

Article

# Influence of Humidity on Performance of Single Chamber Air-Cathode Microbial Fuel Cells with Different Separators

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**Abstract:** The maximum performance of microbial fuel cells (MFCs) is significantly affected by the reduction reactions in the cathode, but their optimum condition is not fully understood yet. The air-cathode MFC operations with different separators (Nafion 117 and polypropylene (PP80)) were evaluated at various relative humidity (RH) at the cathode chamber. Air cathode MFCs with a Nafion 117 separator at RH of  $90 \pm 2\%$  produced the highest cell voltage of 0.35 V (600  $\Omega$ ) and power density of 116 mW/m<sup>2</sup>. With a PP80 separator, the maximum power generation of 381 mW/m<sup>2</sup> was obtained at a relatively lower RH of  $30 \pm 2\%$ . The cyclic voltammogram and Tafel analysis indicated that the best performance of cathodic oxygen reduction reactions could be observed at 90% RH for Nafion and 50% RH for the PP80 separator. Additionally, the RH conditions also affected the anodic reactions and oxygen mass transfer rates to the anode chamber through the cathode and separators. This study suggests that the optimum RH condition at the cathode is important in order to obtain a high performance of MFC operations and needs to be controlled at different optimum levels depending on the characteristics of the separators.

**Keywords:** air-cathode; relative humidity; microbial fuel cell; dissolved oxygen; polypropylene

## 1. Introduction

The increase in global population and energy consumption of fossil fuels has led to an environmental crisis with a rise in global temperatures. In this regard, the research community is in search of eco-friendly energy production technologies with sustainable processes. The energy generation by use of microorganisms is promising owing to their eco-friendly nature and self-regenerative capability compared to other methods. A microbial fuel cell (MFC) produces electric energy directly from the oxidation of organic matter in waste through the metabolic processes of electrochemically active microorganisms on anode electrode. The electrochemically active microbes such as *shewanella oneidensis* and *Geobacter sulfurreducens* along with other microbes in wastewater have been known to transfer electrons from organic wastes to the anode electrode for sustainable power generation [1–3]. Therefore, MFCs are in the spotlight as a microbial technology that can generate electricity with simultaneous wastewater treatment (i.e., organic reduction in wastes). Generally, an MFC is composed of an anode, cathode and a separator; in which the electrons generated from the anode flow to cathode via an external circuit. The protons are diffused from the anode to the cathode via the separator. At the cathode, both the electrons and protons are combined with oxygen to form water.

In past decades, several research studies on MFCs have been pursued for the intensification of wastewater treatment efficiency and energy production at a low cost. Therefore, various MFC designs have been studied in orientation to commercialization. These include the double chamber aerated cathode MFC, single-chamber air cathode MFC, up flow MFC, stacked MFC, sediment MFC and flat plate MFC. Each of these MFC, reactor configurations include their own merits and demerits [4–6]. Among them, the single chamber air cathode MFC is promising and has been proven to overcome several limitations, such as internal resistance and operational costs. In double chamber MFCs, the aeration of cathode can increase the operational cost and size of the system. Furthermore, the long-distance between the anode and the cathode can trigger a larger internal resistance, which can minimize the energy production [7,8]. In single chamber MFCs, the cathode is directly exposed to air to convert atmospheric oxygen to water.

Several researchers have tried to increase the energy generation in single chamber MFCs by varying electrode distance, separators, electrode materials, biocatalysts and substrates under optimum conditions. These studies have suggested that the cathode oxygen reduction reaction (ORR) is a major limitation to achieving a higher power generation. In this aspect, several research studies in MFC had been carried out to increase cathode performance and to minimize oxygen crossover from cathode to anode. One of the other major issues in single chambered systems is the evaporation of anolyte leading to membrane dehydration and decreasing the overall performance due to the exposure of the cathode to air. These conveyed problems at the air cathode are directly associated with the atmospheric relative humidity (RH) [9–11]. It was proven that the humidity levels at the air cathode MFC play a crucial role in oxygen crossover from the air to the anode part [12]. Moreover, the high RH can lead to water accumulation, which can lead to pore blocking at the cathode and thereby inhibit the ORR on cathode electrode. There are various types of separators used in MFCs that have exhibited a different power efficiency depending on the pore size and thickness [7,8]. Therefore, the RH at the cathode in an MFC can be closely related to the separator type, as it acts as a barrier between the anolyte and cathode. However, no studies were performed to clearly understand the influence of RH on the performance of different separators and overall MFC operation.

