SALINITY EFFECTS ON POLYVINYL ALCOHOL SEPARATORS AND THE USE OF SPRAY-ON SEPARATORS IN AIR-CATHODE MICROBIAL FUEL CELLS

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by

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ABSTRACT

Separators in microbial fuel cells (MFCs) can be used to increase coulombic efficiencies (CEs), but they can also adversely affect power production. A new spray method of PVA separator preparation was compared to the traditional cast preparation method. Anode solution conductivities were varied to span values typical of domestic wastewater (~1 mS/cm) and laboratory solutions (7 and 13 mS/cm). Power densities were unaffected by the addition of a PVA separator onto the Pt catalyst cathode in the low conductivity solution relative to MFCs lacking a separator. However, power densities were reduced by 28% in a 7 mS/cm solution, and by 50% in a 13 mS/cm solution. The use of a separator enabled close placement of the electrodes, which resulted in power production 33% higher than control MFCs with widely spaced, separatorless electrodes in the 1 mS/cm. This low-conductivity condition was the only instance of where the power density was higher than that of the control. The reduced impact on power production in the low ionic conductivity solution was attributed to swelling of the PVA polymer, and the smaller contribution of solution resistance to total resistance in lower conductivity solutions. Addition of PVA onto activated carbon cathodes produced results similar to those obtained with the Pt catalyst, with a 26% reduction in the maximum power density (from 702 ± 29 mW/m² to 519 ± 6 mW/m²) in the 7 mS/cm solution. The reduction in power was reduced to <10% (636 ± 64 mW/m²) when switching to closely spaced electrodes compared to MFCs lacking a separator with widely spaced electrodes in the 7 mS/cm solution. Cast separators on both AC and Pt catalyst cathodes produced power densities 7-8% greater than the spray-on separators in a 7 mS/cm conductivity solution. These results show that spray on separators can be an effective method for insulating closely spaced electrodes in low conductivity solutions and that PVA can be used as a separator in low conductivity solutions to increase CE with minimal effect on power production.
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Chapter 1

Introduction

Two and a half billion people did not have improved sanitation facilities and 768 million people lacked access to an improved drinking water source in 2011 (WHO/UNICEF, 2013). Access to fresh water and adequate sanitation are among the most urgent issues facing the world today. Water shortages are increasingly frequent throughout the world, with forecasts indicating that it will get increasingly worse. In addition, energy is required to treat wastewater to suitable levels for discharge or reuse. Conventional power plants use vast quantities of water to produce electricity, increasing the stress on water supplies. Microbial fuel cells (MFCs) are one promising technology in which wastewater can be treated while also creating electricity, possibly making it an energy neutral process (Logan, 2008).

Air-cathode MFCs (Fig. 1-1) contain exoelectrogenic bacteria that use the anode as their electron acceptor, with oxygen in air used at the cathode as a final electron acceptor. These bacteria oxidize organic matter in wastewater and release electrons to the anode, where they flow through an external circuit, to the cathode and combine with oxygen and protons to create water (Logan, et al., 2006), or with oxygen and water to create hydroxide ions (Popat, et al., 2012). The electricity produced can be utilized to offset other energy requirements for treating wastewater.

Current research is focusing on increasing power and the coulombic efficiency (CE), which is defined as the ratio of coulombs harvested as energy through the external circuit versus the reduction in total coulombs in fuel in the cell. Finding materials that improve performance of these two factors, power and CE, are needed to make this MFC technology competitive as an effective method of wastewater treatment. Separators have been shown to increase the CEs of
MFCs, but often at the cost of lower power density. Separators that can increase CE without a loss in power are needed.

![Figure 1-1: Schematic of an air-cathode MFC.](image)

Polyvinyl alcohol (PVA) has shown promise as a useful separator material for MFCs as it was shown that it could be used to raise the CE and limit power losses due to increased internal resistances (Chen, et al., 2012; Chen, et al., 2013). However, research on this material has been limited to the use of high ionic strength solutions and cast membranes. It was observed in preliminary tests that PVA membranes prepared using the previously reported cast procedure (Chen, et al., 2012) had variable swelling characteristics with changes in solution salinity. Therefore, performance of MFCs with PVA separators could change due to differential swelling of the PVA in different solutions (Fig. 1-2).
Figure 1-2: (A) PVA as cast and (B) after swelling in deionized water.

To improve our understanding of PVA separators in MFCs, there were three objectives to this study.

- To determine the impact of swelling on MFC performance, PVA separators were investigated using Pt catalyst cathodes in MFCs with phosphate buffer solutions (PBSs) of varying molarities (5 mM, 50 mM and 100 mM).
- In order to evaluate a new application method for PVA, a spray-on separator was compared to a cast separator in Pt and activated carbon (AC) catalyst MFCs.
- To determine the effectiveness of PVA separators on a less expensive cathode configuration, testing was done in AC catalyst MFCs.

