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NOVEL CATHODE MATERIALS FOR MICROBIAL FUEL CELLS

A Thesis in

Environmental Engineering

by

Fang Zhang

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The thesis of Fang Zhang 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

Michael A. Hickner
Assistant Professor of Materials Science and Engineering

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 for direct bioelectricity generation. A new and simplified approach for making cathodes for microbial fuel cells (MFCs) was developed by using metal mesh current collectors and inexpensive polymer/carbon diffusion layers (DLs). Rather than adding a current collector to a cathode material such as carbon cloth, we constructed the cathode around the metal mesh itself, thereby avoiding the need for the carbon cloth or other supporting material. Poly(dimethylsiloxane) (PDMS) was used as diffusion layer material, preventing water leakage, limiting oxygen transfer through the cathode and improving coulombic efficiency. Multiple PDMS/carbon layers were applied in order to optimize the performance of the cathode. Two PDMS/carbon layers achieved the highest maximum power density of $1610 \pm 56 \text{ mW/m}^2$ (normalized to cathode projected surface area; $47.0 \pm 1.6 \text{ W/m}^3$ based on liquid volume). The coulombic efficiency of the mesh cathodes reached more than 80%, and was much higher than the maximum of 57% obtained with carbon cloth. These findings demonstrate that cathodes can be constructed around metal mesh materials such as stainless steel, and that an inexpensive coating of PDMS can prevent water leakage and lead to improved coulombic efficiencies.

To further reduce the cost of MFC, an inexpensive activated carbon (AC) air cathode was tested as an alternative to a platinum-catalyzed electrode for oxygen reduction in a MFC. AC was cold-pressed with a polytetrafluoroethylene (PTFE) binder to form the cathode around a Ni mesh current collector. Tests with the AC cathode produced a maximum power density of 1220 mW/m^2 (normalized to cathode projected surface area; 36 W/m^3 based on liquid volume) compared to 1060 mW/m^2 obtained by Pt catalyzed carbon cloth cathode. The coulombic efficiency ranged from 15% to 55%. These findings show that AC is a cost-effective material for achieving useful rates of oxygen reduction in air cathode MFCs.

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Chapter 1

Introduction

1.1 The challenges of energy and global climate change

Abundant and economical energy is the lifeblood of modern civilizations. Our energy requirements are almost fully provided for by carbon-containing fossil sources such as oil, coal and natural gas, which have been formed during many millions of years from plant biomass. Fossil fuels have supported the industrialization and economic growth of countries during the past century. Between 1965 and 2008, the worldwide annual growth rate of primary energy consumption was more than 2% (1, 2). It is estimated that in the United States, the total primary energy consumption will grow by 14.4% from 100.1 quadrillion Btu in 2008 to 114.5 quadrillion Btu in 2035 (3). According to BP Statistical Review of World Energy, oil, coal and natural gas together account for 88% of the world's energy consumption in 2008 (2). However, fossil fuels are non-renewable resources and their availability is insufficient to meet global energy demands. As the total population keeps growing, it is clear that fossil fuels cannot indefinitely sustain a global economic growth.

While the depletion of fossil fuels will cause a shortage of primary energy resources in the long term, the release of large amounts of bound carbon as carbon dioxide and other greenhouse gases into the atmosphere is causing changes in our climate that are altering global patterns of temperature, rainfall and runoff. The Intergovernmental Panel on Climate Change (IPCC) recommends a reduction of global CO₂ emissions by more than 50% in order to stabilize the CO₂ levels in the atmosphere at 550 parts per million volume (ppmv) to curb negative climate effects. However, recent estimates show that CO₂ emissions are still increasing (2). Therefore, the

challenge to the water community is how to achieve energy sustainability of our water infrastructure while relying only on methods of energy production that are carbon neutral.

1.2 Bio-energy production from waste and wastewater

The water infrastructure in the USA requires ~3-5% of the annual electricity production, with ~1.5% of the electricity used for wastewater treatment (4). However, biomass in the wastewater is one source of renewable energy. Rather than expend energy to remove organic matter in wastewater, efforts should be made to recover energy from wastewater, effectively converting the wastewater treatment plants into power plants.

Bio-methane, bio-hydrogen, and bio-electricity production using different microbial systems and reactors draws more attention in wastewater treatment research. Anaerobic digestion for methane production is a well-known and relative mature technology. The final biogas contains 55-75% methane and 25-45% carbon dioxide (5). However, because methanogenic microorganisms have a relative high environmental sensitivity, special attention has been paid to environmental conditions of the reactors, such as temperature, pH and substrate concentration. Hydrogen is a clean, CO₂ neutral energy carrier. The fermentative production of hydrogen is one strategy of generating renewable hydrogen from biomass. However, this process has a relatively low energy recovery due to an incomplete oxidation process. Organic matter is not completely oxidized to CO₂ but to intermediate compounds, like acetic acid or lactate. Thus fermentative hydrogen production needs a subsequent process (5). Microbial fuel cells (MFCs) represent a new approach for bio-electricity generation. MFCs could be modified for other forms of bio-energy, including hydrogen and methane gases.

1.3 Microbial fuel cells for bio-electricity production

Microbial fuel cells (MFCs) are devices that use bacteria as the catalysts to oxidize organic or inorganic matter and generate current (6, 7). It has been known for nearly 100 years that bacteria can be used for electricity generation (8). However, chemical mediators were used in the early experiments, which limited the development of the MFC technology. The breakthrough in MFCs occurred in 1999 when it was recognized that mediators were not necessary. The first mediator-less MFC was developed by Kim et al (9, 10) using a Fe (III) – reducing bacterium, *Shewanella putrefaciens*. From then on, most MFC studies have focused on mediator-less systems. All the MFCs described below are mediator-less MFCs.

In an MFC system, bacteria oxidize organic or inorganic matter and release electrons to the anode and protons into the water. The released electrons flow through the circuit to the cathode, and are then accepted by a terminal electron acceptor (e.g. oxygen or ferricyanide). Those electricity-generating bacteria are termed exoelectrogens, due to their ability to directly transfer electrons exocellularly (11). Virtually any biodegradable organic matter can be used in an MFC, including volatile acids, carbohydrates, proteins, alcohols, and even relatively recalcitrant materials like cellulose. Various oxidants for cathode reduction reaction (electron acceptor) have been used in MFCs, such as oxygen, nitrate, ferricyanide, permanganate, ferric iron (12-14). Wastewater and oxygen are considered to be the most promising electron donor and acceptor as they are practical, sustainable and economical. While the energy captured from wastewater is not enough to power a city, it is large enough to run a treatment plant. Eventually MFC technology would help to achieve energy sustainability of the water infrastructure.

1.4 Objectives

The main challenges for commercializing MFCs are developing materials that are cost effective, efficient in power generation, and identifying architectures that can be used at larger scales. Maximum power densities in most high power MFCs are largely limited by cathode surface area and performance, and the price of cathode materials can account for the greatest percentage of the MFC capital costs. Thus, this thesis focuses on development of cathodes that are inexpensive, scalable, and able to produce high power.

Objective 1: Develop a new cathode structure that is built by adding a conductive coating and catalyst onto a metal mesh current collector, and by using a coating on the air-facing side that consists of an inexpensive polymer in order to reduce the cost of the diffusion layer.

Objective 2: Examine the use of an activated carbon mesh cathode which avoids the use of precious Pt catalysts.

1.5 Organization of this thesis

This thesis is organized in the chapters that follow into a literature review of the materials used in MFCs, and then two chapters that address the stated main objectives.

Chapter 3 focuses on the development of a new cathode structure that integrates a metal mesh current collector, an inexpensive polymer, and a Pt catalyst so that carbon cloth or other supporting materials are no longer needed. The results of this work was summarized in a paper by Zhang F., Saito T., Cheng S., Hickner M. A., Logan B. E., titled “Microbial fuel cell cathodes with poly(dimethylsiloxane) diffusion layers constructed around stainless steel mesh current collectors”, and it was published in *Environmental Science and Technology*. Dr. Tomonori Saito

and Dr. Michael Hickner helped to prepare the polymer, and I did all the experiments, including cathode preparation and all other tests. Dr. Shaoan Cheng provided many useful suggestions and assistance throughout my experiment. I prepared the manuscript, and all the co-authors contributed to the writing of the final paper.

Chapter 4 addresses the performance of high surface area activated carbon cathode which avoids the use of precious metals such as platinum, or the use of other metal catalysts, in MFCs. The results of this work was summarized in a paper by Zhang F., Cheng S., Pant D., Bogaert G. V., Logan B. E., titled “Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell”, and published in *Electrochemistry Communications*. I did the tests on the cathodes prepared by Dr. Deepak Pant and Dr. Gilbert Van Bogaert. I also prepared the original manuscript and all the co-authors contributed to the revision and final writing.