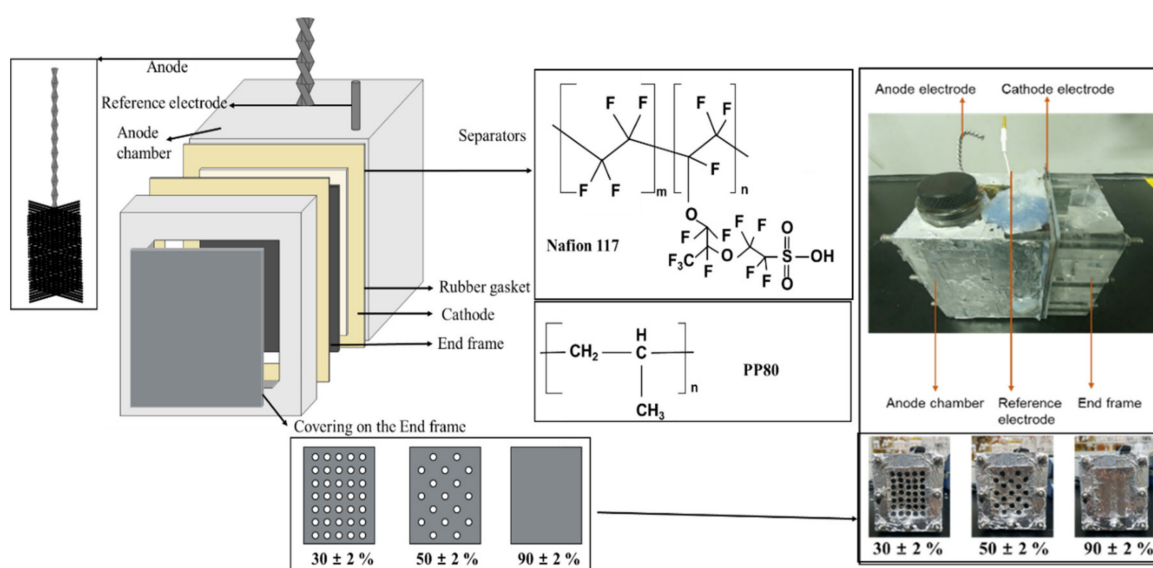
In this study, we have investigated the performance of a single chamber air cathode MFC with different separators (Nafion 117 and polypropylene (PP80)) and RH conditions (30%, 50% and 90%) at the cathode. The PP80 separator was chosen on the basis of our earlier studies, which had exhibited a similar/higher power generation to Nafion 117 [7]. Voltage and power densities were evaluated with the variations in the separator and the RH. Electro kinetic analysis such as cyclic voltammetry (CV) was pursued to evaluate the catalytic performance of the cathode at various operational conditions. The oxygen crossover from the anode to the cathode was also evaluated in abiotic MFCs under different RH conditions. The influence of RH on the coulombic efficiency (CE) was calculated and contemplated with the oxygen crossover.

## 2. Materials and Methods

### 2.1. Construction of Single Chamber Air-Cathode Microbial Fuel Cell

Two similar single chamber air-cathode MFCs were designed and constructed as per our previous studies, with the exception of the separator [13]. Two different separators of Nafion-117 and PP80 were used for ion transports under different RH conditions at the cathode. A cover prearrangement with foil (45 mL of total volume with inner dimensions of  $1.5 \times 5 \times 6 \text{ cm}^3$ ) was made at the cathode with ingrained punched holes on the air facing side to alter the RH. The variation in RH was tweaked by altering the number of holes or by making an elongated vertical hole on the cathode cover foil, and thereby adjusting the RH at the cathode. The humidity around the cathode was regulated in the range of 30%~90% (Figure 1). A hole for the humidity detection sensor was placed at the top of the cathode cover (Figure 1) [9]. Additionally, a humidifier was placed near to the MFC, for maintaining the constant required humidity conditions during operation. A sufficient distance was maintained between

the humidifier and the MFC to avoid any decremental effects in the cathode ORR. The anode electrode for development of bioelectrogens was placed at a distance of 3 cm from cathode. The working volume of the anode chamber was 205 mL (total volume = 210 mL). The pretreated Nafion-117 (PEM; Dupont Co., Wilmington, North Carolina, USA) separator and the size-selective separators of non-woven fabrics PP80 (Non-Woven Tech Co., Busan, Korea) were tested at different relative humidity conditions. The separators were placed between the anode chamber and the cathode and supported by two silicone gaskets to minimize water leakage. Both the MFCs were operated under similar conditions, except for the difference in separator type. The anode chamber and the cathode were held together by coated screws. A commercial wet-proofed platinum-coated carbon cloth ( $0.5 \text{ mg/cm}^2$ ;  $30 \text{ cm}^2$ , Fuel Cell Earth, Woburn, MA, USA) was used for the cathode. A plain carbon fiber brush ( $3 \times 2.5 \text{ cm}^2$ , Kemsung brush, Gyeonggi-do, Korea) was used for the anode. The Ag/AgCl (+197 mV vs. SHE) reference electrode was placed near to the anode electrode to measure electrode potentials. Both the anode and the cathode were connected externally by placing a resistance of  $600 \Omega$  in the external circuit.



