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Single-Step Fabrication Using a Phase Inversion Method of Poly(vinylidene fluoride) (PVDF) Activated Carbon Air Cathodes for Microbial Fuel Cells

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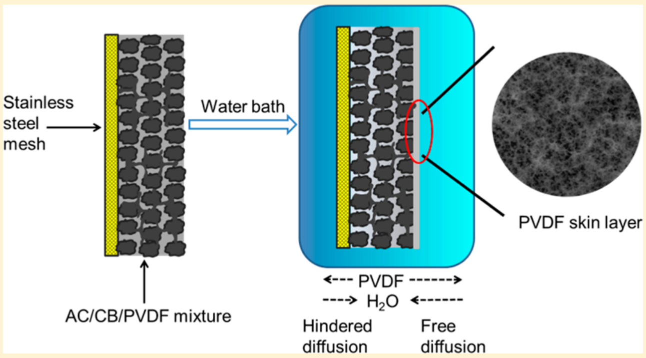
Ⓢ *Supporting Information*



ABSTRACT: Air cathodes used in microbial fuel cells (MFCs) need to have high catalytic activity for oxygen reduction, but they must also be easy to manufacture, inexpensive, and watertight. A simple one-step, phase inversion process was used here to construct an inexpensive MFC cathode using a poly(vinylidene fluoride) (PVDF) binder and an activated carbon catalyst. The phase inversion process enabled cathode preparation at room temperatures, without the need for additional heat treatment, and it produced for the first time a cathode that did not require a separate diffusion layer to prevent water leakage. MFCs using this new type of cathode produced a maximum power density of 1470 ± 50 mW m^{-2} with acetate as a substrate, and 230 ± 10 mW m^{-2} with domestic wastewater. These power densities were similar to those obtained using cathodes made using more expensive materials or more complex procedures, such as cathodes with a polytetrafluoroethylene (PTFE) binder and a poly(dimethylsiloxane) (PDMS) diffusion layer, or a Pt catalyst. Even though the PVDF cathodes did not have a diffusion layer, they withstood up to 1.22 ± 0.04 m of water head (~12 kPa) without leakage, compared to 0.18 ± 0.02 m for cathodes made using PTFE binder and PDMS diffusion layer. The cost of PVDF and activated carbon (\$3 m^{-2}) was less than that of the stainless steel mesh current collector (\$12 m^{-2}). PVDF-based AC cathodes therefore are inexpensive, have excellent performance in terms of power and water leakage, and they can be easily manufactured using a single phase inversion process at room temperature.

■ INTRODUCTION

Microbial fuel cells (MFCs) are being developed to recover energy during wastewater treatment by generating electricity from organic matter using exoelectrogenic bacteria.[1−5] Air cathodes are used in MFCs to avoid the energy demands needed for aerating wastewater.[6,7] Platinum catalysts promote high oxygen reduction reaction activity in MFC cathodes, but practical MFC applications on larger scales will need to avoid using cathodes containing precious metals or other expensive materials. Activated carbon (AC) has been shown to be an effective catalyst for oxygen reduction in MFCs, as it produces power densities similar to cathodes made with Pt, the performance of AC is relatively well maintained over time[6,8,9] and AC is inexpensive (~\$1.4 kg^{-1}). Different temperature and pressure treatments of AC have been used to further enhance cathode performance, but they increase energy input and complicate fabrication procedures, resulting in higher cost materials.[10]

In addition to having good performance with inexpensive materials, cathodes used in MFCs must be watertight so that they do not leak when used in larger-scale reactors, and they must be easy to mass produce. Polytetrafluoroethylene (PTFE) is often used as a catalyst binder, but some of these types of cathodes cannot withstand high water pressures. For example, cathodes made by a common batch-pressing method using a PTFE/AC mixture on stainless steel mesh current collector, with a diffusion layer of poly(dimethylsiloxane) (PDMS)/carbon black (CB) to minimize water leakage, produced a good