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Chapter 2

Literature Review

Microbial fuel cells (MFCs) represent a new approach for bio-electricity production (1-4). One of the most promising applications of MFCs is wastewater treatment, as organic matter can be removed while at the same time producing power. In an MFC, bacteria growing on the anode oxidize organic matter and release electrons to the anode and protons into the solution (Figure 2.1). Scale-up is an important issue for the practical application of MFCs. The main challenges are developing materials that are cost-effective, efficient in power generation, and identifying architectures that can be used at large scales. This chapter will emphasize on the materials used in MFCs.

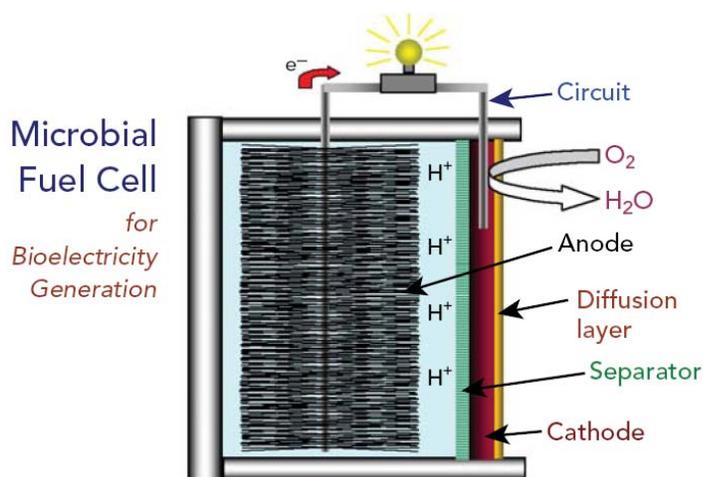


Figure 2.1: Example of an MFC where the anode is made of an electrically conductive graphite fiber brush and the cathode is carbon cloth containing a catalyst on the water-facing side to catalyze oxygen reduction (not shown) and a diffusion layer on the air side (to prevent water loss and reduce oxygen diffusion into the chamber). This MFC design contains a separator that is placed between the electrodes to insulate the cathode against contacting the anode, while allowing for charge transfer (from ref. 5).

2.1 Anode materials

The application of MFCs for wastewater treatment or bio-energy production requires the use of inexpensive anode materials that are electrochemically and biologically stable, and that have a high specific surface area and electrical conductivity. Various types of materials have been used as the anode, most of which are carbon-based materials, including carbon paper, cloth, felt or mesh (6-10); plain graphite or graphite sheets, rods, form and granules (11-14); reticulated vitreous carbon (RVC) (15); high surface area graphite fiber brush electrodes (16). The best performance of these materials depends on many factors, such as electrode spacing, solution conductivity, and substrate.

Carbon materials have high conductivity and are well suited for bacterial growth. Carbon paper is a slightly brittle while carbon cloth is more flexible and appears to have greater porosity than carbon paper. With flat carbon cloth electrodes, it has been shown that reducing electrode spacing from 4 to 2 cm increased power from 720 to 1210 mW/m² (18 to 60 W/m³) with an air cathode due to the decrease of internal resistance (6). However, carbon cloth purchased for fuel cell applications can be expensive (ca. \$1000/m²) and materials of lower cost need to be examined. RVC which has excellent conductivity has been used in the continuous upflow MFCs and the maximum power density of 170 mW/m² was produced at a current density of 516 mA/m² (15). The disadvantage of this material is that it is quite brittle. Chaudhuri et al. (8) compared current densities using a graphite rod, graphite felt and graphite foam, and found that increasing the accessible surface area increased current density. Graphite granules also have good conductivity and have been used in packed-bed reactors as both anodes and cathodes. Graphite granules, with specific surface areas of 817-2720 m²/m³ and a porosity of 0.53, were used as the anode material in a tubular packed-bed reactor, producing 48 W/m³ with acetate and 38 W/m³ with glucose (12). When this material was used for both the anode and cathode, a 6-cell stacked

MFC generated 258 W/m^3 using acetate (13). In order to make the complete bed conductive, the granules must make good electrical contact with each other. However, due to the shape of granules and the bed porosity, they can connect at only a small fraction of the total surface area. Granules are also very dense and thus must be held in containers with sufficient structural strength, and the medium could clog due to relatively low porosities.

A graphite fiber brush electrode was developed for scaling up MFCs that used a twisted core titanium wire as the current collector. Graphite brush electrodes are constructed using graphite fibers having small diameters and thus can have an extremely high surface area. Testing of the small brush anode in a cubic MFC produced a power of 2400 mW/m^2 (normalized to cathode projected surface area, 73 W/m^3 based on liquid volume) with an air cathode at a current density of 0.82 mA/cm^2 in a 200 mM phosphate buffer (16). One limitation of the brush architecture is that the minimum electrode spacing is constrained by the brush size. Recently a flat carbon mesh material was investigated by Wang et al. (9) with different pretreatment methods and heat-treatment was found to be an effective pretreatment to remove the contaminants that interfered with charge transfer. Power generated by heat-treatment carbon mesh anode was only 7% lower than that achieved with ammonia treated carbon cloth. The advantage of carbon mesh is that it is very inexpensive, but the weave of the carbon mesh has so far been too loose to prevent water leakage when used as a cathode.

2.2 Cathode materials

The design of the cathode is the single greatest challenge for making an MFC a useful and scalable technology (1). The same materials that have been described for anodes have also been used as cathodes. Thus different types of carbon and graphite materials have been used commonly as cathode materials in different studies. Various oxidants have been used as the

electron acceptor in MFCs, whose reduction reactions occur at the cathodes, such as oxygen (17), ferricyanide (12, 13), permanganate (18), and nitrate (19). The cathode materials and architectures depend on the properties of electron acceptors. In this part, I will focus on air-cathodes where oxygen is the terminal electron acceptor, as these types of electrodes will ultimately be the type of cathodes used in larger systems due to the availability and sustainability of oxygen.

Carbon cloth or paper is the most common cathode material used for air-cathode MFCs. There are commercially available carbon cloth or paper materials with pre-loaded platinum (Pt) catalyst on one side. However, one can make electrodes that will perform better than commercially manufactured electrodes with the same Pt loading. A catalyst paste can be made from commercially available Pt (10 wt% Pt/C, E-TEK) which is mixed with chemical binder such as 5% Nafion solution (7 μL binder per mg-Pt/C catalyst) and then air dried for 24 hours at room temperature. Cheng et al. (20) found that varying the Pt content from 0.1-2 mg/cm^2 did not appreciably affect power densities in air-cathode MFCs. When the Pt loading on cathode was reduced from 0.5 mg/cm^2 to 0.1 mg/cm^2 , the maximum power density of MFC was reduced on average by 19% (Nafion binder, flat carbon cloth anode). Plain carbon cloth cathode without catalyst produced power of 93 mW/m^2 , which was 73% lower than that obtained with Pt (0.1 mg/cm^2 , Nafion binder). In order to decrease water loss and increase coulombic efficiency (CE, recovery of electrons as current from substrate), a hydrophobic polytetrafluoroethylene (PTFE) diffusion layer was added to the air-side of the cathode. Four PTFE diffusion layers (DLs) had the highest power of 538 mW/m^2 , and more DLs decreased the power due to insufficient oxygen transfer through the DL (21). While carbon cathodes with Pt are effective in producing power, they are expensive and would have a prohibitive cost for large scale applications. For example, carbon cloth, as mentioned before, is ca. $\$1000/\text{m}^2$ for fuel cell grade; and Pt costs $\$700/\text{m}^2$.

Alternatives of lower cost to carbon cloth such as membranes and canvas cloth have been tested (22-24). Based on a tubular architecture, Zuo et al. (23) tested an ultrafiltration (UF) membrane coated with a conductive graphite paint and a non-precious metal catalyst (CoTMPP), and produced power density of 17.7 W/m^3 . However, the UF membrane caused a large increase in internal resistance, resulting in this relatively lower power density. Flat cation, anion exchange membranes (AEM, CEM), and UF membranes using the same coating were tested later (24). The highest maximum power of 449 mW/m^2 was produced by an AEM cathode due to the lower internal resistance of AEM membrane. Zhuang et al. (22) used canvas cloth coated with Ni or graphite based conductive paint and another non-precious catalyst MnO_2 , and made it into tubular reactor of 170 mL (empty volume). Ni paint was found to be better than graphite paint and produced power density of 9.87 W/m^3 . This cathode assembly costs only 5% of the membrane cathodes. One drawback of these systems is that the supporting materials are non-conductive and power is limited by the conductivity of cathode supporting materials. To solve this problem, stainless steel mesh was used as a current collector which was pressed against the conductive paint of AEM membrane and increased the power by 28% with a 38% reduction of internal resistance (24).