**Figure 1.** Exploded schematic view and photograph of a single chamber the air-cathode microbial fuel cell (MFC) with an end frame for controlling relative humidity.

## 2.2. Biofilm Formation and Operation

The inoculum for the development of bioexoelectrogenic biofilm on the anode was established by using domestic wastewater (2 g/L of acetate) collected from Giheung Respia wastewater treatment plant (Yongin, Korea). After noting repeatable maximum stable power generations, the wastewater was replaced with a growth medium (GM) consisting of vitamin (5 mL/L), mineral (12.5 mL/L) and sodium acetate (2 g/L) as a substrate. The GM was prepared as described in earlier studies of MFCs [14]. In order to avoid mass transfer limitations, the anolyte of the MFC was continuously stirred by placing reactors on a magnetic stirrer plate. Both the MFCs were operated in a fed batch mode, in a temperature-controlled incubator at  $30 \pm 1 \text{ }^\circ\text{C}$  (Vision Inc., Daejeon-Si, Korea). Prior to sealing, the anolyte was sparged with argon gas for 15 min to sustain anaerobic conditions. The GM in the anode was replaced after every 2–4 days due to the decline in the maximum stable voltage with respect to substrate degradation. The humidifier was set nearby the MFC to control and maintain the desired humidity at the cathode. All the experiments were conducted in repeatable cycles.

## 2.3. Measurement and Analysis

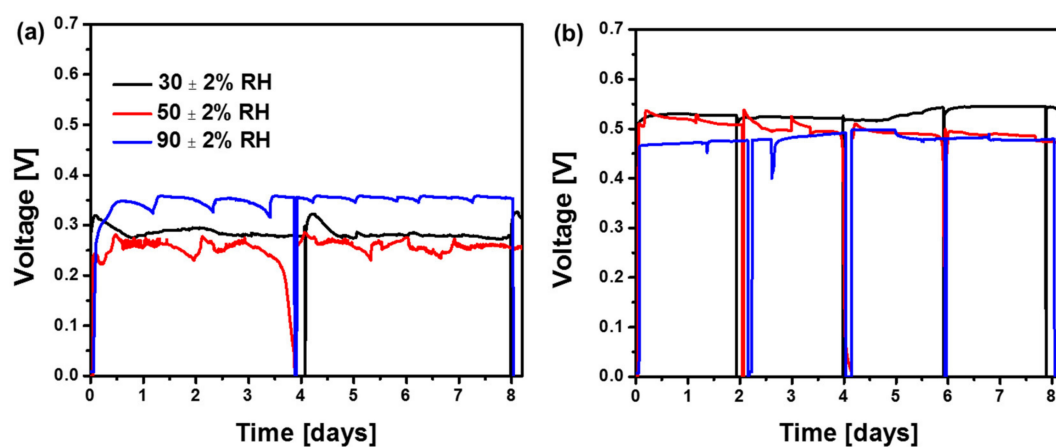
The cell voltage across the anode and the cathode was monitored for every five minutes by using the digital data acquisition system (KEITHLEY, Digital multimeter, Fort Worth, Texas, USA) across

an external resistance of  $600 \Omega$ . Polarization analysis was carried out at different RH, by connecting the MFC to a resistance box and by varying the external resistance from  $10 \Omega$  to  $4000 \Omega$ . During the polarization analysis, the anode and cathode potentials were noted by using Ag/AgCl (+197 mV vs. SHE) as a reference electrode (Bioanalytical Systems Inc, West Lafayette, IN, USA) [15]. The current and power were derived from the voltage by using Ohms law. The current densities and power densities were calculated on the basis of the cathode's surface area ( $30 \text{ cm}^2$ ). The cyclic voltammetry (CV) analysis was pursued with potentiostat (Versa Stat 3, Princeton Applied Research, Berwyn, PA, USA) in a three-electrode system by using the cathode as a working electrode. The anode and Ag/AgCl served as a counter and reference electrode, respectively. The CV analysis was pursued at a scan rate of  $5 \text{ mV/s}$ , within a potential window of  $-0.7$  to  $0.7 \text{ V}$  vs. Ag/AgCl. The oxygen crossover from cathode to anode at different RH values was noted by monitoring the dissolved oxygen (DO) concentration in abiotic MFCs with an RDO meter (Portable Meter, Orion STAR A323, Waltham, MA, USA). The RH in the cathode cover was determined by using a humidity sensor (Digitales Thermo Hygrometer, Waltham, MA, USA). The Columbic efficiencies (CE), oxygen mass transfer ( $K_o$ ) and diffusion coefficients ( $D_o$ ) were calculated as described in previous studies [7,9,16].

