Spray-on polyvinyl alcohol separators and impact on power production in air-cathode microbial fuel cells with different solution conductivities

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Highlights
- Polyvinyl alcohol (PVA) separators were prepared with spray-on and cast methods.
- PVA separators increased power with closely spaced electrodes versus spaced electrodes.
- Power densities with PVA spray-on or cast separators are similar.
- Separator effect on power density is decreased in lower conductivity solutions.

Graphical abstract

Abstract
Separators are used to protect cathodes from biofouling and to avoid electrode short-circuiting, but they can adversely affect microbial fuel cell (MFC) performance. A spray method was used to apply a polyvinyl alcohol (PVA) separator to the cathode. Power densities were unaffected by the PVA separator (339 ± 29 mW/m²), compared to a control lacking a separator in a low conductivity solution (1 mS/cm) similar to wastewater. Power was reduced with separators in solutions typical of laboratory tests (7–13 mS/cm), compared to separatorless controls. The PVA separator produced more power in a separator assembly (SEA) configuration (444 ± 8 mW/m²) in the 1 mS/cm solution, but power was reduced if a PVA or wipe separator was used in higher conductivity solutions with either Pt or activated carbon catalysts. Spray and cast PVA separators performed similarly, but the spray method is preferred as it was easier to apply and use.

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1. Introduction

Microbial fuel cells (MFCs) produce power through the bacterial 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 produce hydroxide ions (Popat et al., 2012) at the air cathode. Power production can be increased in MFCs by using closely spaced electrodes (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; Zhang et al., 2013).
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, thereby limiting the amount of oxygen available to bacteria in the system, but they create pH gradients due to selective ion transport by the membranes (Zhang et al., 2010b; 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 (Zhang et al., 2010c).

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, 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 phosphate buffer solution, PBS) and ~22 mS/cm conductivity (200 mM PBS) (Chen et al., 2012, 2013), but for wastewater treatment applications the solutions will have very low conductivities (~1 mS/cm, similar to that of a 5 mM PBS solution). 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).

The main objective of this work was to evaluate the effect of solution salinity on the properties and performance of the cast PVA separators 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. A second objective was to examine MFC performance using a simple spray-on application method for applying the PVA separator directly to the cathode.

2. Methods

2.1. MFC reactors, electrodes and solutions

MFCs were single-chamber, cubic-shaped reactors (2 cm long cylindrical chamber; 12 mL liquid volume) constructed as previously described (Zhang et al., 2010b). 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 et al., 2010a), with the Pt catalyst layer facing the solution. Activated carbon (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 et al., 2009a), and used in the MFCs with the nickel mesh facing the solution. Electrodes were used in a spaced electrode configuration (SPA, 1.25 cm spacing), with the anode on the opposite side of the MFC chamber than the cathode, or in the SEA configuration (0.75 cm spacing) (Fig. 1), with the anode and cathode on the same side of the MFC chamber, with a separator placed in between.

MFCs were inoculated with the effluent from MFCs operated for over one year. Solutions used for all tests contained 1 g/L sodium acetate and trace vitamins (5 mL/L) and minerals (12.5 mL/L). The concentration of the PBS was varied from a conductivity typical of wastewater, of 1 mS/cm (5 mM PBS; 458 mg Na₂HPO₄, 245 mg NaH₂PO₄·H₂O, 31 mg NH₄Cl, 13 mg KCl), to higher conductivities typical of laboratory tests: 7 mS/cm (50 mM PBS; 4.58 g Na₂HPO₄, 2.45 g NaH₂PO₄·H₂O, 0.31 g NH₄Cl, 0.13 mg KCl) and 13 mS/cm (100 mM PBS; 9.16 g Na₂HPO₄·12H₂O, 4.90 g NaH₂PO₄·H₂O, 0.62 g NH₄Cl, 0.26 g KCl). Reactors were fed in batch mode and operated at room temperature (19–27 °C). MFCs were tested in duplicate, with the exception of the 50 mM testing on Pt, which occurred in 8 MFCs to ensure that all reactors were running in parallel.

2.2. Separators

PVA was prepared in water (8% w/w) with a porogen (5.6% of tetrabutylammonium chloride by weight) 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, as determined by a gravimetric analysis before and after applying the PVA, 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 structure which resulted in the nickel mesh current collector facing the solution in the MFC. A larger amount of PVA was needed to both fill the space between the nickel mesh pores, and produce a separator that was thick enough to provide insulation against short-circuiting of the electrodes.

Spray separators were compared to cast PVA separators (10.8 ± 0.4 mg PVA/cm²) made using polytetrafluoroethylene (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 h drying at 50 °C used previously, to simplify the cast preparation.
Preliminary tests (unpublished) indicated that these two drying conditions yielded similar power densities (data not shown). The dried 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.

