Power Densities Using Different Cathode Catalysts (Pt and CoTMPP) and Polymer Binders (Nafion and PTFE) in Single Chamber Microbial Fuel Cells

SHAOAN CHENG,† HONG LIU,† AND BRUCE E. LOGAN*†‡
Department of Civil and Environmental Engineering and The Penn State Hydrogen Energy (H2E) Center, The Pennsylvania State University, University Park, Pennsylvania 16802

Cathode catalysts and binders were examined for their effect on power densities in single chamber, air-cathode, microbial fuel cells (MFCs). Chronopotentiometry tests indicated that the cathode potential was only slightly reduced (20–40 mV) when Pt loadings were decreased from 2 to 0.1 mg cm\(^{-2}\), and that Nafion performed better as a Pt binder than poly(tetrafluoroethylene) (PTFE). Replacing the precious-metal Pt catalyst (0.5 mg cm\(^{-2}\); Nafion binder) with a cobalt material (cobalt tetramethylphenylporphyrin, CoTMPP) produced slightly improved cathode performance above 0.6 mA cm\(^{-2}\), but reduced performance (<40 mV) at lower current densities. MFC fed batch tests conducted for 35 cycles (31 days) using glucose showed that replacement of the Nafion binder used for the cathode catalyst (0.5 mg of Pt cm\(^{-2}\)) with PTFE reduced the maximum power densities (from 400 ± 10 to 480 ± 20 mW m\(^{-2}\)) to 331 ± 3 to 360 ± 10 mW m\(^{-2}\). When the Pt loading on cathode was reduced to 0.1 mg cm\(^{-2}\), the maximum power density of MFC was reduced on average by 19% (379 ± 5 to 301 ± 15 mW m\(^{-2}\); Nafion binder). Power densities with CoTMPP were only 12% (368 ± 8 mW m\(^{-2}\)) lower over 25 cycles than those obtained with Pt (0.5 mg cm\(^{-2}\); Nafion binder). Power densities obtained using with catalysts on the cathodes were ~4 times more than those obtained using a plain carbon electrode. These results demonstrate that cathodes used in MFCs can contain very little Pt, and that the Pt can even be replaced with a non-precious metal catalyst such as a CoTMPP with only slightly reduced performance.

Introduction

A microbial fuel cell (MFC) is a device that uses bacteria to catalyze the conversion of organic matter into electricity (1–9). Substrate is oxidized by bacteria generating electrons and protons at the anode. Electrons are transferred through an external circuit while the protons diffuse through the solution to the cathode, where electrons combine with protons and oxygen to form water. It is now known that no exogenous mediators need to be added into an MFC (10, 11). It has been found that several microorganisms including *Shewanella putrefaciens* (4, 12, 13), *Geobacteraceae* (5, 14–17) *Clostridium butyricum* (18), and *Rhodofex ferrireducens* (19) can produce electricity in the absence of exogenous mediators from chemicals such as glucose, acetate, lactate, pyruvate, and formate. Mixed cultures of bacteria have been also reported to generate electricity from domestic wastewater (6–8, 20) and marine sediments (4, 15).

The performance of an MFC is influenced by several factors including the microbial activity, chemical substrate (fuel), type of proton exchange material (or even absence of this material), resistance of the circuit, and anode and cathode materials (4–6, 8, 9, 19, 21–23). The cathode performance is an important factor to the performance of an MFC due to the poor kinetics of oxygen reduction in the medium (6, 24). Cathode performance can be improved if Pt catalysts can be made more effective at room temperature, if the internal resistance of the reactor is reduced, or if more effective oxidants than oxygen (such as ferricyanide) are used. For example, power densities of MFCs have been increased by replacing aqueous cathodes with either direct-air carbon cathodes containing Pt (8, 24) or graphite electrodes containing Fe\(^{3+}\) (22). Oh et al. (9) found that the maximum power achieved using ferricyanide ion as oxidant in the cathode chamber was 50–80% greater than that obtained with dissolved oxygen and Pt. Power densities as large as 6000 mW m\(^{-2}\) have been reported for MFCs using ferricyanide (23). However, ferrocyanide must be replaced after it is reduced, while systems using oxygen can be continuously operated and therefore self-sustaining.

