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Performance and stability of different cathode base materials for use in microbial fuel cells

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HIGHLIGHTS

- Carbon cloth base material is more stable than stainless steel in some applications.
- Finer stainless steel mesh sizes outperformed more coarse mesh sizes.
- Potential for corrosion exits for metal base materials in MFC cathodes.
- Potential for salting out exists for metal based materials in MFC cathodes.

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ABSTRACT

Metal supporting materials are increasingly being used as base materials for microbial fuel cell (MFC) cathodes. However, the potential for corrosion may limit their use as base materials of MFCs during scale-up and long-term operation. In this study, the electrochemical performance, power generation in MFCs, hydrostatic pressure tolerance, and stability of activated carbon (catalyst) cathodes with carbon cloth or different size metal mesh as base materials are investigated. Electrochemical testing results show that the finest stainless steel mesh (250 × 250 openings per inch) outperforms carbon cloth cathodes by 10–40% at current densities ranging from 6 to 11.2 A m^{-2} over the typical cathode operating range of 0.1 V–0 V. When tested in MFCs, however, carbon cloth based cathodes out perform all stainless steel mesh cathodes by as much as 34%, reaching 1.72 W m^{-2}; probably due to the corrosion and salt build-up on the surface of the stainless steel mesh cathodes. Carbon cloth cathodes also maintained high static pressure heads of 1.9 m. The high electrochemical performance, hydrostatic pressure tolerance, and corrosion resistance of carbon cloth suggest that carbon fiber based materials may be more suitable than metal based materials for use as MFC cathodes base material for some applications.

1. Introduction

Microbial fuel cell (MFC) technology has the unique ability to convert the organic matter in wastewater directly into electricity while treating the wastewater at the same time. Many advances have been made in gaining a fundamental understanding of interactions in MFC systems, from microbe/electrode interactions to electrochemical reactions [1–8]. Building on this knowledge, improvements in MFC architecture have led to significant increases in MFC performance [4,9–12]. However, power densities are still too low for practical applications. At this point in many MFC systems, the cathode is typically the major limiting factor to current generation and also represents a significant portion of the total cost [3,13]. As a result, making improvements to cathode architecture presents the most immediate need in order for practical application of MFCs for wastewater treatment to be realized.

Among the different types of cathodes that have been used in MFCs, air cathodes have demonstrated the capability of generating high power densities in MFCs, representing a great potential for practical applications. Air-cathodes used in MFCs typically consist of a catalyst layer, gas diffusion layer, and a conductive base material. The catalyst layer, which is the site of the oxygen reduction reaction (ORR), is attached to the solution facing side of the cathode. The gas diffusion layer, is fixed to the air-facing side of the supporting base material, and allows for oxygen diffusion into the cathode structure while preventing leakage of the solution from the MFC. The base material is used as both a current collector and a

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supporting material, for the catalyst layer and gas diffusion layer.

The use of conductive carbon fabrics as base materials for MFC air-cathodes is very common, as carbon fabrics are known for their high strength, good conductivity and chemical stability [13–15]. The electrical properties of carbon fabrics can be controlled through the method in which carbon fibers are formed and through the raw material used to form carbon fibers. Carbon fibers typically have a diameter around 10 μm and are assembled into bundles that contain 1000 to 10,000 fibers [14]. As a result, carbon cloth can be produced with much higher surface area compared to other supporting materials used for electrode base materials in MFCs.

Due to lower cost and higher conductivity than many carbon based materials, stainless steel mesh [16–20], nickel mesh [21,22], and nickel foam [23] have been investigated as new base materials for MFC cathodes. However, recent studies have shown that corrosion of stainless steel mesh [24] and nickel foam [25] is possible when used in MFCs, which results in an increased ohmic resistance and a decreased performance [23,25]. For example, greater than 33% decrease in maximum power due to corrosion, which has been attributed to adsorbed protons at the interface of activated carbon and stainless steel mesh, has been shown to occur after acid pretreatment of activated carbon [24,26]. A similar decrease in power density was shown to occur as a result of corrosion due to low cathode potentials at which corrosion is more thermodynamically favorable [25]. This suggests that metal based electrode supporting materials may lack the stability needed and therefore may be limited in their application in MFCs for treating certain types of wastewaters.

