the headspace of the wastewater and air (control) sample tubes. A gas chromatograph (GC) (model 2610B; SRI Instruments) was then used, as previously described, to analyze the headspace [38]. Using environmental initial conditions (at day 0) and the oxygen peaks from the GC analysis, HBOD₃ was calculated using Equation 4.

\[
HBOD_3 = \left( P_0 - 0.01p_{0,w}r_0 \right) \left( 1 - \frac{A_3}{A_{0,3}} \right) \left[ \frac{107.2}{T_0 + 273.15} \left( \frac{V_T}{V_L} - 1 \right) + \frac{DO}{760 - p_{0,w}} \right]
\]

Eq. 4

Where, \( P_0 \) is the air pressure at day 0 [mmHg], \( p_{0,w} \) is the vapor pressure of water at temperature of sample on day 0 [mmHg], \( r_0 \) is the relative humidity of air on day 0 [%], \( A_3 \) is the oxygen peak area of sample on day 3 [mV-s], \( A_{0,3} \) is the oxygen peak area of air control [mV-s], \( T_0 \) is the temperature of air on day 0 [°C], \( DO \) is the dissolved oxygen concentration in water at temperature \( T_0 \) [mg/L], \( V_T \) is the total volume of an empty test tube [mL], and \( V_L \) is the volume of sample placed in the test tube [mL]. Three-day headspace biochemical oxygen demand (HBOD₃)
values are assumed to be equivalent to five-day biochemical oxygen demand (BOD₅) values based on previous tests at this wastewater treatment plant [39] and were measured for 30% of the wastewater samples (other samples were lost due to equipment failure or unavailability). All BOD₅ calculations were estimated assuming a COD: BOD₅ ratio equal to two, based on typical values [40].

3.4 Experimental conditions

Experiments were conducted in duplicate in a constant temperature room (30°C). The inoculation procedure consisted of filling the reactor body with wastewater daily until bacteria in the wastewater colonized the electrode and began to produce electricity (approximately 3 to 5 days). The MFC was then operated in fed-batch mode, with the MFC refilled when the voltage dropped below 30 mV (1000 Ω external resistance), except as noted.

3.5 Calculations and measurements

Voltages were measured every 20 minute using a data acquisition system (Model 2700, Keithley Instrument). Polarization curves were produced by two different methods: single-cycle and multiple-cycle. The single-cycle power curves were produced by changing the external resistance every 20 minutes, beginning with open circuit (infinite Ω) and reducing stepwise to 200 Ω. This method was originally used, until extreme power overshoot was identified, at which time the multiple-cycle method was used. The multiple-cycle power curves were done using a complete fed-batch cycle for each resistance, in order to allow the bacteria to acclimate to the given resistance. The range of resistances remained the same as that used in the single-cycle method. Current, \( I \) [mA], was calculated according to Eq. 2, where \( V \) is the voltage [mV] and \( R \) is
the external resistance [$\Omega$]. Power, $P$ [mW], was calculated according to Eq. 1 with the appropriate unit conversions. Current density [mA/cm$^2$] and power density [mW/m$^2$] were determined by normalizing by the cross sectional area of the cathode, $A$ [cm$^2$] and applying appropriate unit conversions. Internal resistance was determined from the power density curves, where the maximum power density was achieved when the external and internal resistances ($R_{int}$) were equal. Therefore, using Eq. 3 at the maximum power density, $R_{int}$ was calculated for the various reactor configurations.

COD removal ($\Delta$COD) [%], was calculated according to Equation 5.

$$\Delta COD = \left( \frac{COD_{in} - COD_{out}}{COD_{in}} \right) \times 100$$

Eq. 5

Coulombic efficiency, $CE$ [%] was computed using Equation 6.

$$CE = 8\int_0^{t_b} I \cdot dt / F \cdot v_{an} \cdot \Delta COD$$

Eq. 6

Where, $t_b$ is single-cycle time (sec), $F$ is Faraday’s constant (95,485 C/mol), $v_{an}$ is the volume of the anode compartment (14 cm$^3$), and $\Delta COD$ is the difference between $COD_{influent}$ and $COD_{effluent}$ [mg/L].

Anode potentials were measured using reference electrodes (RE-5B; BASi, West Lafayette, IN) placed centrally in solution in the reactor configurations. Cathode potentials were not measured directly; they were computed using measured whole cell and anode potentials. All potentials were reported with respect to a Ag/AgCl reference electrode [25].

In order to determine the mass transfer coefficient for each cathode prior to its use in an MFC, dissolved oxygen (DO) measurements were taken over time and used to calculate the rate of transfer. DO measurements were done under constantly stirred conditions in a 4 cm cube reactor using distilled water medium and a fiber optic dissolved oxygen probe (FOXY oxygen probe, SF2000, Ocean Optics, Dunedin, FL). A two-point calibration was used, with each point corresponding to an oxygen concentration of 0 mg/L (DI water with sodium thiosulfate) and 7.44
mg/L (aerated DI water). Electrode spacing for all DO tests was 4 cm, with the probe located halfway between the cathode and anode (approximately 2 cm distance from each). Prior to beginning each test, the reactor was filled with distilled water in an anaerobic glove box to ensure an initial oxygen concentration of 0 mg/L within the reactor. Each oxygen probe test was conducted for at least 3 hours (in duplicate), with oxygen concentration readings collected every 1 second by Ocean Optics OOI Sensors data acquisition software. In order to determine the mass transfer coefficient, \( k \) [cm/s], the flux equation was integrated and solved in terms of \( k \) [41], resulting in Equation 7.