MFCs produce lower power densities than other types of fuel cells, but their most promising application in the near future is likely to be as a process for wastewater treatment (7, 25). Reducing the cost of the materials used to make MFCs is essential for building an economical treatment system. The typical manufactured components of an MFC are a proton exchange membrane (PEM), Pt catalyst on the cathode, and carbon electrodes. However, recent studies have shown that the proton exchange membrane is not needed for the operation of MFCs (8, 14) and that removing it actually increases maximum power densities (8). Pt is an effective catalyst used for both electrodes in hydrogen fuel cells, but it is an expensive component of the MFC cathode. While alternatives to Pt have been sought, none have approached the performance of Pt in hydrogen fuel cells (26). Pt is used on the cathode in air-cathode MFCs, so minimizing or eliminating the need for Pt can reduce the system capital costs. In most MFC studies commercially produced cathode electrodes are used that contain 0.5 mg cm\(^{-2}\) Pt loading (8), although graphite electrodes containing 0.28 mg/cm\(^{2}\) Pt have also been used (24).

The effect of different Pt loadings has not been previously examined for MFCs, and few alternatives to Pt have been explored for use in air-cathode MFCs. The effect of Pt loading on power generation has been examined for other types of fuel cells, but these systems operate under much different conditions of pH (highly acid or alkaline conditions; refs 27–29) and temperature (50–1000 °C), and therefore the results are not directly translatable to the performance of MFCs. Maximum power densities in aqueous cathode MFCs can be reduced by an order of magnitude when Pt is not used on the cathode (30). When Pt is used as a catalyst on a carbon electrode, it is usually bound to the electrode substrate using a polymer. Perfluorosulfonic acid (Nafion) and poly(tetrafluoroethylene) (PTFE) are two commonly used binders for Pt in chemical fuel cells (31–33), but Nafion can cost 500 times more than PTFE (mass basis). Nafion is a
proton conductive polymer that has hydrophilic ionic clusters, a hydrophobic base, and a transition region that allows for effective proton transfer to the catalyst. PTFE is a highly hydrophobic material that is useful in limiting water leakage through the cathode in an MFC and it is well-known to have good oxygen transfer properties, but unlike Nafion it is not an electrolyte. In addition, because PTFE is highly hydrophobic, it can cause the environment of the catalyst to become too dry, limiting effective proton transfer to the catalyst. The effect of different binders on the performance of air-cathode MFCs has not been previously addressed.

In this study, we examined the effect of Pt loading (0.1–2 mg cm\(^{-2}\)) using two different binders on the electrochemical performance of the cathodes in a bacteria-free electrochemical cell using chronopotentiometry. We then evaluated the performance of cathodes having a fixed Pt content, and two different binders, over many feeding cycles in fed batch MFC systems in terms of power densities and Coulombic efficiencies. We also compared the performance of the Pt-containing cathodes to that of an inexpensive metal\-based catalyst (cobalt tetramethylphenylporphin, CoTMPP) using chronopotentiometry and in fed batch MFC tests.

**Materials and Methods**

**Electrodes.** The cathode electrodes used in electrochemical cell tests had a projected surface area of 0.64 cm\(^2\), while both electrodes used in MFC had a projected surface area of 7 cm\(^2\). Anodes were made of non-wet-proofed carbon cloth (type A, E-TEK). For Pt-containing cathodes, a commercial Pt catalyst (10 wt % Pt/C, E-TEK) was mixed with a chemical binder (5% Nafion solution or 2% PTFE suspension) to form a paste (7 mL of binder per mg of Pt/C catalyst). The paste was applied to one side of the wet-proofed carbon cloth (30 wt %, type B, E-TEK), and dried at room temperature for 24 h (Nafion) or at 350 °C for 0.5 h (PTFE). The Pt content was varied in the range of 0.1–2 mg cm\(^{-2}\) by changing the mass of Pt catalyst used in the paste. Pt loadings less than 0.1 mg cm\(^{-2}\) were not tested as it was not possible using our application method to evenly apply the paste onto the cathode at lower Pt loadings.