### 3. Results and Discussion

#### 3.1. MFC Power Generation with Different Separators and Relative Humidity Conditions

The voltage was measured during MFC operations with Nafion 117 and PP80 as the separators under three different relative humidity (RH) conditions. The RH values of  $30 \pm 2\%$ ,  $50 \pm 2\%$  and  $90 \pm 2\%$  were maintained by using a humidifier during the operation. MFC operation with Nafion 117 at an RH of  $90 \pm 2\%$  exhibited a maximum stable voltage generation of  $0.35 \text{ V}$  with an external resistance of  $600 \Omega$  (Figure 2). This maximum voltage generation was 1.34 and 1.25-fold higher than the operations with  $50 \pm 2\%$  RH ( $0.26 \text{ V}$ ) and  $30 \pm 2\%$  RH ( $0.28 \text{ V}$ ), respectively. The cathode and anode potential at  $90 \pm 2\%$  RH were noted to be  $-0.180 \text{ V}$  and  $-0.523 \text{ V}$  vs. Ag/AgCl, respectively. MFC operations with  $30 \pm 2\%$  and  $50 \pm 2\%$  RH exhibited a lower cathode potential of  $-0.189 \text{ V}$  and  $-0.261 \text{ V}$ , respectively, thereby suggesting that a higher RH condition in the cathode is beneficial for efficient cathodic oxygen reduction reaction (ORR) reactions with a Nafion 117 separator. Additionally, the higher power density at  $90 \pm 2\%$ , is possibly due to higher proton or hydroxyl ion transports on the cathode [9]. The anode potentials were increased with the decrease in RH levels in the cathode part, and the increased values were  $-0.512 \text{ V}$  and  $-0.473 \text{ V}$  for  $50 \pm 2\%$  RH and  $30 \pm 2\%$  RH %, respectively. This result suggest that higher RH conditions have a negative effect on both anode and cathode performance.



**Figure 2.** Voltage generation from a single chamber air cathode MFC at different relative humidity (RH:  $30 \pm 2\%$ ,  $50 \pm 2\%$  and  $90 \pm 2\%$ ) conditions with (a) Nafion 117 and (b) PP80 as a separator.

On the other hand, the MFC operation with PP80 as a separator exhibited a maximum stable voltage generation of 0.53 V at a relatively lower RH of  $30 \pm 2\%$ . This voltage generation was noted to be 1.51 times higher than the MFC operation with Nafion 117 at  $90 \pm 2\%$  RH. In addition, the maximum voltage generation at  $30 \pm 2\%$  RH was 1.06 and 1.10 times higher than the voltage generation noted at  $50 \pm 2\%$  RH (0.50 V) and  $90 \pm 2\%$  RH (0.48 V), respectively. The cathode and anode potentials at  $30 \pm 2\%$  RH were 0.043 V and  $-0.487$  V, respectively. The cathode potential at higher RHs was found to be similar to the value with 30%, and the values were 0.047 V and 0.049 V at  $50 \pm 2\%$  and  $90 \pm 2\%$  RH, respectively. This result indicates that the variation in RH in the cathode with a PP80 separator does not affect much the ORR reactions with  $1000 \Omega$  external resistance. Moreover, the cathode potential with PP80 was much higher than the values with Nafion 117, which might be due to a larger pore size of PP80 ( $30 \mu\text{m}$  vs.  $50 \times 10^{-4} \mu\text{m}$  for Nafion 117) resulting in more oxygen and proton transports for an efficient ORR environment on the cathode electrode [7,17]. However, the increase in anode potential with the increase in RH levels was observed, and the values were  $-0.437$  V and  $-0.430$  V at  $50 \pm 2\%$  and  $90 \pm 2\%$  RH, respectively. This was in a good agreement with earlier studies of MFCs with a Nafion 117 separator, in which the power generation was decreased with an increase in humidity from 0% to 100% [10].