The studies above also investigated non-precious metal catalysts to replace Pt. Non-precious metal catalysts have been studied and some of them have achieved equal or better performance compared to the Pt-based carbon cathodes. Zhao et al. (25) tested two different transition metal catalysts, iron(II) phthalocyanine (FePc) and cobalt tetramethoxyphenylporphyrin (CoTMPP). In electrochemical tests, both of them showed comparable or better capabilities than Pt-based cathodes at current densities above 0.2 mA/cm^2 . At higher current densities, CoTMPP performed slightly better than FePc. Yu et al. (26) examined different metal TMPP and metal Pc with different carbon support. They showed that catalyst activity could be improved by using a carbon support with a higher surface area (e.g. Ketjenblack carbon). With FePc on Ketjenblack

carbon as cathode catalyst, a power density of 634 mW/m^2 was achieved in a 50 mM phosphate buffer at $\text{pH } 7$, which was higher than that obtained using the Pt cathode (593 mW/m^2) under the same conditions. Cheng et al. (20) also reported that replacing Pt with CoTMPP improved cathode performance when the current density was above 0.6 mA/cm^2 . Fed-batch MFC tests showed that using CoTMPP (0.6 mg/cm^2) produced a maximum power of 369 mW/m^2 , which is 9% higher than that with Pt loading of 0.1 mg/cm^2 . Using CoTMPP loading of 1.2 mg/cm^2 with graphite brush anode produced power of 2400 mW/m^2 in a 200 mM phosphate buffer which is the highest power achieved in an air-cathode system (16).

The activity of a catalyst is often assessed by comparing current or power densities to those with plain electrodes of the same surface area. However, by significantly increasing the cathode surface area, it is possible to decrease the oxygen reduction over-potential and substantially increase the performance of plain cathodes (27, 28). Freguia et al. (28) used plain granular graphite which had nanoscale pores and thus high surface area as cathode and produced power of 50 W/m^3 (normalized to cathode liquid volume) or 21 W/m^3 (cathode total volume) in a continuous MFC fed with acetate. Non-catalyzed graphite plates were used in another research to treat acidogenic wastewater (27).

A binder is needed when applying the catalyst to the supporting material in order to bind the catalyst particles to the surface. Nafion is the most widely used binder material due to its high proton conductivity and oxygen permeability, but it is quite expensive ($\$1000/\text{m}^2$). PTFE suspension has been tested as binder materials in MFC and produced less power (360 mW/m^2) than cathodes with Nafion binder (480 mW/m^2) (20). However, cathodes with PTFE binder showed better long time stability than those with Nafion binder. Recently, poly(phenylsulfone) (Radel) sulfonated to various ion exchange capacities (IEC) were tested as a new binder material for air-cathode MFC. It is found that unsulfonated Radel had the most stable performance during more than 20 cycles and eventually had the comparable performance with Nafion binder (29).

2.3 Membranes and separators

Membranes are often used as separators between anode and cathode chambers in two-chamber MFCs with dissolved oxygen or ferricyanide as the electron acceptors. The use of membranes in MFCs increases CE but also increases internal resistance that decreases power production (12, 23, 24, 30-32). When a proton exchange membrane (Nafion) was hot-pressed to a carbon cloth air-cathode, the CE increased from 9–12% to 40–50%, but power was reduced from 12.5 to 6.6 W/m³ (17). Therefore, membranes are not necessary for air-cathode MFCs that are for high power production. Kim et al. showed that Nafion did not affect the internal resistance of the reactor when placed in between the electrodes instead of being hot-welded to the electrode (31).

In order to decrease the internal resistance and increase power output, a separator is usually needed to minimize the space between anode and cathode. An ideal separator material should have a high proton permeability to ensure that the material does not inhibit proton transfer to the cathode, a low oxygen transfer coefficient to improve CE, and be relatively non-biodegradable. Fan et al. (10) sandwiched a material called J-cloth between anode and cathode in an air-cathode MFC which significantly decreased the internal resistance due to the decreased electrode spacing, and thus increased the power up to 627 W/m³ in fed-batch mode and 1010 W/m³ in continuous flow mode. However, this separator material is not biologically stable. Recently, Zhang et al. (32) compared performances of different separators including glass fiber, J-cloth, and CEM. Glass fiber was found to be a better material compared to J-cloth and CEM. With glass fiber thickness of 1.0 mm, two sets of cathode assembly increased power density from 150 W/m³ to 696 W/m³ by reducing the electrode spacing from 2 cm to 0.3 cm.

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Chapter 3

Microbial fuel cell cathodes with poly(dimethylsiloxane) diffusion layers constructed around stainless steel mesh current collectors¹

Abstract

A new and simplified approach for making cathodes for microbial fuel cells (MFCs) was developed by using metal mesh current collectors and inexpensive polymer/carbon diffusion layers (DLs). Rather than adding a current collector to a cathode material such as carbon cloth, we constructed the cathode around the metal mesh itself, thereby avoiding the need for the carbon cloth or other supporting material. A base layer of poly(dimethylsiloxane) (PDMS) and carbon black was applied to the air-side of a stainless steel mesh, and Pt on carbon black with Nafion binder was applied to the solution-side as catalyst for oxygen reduction. The PDMS prevented water leakage and functioned as a DL by limiting oxygen transfer through the cathode and improving coulombic efficiency. PDMS is hydrophobic, stable, and less expensive than other DL materials, such as PTFE, that are commonly applied to air cathodes. Multiple PDMS/carbon layers were applied in order to optimize the performance of the cathode. Two PDMS/carbon layers achieved the highest maximum power density of $1610 \pm 56 \text{ mW/m}^2$ (normalized to cathode projected surface area; $47.0 \pm 1.6 \text{ W/m}^3$ based on liquid volume). This power output was

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comparable to the best result of $1635 \pm 62 \text{ mW/m}^2$ obtained using carbon cloth with three PDMS/carbon layers and a Pt catalyst. The coulombic efficiency of the mesh cathodes reached more than 80%, and was much higher than the maximum of 57% obtained with carbon cloth. These findings demonstrate that cathodes can be constructed around metal mesh materials such as stainless steel, and that an inexpensive coating of PDMS can prevent water leakage and lead to improved coulombic efficiencies.

3.1 Introduction

A microbial fuel cell (MFC) is a novel technology that can be used for direct bioelectricity generation (1-6). One of the most promising applications for MFCs is wastewater treatment, as organic matter can be removed while at the same time producing power (1-3). Various oxidants have been used as the electron acceptor at the cathode (1, 3, 7-11), but oxygen is the most promising electron acceptor for MFC applications because it is freely available, sustainable, and oxygen reduction is a well studied and widely applied reaction. Air cathode MFCs, which have cathodes exposed to air on one side and water on the other, are the most practical approach for designing MFC cathodes due to not having to aerate the water, and their ability to generate high power densities (7-9, 12).

Scale-up is an important issue for practical applications of MFCs for wastewater treatment and bio-energy production. The main challenges for commercializing scalable MFCs are developing materials that are cost effective, efficient in power generation, and identifying architectures that can be used at larger scales. Maximum power densities in most high power MFCs are largely limited by cathode surface area and performance (9, 12-13), and the price of cathode materials can account for the greatest percentage (47%) of the MFC capital costs (14). Most laboratory MFCs use small electrodes made of carbon cloth or paper or gas-permeable membranes coated with conductive paints. Carbon cloth purchased for fuel cell applications can be expensive (*ca.* \$1000/m²). Recent tests have shown very promising results for overcoming the high costs of the anode by using a very inexpensive carbon mesh (\$10-40/m²) (15). The weave of the carbon mesh is very loose, and thus we found it could not be water sealed when used as a cathode (unpublished data). Tubular cathodes can be designed to provide high surface areas needed for cathodes (13, 16-19), and tubes made of carbon cloth can provide power output similar to that of flat carbon cloth on the basis of equivalent projected surface area (13), but the

carbon cloth can be expensive. To reduce the cost of a tubular cathode, one approach has been to use a membrane as the supporting material for the application of a conductive coating and catalyst (16, 20). Power densities have so far been low with these alternative materials, for example 403 mW/m^2 using two ultrafiltration membrane tube cathodes and a flat carbon paper anode. Power was increased (450 mW/m^2) using a less expensive and flat anion exchange membrane (AEM) and a graphite fiber brush anode.

Scaling up MFCs with carbon cloth or coated membranes alone is likely not practical as the resistance of these materials becomes large as the reactor size increases. The electrical resistivity of carbon materials is relatively high which can produce high electrode ohmic losses in large-scale systems. For example the electrical resistivity of graphite is $1375 \mu\Omega \text{ cm}$, compared to only $42 \mu\Omega \text{ cm}$ for titanium (14). To avoid having large resistances, metal current collectors are often used with carbon materials to reduce the overall resistance of the cathode. In one recent approach for the MFC anode, a graphite fiber brush electrode was developed that used a twisted core titanium wire as the current collector (12). The graphite fibers provide a high surface area for bacteria, and as they are only 1.3 to 2.5 cm long in these brushes, voltage losses across the length of the fibers are small. Electrons can flow along the titanium wire which has a much lower electrical resistivity. Brushes have also been used as cathodes for sediment MFCs in natural systems, where dissolved oxygen is available in the water, but the cost for aeration in an engineered system and the low power densities typically produced by the sediment MFC architecture would likely prohibit the use of brush cathodes in wastewater treatment systems. Current collectors have been used to improve performance of MFC cathodes. For example, power was increased from 450 mW/m^2 to 575 mW/m^2 by adding a piece of stainless steel mesh to the surface of the conductive coating on an AEM cathode (20). The performance of these membrane cathodes has so far been low due to the high internal resistance of these relatively thick cathodes.