This thesis is organized into 4 chapters. In chapter 2, I review the literature on separators and electrodes in MFCs, as well as the effects that salinity can have on MFC performance and membrane properties. Chapter 3 is written as a complete study in a format suitable for publication in a technical journal. In chapter 4, I discuss future work needed in the area of PVA separator research. I prepared all materials, except as mentioned in chapter 3 for VITO AC cathodes. Advice on experimental design was provided by Dr. Xiaoyuan Zhang and Dr. Bruce Logan.
Researchers have made great strides in advancing MFCs by improving coulombic efficiencies and power densities. Research is still needed in order to bring the cost of MFC materials down, to find the best possible components, and to ensure those components work in a variety of different conditions. In this section, I review separators used in MFCs, electrode catalyst types and configurations, and the effects of salinity on MFC performance and membrane properties.

2.1 Separators

Separators, as used in MFCs, are materials used to increase CE by lowering oxygen intrusion into the anode chamber and to allow close electrode spacing by preventing the electrodes from touching and short-circuiting. J-Cloth was one of the first separators shown to effectively increase CEs in MFCs without a large decrease in power density (Fan, et al., 2007). CE was doubled with the use of two layers of J-Cloth, from 35% in a separatorless MFC to 71% with the separator. This increase in CE was attributed to a decrease in oxygen flux into the anode chamber. By avoiding the possibility of the electrodes short-circuiting, the addition of the J-Cloth separator also made a closely spaced electrode configuration possible, which increased power densities to 170 W/m$^3$. This was more than twice the power density of 80 W/m$^3$ produced in the MFC without a separator. The main problem with J-Cloth is that it is biodegradable, making it unsuitable for long-term use (Zhang, et al., 2009b).

Glass fiber mats, such as those used in lead acid batteries, have been studied in MFCs with good results (Zhang, et al., 2009b). They are inexpensive, but questions have been raised
about their long-term durability (Chen, et al., 2012; Li, et al., 2011). Peak CE in a single-chamber MFC with closely spaced electrodes was greater than 80%, and power densities were 33% higher than a single-chamber MFC with no separator and electrodes spaced 2 cm apart. The use of glass fiber separators have also been shown to reduce start up time of MFCs and improve anode performance (Zhang, et al., 2013)

Cation exchange membranes (CEMs) and anion exchange membranes (AEMs) have also been used as separators in MFCs with some success. CEs with these membranes were generally high, with peak values between 41-72% (Kim, et al., 2007). Power densities were low, with 610 mW/m² being produced in a cubic MFC with an AEM and 480 mW/m² being produced in the same configuration with a CEM. The lower power densities have been attributed to increased internal resistance in the cell and potential losses associated with pH gradients formed by the preferential flow of ions (Rozendal, et al., 2007).

PVA has recently been shown to increase CEs while limiting power losses in MFCs (Chen, et al., 2012; Chen, et al., 2013). The use of PVA separators on Pt catalyst cathodes in a high salinity solution (200 mM PBS, 22 mS/cm) produced peak CEs ranging from 81-95%, while limiting power loss, compared to 15% for a control with no separator during the initial cycles. After 17 cycles, the MFCs with PVA had higher power densities (1223 mW/m²) than the control (1112 mW/m²), which was believed to be due to the inhibition of bacterial growth on the cathode by the PVA membrane. In tests using PVA separators in activated carbon catalyst MFCs, with 50 mM PBS (7 mS/cm), results were similar to those previously reported on in 200 mM PBS with Pt catalyst cathodes, with a peak CE of 89% and peak power densities only 10% less than the control with no separator during the initial cycles. The high power density with high CE did not fall on a trendline identified in a previous study that showed decreasing power with increasing CE (Chen, et al., 2012; Fig. 2-1).
2.2 Electrodes

Pt catalyst cathodes have traditionally been used in MFC testing due to the high power densities achieved compared to graphite or carbon cathodes (Cheng, et al., 2006a; Duteanu, et al., 2010). Pt works well as a catalyst due to its low activation energy for oxygen reduction, but it is expensive (Duteanu, et al., 2010; Pant, et al., 2010) and power densities drop off relatively quickly over time (Zhang, et al., 2014). AC cathodes have shown promise in being able to produce, and sustain over time, power densities that can be higher than MFCs using Pt catalyst cathodes (Zhang, et al., 2009a; Zhang, et al., 2014). Maximum power densities achieved with AC mixed with carbon black (1560 mW/m²) were 7% higher than those achieved with Pt (1460 mW/m²) after one week of operation. Over time, the performance of the AC/CB only decreased by 4% after 3.5 months, whereas the performance of the Pt decreased by 55%.
Anode configuration can affect MFC performance. Anode thickness has been investigated by varying the thickness of carbon felt anodes. Power densities were increased from 604 mW/m² with a 0.32 cm thick anode to 1048 mW/m² with a 1.27 cm thick anode in a spaced configuration without a separator. Brush anodes have been compared to flat mesh anodes in MFCs with closely spaced electrodes separated by glass fiber (GF). Maximum power densities, using 1GF separator after 30 days with the brush anodes was 220 mW/m², which was considerably higher than the 80 mW/m² produced with the flat anode (Hays, et al., 2011). After 114 days, the power density decreased to 130 mW/m² with the brush anode and to 42 mW/m² with the flat anodes. Both types of anodes yielded similar results after 30 days when 2 GF separators were used, with brush anodes producing 240 mW/m² and flat anodes producing 230 mW/m². However, after 114 days, the maximum power had dropped to 45 mW/m² with flat anodes, while power remained relatively constant at 230 mW/m² for the brush anodes.

