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Effects of brush lengths and fiber loadings on the performance of microbial fuel cells using graphite fiber brush anodes

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ABSTRACT

An alternative method for fabricating graphite fiber brush (GFB) electrodes was proposed. Two series of GFB electrodes with different lengths (L) and loaded fiber masses (m) were fabricated. The effects of m/L on the biomass distribution, active biomass content, electrochemical behavior and MFC performance were investigated. For the electrodes with a similar m but different L, substrate supply within the interior of GFB electrodes improved with L, leading to higher biomass content and consequently the improved performance. However, a complex trend was found for the electrodes with different m and similar L, due to the opposing trends of substrate supply and actual functional area for electrochemically active bacteria with m. Furthermore, m-normalized biomass content and power density of the GFB electrodes increased with decreasing of m/L ratio due to the improved graphite fiber utilization until 0.014 g mm $^{-1}$, below which they remained constant since the utilization of graphite fibers plateaued.

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1. Introduction

Microbial fuel cell (MFC) is a promising technology for recovering electricity from wastewater. However, its practical application is limited by cell performance due to the sluggish kinetics of the electrochemical interactions between the anode and electrochemically active bacteria (EABs) [\[1,2\].](#page--1-0) It has been demonstrated that using high specific surface area electrodes can substantially improve cell performance since it's beneficial for EAB adhesion and biofilm formation $[3-6]$ $[3-6]$ $[3-6]$.

However, the inherent clogging problem would induce proton diffusion limitation and insufficient substrate supply inside the interior of the electrode, leading to decreased utilization of carbon materials $[7-10]$ $[7-10]$ $[7-10]$. Recently, many open macroscale porous anodes, such as graphene-coated sponges [\[7\],](#page--1-0) carbon nanotube-textile composite [\[8\],](#page--1-0) carbonized kenaf stem [\[9\]](#page--1-0) and electrospun carbon fiber nonwovens [\[10\]](#page--1-0) have been developed for increasing performance by improving the internal microbial colonization, efficient substrate transport and product removal.

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Among these anodes, graphite fiber brushes (GFB) are considered to be one of the most suitable electrodes $[11-13]$ $[11-13]$ $[11-13]$ because of the open structure, low electrode resistance, and most importantly, low cost as well as ease of fabrication. Although promising, a full understanding is still lacking on the impact of manufacturing parameters on the performance. One of the parameters, that differentiates individual GFB electrodes, is their loaded fiber masses (fiber loadings) on the electrodes. However, GFB electrodes with different fiber loadings and the same brush length provide not only various total BET (Brunauer–Emmer–Teller) surface areas but also different number of graphite fibers per length, both affect bacterial adhesion, biomass growth, substrate accessibility and product removal of the electrodes. Additionally, the conventional method doesn't ensure a proper distribution of graphite fibers along the twisted titanium core because of random fiber distribution along the folded titanium wire before twisting (Fig. 1a), adding extra difficulty in optimizing brush architectures for larger applications [\[11\]](#page--1-0). Although decreasing the fiber loading on a GFB electrode can increase the startup time of a MFC [\[13\],](#page--1-0) additional studies are still indispensable to correlate the relationship between manufacturing parameters of GFB electrodes and electricity generation of a MFC.

In this study, an alternative method is proposed for fabricating a GFB electrode with well-defined structural properties. Two series of GFB electrodes with a different number of graphite fibers per length were prepared. Doing so, it was possible to draw correlations between the manufacturing parameters of the GFB electrodes and their performance in MFCs.

2. Materials and methods

2.1. Electrode fabrication

The graphite fibers (Shenyang, China) with a diameter of 6.8 \pm 0.4 µm (n = 100) and a specific BET surface area of 2.36 \times 10³ cm² g⁻¹ were used directly without further treatment. In order to ensure regular distribution of graphite fibers along the twisted titanium core, the reported method [\[11\]](#page--1-0)

Fig. 1 – Schematic illustration of the conventional (a) and modified method (b) for fabricating graphite fiber brush electrodes.

(Fig. 1a) was modified as follows (Fig. 1b): A titanium wire was folded and twisted to form a succession of regular loophole openings. Several graphite fiber bundles, with the same appropriate mass and length, were fit into each loop. Then, the twisting movement was continued so that the graphite fibers in each bundle were crimped to form a spiral structure. The equal fiber loading in each loop-hole opening, i.e. the repeatable fiber distribution along the titanium cores, was ensured by the proposed method. Therefore, a series of well-defined GBF electrodes with different fiber loads and brush lengths can be manufactured by controlling the mass of each graphite fiber bundle and the number of loop-hole openings used.

The number of graphite fibers per length (D_f , mm^{-1}) of the GFB electrode can be expressed by the following equation, assuming all the graphite fibers with the same diameter.

$$
D_{\rm f} = \frac{m}{m_0 L} \tag{1}
$$

where m and m_0 is the fiber loading on the electrodes (g) and the mass of a single graphite fiber (g), respectively. L is the length of the GBF electrodes (mm). From Eq. (1), D_f is proportional to m/L at a constant m_0 . Therefore, D_f can be quantified by the m/L ratio. In this study, two series of the GFB electrodes were fabricated [\(Table 1\)](#page--1-0). The 1st series was prepared by varying L at a nearly constant m (~0.7 g), leading to different D_f (or m/L) values but nearly unchanged total BET surface area, since the total BET surface area is only proportional to the m value. To confirm the results obtained from the 1st series, the 2nd series was fabricated by varying m with a constant L (30 mm). Different from the 1st series, the 2nd series provided different D_f (m/L) values together with various total BET surface areas. The outer diameter for all the electrodes was fixed at 25 mm. The electrode samples in [Table 1](#page--1-0) were denoted using the notation "E-m-L", where m stands for the graphite fiber loading and L the electrode length.

2.2. MFC construction and operation

The effects of m and L on the electricity generation were studied in five parallel dual-compartment MFCs at 25 ± 2 °C. The anodic (30 \times 40 \times 70 mm) and cathodic (30 \times 80 \times 70 mm) chamber equipped with Ag/AgCl reference electrodes (0.198 V vs. SHE) were separated by a proton exchange membranes (30 \times 70 mm, Nafion 117, Dupont). For all the experiments a plain carbon cloth (30 \times 70 mm) was used as the cathode.

The MFCs were inoculated from the effluent of an active, acetate-fed MFC. The components of anodic culture medium were the same with Ref. [\[10\]](#page--1-0). The deoxygenated catholyte containing 100 mM $K_3[Fe(CN)_6]$ and 50 mM phosphate buffer were supplied at 30 mL $\rm h^{-1}.$

2.3. Measurements and calculations

The total active biomass on the electrodes was analyzed according to the reported procedure [\[14\]](#page--1-0). To obtain the information on the biomass distribution on the graphite fibers, the difference in the biofilm morphology between the tips and bases of graphite fibers were characterized by a TESCAN VEGA SEM (scanning electron microscope) system. SEM Sample preparation was based on our previous report [\[6\]](#page--1-0)

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