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

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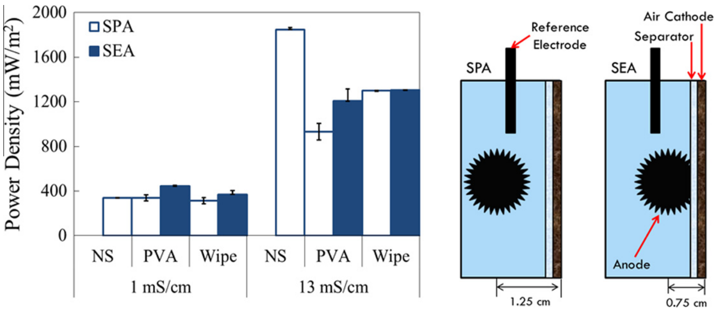
HIGHLIGHTS

- 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



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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/m^2), 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/m^2) 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.

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).

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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/cm^2 10% Pt on Vulcan XC-72 with 33.3 μL/cm^2 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.

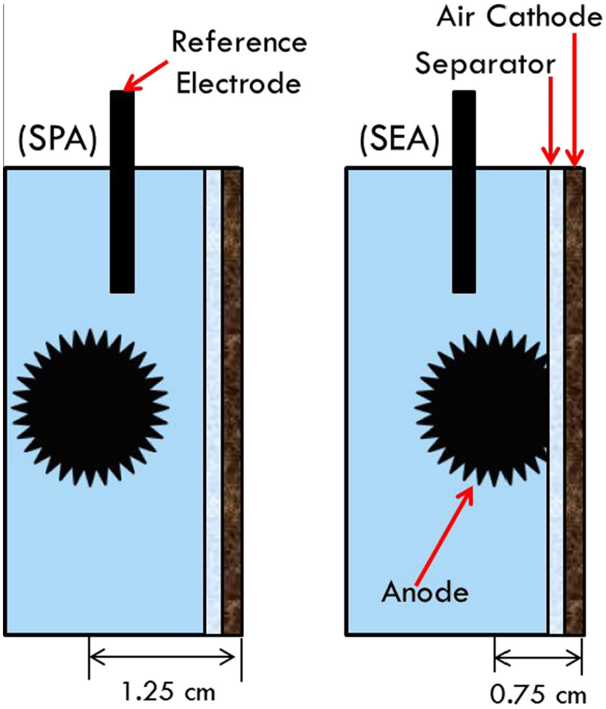

Fig. 1. Configurations for spaced electrode (SPA) and separator electrode assembly (SEA) testing.

MFCs were inoculated with the effluent from MFCs operated for over one year. 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 Na_2HPO_4, 245 mg $NaH_2PO_4 \cdot H_2O$, 31 mg NH_4Cl, 13 mg KCl), to higher conductivities typical of laboratory tests: 7 mS/cm (50 mM PBS; 4.58 g Na_2HPO_4, 2.45 g $NaH_2PO_4 \cdot H_2O$, 0.31 g NH_4Cl, 0.13 mg KCl) and 13 mS/cm (100 mM PBS; 9.16 g Na_2HPO_4, 4.90 g $NaH_2PO_4 \cdot H_2O$, 0.62 g NH_4Cl, 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/cm^2, 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/cm^2 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/cm^2) 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.