2.3 Salinity

Increasing buffer concentrations over certain ranges in MFCs can have a positive effect on power density (Min, et al., 2008; Nam, et al., 2010). Maximum power density seen in a two-chamber MFC operated using a wastewater/acetate medium was increased from 70 mW/m² to 320 mW/m² with the addition of 100 mM PBS (Min, et al., 2008). Comparison of 4 different buffers (PBS, MES, HEPES and PIPES) at the same molarity (50 mM) resulted in power densities that ranged from 204 mW/m² to 410 mW/m² (Fig. 2-2a; Nam, et al., 2010). When NaCl was added to these same 4 buffers to create solutions with the same conductivity (8.2 mS/cm), the power densities were more consistent among the different buffer types, with a range of 437 mW/m² to 459 mW/m² (Fig. 2-2b), indicating that conductivity was a major factor in power generation with different buffer types. The buffer helps to improve power, however, as it was also
shown in a two-chamber MFC that a 50 mM PBS solution (590 mW/m²) had higher power densities than 120 mM (477 mW/m²) or 240 mM (491 mW/m²) NaCl solutions, even though the NaCl solutions had higher conductivities (Ahn, Logan, 2013). Variations in salinity have also been shown to affect ion transport properties and resistances in membranes (Dlugolecki, et al., 2010). Increasing salinity has been shown to decrease resistance and swelling in ion exchange membranes (Urano, et al., 1986; Dlugolecki, et al., 2010).

Figure 2-2: Power densities and cell voltages of MFCs with different buffers at the same molarity (A, D) and at the same conductivity (B, E) (Nam, et al., 2010).
Chapter 3

Analysis of Polyvinyl Alcohol Separators in Microbial Fuel Cells

3.1 Abstract

Separators are used to protect cathodes from fouling and to avoid electrode short-circuiting, but they can affect microbial fuel cell (MFC) performance. A spray method was used to apply a polyvinyl alcohol (PVA) separator to the cathode. MFC performance was affected by solution salinities due to changes in separator water uptake and its thickness. Power densities were unaffected using the separator in a 1 mS/cm conductivity solution (5 mM phosphate buffer solution; PBS) compared to a separatorless control, but they were reduced by 28% in a 7 mS/cm conductivity solution (50 mM PBS), and by 50% in a 13 mS/cm conductivity solution (100 mM PBS) in MFCs containing a Pt catalyst cathode. With an activated carbon cathode, maximum power densities were reduced by the addition of a PVA separator from 702 ± 29 mW/m² to 519 ± 6 mW/m² (50 mM PBS) with widely spaced electrodes, and to 636 ± 64 mW/m² with closely spaced electrodes. Spray and cast PVA separators performed similarly, but the spray method was easier to apply.

3.2 Introduction

Microbial fuel cells (MFCs) produce power through the oxidation of organic material in wastewater (Logan, 2008). Electrons released at the anode by exoelectrogenic bacteria flow through an external circuit, and combine with oxygen and protons to create water (Logan, et al., 2006), or oxygen and water to create hydroxide ions (Popat, et al., 2012) at the air cathode. Power production can be increased in MFCs by using closely spaced electrodes (SPA) (Liu et al., 2005),
but this can lower coulombic efficiency (CE) due to oxygen utilization by bacteria on the anode (Cheng et al., 2006a). Care must be taken to prevent the electrodes from making direct contact, as this would result in short-circuiting. Using a separator insulates the electrodes from direct contact, and increases CE by limiting oxygen intrusion into the anode chamber. However, the presence of the separator can lower power densities by increasing the ohmic resistance of the cell despite the closer electrode spacing (Rozendal, et al., 2007).

A variety of separator materials have been examined in MFCs. Cloth separators (J-cloth, JC) increased power when the electrodes were used in a separator electrode assembly (SEA) configuration, with the electrodes on either side of the separator (Fan, et al., 2007), but their long-term use was limited due to biodegradation of the cloth by microorganisms (Zhang, et al., 2009b). Cation exchange membranes (CEMs) and anion exchange membranes (AEMs) increase CEs in MFCs by reducing oxygen intrusion through the cathode, but create pH gradients due to selective ion transport by the membranes (Zhang, et al., 2010; Rozendal, et al., 2007). Examination of a wide range of other types of materials has similarly shown that there is generally a trade off in increased CE with reduced power (Chen, et al., 2012).