\[
k = \frac{-v_{an}}{A \cdot t} \ln \left( \frac{C_s - C}{C_s} \right)
\]

Eq. 7

Where \( v_{an} \) in this case is 28 mL, \( t \) is the time [sec], \( C_s \) is the bulk oxygen concentration in solution (7.63 mg/L), and \( C \) is the measured oxygen concentration at the electrode over time [mg/L]. The graph of oxygen concentration vs. time showed a linear increase and therefore constant slope over the first approximately 3000 points, before the values began to plateau. It was determined that the most consistent slope of the linear region of the plot occurred between time points 1100 and 2100 seconds, and therefore this was the range used for calculating \( k \), which is equal to the slope of the linear portion of the graph. Extended calculations can be seen in Appendix B.
4.1 Performance of anode materials over time

4.1.1 Voltage generation

The MFCs with brush anodes maintained stable voltage generation over time, averaging 350 ± 35 mV (B-GF1) and 370 ± 35 mV (B-GF2). There were significant changes in the maximum voltage achieved during each feed cycle for the mesh anode configurations. The maximum voltages achieved by the mesh reactors were 260 mV (M-GF1) and 370 mV (M-GF2), while the average voltages over the 100 days of operation were only 87 ± 63 mV (M-GF1) and 200 ± 82 mV (M-GF2). After only 20 days of operation, the voltage generation for M-GF1 dropped below 200 mV, where it stayed for the remainder of the experiment. Separators and cathodes were replaced when it was anticipated that material deterioration was contributing to a decrease in voltage generation. Sudden increases in the voltages of the mesh reactors were attributed to these replacements (Figure 4-1).
Figure 4-1: Voltage profile for membrane electrode assembly reactor configurations, where “voltage” refers to the maximum voltage achieved during each feed cycle. A brush or mesh anode is denoted by “B” or “M” and a glass fiber (GF) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.

4.1.2 Power density curves

After one month of operation, maximum power densities of 240 ± 22 mW/m² (B-GF2) and 220 ± 1.2 mW/m² (B-GF1) were produced. Configuration M-GF2 produced a similar power density at 230 ± 3.3 mW/m², while M-GF1 achieved considerably lower power generation at 80 ± 9.6 mW/m². M-GF1 consistently generated the lowest power over the length of the experiment. Over time the performance of both M-GF1 and M-GF2 significantly decreased. After four months of operation, the maximum power production from M-GF2 diminished to 45 ± 12 mW/m², similar to that of M-GF1 at that time (42 ± 15 mW/m²). After four months, the power density of
B-GF1 also decreased to $130 \pm 55$ mW/m$^2$, while the power density of B-GF2 remained at $230 \pm 9.3$ mW/m$^2$ (Figure 4-2).
Figure 4-2: Power density curves for membrane electrode assembly reactor configurations at day 13 (A.) and at day 102 (B.). A brush or mesh anode is denoted by “B” or “M” and a glass fiber (GF) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.

4.1.3 Electrode potentials

The electrode potentials show the influence of each electrode on the overall whole cell potential. One concern was that anode potentials remain balanced; too low or high of an anode potential could have reduced voltage and power production. In these experiments, anode and whole cell potentials were measured, and cathode potentials were calculated based on those values.

The anode potential in M-GF1 was nearly 0 mV vs. Ag/AgCl at day 54 and -85 mV vs. Ag/AgCl at day 86, showing that the low whole cell potential was due to poor anode performance throughout the experiments. M-GF2 showed opposite trends from what were expected. The anode potential became slightly more positive over time, which led to a decrease in cathode and whole cell potentials. This may have been a direct correlation to a failing biofilm community. The anode potentials of B-GF1 and B-GF2 became increasingly negative with time, indicating a more mature, secure biofilm, which also correlated to a higher whole cell potential (Figure 4-3). The potentials of the brush anode configurations further reinforced their stability and ability to produce consistent results over a long period of time.
Figure 4-3: Electrode potentials for membrane electrode assembly reactor configurations at two time points, where WC represents “Whole Cell”, C represents “Cathode”, and A represents “Anode” potentials. A brush or mesh anode is denoted by “B” or “M” and a glass fiber (GF) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.

4.2 Performance of carbon mesh anode MFCs with additional cathode diffusion layers

4.2.1 Voltage generation

There was a direct relationship between the number of diffusion layers and increased voltage. The G2-PG configuration had the lowest $k$-value, and therefore the least oxygen diffusion, with an average voltage of $310 \pm 52$ mV. The control (PG) produced an average
voltage of only 180 ± 65 mV. The correlation between additional DLs and increased voltages was evident in the remaining reactors, which produced average voltages of 280 ± 62 mV (PS-PG), 250 ± 53 mV (G1-PG), and 210 ± 59 mV (PL-PG) (Figure 4-4). The outliers are assumed to be attributed to differences in wastewater samples.

