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Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell

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ABSTRACT

An inexpensive activated carbon (AC) air cathode was developed as an alternative to a platinum-catalyzed electrode for oxygen reduction in a microbial fuel cell (MFC). AC was cold-pressed with a polytetrafluoroethylene (PTFE) binder to form the cathode around a Ni mesh current collector. This cathode construction avoided the need for carbon cloth or a metal catalyst, and produced a cathode with high activity for oxygen reduction at typical MFC current densities. Tests with the AC cathode produced a maximum power density of 1220 mW/m^2 (normalized to cathode projected surface area; 36 W/m^3 based on liquid volume) compared to 1060 mW/m^2 obtained by Pt catalyzed carbon cloth cathode. The Coulombic efficiency ranged from 15% to 55%. These findings show that AC is a cost-effective material for achieving useful rates of oxygen reduction in air cathode MFCs.

1. Introduction

A microbial fuel cell (MFC) is a novel technology for direct bioelectricity generation from biomass [1–5]. Reducing the cost of the materials used in MFCs is essential for practical applications. The cathode accounts for the greatest percentage of the total capital cost [6], and cathode surface area and materials generally limit higher power production in MFCs [7–9]. Therefore, identifying low-cost materials and efficient cathode architectures are important for improving cost effectiveness and performance of MFCs.

Carbon based materials are widely used as the electrode for air cathode MFCs. The high cost of some of these materials, such as carbon cloth (ca. $\$1000/m^2$), prohibits the use of this material for large scale systems. While low cost cathodes have been made by applying conductive coatings inexpensive membranes, power densities have been relatively low [10,11]. Since a current collector will be needed to construct larger electrodes, we recently investigated an alternative approach based on constructing the cathode around the current collector by coating a stainless steel mesh with a catalyst and a film to prevent water flow through the electrode [12]. This approach greatly reduced the electrode cost, but platinum was needed as a catalyst. Alternatives to Pt include CoTMPP (0.6 or 1.2 mg/cm^2) and iron phthalocyanine (1.0 mg/cm^2) [7,13–15]. Other metals such as manganese dioxide (MnO_2) can also improve cathode performance [16]. While these catalysts greatly reduce the cathode costs compared to Pt, the high loading needed to equal the performance of Pt can result in high overall costs. For example, using CoTMPP at 0.6 mg/cm^2 ($30/g) costs $\$180/m^2$ compared to $\$140–700/m^2$ for Pt (0.1–0.5 mg/cm^2, $140/g) [11].

Promising alternatives to metal-catalyzed cathodes are biocathodes and very high surface area materials such as graphite granules and activated carbon (AC) [17–19]. Biocathodes use bacteria to catalyze oxygen reduction, but so far both biocathodes and graphite granule cathodes have been limited to systems that require aeration of the water to provide dissolved oxygen [18]. Aeration is a highly energy intensive process, and should be avoided for MFCs. AC is inexpensive and is more highly porous than graphite, and it has previously been used with precious metal catalysts such as Pt and Pd in hydrogen fuel cells [20]. An AC cloth air cathode was developed that used ethylenediaminetetraacetic acid (EDTA) chelated iron as a catalyst, achieving a power density of 40 W/m^3 [19]. However, this system required the use of a cation exchange membrane and a sprinkler system to continuously apply a 0.7% NaCl solution over the cathode. The use of a membrane can increase system cost, and the need for wetting the cathode could complicate operation.

In this study, we examined the use in an MFC of a simple AC air cathode that does not require any additional metal catalysts for efficient oxygen reduction. We built the AC air cathode around a nickel (Ni) mesh current collector in order to allow for ease in scale up to larger cathode sizes. We show that this metal mesh AC cath-

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ode is a high performance and cost-effective method for constructing MFCs.

2. Materials and methods

2.1. Electrodes

Cathodes were constructed at VITO (Belgium) by pressing at 150 bar a mixture of AC (70–90 wt%; Norit SX plus, Norit Americas Inc., TX) and polytetrafluoroethylene (PTFE) binder on top of a Ni mesh current collector (#53 mesh, 330 µm opening, 150 µm wire diameter) to form a cathode 0.45 mm thick (final weight ~1 kg/m^2). A PTFE diffusion layer (70% porosity, 0.13 kg/m^2) was added to the air-side of the cathode, except as noted. In some cases the same cathode additionally contained a Pt/Pd catalyst. These cathodes were compared to a carbon cloth cathode made as previously described (Pt loading of 0.5 mg/cm^2, Nafion binder) [8,14]. Anodes were ammonia gas treated graphite fiber brushes (25 mm diameter × 25 mm length; fiber type PANEX 33 160K, ZOLTEK) [7].

