Power generation in dual chamber microbial fuel cells using dynamic membranes as separators

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ABSTRACT

Two dual-chamber microbial fuel cells (MFCs) that use dynamic membranes as separators were designed for power production. The performance of these dynamic membrane microbial fuel cells (DM-MFCs) was studied. Compared to an up-flow dual-chamber MFC (U-MFC), at the total volume of 1.1 L, DM-MFCs achieved a higher maximum power density (1923 mW m^{-3} versus 856 mW m^{-3}). This is because the DM-MFCs have lower membrane resistance (0.6–5.4 Ω), oxygen diffusion coefficient ($D_0 = 1.8 \times 10^{-7}$ cm^2 s^{-1}), and cost (0.3 USD m^{-2}) than other reported separators; e.g., anion exchange membrane (ACM), cation exchange membrane (CEM), ultrafiltration membrane (UFM), and J-cloth. The dynamic membrane is primarily composed of filamentous bacteria and vorticellidae-like protozoa, which tightly attach to the nylon supporting layer. This microorganism layer consumes most of the dissolved oxygen and prevents oxygen transfer from the cathode chamber to the anode chamber, leading to the low D_0 value of the dynamic membrane. Power production of DM-MFCs was further optimized by increasing the NaCl concentration in the influent and the electrode area. The results show that DM-MFCs are feasible and suitable for scaling-up because of their sleeve-shaped configuration. These results indicate that dynamic membranes can be used to increase power production in MFCs relative to traditional separators and DM-MFCs are promising tools for practical applications.

1. Introduction

The fuel cell, a kind of electrochemical device that converts the chemical energy from a fuel into electricity [1], has been considered as a promising green energy conversion technology [2]. Among these, microbial fuel cells (MFCs) are emerging biological tools that can sustainably generate electricity by oxidizing organic and inorganic matter in wastewater and other substrates [3]. By generating power from a renewable substrate that simultaneously treats wastewater, MFCs have been the subject of intense interest over the past decades and shown to have the potential to alleviate future energy crisis [4].

Although research on microbial fuel cells has shown significant development in recent years, there are still many limitations in their practical applications, such as their unstable system performance and high cost [5]. One of the most important constraints is the separators of microbial fuel cells [6]. In an MFC, a separator is used to physically separate anode and cathode chambers [7]. One of the important

functions of separators is to prevent the transfer of dissolved oxygen from the cathode chamber to the anode chamber so that the cathode chamber can maintain an aerobic environment while the anode chamber maintains an anaerobic environment [8].

The use of a separator is associated with three problems: (1) the separator increases the internal resistance of microbial fuel cells [9]; (2) it is difficult to select an ideal separator with low resistance and low oxygen diffusion coefficient; (3) separators increase the cost of an MFC, because the cost of a separator is critical for the development and scaling up of MFCs [10]. These challenges must be overcome for further development of the practical applications of MFCs.

In the past decade, various types of materials have been used as separators, including cation exchange membranes (CEMs) [11], anion exchange membranes (AEMs) [12], ultrafiltration membranes (UFMs) [9,13], and other coarse-pore filters materials; e.g., J-cloth [14] and glass fibers [15]. Although CEM and AEM have been widely used in MFCs because of their high cation or anion conductivity, they also show

relatively high Ohmic resistance and biofilm growth during long-time operations that would deteriorate the MFC performance. Compared to these ion exchange membranes (IEM), UFMs show a lower resistance, higher ability of proton transfer, and better MFC applicability owing to their non-ion selective properties and large pore sizes to facilitate overall charge transfer. Other types of separators, i.e., coarse-pore filters, such as J-cloth and glass fibers, have a lower cost than IEM and UFM and high potential for practical applications in MFCs [6]. These coarse-pore separators are favorable for ion transport and have low Ohmic resistance. Researchers found that the biofilm growth on a J-cloth coarse-pore filter did not reduce the performance of the filter but prevented oxygen diffusion from the cathode chamber to the anode chamber [15]. However, biodegradable characteristics of the cloth limited its practical application.

Inspired by the biofilm growth on coarse-pore filters, we introduce the concept of dynamic membrane bioreactors in MFCs [16]. Dynamic membranes are also called secondary membranes and consist of cheap supporting material, e.g., a membrane, mesh, or a filter cloth [17]. The dynamic layer contains suspended solid particles, e.g., microbial cells and flocs. Organics and colloidal particles, which normally result in the fouling of the membrane, are entrapped in the biomass filtration layer, preventing the fouling of the support material. Dynamic membranes also consume dissolved oxygen and may prevent oxygen diffusion. In addition, because the dynamic layer is *in situ* formed on the supporting layer and can self-upgrade via the metabolism of microorganisms, it can be self-cleaned and is easy to operate [18].

In this study, a novel dynamic membrane MFC with the up-flow mode was designed. A cheap nylon mesh, which is nonbiodegradable, was used as the supporting layer of the dynamic membrane, while the sleeve-shape configuration was used to maintain a low electrode distance and a large separator area when the MFC was scaled up. The performance of the DM-MFC was compared to our previously studied up-flow MFC (U-MFC) [19], which does not have a sleeve-shape configuration or a dynamic membrane. Two DM-MFCs with different sizes were constructed to test the scaling-up property of the DM-MFCs, after the optimization of power production by increasing the NaCl concentration in the influent and the electrode area. Finally, the scalability of the DM-MFC was analyzed.