Cast polyvinyl alcohol (PVA) membranes have been shown to be a promising separator material as their use increased CE with minimal power loss (Chen, et al., 2012; Chen, et al., 2013). However, the performance of the PVA could be affected by solution salinities as this material will swell with a reduction in ionic strength, which could affect performance (Dlugolecki, et al., 2010). PVA separators were previously examined only in highly saline solutions of ~ 7 mS/cm conductivity (50 mM PBS) and ~ 22 mS/cm conductivity (200 mM PBS) (Chen, et al., 2012; Chen, et al., 2013), but for wastewater treatment applications the solutions will have very low conductivities (~ 1 mS/cm; 5 mM PBS). It is also important to avoid separation of the membrane from the cathode, as water trapped between a membrane and cathode can reduce performance (Zhang, et al., 2010b).
A simple spray-on application method was examined here for applying the PVA separator directly to the cathode. The effect of solution salinity on the properties and performance of the cast PVA separators was evaluated by varying the concentration of the PBS between a concentration (5 mM PBS) that had a solution conductivity similar to domestic wastewater (~1 mS/cm), to that more typically used in laboratory experiments of 7 mS/cm (50 mM PBS) or 13 mS/cm (100 mM PBS). PVA was applied to the water side of cathodes containing a Pt or activated carbon (AC) catalyst, and subsequent MFC performance was examined using spaced electrodes or SEA configurations.

3.3 Experimental

3.3.1 Separators

PVA separators were made from an 8% PVA solution in water (w/w) with a porogen (5.6% of tetrabutylammonium chloride by weight) added as previously described (Chen, et al., 2012). Spray-on PVA separators were applied with an air brush in multiple layers (8-15 layers, depending on cathode type). Pt cathodes were made with a PVA loading of 10.0 ± 1.4 mg/cm², determined by a mass balance of the beginning and ending mass, with the PVA applied directly on top of the catalyst layer. AC cathodes were made with a higher loading of 19.5 ± 0.1 mg/cm² due to a different cathode configuration which used a nickel mesh current collector that was facing the solution in the MFC. A larger amount of PVA was needed to both fill the space between the mesh pores, and produce a separator that was thick enough to provide insulation against short-circuiting of the electrodes. Cast PVA separators were made with a PVA loading of 10.8 ± 0.4 mg PVA/cm² in PTFE molds as previously described (Chen et al., 2012), but with different drying conditions. Cast separators were dried for a minimum of 48 h at room
temperature (19-27° C) rather than the 36 hours drying at 50° C used previously. Once cast, the separators were placed in the medium used in MFCs to allow the membranes to swell prior to insertion into the MFCs. All loadings reported here include water trapped in the PVA matrix, as the measurements were taken at ambient, non-desiccated conditions. All references to PVA separators are of the cast variety, unless otherwise noted.

The characteristics and performance of the PVA separators were compared to cloth separators (Dupont Sontara, style 8864) that have previously been shown to increase CE with relatively small power losses (Wei, et al., 2013). These cloth separators are referred to as wipe separators as the material is sold as a wipe or cleaning cloth. A polypropylene mesh support (No.145872, Spectrum Medical Industries Inc., CA.) was used to press the separator onto the cathodes, or it was placed directly onto the cathode in separatorless controls.

3.3.2 MFC Reactors

Anodes were heat-treated (450° C, 30 min), graphite fiber brushes twisted between two titanium wires (Logan, et al., 2007). Cathodes with a Pt catalyst layer (5 mg/cm² 10% Pt on Vulcan XC-72 with 33.3 μL/cm² of 5 wt % Nafion as binder) were constructed with a stainless steel mesh support and a poly(dimethylsiloxane)(PDMS) diffusion layer as previously described (Zhang, F., et al., 2010), with the Pt catalyst layer facing the solution. AC cathodes were made using a nickel mesh (VITO, Belgium), with the AC between the mesh and a polytetrafluoroethylene (PTFE) diffusion layer as previously described (Zhang, F., et al., 2009), and used in the MFCs with the nickel mesh facing the solution.

MFCs were single-chamber, cubic-shaped reactors (2 cm long cylindrical chamber; 12 mL liquid volume) constructed as previously described (Zhang, X., et al., 2010). Electrodes were
used in a spaced electrode configuration (SPA, 1.25 cm spacing) or in the SEA configuration (0.75 cm spacing) (Fig. 3-1).

