Journal of Power Sources xxx (2017) 1–8

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Combined carbon mesh and small graphite fiber brush anodes to enhance and stabilize power generation in microbial fuel cells treating domestic wastewater

Shijia Wu [a], Weihua He [b], Wulin Yang [c], Yaoli Ye [c], Xia Huang [a, **], Bruce E. Logan [c, *]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, PR China
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No. 73 Huanghe Road, Nangang District, Harbin 150090, PR China
[c] Department of Civil and Environmental Engineering, 212 Sackett Building, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- A novel composite anode was developed that combined brushes and carbon mesh.
- The composite anode had higher power output and CEs than either of the other anodes.
- Power overshoot was mitigated with the composite anode MFCs at higher CODs.
- MFCs with the composite anode had less cathode biomass growth.
- The carbon mesh with biofilms in the composite anode also functioned as a separator.

ARTICLE INFO

Article history:
Received 6 November 2016
Received in revised form
19 December 2016
Accepted 9 January 2017
Available online xxx

Keywords:
Microbial fuel cells
Power generation
Oxygen contamination
Power overshoot
Anode configurations

ABSTRACT

Microbial fuel cells (MFCs) need to have a compact architecture, but power generation using low strength domestic wastewater is unstable for closely-spaced electrode designs using thin anodes (flat mesh or small diameter graphite fiber brushes) due to oxygen crossover from the cathode. A composite anode configuration was developed to improve performance, by joining the mesh and brushes together, with the mesh used to block oxygen crossover to the brushes, and the brushes used to stabilize mesh potentials. In small, fed-batch MFCs (28 mL), the composite anode produced 20% higher power densities than MFCs using only brushes, and 150% power densities compared to carbon mesh anodes. In continuous flow tests at short hydraulic retention times (HRTs, 2 or 4 h) using larger MFCs (100 mL), composite anodes had stable performance, while brush anode MFCs exhibited power overshoot in polarization tests. Both configurations exhibited power overshoot at a longer HRT of 8 h due to lower effluent CODs. The use of composite anodes reduced biomass growth on the cathode (1.9 ± 0.2 mg) compared to only brushes (3.1 ± 0.3 mg), and increased coulombic efficiencies, demonstrating that they successfully reduced oxygen contamination of the anode and the bio-fouling of cathode.

1. Introduction

Microbial fuel cells (MFCs) are bioelectrochemical devices that are being investigated for accomplishing wastewater treatment and energy production due to their ability to generate electricity from the degradation of organic matter in the wastewater [1,2]. Air-cathode MFCs are the most promising design for practical applications since they use passive transfer oxygen to the cathode, avoiding energy needed for water aeration [3]. Scaling up MFCs to treat real wastewaters, such as domestic wastewater which has a low conductivity (~1 mS cm^{-1}), requires a compact design with closely spaced electrodes to minimize solution and electron transfer resistances [4]. To avoid direct electrode contact when the anode and cathode placed next to each other, a cloth or battery separator is placed between the electrodes, creating a configuration

* Corresponding author.
** Corresponding author.
E-mail addresses: xhuang@tsinghua.edu.cn (X. Huang), blogan@psu.edu (B.E. Logan).

http://dx.doi.org/10.1016/j.jpowsour.2017.01.041
0378-7753/

known as a separator electrode assembly (SEA) design [5]. Although the SEA designs should generate higher power densities than MFCs with greater spacing between the electrodes due to the reduction in ohmic resistance [6], close electrode spacing can result in decreased power generation due to oxygen crossover through the cathode, which reduces the activity of exoelectrogens on the anode [7]. Power generation using a flat carbon cloth anode decreased when it was moved from 2 cm to 1 cm near a cathode in the absence of a separator [7], and power generation could not be maintained using wastewater with a carbon mesh anode placed directly against the separator in an SEA configuration [8].

