

Porosity and Biofilm Attachment on Carbon Anode Materials for Honeycomb Microbial Fuel Cell

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ABSTRACT

Microbial fuel cells (MFCs) mainly generate energy through microbial metabolism, and microorganisms attachment to the anode plate to form biofilms. For MFCs experiments, the plate material needs to have good electrical conductivity, chemical stability and biocompatibility. At present, carbon electrode plates are often used in MFCs, but different porosities influence the microbial adhesion. Thus, this study uses a carbon cloth, a carbon felt, and a graphite felt to explore the effect on biofilms under the carbon electrode plates of different porosities in honeycomb mesh continuous microbial fuel cells (HC-MFCs). The results show that the currents of carbon felt, graphite felt, and carbon cloth are 34.09 mA, 30.02 mA, and 3.08 mA. It is found that the carbon felt and graphite felt have higher electrical results than carbon cloth, mainly due to the high porosities of the carbon and graphite felt. In addition, the electrode material affects the formation of biofilms and further the electrical performance of MFCs. Through the internal resistance of the system equivalent circuit analysis, the results of the anode activation impedance (R_2) and anode electrical double layer (C_1) show that compared with carbon felt and graphite felt, carbon cloth has a higher resistance value and biofilm formation, which makes it worse in electrical performance of HC-MFC. Therefore, it can be known that the higher material porosity will affect the biofilm formation. This study is aimed to provide MFC research on porosity and biofilm.

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INTRODUCTION

Microbial fuel cells (MFCs) are recognized as a green energy with the capability to degrade organic waste while generating electricity (Santoro et al. 2017). MFCs are similar to conventional fuel cells except it uses bio-catalytic abilities of microorganisms that is capable of utilizing various organic fuels sources (Du et al. 2007). The MFCs consists of the anode where the microorganisms are situated and the anaerobic process is performed and the cathode where the aerobic process is administered and the oxygen and hydrogen are permitted through proton exchange membrane (Du et al. 2007). Recent studies suggests advances in MFCs have been achieved. Slate et al. (2019) performed a review of current technologies used in MFCs highlighting the challenges in the electron transfer process of microorganisms. Do et al. (2020) conducted a critical review of recent advances of MFC-based biosensor for real-time wastewater monitoring. Kabutey et al. (2019) reviewed the various configurations of plant-based MFCs and have discussed the potential applications in wastewater treatment, surface remediation, bio-sensing, and greenhouse gas avoidance. Farber et al. (2020) performed a computational fluid dynamic analysis on the generation of electricity in an MFC with textile-based carbon fiber anodes. Kaur et al. (2020) reported the recent advancement on the nanomaterial-based electrode material for MFCs. For all types of electrodes, the substrate must have good electrical conductivity, good chemical stability, high mechanical strength, and low cost. With these characteristics, carbonaceous material has become the most widely used material for MFCs. In addition, good biocompatibility, good chemical stability, high electrical conductivity, and relatively low cost of carbonaceous material makes it the preferred choice for MFCs (Rahimnejad, Adhami et al. 2015).

The most common materials used in anodes are made of carbon materials. These materials include:

graphite fiber brushes, carbon cloth, graphite rods, carbon paper, reticulated glassy carbon (RVC), and carbon felt because of their stability in microbial cultures. High electrical conductivity and wide surface area are favored in such system to have better performance (Logan et al. 2006). According to a report by Wei et al. (2011) provides greater surface area and power generation efficiency during growth, among which Chaudhuri and Lovley (2003) compared the performance of graphite rods, graphite felts, and stone-foamed foams based on the surface area of the resulting electrodes. Similar current and biomass were obtained from graphite rods and graphite felt electrodes, and the current density generated by graphite foam electrodes was 2.4 times that of graphite rod electrodes, and the battery density was 2.7 times that of graphite rods. According to the above literature, under the polar plates as the same carbon materials, the difference in porosity will affect the power generation efficiency of MFCs. However, the types of materials, and porosity was observed to affect the biofilms (Franks and Nevin 2010, Zhi et al. 2014).