![Diagram showing configurations for Spaced Electrode (SPA) and Separator Electrode Assembly (SEA) testing.](image)

**Figure 3-1:** Configurations for Spaced Electrode (SPA) and Separator Electrode Assembly (SEA) testing.

MFCs were inoculated with the effluent from MFCs operated for over one year. Testing occurred in PBSs with conductivities of 1 mS/cm (5 mM PBS; 458 mg Na$_2$HPO$_4$, 245 mg NaH$_2$PO$_4$·H$_2$O, 31 mg NH$_4$Cl, 13 mg KCl), 7 mS/cm (50 mM PBS; 4.58 g Na$_2$HPO$_4$, 2.45 g NaH$_2$PO$_4$·H$_2$O, 0.31 g NH$_4$Cl, 0.13 mg KCl) and 13 mS/cm (100 mM PBS; 9.16 g Na$_2$HPO$_4$, 4.90 g NaH$_2$PO$_4$·H$_2$O, 0.62 g NH$_4$Cl, 0.26 g KCl). Solutions used for all testing included 1 g/L sodium acetate and trace vitamins (5 mL/L) and minerals (12.5 mL/L). All testing of separators in AC cathode MFCs, and spray applied versus cast separators were made in 7 mS/cm conductivity solution (50 mM PBS). The effect of medium salinity was examined using cast PVA separators on Pt catalyst cathodes in 1 mS/cm, 7 mS/cm, and 13 mS/cm conductivity solutions (5 mM, 50
mM, and 100 mM PBS). Reactors were fed in batch mode and operated at room temperature (19-27° C). MFCs were tested in duplicate for all testing, with the exception of the 50 mM testing on Pt, which occurred in 8 MFCs to ensure that all were running in parallel.

### 3.3.3 Data Analysis

Voltage was measured across an external resistor (1000 Ω) at 20 min intervals with a data acquisition system (34792A, Agilent LXI Data Acquisition/Switch Unit; Santa Clara, CA) connected to a personal computer, with current and power density normalized to the projected surface area of the cathode (7 cm²) as previously described (Logan, 2008). CE was calculated as the ratio of coulombs from the measured current compared to change in substrate based on chemical oxygen demand (COD) (Logan, 2008). In tests using AC cathodes and spray-on or cast separators, polarization data were obtained by varying external resistance from 1000 Ω to 25 Ω in decreasing order over separate cycles at each resistance (multiple cycle method). For tests of the PVA in different salinity solutions, polarization curves were obtained using a single-cycle method where the external resistance was decreased every 20 minutes at the beginning of a single cycle. MFCs used in multi-cycle tests were acclimated at 1000 Ω, but those tested using the single-cycle tests were acclimated at 25 Ω to avoid power overshoot (Zhu, et al., 2013). Cycle times were defined as time from start of the fed batch cycle until the voltage was reduced to <50 mV (AC and spray-on/cast testing) or <20 mV (salinity testing).

Total internal resistance was calculated from the slopes of the linear portions of the polarization curves (Logan, 2008), which varied by test. Components of the internal resistance were analyzed by electrochemical impedance spectroscopy (EIS) using a potentiostat (PC 4/750, Gamry Instruments Inc.; Warminster, PA). Ohmic and charge transfer resistances were obtained by EIS analysis using a single-chamber system (Fig. 3-2), with a set potential of −100 mV versus
a Ag/AgCl reference electrode (+209 mV versus a standard hydrogen electrode, SHE) (RE-5B, Bioanalytical Systems, Inc., West Lafayette, IN) with the separator pressed against the working electrode. Working and counter electrodes were made of carbon cloth with a Pt catalyst and 4 PTFE diffusion layers, and were exposed to air on one side and solution on the other.

![Diagram of EIS Configurations showing the locations of the reference electrode (RE), working electrode (WE), counter electrode (CE) and separator in RO and RCT testing.](Image)

Oxygen permeability through the cathode was examined in terms of an oxygen transfer coefficient, \( k \) (cm/s)(Cheng, et al., 2006b) in order to evaluate how salinity affected the mass transfer characteristics of PVA. An abiotic single-chamber cubic reactor (4 cm length, 28 mL liquid volume) without an anode was used to measure dissolved oxygen concentrations with a non-consumptive oxygen probe (Neofox, Ocean Optics Inc., Dunedin, Fl). Reactors were filled with oxygen-free deionized water, and various concentrations of PBS, and used a Pt/SS cathode with or without a separator. Testing for oxygen permeability occurred in duplicate, with each separator and control being tested twice. Water uptake (%) was calculated as the difference between the saturated and unsaturated weight divided by the unsaturated weight and was averaged from 4 samples. Thickness (µm), measured with a digital micrometer, was averaged from the same 4 samples.
3.4 Results and Discussion

3.4.1 Salinity Effects on PVA Properties

Increasing the solution salinity by changing the solution conductivity decreased water uptake by the PVA separators, and had no effect on the wipe separators (Fig. 3-3A). The PVA separator water uptake ranged from 540% to 840%, but the wipe separators changed very little with an average of 220% for the solutions with the different salinities (Fig. 3-3A). There was no clear trend in the measured PVA separator thickness with solution conductivity. A lack of a trend could be due to the way that the PVA separator thickness was measured, as well as variations in the thickness of dry membranes. The measuring technique also was not very precise, as it is difficult to determine with the digital micrometer where the contact was made with the separator surface. The thickness of a single dry PVA separator also varied by nearly 100% across a single separator, likely due to capillary forces at the edges of the cast molds.

