



# Development of carbon free diffusion layer for activated carbon air cathode of microbial fuel cells



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## HIGHLIGHTS

- A carbon free membrane diffusion layer showed good resistance to water leakage.
- Casting method provides a simplified fabrication procedure of the cathode diffusion layer.
- The membrane diffusion layer has a lower cost than most other materials.

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## ABSTRACT

The fabrication of activated carbon air cathodes for larger-scale microbial fuel cells requires a diffusion layer (DL) that is highly resistant to water leakage, oxygen permeable, and made using inexpensive materials. A hydrophobic polyvinylidene fluoride (PVDF) membrane synthesized using a simple phase inversion process was examined as a low cost (\$0.9/m<sup>2</sup>), carbon-free DL that prevented water leakage at high pressure heads compared to a polytetrafluoroethylene/carbon black DL (\$11/m<sup>2</sup>). The power density produced with a PVDF (20%, w/v) DL membrane of 1400 ± 7 mW/m<sup>2</sup> was similar to that obtained using a wipe DL [cloth coated with poly(dimethylsiloxane)]. Water head tolerance reached 1.9 m (~19 kPa) with no mesh supporter, and 2.1 m (~21 kPa, maximum testing pressure) with a mesh supporter, compared to 0.2 ± 0.05 m for the wipe DL. The elimination of carbon black from the DL greatly simplified the fabrication procedure and further reduced overall cathode costs.

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## 1. Introduction

Microbial fuel cells (MFCs) are devices that can be used to sustainably harvest energy during wastewater treatment by directly extracting electricity from organic matter using exoelectrogenic bacteria (Ahn and Logan, 2010; Bond et al., 2002; Kim et al., 2007; Logan, 2008; Niessen et al., 2004). Electrons released by exoelectrogenic bacteria on the anode are transferred via an external circuit to the cathode, where typically oxygen is reduced (Cheng et al., 2006; Cheng and Logan, 2011). Air cathodes are used to avoid energy demands needed for aeration of wastewater. Activated carbon (AC) air cathodes are now frequently used in MFCs due to the low price of AC (\$1.4/kg) and its good catalytic activity as AC performs similar to or better than Pt catalysts in these systems (Wang et al., 2013; Yang et al., 2014a). Oxygen reduction is a three-phase reaction, in which protons in the solution phase and oxygen in the air phase combine together on the solid AC catalyst phase (Duteanu et al., 2010; Nie et al.,

2011). Therefore, a high performance AC cathode requires a binder that enables efficient proton transfer to the catalyst site but does not inhibit oxygen transfer. Cathodes must also be made using a diffusion layer (DL) so that water does not leak out of the cell.

Cathode materials need to be durable and inexpensive, and the construction of the cathode should require relatively simple procedures and inexpensive equipment with low energy consumption. The cost of the cathode was estimated to be up to 47% of the total cost of all MFC materials, and therefore it is critical to reduce the cathode cost (Rozendal et al., 2008), as larger-scale MFCs will require high cathode specific surface areas (area per volume of the reactor) (Logan et al., 2015). In order to achieve dual goals of being waterproof and oxygen permeable, however, complex procedures have often been used to fabricate DLs. Polytetrafluoroethylene (PTFE), a fluorinated hydrophobic polymer, is commonly applied to the air side of the cathode to produce a DL with the required hydrophobicity (Cheng and Wu, 2013; Dong et al., 2012b). However, PTFE requires high temperature treatment (i.e. 340 °C) to melt the PTFE and form a uniform waterproof polymer film, which therefore results in a complex process that consumes a lot of energy for heating (Dong et al., 2012b). A PTFE film can be

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very dense, and impede oxygen transport, and thus carbon black (CB) powder is usually added to increase the porosity, although this adds another mixing step to the cathode production process (Dong et al., 2012b). A pressurized process stage may also be required as PTFE is not expandable at room temperature (Dong et al., 2012a). A PTFE/CB diffusion layer with a PTFE loading of 450 g/m<sup>2</sup> was estimated to cost \$11/m<sup>2</sup> (Dong et al., 2012b; Yang et al., 2014b). Therefore, fabrication of larger-scale cathodes using PTFE/CB can be both relatively expensive (compared to other DLs), and complex due to the need for both high temperatures and press equipment. Several other DLs have been developed using other materials, but they leak at relatively low water pressures. For example, an inexpensive polymer DL was made from poly(vinylidene fluoride-co-hexafluoropropylene)/CB (PVDF-HFP/CB) mixture at a low PVDF-HFP loading of 44 g/m<sup>2</sup>, at an estimated materials cost of \$1.1/m<sup>2</sup>, but a cathode with this DL leaked at only 41 ± 0.5 cm of water pressure (Yang et al., 2014b). A cloth wipe DL [cloth coated with poly(dimethylsiloxane), PDMS], which costs only \$0.36/m<sup>2</sup> using 121 g/m<sup>2</sup> PDMS, withstood only 19 ± 1 cm of water pressure (Wei et al., 2012; Yang et al., 2014b). In general, the high cost of polymers and high polymer loadings required to make cathodes waterproof makes it a challenge to balance the need for avoiding water leakage but also ensuring sufficient cathode performance relative to power generation.

PVDF is highly hydrophobic fluorinated polymer that can be easily processed at room temperature (Liu et al., 2011). Recently, a simple phase inversion method was used to fabricate an AC air cathode using PVDF to simultaneous form both the catalyst layer (CL) and the DL, which greatly simplified the fabrication procedure (Yang et al., 2014a). During the phase inversion process a porous film of PVDF was formed on the air side of cathode, and small cathodes were shown to not leak at up to 1.2 m of water pressure (Yang et al., 2014a). However, when larger PVDF cathode were used in subsequent tests (unpublished data), leaks developed at much lower water pressures due to an uneven DL formed by the PVDF that left small holes in the DL. Thus, larger-scale cathodes made with PVDF will require an additional DL in order to avoid water leakage.

