Power generation by packed-bed air-cathode microbial fuel cells

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**Highlights**
- Novel and inexpensive packed-bed air-cathodes were developed for MFCs.
- The cathode was a loose bed of activated carbon granules without a binder.
- Power density was positively related to cathode material specific surface area.
- Granular activated carbon and semi-coke air-cathodes were most cost-effective.
- Oxygen transfer limited performance with thicker air-cathodes.

**Abstract**
Catalysts and catalyst binders are significant portions of the cost of microbial fuel cell (MFC) cathodes. Many materials have been tested as aqueous cathodes, but air-cathodes are needed to avoid energy demands for water aeration. Packed-bed air-cathodes were constructed without expensive binders or diffusion layers using four inexpensive carbon-based materials. Cathodes made from activated carbon produced the largest maximum power density of 676 ± 93 mW/m\textsuperscript{2}, followed by semi-coke (376 ± 47 mW/m\textsuperscript{2}), graphite (122 ± 14 mW/m\textsuperscript{2}) and carbon felt (60 ± 43 mW/m\textsuperscript{2}). Increasing the mass of activated carbon and semi-coke from 5 to 15 g significantly reduced power generation because of a reduction in oxygen transfer due to a thicker water layer in the cathode (~3 or ~6 cm). These results indicate that a thin packed layer of activated carbon or semi-coke can be used to make inexpensive air-cathodes for MFCs.

**1. Introduction**
Microbial fuel cells (MFCs) are innovative devices which can generate electricity from biomass using exoelectrogenic bacteria (Logan, 2008, 2009; Lovley, 2008; Rabaey and Verstraete, 2005). Future applications of MFCs include bioelectricity generation, wastewater treatment, desalination, chemical production, and biosensor applications (Cao et al., 2009a,b; Logan and Rabaey, 2012; Lovley, 2008; Rabaey and Verstraete, 2005; Wang et al., 2012). Oxygen in air is the most practical electron acceptor for MFCs since it is readily accessible, sustainable, and environment friendly. Many materials have been tested as the catalyst for oxygen reduction, but often these are examined using aqueous cathodes, where water is aerated to provide dissolved oxygen for the cathode suspended in a catholyte. However, direct air-cathodes are needed to avoid energy demands needed for water aeration.

Air-cathodes are constructed with the catalyst layer directly facing...
the liquid, with the other side that faces the air having diffusion layers to avoid water leakage and to limit oxygen diffusion into the anode chamber (Cheng et al., 2006a; Liu and Logan, 2004).

Precious metals such as platinum (Pt) are commonly used as cathode catalysts, but they are very expensive and the performance drops over time due to chemical and biological fouling (Zhang et al., 2009c). Alternatives to Pt that have been studied for use in MFC cathodes can be divided into three types: transition metal macroyclic compounds, non-noble metallic oxides, and carbon-based materials. Cobalt tetramethylphenylporphin (CoTMP) can produce power densities similar to that of Pt, but CoTMP is used in greater amounts than Pt, making the cost nearly equal for the two materials (Cheng et al., 2006b). Pyrolyzed carbon mixed with iron-chelated ethylenediaminetetraacetic acid (PFeEDTA/C) can produce power densities in MFCs similar to those obtained using a Pt catalyst (Wang et al., 2011), with lower performance using iron(II) phthalocyanine (FePc) (Zhao et al., 2005) and Coprophylalanine (CoNPC) (Kim et al., 2011). Cathodes made with non-noble metallic oxides, such as lead oxide (PbO2), can achieve power densities higher than those using Pt, but leaching of toxic Pb is a problem (Morris et al., 2007). Several manganese oxides (α-MnO2, β-MnO2, and γ-MnO2) have also been tested, but these showed a lower performance than Pt (Zhang et al., 2009b).