In this study, we took a different approach to making cathodes that could be useful for making either planar or tubular types of electrodes. Recognizing that a current collector will be necessary for making larger electrodes, our approach was to build the cathode around the current collector rather than mating a current collector to a preformed cathode structure. To test this concept, we examined the use of porous stainless steel mesh combined with a diffusion layer (DL) coating to prevent water leakage and control oxygen intrusion through the cathode, and a platinum (Pt) catalyst layer for oxygen reduction. We used a poly(dimethylsiloxane) (PDMS) coating to make a DL because it is inexpensive, widely available, stable under typical MFC conditions (neutral pH and ambient temperatures), oxygen permeable, and it is a viscous liquid at room temperature in its uncrosslinked state making it easy to apply the coating to the mesh surface (21). PDMS has a unique semi-organic structure, with a flexible inorganic Si-O backbone that has a very low rotation barrier and a high affinity for oxygen. As a result of its methyl substituents, PDMS liquid is highly hydrophobic and therefore provides a good water seal. In contrast, the commonly used polytetrafluoroethylene (PTFE) is insoluble in common solvents, and special processing must be employed to generate the PTFE emulsion used in DL fabrication. In order to focus on the individual properties of the mesh and DL coating, we used Pt as the catalyst for oxygen reduction, although in future studies non-precious metal catalysts such as CoTMPP and iron phthalocyanine could be used (16, 20, 22-23). We varied the amount of PDMS applied to the metal mesh to optimize cathode performance, and contrasted the performance of this mesh cathode with carbon cloth cathodes, also using PDMS coatings, under otherwise identical experimental configurations. We conducted additional electrochemical tests to examine how cathode performance was related to the different materials. To our knowledge, this is the first time that stainless steel mesh and PDMS have been used in concert to create a simple cathode MFC design.

3.2 Materials and methods

3.2.1 Cathodes

The cathodes developed here are based on integrating the current collector (stainless steel mesh, SS), catalyst (Pt), and diffusion layer (PDMS) into one single cathode structure. The SS mesh (type 304 SS, 90×90, woven wire diameter 0.0055 inches, McMaster-Carr, OH) had 90×90 openings per square inch. PDMS was made using a 10:1 mixture of SYLGARD 184 silicone elastomer base and SYLGARD 184 silicone elastomer curing agent (Dow Corning, MI), that was further diluted to 10 wt% with toluene to decrease the solution viscosity. The PDMS (6.25 mg/cm²) was applied with carbon black (1.56 mg/cm²) to the side of the SS that faced the air. After applying this first PDMS/carbon black as a base layer, additional DLs (one to four layers) containing PDMS/carbon black or only PDMS were applied on top of this base layer at the same mass loading as the original layer. After applying each layer, cathodes were air dried for 2 hours, and then heated at 80 °C for 30 min to crosslink the PDMS oligomers. After applying these DLs, a Pt catalyst layer (5 mg/cm² 10 % Pt on Vulcan XC-72 with 33.3 μL/cm² of 5 wt% Nafion as binder) was applied to the SS mesh on the side facing the solution (see ref. 22 for detailed procedures). Cathodes were also prepared with no coating on the solution-facing side of mesh, or with only a carbon black layer (both with 2 PDMS/carbon DLs on the air side) to determine if these materials had catalytic activity in the absence of Pt.

Carbon cloth (E-Tek, Type B, 30% wet proofing, BASF Fuel Cell, Inc. NJ) was also tested as a cathode supporting material. One or more DLs of PDMS/carbon and the Pt catalyst were applied as described above for the metal mesh cathode. Cathodes were also prepared using previously examined methods consisting of 4 DLs of PTFE as previously described (24).

3.2.2 MFC construction and operation

MFCs were single-chamber cubic-shaped reactors constructed as previously described (8) with an anode chamber 4 cm long and 3 cm in diameter. The anode was an ammonia gas treated graphite fiber brush (25 mm diameter \times 25 mm length; fiber type PANEX 33 160K, ZOLTEK) (12, 25). All reactors were inoculated using a solution from an MFC operated for over 1 year (initially inoculated from the effluent of the primary clarifier of the local wastewater treatment plant). The medium contained acetate as the fuel (0.5 g/L for fixed resistance tests, and 1.0 g/L for polarization tests), and a phosphate buffer nutrient solution (PBS; conductivity of 8.26 mS/cm) containing: Na_2HPO_4 , 4.58 g/L; $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ 2.45 g/L; NH_4Cl 0.31 g/L; KCl 0.13 g/L; trace minerals (12.5 mL/L) and vitamins (5 mL/L) (26). Reactors were all operated in fed-batch mode at 30 °C and were refilled each time when the voltage decreased to less than 20 mV forming one complete cycle of operation.

3.2.3 Calculations and measurements

Voltage (E) across the external resistor (1 k Ω , except as noted) in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I = E/R$), power ($P = IE$) were calculated as previously described (3), with the current density and power density normalized by the projected surface area of the cathode. To obtain the polarization and power density curves as a function of current, external circuit resistances were varied from 1000 to 50 Ω in decreasing order. Each resistor was used for a full fed-batch cycle, and the COD of the solution at the end of the cycle was measured using standard methods (27). The coulombic efficiency (CE) was calculated based on total COD removal over the cycle, as previously described (3). Water losses were measured

daily based on the change in water level in a 5 mL syringe (filled with deionized water) connected to the anode chamber by a needle that pierced a septum on the top of the reactor.

Linear sweep voltammetry (LSV) was used to assess electrochemical performance of the cathodes. Current was measured in 50 mM PBS in the absence of nutrients and exoelectrogens using a potentiostat (PC4/750, Gamry Instruments). A two chamber electrochemical cell with each chamber 2 cm in length and 3 cm in diameter separated by an anion exchange membrane (AMI-7001, Membrane International Inc., NJ) was used for measurements, consisting of a working electrode (cathode with 7 cm² projected surface area), counter electrode (Pt plate with a projected surface area of 2 cm²), and an Ag/AgCl reference electrode (RE-5B; BASi, West Lafayette, IN). The scan rate was 1 mV/s, and potential was scanned from +0.5 V to 0 V (versus standard hydrogen electrode).

Oxygen permeability was measured in terms of oxygen transfer coefficient as previously described (24). The 4-cm cubical reactor used in MFC tests was used for oxygen transport measurements. Dissolved oxygen concentrations were measured using a non-consumptive dissolved oxygen probe (FOXY, Ocean Optics, Inc., Dunedin, FL).

3.3 Results

3.3.1 Performance of SS mesh cathodes in MFCs compared with carbon cloth cathodes

MFCs with SS mesh or carbon cloth cathodes and a Pt catalyst rapidly produced voltage after inoculation, and generated stable voltages at a fixed resistance. Differences in voltage among these reactors at a high external resistance of 1 k Ω were small, although in general the SS mesh produced higher voltages than the carbon cloth cathodes. The largest maximum voltage that was produced over a total of 14 batch cycles of operation was of 602 ± 5 mV (\pm S.D., n=14

cycles) obtained using the SS mesh cathode with 2 PDMS/carbon layers (Figure 3.1). The highest value of carbon cloth cathodes was 585 ± 4 mV for MFCs with 4 PDMS/carbon layers.

