EVALUATION OF CATHODE ELECTRODE PERFORMANCE IN MICROBIAL FUEL CELL BY CYCLIC VOLTAMMETRY

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https://doi.org/10.26782/jmcms.spl.9/2020.05.00021

Abstract

Recently, the Microbial Fuel Cell (MFC) technology has captured the researcher’s attention for potentially solving the energy and environmental problems. In this work, we used cyclic voltammetry (CV) technique to evaluate carbon-based cathode electrode performance in MFC. Although activated carbon sheet (AC) has larger surface area than carbon sheet, experimental results showed that the MFC using carbon sheet for the cathode electrode generated higher power density than the case using AC. Based on the result of CV experiments, we formulate a hypothesis that the above result could be attributed to AC had absorbed more ferrocyanide in the cathodic chamber (ferricyanide turned into ferrocyanide by the oxidation reaction during MFC operation). This led to that the surface area of AC became smaller than that of carbon sheet, as a result, carbon sheet had outperformed AC in the role of the cathode in our MFC experiments.

Keywords: Microbial fuel cell, Carbon sheet, Activated carbon sheet, Cyclic voltammetry

I. Introduction

During the last few decades, energy shortage and environmental pollution have become major problems around the world. Consequently, for solving these problems, renewable energy technologies have been attracted many researchers in recent years [XIV], [II], [XII]. Microbial Fuel Cell (MFC) is one of the attractive technique that substitute for non-renewable energy resources such as oil and coal [IV]. MFC using biomass to generate energy is not only sustainable energy but also environmentally friendly energy production. It generates electricity by degrading organic matters through active microorganisms [VIII], [V], [XIII]. Even though some impressive merits are expected, there are still some problems in terms of output power, efficiently of MFCs performance and so on. Thus, most studies of MFCs are still performed at a laboratory level. To enable the practical application of MFCs, researcher have been focusing on various elements, designing new structures of MFC.
discovering of efficient microbes, new electrode materials and so on[VII], [XV]. It is generally believed that the electrode material is one of the most critical factors determining MFC performance.

General materials for MFC electrodes are metal-based or carbon-based materials. This is because electrodes should provide some requirements such as high conductivity, low cost and large surface area. Comparing these materials, although carbon-based materials show lower conductivity than metal-based material, they have been studied due to the effectiveness in microbial adhesion, stability, and low cost. Therefore, there are a lot of studies using carbon-based materials to improve MFC performance [XVI], [VI], [III].

Activated carbon (AC) is one of the carbon-based materials. It is widely used for the anode electrode to increase the surface area and roughness because of highly porous surface. This porous structure produces higher power generation by adding many microbial cells to the electrode. It is also used for air-cathode due to the characteristics of high absorption capacity of both gases and solutes. Oxygen reduction takes place at a very slow rate on the surface and leads to high overpotential that causes lower current density of MFCs. For solving this electrode overpotential, MFC systems commonly use potassium ferricyanide as an electron acceptor at laboratory. Although the use of potassium ferricyanide allow the MFCs to work more efficiently, it is not practical outside the laboratory due to its toxicity and insufficient deoxidation for long-term electricity generation [XV].

In this paper, the performance of AC sheet for the cathode in MFC with potassium ferricyanide was evaluated by using Cyclic Voltammetry technique and compared with hydrophilic Carbon sheet in terms of internal resistance and power generation.

II. Materials and Method
II.i. MFC Operation Principle

Fig. 1 shows the operation principle of MFC. A microorganism in the anode compartment decomposes organic matter (glucose) to generate electrons and protons, then transfers the electrons to the anode electrode. The electrons from the anode go through the external circuit to the cathode then reduced by an electron acceptor (potassium ferricyanide) in the cathodic compartment. The protons migrate to the cathodic compartment through the membrane to close the circuit.
II.ii. Properties of AC Sheet and Carbon Sheet

Table 1 shows the characteristics of the samples: AC sheet and hydrophilic carbon sheet. These sheets were provided by AZUMI FILTER PAPER.