In addition, the biofilms studied in MFCs are formed by stacking organisms and transferring electrons to anode plates (Logan 2009). Therefore, the material of the anode plate is an important factor for the biofilm. According to Lin et al. (2018), the formation of biofilm is influenced by temperature, external impedance, plate material, anode matrix species, and biological community. Moreover, the reaction area of the plate material, effects of biocompatibility, porosity, and chemical properties are among the factors were recognized to affect the biofilm formation. Wei et al. (2011) also discussed the types and modification methods of anode plate materials, which modify the adhesion of the microorganisms in the MFC. Based from these recent studies, it is known that the formation of biofilms is susceptible to the influence of plate materials and special systems. Therefore, in this study, the effects of porosity on biofilms in different types of carbon material plates (carbon cloth, carbon felt, and graphite felt) will be analyzed in a continuous honeycomb microbial fuel cell system and alternating current (AC) impedance analysis.

MATERIALS AND METHODS

Chamber Design

In this experiment, a continuous Honeycomb Microbial Fuel Cells (HC-MFCs) was designed (as shown in Figure 1). The cathode cell was ($L \times W \times D$: 5 cm $\times$ 5 cm $\times$ 6 cm) and using proton exchange membrane nafion 117 (5 cm $\times$ 5 cm, 25 cm²), the anode cell is ($L \times W \times D$: 7 cm $\times$ 5 cm $\times$ 8 cm) and continuous flow field, the flow rate is controlled at 438 mg / L, A honeycomb design (inner $L \times W \times D$: 5 cm $\times$ 5 cm $\times$ 8 cm) was used for rectification before

and after (Figure 1). In this experiment, the material of the cathode / anode plate is carbon cloth (Carbon Cloth, CC), carbon felt (Carbon Felt, CF), and graphite felt (Graphite Felt, GF), and the reaction area is 25 cm². However, according to the literature, it can be known that the porosity of the three carbon material plate (CC, CF, GF) is 80%, 40%, and 60% (Morozan, Stamatina et al. 2007, Wei, Liang et al. 2011, Sonawane, Yadav et al. 2017).



Fig. 1. The honeycomb microbial fuel cells experimental tank.

MFCs Experimental Operations

The wastewater is domestic wastewater, which is taken from Luodong Wastewater Treatment Plant. The characteristics of wastewater are shown in Table 1. Before the experiment, the graphite felt was hydrophobic and had to be pretreated to become hydrophilic in order to facilitate the adhesion of microorganisms. First, the graphite felt was soaked with RO water and heated at 90 °C for 3 hours with water insulation. For proton exchange membrane pre-treatment, use 0.05 M H₂O₂ (950 ml H₂O and 50 ml H₂O₂), heat it under water for 1 hour (70 °C), soak it with DI water, and then use 1 mole sulfuric acid (947 ml H₂O and 3 ml of H₂SO₄) was immersed for 1 hour, then removed and immersed in DI water (Chen, Wang et al. 2018).

Table 1. Specific data for the tank vehicle.

Parameter	Value
COD	218 ppm
pH	7.028
Conductivity of anode chamber solution	2.40 mS/cm

In addition, for domestication, an external resistor of 1 K Ω (Ren, Yan et al. 2011, Ahn and Logan 2012) is required in the microbial culture, and the matrix is added step by step, so that the microorganisms gradually adapt to and attach to the electrode plate, and use the instrument to conduct electricity monitoring, but when the power drops below 10% of the original maximum power or the cathode / anode liquid level is too low, the solution

needs to be replaced.

The anode solution was 50 mM phosphate buffer nutrient solution (PBS, Na_2HPO_4 , 4.58 g / L; $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 2.45 g / L; NH_4Cl , 0.31 g / L; KCl , 0.13 g / L), which contains phosphate buffer and matrix (sodium acetate) dissolved in RO water. The cathodic solution was configured with a 50 mM potassium ferricyanide / phosphate buffer at 1:1 (Chen, Wang et al. 2018).

Measurement Method

In this study, an electrochemical analyzer was used for electrical measurement and an AC impedance analyzer was used to analyze the internal impedance in a microbial fuel cell. The measurement was performed at an open circuit voltage (OCV) and a scanning frequency of 100K Hz to 0.1 Hz every 60 seconds, data is recorded and monitored by connecting to a personal computer.

RESULTS AND DISCUSSIONS

This study is aimed to explore the effects of the carbon materials with different porosity on the continuous MFC honeycomb network electricity. The results on the electrical analysis and polarization loss are discussed.

