Microbial Fuel Cell Cathodes With Poly(dimethylsiloxane) Diffusion Layers Constructed around Stainless Steel Mesh Current Collectors

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A new and simplified approach for making cathodes for microbial fuel cells (MFCs) was developed by using metal mesh current collectors and inexpensive polymer/carbon diffusion layers (DLs). Rather than adding a current collector to a cathode material such as carbon cloth, we constructed the cathode around the metal mesh itself, thereby avoiding the need for the carbon cloth or other supporting material. A base layer of poly(dimethylsiloxane) (PDMS) and carbon black was applied to the air-side of a stainless steel mesh, and Pt on carbon black with Nafion binder was applied to the solution-side as catalyst for oxygen reduction. The PDMS prevented water leakage and functioned as a DL by limiting oxygen transfer through the cathode and improving coulomibic efficiency. PDMS is hydrophobic, stable, and less expensive than other DL materials, such as PTFE, that are commonly applied to air cathodes. Multiple PDMS/carbon layers were applied in order to optimize the performance of the cathode. Two PDMS/carbon layers achieved the highest maximum power density of 1610 ± 56 mW/m² (normalized to cathode projected surface area; 47.0 ± 1.6 W/m² based on liquid volume). This power output was comparable to the best result of 1635 ± 62 mW/m² obtained using carbon cloth with three PDMS/carbon layers and a Pt catalyst. The coulombic efficiency of the mesh cathodes reached more than 80%, and was much higher than the maximum of 57% obtained with carbon cloth. These findings demonstrate that cathodes can be constructed around metal mesh materials such as stainless steel, and that an inexpensive coating of PDMS can prevent water leakage and lead to improved coulombic efficiencies.

Introduction

A microbial fuel cell (MFC) is a novel technology that can be used for direct bioelectricity generation (1–9). One of the most promising applications for MFCs is wastewater treatment, as organic matter can be removed while at the same time producing power (1–3). Various oxidants have been used as the electron acceptor at the cathode (1, 3, 7–11), but oxygen is the most promising electron acceptor for MFC applications because it is freely available, sustainable, and oxygen reduction is a well studied and widely applied reaction. Air cathode MFCs, which have cathodes exposed to air on one side and water on the other, are the most practical approach for designing MFC cathodes due to not having to aerate the water, and their ability to generate high power densities (7–9, 12).

Scale-up is an important issue for practical applications of MFCs for wastewater treatment and bioenergy production. The main challenges for commercializing scalable MFCs are developing materials that are cost-effective, efficient in power generation, and identifying architectures that can be used at larger scales. Maximum power densities in most high power MFCs are largely limited by cathode surface area and performance (9, 12, 13), and the price of cathode materials can account for the greatest percentage (47%) of the MFC capital costs (14). Most laboratory MFCs use small electrodes made of carbon cloth or paper or gas-permeable membranes coated with conductive paints. Carbon cloth purchased for fuel cell applications can be expensive (ca. $1000/m²). Recent tests have shown very promising results for overcoming the high costs of the anode by using a very inexpensive carbon mesh ($10–40/m²) (15). The weave of the carbon mesh is very loose, and thus we found it could not be water sealed when used as a cathode (unpublished data). Tubular cathodes can be designed to provide high surface areas needed for cathodes (13, 16–19), and tubes made of carbon cloth can provide power output similar to that of flat carbon cloth on the basis of equivalent projected surface area (13), but the carbon cloth can be expensive. To reduce the cost of a tubular cathode, one approach has been to use a membrane as the supporting material for the application of a conductive coating and catalyst (16, 20). Power densities have so far been low with these alternative materials, for example 403 mW/m² using two ultrafiltration membrane tube cathodes and a flat carbon paper anode. Power was increased (450 mW/m²) using a less expensive and flat anion exchange membrane (AEM) and a graphite fiber brush anode.

Scaling up MFCs with carbon cloth or coated membranes alone is likely not practical as the resistance of these materials becomes large as the reactor size increases. The electrical resistivity of carbon materials is relatively high which can produce high electrode ohmic losses in large-scale systems. For example the electrical resistivity of graphite is 1375 µΩ cm, compared to only 42 µΩ cm for titanium (14). To avoid having large resistances, metal current collectors are often used with carbon materials to reduce the overall resistance of the cathode. In one recent approach for the MFC anode, a graphite fiber brush electrode was developed that used a twisted core titanium wire as the current collector (12). The graphite fibers provide a high surface area for bacteria, and as they are only 1.3–2.5 cm long in these brushes, voltage losses across the length of the fibers are small. Electrons can flow along the titanium wire which has a much lower electrical resistivity. Brushes have also been used as cathodes for sediment MFCs in natural systems, where dissolved oxygen is available in the water, but the cost for aeration in an engineered system and the low power densities typically produced by the sediment MFC architecture would likely prohibit the use of brush cathodes in wastewater treatment systems. Current collectors have been used to improve performance of MFC cathodes. For example, power was increased from 450 to 575 mW/m² by adding a piece of...
stainless steel mesh to the surface of the conductive coating on an AEM cathode (20). The performance of these membrane cathodes has so far been low due to the high internal resistance of these relatively thick cathodes.