Cathodes containing PVA separators were also compared to cloth separators (Dupont Santara, style 8864) that were previously 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. All separators or plain cathodes were covered with a polypropylene mesh support (No. 145872, Spectrum Medical Industries Inc., CA). The mesh was needed to press the cloth and membrane separator onto the cathodes, and therefore it was used in other tests to maintain similar test conditions.

2.3. Analysis

Voltage was measured across an external resistor (1000Ω) 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, MFCs were acclimated at 1000Ω, and polarization data were obtained by varying external resistance from 1000Ω to 25Ω in decreasing order over separate cycles at each resistance (multiple cycle method). For tests of PVA in different salinity solutions, reactors were acclimated to 25Ω, prior to polarization tests, to avoid power overshoot (Zhu et al., 2013). Polarization curves were then obtained using a single-cycle method where the external resistance was decreased every 20 min at the beginning of a single cycle. 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 polarization curves where they appeared to be most linear near the maximum power densities (Logan, 2008). Components of the internal resistance were analyzed using electrochemical impedance spectroscopy (EIS) and a potentiostat (PC 4/750, Gamry Instruments Inc.; Warminster, PA). Ohmic and charge transfer resistances were obtained by EIS analysis 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 (water side) and 4 PTFE diffusion layers (air side).

Oxygen permeability of 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. Tests for oxygen permeability were conducted using duplicate reactors, with each separator or 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. Results and discussion

3.1. Salinity effects on PVA properties

Increasing the solution salinity decreased water uptake by the PVA separators, but it had no effect on water uptake of the wipe separators (Fig. S1). The PVA separator water uptake ranged from 540% to 840%, with the wipe separators absorbing a relatively constant amount of water (20%) in solutions with different salinities. Despite these changes in water uptake, there was no clear trend in the PVA separator thickness with solution conductivity (Fig. S1). 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 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 varied for the different separator conditions, but did not show any significant trends with salinity. The oxygen mass transfer coefficient for PVA separators in various solutions was constant at 50 ± 10 × 10⁻⁵ cm/s (both DI water and 100 mM PBS). Controls lacking a separator had mass transfer coefficients that ranged from 180 ± 10 × 10⁻⁵ cm/s in DI water, to 210 ± 10 × 10⁻⁵ cm/s in 100 mM PBS (Fig. S1). Wipe separators had oxygen mass transfer coefficients of 80 ± 0 × 10⁻⁵ cm/s (DI water) and 60 ± 0 × 10⁻⁵ cm/s (100 mM PBS). The lower oxygen transfer rates obtained with separators was expected based on previous results (Chen et al., 2012).

3.2. 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 ± 3 mW/m² was the same as that with a PVA separator (339 ± 29 mW/m²) (Fig. 2). There was a 7% reduction in power in this solution using a wipe separator (313 ± 27 mW/m²). The impact of the separator was more apparent at higher conductivities. At a conductivity of 7 mS/cm (50 mM PBS), the maximum power density without a separator increased to 1228 ± 55 mW/m² due to the increased solution conductivity, but the use of a PVA separator reduced power by 28% (889 ± 0 mW/m²), similar to that obtained using wipe separators (30% reduction, 853 ± 60 mW/m²) (Fig. 2). 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/m², using the spaced electrode configuration. Adding a PVA separator decreased the maximum power density by almost 50% (932 ± 76 mW/m²), compared to only a 33% decrease using the wipe separators (1239 ± 19 mW/m²) in this solution (Fig. 2).

The use of the separator allowed operation of the reactors in the SEA configuration. Switching reactors from the SPA to the SEA configuration increased 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 that of the SPA configuration control without a separator. In the 1 mS/cm (5 mM PBS) reactor, power densities versus the control were 32% higher with PVA separators (444 ± 8 mW/m²), compared to an increase of 10% higher with wipe separators (370 ± 34 mW/m²) (Fig. 2). In 7 mS/cm (50 mM PBS) SEA testing, power densities were decreased by 22% with
PVA separators (956 ± 51 mW/m²) and by 29% with wipe separators (877 ± 53 mW/m²) compared to separatorless controls in the SPA configuration (Fig. 2). In 13 mS/cm (100 mM PBS) SEA testing, power densities were lower than the control by 35% with PVA separators (1207 ± 110 mW/m²), and 29% lower with wipe separators (1303 ± 5 mW/m²) (Fig. 2).

The reduction in power production in MFCs with solution conductivity observed here is well known, and consistent with previous reports (Cheng and Logan, 2007). However, it has not been previously shown that a change in solution conductivity can affect the separator itself, and thus alter power production. Using PVA separators in the SEA configuration increased power production by 32% compared to the spaced electrode configuration (no separator) in the 1 mS/cm solution (Fig. 2). This increase was greater than that obtained using wipe separators (10%) in these same configurations. This finding on the impact of the separator at this low solution conductivity is important because a conductivity of 1 mS/cm is typical for a domestic wastewater. Therefore, it is only in laboratory solutions that have high solution conductivities of 7 mS/cm (50 mM PBS) and 13 mS/cm (100 mM PBS) where loss of power density due to separators will be significant. This lack of impact of the separator in the low conductivity solution was due to its insignificant contribution to the total resistance, as explained below.