Recent studies have compared the performance of metal based activated carbon cathodes to carbon cloth based cathodes using platinum as the catalyst in MFCs [21,22,27], demonstrating comparable results between the two materials for both electrochemical and MFC tests. However, only one metal mesh size was used to make the comparison in these studies and a comparison between based materials with the same catalyst (activated carbon) was not made. One study examined the effect of different metal mesh sizes on performance, focused on more coarse mesh sizes (ranging from 30 × 30 to 120 × 120 openings per inch) and a comparison with carbon fiber based materials was not made [28]. Finer metal mesh sizes have the potential to lead to better performance, compared to more coarse mesh sizes, due to their larger specific surface area. Furthermore, hydrostatic pressure tolerance and stability of MFC base materials, which are critical for large scale and long term operation, have not been well studied.

In this study, the performance and stability of activated carbon cathodes with stainless steel mesh or carbon cloth based materials were investigated. The electrochemical performance in both electrochemical cells and MFCs and the hydrostatic pressure tolerance of cathodes fabricated under different conditions were characterized. Stability as determined by susceptibility to corrosion and salt build-up on the cathode surface were also examined and discussed.

2. Experimental

2.1. Cathode fabrication

Cathodes were constructed with carbon cloth (**CC**, fuelcellearth.com) or of stainless steel mesh of four different sizes (mcmaster.com) as the base material, activated carbon powder (AC, VWR) as the catalyst, carbon black (Vulcan XC-72R) to increase conductivity, and PTFE as the binder. The stainless steel mesh sizes, characterized by the number of openings per inch, were 250 × 250 (**SS-250**), 200 × 200 (**SS-200**), 150 × 150 (**SS-150**), and 100 × 100 (**SS-100**). Activated carbon and carbon powder were combined at mass ration of 9:1 (AC:CP) and mixed with ethanol for 15 min. PTFE (60 wt%) was then added to the mixture at a mass ratio of 3:1 (AC to PTFE) and heated at 50 °C until a slurry was formed. The slurry was then applied evenly to the solution facing side of the carbon cloth cathode, air-dried overnight, and pressed at ~100 psi at activated carbon mass loading of 17.5 mg cm^{-2}. The other side of the carbon cloth, the air facing side, was prepared prior to the addition of the catalyst by applying diffusion layers as previously reported [29]. Additional cathodes were also constructed with the same procedure as above without the pressing step.

2.2. Electrochemical analysis

Cathode polarization curves were generated using linear sweep voltammetry with a potentiostat (G300, Gamery Instruments, Inc.) in a three-electrode electrochemical test cell. The test cell was constructed from PVC and measured 3 cm in diameter by 2 cm in length (empty bed volume of ~12 ml). The test cell consisted of a cylindrical single-chamber with the working electrode (cathodes with area equal to 0.7 cm^2) placed at one end of the chamber and the counter electrode (anode) placed at the other end. The reference electrode consisted of a Ag/AgCl reference (MF-2052 RE-5B, Bioanalytical Systems, USA) placed in a 200 μl pipet tip which was modified by heating and bending so that the tip faced the working electrode. The counter electrode consisted of a square piece of platinum foil (2.12 × 2.12 cm^2). Tests were conducted in a medium solution containing the following (per liter): KCl, 0.13 g; NH_4Cl, 0.31 g; $NaH_2PO_4{}^*H_2O$, 2.92 g; and $Na_2HPO_4{}^*7H_2O$, 7.735 g. LSV experiments were conducted by varying potential from +300 mV to −200 mV at a scan rate 0.1 mV s^{-1}.

2.3. Pressure tests

Pressure tolerance of cathodes was determined by measuring the static pressure head. The testing device consisted of a test piece holder (cathode test piece area equal to 7 cm^2) constructed from PVC piping and attached to a tube 2.5 m in length. The apparatus was filled with growth medium solution prepared as previously described [10]. Starting at 10 cm the tubing was raised in 5 cm increments above the test piece holder and left to stand for several hours. Tests were ended when medium solution leaked through the cathode. The pressure tolerance was recorded as the static head measurement prior to the height at which leaking occurred. The average and standard deviation of 3–4 cathodes was reported for each test condition.

2.4. MFC construction & operation

Cube-MFCs were used to determine cathode performance. The MFCs were constructed as previously described [10] with an empty bed volume ~ 12 ml. Carbon cloth (CCP, fuelcellearth.com) was used as the anode material while cathodes were as described above. All data for cathodes presented in this study was obtained by placing new cathodes into fully operational cube-MFCs. Polarization curves were generated as previously described [30] once the voltage had stabilized, typically within 5–6 batches after cathodes were placed in MFCs. MFCs were inoculated as previously described [11] using a medium solution containing the following (per liter): acetate, 5.9 g; KCl, 0.13 g; NH_4Cl, 0.31 g; $NaH_2PO_4{}^*H_2O$, 2.92 g; and $Na_2HPO_4{}^*7H_2O$, 7.735 g. All experiments were conducted in duplicate or triplicate.