Oxygen transfer coefficients showed variation with salinity change in the control lacking a separator, with values of $180 \times 10^{-5} \pm 10 \times 10^{-5}$ cm/s in DI water and $210 \times 10^{-5} \pm 10 \times 10^{-5}$ cm/s in 100 mM PBS (Fig. 3-3B), but statistical analysis revealed no significant trend. There was no change in the oxygen mass transfer coefficients with PVA separators in various solutions, with a value of $50 \times 10^{-5} \pm 10 \times 10^{-5}$ cm/s in both DI water and 100 mM PBS. Wipe separators had an oxygen transfer coefficient of $80 \times 10^{-5} \pm 0$ cm/s in DI water, which was slightly higher than the $60 \times 10^{-5} \pm 0$ cm/s calculated in 100 mM PBS. The lower oxygen transfer rates with separators follow the trend of increased CE but lower power density that would be expected.
Figure 3-3: Water uptake (Closed symbols; A), thickness (Open symbols; A) and oxygen transfer coefficients (B) of PVA, wipe and NS conditions as a function of PBS molarity. (Error bars are standard deviations of 4 tests. Some error bars are smaller than the symbol size.).

3.4.2 **Salinity Effects on PVA Power Densities using Pt cathodes**

There was little impact of the PVA separator on power generation in the lowest conductivity solution, but power was reduced in higher conductivity solutions. In the lowest conductivity solution of 1 mS/cm (5 mM PBS) in the spaced electrode configuration, the maximum power density without a separator of $336 \pm 3$ mW/m$^2$ was the same as that with a PVA separator ($339 \pm 29$ mW/m$^2$), compared to 7% less power with the wipe separators ($313 \pm 27$ mW/m$^2$) (Fig. 3-4A). The impact of the separator was more substantial as conductivity increased. At a conductivity of 7 mS/cm (50 mM PBS), the maximum power density without a separator was increased to $1228 \pm$
55 mW/m$^2$, but the PVA separator reduced power by 28% (889 ± 0 mW/m$^2$), which was similar to that of the wipe separators (30% reduction, 853 ± 60 mW/m$^2$) (Fig 3-4B). In the highest conductivity solution of 13 mS/cm (100 mM PBS), the maximum power density for the MFC without a separator was 1848 ± 18 mW/m$^2$, using the spaced electrode configuration. Adding a PVA separator decreased the maximum power density by almost 50% (932 ± 76 mW/m$^2$), compared to only a 33% decrease using the wipe separators (1239 ± 19 mW/m$^2$) in this solution (Fig 3-4C).

The use of the separator allowed operation of the reactor in the SEA configuration. Switching reactors from the spaced to the SEA configuration produced increases in power densities in all cases. However, only for the case of the 1 mS/cm solution was the power density higher in the SEA configuration than the spaced electrode control (no separator). In the 1 mS/cm (5 mM PBS) reactor power densities versus the control were 32% higher with PVA separators (444 ± 8 mW/m$^2$) and 10% higher with wipe separators (370 ± 34 mW/m$^2$)(Fig. 3-4A). In 7 mS/cm (50 mM PBS) SEA testing, power densities versus the control were decreased by 22% with PVA separators (956 ± 51 mW/m$^2$) and by 29% with wipe separators (877 ± 53 mW/m$^2$)(Fig. 3-4B). In 13 mS/cm (100 mM PBS) closely spaced electrode testing, power densities were lower than the control by 35% with PVA separators (1207 ± 110 mW/m$^2$), and 29% lower with wipe separators (1303 ± 5 mW/m$^2$) (Fig. 3-4C).
The reduction in power production in MFCs with solution conductivity observed here is well known, and consistent with previous reports (Cheng, Logan, 2007). However, it has not been
previously shown that a change in solution conductivity can affect the separator itself, and thus also alter power production. Using PVA separators in the SEA configuration produced a 32% increase in power production than the spaced electrode configuration (no separator) in the 1 mS/cm solution (Fig. 3-5), which was greater than the increase seen with wipe separators (10%) in the same configuration. This finding is important because this conductivity is most representative of a typical domestic wastewater. In typical laboratory solutions of 7 mS/cm (50 mM PBS) and 13 mS/cm (100 mM PBS) loss of power density due to separators was significant, likely due to the insignificant contribution of the ohmic resistance to the total resistance, as further examined below.

