Bioresource Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

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

Development of anode zone using dual-anode system to reduce organic matter crossover in membraneless microbial fuel cells

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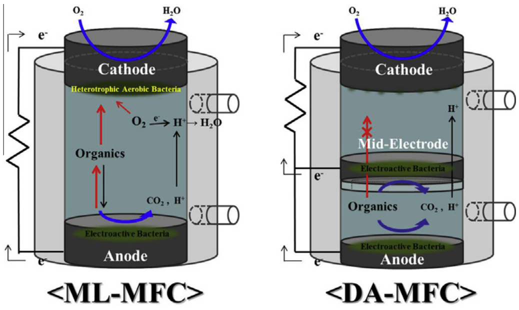
HIGHLIGHTS

- ML-MFCs suffer from organic crossover to the cathode.
- The development of an anode zone using a dual-anode system was demonstrated.
- ML-MFC studies should consider anode zone characterizations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 26 February 2016
Accepted 1 March 2016
Available online xxxx

Keywords:
Microbial fuel cell
Membraneless MFC
Organic crossover
Dual-anode system
Anode zone

ABSTRACT

To prevent the occurrence of the organic crossover in membraneless microbial fuel cells (ML-MFCs), dual-anode MFC (DA-MFC) was designed from multi-anode concept to ensure anode zone. The anode zone addressed increase the utilization of organic matter in ML-MFCs, as the result, the organic crossover was prevented and performance of MFCs were enhanced. The maximum power of the DA-MFC was 0.46 mW, which is about 1.56 times higher than the ML-MFC (0.29 mW). Furthermore, the DA-MFC had advantage in correlation of organic substance concentration and dissolved oxygen concentration, and even electric over-potential. In addition, in terms of cathode fouling, the DA-MFC showed clearer surface. Hence, the anode zone should be considered in the advanced ML-MFC for practically use in wastewater treatment process, and also for scale–up of MFCs.

1. Introduction

Microbial fuel cells (MFCs) are a technology that employs microorganisms as a biocatalyst, leading to the generation of electricity (Du et al., 2007; Kim et al., 1999). Their use is considered a sustainable technique for wastewater treatment processes due to their simultaneous ability to both generate energy as well as treat organic matter (Jiang et al., 2010; Liu et al., 2004; Wang et al., 2015). MFCs commonly consist of an anode and cathode, possibly separated by a proton exchange membrane (Kim et al., 2013; Logan et al., 2006; Ren et al., 2007). However, in terms of full-scale application in wastewater treatment, there are inherent limitations due to biofouling on the membrane surface in addition to their high cost. In particular, biofouling leads to a decrease in MFC performance because of the interruption of proton migration and competition for substrate utilization (Choi et al., 2011; Xu et al., 2012).

Hence, membraneless MFCs (ML-MFCs) have been suggested by Jang et al. (2004) as an alternative due to simple configuration, lack of membrane, and associated biofouling limitations (You et al., 2006; Zhu et al., 2011). Furthermore, the no membrane design improves the economic feasibility by reducing the initial investment and operational costs pertaining to membrane maintenance

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http://dx.doi.org/10.1016/j.biortech.2016.03.012
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Please cite this article in press as: Kim, J., et al. Development of anode zone using dual-anode system to reduce organic matter crossover in membraneless microbial fuel cells. Bioresour. Technol. (2016), http://dx.doi.org/10.1016/j.biortech.2016.03.012

(Ghangrekar and Shinde, 2007; Lee and Nirmalakhandan, 2011). Based on these advantages, current ML-MFC studies have spotlighted and developed an adequate system for wastewater applications. Notably, the bipolar plate-electrode assembly (BEA) structure, which makes ML-MFCs scalable, modulable, and stackable in series connection, is regarded as a key directional architecture for ML-MFC developments (An et al., 2014).

However, ML-MFCs still suffer from specific restrictions due to structural weaknesses. Specifically, because of the no membrane design configuration, electrolyte mixing on both sides of the anode and cathode commonly occurs because of migration, convection, and diffusion (Tartakovsky and Guiot, 2006). This issue deteriorates the performances of ML-MFCs due to oxygen and substrate crossover to the anode and cathode, causing a low coulombic efficiency and power density (Du et al., 2011; Wang et al., 2013). Another major weakness of ML-MFCs is that biofilms form on the cathode surface, in which diffused organic matter interacts with heterotrophic aerobic bacteria from the air or inoculum medium (Yuan et al., 2013; Zhang et al., 2012). This issue is critical, as it lowers the oxygen reduction reaction (ORR) kinetics of the cathode due to excessive consumption of dissolved oxygen (DO) and the formation of a mixed potential (An et al., 2011; Harnisch and Schröder, 2009).

Therefore, MFC research has been focusing on biofilm formation on the cathode surface and attempting to overcome the high reduction overpotential in ML-MFCs. For instance, Harnisch et al. (2009) reported on the use of pyrolysed iron (Π) phthalocyanines (pyr-FePc) catalyst as an alternative to prevent the formation of mixed potentials that occur by biofilm formation. In addition, Ma et al. (2015) revealed efficient antibacterial ORR catalysts ($AgNPs/Fe_3O_4/GC$) based on the synergistic effects of Ag/NPs, Fe_3O_4, and graphitic carbon that inhibit the overgrowth of biofilms on the cathode surface and improve ORR kinetics. Despite these contributions, however, advanced ML-MFCs do not practically remove floating organic matter that leads to a low coulombic efficiency, caused by substrate losses in the anode (Hu, 2008). In addition, Rismani-Yazdi et al. (2008) reported that organic matter and its oxidation products may result in corruption of the cathode catalyst and structural modifications on the cathode surface. Indeed, fundamental solutions to reduce diffused organic matter in ML-MFCs have yet to be found.

