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Short communication

Air humidity and water pressure effects on the performance of air-cathode microbial fuel cell cathodes

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HIGHLIGHTS

- High humidity or increased water pressure reduced power production.
- Cathode performance decreased due to water flooding and salt precipitation.
- Water flooding would have hindered oxygen transport to the catalyst.
- Cathode performance could be restored by cleaning with low concentration acid.

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ABSTRACT

To better understand how air cathode performance is affected by air humidification, microbial fuel cells were operated under different humidity conditions or water pressure conditions. Maximum power density decreased from 1130 ± 30 mW m^{-2} with dry air to 980 ± 80 mW m^{-2} with water-saturated air. When the cathode was exposed to higher water pressures by placing the cathode in a horizontal position, with the cathode oriented so it was on the reactor bottom, power was reduced for both with dry (1030 ± 130 mW m^{-2}) and water-saturated (390 ± 190 mW m^{-2}) air. Decreased performance was partly due to water flooding of the catalyst, which would hinder oxygen diffusion to the catalyst. However, drying used cathodes did not improve performance in electrochemical tests. Soaking the cathode in a weak acid solution, but not deionized water, mostly restored performance (960 ± 60 mW m^{-2}), suggesting that there was salt precipitation in the cathode that was enhanced by higher relative humidity or water pressure. These results showed that cathode performance could be adversely affected by both flooding and the subsequent salt precipitation, and therefore control of air humidity and water pressure may need to be considered for long-term MFC operation.

1. Introduction

Microbial fuel cells (MFCs) are devices in which exoelectrogenic bacteria oxidize organic compounds and transfer electrons to an electrode [1–3]. These electrons flow to the cathode through an external circuit, with protons transferred through the solution. Electrons combine with protons and oxygen at the cathode to form water [1–3]. MFCs have the advantage compared to conventional wastewater technologies of direct energy production from wastewater along with treatment [3]. The maximum power output of MFCs has increased by several orders of magnitude over the last decade by reducing the overpotentials of the electrodes and ohmic losses of the system [4,5]. Scaling up and practical application of MFCs, however, still requires further improvement in performance, which can be obtained through a better understanding of the reaction kinetics and potential losses at the electrodes.

Cathode performance usually limits power production in MFCs due to the slow kinetics of the oxygen reduction reaction (ORR) in the neutral pH solutions needed for bacterial growth in single-chamber, air-cathode MFCs [5,6]. Pt is useful for catalyzing the ORR, although many other catalysts can be used, such as carbon-based nanomaterials, metal tetramethoxyphenylporphyrin (MPP) and manganese oxide [7–9]. Most of these catalysts are applied as a thin layer using a binder, such as Nafion, to a conductive surface such as carbon paper, carbon cloth, or a metal mesh. Activated carbon can also be used, but typically it is applied as a much thicker layer [10,11]. The performance of these catalysts for ORR depends on the simultaneous presence of oxygen, protons and electrons,

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which can be affected by various factors including catalyst loading, hydrophobicity and ion conductivity of binder materials, solution conductivity and pH.

Water content of an air-cathode is well known to affect the performance of hydrogen fuel cells with proton exchange membranes (PEMs) [12]. The feed gas of a PEM fuel cell is usually humidified to ensure hydration of the Nafion membrane for good proton conductivity, particularly at low current densities. At high current densities, however, the rate of water production is quite high and excessive humidification can lead to over accumulation of water (flooding) which reduces performance due to water blocking the pores in the diffusion and catalyst layers. MFCs have much different operating conditions and current densities than hydrogen PEM fuel cells. The MFC cathode is directly facing the solution (water), and this condition makes water flooding of the catalyst much more likely because water is used for proton conduction to the catalyst layer rather than a PEM. Current densities are low, so that water in the cathode is primarily controlled by seepage into the cathode rather than water production. Binder properties are especially important relative to water seepage and the steady state water content in the cathode. Nafion is typically used as a binder for Pt catalyst, but the use of more hydrophobic polydimethylsiloxane (PDMS) binders can improve performance due to the high hydrophobicity or increased surface area for oxygen reduction [13,14]. Performance is also affected by oxygen transfer to the cathode [15]. Diffusion layers are applied to the air-side of cathodes, primarily to prevent water leaking through the cathode, but they also affect oxygen transfer to the catalyst sites as well as water content in the cathode layer. Hydrophobic materials such as polytetrafluoroethylene (PTFE) and PDMS are also used to avoid water losses by seepage through the cathode, but evaporative losses still occur. The relative humidity of air should affect evaporative losses through the cathode, but issues related to water content of the cathode, especially with respect to air humidification or water pressure, have not been previously studied in MFCs.