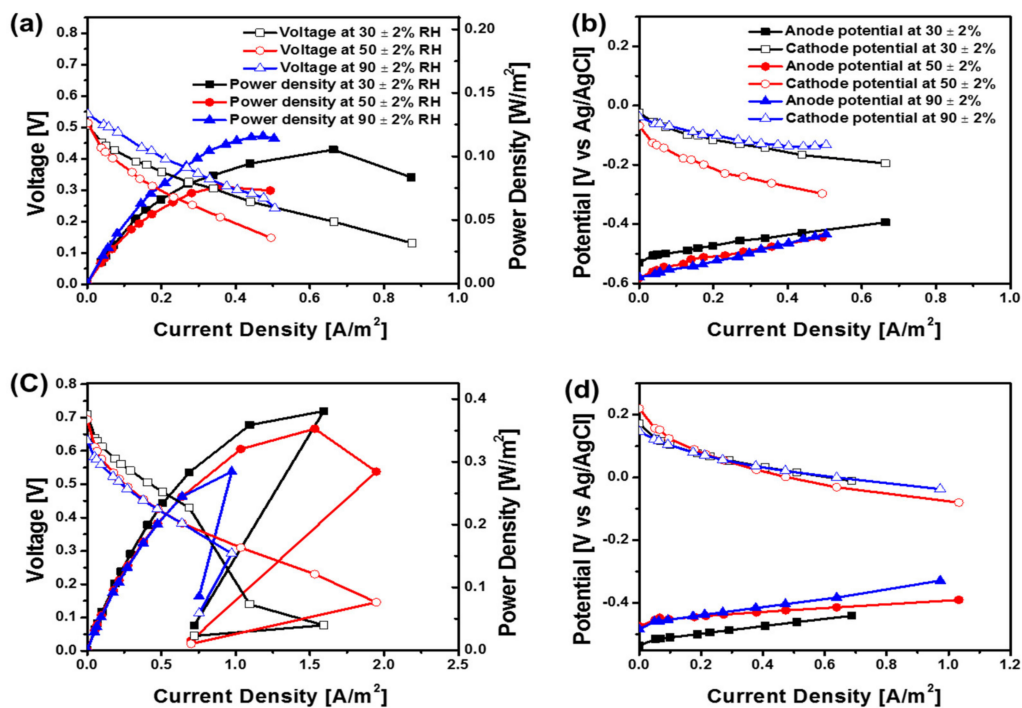
### 3.2. Polarization Performance of Air-Cathode MFCs

During the polarization analysis, the various resistances (4000 to  $10 \Omega$ ) were used to evaluate the maximum power density of air-cathode MFCs by using a resistance box. The polarization and I-V curve at different RHs with respect to current density were shown in Figure 3. The open circuit cell voltage (OCV) of the air cathode MFC with Nafion 117 at  $90 \pm 2\%$  RH was noted as 0.542 V. The open circuit cathode potential (OCP) and anode potential (OAP) were  $-0.038$  V and  $-0.580$  V, respectively. With a decrease in RH to  $50 \pm 2\%$  and  $30 \pm 2\%$ , the measured OCV was noted to be 0.514 V (OCP =  $-0.068$  V and OAP =  $-0.58$  V) and 0.505 V (OCP =  $-0.025$  V and OAP =  $-0.53$  V), respectively. At  $90 \pm 2\%$  RH, the maximum power density of  $116 \text{ mW/m}^2$  was noted at a current density of  $0.473 \text{ A/m}^2$ . This was found to be 1.10 and 1.52-fold higher in comparison to the MFC operation at an RH of 30% and 50%, respectively.

In earlier studies of MFC, Ahn et al. (2014) reported that the maximum power density of  $1130 \pm 30 \text{ mW/m}^2$  with Nafion was noted at 0% RH (a dry air), and this was decreased to  $980 \pm 80 \text{ mW/m}^2$  with an increase in RH to 100% [10]. The decrease in power density at 100 % RH might be due to water flooding at the cathode, leading to the blockage of oxygen transport from the air to the catalytic layer [9,18,19]. The different trend in power density at RH conditions in this study might be due to the variation in operational conditions such as the reactor volume (28 mL vs 200 mL), substrate concentration (1 g/L vs. 2 g/L) and electrode surface area ( $7 \text{ cm}^2$  vs  $30 \text{ cm}^2$ ) [10]. At an RH of  $50 \pm 2\%$ ; the maximum power density was  $76 \text{ mW/m}^2$  at a current density of  $0.356 \text{ A/m}^2$ . Whereas, with an MFC operation at  $30 \pm 2\%$  of RH, the maximum power density was noted to be  $105 \text{ mW/m}^2$  at a current density of  $0.663 \text{ A/m}^2$ .

With PP80, the open-circuit cell voltages (OCVs) of the air cathode MFC at  $30 \pm 2\%$ ,  $50 \pm 2\%$  and  $90 \pm 2\%$  were 0.71 V (OCP = 0.173 V and OAP =  $-0.537$  V), 0.694 V (OCP = 0.220 V and OAP =  $-0.474$  V) and 0.631 V (OCP = 0.147 V and OAP =  $-0.484$  V), respectively. The average OCPs ( $0.180 \pm 0.037$  V) with PP80 were much higher than the values ( $-0.044 \pm 0.022$  V) with Nafion, although the same cathode electrode was used in both reactor operations. This observation suggests that PP80 is a more favorable separator for cathodic oxygen reductions in single chamber MFCs. The highest OCP values were obtained as the RH condition was adjusted at 50%. However, in terms of OAP, the most negative values of OAPs were obtained at 30% compared with other RH conditions. The maximum power density of  $381 \text{ mW/m}^2$  was noted at a lower RH of  $30 \pm 2\%$ , which was about 3 times higher than the operation with Nafion at 90% RH. At the other RHs, the maximum power densities were  $352 \text{ mW/m}^2$  and  $284 \text{ mW/m}^2$  at  $50 \pm 2\%$  and  $90 \pm 2\%$  RH, respectively. These results suggest that the different optimum RH conditions at the cathode are required to obtain a high performance of MFCs depending