Electrical Analysis of Carbon Plates with Different Porosities

Three different carbon materials (CC, CF and GF) were considered due to the influence of the electrode plate on the electrical properties of MFC. Mustakeem (2015) have utilized various carbon-based electrodes such as graphite rod, carbon fiber brush, carbon cloth, carbon felt. The electrical results are shown in Figure 2 wherein the limiting currents of CF, GF, and CC are 34.09 mA, 30.02 mA, and 3.08 mA, respectively.

The results of Mustakeem (2015) on various carbon-based electrodes agreed with the power trend results in this study as shown in Figure 2. With CF having higher limiting current results, it may due to the effect of porosity in the carbon material. According to Li et al. (2018), the characteristics, surface area, porosity, and surface area reported in electrode plate materials will affect biofilms, which in turn affects the electrical performance of MFCs. In addition, Chaudhuri et al. and Lovley (2003) report compared the properties of graphite rods, graphite felt, and graphite foam. Similar current and biomass were obtained from graphite rod and graphite felt electrodes, and the current density generated by graphite foam electrodes was 2.4 times that of graphite rod electrodes, and the battery density was 2.7 times that of graphite rods. According to the above literature, it can be known that under different porosities, electrical properties will be affected. It is found through electrical analysis that the higher the

electrical properties, the lower the porosity. However, in the MFCs experiment, a biofilm is formed on the surface of the anode plate, and the biofilm is mainly generated by microorganisms attached to the polar plate. Based on Manohar et al. (2008), it was found that the resistance of the anode would be reduced under the condition of including biofilm, indicating that the formation of biofilm on the surface of the anode can help reduce anode charge transfer resistance and increase electron transfer (Sekar and Ramasamy 2013). In addition, Li et al. (2018) knows that the formation of biofilms is affected by the material of the plate, and the formation of biofilms will also affect the internal resistance of the system in MFCs, and cause polarization loss. The report by Wen et al. (2009) states that the polarization curve can be used to determine whether or not it is affected by the loss of internal resistance. Therefore, in the electrical results of this study, it is speculated that MFCs are caused by the internal resistance of the system. Moreover, the effects of various internal impedances (activation impedance, ohmic impedance, and concentration impedance) in HC-MFCs will be explored through AC impedance analysis.

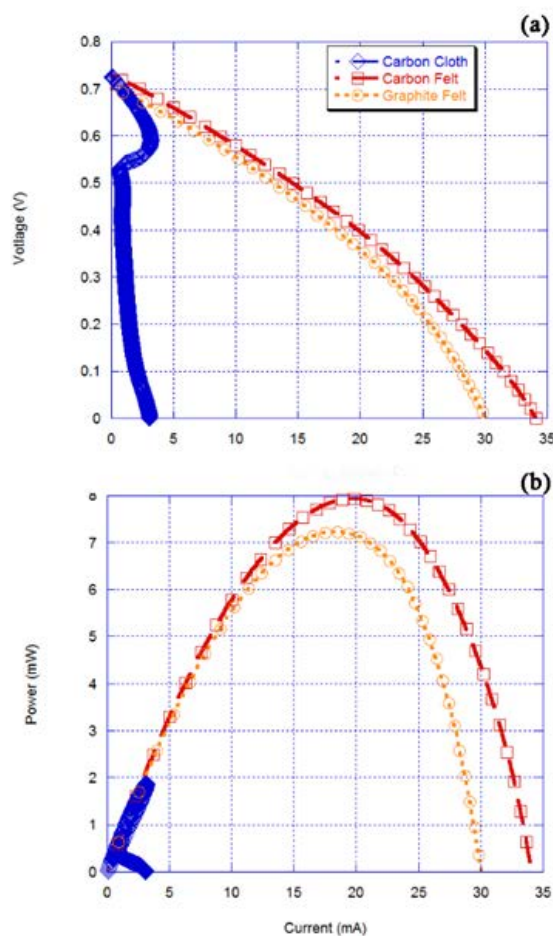


Fig. 2. Electrical characteristics of three different carbon materials (a) I-V curve (b) P-I curve.

AC Impedance Analysis of HC-MFCs

Since different electrode materials will affect the biofilm, and then affect the electrical performance of MFCs, and the formation of biofilms will affect the internal resistance of MFCs, the internal resistance analysis is performed by equivalent circuits in this study. Figure 3 is the equivalent circuit model of this study wherein the impedance W_2 is negligible and assumed to be ignored. R_1 is the ohmic impedance, R_2 is the anode activation impedance, R_3 is the cathode activation impedance, Q_1 is the anode electrical double layer, and W is the concentration impedance.