Figure 4-4: Voltage profile for membrane electrode assembly reactor configurations with additional diffusion layers, where “voltage” refers to the maximum voltage achieved during each feed cycle. A pulp laminated glass fiber (PG) or glass fiber (GF) separator was used with a generic cling wrap or PDMS diffusion layer as denoted by “G” or “P”. PG and GF2 are controls with no additional DLs.
4.2.2 Power density curves

Maximum power density values followed the same trend as voltage; the reactors with additional diffusion layers outperformed the controls that had no additional DLs (GF2 and PG). The two MFCs with the least oxygen permeable cathodes reached comparable maximum power densities of 150 ± 22 mW/m² (G2-PG) and 140 ± 6.4 mW/m² (PS-PG). The remaining setups followed the trend, producing maximum power densities of 110 ± 14 mW/m² (G1-PG), 70 ± 31 mW/m² (PL-PG), 46 ± 2.4 mW/m² (PG), and 44 mW/m² (GF2). Power overshoot was evident in the single-cycle polarization curves (Figure 4-5A), so multiple-cycle curves (Figure 4-5B) were performed to attempt to overcome this phenomenon. The multiple-cycle polarization curve method was successful in delaying the onset of power overshoot, although it did not entirely prevent it. Power overshoot was observed during the multiple-cycle method in reactors G1-PG, G2-PG, and GF2, but not until the final applied R_{ext} (200 Ω). In both cases, increasing the diffusion layers increased the power production, but never produced power comparable to that of the original mesh MEA configuration (M-GF2: 230 mW/m²).
Figure 4-5: Power density curves for membrane electrode assembly reactor configurations with additional diffusion layers using (A.) single-cycle and (B.) multiple-cycle polarization methods. A pulp laminated glass fiber (PG) or glass fiber (GF) separator was used.
with a generic cling wrap or PDMS diffusion layer (DL) as denoted by “G” or “P”. PG and GF2 are controls with no additional DLs.

4.2.3 Electrode potentials

The anode and whole cell potentials were measured for the two highest performance MEA reactors with additional diffusion layers (G2-PG and PS-PG) during each external resistance (R_{ext}) of the multiple-cycle power density curve (Figure 4-6). The brush control anode potentials (B-PG) remained consistent despite the R_{ext} changes; however, the average anode potentials of the reactors with additional DLs fluctuated greatly, especially during tests with lower resistances. The generic cling wrap DL reactor (G2-PG) had more negative anode potentials than the PDMS DL reactor (PS-PG) for all R_{ext} except for 700 Ω. All of the anode potentials, except the brush control, converged at an R_{ext} of 500 Ω (PG: -37 mV vs. Ag/AgCl, PS-PG: -76 ± 91 mV vs. Ag/AgCl, G2-PG: -94 ± 89 mV vs. Ag/AgCl) suggesting that the more positive anode potentials caused the low whole cell potentials at low resistances, and contributed to the presence of power overshoot. The corresponding power density curves can be found in Appendix D (Figure D-6).
Figure 4-6: Electrode potentials for membrane electrode assembly reactor configurations with additional diffusion layers at various $R_{ext}$: (A) anode potentials, and (B) whole cell potentials. A pulp laminated glass fiber (PG) separator was used and a brush or mesh anode was
denoted by “B” or no specification. Generic cling wrap or PDMS diffusion layers were used as denoted by “G2” or “PS”.

4.3 Coulombic efficiency (CE) and COD removal (ΔCOD)

4.3.1 CE

The CE (%) for all four configurations peaked during the first month of operation; the maximum values were 22 ± 0.37% (M-GF2), 8.2 ± 0.14% (M-GF1), 10 ± 1.1% (B-GF1), and 13 ± 2.9% (B-GF2). After the first month of operation, the CE achieved by B-GF1 and B-GF2 remained slightly higher (average values: 5.6% and 7.2%) than that of M-GF1 and M-GF2 (average values: 1.8% and 4.6%) (Figure 4-7).

![Graph](attachment:image.png)

Figure 4-7: CE for membrane electrode assembly reactor configurations over time. A brush or mesh anode is denoted by “B” or “M” and a glass fiber (GF) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.
The addition of DLs produced higher CE values relative to the control reactors. At day 34, there was a direct correlation between the number of diffusion layers and an increase in CE. After this time the generic cling wrap DL reactors (G1-PG and G2-PG) outperformed the PDMS DL reactors (PS-PG and PL-PG). The correlation between number of diffusion layers and increased CE was seen on day 34, where CEs of 15 ± 2.6% (G2-PG), 12 ± 2.6% (PS-PG), 11 ± 1.3% (G1-PG), and 11 ± 1.3% (PL-PG) were achieved. The ability of reactors with generic cling wrap DLs (G1-PG and G2-PG) to produce higher CEs than reactors with PDMS DLs (PS-PG and PL-PG) was supported by the average CE values over time, which were 12 ± 4.3% (G2-PG), 9.1 ± 2.0% (G1-PG), 7.6 ± 4.9% (PS-PG) and 7.3 ± 4.5% (PL-PG) (Figure 4-8).

Figure 4-8: CE for membrane electrode assembly reactor configurations with additional diffusion layers over time. A pulp laminated glass fiber (PG) or glass fiber (GF) separator was used with a generic cling wrap or PDMS diffusion layer as denoted by “G” or “P”. PG and GF2 are controls with no additional DLs.
CE values were also determined at each applied external resistance during the multiple-cycle polarization curve method. At external resistances of 500 Ω, 300 Ω, and 200 Ω, CE values diminished to < 5%, as whole cell potentials simultaneously declined, suggesting that the biofilm was not able to generate current at these low resistances. However, at 700 Ω, the reactors with additional diffusion layers performed similarly or better than the mesh and brush controls (PG: 6.6%, B-PG: 4.5 ± 0.06%, PS-PG: 6.6 ± 2.8%, G2-PG: 8.3 ± 1.5%) (Figure 4-9).