The effect of air relative humidity and water pressure on the cathode performance was examined here using MFCs and electrochemical tests. In MFC tests, the humidity of the air was varied for extended periods of time to achieve steady operating conditions. To determine how water pressure might affect the cathode performance, the cathode orientation was changed from a vertical orientation, where water pressure varies from the bottom to the top of the cathode, to a horizontal orientation with the cathode on the reactor bottom, with water resting on top of the cathode. We evaluated these different conditions using standard Pt/C cathodes with a Nafion binder [4], monitoring changes in power densities and coulombic efficiencies (CEs).

2. Experimental

2.1. MFC construction

Single-chamber cubic-shaped MFCs were constructed with an anode chamber volume of 28 mL (4 cm length and 3 cm diameter) as previously described [16]. Each reactor contained a graphite fiber brush anode which was heat treated at 450 °C for 30 min before use. The cathode (7 cm^2) was wet-proofed carbon cloth (type B-1B, E-TEK) containing a 0.5 mg Pt cm^{-2} of Pt catalyst layer (10% Pt on Vulcan XC-72, BASF Fuel Cells, Inc) with a Nafion binder (33.3 μL cm^{-2} of 5 wt% Nafion solution) and four PTFE diffusion layers [4]. The medium contained sodium acetate as the fuel (1 g L^{-1}) and a 50 mM phosphate buffer nutrient solution (PBS) (Na_2HPO_4, 4.58 g L^{-1}; $NaH_2PO_4 \cdot H_2O$ 2.45 g L^{-1}; NH_4Cl 0.31 g L^{-1}; KCl 0.13 g L^{-1}; trace minerals and vitamins; conductivity of 6.82 mS cm^{-1}).

2.2. MFC operation

Anodes were pre-acclimated in other reactors and transferred to reactors with new cathodes before fed-batch operations. Cathodes were normally oriented in a vertical direction (on the side of the reactor). However, the cathode in one reactor was placed in a horizontal position (on the bottom) to produce a higher and more uniform water pressure than the vertical cathode position. All MFCs were run in relative humidity (RH)-controlled plastic chambers (27 cm long, 21 cm wide, and 13 cm tall). Water saturated air was prepared by bubbling air through a bottle containing water and dry air was prepared by passing the air through an anhydrous Drierite column (WH Hammond, Drierite Co., Xenia, USA). A constant relative humidity was obtained by mixing water saturated air with dry air at a given ratio. Humidity and temperature inside the chamber were monitored with a OM-EL-USB-2-LCD temperature and relative humidity logger (Omega Engineering Inc., Stanford, CT, USA). The air flow rate through the RH-controlled chambers was 0.14 m^3 h^{-1} (5 ft^3 h^{-1}), producing an air retention time of 5.2 min. The MFCs were first run at 0% RH and the RH was subsequently increased by 20–100% RH, and then back to 0% RH. Reactors were refilled with 28 mL of medium when the voltage dropped below 30 mV. At each RH condition, the MFCs ran for at least three batch cycles (approximately 1.5 days for each cycle).

2.3. Measurements and electrochemical analysis

The voltage (U) across an external resistor (100 Ω) in the MFC circuit was monitored at 20 min intervals using a multimeter (Keithley Instruments, OH) connected to a personal computer. The current (I, A) was computed by $I = UR^{-1}$ where R is the resistance (Ω) and U is the voltage across the resistor. The power output of the cells (P, W) was calculated as $P = IU$ and normalized by cathode area. Maximum power was obtained by fixing the external resistance at 100 Ω, which was the resistance that produced the maximum power in polarization tests using the same type of cathode [17]. Coulombic efficiencies were calculated as the ratio of total recovered coulombs to the theoretical amount of electrons derived from the oxidation of acetate to carbon dioxide. Total chemical oxygen demand (COD) was measured according to the Standard Methods (TNT plus COD reagent; HACH company) [18].

Linear sweep voltammetry (LSV) was performed at 1 mV s^{-1} on the cathodes with a clean carbon fiber brush as a counter electrode using a potentiostat (BioLogic, VMP3) and data was recorded and analyzed with EC-Lab V10.02 software. The reactor was filled with 28 mL of 50 mM PBS solution and equipped with an Ag/AgCl reference electrode (+209 mV versus SHE; RE-5B; BASi).

3. Results and discussion

3.1. Effect of relative humidity and cathode orientation on MFC performance

Increased air humidity adversely affected the power production of MFCs in both vertical and horizontal cathode positions. As the RH increased, the power production showed a steady decrease (Fig. 1A). Dry air (0% RH) produced a maximum power density of 1130 ± 30 mW m^{-2} with a vertical cathode, but this decreased by 13% (980 ± 80 mW m^{-2}) with 100% RH air. One possible reason for decreased performance in power production was water flooding in the cathode [19] as a result of the increasing RH of air. An increase in water content could have reduced oxygen transport to the cathode catalyst layer [20] and thus lowered power production.