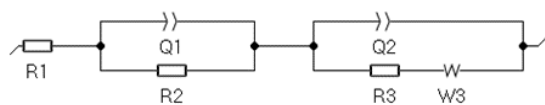


Fig. 3. Analysis of MFCs equivalent circuit.

The results of the AC impedance analysis are shown in Table 2. The results of R_1 are very similar due to the results obtained using the same PBS (Wang et al. 2018). The impedance of CF and GF in the W (concentration impedance) portion is greater than CC, and it is speculated that the loss in concentration is accumulated on the anode surface through substrate availability and product accumulation on the anode surface (Helder et al. 2012).

Table 2. Internal resistance analysis of HC-MFCs by equivalent circuit.

Kinds	R_1 (Ω)	R_2 (Ω)	Q_1 (C)	R_3 (Ω)	$W(C)$
CC	6.205	125.7	0.632	2.129	9.023
CF	6.377	2.396	0.137	13.92	120
GF	5.401	3.833	10.09×10^{-6}	19.9	674

Therefore, CF and GF have higher concentration impedance. In the results of R_2 , it was found that CC had a higher effect than CF and GF, and their individual values were 125.7, 2.396, and 3.833%. It is speculated that it may be due to the influence of biofilms, but according to Manohar et al. (Manohar et al. 2008), it was found that the resistance of the anode would be reduced under the conditions including biofilms, indicating that the formation of biofilms on the anode surface helps reduce the resistance. This increases the anode charge transfer resistance. However, the results at R_2 show a higher anode activation impedance compared to CF and GF. It can be known that in the HV-MFC experiment, the biofilm is generated on the anode electrode plate, which increases the anode activation resistance, and R_2 is related to the electron or ion accumulation phenomenon in the biofilm or

substrate (Kang et al. 2017). And Wen et al. (Wei et al. 2011) report stated that different electrode materials can affect the formation of biofilms. Therefore, it can be known that the use of carbon electrode plates with different porosities will affect the adhesion of biofilms, and then the system electrical properties.

CONCLUSIONS

This study investigates the effects of carbon plates with different porosities on biofilms in HC-MFCs. It was found that carbon cloth (CC), carbon felt (CF), and graphite felt (GF) were used as the electrode plate materials, and the porosities were 80%, 40%, and 60%, respectively, and the limiting current results were 3.08 mA and 34.09 mA and 30.02 mA, respectively. It can be seen that carbon felt has higher electrical performance, and the higher the porosity, the lower the current. Since different electrode materials will affect the biofilm and further affect the electrical performance of MFC, it can be known from the results of AC impedance analysis that C_1 is related to the electron or ion accumulation phenomenon in the biofilm or substrate and R_2 represents the anode activation impedance. The results of R_2 and Q_1 have a higher impedance in CC than CF and GF, so carbon electrode plates with different porosities will have an impact on the biofilm formation. This research will be helpful for microbial fuel cell research on porosity and biofilm.

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蜂巢網微生物燃料電池碳 陽極材料孔隙度和生物膜 附著

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摘要

微生物燃料電池主要通過微生物附著在陽極板上形成生物膜及微生物代謝產生電能，微生物燃料電池電極板材料需具良好導電性、化學穩定性和生物相容性。碳電極板常用於微生物燃料電池，但不同孔隙率將會影響微生物附著力及影響系統產電效能，故本研究將選用碳布、碳氈及石墨氈分別探索其對蜂巢網連續微生物燃料電池中不同孔隙率碳電極板生物膜生長影響，結果表明，碳氈、石墨氈及碳布電流分別為 34.09 mA、30.02 mA 和 3.08 mA；碳氈和石墨氈產電能力高於碳布，主要是因為碳氈和石墨氈之高孔隙率。實驗通過系統等效電路內阻分析、陽極活化阻抗 (R2) 及陽極電雙層 (C1) 結果並與碳氈和石墨氈相比對，發現碳布具更高電阻值和更厚的生物膜形成，這將使得蜂巢網連續微生物燃料電池產電性能更差，如此結果可發現較高材料孔隙率將會影響生物膜形成造成最終系統電性表現。