Figure 4-9: CE for membrane electrode assembly reactor configurations with additional diffusion layers at varied external resistances, where “1k after” refers to the time point when the reactor had been returned to an $R_{ext}$ of 1k Ω for three feed-cycles. A pulp laminated glass fiber (PG) separator was used and a brush or mesh anode was denoted by “B” or no specification. Generic cling wrap or PDMS diffusion layers were used as denoted by “G2” or “PS”.
4.3.2 ΔCOD

The COD removals achieved in the carbon mesh MFCs (M-GF1 and M-GF2) were significantly lower than those in the brush MFCs (B-GF1 and B-GF2) (Figure 4-10). After 21 days, while brush and mesh reactor voltage and power generation were still relatively similar (excluding M-GF1), mesh anode reactors produced lower ΔCOD values (M-GF1: 58 ± 0.3 mg/L; M-GF2: 59 ± 3.1 mg/L), while brush anode reactors had improved ΔCOD values (B-GF1: 83 ± 0.1 mg/L; B-GF2: 82 ± 6.8 mg/L). However, after 144 days, the ΔCOD values for the mesh reactors had recovered to 89% (M-GF1) and 91% (M-GF2). COD readings were not done at this time for B-GF1 and B-GF2. Therefore, the reason for this increase is not known.

Figure 4-10: COD removal for membrane electrode assembly reactor configurations over time. A brush or mesh anode is denoted by “B” or “M” and a glass fiber (GF) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.
An increase in the number of diffusion layers also increased the maximum COD removal achieved by each reactor over the lifetime of the study. Reactor configuration G2-PG reached a maximum ΔCOD value of 99%, while the remaining reactors achieved maximum COD removals of 94% (PS-PG), 91% (G1-PG), and 89% (PL-PG) (Figure 4-11). These measurements reinforced the idea that increasing the number of DLs increased the performance of the reactor, as seen in the other tests. However, the ΔCOD test revealed that the control reactors reached higher ΔCODs (PG: 93 ±1.9%; GF2: 90%) than reactors with additional DLs (G1-PG and PS-PG). There was no consistent correlation over time between the amount of oxygen diffusion through the cathode and the corresponding ΔCOD.

Figure 4-11: COD removal for membrane electrode assembly reactor configurations with additional diffusion layers over time. A pulp laminated glass fiber (PG) or glass fiber (GF) separator was used with a generic cling wrap or PDMS diffusion layer as denoted by “G” or “P”. PG and GF2 are controls with no additional DLs.
COD removal was measured at each of the external resistances used during the multiple-cycle polarization curve method over a single fed-batch cycle. Slight declines in ΔCOD were noticed at R\textsubscript{ext} of 300 Ω. However, large drops in ΔCOD were evident when R\textsubscript{ext} was reduced to 200 Ω, at which time all reactors except the brush control produced much lower ΔCODs (PG: 29%, PS-PG: 48 ± 5.7%, G2-PG: 51 ± 16%). ΔCOD values recovered after the polarization curve was finished and an R\textsubscript{ext} of 1k Ω was reinstated. No clear trends were noted throughout this test (Figure 4-12).

**Figure 4-12**: COD removal for membrane electrode assembly reactor configurations with additional diffusion layers at varied external resistances, where “1k after” refers to the time point when the reactor had been returned to an R\textsubscript{ext} of 1k Ω for three feed-cycles. A pulp laminated glass fiber (PG) separator was used and a brush or mesh anode was denoted by “B” or no specification. Generic cling wrap or PDMS diffusion layers were used as denoted by “G2” or “PS”.
4.4 Performance of different substrates

4.4.1 Wastewater properties

Wastewater properties varied seasonally in regards to flowrate, organic content, and ionic strength. Specifically, flowrates to the PSU wastewater treatment plant decreased during the summer months, spring break, and Christmas holiday due to a reduction in the number of people in town. These decreases were not only attributed to the reduction in number of students contributing to campus flow during these times, but also a decline in flow from the borough, suggesting a reduction in the non-student population of State College, as well (Figure 4-13).

![Figure 4-13: Penn State wastewater treatment plant monthly flow rates over 1 year [1].](image-url)
4.4.1.1 pH and conductivity

The average pH for PSU domestic wastewater effluent over an approximately 18 month period was 7.5 ± 0.4 (n = 28), with a maximum value of 8.1 and a minimum of 6.7. The PSU wastewater treatment plant primary clarifier effluent conductivity ranged from 1310 to 1820 mS/cm², with an average of 1494 ± 150 (n = 28) (Figure 4-14). These low conductivities directly affected the internal resistances experienced by each of the reactor setups (Table 4-1). No evident correlation was made between the changes in flowrates, pH, and conductivity for the wastewater samples.