2.2. MFC construction and operation

MFC tests were conducted using single-chamber, cubic-shaped MFC reactors containing a cylindrical anode chamber 4-cm long and 3-cm in diameter [21]. Reactors were inoculated with solution from an MFC operated for over 1 year (initially inoculated using primary clarifier effluent from a local wastewater treatment plant). The anode was placed horizontally in the cylindrical chamber with the end 1 cm from the cathode. All reactors were operated at 30 °C, and fed a medium containing acetate (1.0 g/L), a phosphate buffer solution (PBS; 50 mM; Na_2HPO_4 4.58 g/L, $NaH_2PHO_4 \cdot H_2O$ 2.45 g/L, NH_4Cl 0.31 g/L, KCl 0.13 g/L; conductivity of 6.82 mS/cm), and a trace mineral (12.5 mL/L), and vitamin (5 mL/L) solution [21].

2.3. Calculations

Voltage (E) across the external resistor in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I = E/R$), power ($P = IE$), and coulombic efficiency (CE) were calculated as previously described [2], with the current and power normalized by the projected surface area of the cathode or the reactor volume. Power density curves were obtained by varying external circuit resistance, with a single resistor used for a full batch cycle.

Linear sweep voltammetry (LSV) was used at a scan rate of 1.0 mV/s to evaluate the electrochemical performance of the cathodes as previously described [12]. Energy dispersive X-ray spectroscopy (EDS) was performed to analyze the elemental composition at a sampling depth of up to 1–2 µm. Plain AC cathodes and AC cathodes with Pt/Pd were analyzed by EDS at 20 kV (Quanta 200, FEI, OR).

3. Results and discussion

3.1. MFC performance

Plain AC cathodes produced a maximum power density of 1220 ± 46 mW/m^2 with a PTFE diffusion layer, and 1150 ± 57 mW/m^2 without a diffusion layer (Fig. 1A). In addition to a lower power density, the AC cathode lacking the PTFE layer also exhibited more erratic performance, as shown by high standard deviations for values obtained in duplicate tests (Fig. 1A). For comparison with cathodes previously used in this reactor, a maximum power density of 1060 mW/m^2 was produced using a carbon cloth cathode with Pt (0.5 mg/cm^2). Power production was increased by only 16% (1415 mW/m^2) by adding a Pt/Pd catalyst, compared to much large increases observed for carbon cloth with Pt [14].

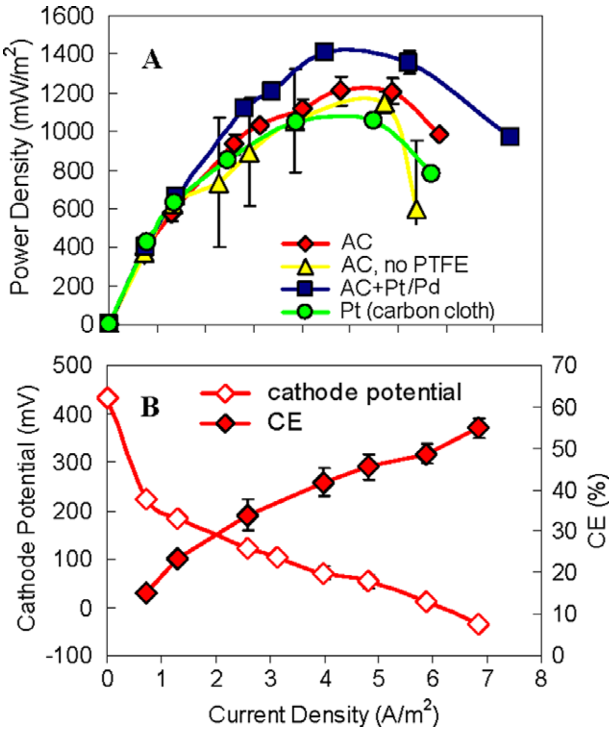

Fig. 1. (A) Power density of plain AC and AC containing Pt/Pd cathodes with a PTFE diffusion layer, and AC without PTFE. (B) Cathode potentials and CE of plain AC and AC with PTFE (error bars ± SD based on measurement of two duplicate reactors or multiple tests).

The open circuit cathode potential of the AC cathode with a PTFE diffusion layer was 430 mV, and decreased from 222 mV at a current density of 0.7 A/m^2 (1000 Ω) to −34 mV at a current density of 6.9 A/m^2 (50 Ω). CE increased from 15% to 55% with increasing current density (Fig. 1B).