2. Experimental

2.1. DM-MFCs set-up

A DM-MFC reactor was constructed in a cylindrical Plexiglas tube. In the center of the reactor, a hollowed smaller tube acted as an anode chamber, while the outside part of the anode chamber acted as a cathode chamber (Fig. 1). The anode and cathode compartments were separated by a nylon mesh (0.03 cm pore diameter, 0.0225 cm thick, Huawei Co., Beijing, China), used as a dynamic membrane supporting layer (Fig. 1). A tubular shape carbon felt (5 cm thick, $60.5\,m^2\,g^{-1}$ specific surface area, Sanye Co. Beijing, China) and an activated carbon fiber felts (ACFF) (5 cm thick, $1000\,m^2\,g^{-1}$ specific surface area, Senxin Co., Liaoning Province, China) were used as anode and cathode, respectively. These tubular shape electrodes were connected to the circuit by graphite rods and then placed vertically in the anode and cathode chambers (Fig. 1). Ag/AgCl reference electrodes (Luosu Co., Shanghai, China) were inserted into each chamber to test electrode potentials. The influent was pumped from the bottom of the anode chamber with an up-flow mode, passed through the dynamic membrane separator into the cathode chamber, and then flowed out from the reactor. To test the scalability of DM-MFC, a larger DM-MFC (denoted as DM-MFC(L)) with the same configuration was also constructed (the smaller DM-MFC is denoted hereafter as DM-MFC(S)). The basic parameters of these two DM-MFCs are listed in Table 1. To compare the power production of DM-MFC with other dual-chamber MFCs, our previously studied up-flow MFC (U-MFC), whose empty volume is similar to that of DM-

MFC(S), was used here. The detailed information of U-MFC is listed in supplementary material. The parameters of the U-MFC are listed in Table 1 and in the supporting information. To optimize the power production of DM-MFCs, NaCl salts were added in the influent at various NaCl concentrations ($0.04\,mol\,L^{-1}$, $0.08\,mol\,L^{-1}$, $0.12\,mol\,L^{-1}$) to increase electrolyte conductivity. Power production of DM-MFCs was further optimized by increasing the anode area followed by the increase in the cathode area (electrode area information is listed in Table S1).

2.2. Inoculation and operation

The anode of DM-MFCs and U-MFC were inoculated using granular anaerobic wastewater sludge from the Gaobeidian Domestic Wastewater Treatment Plant in Beijing, China. After being washed three times with distilled water, 100 mL of the sludge was added to 500 mL of a nutrient solution containing glucose ($200\,mg\,L^{-1}$ COD), NH_4Cl, and NaH_2PO_4 such that the COD:N:P ratio was 100:5:1 by weight. The sludge was cultivated for one week at 35 °C and the resulting suspension was used to inoculate the anode material.

The DM-MFCs and U-MFC were fed a synthetic medium containing $500\,mg\,COD\,L^{-1}$ of glucose, $1000\,mg\,L^{-1}$ of $NaHCO_3$, $95.5\,mg\,L^{-1}$ of NH_4Cl, $19.25\,mg\,L^{-1}$ of NaH_2PO_4, and $0.08\,mol\,L^{-1}$ NaCl. Various NaCl concentrations ($0.04\,mol\,L^{-1}$, $0.08\,mol\,L^{-1}$, and $0.12\,mol\,L^{-1}$) were used to investigate DM-MFC optimization. If not otherwise specified, the NaCl concentration is $0.08\,mol\,L^{-1}$. No trace metals or buffers were added. The substrate was pumped into the bottom of the anode chamber using a peristaltic pump (Lange Co., Hebei Province, China) (Fig. 1). The flow rate was adjusted to keep a constant hydraulic retention time of 1 d. The cathode chamber was continuously aerated using a circular aeration pipe placed at the bottom of the cathode chamber, producing a dissolved oxygen concentration of $6-7\,mg\,L^{-1}$. All experiments were conducted in duplicate at room temperature.

2.3. Characterizations and calculations

Cell voltage (V) across a resistor (R) was determined in relation to Ag/AgCl reference electrodes (Shanghai, China) and measured using a data acquisition system (AD8223h, Beijing, China). Data were recorded on a personal computer every 10 min. Polarization curves were constructed by varying the resistance in the circuit from $10\,\Omega$ to $100,000\,\Omega$. For each change in external resistance, data were recorded at least 2 h after a stable voltage was achieved. Internal resistance was calculated by applying the polarization slope method to the linear portion of the current (I) versus voltage (V) plot [20]. Power was calculated using the equation, $P = I \times V$, normalized to the reactor net volume for comparison with published power density values [21].

The total resistance R_t, anode resistance R_a, and the cathode resistance R_c of MFCs were calculated by the polarization slope method, using the linear portion of the plots of current (I) versus voltage (V), anode potential, and cathode potential, respectively. Membrane resistance R_m is calculated by subtracting R_a and R_c from R_t.

Surface morphologies of dynamic membranes were observed using scanning electron microscope (SEM) (FEIQUANTA 200, Netherlands). Before scanning, dynamic membrane samples were pretreated as follows [22]: samples were immersed in 2.5% pentanediol solution for 4 h and cleaned three times with deionized water. They were then immersed in 1% osmic acid solution for 2–4 h and cleaned three times with phosphate buffer. Next, the samples were dehydrated using 30%, 50%, 70%, 85%, and 95% ethanol solution, successively. They were treated twice with isoamyl acetate and dried using a CO_2 critical point drying machine (CPD030 Critical Point Dryer). Finally, after metal spraying treatment, the samples were scanned [23,24].

The oxygen transfer coefficient (k_0) of dynamic membrane separators can be obtained using Eq. (1) [9], where V_a is the liquid volume in the anode chamber, A is the membrane cross-sectional area, $C_{1,0}$ is the saturated dissolved oxygen (DO) concentration in the cathode chamber,