Figure 4-14: Domestic wastewater, from PSU primary clarifier, properties: pH and conductivity.
COD and HBOD measurements varied over time with different wastewater samples. The average measured HBOD₃ value was 200 ± 40 mg/L. The calculated average COD reading over time was 410 ± 45 mg/L. The typical ratio of COD: BOD₅ is 2 [39] and the COD: HBOD₃ ratio determined here was 2.03 ± 0.2 [40] (Figure 4-15). The fact that this calculated COD:BOD₅ ratio is close to 2 suggests that the assumption that the HBOD₃ was approximately equal to the BOD₅ was valid.
Figure 4-15: Domestic wastewater, from PSU primary clarifier, properties over time: three-day headspace biochemical oxygen demand (HBOD₃) and chemical oxygen demand (COD) refer to the primary y-axis; COD:HBOD₃ and COD:BOD₅ ratios refer to the secondary y-axis, where * denotes an accepted value.

The effluent BOD₅ values for each reactor configuration were determined based on the typical value for COD:BOD₅ (2.0) found in the literature [40]. The effluent BOD₅ ranged from 24.2 mg/L to 79.9 mg/L depending upon the reactor configuration (Table 4-2). EPA guidelines require secondary wastewater treatment to remove 85% of the BOD₅ content in the wastewater [42]. For the samples tested here, that would result in an average effluent BOD₅ concentration of 29.3 mg/L. The two reactors with the least oxygen diffusion through the cathode (G2-PG and PS-PG) were the only configurations that met this effluent requirement.
Table 4-2: Wastewater effluent COD and BOD₅ values

<table>
<thead>
<tr>
<th>reactor configuration</th>
<th>Avg delta COD (%)</th>
<th>effluent COD (mg/L)</th>
<th>effluent BOD₅ (mg/L)</th>
</tr>
</thead>
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<tr>
<td>M-GF1</td>
<td>70.3</td>
<td>115.8</td>
<td>57.9</td>
</tr>
<tr>
<td>M-GF2</td>
<td>58.4</td>
<td>162.2</td>
<td>81.1</td>
</tr>
<tr>
<td>B-GF1</td>
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<td>33.7</td>
</tr>
<tr>
<td>B-GF2</td>
<td>80.2</td>
<td>77.2</td>
<td>38.6</td>
</tr>
<tr>
<td>GF2</td>
<td>82.1</td>
<td>69.8</td>
<td>34.9</td>
</tr>
<tr>
<td>PG</td>
<td>84.9</td>
<td>58.9</td>
<td>29.4</td>
</tr>
<tr>
<td>PS-PG</td>
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<td>57.7</td>
<td>28.9</td>
</tr>
<tr>
<td>PL-PG</td>
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</tr>
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<td>G2-PG</td>
<td>87.4</td>
<td>49.1</td>
<td>24.6</td>
</tr>
</tbody>
</table>

4.5 Performance of acetate-fed reactors

Many MFCs were evaluated using acetate as a substrate, which commonly consisted of 1g/L sodium acetate (NaAc) in 50 mM phosphate buffer solution (PBS). The average COD value of NaAc is 780 mg/L; and the average conductivity is 6900 μS/cm. It is assumed, based on the typical COD: BOD₅ ratio of 2 that this COD value would correlate to a BOD₅ value of 390 mg/L. The high organic loading and ionic strength of acetate at this concentration contributed to more ideal performance of MFCs fed 1 g/L acetate substrate. Fang Zhang (unpublished data, this laboratory) performed MEA setup acetate-fed reactors, which achieved much higher maximum power values (Mesh anode: 960 mW/m²; Brush anode: 1300 mW/m²) than wastewater-fed reactors (Figure 4-16).
Figure 4-16: Power density curves for membrane electrode assembly reactor configurations with activated carbon cathodes, and either carbon mesh or brush anodes with glass fiber separators (0.9, 1.2 or 2.4 mm, as specified in legend), fed sodium acetate (NaAc) or domestic wastewater (WW).
Chapter 5

Discussion

5.1 Performance of anode materials

The use of brush anodes in MFCs provided a quicker startup time and more reliable performance over an extended period of time than mesh anodes. Brush anodes provided a large surface area for bacterial adhesion, and thus the opportunity for a well-established bacterial community. The mesh anodes had less available surface area for bacterial adhesion and more opportunity for oxygen contamination of the anode due to the mesh anode being entirely pressed up against the separator in the MEA configuration. On the other hand, the brush anode had the opportunity for some of the fibers to be in solution, away from the separator, thus providing a more ideal location with less oxygen intrusion to the bacterial community.

The poor performance achieved from the mesh M-GF1 MFC was likely due to the rapid deterioration of the glass fiber separator material. Separator replacements were made when voltage began to drop to try to improve the performance of the MFCs. During the replacements in the mesh anode MFCs, much of the perimeter of the glass fiber separators had disintegrated, allowing for contact of the electrodes and short circuiting. There was also distinct biofilm growth on the removed separator, although the extent to which this may have affected power production is not known. Similar material replacements were made in the brush configurations even though these MFCs had consistent voltage generation (indicating stable reactor performance) in order to be able to directly compare results of the brush and mesh anode performances in MFCs. As expected, the new materials had no effect on reactor voltage demonstrating that material
deterioration did not affect the voltage generation in the brush setups in the same way as the mesh setups.