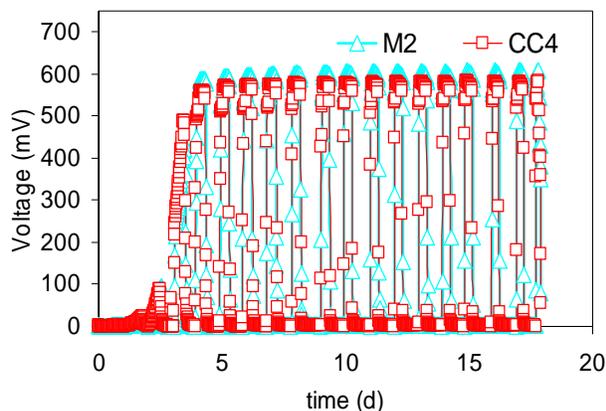


Figure 3.1: Voltage generation of SS mesh cathode and a Pt catalyst with 2 PDMS/carbon DLs (M2) and carbon cloth cathodes with 4 DLs (CC4) versus time, with 50mM PBS buffer and 0.5g/L sodium acetate. (Best two cases among each group in voltage generation)

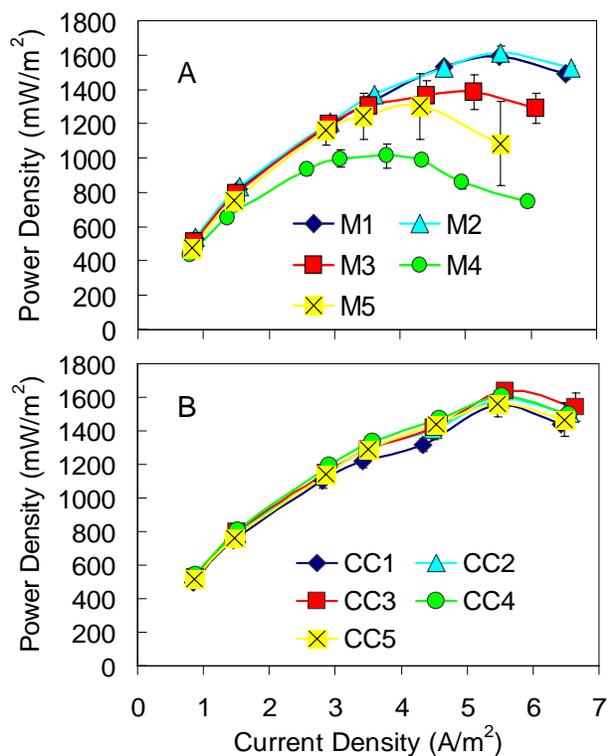


Figure 3.2: Power density of (A) SS mesh with Pt catalyst and 1-5 layers of PDMS/carbon DLs (M1-M5) and (B) carbon cloth cathodes with Pt and the same DLs (CC1-CC5) as a function of

current density (normalized to cathode surface area) obtained by varying the external circuit resistance (1000-50 Ω). (Error bars \pm SD based on measurement of two duplicate reactors.)

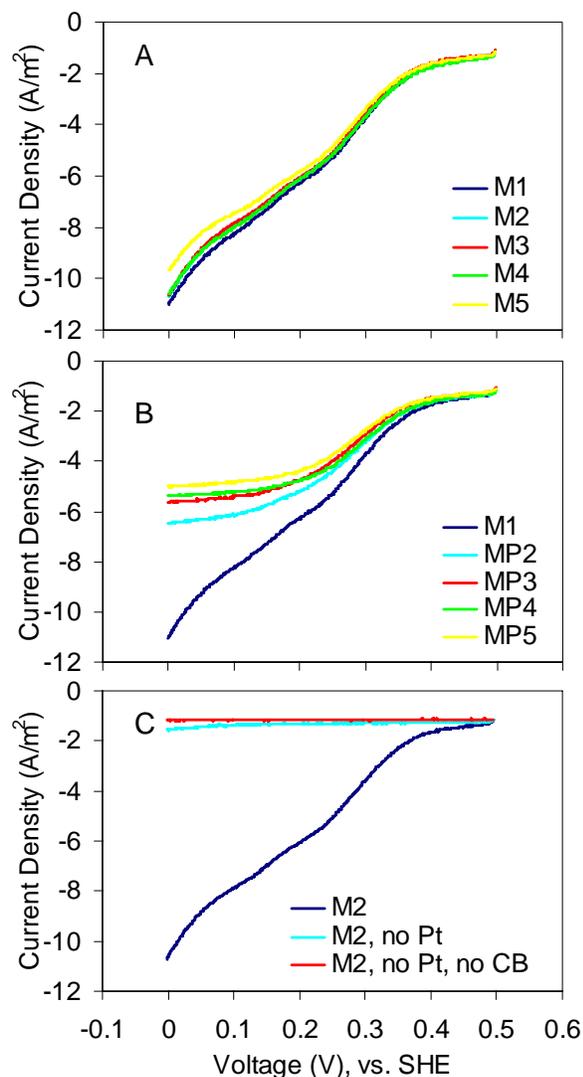


Figure 3.3: LSV of SS mesh cathodes (A) with a Pt catalyst and 1-5 PDMS/carbon DLs (M1-M5) (B) M1 compared with ones with additional PDMS layers (MP2-MP5), both with Pt catalyst. (C) M2 compared with the one with only carbon black (M2, no Pt), and one with no coating on the solution-facing side (M2, no Pt, no CB).

Large differences in power production were observed based on polarization data. The largest maximum power density using a SS mesh cathode of 1610 ± 56 mW/m² (\pm S.D. for duplicate reactors) was achieved with 2 PDMS/carbon layers. This power was similar to that

produced with a single layer ($1592 \pm 19 \text{ mW/m}^2$), but three or more layers decreased performance to as little as 1010 mW/m^2 (Figure 3.2A). Maximum power densities produced using carbon cloth cathodes with PDMS/carbon layers varied over a smaller range of $1553 \pm 19 \text{ mW/m}^2$ (1 DL) to $1635 \pm 62 \text{ mW/m}^2$ (3 DLs) (Figure 3.2B). Thus, there was much less of an effect of the number of layers on power generation with the carbon cloth material than with the SS mesh.

3.3.2 Performance of SS mesh cathodes in electrochemical tests

LSV tests were conducted using SS mesh cathodes to evaluate the electrochemical performance of the cathodes in the absence of bacteria. All voltammograms with the SS mesh cathodes containing a Pt catalyst and 1-5 PDMS/carbon layers had similar current densities at a given applied voltage (Figure 3.3A). The cathode that had the largest current response had only 1 PDMS/carbon base layer. Current densities with the SS mesh cathodes with 2-4 layers had only slightly reduced activities compared to the single PDMS/carbon base layer. This small decrease suggests that the different performance of the SS mesh cathodes with a different number of DLs in MFC tests was not due to their oxygen reduction kinetics, but rather other effects such as development of a cathode biofilm (22, 28) or oxygen intrusion through the DLs and the effects on the bacteria in the anode chamber.

Voltammograms were also conducted using the SS mesh containing only PDMS (no carbon black) applied to the PDMS/carbon base layer. These cathodes with one to four additional PDMS layers showed poorer electrochemical performance, and had a much wider variation in electrochemical performance, than the SS cathodes with both PDMS and carbon (Figure 3.3B). With only PDMS, electrochemical performance decreased with the additional layers. This decrease indicates that the carbon black material is needed with PDMS to ensure good electrochemical performance. When cathodes with 2 PDMS/carbon DLs were examined using

LSV that had only carbon black on the side of the SS mesh facing solution (no Pt), there was little current over the range of voltages examined (Figure 3.3C). In addition, cathodes prepared without carbon black or Pt were similarly ineffective at oxygen reduction. These results show that the SS and carbon black did not catalyze oxygen reduction.

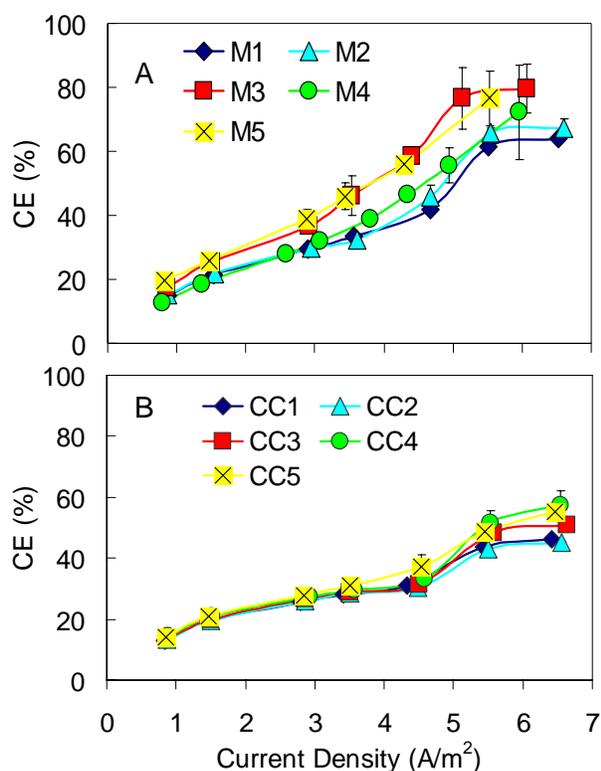


Figure 3.4: CE of (A) SS mesh with Pt catalyst and 1-5 layers of PDMS/carbon DLs (M1-M5) and (B) carbon cloth cathodes with Pt and the same DLs (CC1-CC5) as a function of current density (normalized to cathode surface area) obtained by varying the external circuit resistance (1000-50 Ω). (Error bars \pm SD based on measurement of two duplicate reactors.)