Table 1: characteristics of the samples

| Samples                          | C1P1AC1 (Activated Carbon) | C1P-2 (Carbon) |
|---------------------------------|-----------------------------|---------------|
| Compounding ratio (%)          | Activated carbon:60         | Carbon fiber:50 |
|                                 | Carbon fiber:20             | Cellulose fiber:50 |
| Paper weight (g/㎡)             | 51                          | 51            |
| Thickness (mm)                  | 0.23                        | 0.26          |
| Density (g/㎤)                  | 0.24                        | 0.20          |
| Specific surface area of AC powder (㎡/g) | 1450                  | —             |

II.iii. Cyclic Voltammetry

Cyclic Voltammetry (CV) were performed with ALS model 1200 (BAS). The setup is shown in Fig. 2. In this study, all CV measurements were carried out in three-
electrode measurement setup. Working electrode (WE) was each sample’s electrode (1.5cm²), and counter electrode (CE) was AC sheet whose surface area is 2cm². Reference electrode (RE) was Ag/AgCl | KCl (sat) for the measurements. Buffer solutions were 0.01mol/L phosphate, buffered saline (purchased from Wako). All CV measurements were recorded at room temperature of 25 ℃, varying given voltage from 0.5V to −0.3V and the scan rate was 0.01V/s. We observed CV results for the heterogeneous rate and surface area of AC sheet and Carbon sheet electrodes against reversible one-electron-change reduction (equation (1)).

\[
[\text{Fe(CN)}_6]^{3-} + e^- \rightleftharpoons [\text{Fe(CN)}_6]^{4-}
\] (1)

The area of reaction was evaluated from following equation.

\[
i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}C^*
\] (2)

At 25 ℃ where \(i_p\) is the peak current, \(n\) is number of electrons transferred, \(A\) is the electrode surface area (usually treated as the geometric surface area of WE), \(D\) is the diffusion coefficient, \(v\) is the scan rate was and \(C^*\) is the electrode’s surface concentrate of molecules that is electrolyte in bulk solution (potassium ferricyanide). It means that the peak current is proportional to the electrode surface area when other elements are constant[I], [IX], [XI], [X].

Fig. 2: Setup of CV experiment

II.iv. Microbial Biofilm

In this study, *Escherichia coli* (*E. coli*) was used as the biocatalyst because it is easy to culture. It was grown in Lysogeny Broth medium (LB, 10g/L Tryptone, 5g/L Yeast extract, 10g/L NaCl and NaOH to adjust PH=7.0). After inoculating bacterial cells to 40ml LB medium contained in a plastic cup, it was put in a shaking incubator at 30 ℃ for 72 hours. After that a AC sheet (anode electrode) with the size of 4.5 cm² (1.5cm × 3cm) were immersed in the medium at 30 ℃ for 48 hours to form the bacterial biofilm. For avoiding the adhesion dead cell and excreta on the AC sheet surface, the sheet was put vertically in the medium by using a paper stand as shown in
Fig. 3. This AC sheets were used for anode electrode when the power output test was performed.

Fig. 3: The setup for biofilm formation at the anode electrode surface

II.v. Power Output of the MFC

MFC construction used in this study was double chamber type and was made of acryl transparent board. The volume of both anodic and cathodic compartments was $9\text{cm}^3$ ($1.0\text{cm} \times 3.0\text{cm} \times 3.0\text{cm}$). Proton exchange membrane (PEM, Nafion$^\text{R}$ membrane) was sandwiched between the anode and cathode compartments. The size of PEM was $3\text{cm}^2$ ($1.5\text{cm} \times 2\text{cm}$). Fig. 4 displays the configuration of the MFC. The anode chamber was filled with 6ml medium composed of 10g/l glucose, 5g/l yeast extract, 10g/l NaH$_2$CO$_3$, and 8.5g/l NaH$_2$PO$_4$, while the cathode chamber was filled with different concentration of potassium ferricyanide solution (1mM, 10mM, 50mM) in distilled water (6ml).

The output voltage of this MFC was monitored by using a data acquisition system (DAQ, National Instrument) and recorded the reading via a customized Lab-View interface. The circuit was closed by an external resistor between the anode and cathode. The current through resistor was calculated based on the discharging voltage using Ohm’s law.

Fig. 4: Configuration of the MFC

III. Result and Discussion

For the CV experiment, the concentration of ferricyanide in the electrolyte (1mM, 5mM, 10mM, 50mM in distilled water) was the main parameter for the evaluation of the surface area of the WE. Fig. 5 (a) (b) showed the Voltammogram of the carbon sheet and AC sheet, respectively. Fig. 5 (a) indicates that peak current increase proportionally with the concentration of potassium ferricyanide. This
phenomenon was explained by the Equation (2). Figure 5 (b) showed the peak current of AC sheet higher than that of carbon sheet by each concentration of ferricyanide; however, it was not proportional to the increase of the concentration of potassium ferricyanide. Moreover, in the case of higher concentration (50mM), peak currents of AC sheet and carbon sheet were recorded almost the same values (Figure 5 (c)). According to Equation (2), this result suggests that each surface area was almost the same.