The large drop in power and voltage generation that occurred with the mesh anode reactor with the thin (1.2 mm) separator (M-GF1) did not also occur with the brush anode reactor (B-GF1) with the same separator. While some of the brush fibers were pressed up against (and potentially through) the separator, most of the brush fibers were located away from the separator in solution in the B-GF1 reactor. In the mesh anode configuration (M-GF1), the entire anode was pressed flat against the separator. Therefore, it was assumed that short circuiting occurred in the mesh anode reactor (M-GF1) but not in the brush anode reactor (B-GF1). There is a possibility that some short circuiting occurred in the brush anode reactors, but there were no visible declines in the voltage or power generation. This is further evidence that brush anodes were more stable than mesh anodes for use in the MEA.

The low current densities shown in the power density curves (Figure 4-2) suggested the occurrence of an unstable anode biofilm. The single-cycle power density curves from the brush reactors (B-GF1 and B-GF2) showed that much lower current densities could be produced on day 102 compared to day 13 (Figure 4-2). This decrease in current density indicated that the biofilm was producing fewer electrons, and may have implied a failing biofilm. It was assumed that power overshoot occurred because the bacteria were not given enough time to adapt to new conditions and power doubled back to previous currents. The evidence of this phenomenon was present in all four reactor configurations, and the different current densities which were achieved when using brush anodes versus mesh anodes were attributed to different bacterial communities on each anode. However, much lower power outputs were achieved by the mesh anode reactors (M-GF1 and M-GF2) relative to the brush anode reactors (B-GF1 and B-GF2), suggesting either the enriching of non-exoelectrogenic bacteria or an unhealthy biofilm. In later tests, the presence of power overshoot was minimized by using the multiple-cycle power density curves.
Over time, the performance of both mesh anode reactors (M-GF1 and M-GF2) deteriorated, with M-GF2 power densities and voltages falling to match those of M-GF1. The extremely low (near zero) anode potential in the M-GF1 MFC accounted for the low whole cell potential (Figure 4-3). The M-GF2 MFC had increasingly more positive anode potentials, which corresponded to decreased whole cell voltages over time. However, the anode potentials of both brush reactors (B-GF1 and B-GF2) became more negative over time, verifying their increased cell voltages, and thus, stability, over time.

5.2 Performance of carbon mesh anode MFCs with additional cathode diffusion layers

As hypothesized, additional diffusion layers resulted in higher voltage generation and power production, relative to the control reactors. The direct correlation between diffusion layers and higher performance suggested that minimizing oxygen diffusion through the cathode helped keep the anode anaerobic and thus increased performance of the reactor. However, the reactors with additional DLs and their controls underperformed compared to the original MEA reactor (M-GF2), with an identical setup. The differences in performance were attributed to different inocula and wastewater feed sources throughout experimentation.

The multiple-cycle polarization curves for the MEA reactors with additional DLs produced some unusual shapes of the curves, different than the “typical” polarization curve (shaped comparably to an upside-down parabola). At an $R_{\text{ext}}$ of 700 $\Omega$, the polarization curves for three of the four MEA reactor setups with additional DLs (PL-PG, G1-PG, G2-PG) converged on each other rather than continuing outward to produce a “typical” curve (Figure 4-5B). Some suggested reasons are: the failure of the biofilm to adapt to an external resistance lower than that which it had previously been exposed to (1000 $\Omega$); the possibility of a low organic loading wastewater sample; and the rate of oxygen diffusion through the cathode being slowed (by four
orders of magnitude) due to the liquid accumulation between the generic cling wrap DLs. The unusual curve shapes were most likely caused by the inability of the biofilms to adjust to resistances lower than those at which they were originally acclimated (< 1000 Ω). The multiple-cycle curves show that it is difficult to produce polarization curves without power overshoot using MEA configuration reactors and a wastewater feed source.

5.3 CE and ΔCOD

Brush anodes consistently produced higher CEs than mesh anodes over time, although the maximum CE was achieved by the mesh anode reactor configuration M-GF2 (22 ± 0.37%). CE is dependent on current and COD of a given sample. Therefore, low CE values were expected in the MEAs because of the generation of low current densities (< 0.12 mA/cm²) recorded in the polarization curves. In all experiments, after approximately one month of operation, the CE values became consistent, which indicated a mature biofilm acclimated to its environment.

One likely cause of the low CEs was an excess of oxygen in solution which created an aerobic environment at the anode. Excess oxygen leakage through the cathode to the anode may have caused “competitive electron scavenging” leading to aerobic respiration, which would have provided the bacteria alternative to reducing the anode, and resulted in low CEs [13]. This theory was supported with the addition of diffusion layers positively influencing the CE. The reactors with additional diffusion layers achieved higher CE values relative to the controls without additional DLs. Specifically, the generic cling wrap DL reactors produced higher CEs than the PDMS DL reactors, suggesting that the PDMS may have hindered the reduction reaction at the cathode. However, the maximum CE previously achieved (M-GF2: 22 ± 0.37%) was not able to be reproduced by any of the reactors containing additional DLs. Overall, the CE values achieved
by MEA configurations fed wastewater were low (<25%), even when utilizing additional
diffusion layers.

