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A high-performance rotating graphite fiber brush air-cathode for microbial fuel cells

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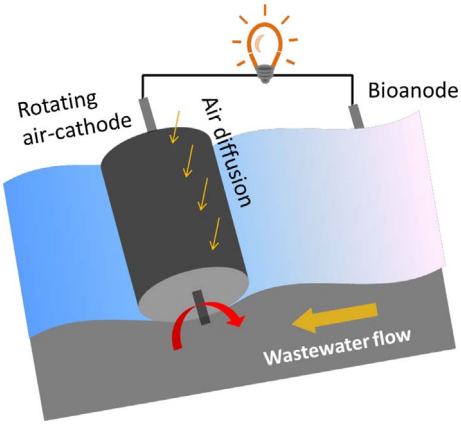
HIGHLIGHTS

- A binder-free rotating air-cathode is presented for enhancing ORR electrocatalysis in MFCs.
- It provided more three-phase oxygen reduction interface and enhanced mass transfer.
- It showed enhanced ORR electrocatalysis under a slow speed rotation conditions.
- It could be arranged horizontally in practically relevant systems to avoid water leaking.
- Bioenergy harvested by the MFCs or the flow of wastewater would be used to rotate such air-cathodes.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFC) represent an emerging technology to harvest electric energy from waste streams like wastewaters. To further increase MFC performance, the individual fuel cell processes, such as the cathodic oxygen reduction (ORR) need to be further improved. The commonly used, two-dimensional air-cathodes usually show limited performance due to a low three-phase ORR interface and a low oxygen mass transfer rate. To address these issues, a binder-free rotating three-dimensional air-cathode that provides a larger three-phase ORR interface and an enhanced oxygen mass transfer rate is reported in this paper. The cathode is prepared by coating a self-supporting N and P co-doped carbon ORR catalyst layer onto a graphite fiber brush current collector (GB/NPC). No binder and diffusion layer are used to avoid the limitations associated with these components. The electrochemical tests demonstrate enhanced ORR electrocatalysis under rotation conditions. In MFCs, a high performance was achieved by operating the GB/NPC air-cathode at a slow rotation speed. For example, at 20 rpm, it delivered three times higher cathodic current (1.02 ± 0.05 mA cm^{-2}) and two times higher power output (879 ± 16 mW m^{-2}, normalized to the projected surface area of air-cathode) than its counterpart non-rotating, static air-cathode (0.35 ± 0.03 mA cm^{-2} and 486 ± 11 mW m^{-2}, respectively). The rotating conditions increased the availability of catalytic sites for the ORR, and improved oxygen diffusion and OH^- transport at or within the air-cathode. This study thus presents a promising approach for enhancing the performance of air-cathodes, which is often the major performance-limiting component of the MFCs.

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1. Introduction

As an emerging wastewater treatment and bioenergy recovery approach, research domains and application range of microbial fuel cells (MFCs) are expanding rapidly [1–3]. This microbial electrochemical technology takes advantage of mixed cultures containing electroactive bacteria to mineralize the organic waste present in wastewaters and to generate electric power simultaneously. It has the potential to reduce the energy consumption of wastewater treatment process and to recover the bioenergy contained in different types of wastewaters [4,5]. The realization of practical applications of the MFC technology is still hampered by (i) comparatively low current or power outputs, which limits its efficiency of pollutant removal, (ii) its high capital cost and (iii) poor long-term operational stability of the cathode. Thus, increasing power generation and long-term stability at decreased cost level, is the key to achieve its real-world applications [6–9].

The cathode is widely regarded as the major performance-limiting component of the MFCs [8,10,11]. Over the past decade, several studies have focused on the development of noble-metal free ORR cathode catalysts to replace high-cost, precious metal catalysts. A series of such ORR catalysts, including heteroatom-doped carbon [12–14], metal oxides and activated carbon [15] and Fe, Co, Ni and Mn catalysts has been explored [8,10,11,16–18]. Beside the catalytic activity of ORR catalysts, the quantity of active catalytic sites, mass transport of OH^-, the rates of electron transfer and oxygen diffusion also greatly affect the cathode performance. The most feasible cathode configuration for large-scale application of MFCs, e.g., for wastewater treatment, is the air-cathode because its use solves the issue of limited oxygen solubility in water, and makes purging obsolete thus greatly reduces the energy consumption for wastewater treatment [19,20]. The non-limiting availability of oxygen at the air-cathodes, ultimately, makes it possible to achieve higher current densities.

