Journal of Power Sources 332 (2016) 447–453

Contents lists available at ScienceDirect

Journal of Power Sources

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

Pressurized air cathodes for enhanced stability and power generation by microbial fuel cells

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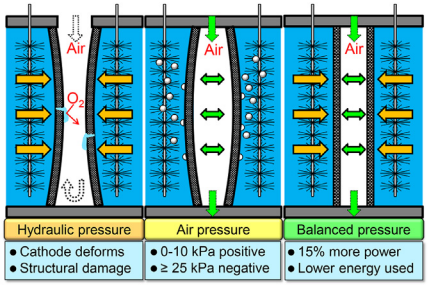
HIGHLIGHTS

- Air pressure of 10 kPa alone enhanced cathode performance by 17%.
- High gas pressure (≥25 kPa) alone resulted in poor performance and air leakage.
- Best results with balanced and higher air and water pressure.
- Balanced pressures stabilized and enhanced power output of MFCs by 15%.
- Cathodes functioned normally with an oxygen partial pressure >12.5 kPa.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 June 2016
Received in revised form
9 September 2016
Accepted 20 September 2016

Keywords:
Microbial fuel cell
Hydraulic pressure
Gas pressure
Electrode spacer
Oxygen partial pressure

ABSTRACT

Large differences between the water and air pressure in microbial fuel cells (MFCs) can deform and damage cathodes. To avoid deformation, the cathode air pressure was controlled to balance pressure differences between the air and water. Raising the air pressures from 0 to 10 kPa at a set cathode potential of −0.3 V (versus Ag/AgCl) enhanced cathode performance by 17%, but pressures ≥25 kPa decreased current and resulted in air leakage into the solution. Matching the air pressure with the water pressure avoided cathode deformation and improved performance. The maximum power density increased by 15%, from 1070 ± 20 to 1230 ± 70 mW m^{-2}, with balanced air and water pressures of 10 −25 kPa. Oxygen partial pressures ≥12.5 kPa in the cathode compartment maintained the oxygen reduction rate to be within 92 ± 1% of that in ambient air. The use of pressurized air flow through the cathode compartments can enable closer spacing of the cathodes compared to passive gas transfer systems, which could make the reactor design more compact. The energy cost of pressurizing the cathodes was estimated to be smaller than the increase in power that resulted from the use of pressurized cathodes.

1. Introduction

Sustainable processes and resource recovery from wastewaters have received great attention for the treatment of domestic and

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http://dx.doi.org/10.1016/j.jpowsour.2016.09.112
0378-7753/

industrial wastewaters [1]. Microbial fuel cells (MFCs) are being developed as an alternative to traditional treatment processes due to simultaneous removal of organic matter in the wastewater and energy recovery [2–4]. In MFCs, the chemical energy in the organic matter is transformed by microbial communities on the anode and released as electrical current, typically with oxygen reduction at the cathode [5]. In the last decade, many advances in our understanding of the factors that limit power generation, and the development of low cost materials, have improved both performance and the economic outlook for using MFCs for wastewater treatment [6–10]. One of the remaining challenges for commercialization of MFC is development of larger-scale systems capable of continuous and stable treatment of wastewater [11].

Cathode performance typically limits power production by MFCs [12]. Improvements of the cathode materials and designs have led to considerable power density increases in MFCs [13]. Various materials have been used to make cathodes, including carbon cloth and carbon mesh with platinum catalysts [14,15], stainless steel mesh and activated carbon catalysts [16,17] and nickel foam carbon cathodes [18]. Of these materials, the greatest promise for economical construction of cathodes and long-term performance are those made using activated carbon with stainless steel current collectors [16,17]. One challenging for constructing larger cathodes using these materials is maintaining performance with higher hydraulic pressures that result with larger systems. Hydraulic pressure can deform the hydrophobic diffusion layer and lead to water leakage, cathode flooding, and structural deformation of the cathode, resulting in reduced performance or even cathode failure [19,20].

To avoid deformation of the cathode, high porosity plastic mesh spacers have been proposed that can fit between adjacent cathodes and provide structural support while allowing passive air flow between the electrodes [21]. However, the use of plastic mesh spacers was found to inhibit power production due to a lack of sufficient air flow [22]. Rigid wire spacers, which had a higher porosity and excellent mechanical strength, were found to produce much better performance in a larger-scale MFC (200 cm^2 effective cathode area). However, larger reactors that are needed to further scale up these systems could have cathode areas of ~1 m^2, which would present even greater challenges for allowing air flow while avoiding deformation of the cathodes due to the increased water pressure. The distance between the cathodes could be increased to allow better air flow. However, compact and modular designs are needed to produce MFCs with a high cathode specific surface area (total cathode area per total volume of the reactor) and thus a good volumetric power [2,12]. High hydraulic pressures will also press the spacer onto the cathode surface, which could reduce the area of the cathode for oxygen transfer (called the “shadow effect”) [22], or even deform or damage the cathode.