COD removal values were consistently higher with brush anodes relative to mesh anodes,
which was most likely a result of a more stable biofilm forming on the anode. The COD removal
remained high over time with the addition of cathodic diffusion layers, suggesting that the
addition of DLs neither positively nor negatively influenced the ability of the anodic biofilms to
oxidize organic material (Figure 4-11). The low COD removals for the G2-PG MFC (Figure 4-
12) were likely due to the visible accumulation of liquid between the diffusion layers of one of
the duplicate MFCs. The bubbles would slow the rate of reduction at the cathode because of
excess oxygen blockage and prevention of water evaporation out of the reactor. However, the
formation of bubbles in the generic cling wrap DLs was not consistent, and sometimes the
bubbles were not evident at all, suggesting an incomplete seal of the DL over the cathode. Due to
the inconsistency, the effect of the cling wrap on cell performance could not be determined.

There are a number of possibilities that could explain the increase in ΔCOD which
occurred at day 120 in the mesh reactors. These include: a change in bacterial community, a
change in wastewater sample, or acclimation of the biofilm to the anode. The increase in ΔCOD
at day 120 in mesh anode reactors (M-GF1 and M-GF2) happened with simultaneously constant
CE values. Therefore, it is possible that the bacterial community changed from a predominantly
exoelectrogenic population to other microorganisms that utilized the food source but did not
produce current. This would have produced high ΔCOD values, while not necessarily recovering
the electrons as current, thus lowering the CE. This bacterial shift may have been caused by
excess oxygen leakage through the cathode to the anode, which allowed for aerobic bacterial
communities to take over in place of exoelectrogens. The ΔCOD may also have been a result of a
change in the composition of the wastewater sample; a higher influent COD could have led to a
higher COD removal rate. Finally, further acclimation of bacteria to the carbon mesh anode may
also have caused the increased ΔCOD, though this is unlikely given the amount of time that had already passed.

The formation of a cathodic biofilm, which was evident in many of the MEA configurations upon dismantling the reactors, could also have influenced the CE and bacterial communities. These biofilms provided an oxygen barrier and, over time, this additional blockage of oxygen may have contributed to the higher CE values. The biofilm may also have caused a change in the bacterial community on the anode because of the blocked oxygen and the presence of another biofilm in solution, or hindered proton transfer to the cathode. It is unknown what effect this biofilm had exactly, but assumed that it influenced the performance of the reactors.

5.4 Performance of acetate-fed reactors

Acetate-fed reactors produced higher power densities than wastewater-fed reactors using both brush and mesh anodes. The maximum power densities achieved with acetate-fed MEA reactors using either mesh or brush anodes were both over 4 times higher than those of wastewater-fed reactors (Figure 4-16). Since these reactors are identical except for the feed, the solution characteristics and the substrate concentration and biodegradability are producing the different outcomes. The low conductivity of wastewater caused high solution resistance. Although the close electrode spacing used in the MEA configuration helped minimize the effect of solution resistance, wastewater fed reactors still had higher solution resistances than acetate fed reactors. This was partially due to the low solution conductivity of wastewater that correlated to high solution resistance, and thus allowed for less transfer of electrons through solution than with acetate. In MFCs, the use of high ionic strength solutions resulted in low internal resistances in reactors, which typically correlated to higher power outputs.
Another reason for the increased performance seen from acetate-fed reactors was due to the nearly double (1.93 times) organic loading to that of wastewater. This ensured an adequate amount of organic matter for the bacteria to break down, and allowed for longer cycle times between feeding. The excess organic matter in an acetate feed source produced a plateau of the maximum voltage (Figure E-3) contrary to the single peak seen in the voltage curves of wastewater fed reactors (Figure ED-1). Higher organic loadings correlated to more evident plateaus in isolated single-cycle voltage vs. time curves (Appendix E).
Chapter 6

Conclusions

Brush anode configurations were more difficult to construct than configurations with flat mesh anodes. However, it was found that brush anodes generated consistently higher voltage and power relative to the proposed carbon mesh anode. In addition, brush anode configurations achieved higher COD removal rates relative to mesh anodes as well as higher maintained CEs over time.

Diffusion layers were added in an effort to optimize the use of carbon mesh anodes for the MEA configuration. The carbon mesh anodes with additional diffusion layers outperformed the reactors with no additional diffusion layers in terms of both power and voltage generation. In addition, there was a direct correlation between CE and number of diffusion layers. However, when compared with the original setups, they did not perform better than either mesh or brush anode MEAs. This indicated that the addition of diffusion layers helped improve the performance of carbon mesh anodes, but for long term use, brush anodes offered more consistent, dependable results for use in the MEA configuration than carbon mesh anodes.
Chapter 7

Future Work

The inconsistent results which come from the use of carbon mesh anodes in MFCs leads to the need for more experimentation to idealize the use of flat anode materials. There are additional areas which could be researched to help better understand the materials used in MFCs.

1. The research of more durable, inexpensive separator materials, such as cleaning wipe materials and polymer separators, is needed to add to the understanding of the MEA configuration. Focusing on the degradability of the separator will allow for analysis of the effect of short circuiting on reactor performance and will help to determine which separator materials will be able to be used for long term application at a wastewater treatment plant.

2. Determining the point at which oxygen limitations hinder cathode performance will be important to understand the effect oxygen intrusion has on anode performance. This should be done by adding DLs onto activated carbon cathodes until the measured oxygen transfer coefficient, $k$, is approximately zero. Additional cathodes with slightly less oxygen hindrance should also be tested to find the most ideal k-value for maximizing the performance of the MFC.