3.4.3 PVA on Activated Carbon Cathodes

The effect of PVA separators on power production using the AC cathode catalyst in MFCs was consistent with that observed with the Pt cathode catalyst. The use of a PVA separator in the spaced electrode configuration lowered power densities in AC catalyst MFCs by 26%
versus the separatorless control (519 ± 6 mW/m² vs 702 ± 29 mW/m²) (Fig. 3-6A). Wipe separators reduced power by 30% (488 ± 6 mW/m²). Changing to a closely spaced electrode configuration reduced the impact of the separator, with power densities 9% lower with PVA (636 ± 64 mW/m²) and unchanged with wipe separators (701 ± 57 mW/m²) (Fig. 3-6A), versus the separatorless, spaced electrode control. Anode potentials for testing in both SPA and SEA were all similar (Fig. 3-6C), indicating that the difference in power production was primarily due to differences at the cathode side of the system.

The 26% decrease in power density when PVA was added into the spaced electrode format was larger than the 10% reduction in power previously obtained by others using a PVA separator on an AC cathode (Chen, et al., 2013). The differences in power reduction could be due to different cathode binders (Q-FPAE) and diffusion layers (PTFE) than those used here. Previous tests were also conducted at a higher temperature (30° C) than the room temperature used here.
Figure 3-6: (A) Power density curves (Solid symbols, SEA format; Open symbols, SPA format), (B) Cell voltages, and (C) Electrode potentials (Cathodes: solid lines; Anodes: dashed lines) for testing on AC cathodes.
3.4.4 Spray-on vs Cast PVA Separators

With cast separators, the power densities of $942 \pm 43 \text{ mW/m}^2$ were 7% higher than spray-on separators ($873 \pm 33 \text{ mW/m}^2$) on Pt catalyst cathodes (Fig. 3-7). Similarly, the power densities of $718 \pm 74 \text{ mW/m}^2$ with cast separators were 8% higher than spray-on separators ($664 \pm 67 \text{ mW/m}^2$) on AC catalyst cathodes. PVA loading on the AC cathodes ($19.5 \pm 0.1 \text{ mg PVA/cm}^2$) was roughly twice as much as the loading on the Pt cathodes ($10.0 \pm 1.4 \text{ mg/cm}^2$) due to the cathode configuration that required the PVA to completely cover the metal mesh. This only had a small impact on power production. Further research is needed to determine if changing the cathode configuration to allow a lower loading rate of PVA onto the AC catalyst layer will produce better results than the cast separators.
Figure 3-7: Test data for cast (closed symbols) and spray-on (open symbols) PVA separators in SEA on Pt and AC cathodes showing: (A) Power density curves, (B) Cell voltages, and (C) Electrode potentials (Cathodes: solid lines; Anodes: dashed lines).
3.4.5 Resistance

The effect of separators on ohmic resistance was highest in the lowest conductivity solution of 1 mS/cm (5 mM PBS) (Figure 3-8). In 1 mS/cm conductivity solution (5 mM PBS), addition of PVA and wipe separators increased ohmic resistance from 120 Ω (no separator) to 140 Ω. In both of the higher conductivity solutions (7 mS/cm, 50 mM PBS; 13 mS/cm, 100 mM PBS), ohmic resistance was unchanged with the addition of a separator. Ohmic resistance was 20 Ω in the 50 mM PBS and 10 Ω in the 100 mM PBS. Charge transfer resistance at a set potential of −100 mV increased in 1 mS/cm (5 mM PBS) with the addition of separators, but there was no clear trend in resistance at higher PBS concentrations. The charge transfer resistance in the 7 mS/cm solution increased from 30 ± 0 Ω (no separator) to 70 ± 10 Ω with the addition of PVA separators, and to 50 ± 0 Ω with wipe separators. In the 13 mS/cm solution (100 mM PBS), there was no difference in charge transfer resistance between testing with and without a separator.

![Graph showing resistance values for different conditions and separators.

