



## 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  $1130 \pm 30 \text{ mW m}^{-2}$  with dry air to  $980 \pm 80 \text{ mW m}^{-2}$  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 ( $1030 \pm 130 \text{ mW m}^{-2}$ ) and water-saturated ( $390 \pm 190 \text{ mW m}^{-2}$ ) 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 ( $960 \pm 60 \text{ mW m}^{-2}$ ), 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.

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## 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 quite 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<sup>2</sup>) was wet-proofed carbon cloth (type B-1B, E-TEK) containing a 0.5 mg Pt cm<sup>-2</sup> of Pt catalyst layer (10% Pt on Vulcan XC-72, BASF Fuel Cells, Inc) with a Nafion binder (33.3 μL cm<sup>-2</sup> of 5 wt% Nafion solution) and four PTFE diffusion layers [4]. The medium contained sodium acetate as the fuel (1 g L<sup>-1</sup>) and a 50 mM phosphate buffer nutrient solution (PBS) (Na<sub>2</sub>HPO<sub>4</sub>, 4.58 g L<sup>-1</sup>; NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O 2.45 g L<sup>-1</sup>; NH<sub>4</sub>Cl 0.31 g L<sup>-1</sup>; KCl 0.13 g L<sup>-1</sup>; trace minerals and vitamins; conductivity of 6.82 mS cm<sup>-1</sup>).

### 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., Stamford, CT, USA). The air flow rate through the RH-controlled chambers was 0.14 m<sup>3</sup> h<sup>-1</sup> (5 ft<sup>3</sup> h<sup>-1</sup>), 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

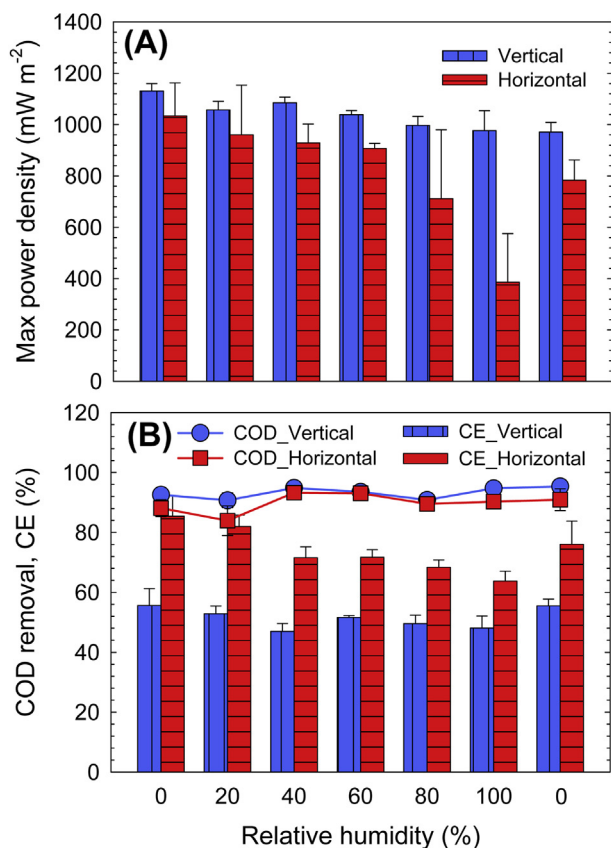
The voltage ( $U$ ) across an external resistor (100 Ω) in the MFC circuit was monitored at 20 min intervals using a multimeter (Keithley Instruments, OH) connected to a personal computer. The current ( $I$ , A) was computed by  $I = UR^{-1}$  where  $R$  is the resistance (Ω) and  $U$  is the voltage 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<sup>-1</sup> 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<sup>-2</sup> with a vertical cathode, but this decreased by 13% (980 ± 80 mW m<sup>-2</sup>) 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.



**Fig. 1.** (A) Maximum power densities, (B) COD removals and CEs as a function of relative humidity of air in MFCs with different cathode positions.

Changing the cathode orientation from vertical to horizontal with the cathode on the bottom, reduced power production for all RH conditions (Fig. 1A). The horizontal cathode produced a maximum power density of  $1030 \pm 130 \text{ mW m}^{-2}$  with dry air, with decreased power as the RH was increased. When 100% RH air was used with the horizontal cathode orientation, power decreased by 62% to only  $390 \pm 190 \text{ mW m}^{-2}$ . Lower initial power production and further decreases with increasing humidity for the horizontal cathode were assumed to be due to water flooding [19] as a result of the increased water pressure on the cathode. The higher water content inside the cathode would have hindered oxygen transport to the catalyst by blocking the pores and flooding the catalyst layer [20].

To test whether the effect of relative humidity and cathode orientation on the MFC performance was reversible, MFCs operated with 100% RH were switched back to 0% RH. Performance was only partially recovered from the first batch cycle, with the vertical orientation improving the most, with 86% ( $970 \pm 40 \text{ mW m}^{-2}$ ) of the original power production recovered. For the horizontal orientation, the use of the dry air also improved performance but only to 76% ( $780 \pm 80 \text{ mW m}^{-2}$ ) of that previously obtained. These results suggested that once the cathodes were flooded, there were other changes that had occurred over time that did not allow the original cathode performance to be recovered. This lack of full recovery could be due to biofilm formation or salt accumulation in the cathode, as further examined below in electrochemical tests.