Carbon-based catalysts show great promise for oxygen reduction in MFCs due to their low cost and good performance. Activated carbon (AC) is a particularly promising material (Dong et al., 2012a,b; Wei et al., 2012; Zhang et al., 2009a) but when AC or other materials have been used as air-cathodes, a binder has been used to hold the materials together. Different types of catalyst binders have been used, and some of these materials are quite expensive. For example, Nafion is often used as a Pt catalyst binder, but its cost can be nearly equal to that of Pt in these cathodes (Zhang et al., 2012). AC cathodes are commonly constructed using a less expensive polytetrafluoroethylene (PTFE) binder. AC cathodes made by cold-pressing the AC onto a nickel mesh current collector using a PTFE binder, by a proprietary process, produced power densities comparable to those obtained with carbon cloth cathodes containing Pt and Nafion (Zhang et al., 2009a). AC has also been used with a PTFE binder in a rolling/press construction process that pressed the catalyst and binder onto a stainless steel mesh (Dong et al., 2012a,b). The mass of AC used can affect performance. In one series of tests, it was found that an AC loading rate of 43 mg/cm² was optimal (range of 7 mg/cm² to 171 mg/cm²) based on cathodes made using a cold-pressed, batch application process (Wei et al., 2012).

Diffusion layers have been used to prevent water leakage for all previously tested air-cathodes, but the number of diffusion layers and the types of materials vary (Cheng et al., 2006a; Zhang et al., 2011). Four PTFE layers are commonly used as diffusion layers for air-cathodes, based on optimization tests using Pt catalysts and carbon cloth (Cheng et al., 2006a). Alternatively, polydimethylsiloxane (PDMS) has also been used as a less expensive alternative to PTFE as a diffusion layer (Zhang et al., 2010a). When separators are used between closely spaced electrodes, minimizing the number of diffusion layers can improve the performance by maximizing oxygen transfer through the cathode (Zhang et al., 2011).

In order to avoid the need for expensive binders, diffusion layers, or the need for water aeration with carbon-based catalysts, a unique air-cathode design was investigated here. Carbon catalysts were packed onto a current collector, with the cathode oriented horizontally on top of the liquid anode chamber, avoiding the need for a binder. In addition, no diffusion layer was needed as there was no hydrostatic pressure on the cathode as in the previous air-cathode designs. Four inexpensive carbon-based materials previously examined as aqueous cathodes (Wei et al., 2011) were tested here as direct air-cathode catalysts in this new configuration: granular activated carbon, granular semi-coke, carbon felt cubes, and granular graphite. The performance of these packed-bed air-cathodes was evaluated in MFCs based on maximum power in polarization tests. Material characteristics, including specific area and total surface area, were examined and different amounts of two of the materials (activated carbon and semi-coke) were used to construct the cathode layer and examined to see the effect on performance. Dissolved oxygen concentrations were monitored within the cathode during MFC operation to measure oxygen transfer across the cathode, as oxygen crossover is an important factor in MFC performance.

2. Methods

2.1. Cathode materials

The four carbon based materials used in the cathode all varied in size and composition (Supplementary Fig. S1). Granular activated carbon (GAC) was coal-based and of a cylindrical shape, with a diameter of ~0.2 cm and lengths of ~0.3 to 1 cm (Beijing Weishi-mei Environmental Science and Technology Co. Ltd., China). Granular semi-coke (GS) had lengths of ~0.3 to 0.5 cm (China Electric Power Research Institute). Carbon felt cubes (CFC) had a slightly longer length of ~1 cm, and a thickness of ~0.5 cm (Beijing Sanye Carbon Co., Ltd., China). Granular graphite (GG) particles were cylindrical, with a diameter of ~0.8 cm and lengths of ~0.5 to 1 cm (Beijing Sanye Carbon Co. Ltd., China). All these carbon materials were cleaned in 20% HCl solution for 24 h to solubilize and remove trace metals, and then washed with deionized water prior to drying at room temperature.

2.2. MFC construction and operation

Packed-bed air-cathode MFCs were constructed with the anode chamber at the bottom, an anion exchange membrane (AEM, AMI-7001, Membrane International, USA) as a separator in the middle, and a cathode chamber open to the air on the top (Fig. 1). Titanium mesh was placed on the surface of the separator and used as a current collector. To compare performances of the different materials on a relatively common height basis, 5 g of GAC, GS and GG, or 2 g of CFC were added onto the current collector to form packed-beds of ~1 cm (7 cm² projected area). A mass of 5 g of GS was the minimum needed to form a single layer that completely covered the whole membrane. To further study the effect of the amount of the material and cathode height on performance, 10 g (~3 cm) and 15 g (~6 cm) of GAC or GS were used in further tests and an additional titanium mesh was added as a second current collector. A catholyte consisting of a 50 mM phosphate buffer solution (PBS; 4.57 g/L Na2HPO4, 2.45 g/L NaH2PO4·H2O, 0.31 g/L NH4Cl and 0.13 g/L KCl) was used to fill the packed bed to the top of the packed materials, and after each cycle the catholyte was refilled to the same height.