In order to prevent water leakage through AC cathodes, the use of an additional and separate PVDF membrane was examined here as a DL that could be easily added to the cathode to make it consistently waterproof at relatively high (~2 m) water pressures. Hydrophobic PVDF membranes have long been used in membrane-based processes such as membrane distillation that allow for gas permeation but not liquid flow (Tomaszewska, 1996; Wang et al., 2008). The PVDF membrane properties have been thoroughly investigated for membranes made with established and commercialized fabrication procedures (Nejati et al., 2015). PVDF membranes are highly resistant to leakage, as shown by a critical liquid entry pressure (LEP) for water of 0.13 MPa for a 15% (w/w) PVDF hollow fiber membrane (Tan et al., 2006). Thus, very large PVDF membranes could be used as a waterproof DL for an AC cathode. The performance of cathodes with DL membranes made with different amounts of PVDF was evaluated here under both abiotic in electrochemical tests, and under biotic conditions in MFCs. The mechanical stability of the DLs was examined relative to leakage using a lab-designed water pressure test system.

## 2. Methods

### 2.1. Membrane fabrication

Membrane casting solutions of 15%, 20% and 25% (w/v) PVDF were prepared by dissolving PVDF powder (~534,000 Da; Sigma

Aldrich) in *N,N*-dimethylacetamide (DMAc, anhydrous, 99.8%, Sigma Aldrich) and vigorously stirring using a stir bar at 60 °C for over 6 h, until the solution became homogeneous and transparent. A slow stirring process was continued for another 2 h to remove bubbles in the solution. The solution was then cast onto a clean glass plate with a doctor blade (Microm II, Gardco, USA) set at a height of 200 μm, and exposed to air for 30 s. The glass plate was then immersed in a distilled water bath, in which the phase inversion process took place. After 10 min, the membrane was transferred to an ethanol/water (1:1, v/v) bath for 6 h and then to a pure ethanol bath for another 24 h (Fig. S1). This solvent exchange procedure was adopted to prevent the shrinkage of the PVDF membranes. The PVDF membrane was then air dried in a fume hood for 10 min to restore hydrophobicity, and stored in sealed plastic bag at room temperature prior to use.

### 2.2. Cathode fabrication and operation

The AC catalyst layer was prepared by mixing AC powder (Norit SX plus, Norit Americas Inc., TX) with PVDF (5% w/v) PVDF and carbon black (CB; Vulcan XC-72, Cabot Corporation, USA) powder at a mass ratio of AC:CB:PVDF = 30:3:5, with an AC catalyst loading of 26.5 mg/cm<sup>2</sup> as previously described (Yang et al., 2014a). The mixture was spread directly onto an 11.3 cm<sup>2</sup> circular section of stainless steel mesh (50 × 50, type 304, McMaster-Carr, USA) with a spatula (except as noted). The mesh with the catalyst was then immersed into deionized (DI) water for 15 min at room temperature to leach out DMAc solvent, and air dried in a fume hood overnight prior to use. The final cathode was produced by attaching the DL onto the CL (fixed by rubber O ring) with the dense skin layer facing the CL. The cathode was positioned in the reactor with the DL facing the air side and CL towards the solution side. A PDMS/CB wipe DL [cloth coated with PDMS/CB mixture] was used as an established control as it has been used in many other studies (Luo et al., 2011; Zhang et al., 2010); it was prepared as previously described (Wei et al., 2012).

The cathodes were operated in cubic single-chamber MFCs (except as noted) constructed from a Lexan block 4 cm in length, with an inner chamber diameter of 3 cm (Logan et al., 2007). The anodes were graphite fiber brushes (2.5 cm in both diameter and length, heat treated at 450 °C in air for 30 min) placed horizontally in the center of MFC chambers (Logan et al., 2007). Anodes were acclimated by operation for over one year in a previous MFC at a constant temperature (30 °C), with a fixed external resistance (1000 Ω). The medium contained 1 g/L sodium acetate dissolved in 50 mM phosphate buffer solution (PBS; Na<sub>2</sub>HPO<sub>4</sub>, 4.58 g/L; NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, 2.45 g/L; NH<sub>4</sub>Cl, 0.31 g/L; KCl, 0.31 g/L; pH = 6.9; conductivity of κ = 6.9 mS/cm) amended with 12.5 mL/L minerals and 5 mL/L vitamins (Yang et al., 2014a).

### 2.3. Cathode performance characterization

Electrochemical cathode tests were conducted in a two-chamber electrochemical cell assembled by bolting two 2-cm wide cubes separated by an anion exchange membrane (AEM; AMI-7001, Membrane International Inc., USA). The counter electrode was a 7 cm<sup>2</sup> diameter platinum plate. An Ag/AgCl reference electrode (RE-5B, BASi, West Lafayette, IN; +0.209 V vs a standard hydrogen electrode, SHE) was placed in the cathode chamber close to cathode. Electrochemical measurements were conducted with a multichannel potentiostat (VMP3 Workstation, Biologic Science Instruments, USA) in a constant temperature room at 30 °C. A step current method was used to obtain the cathode polarization curve by applying lower currents (0 mA, 1 mA, 2 mA, and 3 mA) for 30 min and higher currents (4 mA, 5 mA, 6 mA, 7 mA, 8 mA, 9 mA

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