COD removals were above 90% for all test conditions, consistent with previous MFC tests [21]. MFCs with horizontal cathodes had COD removals of  $90 \pm 1\%$ , which was only slightly less on average

than the COD removal of the vertical cathodes ( $95 \pm 2\%$ ) at 100% RH, but several COD removals were the same in several tests (Fig. 1B).

The cathode orientation produced a much greater change in the CE than changes in RH. The CEs for the horizontal cathode averaged  $74 \pm 8\%$ , while the CEs for the vertical cathodes were significantly lower at  $51 \pm 3\%$  ( $p < 0.001$ , Student's *t*-test). The change in the CE due to RH was also greater for the horizontal cathodes than for the vertical cathodes. CE is well known to be a function of the current density in MFC tests with vertical cathodes, with CE positively correlated with current [15,21]. However, that explanation for the change in CE with current cannot explain results here as the vertical cathodes had higher current densities, but lower CEs, than horizontal cathodes. Thus, the CE here was affected by the combination of the horizontal orientation and increased RH, which both increased water pressure on the cathode. Higher water contents resulted from higher water pressures that hindered oxygen transfer through the catalyst layer into the cathode chamber [20]. Thus, the CE increased even though the maximum power was lower with horizontal cathodes.

### 3.2. Electrochemical studies

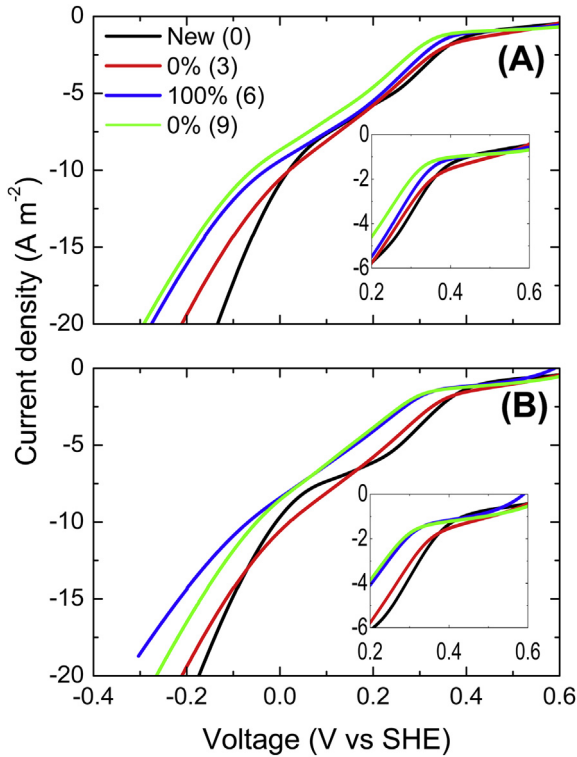
Biofilm formation on the cathodes over time can reduce oxygen transfer into the anolyte and increase CE [22,23]. Thus, the difference in the 0% RH case between the beginning and the end of the RH experiments could have been partly due to biofilm formation. New cathodes were therefore made and LSV tests were conducted to confirm that the changes in performance with humidified air were mainly due to the decreases in cathode catalyst performance rather than biofilm formation. To minimize the deterioration of cathode performance by increased operation time, RH of air was changed directly from 0% to 100% and back to 0% after three fed batch cycles at each condition.

Cathodes placed in a vertical position exhibited better electrochemical performance than those in a horizontal position (Fig. 2). Significantly lower currents were obtained when cathodes were tested with 100% RH air. The current density with horizontal cathode decreased significantly over the entire potential range (Fig. 2A), while that of vertical cathode decreased only when the potential was lower than 0.2 V (Fig. 2B).

Cathode LSV tests were repeated 3 more times after running the MFC at the 0% RH air condition to examine the reversibility of the effect of humidity on cathode performance. However, the current densities did not recover to the original values over the range of potentials. These changes observed in LSV tests were consistent with previous MFC results, where a high RH would lead to a decreased power production, but a low RH afterward could not recover the original power production. These results suggested that the cathode performance decreased irreversibly when cathodes were exposed to humid air, and thus biofilm formation was not the main reason for power changes in MFC tests. Further tests were therefore conducted to determine the main cause of the decreased performance by trying to restore cathode performance using different approaches.