During initial MFC tests, we observed appreciable water losses based on the development of a headspace in the anode chamber. We therefore pierced the septum on the top of the reactor with a needle connected to a 5 mL syringe containing deionized water, and measured daily water losses of 10–15% of the liquid in the reactor. The inclusion of a PTFE diffusion layer did not substantially affect water losses, suggesting that water losses were due to evaporation and not flow thorough the cathode. Water losses could be reduced in the future by using more dense diffusion layers.

3.2. Electrochemical performance

LSV tests were conducted to evaluate the electrochemical performance of the AC cathodes. Plain AC cathodes were compared to carbon cloth and AC cathodes containing Pt/Pd. At a current density of less than 3.9 A/m^2, the AC cathode exhibited better electrochemical performance than Pt loaded carbon cloth cathode (Fig. 2). Addition of Pt/Pd to the AC cathode improved performance, with the higher current densities produced at all voltages compared to the other two cathodes.

3.3. Elemental composition

EDS analysis showed that for plain AC from cathode, carbon and fluorine were two most abundant elements, with trace amounts of

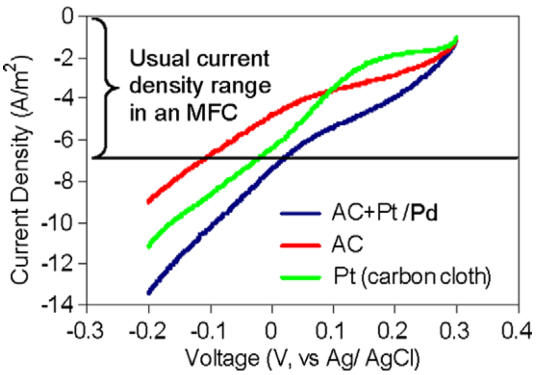

Fig. 2. LSV of plain AC, AC with Pt/Pd and Pt catalyzed carbon cloth cathode.

Table 1
Elemental composition of plain AC and AC with Pt/Pd.

Elements	Plain AC (%)	AC with Pt/Pd (%)
C	66.54	80.45
Si	0.24	0.44
Ca	0.04	0.04
Fe	0.15	0.14
S	0.12	–
Cl	0.05	–
Al	0.02	0.03
Ni	0.2	0.06
F	32.64	11.75
Pt	–	4.42
Pd	–	2.52
Cu	–	0.14
Na	–	0.01

calcium, iron, aluminium, and nickel (Table 1). The presence of fluorine was due to the use of the PTFE binder, and the Ni on the AC was likely due to the process of pressing the AC onto the Ni mesh. The acid washed AC used here should have had a low metal content. Analysis of the AC containing Pt/Pd showed that it contained at the surface 4.42% Pt and 2.52% Pd (Table 1). These two precious metal catalysts were responsible for the improved performance of the AC electrode.

3.4. Performance and cost of materials

The performance of the AC cathodes was due to the high surface area of the material, combined with the effective current collection by the Ni mesh. The PTFE diffusion layer contributed to consistent performance, although it did not sufficiently limit water losses through the cathode. Such water losses may not be important in continuous flow systems, but in fed-batch systems this results in the development of a headspace.

The cost of the AC cathodes cannot be predicted with any certainty, but we estimate a reasonable market price to be \$50–70/m^2 when produced in reasonable sized batches. The price of just the AC is only ca. \$2.60/kg, which is sufficient to produce a 7 m^2 electrode. Building the cathode around the metal mesh lowers the ohmic losses of cathode, and avoids the need for other supporting materials such as membranes. The cost of the cathode can be further reduced to \$20–40/m^2 through using less expensive materials and minimizing the amount of metal used for the current-collecting mesh. Preliminary tests with much less expensive stainless steel mesh have shown MFC performance comparable to that of the Ni mesh (unpublished results). The fact that stainless steel can replace the Ni suggests that the Ni is not acting as an oxygen reduction catalyst. PTFE was used here as a binder and diffusion layer, but it may be possible to use less expensive materials in the future.

4. Conclusions

Inexpensive AC was used at cathode without any metal catalyst for oxygen reduction in an air cathode MFC. The use of this AC cathode in an MFC produced a maximum power density of 1220 mW/m^2 (36 W/m^3) compared to 1060 mW/m^2 obtained by Pt catalyzed carbon cloth cathode, and CE ranging from 15% to 55%. Thus, the use of AC and a metal mesh collector is an efficient and cost-effective method for producing an air cathode for an MFC. Further improvements in the performance of AC cathodes should be possible to limit water losses and further reduce the costs of these cathodes.

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