In a common configuration, two-chambered MFC systems separate the anode and cathode zone for each reaction using a membrane. However, ML-MFCs have difficulties in generating and maintaining a specific anode zone for organic consumption because of the blurry boundary between their two chambers (Liu and Logan, 2004). For this reason, it is necessary to develop an ‘anode zone’ in ML-MFCs that enables them to separate the region for substrate consumption to effectively minimize the impact of organic crossover into cathode area. To secure a more spacious anode zone, multiple-electrode systems having a wider application to ML-MFCs are being investigated, in order increase the high space capability required to scale-up MFCs (Kim et al., 2015a). Thus, the developments of in the anode zone using this concept should be considered for high substrate consumption.

In this study, the dual-anode MFC (DA-MFC) was proposed as a practicable methodology to overcome the structural restrictions of standard ML-MFCs. The mid-electrode in the DA-MFC, which acts as an additional anode between existing electrodes, could increase the anode zone and thus making it more spacious with a longer residence time. This increased anode zone could reduce the crossover of organic matter at a high consumption rate, and thereby overcome extreme oxygen depletion by reducing heterotrophic aerobic bacteria growth on the cathode surface. In addition, the suggested concepts can be recommended for further extension of the anode zone by using a multi-anode concept as a practical approach in wastewater treatment.

2. Methods

2.1. Construction and operation of ML-MFCs and DA-MFCs

An individual MFC was designed and operated by using a cylindrical acrylic reactor (5 cm inner diameter, 9 cm height) in quadruplicate, as described in a previous study (An et al., 2014). In this experiment, the graphite felt (5 cm inner diameter, 2.54 cm thickness) loaded with 1 mg/cm^2 of Pt/C (40% wt. platinum on Carbon Vulcan XC-72; Fuel Cell Earth, USA) was used as the standard cathode electrode in order to prevent a critical decrease of the electrochemical cathode performance. To distinguish between two types of MFC units and prevent wording confusion, DA-MFC was named as an application of the dual-anode system to ML-MFC. The dual-anode system was composed of two graphite felts (5 cm inner diameter, 1.27 cm thickness); the ML-MFC had the same anode electrode volume (5 cm inner diameter, 2.54 cm thickness), and anode units were placed about 2 cm apart on the bottom.

Each MFC unit was inoculated with 157 mL anaerobic digestion sludge, obtained from a brewery wastewater treatment plant (Gwangju, Korea), and anaerobic sludge was replaced with artificial wastewater containing 3 mM acetate medium. At that time, an artificial medium was fed continuously at a hydraulic resistance time (HRT) of 23.78 ± 0.11 h using a peristaltic pump (520Di, Watson-Marlow Pumps Group, UK). When the open circuit voltage (OCV) stabilized, each cell was connected under a 1 kΩ external resistance and operated until the closed circuit voltage (CCV) became stable (Kim et al., 2015b). Each MFC unit was subsequently operated under periodic monitoring, sampling, electrochemical measurements, and biomass analysis during the planned 16 days after CCV stabilization.

2.2. Electrochemical analysis

The voltage from the electrode potentials versus Ag/AgCl reference electrode (MF-2052, BAS Inc., IN, U.S.A.) was measured over the planned 16 days by using a data acquisition system (Multimeter Keithley Instruments Inc., Cleveland, OH, U.S.A.) connected to a personal computer (Kim et al., 2013). The performance of each MFC unit was estimated by ranging the variable external resistances from 100 kΩ to 50 Ω (e.g., 100 kΩ, 50 kΩ, 30 kΩ, 20 kΩ, 15 kΩ, 10 kΩ, 5 kΩ, 1 kΩ, 500 Ω, 100 Ω, and 50 Ω). The current and power of each cell were then calculated using $I = V/R$ and $P = IV$, respectively, where I is the current (mA), V is the voltage (V) in individual units, R is the external resistance (Ω) applied to the units, and P is the power (mW) in the units.

To evaluate the cathode activities based on the bioelectrochemical behavior of cathodic biofilms during long-term operation, linear sweep voltammetry (LSV) tests were employed using a potentiostat (Eco Chemie, Utrecht, The Netherlands) in a three-electrode electrochemical cell. LSV tests were performed in situ by considering cathode and anode as the working and counter electrodes against an Ag/AgCl reference electrode (0.201 V vs SHE) over a potential range from 0.3 V to −0.4 V at a scan rate of 5 mV/s at room temperature (about 20 °C). Typically, the reduction peak current is linearly proportional to the DO concentration as a reactant concentration for ORR (Glazer et al., 2004). Here, the reduction currents were evaluated based on DO concentrations with respect to time.

2.3. Chemical analysis methods

Operation conditions such as DO concentration, conductivity, and pH were periodically measured using an Orion 4 star DO/pH meter and Orion 3-star bench top conductivity meter (Thermo

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