3.3.3 Coulombic efficiency and COD removal

MFC tests with SS mesh cathodes in general produced much higher CEs than those with carbon cloth cathodes (Figure 3.4). In all case, the CE increased with current density, consistent with previous results (12, 20, 24, 25). CEs of the SS mesh cathode ranged from 15% to 64% with

single PDMS/carbon base layer, and only slightly increased when adding the second layer. The highest CE of 80% was obtained when 3 DLs were applied to this cathode. In contrast, the carbon cloth cathodes CEs ranged from 13 to 46% with the first DL, with the highest value of 57% with 4 DLs. COD removals over a cycle of operation ranged from 90% to 95%, and there was no effect of the number of DLs or the type of material (SS or carbon cloth) on COD removal.

3.3.4 Oxygen permeability of the cathodes

PDMS is relatively permeable to oxygen, but increasing the number of PDMS diffusion layers should reduce oxygen transfer due to the increased thickness of the DL. With one base layer of PDMS/carbon on the SS mesh cathode, the oxygen mass transfer coefficient was $1.2 \pm 0.1 \times 10^{-3}$ cm/s. Successive application of multiple PDMS/carbon DLs decreased the oxygen mass transfer coefficient from $1.1 \pm 0.1 \times 10^{-3}$ cm/s (2 layers) to $0.7 \pm 0.1 \times 10^{-3}$ cm/s (5 layers) (Figure 3.5). Addition of only PDMS (no carbon) onto this base layer decreased the mass transfer coefficient to $0.7 \pm 0.1 \times 10^{-3}$ cm/s, with the lowest value of $0.2 \pm 0.1 \times 10^{-3}$ cm/s obtained with four pure PDMS layers. Thus, the addition of carbon with PDMS created a more oxygen permeable material than the PDMS alone. We also prepared a carbon cloth cathode with 4 PTFE layers and obtained an oxygen transfer coefficient of $1.1 \pm 0.1 \times 10^{-3}$ cm/s. This value is lower than previously reported for this procedure with these materials of $2.3 \pm 0.2 \times 10^{-3}$ cm/s (24), perhaps due to differences in batches of the carbon cloth or variations in fabrication procedures by different researchers.

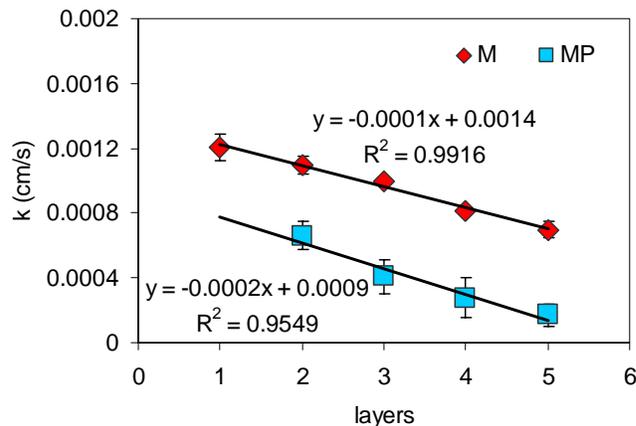


Figure 3.5: Oxygen permeability of SS mesh cathodes with PDMS/carbon DLs (M) or only PDMS DLs (MP), both with a PDMS/carbon base layer and Pt catalyst.

3.3.5 Water loss

The addition of a PDMS layer was important for controlling water loss from the cathode. SS mesh cathode with the base PDMS/carbon layer had an initial water evaporation loss of 5% of the water in the anode chamber each day. Water loss decreased with additional DLs, and was not detectable for cathodes with five DLs. For carbon cloth cathodes, the water loss was larger, decreasing from 10% loss per day with one DL, to 5% loss per day with five DLs. However, as a biofilm developed on the cathodes after several cycles, water loss gradually decreased for both SS and carbon cloth cathodes by *ca.* 20-30%.

3.4 Discussion

Building a cathode from SS mesh is an effective method for creating a cathode that can achieve performance similar to that obtained with carbon cloth electrodes. PDMS mixed with carbon black proved to be effective at reducing water losses and allowing oxygen transfer to the cathode catalyst. The best performance obtained here was with a SS mesh cathode and two

PDMS/carbon layers, resulting in a maximum power density of $1610 \pm 56 \text{ mW/m}^2$ ($47.0 \pm 1.6 \text{ W/m}^3$). In comparison, the best performance with a carbon cloth cathode was $1635 \pm 62 \text{ mW/m}^2$ with three PDMS/carbon layers. The recovery of the substrate as current was also improved using SS mesh cathodes, with CEs ranging from 15-67% for the SS cathodes, compared to 14-51% for the carbon cloth cathodes for the above two cases.

Current collectors will be essential to the performance of larger-scale MFCs, and therefore the integral construction of the cathode around the mesh has substantial advances in simplicity of design and performance compared to previous studies where a current collector was added to other materials. For example, the addition of a current collector to an AEM membrane increased the power density from 450 to 575 mW/m^2 , but in both cases the power produced was substantially less than that achieved here. Although a CoTMPP catalyst was used in this previous study, it has been shown that CoTMPP at a concentration of 0.6 mg/cm^2 produces similar performance to a Pt cathode (0.5 mg/cm^2) (22). Pt was used as the catalyst here for the SS cathodes, but in the future tests should be conducted using alternative metal catalysts such as CoTMPP and iron phthalocyanine. The SS mesh was not optimized for thickness, pore size or type of stainless steel, and the SS used here (type 304) did not show any evidence of corrosion in MFC tests. Corrosion of the cathode metal is not expected as SS is cathodically protected from corrosion at these electrical potentials (29). Others have also found that SS does not corrode when used as the cathode (30, 31). The cost of the type 304 SS mesh was less than $\$50/\text{m}^2$, which is 20 times cheaper than small pieces of fuel-cell grade carbon cloth, and nearly half the price of an AEM membrane ($\$80/\text{m}^2$) based on purchase prices for small quantities (20). The cost for the SS material itself is currently less than $\$3.00/\text{kg}$ (price of Feb. 2009) (32), indicating that the raw material is very inexpensive.

PDMS was also examined here for the first time as a low cost diffusion layer coating for MFC cathodes. Both PDMS and PTFE are hydrophobic, stable polymers, except that PTFE can

be used under highly acidic conditions while PDMS cannot. However, since neutral pH conditions are used in an MFC, PDMS can be substituted for the more expensive PTFE material. We found here that PDMS provided performance comparable to that of PTFE used in previous tests. Carbon cloth with 3 PDMS/carbon DLs achieved maximum power density of 1635 ± 62 mW/m^2 in 50 mM PBS. This value is lower than that achieved by carbon cloth with 4 PTFE DLs (2400 mW/m^2 in 200 mM PBS) mainly due to the lower buffer concentration used in this work (50 mM) which resulted in lower solution conductivity compared to previous tests (12, 33). The cost of PDMS is less than \$1.00/kg, compared to \$1.00-2.00/kg for PTFE (34). It is estimated that PDMS would cost only $\$0.13/\text{m}^2$ when used on a cathode (2 DLs), adding little to the total cathode cost. Thus, the use of PDMS reduces both cathode costs and complexity of construction.

Carbon black is integral for creating a microporous hydrophobic layer that can improve oxygen transport to the Pt catalyst (24, 35). Cathodes with PDMS/carbon DLs had much higher oxygen transfer coefficients than those with PDMS alone, and thus they also had better electrochemical performance (Figure 3.3). Carbon black may also help to increase the specific surface area of cathode which can lower the current density per electrode area, and thus improve oxygen reduction by lowering the over-potential (36). Carbon black alone on the SS mesh did not appreciably catalyze oxygen reduction. The commercial price of carbon black is similar to that of PDMS (less than \$1.00/kg) (37). Because carbon black loading is only 1.56 mg/cm^2 for each layer, however, the use of the carbon black would add only $\$0.02/\text{m}^2$ to the cost of a cathode with two PDMS/carbon DLs.

The combination of SS mesh and PDMS/carbon DLs produced a structure that had an improved CE, compared to carbon cloth cathode, likely as a result of reduced oxygen transfer into the anode chamber. SS mesh cathodes had a CE as high as 80% with 3 PDMS/carbon DLs, over a current density range of $0.8 - 6.6 \text{ A/m}^2$. Carbon cloth cathodes with same DL had CEs that ranged from 13% to 57% over similar current densities. These CEs can be compared with those of

carbon cloth cathodes with 4 PTFE DLs in previous studies that had CEs ranging from 20% to 27% at current densities of 0.8-2.5 A/m² (flat carbon cloth anode) (24), and from 40% to 60% at 0.8-11 A/m² (graphite fibre brush anode) (12). A comparison of these results suggests that high CEs achieved with the SS mesh cathodes are partly due to high current densities. When the current density is increased, the cycle time is reduced, and thus the amount of oxygen that can diffuse into the reactor is substantially reduced in proportion to the cycle time. However, even in the high current density range of >5 A/m², SS mesh cathode had a higher maximum CE than other materials, likely due to the lower oxygen permeability of the mesh DL.