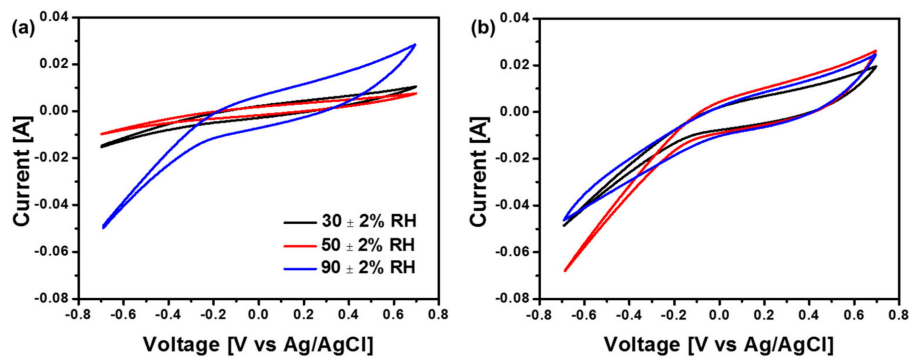
on the separator type. In addition, it was suggested that the RH condition in the cathode had an influence on the redox reactions on both the anode and cathode electrodes.



**Figure 3.** I-V and polarization curve of a single chamber air cathode MFC using (a) Nafion 117 and (c) PP80 at different relative humidity conditions. Variation in individual electrode potentials in relation to current densities by using (b) Nafion 117 and (d) PP80 as a separator.

### 3.3. Cyclic Voltammogram Analysis of Cathode Electrode

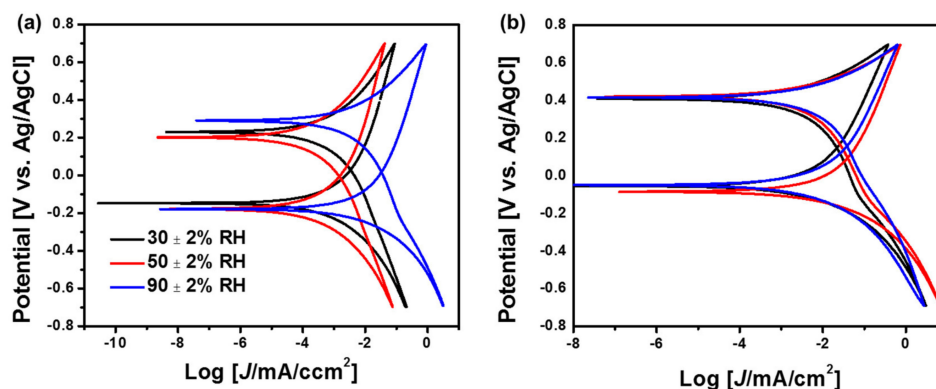
The influence of relative humidity on oxygen reduction at the cathode electrode was analyzed using a cyclic voltammogram (CV) in different RH conditions (30 ± 2%, 50 ± 2% and 90 ± 2%) (Figure 4). The cathode performance in the air-cathode MFC is largely affected by oxygen reduction at the cathode. The air-cathode MFC operation with Nafion 117 at the 90 ± 2% RH condition resulted in a maximum reduction current of −0.051 A, which was a much higher absolute value than at the other conditions. This result also confirms that more a favorable reduction of oxygen on the cathode can be achieved at relatively high RH conditions. The high relative humidity condition at the cathode can elevate ion transports and oxygen solubility on the cathode, which can, in turn, increase the cathode reduction reaction [9]. By decreasing relative humidity at the cathode to 50 ± 2% and 30 ± 2% RH, the reduction current values were observed at −0.007 A and −0.015 A, respectively. Using PP80 as a separator, the maximum reduction current was obtained at an RH of 50 ± 2%, and the value was −0.068 A. These cathode reduction currents at 50 ± 2% RH were higher than with the Nafion 117 (−0.051 A at 90 ± 2% RH), but lower than with the CMI separator (−0.073 A at 88 ± 2% RH) [9]. At the other RH conditions (90 ± 2% and 30 ± 2%), the reduction current values were similarly obtained at −0.046 A and −0.049 A, respectively. CV results with different separators also suggest that the RH condition greatly influences the reduction of oxygen on the electrode. In addition, the variation in reduction current with different separator types can be due to the difference in physical characteristics such as pore size, functionalization and the thickness, which can greatly affect the water flux from the anode to the cathode in air-cathode MFCs [7,20].



**Figure 4.** Cyclic voltammogram analysis of air-cathode MFCs with Nafion 117 (a) and PP80 (b) at different relative humidity (RH).

