Increased performance of single-chamber microbial fuel cells using an improved cathode structure

Shaoan Cheng a, Hong Liu b, Bruce E. Logan a, *

a Department of Civil and Environmental Engineering, The Pennsylvania State University, H2E Center, 212 Sackett Building, University Park, PA 16802, USA
b Department of Biological and Ecological Engineering, Oregon State University, 116 Gilmore Hall, Corvallis, OR 97331, USA

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Abstract

Maximum power densities by air-driven microbial fuel cells (MFCs) are considerably influenced by cathode performance. We show here that application of successive polytetrafluoroethylene (PTFE) layers (DLs), on a carbon/PTFE base layer, to the air-side of the cathode in a single chamber MFC significantly improved coulombic efficiencies (CEs), maximum power densities, and reduced water loss (through the cathode). Electrochemical tests using carbon cloth electrodes coated with different numbers of DLs indicated an optimum increase in the cathode potential of 117 mV with four-DLs, compared to a <10 mV increase due to the carbon base layer alone. In MFC tests, four-DLs was also found to be the optimum number of coatings, resulting in a 171% increase in the CE (from 19.1% to 32%), a 42% increase in the maximum power density (from 538 to 766 mW m⁻²), and measurable water loss was prevented. The increase in CE due is believed to result from the increased power output and the increased operation time (due to a reduction in aerobic degradation of substrate sustained by oxygen diffusion through the cathode).

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1. Introduction

A microbial fuel cell (MFC) uses bacteria to generate electricity from the oxidation of organic matter [1–8]. Bacteria capable of electricity generation have been enriched from domestic wastewater [6], ocean sediments [9], animal wastes [10], and anaerobic sewage sludge [11,12]. Electricity generation is supported by a range of biodegradable substrates, including glucose, acetate, lactate, butyrate, ethanol and organic matter in wastewater [5,13–16]. Several factors affect MFC performance including the microbial inoculum, chemical substrate (fuel), type of proton exchange material (and the absence of this material), cell internal and external resistance, solution ionic strength, electrode materials, and electrode spacing [3–5,13–20]. The cathode is an important factor in the performance of a MFC due to the poor kinetics of oxygen reduction reaction in a neutral pH medium [16,21]. Using more effective catholytes than oxygen, such as ferricyanide, can substantially increase power output [12,17,19]. However, ferrocyanide must be replaced after ferricyanide is converted to ferrocyanide, while systems using oxygen can be continuously operated and therefore, the reaction is self sustaining. Furthermore, a proton exchange membrane (PEM) must be used to prevent ferricyanide from diffusing into the anode chamber. In air-cathode MFCs, removing the PEM increases the maximum power density [5]. Although Pt is an expensive component for MFCs, its construction, it has recently been shown that Pt loading on the water side of an air cathode can be as low as 0.1 mg cm⁻² without affecting power densities, and that Pt can be replaced by less expensive alternatives such as Co-tetramethyl phenylporphyrin (CoTMPP) with only small changes in MFC performance [15,22].
The coulombic efficiency (CE) in MFCs that use oxygen varies widely, ranging from 9–12% for single chamber systems lacking a PEM, to 40–90% for two-chamber systems with aqueous cathodes and a PEM using glucose as substrate [5,21,23]. One of the main reasons for low CEs is loss of substrate due to bacterial oxidation using oxygen as an electron acceptor. Oxygen flux through the air cathode is 3.7 times higher than that through the same cathode containing a Nafion PEM [5]. In addition, there can be evaporative losses of water from the chamber at the cathode surface, which produce a gas phase in the anode chamber. The amount of oxygen needed at the MFC cathode is small compared to that required for hydrogen fuel cells, due to the low current densities (0.03–1.5 mA cm⁻²) [19] in MFCs. Therefore, we hypothesized that power might not be adversely affected by a cathode coating that could reduce water loss, as long as the coating did not completely hinder oxygen diffusion to the Pt catalyst. Such cathode coatings, called diffusion layers (DLs), have been used to improve cathode performance in other types of fuel cells, but these systems operate under much different conditions of pH (pH 7, compared to traditional hydrogen/oxygen fuel cells which can use highly acid or alkaline conditions [24,25]), temperature (20–30 °C, compared to 50–1000 °C), current density (usually <2 mA cm⁻², compared to 100 mA cm⁻²), and water concentration at the cathode (water saturation of the cathode, compared to systems that use a solid electrolyte).