Figure 3-8: Total, charge transfer and ohmic resistances. SPA and SEA Total resistances taken from the linear portion of the MFC polarization data. Charge transfer and ohmic resistances taken from EIS data. Resistances over the complete polarization curves located in the appendix (Fig. S1).
Total internal resistances were calculated over the linear portions of the polarization data, which varied with solution conductivity. In 1 mS/cm solution (5 mM PBS), total internal resistance was calculated over a current range of 0.6-1.7 A/m². In the spaced electrode configuration without a separator, total internal resistance was 320 Ω, which increased only slightly to 340 Ω with the addition of a PVA separator, but decreased to 300 Ω with the addition of wipe separators (Fig.3-8). These variations in resistance were minor in terms of total resistance, and therefore power densities were not significantly affected by the addition of either the PVA or wipe separators (Fig. 3-9). Changing the configuration into closely spaced electrodes decreased the total cell resistance to 210 Ω with PVA separators, and to 230 Ω with wipe separators. Whole cell resistance, calculated over a current range of 2.8-9.1 A/m², in the space electrode configuration operated in 13 mS/cm solution (100 mM PBS) was 70 Ω without a separator. Cell resistance decreased to 60 Ω with the addition of PVA separators and increased to 80 Ω with wipe separators. The lack of significant variation in resistance at this conductivity was unexpected due to the large decrease in power density that was seen with the addition of separators into the system. These calculated resistances could therefore indicate that the polarization curves were not completely linear as assumed. Total internal resistances in the 7 mS/cm solution (50 mM PBS) were calculated over the range of 2.8-6.9 A/m². If all these data are plotted in terms of power versus the inverse of total resistance, we see the overall expected trend of increased power inversely with resistance, but there are large variations at specific values for each case (Fig. 3-10). Due to the small changes in both solution and charge transfer resistance seen in the various conductivity solutions, the main impact on whole cell resistance was likely due to changes in diffusion resistance with and without separators.
Figure 3-9: Power density and resistance comparison as a function of PBS concentration and MFC configuration (Open bars, SPA; Closed bars, SEA).

Figure 3-10: Distribution of power densities versus inverted resistance for 5 mM (green symbols), 50 mM and 100 mM PBS.
3.4.6 Coulombic Efficiencies and Cycle Times

Coulombic efficiencies in the AC cathode MFCs were generally 10-20% higher in the MFCs with PVA or wipe separators (Fig. 3-10). Electrode configuration had little effect on CE values, as there was negligible difference between the spaced electrode and closely spaced configurations. CE increased with current density, with peak values between 65-75% with separators and 60% without a separator. The same trend of increased CE with separators was seen in the testing on Pt cathodes with different PBS concentrations, with the CE increasing inversely with solution conductivity (Figs. S2, S3 & S4).

Spray-on and cast separators had CEs that ranged from 63-74%, with the spray-on separators being lower than the cast at peak power densities (Fig. S5). The lower values in this range of CEs are only slightly higher than CEs measured with the control in both AC (61%, Fig. 3-6) and in Pt (55%, Fig. S3) cathode MFCs.

![Figure 3-11: Coulombic efficiencies for SPA (open symbols) and SEA (closed symbols) testing on AC cathodes.](image)

Cycle times in AC and Pt cathode MFCs increased by 20-50% with the addition of separators, with closely spaced electrode cycle times being longer than spaced electrode cycle...
times. Cycle times with spray-on separators were longer than those with cast separators in both AC (34.5 ± 1.5 hrs vs 27 ± 1.5 hrs) and Pt (23 ± 2.5 hrs vs 18.5 ± 2.5 hrs) cathode MFCs. The increase in cycle time is expected as the addition of the separator reduces oxygen transfer into the anode solution, and thus less substrate is lost to aerobic degradation of the acetate.

3.5 Conclusions

Polyvinyl alcohol can be used as a separator in MFCs with comparable results to wipe separators in both AC and Pt cathode MFCs. In a low conductivity solution, where solution resistance is a main component of total resistance, addition of a PVA separator had no effect on power densities. In higher conductivity solutions, where solution resistance is a smaller part of total resistance, the impact of PVA on power production became larger with solution conductivity. A spray-on separator can be used in place of a cast separator to achieve similar power densities and CEs, but with increased cycle times.
Chapter 4

Future Work

Research on the use of PVA in MFCs could be furthered by investigating the following areas.

- Testing of PVA separators in wastewater is needed to evaluate its durability over time in a more complex medium, as well as the effects on power production and CE.

- Further testing of spray-on separators is needed to achieve the minimum loading rate for electrode insulation with maximum power.

- Alternative porogens should be investigated to identify the most cost efficient materials.
Appendix

Supporting Information

Fig. S1: Total, charge transfer and ohmic resistances. SPA and SEA Total resistances taken from complete MFC polarization data. Charge transfer and ohmic resistances taken from EIS data.
Fig. S2: Comparison of SEA (closed symbols) and SPA (open symbols) testing in 5 mM PBS showing: (A) Cell potentials, (B) Electrode potentials and (C) Coloumbic efficiencies.
Fig. S3: Comparison of SEA (closed symbols) and SPA (open symbols) testing in 50 mM PBS showing: (A) Cell potentials, (B) Electrode potentials and (C) Coloumbic efficiencies.
Fig. S4: Comparison of SEA (closed symbols) and SPA (open symbols) testing in 100 mM PBS showing: (A) Cell potentials, (B) Electrode potentials and (C) Coloumbic efficiencies.
Fig. S5: Coulombic efficiencies for cast (closed symbols) and spray-on (open symbols) PVA separators in SEA on Pt and AC cathodes.
Fig. S6: EIS plots for wipe separators, PVA separators, and the NS control in A) 5 mM PBS, B) 50 mM PBS and C) 100 mM PBS.
References