In this study, we took a different approach to making cathodes that could be useful for making either planar or tubular types of electrodes. Recognizing that a current collector will be necessary for making larger electrodes, our approach was to build the cathode around the current collector rather than mating a current collector to a preformed cathode structure. To test this concept, we examined the use of porous stainless steel mesh combined with a diffusion layer (DL) coating to prevent water leakage and control oxygen intrusion through the cathode, and a platinum (Pt) catalyst layer for oxygen reduction. We used a poly(dimethylsiloxane) (PDMS) coating to make a DL because it is inexpensive, widely available, stable under typical MFC conditions (neutral pH and ambient temperatures), oxygen permeable, and it is a viscous liquid at room temperature in its un-cross-linked state making it easy to apply the coating to the mesh surface (21). PDMS has a unique semiorganic structure, with a flexible inorganic Si–O backbone that has a very low rotation barrier and a high affinity for oxygen. As a result of its methyl substituents, PDMS is highly hydrophobic and therefore provides a good water seal. In contrast, the commonly used polytetrafluoroethylene (PTFE) is insoluble in common solvents, and special processing must be employed to generate the PTFE emulsion used in DL fabrication. In order to focus on the individual properties of the mesh and DL coating, we used Pt as the catalyst for oxygen reduction, although in future studies nonprecious metal catalysts such as Co/TMPP and iron phthalocyanine could be used (16, 20, 22, 23). We varied the amount of PDMS applied to the metal mesh to optimize cathode performance, and contrasted the performance of this mesh cathode with carbon cloth cathodes, also using PDMS coatings, under otherwise identical experimental configurations. We conducted additional electrochemical tests to examine how cathode performance was related to the different materials. To our knowledge, this is the first time that stainless steel mesh and PDMS have been used in concert to create a simple cathode MFC design.

Materials and Methods

Cathodes. The cathodes developed here are based on integrating the current collector (stainless steel mesh, SS), catalyst (Pt), and diffusion layer (PDMS) into one single cathode structure. The SS mesh (type 304 SS, 90 × 90, woven wire diameter 0.0055 in., McMaster-Carr, OH) had 90 × 90 openings per square inch. PDMS was made using a 10:1 mixture of SYLGARD 184 silicone elastomer base and SYLGARD 184 silicone elastomer curing agent (Dow Corning, MI), that was further diluted to 10 wt % with toluene to decrease the solution viscosity. The PDMS (6.25 mg/cm²) was applied with carbon black (1.56 mg/cm²) to the side of the SS that faced the air. After applying this first PDMS/carbon black as a base layer, additional DLs (one to four layers) containing PDMS/carbon black or only PDMS were applied on top of this base layer at the same mass loading as the original layer. After applying each layer, cathodes were air-dried for 2 h, and then heated at 80 °C for 30 min to cross-link the PDMS oligomers. After applying these DLs, a Pt catalyst layer (5 mg/cm² 10% Pt on Vulcan XC-72 with 33.3 μL/cm² of 5 wt % Nafion as binder) was applied to the SS mesh on the side facing the solution (see ref 22 for detailed procedures). Cathodes were also prepared with no coating on the solution-facing side of mesh, or with only a carbon black layer (both with two PDMS/carbon DLs on the air side) to determine if these materials had catalytic activity in the absence of Pt.

Carbon cloth (E-Tek, Type B, 30% wet proofing, BASF Fuel Cell, Inc. NJ) was also tested as a cathode supporting material. One or more DLs of PDMS/carbon and the Pt catalyst were applied as described above for the metal mesh cathode. Cathodes were also prepared using previously examined methods consisting of four DLs of PTFE as previously described (24).