DLs have not been previously investigated for air cathode MFCs. A DL that is hydrophobic can also potentially improve performance by decreasing the water flooding of the cathode. In this paper, we demonstrate that a cathode containing a hydrophobic layer (to reduce water losses) on the air-side of the cathode can significantly increase the coulombic efficiency and power density of an MFC, and reduce water loss through the cathode. Power output and coulombic efficiency of MFCs containing a single carbon/polytetrafluoroethylene (PTFE) base layer was compared to reactors containing additional PTFE DLs.

2. Materials and methods

2.1. MFC electrodes

Anodes were made of non-wet proofed carbon cloth (type A, E-TEK), while cathodes were wet-proofed (30%) carbon cloth (type B, E-TEK). Cathodes were either used as supplied by the manufacturer (No DL), or they were coated on the air-facing side of the cathode with a carbon/PTFE layer (T₄) or one or more additional DLs consisting of PTFE (Fig. 1). The carbon base layer was prepared by applying a mixture of carbon powder (Vulcan XC-72) and 30 wt% PTFE solution (20 µl/mg of carbon powder) onto one side of the carbon cloth, air-drying at room temperature for 2 h, followed by heating at 370 °C for 0.5 h. The carbon loading in this DL was chosen to be 2.5 mg cm⁻² based on a previous report [26]. Additional DLs were made by brushing a PTFE solution (60 wt%) onto the coating side, followed again by drying at room temperature and heating at 370 °C for 10 min. DLs were applied for 2, 4, 6, 8 times (4 mg cm⁻² of PTFE per coating), and are denoted here as T₂, T₄, T₆, and T₈, respectively. Pt catalyst (0.5 mg cm⁻²) was then applied to the water-facing side of the carbon cloth as previously described using Nafion as a binder [15]. In some experiments, a commercially available cathode (CC) containing 0.5 mg cm⁻² Pt (E-TEK) was used for comparison to the laboratory-prepared cathodes. All electrodes had a projected surface area of 7 cm².

2.2. MFC tests

MFC tests were conducted using a single chamber device constructed as previously described [5] and operated with a 1000 Ω external resistor except as noted. MFCs were inoculated with domestic wastewater (pH of 7.3–7.6, chemical oxygen demand (COD) of 200–300 mg L⁻¹) collected from the primary clarifier overflow at the Pennsylvania State University Wastewater Treatment Plant. The wastewater was replaced 3–5 times (i.e., over 72–120 h) to allow a biofilm to form on the anode surface, before the solution was switched to a solution containing glucose (500 mg L⁻¹) and a phosphate buffered nutrient medium (PBM) containing: NH₄Cl (0.31 g L⁻¹); NaH₂PO₄·H₂O (4.97 g L⁻¹); Na₂HPO₄·H₂O (2.75 g L⁻¹); KCl (0.13 g L⁻¹), and a metal (12.5 mL) and vitamin (12.5 mL) solution [27]. The chamber was refilled each time the voltage decreased to less than 20 mV forming one complete cycle of operation. Polarization curves were used to obtain the maximum power density by varying the external resistance using a resistor box (RS-500, Elenco Electronics). All tests were conducted in a 30 °C temperature-controlled room.
2.3. Electrochemical cell tests

Cathode potentials were measured in PBM in the absence of microorganisms by chronopotentiometry using a PC4/750 potentiostat (Gamry Instruments). Measurements were made at different current densities in a three-chambered electrochemical cell containing a working electrode (cathode electrode with 0.64 cm² projected surface area), a counter electrode (platinum plate with a projected surface area of 2 cm²), and an Ag/AgCl reference electrode (EE009 no leak electrode, Cypress Systems) as previously described [15]. The potential for each current was obtained by applying a constant current for 60 min. These potentials were then plotted against current densities to evaluate the performance of cathodes, where a higher potential at same current density indicates improved cathode performance.

2.4. Analytical measurements and calculations

The concentration of organic matter in the MFC was measured as COD using Standard Methods [28]. All samples were filtered through a 0.22 μm (pore diameter) membrane filter prior to COD measurements. COD removal was calculated as $E_{COD} = \left[ (COD_{in} - COD_{out}) / COD_{in} \right] \times 100\%$, where COD$_{in}$ is the influent COD and COD$_{out}$ the effluent COD.