CoTMPP was also examined as an alternative to a Pt-based catalyst as it has been demonstrated to have a high activity for oxygen reduction in direct methanol fuel cells. CoTMPP (Acros) was dissolved in chloroform (0.001 M) and mixed with Vulcan XC-72 carbon (320 mg per 100 mL) as previously described. The mixture was air-dried and then heated in an inert-gas atmosphere at 800 °C for 1 h. The material (0.6 mg cm\(^{-2}\) CoTMPP loading) was applied to carbon cloth using a Nafion binder by the same method described above for the Pt catalyst cathode. A cathode containing only carbon powder (Vulcan XC-72) was prepared as a non-catalyst control.

**MFC Tests.** All MFC tests were conducted using single chamber MFCs constructed as previously described, and operated at a fixed external circuit resistance (1000 Ω). The coated side of the cathode was placed facing the solution, with the uncoated side exposed directly to air. MFCs were inoculated using domestic wastewater (pH 7.3–7.6, chemical oxygen demand (COD) = 200–300 mg L\(^{-1}\)) collected from the primary clarifier of the Pennsylvania State University Wastewater Treatment Plant. The wastewater was replaced three to five times before the solution was switched to solution containing glucose (1 g L\(^{-1}\)) and a phosphate buffered nutrient medium (PBM) containing NH\(_4\)Cl (0.31 g L\(^{-1}\)), NaH\(_2\)PO\(_4\)-2H\(_2\)O (4.97 g L\(^{-1}\)), Na\(_2\)HPO\(_4\)-2H\(_2\)O (2.75 g L\(^{-1}\)), KCl (0.13 g L\(^{-1}\)), and a metal (12.5 mL) and vitamin (12.5 mL) solution (36). The chamber was refilled each time the voltage decreased to less than 50 mV, forming one complete cycle of operation. All tests were conducted in a 30 °C temperature-controlled room.

Glucose utilization was calculated on the basis of change in COD, which was measured using standard methods (37). All samples were filtered through a 0.22 μm (nominal diameter) membrane filter prior to COD measurements.

**Electrochemical Cell Tests.** The cathode potential was measured by applying a constant current in potentiometry tests (chronopotentiometry; ref 38) using a three-chambered electrochemical cell containing a working electrode (cathode electrode with 0.64 cm\(^2\) projected surface area), a counter electrode (platinum plate with a projected surface area of 2 cm\(^2\)), and an Ag/AgCl reference electrode (EE009 no-leak electrode, Cypress Systems). The catalyst-coated side of the cathode was placed facing the solution, with the uncoated side exposed directly to air. Chronopotentiometry studies were conducted using a PC4/750 potentiostat (Gamry Instruments) by applying a constant current for 60 min and recording the stable value of the response potential. A curve of the cathode potentials against current densities was used to evaluate the performance of cathodes. For a fixed current density, the higher the potential the better the performance of the cathode material.

**Calculations.** Cell voltage was recorded using a multimeter and a data acquisition system (Model 2700, Keithly).

Current density in chronopotentiometry tests was calculated as \(J = I/A\), where \(I\) (mA) is the applied constant current and \(A\) (cm\(^2\)) is the projected surface area of the electrode. Power density in MFC tests was calculated according to \(P = \frac{1}{2}V(IA)\), where \(V\) (mV) is the voltage and \(R\) (Ω) is the external resistance. Coulombic efficiency was calculated as \(\eta = \frac{I_{\text{th}}}{C_{\text{n}}} \times 100\%\), where \(I_{\text{th}}\) (C) is the total coulombs calculated by integrating the current over time, and \(C_{\text{n}}\) is the theoretical amount of coulombs available based on measured COD removal in the MFC.