MFC Construction and Operation. MFCs were single-chamber cubic-shaped reactors constructed as previously described (8) with an anode chamber 4 cm long and 3 cm in diameter. The anode was an ammonia gas treated graphite fiber brush (25 mm diameter × 25 mm length; fiber type PANEX 33 160K, ZOLTEK) (12, 25). All reactors were inoculated using a solution from an MFC operated for over 1 year (initially inoculated from the effluent of the primary clarifier of the local wastewater treatment plant). The medium contained acetate as the fuel (0.5 g/L for fixed resistance tests, and 1.0 g/L for polarization tests), and a phosphate buffer nutrient solution (PBS; conductivity of 8.26 mS/cm) containing Na₂HPO₄, 4.58 g/L; NaH₂PO₄ · H₂O 2.45 g/L; NH₄Cl 0.31 g/L; KCl 0.13 g/L; trace minerals (12.5 mL/L) and vitamins (5 mL/L) (26). Reactors were all operated in fed-batch mode at 30 °C and were refilled each time when the voltage decreased to less than 20 mV forming one complete cycle of operation.

Calculations and Measurements. Voltage (E) across the external resistor (1 kΩ, except as noted) in the MFC circuit was measured with 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current (I = EI/R), power (P = IE) was calculated as previously described (3), with the current density and power density normalized by the projected surface area of the cathode. To obtain the polarization and power density curves as a function of current, external circuit resistances were varied from 1000 to 50 Ω in decreasing order. Each resistor was used for a full fed-batch cycle, and the COD of the solution at the end of the cycle was measured using standard methods (27). The coulombic efficiency (CE) was calculated based on total COD removal over the cycle, as previously described (3). Water losses were measured daily based on the change in water level in a 5 mL syringe (filled with deionized water) connected to the anode chamber by a needle that pierced a septum on the top of the reactor.

Linear sweep voltammetry (LSV) was used to assess electrochemical performance of the cathodes. Current was measured in 50 mM PBS in the absence of nutrients and exoelectrogens using a potentiostat (PG/A750, Gamry Instruments). A two chamber electrochemical cell with each chamber 2 cm in length and 3 cm in diameter separated by an anion exchange membrane (AMI-7001, Membrane International Inc., NJ) was used for measurements, consisting of a working electrode (cathode with 7 cm² projected surface area), counter electrode (Pt plate with a projected surface area of 2 cm²), and an Ag/AgCl reference electrode (RE-5B; BASI, West Lafayette, IN). The scan rate was 1 mV/s, and potential was scanned from +0.5 to 0 V (versus standard hydrogen electrode).

Oxygen permeability was measured in terms of oxygen transfer coefficient as previously described (24). The 4 cm cubical reactor used in MFC tests was used for oxygen transport measurements. Dissolved oxygen concentrations were measured using a nonconsumptive dissolved oxygen probe (FOXY, Ocean Optics, Inc., Dunedin, FL).

Results

Performance of SS Mesh Cathodes in MFCs Compared with Carbon Cloth Cathodes. MFCs with SS mesh or carbon cloth cathodes and a Pt catalyst rapidly produced voltage after inoculation, and generated stable voltages at a fixed resistance. Differences in voltage among these reactors at a high
external resistance of 1 kΩ were small, although in general the SS mesh produced higher voltages than the carbon cloth cathodes. The largest maximum voltage that was produced over a total of 14 batch cycles of operation was of 602 (5 mV (S.D., n = 14 cycles) obtained using the SS mesh cathode with 2 PDMS/carbon layers (Figure 1). The highest value of carbon cloth cathodes was 585 (4 mV for MFCs with four PDMS/carbon layers.

Large differences in power production were observed based on polarization data. The largest maximum power density using a SS mesh cathode of 1610 (56 mW/m² (SD for duplicate reactors) was achieved with 2 PDMS/carbon base layer. This power was similar to that produced with a single layer (1592 ± 19 mW/m²), but three or more layers decreased performance to as little as 1010 mW/m² (Figure 2A). Maximum power densities produced using carbon cloth cathodes with PDMS/carbon layers varied over a smaller range of 1553 ± 19 mW/m² (one DL) to 1635 ± 62 mW/m² (three DLs) (Figure 2B). Thus, there was much less of an effect of the number of layers on power generation with the carbon cloth material than with the SS mesh.

Performance of SS Mesh Cathodes in Electrochemical Tests. LSV tests were conducted using SS mesh cathodes to evaluate the electrochemical performance of the cathodes in the absence of bacteria. All voltammograms with the SS mesh cathodes containing a Pt catalyst and 1–5 PDMS/carbon DLs (M1–M5) and (B) carbon cloth cathodes with Pt and the same DLs (CC1–CC5) as a function of current density (normalized to cathode surface area) obtained by varying the external circuit resistance (1000–50 Ω). (Error bars ±SD based on measurement of two duplicate reactors.)