3.3. 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 SPA configuration lowered power densities in AC catalyst MFCs by 26% versus the separatorless control (519 ± 6 mW/m² versus 702 ± 29 mW/m²) (Fig. 3). Wipe separators reduced power by 30% (488 ± 6 mW/m²). Changing to a SEA 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), versus the separatorless, SPA control. Anode potentials for testing in both SPA and SEA were all similar (Fig. 3), indicating that differences in power production were due to cathodes and separators.

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.

3.4. Spray-on versus cast PVA separators

With cast separators, power densities of 942 ± 43 mW/m² with Pt cathode catalysts were 7% higher than with spray-on separators (873 ± 33 mW/m²) (Fig. 4). Similarly, the power densities of 718 ± 74 mW/m² with cast separators were 8% higher than spray-on separators (664 ± 67 mW/m²) on AC catalyst cathodes. PVA loading on the AC cathodes (19.5 ± 0.1 mg PVA/cm²) was roughly twice as much as the loading on the Pt cathodes (10.0 ± 1.4 mg/cm²) due to the cathode configuration that required the PVA to completely cover the metal mesh. The additional PVA loading had only a small impact on power production. PVA
thickness was not compared between cast and spray-on separators, but the general trend is that a thicker separator yields a higher CE, but results in a lower power density. It is likely that the spray-on separators were thicker than the cast separators due to the inclusion of air bubbles in the application process but this only had a minimal effect on performance due to the greater porosity created by those air bubbles. 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 those obtained with cast separators. Long term studies are also needed to determine if fouling or degradation will decrease performance over time.

3.5. Total internal and ohmic resistances

Total internal resistances were calculated over the relatively linear portions of the polarization data, using the current ranges of: 0.6–1.7 A/m² (5 mM PBS, 1 mS/cm), 2.8–6.9 A/m² (50 mM PBS, 7 mS/cm) and 2.8–9.1 A/m² (100 mM PBS, 13 mS/cm). However, there was no clear trend in changes in total internal resistance relative to the addition of a separator in solutions with these different conductivities (Fig. 5). For example, the internal resistance was calculated to be higher using the PVA separator than no separator in the 5 mM PBS solution, but the opposite was observed for the 50 mM PBS solution. The use of the total polarization curve, rather than the more linear portions of the curve, also did not provide any clear trends in internal resistance with the addition of separators (Fig. 52). The lack of clear trends in internal resistance with the presence of separators was likely due to the lack of clearly linear portions in the polarization curves (Fig. 3), which are needed to use this method of estimating internal resistance.

The impact of the separators on ohmic and charge transfer resistances were also evaluated using EIS data (Fig. 5). In general, adding a PVA separator increased the sum of these resistances, but addition of the wipe separator increased the resistance in 5 mM PBS and decreased these two resistances in the 50 mM PBS. While the sum of the charge transfer and ohmic resistances also did not show consistent trends relative to adding a separator, the impact of the diffusion resistance was not included in this analysis as that component was not reliably estimated in our EIS measurements.

Solution conductivity had a greater impact on power density than the presence or absence of a separator. If all the internal resistance data are plotted relative to power versus the inverse of total resistance, we see the overall expected trend of increased power inversely related to resistance (Fig. 5). Thus, the main impact on the whole cell resistances due to the presence of separators was likely due to changes in diffusion resistances, which could not be reliably estimated using EIS data, or calculated as the difference between total internal resistance and the sum of charge transfer and ohmic resistances (Hutchinson et al., 2011).

3.6. 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. 53). Electrode configuration had little effect on CE values, as there was negligible difference between the SPA and SEA configurations. CE increased with current density, with peak values between 65% and 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. S4–S6).

Spray-on and cast separators had CEs that ranged from 63% to 74%, with the spray-on separators being lower than the cast at peak power densities (Fig. 57). The lower values in this range of
CEs are only slightly higher than CEs measured with the control in both AC (61%, Fig. S3) and Pt (55%, Fig. S5) cathode MFCs.

Cycle times in AC and Pt cathode MFCs increased by 20–50% with the addition of separators, with SEA cycle times being longer than SPA cycle times. Cycle times with spray-on separators were longer than those with cast separators in both AC (34.5 ± 1.5 h versus 27 ± 1.5 h) and Pt (23 ± 2.5 h versus 18.5 ± 2.5 h) 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.

4. 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.

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Appendix A. Supplementary data

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References