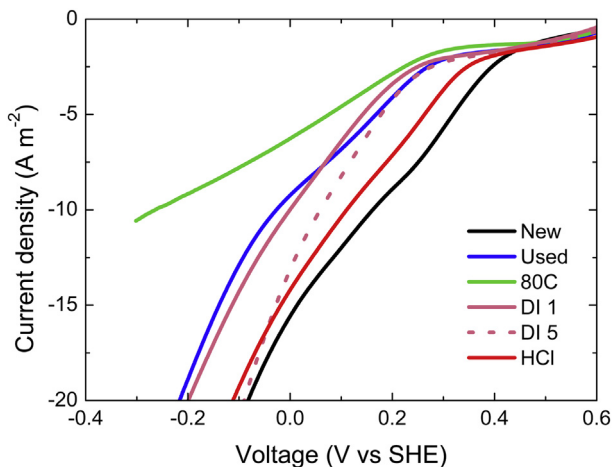
### 3.3. Regeneration of used cathode

The two remaining reasons for decreased cathode performance with an increase in RH or water pressure (cathode orientation) were: water accumulation inside the micro-pore of the cathode that could not be removed just by switching to dry air; and salt precipitation. To distinguish these two possible causes, several different tests were conducted to improve cathode performance following operation under 100% RH conditions. First, used cathodes were removed and dried in an oven at  $80 \text{ }^\circ\text{C}$  for 6–8 h to fully

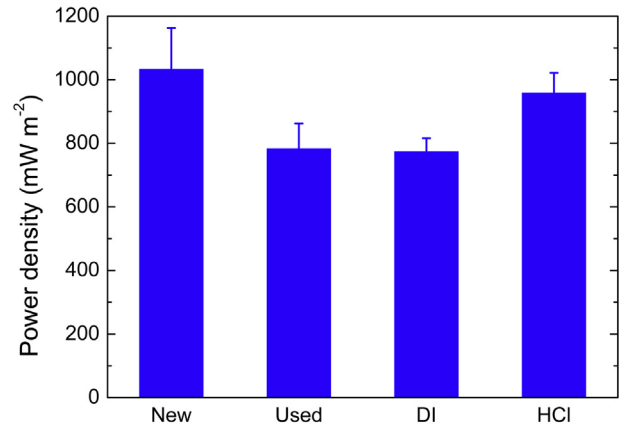


**Fig. 2.** Change of cathode LSVs over time for MFCs using different levels of relative humidity air with vertical (A) and horizontal cathode (B). Numbers in parentheses represent the total number of fed batch cycles before LSV tests were performed.

remove water from the cathode. However, this treatment did not restore current densities in LSV test to those originally obtained with the new cathode (Fig. 3). This indicated that water content alone was not the main reason for the decreased cathode performance with humid air. It was also possible that drying the cathode when it had PBS medium in it also may have resulted in salt precipitation. To remove salts so that they would not remain during the drying process, cathodes were soaked in deionized (DI) water for 1–5 days to dissolve the salts in the cathode in water. The cathode soaked in DI water for 1 day showed slightly improved electrochemical performance in LSV tests, which was similar to that obtained with the used cathode. The performance continued to



**Fig. 3.** LSV curves for the new, used, and regenerated cathodes with various regeneration processes: 80C indicates cathodes were oven dried at 80 °C, DI that they were soaked in DI water, and HCl indicates they were cleaned using 50 mM HCl.



**Fig. 4.** Maximum power production of MFC with new, used, and regenerated cathodes.

improve with longer soaking periods in the DI water, suggesting that re-dissolution of these salts was slow. However, the current densities following extended soaking in the DI water were all still lower in LSV tests than those with the new cathode. To further improve salt dissolution, cathodes were soaked in a low concentration acid solution (60 mM HCl) for 2 days to more effectively dissolve salts that may have precipitated in the cathode. This treatment improved the electrochemical performance to be similar to that of a new cathode, over the entire potential range in LSV tests.

These cleaned cathodes were subsequently tested in MFCs with 0% RH air to confirm the results obtained from LSV tests. The cathodes cleaned using the acid solution produced power densities of  $960 \pm 60 \text{ mW m}^{-2}$ , which was only 7% less than that obtained with new cathode ( $1030 \pm 130 \text{ mW m}^{-2}$ ) (Fig. 4). Cathodes cleaned by soaking in DI water for 5 days produced much lower maximum power densities ( $770 \pm 40 \text{ mW m}^{-2}$ ) that were similar to those obtained with used cathodes ( $780 \pm 80 \text{ mW m}^{-2}$ ).

These results with water soaking and acid-cleaning of the cathodes confirmed that salt precipitation was the main cause of deterioration in cathode performance over time. We hypothesize that a lower RH keeps the cathode drier and reduces the penetration of the salty medium into the cathode and its diffusion layer. When water in the salty medium evaporates, the loss of this water but not the salt, can leave a salt residue that would reduce oxygen transfer and cathode performance. Restoring dry air conditions would not remove the salt obstruction and thus extended soaking and chemical cleaning were needed to restore performance.

#### 4. Conclusions

Cathode performance decreased with an increase in the RH of air, due to water flooding of the cathodes which decreased oxygen transfer to the catalyst sites. Increasing water pressure on the cathode by placing it in a horizontal position on the reactor bottom also reduced performance. Cathode performance could not be fully restored by operation with dry air as operation in high RH conditions or in the horizontal position increased salt precipitation in the cathode. Salts could partly be removed by soaking in DI water, but cleaning with a low concentration acid solution was needed to more fully restore cathode performance.

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