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maximum power density of 1310 ± 70 mW m^{-2}.[11] However, these cathodes leaked with less than one meter head of water pressure.[12] Cathodes made by a rolling-press method using the same binder but with a PTFE/CB diffusion layer on stainless steel mesh current collector had similar power densities but much improved water retention (up to 3 m of water head).[13,14] The PTFE used in the diffusion layer ($9.4 m^{-2}), is relatively expensive as it costs almost as much as the stainless steel current collector (~$12 m^{-2}). The sintering process needed for the diffusion layer (340 °C for 25 min)[12,13] also makes PTFE-based cathodes difficult to mass produce. Poly(vinylidene fluoride) (PVDF) has previously been used in making cathodes, but only as a diffusion layer added on to the air-side of a cathode. Thus, the cathode itself was made using a paste and press type of process, with the diffusion layer added following cathode construction.[12]

A new type of AC cathode was developed in this work using a phase inversion process with a PVDF binder. This new preparation procedure enabled cathode production in a one-step process, without the need for further heat-treatment or the addition of a separate diffusion layer. PVDF is a semicrystalline fluoropolymer that exhibits good physical stability and chemical resistance. It has been used as a binder material in the electrodes of batteries and fuel cells[15,16] and capacitors,[17] but it has always been prepared for these applications as a paste. There has only been one report on the use of PVDF in an MFC cathode, but the cathode was prepared using a typical "mix and paste" approach, rather than a phase inversion approach used here, and the peak power density was relatively low (286 mW m^{-2}) for an air cathode under the tested conditions.[18] PVDF is also used to make microfiltration and ultrafiltration membranes using a diffusion-induced, phase inversion method.[19−21] The phase inversion process occurs at room temperature, making membrane production simple and flexible, allowing large-scale production of low-cost membranes.[19] During the phase inversion process in a water bath, the PVDF diffuses out from the catalyst mixture and precipitates on the cathode surface, forming a thin but dense hydrophobic PVDF skin layer on the surface that is relatively waterproof. Therefore, making a cathode with PVDF by a phase inversion process was hypothesized to be able to accomplish both binding of the catalyst to the current collector and formation of a polymer layer that could withstand high water pressure to avoid the need for a separate diffusion layer. The low cost of the polymer and the ease of the phase inversion process would make the production of the MFC cathodes both simple and inexpensive.

■ MATERIALS AND METHODS

Cathode Fabrication and Operation. PVDF solutions with different concentrations of 5%, 7.5%, and 10% (w/v) were prepared by dissolving PVDF powder (~534 000 Da; Sigma-Aldrich) in *N,N*-dimethylacetamide (DMAc), with vigorous stirring using a stir bar at room temperature (23 ± 1 °C) for over 8 h to completely dissolve the polymer. AC powder (Norit SX plus, Norit Americas Inc., TX) was applied at an optimum AC loading of 26.5 mg cm^{-2}, based on previous experiments. Catalyst mixtures were prepared with different PVDF loadings (all mass ratios) of (1) 8.8 mg cm^{-2}, AC/CB (Vulcan XC-72, Cabot Corporation, USA)/PVDF (10% as prepared) = 30:3:10; (2) 6.6 mg cm^{-2}, AC/CB/PVDF (7.5%) = 30:3:7.5; (3) 4.4 mg cm^{-2}, AC/CB/PVDF (7.5%) = 30:3:5. The mixtures were spread directly onto an 11.3 cm^2 circular section of stainless steel mesh (50 × 50, type 304, McMaster-Carr, USA) with a spatula (except as noted). The cathodes were then immersed into deionized (DI) water for 15 min at room temperature to induce phase inversion. Cathodes were then air-dried in a fume hood for >6 h and stored in DI water prior to tests. The performance of the PVDF cathodes was compared to controls made with an AC (26.5 mg cm^{-2}), CB, and a PTFE (60%) emulsion at a AC/CB/PTFE ratio of 9:1:0.9 (w/w) with a PDMS (12.1 mg cm^{-2}) wipe diffusion layer.[11]