Cell voltage was recorded using a multimeter and a data acquisition system (Model 2700, Keithly). Current density was calculated as $i = I/A = V/RA$, where $V$ (mV) is the voltage, $I$ (mA) the current density in electrochemical tests, $R$ (Ω) the external resistance, and $A$ (cm²) the projected surface area of the studied electrode. Power density was calculated according to $P$ (mW m⁻²) = $10 \times iV$ (10 needed for the given units). Coulombic efficiency was calculated as $CE = C_{th}/C_{p} \times 100\%$, where $C_{p}$ is the total coulombs calculated by integrating the current over time, and $C_{th}$ is the theoretical amount of coulombs available based on the COD removed in the MFC.

Oxygen permeability of a cathode was characterized in terms of a mass transfer coefficient, $k$ (cm s⁻¹), calculated from a mass balance on oxygen concentration in the anode chamber over time, as

$$k = \frac{v}{At} \ln \left( \frac{C_{s} - C}{C_{s}} \right), \quad (1)$$

where $v$ is the volume of the chamber (28 ml), $A$ the cross-sectional area (7 cm), $C_{s}$ the bulk oxygen concentration of the solution at time $t$, and $C_{s}$ the concentration at the air side of the cathode (assumed to be the saturation concentration of oxygen in water, or 7.8 mg L⁻¹). The diffusion coefficient ($D$) for the cathode can be estimated as $k = D/L$, assuming a constant cathode thickness of $L = 0.7$ mm.

Oxygen concentrations were measured using a non-consumptive dissolved oxygen probe (FOXY, Ocean Optics, Inc., Dunedin, FL) fixed in the center of the anode chamber filled with deionizer water. Before measurement, the water used for MFC tests was degassed by stirring in an anaerobic box (Coy Scientific) for at least 48 h to remove oxygen. Water was added to the anode chamber, and dissolved oxygen concentrations were recorded continuously for 5 h after exposure to air.

3. Results

3.1. Cathode performance in electrochemical cell tests

Cathodes were initially evaluated on the basis of final potentials in electrochemical tests (no bacteria). As expected, application DLs had no effect on the open circuit potential (OCP) of the cathodes, with all values equal to $302 \pm 4$ mV (vs Ag/AgCl). The application of the initial carbon base layer to the cathode ($T_0$) increased the potential by less than 10 mV, compared to a plain cathode (No DL) (Fig. 2). Application of successive PTFE DLs increased the cathode potentials for up to four-PTFE coatings ($T_4$), but additional DLs ($T_6$ and $T_8$) decreased the current density in the region of 0.1–1 mA cm⁻². The maximum potential difference between the $T_4$ cathode and the cathode lacking a DL was 117 mV at 0.6 mA cm⁻². The potentials produced by the commercially available cathode (CC) were lower than those obtained using the other cathodes.

3.2. MFC performance

The performance of the cathodes was examined in MFC tests following acclimation and steady state performance of the system. The maximum power density of the MFC with a cathode lacking a diffusion layer (No DL) was $538 \pm 6$ mW m⁻². Coating the cathode with the initial carbon layer ($T_0$) increased the maximum power density by 15% to $620 \pm 5$ mW m⁻², but the overall CE decreased.

![Fig. 2. Cathode potential as a function of current density measured in the electrochemical cell for the cathodes with different diffusion layers: without diffusion layer (No DL); carbon layer only ($T_0$); carbon layer with 2 ($T_2$), 4 ($T_4$), 6 ($T_6$) and 8 PTFE layers ($T_8$); commercially available cathode (CC). The inset shows the potential relative to the CC cathode.](image-url)
slightly from 19.1% to 17.9%. When additional DLs were applied, the maximum power density increased to 766 mW m\(^{-2}\) for the cathode containing four DLs (Fig. 3A). This power density is 42% greater than that obtained without a DL, and is 62% higher than that obtained with the commercially prepared cathode. Further increasing additional DLs reduced the maximum power density, resulting in 633 ± 7 mW m\(^{-2}\) for the 8-PTFE DL coating.

The CE increased with successive application of DLs. The CE ranged from 13–20% in the absence of the DL, and increased to 20–27% for the four DLs (Fig. 3B). The CE continued to increase with successive DLs, ranging from 21% to 32% for the 6 DLs to a maximum of 32% for the 8 DLs. The CE for the 8 DLs is about twice that obtained using the commercial cathode. Application of the DLs had no significant effect on COD removal, which ranged from 90% to 95%.