FIGURE 1. Voltage generation of SS mesh cathode and a Pt catalyst with two PDMS/carbon DLs (M2) and carbon cloth cathodes with four DLs (CC4) versus time, with 50 mM PBS buffer and 0.5 g/L sodium acetate. (Best two cases among each group in voltage generation).

FIGURE 2. Power density of (A) SS mesh with Pt catalyst and 1–5 layers of PDMS/carbon DLs (M1–M5) and (B) carbon cloth cathodes with Pt and the same DLs (CC1–CC5) as a function of current density (normalized to cathode surface area) obtained by varying the external circuit resistance (1000–50 Ω). (Error bars ±SD based on measurement of two duplicate reactors.)

FIGURE 3. LSV of SS mesh cathodes (A) with a Pt catalyst and one to five PDMS/carbon DLs (M1–M5) (B) M1 compared with ones with additional PDMS layers (MP2–MP5), both with Pt catalyst. (C) M2 compared with the one with only carbon black (M2, no Pt), and one with no coating on the solution-facing side (M2, no Pt, no CB).
We also prepared a carbon cloth cathode with four PTFE layers and obtained an oxygen transfer coefficient of $1.1 \pm 0.1 \times 10^{-3}$ cm/s. This value is lower than previously reported for this procedure with these materials of $2.3 \pm 0.2 \times 10^{-3}$ cm/s (24), perhaps due to differences in batches of the carbon cloth or variations in fabrication procedures by different researchers.

**Water Loss.** The addition of a PDMS layer was important for controlling water loss from the cathode. SS mesh cathode with the base PDMS/carbon layer had an initial water evaporation loss of 5% of the water in the anode chamber each day. Water loss decreased with additional DLs, and were not detectable for cathodes with five DLs. For carbon cloth cathodes, the water losses were larger, decreasing from 10% loss per day with one DL, to 5% loss per day with five DLs. However, as a biofilm developed on the cathodes after several cycles, water loss gradually decreased for both SS and carbon cloth cathodes by ca. 20–30%.

**Discussion**

Building a cathode from SS mesh is an effective method for creating a cathode that can achieve performance similar to that obtained with carbon cloth electrodes. PDMS mixed with carbon black proved to be effective at reducing water losses and allowing oxygen transfer to the cathode catalyst. The best performance obtained here was with a SS mesh cathode and two PDMS/carbon layers, resulting in a maximum power density of 1610 $\pm$ 56 mW/m$^2$ (47.0 $\pm$ 1.6 W/m$^3$). In comparison, the best performance with a carbon cloth cathode was 1635 $\pm$ 62 mW/m$^2$ with three PDMS/carbon layers. The recovery of the substrate as current was also improved using SS mesh cathodes, with CEs ranging from 15–62% for the SS cathodes, compared to 14–51% for the carbon cloth cathodes for the above two cases.

Current collectors will be essential to the performance of larger-scale MFCs, and therefore the integral construction of the cathode around the mesh has substantial advances in simplicity of design and performance compared to previous studies where a current collector was added to other materials. For example, the addition of a current collector to an AEM membrane increased the power density from 450 to 575 mW/m$^2$, but in both cases the power produced was substantially less than that achieved here. Although a CoTMPP catalyst was used in this previous study, it has been shown that CoTMPP at a concentration of 0.6 mg/cm$^2$ produces similar performance to a Pt cathode (0.5 mg/cm$^2$) (22). Pt was used as the cathode here for the SS cathodes, but in the future tests should be conducted using alternative metal catalysts such as CoTMPP and iron phthalocyanine. The SS mesh was not optimized for thickness, pore size or type of stainless steel, and the SS used here (type 304) did not show any evidence of corrosion in MFC tests. Corrosion of the cathode metal is not expected as SS is cathodically protected from corrosion at these electrical potentials (29).

Others have also found that SS does not corrode when used as the cathode (30, 31). The cost of the type 304 SS mesh was less than $50/m$^2$, which is 20 times cheaper than small pieces of fuel-cell grade carbon cloth, and nearly half the price of an AEM membrane ($80/m^2$) based on purchase prices for small quantities (20). The cost for the SS material itself is currently less than $3.00/kg (price of Feb. 2009) (32), indicating that the raw material is very inexpensive.

PDMS was also examined here for the first time as a low cost diffusion layer coating for MFC cathodes. Both PDMS and PTFE are hydrophobic, stable polymers, except that PTFE can be used under highly acidic conditions while PDMS cannot. However, since neutral pH conditions are used in an MFC, PDMS can be substituted for the more expensive PTFE material. We found here that PDMS provided performance than those with carbon cloth cathodes (Figure 4). In all case, the CE increased with current density, consistent with previous results (12, 20, 24, 25). CEs of the SS mesh cathode ranged from 15 to 64% with single PDMS/carbon base layer, and only slightly increased when adding the second layer. The highest CE of 80% was obtained when three DLs were applied to this cathode. In contrast, the carbon cloth cathodes CEs ranged from 13 to 46% with the first DL, with the highest value of 57% with four DLs. COD removals over a cycle of operation ranged from 90 to 95%, and there was no effect of the number of DLs or the type of material (SS or carbon cloth) on COD removal.