**Results**

**Performance of Pt Cathodes with Different Pt Loadings and Binders.** To assess the effect of the Pt loading on their performance at the current densities typical of MFCs, electrodes were tested using chronopotentiometry at Pt loadings ranging from 0.1 to 2 mg cm\(^{-2}\) with Nafion or PTFE as the binder. At a Pt loading of 0.5 mg cm\(^{-2}\) (Nafion binder), the cathode potential rapidly decreased from 307 to −239 mV for current densities up to 2 mA cm\(^{-2}\) (Figure 1A). These potentials are much lower than those theoretically possible under these solution conditions (620 mV vs Ag/AgCl for 25 °C at pH 7) or those theoretically possible in hydrogen fuel cells under more acidic conditions and at higher temperatures (1030 mV vs Ag/AgCl, pH 0, 80 °C) where the cathode is in contact with a PEM and not water.

There was only a small change in the potential when the Pt loading was changed within a range of 0.1–2 mg cm\(^{-2}\). The difference in the potential of the other cathodes relative to that of the cathode with a Pt loading of 0.5 mg/cm\(^2\) (\(E - E_{0.5}\)) was typically less than 10–20 mV (Figure 1A). Similar results were obtained using PTFE as a binder for Pt loadings of 0.25–1 mg cm\(^{-2}\) (Figure 1B). The potential decreased rapidly from 288 to −257 mV at current densities up to 2 mA cm\(^{-2}\). The potential differences (\(E - E_{0.5}\)) of the cathodes with various Pt loadings relative to that obtained at 0.5 mg cm\(^{-2}\)Pt was generally less than 10–15 mV, or only a difference of 4–10% in potential at a current density of 1 mA cm\(^{-2}\) (Figure 1B).

A comparison of the two different bonding materials at a fixed Pt loading of 0.5 mg cm\(^{-2}\) showed that Nafion produced slightly more positive potentials than PTFE when compared at the same current density (Figure 2). For example, at 1 mA cm\(^{-2}\), the measured potential with Nafion was 12% more positive than that obtained using PTFE as the binder.

**Performance of the CoTMPP Cathode.** The performance of a CoTMPP cathode (Nafion binder) was compared to Pt
catalyst cathodes (Nafion or PTFE binders) using chronopotentiometry. At current densities above 0.6 mA cm\(^{-2}\), the potentials produced using CoTMPP were 3–15 mV more positive than those using Pt and Nafion (Figure 2). At lower current densities (<0.6 mA cm\(^{-2}\)) the CoTMPP cathode potential was up to 36 mV more negative than that obtained with Pt (Nafion binder). Potentials produced with CoTMPP were consistently more positive (1–35 mV) than Pt cathodes using a PTFE binder (see inset in Figure 2). In all cases the Pt and CoTMPP catalyst potentials were substantially more positive than those obtained using a plain carbon cathode (prepared in the same manner as the other cathodes, and containing the carbon paste, but lacking a catalyst).

**MFC Performance Using a Pt Catalyst with Different Binders.** The performance of the Pt catalyst (0.5 mg cm\(^{-2}\) Pt) with a Nafion or PTFE binder was examined in MFCs operated in a fed batch mode over 31 days (35 cycles). Following acclimation, glucose was used as a substrate during the tests with each cycle requiring ~24 h before the voltage was reduced to below <50 mV. The maximum voltage produced with the Nafion binder varied between 0.5 and 0.6 V each time the MFC was refilled, with this voltage generally decreasing over time (Figure 3A). For example, the maximum power density achieved in the MFC decreased from an average of 480 ± 20 mW m\(^{-2}\) (±SD (standard deviation)) based on the averages of the maximum voltages for the first three cycles; range of 464–508 mW m\(^{-2}\); Figure 3B) to 400 ± 10 mW m\(^{-2}\) (last three cycles; range of 390–414 mW m\(^{-2}\); Figure 3C). The current density ranged from 0.075 to 0.102 mA cm\(^{-2}\). Although the maximum power density decreased, the Coulombic efficiency increased during the same period from 8.9 ± 0.4% to 18.6 ± 0.5% (Figure 3D).