Fig. 1. (A) Schematic and (B) photo of packed-bed air-cathode MFC.
The anode was a graphite fiber brush with a core of two twisted titanium wire current collectors (Logan et al., 2007) that was heat treated in a muffle furnace at 450 °C for 30 min (Wang et al., 2009). Anodes were all first acclimated in single-chamber MFCs with liquid volume of 21 mL (inoculated from MFCs operated for over one year) that had carbon cloth air-cathodes with 0.5 mg/cm² platinum catalyst and four polytetrafluoroethylene (PTFE) diffusion layers (Cheng et al., 2006a). All MFCs were fed with 1 g/L acetate in 50 mM PBS amended with 12.5 mM/L mineral and 5 mM/L vitamin solutions (Logan et al., 2007), and operated at 30 ± 1 °C. After all anodes exhibited stable and parallel performance (~20 cycles of 2 days each), they were used in packed-bed air-cathode MFCs.

2.3. Analysis of MFCs

Voltages (E) were recorded across an external resistance (R) at 20 min intervals using a data acquisition system (2700, Keithley Instrument, USA) connected to a personal computer. After stable and repeatable voltages were generated by packed air-cathode MFCs for at least two cycles, polarization tests were conducted after 2 h of operation for the reactor initially operated at 1000 Ω external resistance. Polarization data were obtained by varying external resistance in decreasing order (from 1000 to 50 Ω) with 20 min intervals at each resistance (except for 1000 Ω, 2 h). Current densities (i) and power densities (P) were normalized by packed-bed air-cathode projected area (A = 20 cm²), using i = E/RA and P = E/R (Logan et al., 2006). The power densities (P) were also normalized by the weight of cathode materials (M), using P = iE/M. Anode potentials were reported versus an Ag/AgCl reference electrode (+0.211 V vs. a standard hydrogen electrode; RE-5B; BASi, West Lafayette, USA).

Dissolved oxygen (DO) of the catholyte was monitored using a non-consumptive DO probe (Foxy-18G, Ocean Optics Inc., USA). The DO probe was calibrated by two points using water saturated and air saturated with nitrogen gas.

2.4. Water layer effect test

To further understand the effect of the water layer separate on performance, additional experiments were conducted using a commercially produced AC cathode previously used in MFC tests (Zhang et al., 2009a). This cathode contained AC powder (Norit SX plus, Norit Americas Inc., USA), a PTFE binder, and a Ni mesh current collector (#53 mesh, 330 µm diameter) but no diffusion layers (VITO, Mol, Belgium). The MFCs were initially operated in the same orientation as the packed-bed cathodes (cathode facing up into the air) without a water layer. After 1 month, 50 mM PBS was poured onto the surface of the cathode. After 1 month, 50 mM PBS was poured onto the surface of the cathode (7 cm²) and the performance was compared using polarization data before and after water addition.

3. Results and Discussion

3.1. Power generation with different carbons

The maximum power densities were significantly altered by the use of the different carbon based materials (Fig. 2). MFCs with GAC produced the largest maximum power density of 676 ± 93 mW/m² (1.8 A/m²; normalized by projected air-cathode area, 7 cm²), followed by GS (376 ± 47 mW/m²), GG (122 ± 14 mW/m²) and CFC (60 ± 43 mW/m²) (Table 1). The anodes of the different MFCs all had similar performance, and thus the differences in power were due to the cathode performance (Fig. 2). This general trend in performance based on the type of material used to make the air-cathodes here is similar to that reported by Wei et al. (2011) when these materials were used as aqueous biocathodes, in an air-sparged solution (i.e., GAC followed by GS, GG, and CFC). However, the power densities were all much greater here than those reported with the aqueous biocathodes. The CFC material produced a lower maximum power density here that obtained in an MFC with an up-flow MFC with an aqueous cathode (315 mW/m²) (Deng et al., 2010). The CFC material was much lighter than the other three materials, and thus only 2 g was sufficient to cover
the membrane and produce the same height of the packed-bed air-cathode (~1 cm; 5 g for GAC, GS and GG). The maximum power density of CFC normalized by the weight was 21 ± 15 mW/kg, slightly higher than GG (17 ± 2 mW/kg), but still much lower than GAC (95 ± 13 mW/kg) and GS (53 ± 7 mW/kg). In all cases here, the use of the direct air-cathode, as opposed to an aqueous cathode which requires an air sparged liquid, avoided the need for energy intensive aeration. The duration of each cycle of the best two packed-bed air-cathode MFCs (GAC and GS) was ~72 h and voltage generation was stable throughout the cycle (Supplementary Fig. S2).

