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Anion exchange polymer coated graphite granule electrodes for improving the performance of anodes in unbuffered microbial fuel cells



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HIGHLIGHTS

• The performance of QDPSU and Nafion coated anodes is relatively stable without PBS.

• QDPSU and Nafion coatings served as a solid state buffer.

• QDPSU provided a favorable microenvironment for the anodic biofilm.

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ABSTRACT

In this paper, graphite granule composite electrodes are prepared for microbial fuel cells (MFCs) by coating commercial graphite granules with the mixture of quaternary DABCO polysulfone or Nafion ion exchange polymer and carbon black. The results of electrochemical impedance spectroscopy (EIS) suggest that the addition of carbon black could significantly improve the electrical conductivity of graphite granule anodes. When phosphate buffer solution (PBS) is replaced by NaCl solution, the current densities of the pristine anode, 0.08 g Nafion coated ande and 0.16 g QDPSU coated anode decrease by 52.6%, 20.6% and 10.3% at -0.2 V (vs. Ag/AgCl), respectively. The solution resistance of ion exchange polymer coated anode sis more stable in comparison with that of pristine anode. After 40 operational days, the performance drop of 0.16 g QDPSU coated anode when switching the solution from PBS to NaCl is still smaller than that of pristine anode. However, 0.08 g Nafion coated anode shows the similar performance in NaCl solution to the pristine anode after long term operation. This study reveals that QDPSU anion exchange polymer is more suitable for the anode modification. The QDPSU coated anode promises a great potential for three-dimensional anode based MFCs to treat domestic wastewater.

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1. Introduction

Microbial fuel cells (MFCs) can directly convert organic matter in wastewater into electricity. MFCs can be modified for applications of denitrification [1], dye decolorization [2], heavy metal recovery [3] and chemical bio-synthesis [4,5]. However, because of mild operating conditions and requisite of bacteria catalyzed electrodes, the performance of MFCs is significantly lower than that of

* Corresponding author. E-mail address: xu.wang@whu.edu.cn (X. Wang). conventional fuel cells (e.g., direct alcohol fuel cells). Extensive efforts have been made to improve the cell performance and reduce costs, including improvement of reactor design [6,7], adoption of three-dimensional electrodes [8], modification of electrodes [9], enrichment of highly specialized microbial communities [10], application of low cost highly active catalysts and biocatalysts [11,12], and optimization of operating conditions [13].

The anodes of MFCs are attached with microorganisms that facilitate the oxidation of organic matter in wastewater. The anode performance has a great impact on the MFC performance [8]. In comparison to the use of two-dimensional electrodes (e.g. carbon cloth or carbon paper), three-dimensional electrodes have higher surface to volume ratios of up to $6.0 \times 10^6 \text{ m}^2 \text{ m}^{-3}$ which increases the attachment of bacteria and improves the anode performance [14]. A number of electrode materials were investigated including graphite granules [15], carbon brush [8], granular activated carbon [16], and nanofiber textile [17]. Lately, a maximum power density of 2420 mW m⁻² was achieved using a polypyrrole/poly(vinyl alcohol-*co*-polyethylene) nanofibers/poly(ethylene terephthalate) (PPy/NFs/PET) nanofiber anode [17]. The distance of twodimensional anode and cathode can be easily minimized and thus the ionic resistance can be effectively reduced. For a threedimensional anode based MFC, the distance between the internal parts of the anode to cathode is relatively large. Therefore, the ionic resistance in three-dimensional anode based MFCs becomes a significant factor for limiting the performance of enlarged MFCs

when treating domestic wastewater which has a low ionic conductivity (~1 mS cm⁻¹).

Although anode materials have been modified with metal oxides, electron conductive polymers, carbon materials [9,18–22], there are few reports on modifying anodes for increasing the ionic conductivity. According to our previous report, quaternary DABCO polysulfone (QDPSU) can accelerate OH⁻ ion transfer of the air cathode resulted in better performance than that of the air cathode using Nafion ionomer [23]. Wang et al. observed the similar phenomenon using an anion exchange resin modified activated carbon (AC) for air cathode MFCs [24].

In this paper, anion exchange polymer is applied on a graphite granules anode (as shown in Fig. 1a). The QDPSU anion exchange polymer and cation exchange membrane (Nafion[®]117) can form a



Fig. 1. Schematic diagrams of a) anion exchange polymer and carbon black coated graphite granular anode, b) ion transport in a dual-chamber MFC with a QDPSU coated anode.

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