When PTFE was used as the Pt (0.5 mg cm\(^{-2}\)) binder on the cathode, the maximum cell voltage was slightly lower (<0.5 V) than that obtained with Nafion (Figure 4A). However, the maximum voltage for each cycle did not decrease as much over the operation period using PTFE as the binder as it did with Nafion. The maximum power density for the PTFE cathode with Pt decreased only 9%, or from 360 ± 10 mW m\(^{-2}\) (cycles 2–4) to 331 ± 3 mW m\(^{-2}\) (last three cycles) compared to a 19% decrease using Nafion (Figure 4B). The Coulombic efficiency also varied over a smaller range during the same period, or from 9.5 ± 1.5% to 13.1 ± 0.3%.

When the Pt loading was reduced to 0.1 mg cm\(^{-2}\) (Nafion binder), the maximum power density of MFC averaged 340 ± 20 mW m\(^{-2}\) (from 379 to 301 mW m\(^{-2}\) for 24 cycles of operation (Figure 5A). These maximum power densities were 19% lower on average than those obtained with 0.5 mg cm\(^{-2}\) Pt and the same binder. The Coulombic efficiency ranged from 4.5% to 7.5%, which is about half that obtained at the higher Pt loading with a Nafion binder (Figure 5B).

**MFC Performance Using a CoTMPP Cathode or in the Absence of a Catalyst.** In tests using CoTMPP as the cathode catalyst, the power density was 369 ± 8 mW m\(^{-2}\) on average (range from 397 to 361 mW m\(^{-2}\); 25 cycles), which is 12% lower than that obtained with Pt (0.5 mg cm\(^{-2}\); Nafion binder) (Figure 5A). The Coulombic efficiency ranged from 7.9% to 16.3% (Figure 5B), similar to that obtained with 0.5 mg cm\(^{-2}\) Pt and Nafion (Figure 3D).

In the absence of a cathode catalyst, the average power density was reduced to 93 ± 13 mW m\(^{-2}\) (range from 104 to 88 mW m\(^{-2}\)). This power density is 73% lower than that obtained with Pt (0.1 mg cm\(^{-2}\); Nafion binder). The Coulombic efficiency, however, was 10–20% lower than that obtained with Pt (0.1 mg cm\(^{-2}\); Nafion binder) (Figure 5B).

**Discussion**

MFC tests at a fixed Pt loading (0.5 mg cm\(^{-2}\)) demonstrated that Nafion was a better binder than PTFE on the basis of maximum power densities measured in 35 repeated fed batch cycles. The maximum power density with Nafion averaged 480 mW m\(^{-2}\), while that obtained with PTFE was 14% less at the same Pt loading. Reducing the Pt loading from 0.5 to 0.1 mg cm\(^{-2}\) (Nafion binder) produced a similar reduction in power, averaging 19% less than that obtained at the higher Pt loading. CoTMPP proved to be a suitable replacement for Pt on the MFC cathode. In fed batch tests over many cycles, the maximum power density using CoTMPP was actually 8.5% greater than that obtained at the lower Pt loading (0.1 mg cm\(^{-2}\)) using a Nafion binder, and 5.4% greater compared to that using a PTFE binder even at the higher Pt loading (0.5 mg cm\(^{-2}\) Pt). The maximum power with CoTMPP produced only 12% less power than the Pt catalyst (Nafion binder) at the higher Pt loading (0.5 mg cm\(^{-2}\)). The Coulombic efficiency of the CoTMPP was also similar to that obtained with the higher Pt loading and Nafion binder, indicating that there was greater overall conversion of substrate into electricity.