These experiments have shown that using SS mesh for the cathode supporting material substantially lowers the cost of the cathode, and eliminates the need for the carbon cloth material. Catalysts lacking precious metals, and cathodes that use binders that are less expensive than Nafion used here, are currently under investigation for further reducing the cost of the cathodes. The use of SS mesh has advantages over other membrane materials in that it is very flexible and thus it should be possible to make it into tubular structures that have good mechanical strength. Further development of materials in MFCs based on tubular SS mesh cathodes and graphite fiber brush anodes will be helpful in reducing the cost, and improving the performance of MFCs, so that they can be used for economical wastewater treatment and bioenergy production.

3.5 Acknowledgments

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Chapter 4

Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell²

Abstract

An inexpensive activated carbon (AC) air cathode was developed as an alternative to a platinum-catalyzed electrode for oxygen reduction in a microbial fuel cell (MFC). AC was cold-pressed with a polytetrafluoroethylene (PTFE) binder to form the cathode around a Ni mesh current collector. This cathode construction avoided the need for carbon cloth or a metal catalyst, and produced a cathode with high activity for oxygen reduction at typical MFC current densities. Tests with the AC cathode produced a maximum power density of 1220 mW/m² (normalized to cathode projected surface area; 36 W/m³ based on liquid volume) compared to 1060 mW/m² obtained by Pt catalyzed carbon cloth cathode. The coulombic efficiency ranged from 15% to 55%. These findings show that AC is a cost-effective material for achieving useful rates of oxygen reduction in air cathode MFCs.

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4.1 Introduction

A microbial fuel cell (MFC) is a novel technology for direct bioelectricity generation from biomass (1-5). Reducing the cost of the materials used in MFCs is essential for practical applications. The cathode accounts for the greatest percentage of the total capital cost (6), and cathode surface area and materials generally limit higher power production in MFCs (7-9). Therefore, identifying low-cost materials and efficient cathode architectures are important for improving cost effectiveness and performance of MFCs.

Carbon based materials are widely used as the electrode for air cathode MFCs. The high cost of some of these materials, such as carbon cloth (ca. \$1000/m²), prohibits the use of this material for large scale systems. While low cost cathodes have been made by applying conductive coatings inexpensive membranes, power densities have been relatively low (10, 11). Since a current collector will be needed to construct larger electrodes, we recently investigated an alternative approach based on constructing the cathode around the current collector by coating a stainless steel mesh with a catalyst and a film to prevent water flow through the electrode (12). This approach greatly reduced the electrode cost, but platinum was needed as a catalyst. Alternatives to Pt include CoTMPP (0.6 mg/cm² or 1.2 mg/cm²) and iron phthalocyanine (1.0 mg/cm²) (9, 13-15). Other metals such as manganese dioxide (MnO₂) can also improve cathode performance (16). While these catalysts greatly reduce the cathode costs compared to Pt, the high loading needed to equal the performance of Pt can result in high overall costs. For example, using CoTMPP at 0.6 mg/cm² (\$30/g) costs \$180/m² compared to \$140–700/m² for Pt (0.1–0.5 mg/cm², \$140/g) (11).

Promising alternatives to metal-catalyzed cathodes are biocathodes and very high surface area materials such as graphite granules and activated carbon (AC) (17-19). Biocathodes use bacteria to catalyze oxygen reduction, but so far both biocathodes and graphite granule cathodes

have been limited to systems that require aeration of the water to provide dissolved oxygen (18). Aeration is a highly energy intensive process, and should be avoided for MFCs. AC is inexpensive and is more highly porous than graphite, and it has previously been used with precious metal catalysts such as Pt and Pd in hydrogen fuel cells (20). An AC cloth air cathode was developed that used ethylenediaminetetraacetic acid (EDTA) chelated iron as a catalyst, achieving a power density of 40 W/m^3 (17). However, this system required the use of a cation exchange membrane and a sprinkler system to continuously apply a 0.7% NaCl solution over the cathode. The use of a membrane can increase system cost, and the need for wetting the cathode could complicate operation.

In this study, we examined the use in an MFC of a simple AC air cathode that does not require any additional metal catalysts for efficient oxygen reduction. We built the AC air cathode around a nickel (Ni) mesh current collector in order to allow for ease in scale up to larger cathode sizes. We show that this metal mesh AC cathode is a high performance and cost-effective method for constructing MFCs.

4.2 Materials and methods

4.2.1 Electrodes

Cathodes were constructed at VITO (Belgium) by pressing at 150 bar a mixture of AC (70–90 wt%; Norit SX plus, Norit Americas Inc., TX) and polytetrafluoroethylene (PTFE) binder on top of a Ni mesh current collector (#53 mesh, 330 μm opening, 150 μm wire diameter) to form a cathode 0.45 mm thick (final weight $\sim 1 \text{ kg/m}^2$). A PTFE diffusion layer (70% porosity, 0.13 kg/m^2) was added to the air-side of the cathode, except as noted. In some cases the same cathode additionally contained a Pt/Pd catalyst. These cathodes were compared to a carbon cloth cathode

made as previously described (Pt loading of 0.5 mg/cm^2 , Nafion binder) (7, 14). Anodes were ammonia gas treated graphite fiber brushes (25 mm diameter \times 25 mm length; fiber type PANEX 33 160K, ZOLTEK) (9).

4.2.2 MFC construction and operation

MFC tests were conducted using single-chamber, cubic-shaped MFC reactors containing a cylindrical anode chamber 4-cm long and 3-cm in diameter (21). Reactors were inoculated with solution from an MFC operated for over 1 year (initially inoculated using primary clarifier effluent from a local wastewater treatment plant). The anode was placed horizontally in the cylindrical chamber with the end 1 cm from the cathode. All reactors were operated at 30°C , and fed a medium containing acetate (1.0 g/L), a phosphate buffer solution (PBS; 50 mM; Na_2HPO_4 4.58 g/L, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ 2.45 g/L, NH_4Cl 0.31 g/L, KCl 0.13 g/L; conductivity of 6.82 mS/cm), and a trace mineral (12.5 mL/L), and vitamin (5 mL/L) solution (21).

4.2.3 Calculations

Voltage (E) across the external resistor in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I = E/R$), power ($P = IE$), and coulombic efficiency (CE) were calculated as previously described (3), with the current and power normalized by the projected surface area of the cathode or the reactor volume. Power density curves were obtained by varying external circuit resistance, with a single resistor used for a full batch cycle.

Linear sweep voltammetry (LSV) was used at a scan rate of 1.0 mV/s to evaluate the electrochemical performance of the cathodes as previously described (12). Energy dispersive X-

ray spectroscopy (EDS) was performed to analyze the elemental composition at a sampling depth of up to 1–2 μm . Plain AC cathodes and AC cathodes with Pt/Pd were analyzed by EDS at 20 kV (Quanta 200, FEI, OR).

4.3 Results and discussion

4.3.1 MFC performance

Plain AC cathodes produced a maximum power density of $1220 \pm 46 \text{ mW/m}^2$ with a PTFE diffusion layer, and $1150 \pm 57 \text{ mW/m}^2$ without a diffusion layer (Figure 4.1A). In addition to a lower power density, the AC cathode lacking the PTFE layer also exhibited more erratic performance, as shown by high standard deviations for values obtained in duplicate tests (Figure 4.1A). For comparison with cathodes previously used in this reactor, a maximum power density of 1060 mW/m^2 was produced using a carbon cloth cathode with Pt (0.5 mg/cm^2). Power production was increased by only 16% (1415 mW/m^2) by adding a Pt/Pd catalyst, compared to much large increases observed for carbon cloth with Pt (14).

The open circuit cathode potential of the AC cathode with a PTFE diffusion layer was 430 mV, and decreased from 222 mV at a current density of 0.7 A/m^2 (1000Ω) to -34 mV at a current density of 6.9 A/m^2 (50Ω). CE increased from 15% to 55% with increasing current density (Figure 4.1B).

During initial MFC tests, we observed appreciable water losses based on the development of a headspace in the anode chamber. We therefore pierced the septum on the top of the reactor with a needle connected to a 5 mL syringe containing deionized water, and measured daily water losses of 10–15% of the liquid in the reactor. The inclusion of a PTFE diffusion layer did not substantially affect water losses, suggesting that water losses were due to evaporation and not

flow through the cathode. Water losses could be reduced in the future by using more dense diffusion layers.