**Oxygen Permeability of the Cathodes.** PDMS is relatively permeable to oxygen, but increasing the number of PDMS diffusion layers should reduce oxygen transfer due to the increased thickness of the DL. With one base layer of PDMS/carbon on the SS mesh cathode, the oxygen mass transfer coefficient was $1.2 \pm 0.1 \times 10^{-3}$ cm/s. Successive application of multiple PDMS/carbon DLs decreased the oxygen mass transfer coefficient from $1.1 \pm 0.1 \times 10^{-3}$ cm/s (two layers) to $0.7 \pm 0.1 \times 10^{-3}$ cm/s (five layers) (Figure 5). Addition of only PDMS (no carbon) onto this base layer decreased the mass transfer coefficient to $0.7 \pm 0.1 \times 10^{-3}$ cm/s, with the lowest value of $0.2 \pm 0.1 \times 10^{-3}$ cm/s obtained with four pure PDMS layers. Thus, the addition of carbon with PDMS created a more oxygen permeable material than the PDMS alone.
comparable to that of PTFE used in previous tests. Carbon cloth with three PDMS/carbon DLs achieved maximum power density of 1635 ± 62 mW/m² when used on a cathode (two DLs), mainly due to the lower buffer concentration used in this work (50 mM) which resulted in lower solution conductivity compared to previous tests (12, 33). The cost of PDMS is less than $1.00/kg, compared to $1.00–2.00/kg for PTFE (34). It is estimated that PDMS would cost only $0.13/m² when used on a cathode (two DLs), adding little to the total cathode cost. Thus, the use of PDMS reduces both cathode costs and complexity of construction.

Carbon black is integral for creating a microporous hydrophobic layer that can improve oxygen transport to the Pt catalyst (24, 35). Cathodes with PDMS/carbon DLs had much higher oxygen transfer coefficients than those with PDMS alone, and thus they also had better electrochemical performance (Figure 3). Carbon black may also help to increase the specific surface area of cathode which can lower the current density per electrode area, and thus improve oxygen reduction by lowering the overpotential (36). Carbon black alone on the SS mesh did not appreciably catalyze oxygen reduction. The commercial price of carbon black is similar to that of PDMS (less than $1.00/kg) (37). Because carbon black loading is only 1.56 mg/cm² for each layer, however, the use of carbon black would add only $0.02/m² to the cost of a cathode with two PDMS/carbon DLs.

The combination of SS mesh and PDMS/carbon DLs produced a structure that had an improved CE, compared to carbon cloth cathode, likely as a result of reduced oxygen transfer into the anode chamber. SS mesh cathodes had a CE as high as 80% with three PDMS/carbon DLs, over a current density range of 0.8–6.6 A/m². Carbon cloth cathodes with same DL had CEs that ranged from 13 to 57% over similar current densities. These CEs can be compared with those of carbon cloth cathodes with four PTFE DL in previous studies that had CEs ranging from 20 to 27% at current densities of 0.8–2.5 A/m² (flat carbon cloth anode) (24), and from 40 to 60% at 0.8–11 A/m² (graphite fiber brush anode) (12). A comparison of these results suggests that high CEs achieved with the SS mesh cathodes are partly due to high current densities. When the current density is increased, the cycle time is reduced, and thus the amount of oxygen that can diffuse into the reactor is substantially reduced in proportion to the cycle time. However, even in the high current density range of >5 A/m², SS mesh cathode had a higher maximum CE than other materials, likely due to the lower oxygen permeability of the mesh DL.

These experiments have shown that using SS mesh for the cathode supporting material substantially lowers the cost of the cathode, and eliminates the need for the carbon cloth material. Catalysts lacking precious metals, and cathodes that use binders that are less expensive than Nafion used here, are currently under investigation for further reducing the cost of the cathodes. The use of SS mesh has advantages over other membrane materials in that it is very flexible and thus it should be possible to make it into tubular structures that have good mechanical strength. Further development of materials in MFCs based on tubular SS mesh cathodes and graphite fiber brush anodes will be helpful in reducing the cost, and improving the performance of MFCs, so that they can be used for economical wastewater treatment and bioenergy production.

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Literature Cited