Chronopotentiometric tests were successful in predicting the relational performance of the different catalysts and binders, although the actual performance differences were larger than the differences implied by the electrochemical tests. On the basis of maximum power densities, the performance of the different systems can be ordered according to the following: 0.5 mg cm\(^{-2}\) Pt and Nafion binder > CoTMPP > 0.5 mg cm\(^{-2}\) Pt and PTFE binder > 0.1 mg cm\(^{-2}\) Pt and Nafion binder > plain carbon electrode. This is the same order expected from the chronopotentiometric tests at current densities similar to that produced in the MFC tests (<0.5 mA cm\(^{-2}\)). Thus, chronopotentiometry tests were useful as a rapid method of evaluating and ranking the different electrode materials and preparation techniques.
In general, there were larger differences in the maximum power densities measured in MFC tests than those found for the differences in potentials measured in chronopotentiometric tests. In addition, there were changes in the maximum power densities observed over time in MFC tests that could not be anticipated from the chronopotentiometric tests. Thus, some of the differences in maximum power densities observed for the different catalysts and binders during the MFC tests must result from other factors, such as biofilm formation on the cathodes and the effects of chemicals produced by the bacteria during glucose oxidation. Upon completion of the MFC fed batch cycle tests, for example, it was observed that the biofilm formed on PTFE cathode was thin and loose compared to that formed on Nafion cathode. While we cannot conclusively link this qualitative difference in the biofilm to the performance of the two systems, we do note that biofilm formation is a function of the hydrophobicity of the surface (39–41). It seems that biofilm formation on the cathode surface contributed to the increase in Coulombic efficiency with the operation time of MFC according to the results using different binders.

The function of a catalyst binder should not be confused with the function of a PEM, although the same materials can be used for both. Ideally, the main function of the binder is to hold the catalyst in contact with the conductive electrode surface, providing the catalyst as a site for the reaction of oxygen, protons, and electrons. The purpose of a PEM is to conduct protons from the anode to cathode. In an MFC, water is the proton carrier between the electrodes. Removing the PEM in an MFC can increase power (8), while the binder may increase or decrease power depending on the nature of the material. The lack of a PEM does reduce the Coulombic efficiency compared to MFCs with a PEM, as previously noted (8). The Coulombic efficiencies obtained here, while low, are
consistent with values previously reported for this system (8, 14).

The relatively small effect of different Pt loadings on the performance of MFCs is different from what could be expected from hydrogen fuel cells, where the performance is greatly affected by Pt loading. It has been reported that the power density of a hydrogen fuel cell decreased by a factor of 2 when the Pt loading was reduced from 0.387 to 0.074 mg cm$^{-2}$ (also using E-TEK materials, but with 40% Pt/C) (42). These different results likely arise from the different operating conditions of hydrogen fuel cells and MFCs, such as electrolyte, temperature, and current density. For example, the water content of the cathode in a hydrogen fuel cell is controlled to prevent cathode flooding, while there is no PEM in the MFC used here and the cathode is placed directly in contact with water. Hydrogen fuel cells operate at higher temperatures (50–80 °C) and at current densities of 100 mA cm$^{-2}$ or more, while MFCs operate at much lower temperatures that bacteria can tolerate (30 °C in the present study), and produce current densities below 1 mA cm$^{-2}$. Thus, it is difficult to predict the magnitude of differences in these systems produced solely by the materials used.

While it has been shown here that the performance of Pt cathode with Nafion is better than that with PTFE, this comparison does not consider the cost of these two chemicals. Lowering the Pt loading by a factor of 5 reduced overall performance by a factor of only 1.2, a difference that might be acceptable given the cost of the catalyst and the large surface areas needed for MFC operation. The CoTMP material showed excellent promise as an alternative to Pt for MFCs, but additional studies on loadings and long-term stability of this material compared to Pt are needed. Thus, further comparisons of the different cathode materials and catalysts based on construction costs and long-term stability are needed to better compare all aspects of using materials in MFCs.

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Supporting Information Available

Electrochemical cell used to examine cathode performance as a function of Pt loading and chemical binder. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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