The commonly used air-cathode is based on an ORR catalytic layer and a waterproof, air-breathing diffusion layer, which are bonded onto the both sides of a current collector using polymer binders [19–21]. However, it shows limited performance despite the use of highly active ORR catalysts. The possible reasons are: (i) its two-dimensional (2D) three-phase ORR interface, which provides a limited surface area and catalytic sites for ORR, (ii) its operation under static conditions, which lead to a low oxygen mass transfer rate, and (iii) the use of polymer binder, which covers a large number of active sites of ORR catalyst and obstructs the oxygen diffusion through such cathode. The use of binder and additional diffusion layer adds to the cost and importantly, leads to a high electrode resistance, which decreases the electron transfer rate. Moreover, the biofouling and salt deposition also greatly decrease the long-term stability of the 2D air-cathodes [22–27].

It was reported recently that increasing the exposed area of the air-cathode could enhance the power density of MFCs [28]. Inspired by the rotating biological contactor, developed to improve oxygen diffusion to the attached biofilms for aerobic bacterial metabolism of organic waste [29], a rotating cathode loaded with Pt catalyst was firstly attempted by He et al. in 2007 to improve the availability of oxygen to the cathode in a sediment MFC [30]. About 70% power output improvement by the rotating cathode compared to a non-rotating cathode was reported. The contribution of rotation to the real ORR catalytic performance of the rotating cathode was, however, not studied in this case. Notably, no research has been conducted on the use of such approach for typical MFCs proposed for harvesting bioenergy from different wastewaters so far. Therefore, in order to address the limitations as mentioned earlier for routinely used 2D air-cathodes; the approach of using rotating air-cathodes was thoroughly investigated in this study. Fig. 1 shows a proposed schematic of the MFC equipped with the rotating air-cathode for harvesting bioenergy from the practical wastewater treatment process.

The air-cathode was prepared by binder-free coating of N, P co-doped carbon ORR catalyst onto a graphite fiber brush current collector

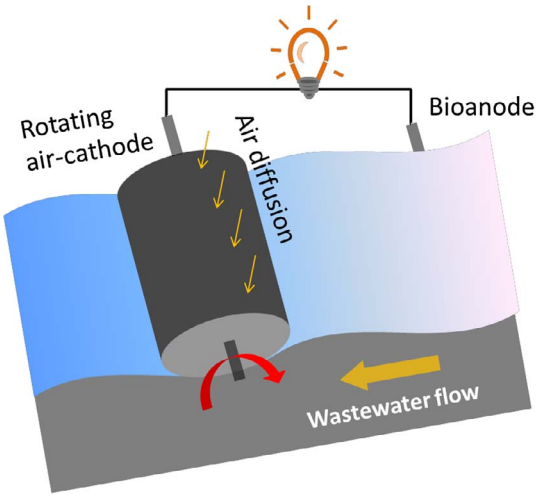

Fig. 1. Schematic of the MFC equipped with a rotating air-cathode for harvesting energy from the practical wastewater treatment process. The rotating air-cathode can be arranged horizontally and driven by the flow of wastewater or by the power that is generated by the wastewater treating MFCs when it is used for practical wastewater treatment.

(denoted as GB/NPC). It was first characterized electrochemically for ORR reaction and then tested in practically relevant two-chambered MFCs under static and rotating conditions. The effect of rotating speed on the performance of the GB/NPC air-cathode was studied systematically. The MFC equipped with the rotating air-cathode was able to harvest two times more electric power than its counterpart, non-rotating, static air-cathode. The slow rotation of the air-cathode may be driven by the wastewater flow without any external energy consumption. This approach is easier to scale up because of the possibility to arrange such cathodes horizontally at the surface of the wastewater stream and thereby avoid the concern of water leaking that usually occurs with the vertically arranged 2D air-cathodes. With this study, we thus present a novel design and operational approach for enhancing the performance of the air-cathode, which is the major performance-limiting component of the MFCs.

2. Experimental

2.1. Materials

Graphite fiber brushes (GBs) with the size of 26 mm in diameter and 42 mm in length were made by fixing graphite fibers (TORAY) on a twisted titanium wire and had a projected area of approximate 10.9 cm^2 (calculated by multiplying the diameter and the length) and surface area of 34.2 cm^2. The twisted titanium wire had a diameter of about 2 mm. All chemicals including ammonium persulfate, aniline and phytic acid (PA) (50 w/w in water) were purchased from Sigma Aldrich.

2.2. Preparation and characterization of the GB/NPC cathode

GBs were first immersed into a 50% (w/w) concentrated sulfuric acid for five minutes to improve their hydrophilicity and then washed with distilled water for three times before further use. Polyaniline (PANi) was grown onto the GB by a chemical oxidative polymerization process. The polymerization was carried out at a temperature range of 0 to 5 °C, based on the protocol published elsewhere [31]. Briefly, separate solutions of 0.06 M aniline and 0.015 M ammonium persulfate were prepared by dissolving 0.559 g and 0.342 g, respectively in 100 mL 2 M HCl solution. Both solutions were then mixed vigorously, and the GB electrode was immersed into this mixture immediately. After oxidative polymerization for about 12 h, the composite GB/PANi