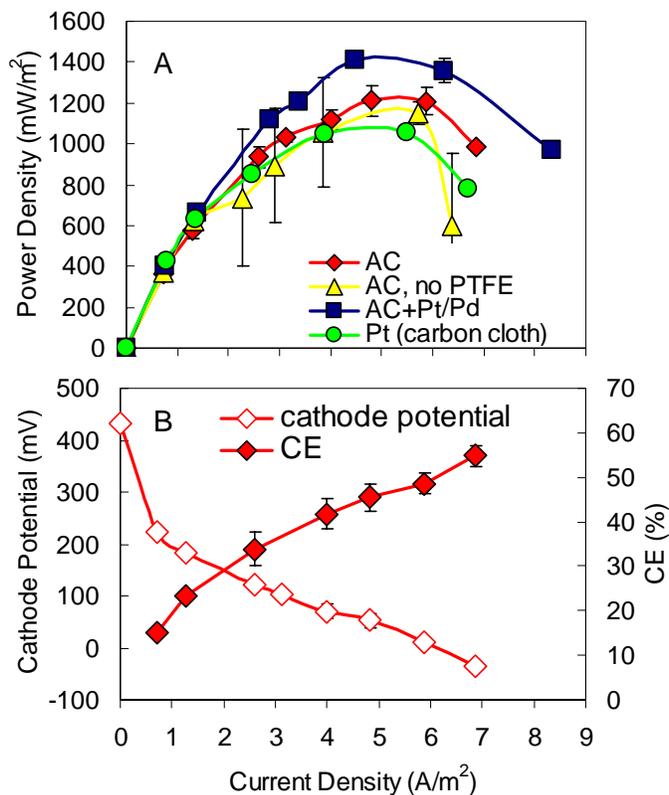


Figure 4.1: (A) Power density of plain AC and AC containing Pt/Pd cathodes with a PTFE diffusion layer, and AC without PTFE. (B) Cathode potentials and CE of plain AC and AC with PTFE (Error bars \pm SD based on measurement of two duplicate reactors or multiple tests).

4.3.2 Electrochemical performance

LSV tests were conducted to evaluate the electrochemical performance of the AC cathodes. Plain AC cathodes were compared to carbon cloth and AC cathodes containing Pt/Pd. At a current density of less than 3.9 A/m^2 , the AC cathode exhibited better electrochemical performance than Pt loaded carbon cloth cathode (Figure 4.2). Addition of Pt/Pd to the AC cathode improved performance, with the higher current densities produced at all voltages compared to the other two cathodes.

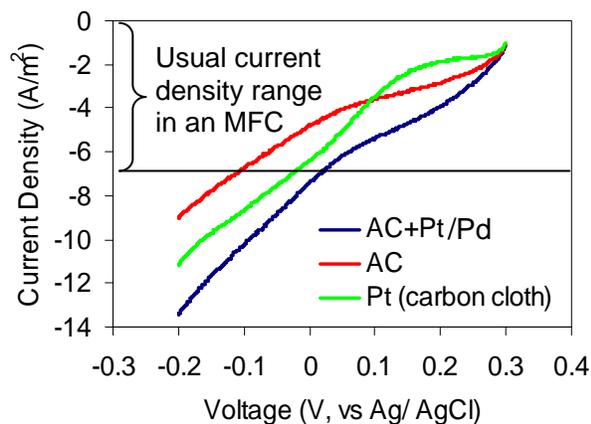


Figure 4.2: LSV of plain AC, AC with Pt/Pd and Pt catalyzed carbon cloth cathode.

4.3.3 Elemental composition

EDS analysis showed that for plain AC from cathode, carbon and fluorine were two most abundant elements, with trace amounts of calcium, iron, aluminum, and nickel (Table 4.1). The presence of fluorine was due to the use of the PTFE binder, and the Ni on the AC was likely due to the process of pressing the AC onto the Ni mesh. The acid washed AC used here should have had a low metal content. Analysis of the AC containing Pt/Pd showed that it contained at the surface 4.42% Pt and 2.52% Pd (Table 4.1). These two precious metal catalysts were responsible for the improved performance of the AC electrode.

4.3.4 Performance and cost of materials

The performance of the AC cathodes was due to the high surface area of the material, combined with the effective current collection by the Ni mesh. The PTFE diffusion layer contributed to consistent performance, although it did not sufficiently limit water losses through

the cathode. Such water losses may not be important in continuous flow systems, but in fed-batch systems this results in the development of a headspace.

Table 4.1: Elemental composition of plain AC and AC with Pt/Pd

Elements	Plain AC (%)	AC with Pt/Pd (%)
C	66.54	80.45
Si	0.24	0.44
Ca	0.04	0.04
Fe	0.15	0.14
S	0.12	-
Cl	0.05	-
Al	0.02	0.03
Ni	0.2	0.06
F	32.64	11.75
Pt	-	4.42
Pd	-	2.52
Cu	-	0.14
Na	-	0.01

The cost of the AC cathodes cannot be predicted with any certainty, but we estimate a reasonable market price to be \$50–70/m² when produced in reasonable sized batches. The price of just the AC is only *ca.* \$2.60/kg, which is sufficient to produce a 7 m² electrode. Building the cathode around the metal mesh lowers the ohmic losses of cathode, and avoids the need for other supporting materials such as membranes. The cost of the cathode can be further reduced to \$20–40/m² through using less expensive materials and minimizing the amount of metal used for the current-collecting mesh. Preliminary tests with much less expensive stainless steel mesh have shown MFC performance comparable to that of the Ni mesh (unpublished results). The fact that stainless steel can replace the Ni suggests that the Ni is not acting as an oxygen reduction catalyst. PTFE was used here as a binder and diffusion layer, but it may be possible to use less expensive materials in the future.

4.4 Conclusions

Inexpensive AC was used at cathode without any metal catalyst for oxygen reduction in an air cathode MFC. The use of this AC cathode in an MFC produced a maximum power density of 1220 mW/m^2 (36 W/m^3) compared to 1060 mW/m^2 obtained by Pt catalyzed carbon cloth cathode, and CE ranging from 15% to 55%. Thus, the use of AC and a metal mesh collector is an efficient and cost-effective method for producing an air cathode for an MFC. Further improvements in the performance of AC cathodes should be possible to limit water losses and further reduce the costs of these cathodes.

4.5 Acknowledgements

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Chapter 5

Conclusions

Cathode materials (carbon cloth, Nafion, platinum) are the most expensive components in MFC reactors. It was shown here that this is possible to substantially lower the cathode costs by avoiding the use of carbon cloth, or platinum, and an inexpensive polymer was used as the diffusion layer.

Building cathodes around stainless steel mesh current collectors is a promising method for creating a cost effective cathode that can achieve performance similar to that obtained with carbon cloth cathodes. Inexpensive PDMS polymer mixed with carbon black was shown to be effective in preventing water loss, allowing oxygen diffusion to the cathode and improving CE of the MFCs. SS mesh cathode with two PDMS/carbon layers achieved the best performance among the mesh cathodes, producing a maximum power density of $1610 \pm 56 \text{ mW/m}^2$ ($47.0 \pm 1.6 \text{ W/m}^3$) with CEs ranging from 15-67%, compared to the maximum power density of $1635 \pm 62 \text{ mW/m}^2$ with CEs ranging from 14-51% produced by carbon cloth cathodes (3 DLs). It costs only $\$50/\text{m}^2$ for SS mesh and $\$0.13/\text{m}^2$ for 2 layers of PDMS, which substantially lowers the cathode costs.

Inexpensive AC was used at cathode without any metal catalyst for oxygen reduction in an air cathode MFC. This AC cathode produced a maximum power density of 1220 mW/m^2 (36 W/m^3) compared to 1060 mW/m^2 obtained by Pt catalyzed carbon cloth cathode, with CE ranging from 15% to 55%. Thus, the use of AC and a metal mesh collector is an efficient and cost-effective method for producing an air cathode for an MFC.

Chapter 6

Future Work

This was the first study to integrate metal mesh current collectors with PDMS diffusion layers, or to use AC for oxygen reduction in MFCs. There are still challenges to be addressed for improving the performance of these cathodes.

1. The mesh size needs to be optimized for better performance. It is expected that mesh size can affect mass transfer, and also the current distribution on the cathode. However, additional investigations are needed to examine how mesh size affects the reactor performance in order to optimize the system.
2. Further improvements in the performance of AC cathodes should be possible by limiting water losses by decreasing the porosity of the PTFE diffusion layer, or using other diffusion layer materials such as PDMS. Particle sizes or type of AC and binder can be optimized to improve performance. Integration of SS mesh current collectors, PDMS diffusion layers, and AC together can help to further lower the cathode cost and produce less expensive cathodes for wastewater treatment.
3. Long term stability of these metal mesh cathodes needs to be further examined. While corrosion was not observed in short-term tests, it may be that over time there is cathode corrosion and therefore performance could be affected.
4. Oxygen reduction mechanisms using AC need to be further studied. We believe that the high surface area of AC significantly lowers the current densities, thus lowers the oxygen reduction over-potentials. However, we still lack knowledge of oxygen reduction kinetics or mechanisms on AC cathodes in MFCs.

5. Actual wastewater, such as domestic and industrial wastewater should be further explored using these AC metal mesh cathodes. It will be beneficial for their application in wastewater treatment to use scaled up reactor designs and continuous flows. Separators could be used to reduce the electrode spacing for higher volumetric power production.