Previous reports of different ACs used in MFC cathodes have concluded that surface area is an important factor in cathode performance (Dong et al., 2012a). Here, the two best performing carbon materials also had the highest specific surface areas (Table 1). GAC had the largest specific area of 686 m²/g, followed by GS (236 m²/g) (Table 1). These surface areas are about three orders of magnitude higher than those of GG and CFC. Based on the mass of packed-bed air-cathode materials, total surface areas were calculated and relative values were as follows: GAC > GS > GG > CFC, which were in consistence with power density results (Table 1).

3.2. Power generation for different amount of GAC and GS

Since cathode performance was positively related to the total surface area of the material, different masses of GAC and GS were used for packed-bed air-cathode to see if the power generation could be improved by increasing the catalyst mass. However, power was decreased by adding additional catalyst, with the maximum power density decreasing to 115 ± 28 mW/m² (1.0 A/m²) when using 15 g of GAC. This was only 17% of that obtained with 5 g GAC (676 ± 93 mW/m²) (Fig. 3). The maximum power density was further decreased when the mass of GAC was increased to 30 g (55 ± 12 mW/m²) (Fig. 3). The anodes all had similar performance in these tests, and thus the decreases in power were due to cathode performance (Fig. 3). Adding more GS also significantly reduced performance with 80 ± 16 mW/m² with 15 g of catalyst, and 18 ± 3 mW/m² with 30 g, compared to 376 ± 47 mW/m² with 5 g (Supplementary Fig. S3).

3.3. Dissolved oxygen of packed-bed air-cathode

Previous studies have shown that air-cathode performance was positively correlated with the oxygen transfer coefficient (Zhang et al., 2011), and lower DO concentrations are known to affect the performance of liquid phase cathodes (Oh et al., 2004). Therefore the DO concentration of the catholyte was measured in an operating MFC to determine if oxygen concentrations in the cathode were affecting performance here. At a fixed external resistance (1000 Ω), the height of the cathode layer and water was ~1 cm using 5 g of GAC or GS. DO concentrations in the cathode/catholyte at a distance very close to the separator (0.2 cm) with 5 g of the GAC or GS were 7.1 mg/L and 6.7 mg/L (Fig. 4), which is close to DO saturation (7.56 mg/L in 50 mM PBS). When 15 g of one of these materials was used, the cathode height increased from ~3 cm, and the DO concentration at the same distance (0.2 cm) from the separator was reduced by 84% to only 1.1 mg/L (Fig. 4). At greater distances of 1.5 cm and 2.5 cm, DO concentrations were slightly higher with 1.7 mg/L (GAC) and 1.4 mg/L (GS) at 1.5 cm, and 3.8 mg/L (GAC and GS) at 2.5 cm (Fig. 4). Previous studies have shown that DO concentrations below ~3 mg/L reduce power generation in aqueous cathode MFCs (Oh et al., 2004). These results therefore show that lower DO concentrations due to the longer diffusion path for oxygen with the increased water heights, was the main factor in reduced MFC performance.

Increasing the current density by using a lower external resistance (150 Ω) further reduced DO concentrations within the cathode solution due to increased rates of oxygen utilization by the cathode. Compared to current densities produced using the 1000-Ω external resistance, the DO concentrations at 0.2 cm and 150 Ω were reduced by 36% to 0.7 mg/L for 15 g of GAC, and by

Fig. 3. (A) Power densities and (B) electrode potentials (cathode, filled symbols; anode, open symbols) as a function of current density in MFCs using different amounts of granular activated carbon (GAC) for packed-bed air-cathode.