Furthermore, the electrochemical behavior of the cathode for oxygen reduction was evaluated by deriving the Tafel slope from the cyclic voltametric data (Figure 5). The Tafel slope can be one of the crucial parameters in determining the reaction kinetics at the cathode electrode of MFCs. The lower Tafel slope suggests the higher electrocatalytic activity in terms of oxygen reduction. The MFC operations with variations in RH and the separator exhibited a different Tafel slope and exchange current density ( $i_0$ ) based on cathodic performance. The MFC operation with Nafion 117 at  $90 \pm 2\%$  RH exhibited a lower Tafel slope of 0.424 V/decade and a higher  $i_0$  of 0.077 mA/cm<sup>2</sup> than at the other RH conditions (Table 1). The Tafel slope and exchange current density values with  $30 \pm 2\%$  RH were 0.455 V/decade and 0.006 mA/cm<sup>2</sup>, and with  $50 \pm 2\%$  RH, they were 0.448 V/decade and 0.002 mA/cm<sup>2</sup>. The lower Tafel slope and larger  $i_0$  at  $90 \pm 2\%$  RH, signifies the high oxygen reduction at the cathode and these are in good agreement with the high cathode potentials and power densities noted during polarization.

An MFC operation with PP80 as a separator at  $50 \pm 2\%$  RH exhibited a lower Tafel slope and  $i_0$  of 0.501 mV/decade and 0.323 mA/cm<sup>2</sup>, respectively. The similar Tafel slope was noted with  $30 \pm 2\%$  RH (0.516 mV/decade), however  $i_0$  was noted to be 48.3% (0.156 mA/cm<sup>2</sup>) smaller in comparison to MFC operation at  $50 \pm 2\%$  RH. The Tafel slope and  $i_0$  at  $90 \pm 2\%$  RH was noted to be 0.704 V/decade and 0.290 mA/cm<sup>2</sup>, respectively. The derived maximum  $i_0$  with PP80 at 50% RH is about 4 times higher than the maximum value with Nafion at 90%, suggesting the better ORR at the cathode with PP80 over Nafion 117, which was in a good agreement with the polarization and CV analysis in terms of cathodic performance. The  $i_0$  noted in present study were found to be smaller in comparison with other studies of MFCs. Xu et al., operated a double chamber MFC with a Prussian blue/graphene cathode and noted an  $i_0$  of 12.78 mA/cm<sup>2</sup> [21]. This difference in  $i_0$  in relation to ORR might be due to the variation in operational conditions such as reactor configurations, cathode humidity and cathode catalyst.



**Figure 5.** Tafel analysis derived from the voltametric profiles during forward and reverse scans of Nafion 117 (a) and PP80 (b) at different relative humidity (RH).

**Table 1.** Tafel slope and exchange current densities at different RHs and separators noted in a single chamber air cathode MFC.

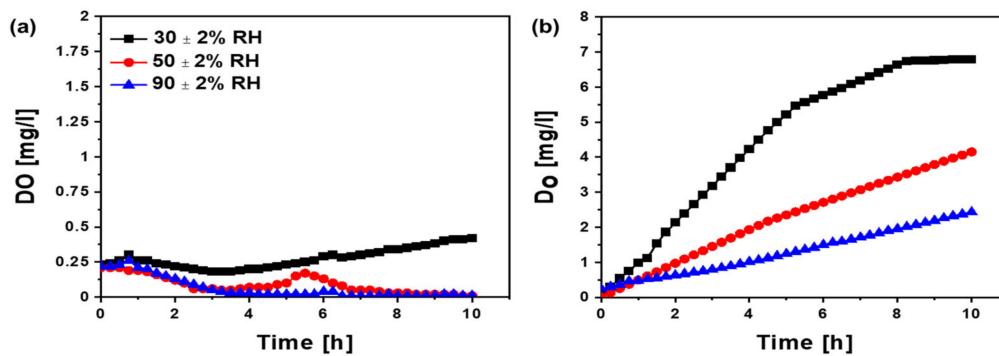
Relative Humidity (%)	Nafion		PP80	
	Tafel Slope (mV/decade)	Exchange Current Density (mA/cm <sup>2</sup> )	Tafel Slope (mV/decade)	Exchange Current Density (mA/cm <sup>2</sup> )
30 ± 2	0.455	0.006	0.516	0.156
50 ± 2	0.448	0.002	0.501	0.323
90 ± 2	0.424	0.077	0.704	0.290