In order to avoid large pressure differences across the air cathode surface, as well as to improve the cathode performance by providing a higher partial pressure of oxygen, we developed the pressurized air cathodes for MFCs. An MFC reactor was designed that allowed both water and air pressure to be independently varied to conduct the pressure tests on the air cathodes. The performance of the cathodes was initially examined in electrochemical tests at set potentials with imbalanced (only air pressure) or balanced pressures across the cathode. Cathodes with pressurized air were then examined in MFCs at balanced pressures that spanned ambient pressure, to water pressures comparable to meter-scale hydraulic pressures. The energy costs to provide pressurized air flow into a cathode chamber were examined through an energy analysis for different cathode current densities, to determine if the energy cost of producing high air pressures was reasonable.

2. Materials and methods

2.1. Reactor construction

An MFC reactor setup, which allowed independent adjustment of the air and hydraulic pressures, was developed for electrochemical and MFC tests under various pressure conditions. The test reactors were built from 4-cm thick blocks of polycarbonate that were drilled to contain two cylindrical anode compartments (each 3 cm in diameter) and a single cathode chamber between the anode chambers formed by the air cathodes on each side of the reactor (Fig. 1). Each of the chambers could be operated at a specific set pressure. The cathode chamber contained two adapters (NPT male adapter to hose barb, 1/4″ NPT to 1/4″ ID, Cole-Parmer) for air flow, which were screwed into the opposite sides of the cathode compartment (Fig. 1). One adapter was connected to the outlet valve of the air supply pipe, while the other one was connected to a gas flow meter (Fig. S1). Gas pressures in the cathode chamber were set by monitoring pressure using a low-pressure gauge (Ashcroft low-pressure gauge, 0–50 kPa, Cole-Parmer, USA) connected into the top of the cathode compartment, and adjusting the gas flow and backpressure with a valve. Pressure in the anode chambers was controlled by connecting a tube of water, using straight barbed fittings glued to the sides of the cover plates of anode compartments, to a tube that could be filled with water to a total height of ~2.5 m (Fig. S1), allowing pressure adjustments to up to 25 kPa above ambient pressure. All connections were sealed with silicon to make them water and gas tight.

2.2. Electrodes and operation

Cathodes were made as previously described [9,16], and contained three layers: catalyst layer (water side), current collector, and diffusion layer (air side). The diffusion layer was made of a mixture of carbon black (CB, 25 mg cm^{-2}) and PTFE (37.5 mg cm^{-2}) [16]. The diffusion layer was hot pressed on the current collector at 70 °C with a pressure machine (Carver press, Model 4386, Carver Inc., IN, USA) and then heat treated at 340 °C for 15 min [23]. The current collector was made from stainless steel mesh (42 × 42 Mesh, type 304, McMaster-Carr, USA). The catalyst layer was made from activated carbon (AC) powder (26.5 mg cm^{-2}, Norit SX plus, Norit Americas Inc., USA) [9] mixed with a polytetrafluoroethylene binder (PTFE, 60%; 6.5 mg cm^{-2}, PTFE) [16]. The mixed AC and PTFE suspension was added to an appropriate amount of ethanol, and stirred in a water bath with ultrasonication at 80 °C until it formed an adhesive paste due to the evaporation of ethanol. The heating temperature of 80 °C was chosen according to the boiling point of ethanol. The catalyst layer paste was then pressed onto the opposite side of the current collector containing the diffusion layer, and dried at ambient temperature.

Anodes used in MFCs were graphite fiber brushes (2.5 cm diameter, 2.5 cm long) that were heat treated in air at 450 °C for 30 min [24]. The brushes were placed into the middle of the anode chamber, with the ends connected to the circuit through a hole in the center of a solid cover plate (Fig. 1). The anodes were inoculated with effluent of another well acclimated cubic MFC, and acclimated to the acetate medium for over six months. Electrochemical tests of cathodes were made using a platinum mesh counter electrode (1 cm × 2.0 cm, dual layers, 52 mesh, Sigma-Aldrich Co.). All tests were conducted in a constant temperature (30 °C) room.

2.3. Measurements settings

Abiotic electrochemical tests were conducted using cathodes as the working electrodes, platinum mesh counter electrodes, and a