Cubic single-chamber MFCs were used in all tests (except as noted). They were constructed from a Lexan block 4 cm in length, with an inside cylindrical chamber having a diameter of 3 cm.[22] The anodes were graphite fiber brushes (2.5 cm in both diameter and length, heat treated at 450 °C in air for 30 min) that were placed horizontally in the middle of the MFC chambers.[22] Anodes were fully acclimated by operation for over one year at a constant temperature (30 °C) and a fixed external resistance (1000 Ω). The medium contained 1 g L^{-1} sodium acetate dissolved in 50 mM PBS buffer amended with 12.5 mL L^{-1} minerals and 5 mL L^{-1} vitamins (except as noted).

In larger-scale MFC tests, PVDF cathodes (7 cm × 10 cm, with 5 cm × 7 cm exposed to the air) were constructed and tested in a multibrush anode reactor (130 mL) fed with domestic wastewater as previously described (see also Figure S3, Supporting Information).[23] Carbon cloth-based cathodes with a platinum catalyst (ETEK C1-10 10% Pt on Vulcan XC-72) and a PTFE diffusion layer was prepared as previously described,[24] and used as a Pt catalyst control.

Measurements. MFC power curves were obtained by decreasing the external resistance from 1000 through 500, 200, 100, 75, 50, to 20 Ω at 20 min intervals. Coulombic efficiencies were calculated at a resistance of 1000 Ω based on changes in chemical oxygen demand (COD) concentration, as previously described. Cathode polarization measurements were conducted with new cathodes in a two chamber electrochemical cell (2 cm length, 3 cm diameter, with a Nafion membrane and Pt counter electrode) using a step current method, with a series of different set currents after the cell was acclimated under open circuit conditions for 1 h. The lower currents (1, 2, 3, and 4 mA) were applied for 1 h, and the higher currents (5, 6, 7, 8, 9, and 10 mA) were applied for 30 min to obtain steady-state conditions. A fully assembled reactor was used to determine the maximum water pressure (in cm of static head) that would produce water leakage through the cathodes as previously described.[12] A rubber ring covered with at least three layers of Teflon tape was used to seal the edge during the pressure test. All tests were conducted with duplicate cathodes.

■ RESULTS AND DISCUSSION

Cathode Performance Using Acetate. A maximum power density of 1470 ± 50 mW m^{-2} was produced by MFCs with PVDF cathodes (8.8 mg cm^{-2}) with the SS mesh facing the water side and the PVDF-AC catalyst layer facing the air side of the cell, using acetate as the fuel (Figure 1A). A similar power density (1450 ± 10 mW m^{-2}) was produced using a cathode made with a PTFE binder, but this cathode required a diffusion layer to avoid water leakage. The columbic efficiency of the PTFE cathode was 20 ± 5%, which was higher than PVDF or reversed PVDF cathode (both had CEs of 13 ± 1%). Although the decrease in the CE results in less production of electricity from the substrate, this can lead to faster removal of the organic matter, which can be desirable as it can reduce the time needed for wastewater treatment.[25] Future studies employing separators could be conducted to increase CE while