Fig. 4. DO concentrations in catholytes of granular activity carbon (GAC) and granular semicoke (GS) packed-bed air cathode MFCs. The catholyte for 5 g GAC and GS was added to a height of ~1 cm, reaching the top of the packed-bed air-cathode material, and for 15 g GAC and GS the catholyte height was ~3 cm. DO concentrations were tested at a height of 0.2 cm for 5 g GAC and GS MFCs and at a height of 0.2, 1.5, and 2.5 cm for 15 g GAC and GS MFCs. The MFCs were operated with (A) 1000 Ω resistor and (B) 150 Ω resistor.
45% to 0.6 mg/L for 15 g of GS (Fig. 4). At distances of 1.5 cm and 2.5 cm, the DO concentrations were reduced by 47% to 55%. These results demonstrate that adding more catalyst did not increase power due to the depressed DO concentrations in the catholyte.

3.4. Water layer effect on cathode performance

The effect of this water layer was also examined using an AC cathode containing a PTFE binder that has been used in previous MFC studies (Zhang et al., 2009a). The maximum power density with this AC-binder cathode was 981 ± 185 mW/m$^2$ (3.7 A/m$^2$) (Fig. 5) in the absence of the water layer. When the water was added on top of the cathode to a height of 0.5-cm, the maximum power density decreased by 57% to 420 ± 12 mW/m$^2$ (1.7 A/m$^2$) (Fig. 5). This shows that water flooding, and the reduced oxygen transfer through the water layer to the cathode, resulted in a significant reduction in power. This power density with the water layer is actually lower than that produced here using 0.5 g of GAC (676 ± 93 mW/m$^2$) (1.8 A/m$^2$). Thus, the presence of the binder and possible differences in electrical conductivity were less important than the presence of the water layer. However, the water layer was needed here to avoid the lack of poor connectivity of the catalyst with the water.

3.5. Economic assessment

The four carbon-based materials in this study (GAC, GS, CFC and GG) are all many industrial products, with GAC commonly used in water treatment process. According to the current average market prices in China (http://china.alibaba.com), the costs of these materials are: 0.1 to 1 €/kg, GAC; 0.01 to 0.1 €/kg, GS; 0.5 to 3.5 €/kg, GG; and 18 to 65 €/kg, CFC. Based on loading rates in this study (GAC and GS, 7.15 kg/m$^2$), the cost of the cathode carbon would be 0.7 to 7.2 €/m$^2$ for GAC, and 0.1 to 0.7 €/m$^2$ for GS. The cost of current collector (stainless steel mesh) would be 6 to 12 €/m$^2$. The total costs of the packed-bed air-cathode material and current collector are significantly less than those of Pt of 125 €/m$^2$ (assuming 25 €/g, and 0.5 mg/cm$^2$ Pt) (Cheng et al., 2006a) and the activated carbon powder based cathode that used a PTFE binder and a PTFE diffusion layer (52 €/m$^2$, activated charcoal + PTFE layer + current collector) (Pant et al., 2010). MFCs using Pt catalysts can produce higher maximum power densities of 786 ± 65 mW/m$^2$ with an AEM as a separator and a stainless steel mesh (Zhang et al., 2010b), and up to 1815 ± 236 mW/m$^2$ at 30 °C with a glass fiber separator (Zhang et al., 2013). Thus, while the power densities produce here using GAC and GS are lower (676 ± 93 mW/m$^2$ and 376 ± 47 mW/m$^2$), the reduction in cost may make the use of these materials possible for overall economic reasons.

4. Conclusions

Packed-bed air-cathode MFCs constructed with GAC produced the highest maximum power density, followed by GS, GG and CFC. When more GAC or GS was added to increase the total surface area, the power densities were significantly reduced due to resulting lower dissolved oxygen concentrations in the catholyte. Therefore, while the packed-bed configuration can produce power with an inexpensive carbon material, and no binder or diffusion layers are needed, the water height will need to be controlled to optimize power. This configuration using a thin layer of GAC and GS could provide a cost effective alternative to platinum catalyst air-cathodes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.05.014.

References