3. Improved methods for measuring power density in MFCs using wastewater substrates are needed. Power overshoot is a phenomenon which skews the maximum power density values, and therefore needs to be avoided. However, using the whole cycle method, it is difficult to maintain stable reactor and substrate conditions over the length of the polarization test (approximately 7-14 days), especially for
wastewater samples. It is possible that power overshoot could be avoided in single-cycle polarization curves if the reactors were acclimated to lower resistances from the beginning. I recommend starting up reactors at resistances lower than 1000 $\Omega$ and once stable voltage is achieved, producing single-cycle polarization curves. This should reveal the effects of each initial resistance on both maximum power production and power overshoot.
Appendix A

Literature Cited

Appendix B

Oxygen transfer coefficient, k, calculations

METHOD 1: CALCULATION

Integration and solution of flux equation in terms of oxygen diffusion coefficient, k

1. \( \dot{V} \frac{dC}{dt} = JA \)

2. \( J = k(C_s - C) \)

Where: \( J = \text{flux}; V = \text{volume anode chamber (28 mL)}; k = \text{mass transfer coefficient}; C_s = \text{bulk concentration of saturated dissolved oxygen (DO) (7.63 mg/L)}; C = \text{concentration of saturated DO at electrode (2.65} \times 10^{-4} \text{ mol/L)}; \) and \( A = \text{area of cathode (7 cm}^2) \).

3. \( \dot{V} \frac{dC}{dt} = k(C_s - C)A \)

4. \( \int \frac{dC}{C_s - C} = \int \frac{KA}{V} dt \)

5. \( -\ln(C_s - C)|_0^C = \frac{kA}{V} t|_0^t \)

6. \( kt = \frac{-V}{A} \ln \left( \frac{C_s - C}{C_s} \right) \)

7. \( k = \frac{-V}{At} \ln \left( \frac{C_s - C}{C_s} \right) \)
METHOD 2: DATA ANALYSIS

Figure B-1: Example curve from oxygen probe data

1. Plot oxygen vs. time from oxygen probe data

2. Choose linear portion of plot (approximately the first 3000 points of the curve),
   where I chose points 1100-2100.
3. The slope of this linear portion of the curve is equal to the corresponding k-value.
Appendix C

Full cycle Voltage Profiles

Figure C-1: Voltage profile for 2 cm mesh anode “sandwich” setup reactor configuration
Figure C-2: Voltage profile for 2 cm brush anode “sandwich” setup reactor configuration
Figure C-3: Voltage profile for 2 cm mesh anode, activated carbon cathode with PDMS diffusion layers, “sandwich” setup reactor configuration
Figure C-4: Voltage profile for 2 cm mesh anode, activated carbon cathode with generic cling wrap diffusion layers, “sandwich” setup reactor configuration
Figure C-5: Voltage profile for 2 cm mesh anode, activated carbon cathode, “sandwich” setup reactor configurations used as controls for diffusion layer experiments.
Figure D-1: Power density curves for 2 cm mesh and brush anode “sandwich” setup reactor configurations at day 13.
Figure D-2: Power density curves for 2 cm mesh and brush anode “sandwich” setup reactor configurations at day 40.
Figure D-3: Power density curves for 2 cm mesh and brush anode “sandwich” setup reactor configurations at day 56.
Figure D-4: Power density curves for 2 cm mesh and brush anode “sandwich” setup reactor configurations at day 102.
Figure D-5: Power density curves for 2 cm mesh anode, activated carbon cathode with additional PDMS or generic cling wrap diffusion layers, “sandwich” setup reactor configurations at day 23.
Figure D-6: Redo of power density curves for 2 cm mesh anode, activated carbon cathode with additional PDMS or generic cling wrap diffusion layers, “sandwich” setup reactor configurations with brush and mesh control reactors.
Appendix E

Individual Cycles of Acetate-fed and Wastewater-fed Reactors

Figure E-1: Typical 4cm reactor wastewater fed batch cycles
Figure E-2: Typical 4cm reactor 8mM acetate fed batch cycle (similar to conductivity of wastewater)

Figure E-3: Typical 4cm reactor 50 mM acetate fed batch cycle
Figure F-1: Polarization curve for membrane electrode assembly reactor configurations at day 13.

A brush or mesh anode is denoted by “B” or “M” and a glass fiber (gf) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.
Figure F-2: Polarization curve for membrane electrode assembly reactor configurations at day 102. A brush or mesh anode is denoted by “B” or “M” and a glass fiber (gf) separator thickness of 2.4 mm or 1.2 mm is denoted by 2 or 1.
Figure F-3: Polarization curve for membrane electrode assembly reactor configurations with additional diffusion layers using single-cycle polarization methods. A pulp laminated glass fiber (PG) or glass fiber (GF2) separator was used with a generic cling wrap or PDMS diffusion layer (DL) as denoted by “G” or “P” and multiple or a single DL as denoted by 2 or 1. PG and GF2 are controls with no additional DLs.
Figure F-4: Polarization curve for membrane electrode assembly reactor configurations with additional diffusion layers using multiple-cycle polarization methods. A pulp laminated glass fiber (PG) or glass fiber (GF2) separator was used with a generic cling wrap or PDMS diffusion layer (DL) as denoted by “G” or “P” and multiple or a single DL as denoted by 2 or 1. PG and GF2 are controls with no additional DLs.