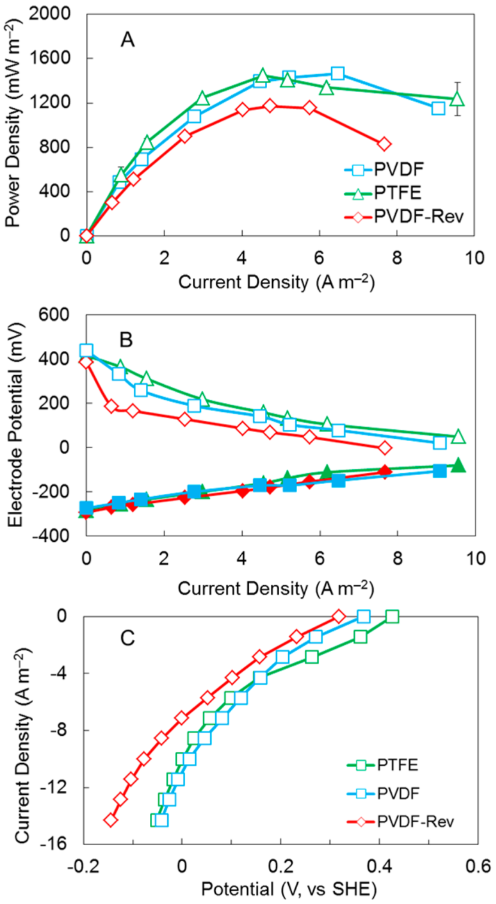

Figure 1. MFC tests: (A) power density curves for a PVDF cathode, reversed-side PVDF cathode, and a PTFE cathode; (B) electrode potentials (solid symbols, anode potentials; open symbols, cathode potentials). (C) Current−voltage (polarization) curves for the same cathodes in an abiotic electrochemical cell.

minimizing biofouling.[26] Using less PVDF for the cathode (4.4 or 6.6 mg cm^{-2}) did not alter power production (Figure S1, Supporting Information). When the PVDF cathode orientation was reversed, with the PVDF-AC layer in contact with the electrolyte (SS mesh on the air side), the maximum power density decreased to 1170 ± 10 mW m^{-2} (Figure 1A). The change in performance was due to more negative cathode potentials, as the anode potentials were not altered by changing the cathode orientation (Figure 1B). The reduction in power when the catalyst faced the electrolyte showed that the cathode composition was asymmetric. During the phase inversion process, it was expected that a more hydrophobic skin layer would form on the cathode. This type of layer would therefore hinder ion diffusion to and from the catalyst surface, which would reduce cathode performance.

Abiotic electrochemical tests with the cathodes similarly showed improved performance of the PVDF cathodes when the catalyst layer was exposed to the air side of the cell, compared to the catalyst layer facing the electrolyte (Figure 1C). Similar overpotentials were obtained using the PVDF cathode and the PTFE cathode with a diffusion layer (Figure 1C).

Water Pressure Resistance. The PVDF cathodes showed good water pressure resistance, tolerating a water pressure head of 1.22 ± 0.04 m (∼12 kPa) for the cathode with 8.8 mg cm^{-2} PVDF loading before showing any water leakage (Figure 2). In contrast, the PTFE cathode showed water leakage at a very low water height of 0.18 ± 0.02 m, despite the use of a diffusion layer. Further evidence of the asymmetric nature of the PVDF cathode was shown by water leakage at a lower water height of 1.02 ± 0.02 m when the cathode orientation was reversed, and the catalyst layer was oriented toward the electrolyte.

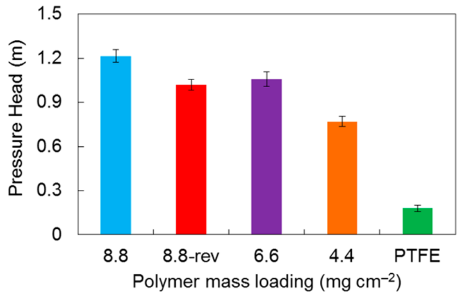

Figure 2. Water pressure resistance of PVDF cathodes with different polymer loadings (8.8, 6.6, and 4.4 mg cm^{-2}) with the polymer layer facing the air, compared to the reversed orientation of a PVDF cathode (8.8 mg cm^{-2}) and a PTFE cathode.