3.3. Oxygen permeability of the cathode

Oxygen diffusion into the anode chamber was reduced through the application of two or more DLs (Fig. 4). The oxygen mass transfer coefficients for the cathode lacking a DL was 3.3×10\(^{-3}\) cm s\(^{-1}\) (Table 1). This value increased slightly (by 18%) with the application of just the carbon layer (T\(_0\)) to 3.9×10\(^{-3}\) cm s\(^{-1}\), perhaps as a result of the heat treatment needed to apply the coating. Successive DL layers decreased the oxygen mass transfer coefficient, to a minimum of 0.6×10\(^{-3}\) cm s\(^{-1}\) for the 8 DL (T\(_8\)). These values for mass transfer coefficients are comparable to those previously reported [29].

### Table 1

<table>
<thead>
<tr>
<th>Cathode</th>
<th>(k \times 10^{-3}) (cm s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>No DL</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>T(_0)</td>
<td>3.9 ± 0.7</td>
</tr>
<tr>
<td>T(_2)</td>
<td>2.9 ± 0.3</td>
</tr>
<tr>
<td>T(_4)</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>T(_6)</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>T(_8)</td>
<td>0.6 ± 0.1</td>
</tr>
</tbody>
</table>

3.4. Water loss

Water loss was greatly reduced by application of DLs to the cathode. Water loss in the MFC using a cathode without DLs (T\(_0\)) at 30 °C was 20% per day. Only 5% of the water was lost using a MFC with 2 DLs, and water loss was not detectable in the MFC with 4 DLs, indicating 4 DLs is optimal for reducing water loss. With a commercial cathode (CC), the water loss was 25% per day. Thus, application of DLs is important for ensuring a consistent water level in the MFC.

4. Discussion

The addition of DLs increased the maximum power and the CE. Four DLs added to a carbon/PTFE base was found to be optimal for increasing power generation by 42% (to 766 mW m\(^{-2}\)) as further DLs decreased the maximum power output. DLs consistently increased CE, with 8 DLs increasing CE by 32%. This increase in CE was 171% higher than that obtained using the same cathode lacking a DL, and 200% higher than that obtained using a commercially available cathode with pre-loaded catalyst.

The application of the DL in a hydrogen fuel cell increases power by improving water and gas transfer [26,30]. We found here that application of the base carbon layer increased the oxygen mass transport coefficient increased by 11%. This increase in oxygen diffusion is useful in a hydrogen fuel cell, but not in a MFC as substrate
loss to aerobic oxidation of the substrate can reduce overall CE. However, an increase in power can partially offset the increased oxygen flux as a higher power density will reduce the overall time needed to fully degrade the substrate. Additional layers of PTFE improved the CE primarily by restricting the oxygen flux into the system, as shown by a reduction in the oxygen mass transfer coefficient (Table 1). The increase in CE can be seen from the larger area under the curve in Fig. 5 for a MFC cycle of operation with a DL, versus a cycle of operation without a DL. The reduction in oxygen flux to the MFC cathode is not necessarily a problem because the current density in a MFC (relative to that in a hydrogen fuel cell) is low, and therefore the oxygen needed is correspondingly low. Therefore, the reduction in oxygen flux that occurred with application of up to four DLs did not limit power generation, and in fact improved both power generation (shown by a higher maximum voltage in Fig. 5) and CE. We think the increased power density produced by the DL resulted from an improved three-phase interface for oxygen reduction by the Pt catalyst. However, the reduction in oxygen transfer eventually had an adverse effect on power generation as more than 4 layers decreased the power output at current densities >0.1 mA cm$^{-2}$ (Figs. 2 and 3A).

Further increases in the maximum power densities produced by MFCs should be possible using these DLs in MFCs with higher current densities. Electrochemical tests indicated that the greatest improvements in the cathode occurred at a current density of $\sim 0.6$ mA cm$^{-2}$ (Fig. 2).

The MFCs operated here produced maximum power densities in the current density range of 0.08–0.3 mA cm$^{-2}$. Thus, these systems did not operate over the range of current densities that can be expected to produce the largest benefits of the DL. Recent advances in MFC architecture and operating conditions have shown that current density can be increased. For example, anode performance can be improved by using different materials [19] and different structures [20], internal resistance can be reduced by advective flow through the anode, reducing the electrode spacing [31], or by increasing ionic strength [20]. Thus, combining these various technologies with a cathode containing an optimum number of DLs will increase power generation and CE of MFCs.

5. Conclusions

Application of a DL, consisting of mixture of PTFE and carbon, can be used to increase the performance of a MFC. It was found here that the application of four DLs (equivalent to 20 mg cm$^{-2}$ of PTFE and 2.5 mg cm$^{-2}$ of carbon) produced the best performance of the MFC by increasing the maximum power density by 42% and the CE by 200%, as compared to a commercially available cathode.

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References