#### 3.4. Oxygen Transport from Cathode to Anode at Varied Relative Humidity Conditions with Different Separators

Relative humidity at the cathode can possibly alter the oxygen mass transports to the anode chamber, which is one of the important factors affecting the overall performance of MFCs. High oxygen diffusion to the anode from the cathode that faced the atmospheric air could reduce bioelectrogenic activities at the anode and also enhance biofilm development on the membrane or the electrodes [22]. In this study, the maximum oxygen transfer coefficient ( $K_o$ ) and diffusion coefficient ( $D_o$ ) values were calculated at the low RH condition ( $30 \pm 2\%$ ) in both Nafion and PP80 (Figure 6). The high  $K_o$  and  $D_o$  in the air-cathode MFC with Nafion 117 at  $30 \pm 2\%$  RH were noted to be  $0.35 \times 10^{-4}$  cm/s and  $0.70 \times 10^{-6}$  cm<sup>2</sup>/s, respectively (Table 2). With the higher RHs of  $50 \pm 2\%$  and  $90 \pm 2\%$ , the  $D_o$  levels were not increased with the prolonged operation, and so the oxygen diffusion was not observed. Likewise, the maximum  $K_o$  and  $D_o$  values with PP80 were observed at  $30 \pm 2\%$  RH, and the values were  $13.60 \times 10^{-4}$  cm/s and  $5.7 \times 10^{-5}$  cm<sup>2</sup>/s, respectively. With an increase in RH to  $50 \pm 2\%$ , the  $K_o$  and  $D_o$  decreased to  $7.81 \times 10^{-4}$  cm/s and  $3.30 \times 10^{-5}$  cm<sup>2</sup>/s, respectively. With a further increase of RH to  $90 \pm 2\%$ , these coefficients were decreased to  $4.15 \times 10^{-4}$  cm/s ( $K_o$ ) and  $1.70 \times 10^{-5}$  cm<sup>2</sup>/s ( $D_o$ ). The  $K_o$  of PP80 at an RH of  $30 \pm 2\%$  is 38 times higher than the Nafion 117, possibly due to the larger pore size of PP80 which could increase the oxygen permeation. The high oxygen diffusion to the anode chamber with PP80 might cause higher anode potentials than the values with Nafion 117 [23,24]. In addition, at higher RHs, water evaporation to the cathode side could be minimized leading to the blockage of pores and forming a dense biofilm at the cathode and thereby minimizing the oxygen cross over from cathode to anode [25].

**The columbic efficiencies (CE) were evaluated at different RHs and separators to understand the relationship between CE and oxygen diffusion as an indicator of reactor performance.** The CE values with Nafion 117 at different humidity conditions of  $30 \pm 2\%$ ,  $50 \pm 2\%$ , and  $90 \pm 2\%$  were 3.2%, 2.6% and 3.2%, respectively. The MFC operations with PP 80 showed the CE values of 5.09%, 2.87% and 2.72% at  $30 \pm 2\%$ ,  $50 \pm 2\%$  and  $90 \pm 2\%$  RHs, respectively. Although more oxygen diffusion with PP80 was observed compared with Nafion in abiotic conditions, similar CE values with PP80 were observed, possibly due to high current generation and biofilm development on the membrane in biotic operations. The CE values noted in this study are relatively low in comparison to other similar studies, which reported 4%~22% of CE with acetate as a substrate [9,22]. This low CE value compared to other studies might be due to the large size of the separators (30 cm<sup>2</sup>) which allowed more oxygen diffusion.





**Figure 6.** Dissolved oxygen levels noted in a single chamber air-cathode MFC with Nafion 117 (a) and PP80 (b) at different relative humidity (RH) conditions.

**Table 2.** Performance parameters of MFC with variations in separator and relative humidity.

Relative Humidity (%)	Voltage (V)		Power Density (mW/m <sup>2</sup> )		<sup>a</sup> Do (cm <sup>2</sup> /s)		<sup>b</sup> CE (%)	
	Nafion	PP80	Nafion	PP80	Nafion	PP80	Nafion	PP80
30 ± 2	0.28	0.53	105	381	$0.70 \times 10^{-6}$	$5.70 \times 10^{-5}$	3.2	5.09
50 ± 2	0.26	0.50	76	352	-	$3.30 \times 10^{-5}$	2.6	2.87
90 ± 2	0.35	0.48	116	284	-	$1.70 \times 10^{-5}$	3.2	2.72

<sup>a</sup> Oxygen diffusion coefficient, <sup>b</sup> Columbic efficiency.

#### 4. Conclusions

The variation in humidity conditions at the cathode of a single chamber MFC had much influence on the overall performance of MFC operations. The optimum RH conditions were obtained at different values depending on the types of separators and operational parameters. MFC operations with Nafion 117 exhibited a higher power density at an RH of 90% than with other RH conditions. With PP80, the maximum power density was obtained at a relatively lower RH of 30%, and the value was 3.3 times higher than with Nafion 117, suggesting PP80 as a favorable separator for high power generation in single chamber MFCs. Additionally, a PP80 separator showed a higher performance in oxygen reduction conductance at all RH conditions. The oxygen diffusion rate was reduced with an increase in RH, but the CE values of MFCs were determined majorly by current generation. This study suggests that the RH condition on the cathode needs to be properly controlled depending on the separator characteristics and other operational conditions (exoelectrogens, temperature, etc.) to achieve the best performance of single chamber MFCs.

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