A reduction in the PVDF loadings resulted in water leakage at lower water heights of 1.06 ± 0.06 m (6.6 mg cm^{-2}) and 0.77 ± 0.04 m (4.4 mg cm^{-2}) compared to higher PVDF loadings. Cathodes with lower PVDF loadings likely had less tolerance to water pressure due to formation of a less dense PVDF network (Figure S2, Supporting Information), even though power production was not affected by the polymer loading (Figure S1, Supporting Information). Thus, the higher PVDF loading of 8.8 mg cm^{-2} was required to avoid water leakage.

MFC Performance with Larger Cathodes and Domestic Wastewater. To demonstrate the scalability of the PVDF cathodes and their suitability for use with actual wastewaters, larger PVDF cathodes were tested in multibrush anode reactors.[23] The maximum power density with the domestic wastewater was 230 ± 10 mW m^{-2} (Figure S4, Supporting Information). This lower power density is consistent with previous reports showing that power production is lower with a domestic wastewater compared to more optimal conditions obtained using acetate in well buffered solutions. This power density was the same as that produced using carbon cloth cathodes with a platinum catalyst (PTFE as diffusion layer) in a separator-free configuration. No water leakage was observed in tests using these larger sized PDVF cathodes, confirming the stability of the process when making larger cathodes. Additional tests with these cathodes have shown that there was no water leakage, even after two months of operation (data not shown).

Materials and Cost Analysis. The PVDF cathodes not only tolerate relatively higher water pressures, but they also are economical to manufacture due to the use of relatively small amounts of inexpensive polymer (Table 1). The overall cost of the PVDF cathode was \$15 m^{-2}, but \$12 m^{-2} of this cost is for the stainless steel mesh. The catalyst layer of the best performing PVDF cathodes required 88 g m^{-2} of polymer, compared to a range of 30 g m^{-2} (PTFE) to 100 g m^{-2} (Nafion) for other cathodes. However, the PVDF cathode did not have a diffusion layer, which greatly reduced polymer requirements. For example, while the cathode prepared by a rolling method used only 45 g m^{-2} for the catalyst layer, 450 g m^{-2} of PTFE was used for the diffusion layer (Table 1), resulting in an overall much higher materials cost. Although the cathode made using a pressing method with PTFE and PDMS cost only \$14 m^{-2} for the materials, the water tolerance was

Table 1. Material and Cost Analysis of Current Activated Carbon Cathodes and Pt/C Cathode[a]

	catalyst layer (g m^{-2})				diffusion layer (g m^{-2})		current collector (\$ m^{-2})						
cathode	Pt	AC	polymer	CB	CB	polymer	carbon cloth	SS mesh	nickel foam	max. power (mW m^{-2})	pressure tolerance (m)	cost (\$ m^{-2})	ref
phase inversion		265	88 (PVDF)	26.5				12		1470 ± 50	1.22 ± 0.04	15	this study
rolling		273	45 (PTFE)		191	450 (PTFE)		12		1355 ± 26	3	25	13,14
		200	60 (PTFE)	8	60	454 (PTFE)			20	1190 ± 50		33	6
pressing		270	30 (PTFE)		31	121 (PDMS)		12		1310 ± 70	0.18 ± 0.02	14	11
brushing	5		100 (Nafion)		15.6	555 (PTFE)	625			1320	1.2 ± 0.07	1814	6,12

[a] Cost estimations were all based on commercial price of materials in bulk quantity, and unit price is provided in Table S1, Supporting Information.

relatively poor (0.18 m) compared to that of the PVDF cathode (1.22 m).

Outlook. Inexpensive PVDF cathodes, fabricated via a simple one-step phase inversion process, withstood high water pressures while achieving good power performance. The cathode fabrication was accomplished by spreading the AC/PVDF/CB mixture onto a stainless steel mesh, followed by immersion in water, making the procedure simple yet efficient compared to previous methods requiring high temperature heat treatments.[13] The durability of the cathodes will now need to be further examined over time, but preliminary tests have shown that the cathodes can produce power levels comparable to other AC or Pt catalyst cathodes, with both acetate and wastewater solutions, and that they do not leak even after two months of operation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Four figures and one table. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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