While the CV method was performing, redox was occurred on the electrode surfaces spreading in electrolyte to the edge of diffusion layer over time. This CV result speculated that ferrocyanide, which reacted from ferricyanide during the experiment, adhered to the AC sheet electrode and led to reduce the effective surface area of the electrode. As a result, it is thought that the AC sheet becomes ineffective in terms of surface area when using as the cathode working with ferricyanide. In general, the peak voltage separation, $\Delta E$, between the oxidation peak voltage and the reduction peak voltage in Voltammogram is one of the elements to measure the reversibility electrochemical reaction.
Fig. 5: Voltammogram of the AC sheet and carbon sheet as the WE with various concentration of potassium ferricyanide (1mM, 5mM, 10mM, 50mM). (a) Carbon sheet WE with potassium ferricyanide concentration: 1mM (blue line), 5mM (red line), 10mM (black line). (b) AC sheet WE with potassium ferricyanide concentration: 1mM (blue line), 5mM (red line), 10mM (black line). (c) Carbon sheet (black line) and AC sheet (red line) with 50mM potassium ferricyanide

As Figure 5 (c) showed, there is a slightly difference between the $\Delta E$ of AC sheet and carbon sheet. Smaller $\Delta E$ indicates high electron transfer rate, therefore, comparing two electrodes, the carbon sheet is better for homogeneous kinetics. This result has relation to the overpotential of the MFC. High electron transfer rate leads to high power density in the case that there is no difference in other conditions in MFC.

Fig. 6 displays the power density outputs of MFCs using AC sheet cathode and carbon sheet cathode respectively with varying concentrations of potassium ferricyanide in the cathode electrolyte (1mM, 10mM and 50mM). These results were calculated from maximum current output at a given external resistance (6700Ω, 4700Ω, 2700Ω, 1800Ω, 1000Ω, 680Ω, 470Ω, 220Ω). From the graph, we evaluated the internal resistances of this MFC. As these results showed, when both AC sheet and carbon sheet were used, the internal resistances were almost the same value (at the point of the maximum power density), depending on the concentration of potassium ferricyanide in the cathode solution. In the case of 50mM and 10mM of the concentration of potassium ferricyanide, the internal resistance was approximately 1kΩ. However, at lower concentration (1mM), the internal resistance was between 2700Ω and 4700Ω. It indicated that there was poor reduction reaction with electrons from the biofilm anode on the cathode electrode surface. Therefore, at lower concentration, overpotential became higher and the total cell resistance became higher. As a result, the power density was considerably lower than the other concentrations. Comparing AC sheet with carbon sheet, the power density of carbon sheet was higher than that of AC sheet. Considering only the condition of 50mM potassium ferricyanide, the difference of electron transfer rate that obtained from the data of CV experiment might bring the difference of the power density.

As shown in Fig. 6, the maximum power density of carbon sheet cathode MFC was 25.6 $\mu$W/cm$^2$ (92.4$\mu$A/cm$^2$), while that of AC sheet cathode MFC was 21.0 $\mu$W/cm$^2$. 

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(83.7µA/cm²). Comparing these performances, the carbon sheet cathode MFC was about 22% higher.

![Power density graph](image)

**Fig. 6:** Power density of the MFCs with varying concentration of potassium ferricyanide (1mM, 10mM, 50mM). The results were calculated from the maximum current density at a given external load (6700Ω, 4700Ω, 2700Ω, 1800Ω, 1000Ω, 680Ω, 470Ω, 220Ω). Carbon sheet: 50mM (orange line), carbon sheet: 10mM (yellow line), carbon sheet: 1mM (green line), AC sheet: 50mM (dark blue line), AC sheet: 10mM (gray line), AC sheet: 1mM (light blue line)

### IV. Conclusion

In this study, we compared the performance of AC sheet cathode and carbon sheet cathode in MFC. Furthermore, the performance of carbon sheet cathode with ferricyanide was better than that of AC sheet cathode due to the higher electron transfer rate. This phenomenon was confirmed by CV experiment. From the result of both power density and CV experiment, we formulated a hypothesis that AC absorbed ferrocyanide during the oxidation reaction at the cathode compartment. It might lead to decrease the effective surface area of AC sheet. In future study, we will conduct a research about high permeance MFCs to prove this hypothesis.

### V. Acknowledgments

We would like to thank Simono, Siraishi, and Suzaki for valuable suggestions. A part of this research was supported by AZUMI FILTERPAPER CO., Ltd.
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