MFCs with graphite fiber brush (GFB) anodes have been shown to produce higher power densities than flat carbon cloth or carbon mesh anodes due to their high specific surface area, high porosity, and low electrical resistance, and they are relatively inexpensive and easy to fabricate [9,10]. Brushes (typically 25 mm in diameter) can be placed close to the cathode in an SEA configuration without impaired power production [8], suggesting that the thick and porous structure helps to maintain the anoxic conditions needed within the anode for electricity generation even with oxygen transfer through the cathode and separator. However, larger brush anodes do not necessarily produce more power than smaller brushes, and thus the size of the brush, its distance from the cathode, and the concentration of organic matter in the solution can all impact performance. Brushes 25 mm in diameter produce stable power in small (28 mL) and larger (ranging from 170 mL to 6.1 L) MFCs when placed near to the cathode using acetate (~1000 mg L^{-1}, equal to ~780 mg L^{-1} of chemical oxygen demand, COD) in a phosphate buffer or domestic wastewater [11–14]. Smaller diameter brushes (8 mm) produced much higher power (1020 mW m^{-2}) than three larger brushes (25 mm, 560 mW m^{-2}) in continuous flow MFC tests using acetate (1000 mg L^{-1}) due to the closer spacing between the center of brushes and the cathode, despite the fact that the larger brushes had more surface area for biofilm growth [11]. When these smaller brushes were used in the same MFCs with lower-strength domestic wastewater (~300 mg-COD L^{-1}), the reactor produced at the start of the fed batch cycle a lower power (~320 mW m^{-2}) as expected due to the lower COD of the wastewater compared to tests with acetate [15]. However, power generation was unstable in continuous flow mode, with two identical reactors producing much lower and much different power densities (150 and 250 mW m^{-2}). Not only was power production erratic, polarization data showed that the anodes could not sustain power at lower resistances, as shown by power overshoot (where the power density curve doubles back to lower current densities as the external resistance was decreased) [15]. It was concluded in that study with low-strength wastewater that power was reduced with small brushes due to the impact of oxygen crossover from the cathode. It is well known that when a thin anode (carbon cloth or carbon mesh) is placed close to the cathode that power decreases due to oxygen crossover, despite the improved reduction in ohmic resistance [7,8,16]. Thicker carbon felt electrodes can increase power with acetate when distant from the cathode and thus not influenced by oxygen crossover, but there is very little impact of anode thickness when they are placed close to the cathode [17]. It has also been shown in several studies that placing any porous material between the electrodes, such as non-conductive separators (cloth, nylon mesh and glass fiber) or an ion exchange membrane, reduces oxygen crossover [18,19]. However, the use of separators or membranes that hinder hydroxide ion from the cathode increases ohmic resistance and thus can decrease power generation [20].

Compact MFC configurations are needed to maximize power production per volume of reactor and make the process more economical. Therefore, while larger brushes (2.5 cm diameter) have stable power generation and more surface area for biofilm growth than small brushes (0.8 cm diameter), they require more anode space and thus constrain the design of more compact reactors. To reduce the impact of oxygen crossover on anode performance, we devised a composite anode configuration where a carbon mesh was placed on the separator and several smaller brushes were pressed against the outer side of the carbon mesh. The air cathode was positioned directly on the other side of the separator, in an SEA configuration. Previous work has shown that using only the mesh, or using only the small brushes, resulted in unstable power production [4,15]. It was hypothesized that the brush and mesh combination could help to sustain current generation by an anaerobic biofilm similar to the situation with larger brushes, but that this combination would occupy less anode space than larger brush anodes. The use of the mesh also was hypothesized to serve as a type of “separator” because placing any porous material on top of the separator would necessarily reduce oxygen transfer to the brush electrodes. In addition, since the mesh and brush are electrically connected and have small ohmic resistance (as discussed below), they would have the same potential. Thus, the brush could act to stabilize the mesh electrode electrical potential, and enable the carbon mesh to function as an additional anode surface area while using very little volume compared to a reactor with larger brushes.

In order to test this composite anode design, we examined power generation and COD removal with the composite anodes using domestic wastewater in two different reactors: small, fed batch MFCs, and larger reactors under continuous flow conditions for three different hydraulic retention times (HRTs). Performance was compared to reactors with mesh or brush anode in the smaller MFCs, but only compared to brushes anode in the larger reactors due to the erratic performance reactors with only flat anodes with domestic wastewater and an SEA configuration. Anode and cathode total biomass were also investigated after long-term operation of MFC with or without the additional carbon mesh to evaluate the growth of biofilm on the electrodes due to the presence of the carbon mesh.

2. Materials and methods

2.1. MFC construction

The composite electrodes were examined in two different MFCs reactors in order to evaluate anode performance under fed-batch and continuous flow conditions. For fed-batch tests, MFCs were smaller cubic-shaped reactors that have previously been examined in many MFC studies [4,8]. The MFCs had a 3 cm diameter anode chamber that was 4 cm in length (28 mL empty bed volume). Three different anodes were used: a single mesh anode; a single brush anode; and a composite anode, with the brush pressed against the carbon mesh. All the anode materials in the experiment were presoaked in acetone overnight and then heated at 450 °C for 30 min prior to use [21]. The carbon mesh (Gaojieshi Graphite Products Co., Ltd., Fujian, China) anode was 3 cm in diameter, and it was placed right on the separator surface and connected to the circuit using a titanium wire (M-MFC) (Fig. 1A). The graphite fiber brush (Mill-Rose, Mentor, OH) was made with two titanium core wires (25 mm diameter) (B-MFC) and compressed against the separator forming a half cylinder (Fig. 1B). For the composite anode, the brush was pressed against the carbon mesh that was placed on the separator (BM-MFC) (Fig. 1C). Cathodes (7 cm^2 projected surface area) were fabricated by a phase inversion technique using a polyvinylidene fluoride binder and a mixture of activated carbon (8.8 mg cm^{-2}) and carbon black (Vulcan XC-72, Calbot Corporation, USA) as previously described [22]. Two layers of textile (46% cellulose, 54%

Please cite this article in press as: S. Wu, et al., Journal of Power Sources (2017), http://dx.doi.org/10.1016/j.jpowsour.2017.01.041