



Cobalt-Intercalated Birnessite-Type Manganese Oxide Catalysts for Low-Cost Cathodes in Microbial Fuel Cells

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Abstract

Microbial fuel cells (MFCs) are a promising technology for solving energy and water pollution problems. However, to promote the practical application of MFC, it is necessary to solve the problems of power output and electrode cost simultaneously. Therefore, transition metal-based catalysts that can improve air cathode functionality without using platinum catalysts, which are commonly used, are attracting attention. In this experiment, a cobalt-intercalated birnessite-type manganese oxide catalyst was used as the cathode of the MFC. In addition, rice husk charcoal from agricultural waste and Sumi ink were used as cathode materials to reduce cost and improve the physical stability of the electrodes. The conductivity of the Sumi ink is expected to compensate for the low conductivity of manganese oxide. The resulting power density was 5.8 times higher with the catalyst than without. It was also confirmed that the fabricated cathode operated for at least 90 days without maintenance.

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Keywords

MnO₂; Co; Catalyst; Sumi ink; Rice husk charcoal

1. Introduction

In the current society, where much energy is obtained from fossil fuels, it is necessary to secure renewable energy sources to establish a sustainable society, considering the finite availability of fossil fuels and their effects on the environment (Tsangas, et al., 2023). Therefore, it is considered important that a large diversity of renewable energy sources be considered for various locations, situations, and costs.

Microbial fuel cells (MFCs) are a technology that generates electrical energy by using electrons released by electrogenic bacteria, which are generally found in rivers, lakes, wastewater, and soil during their biological activity of decomposing organic matter (Xiao, et al., 2022, Nawaz, et al., 2022). Since the organic matter in rivers and wastewater can be practically converted into electrical energy, this technology is expected to be an effective solution to both organic pollution and energy problems (Khandaker, et al., 2021).

In the development of MFCs for practical use, it is required to improve both the output power and the cost of electrodes at the same time (Kumar, et al., 2019). Platinum catalysts are generally used to activate the oxygen reduction reaction (ORR) at the cathode and to increase the power output of MFCs (Jin, et al., 2020). However, the high cost and scarcity of platinum make its practical application as a sustainable energy source difficult. Thus, there is growing interest in using catalysts other than platinum (Rodriguez, et al., 2021, Karthick & Haribabu, 2020).

Catalysts based on manganese dioxide (MnO_x) have been studied as a substitute for platinum catalysts due to their high ORR performance and low cost (Chaturvedi & Kundu, 2021). Birnessite-type MnO_2 has a layered structure formed by MnO_6 octahedra, which has a high surface area and is promising for improving ORR performance (Zhu, et al., 2020). Furthermore, the intercalation of cobalt between MnO_6 layers has been shown to improve the surface area, conductivity, and catalytic activity at the air cathode of aluminum-air batteries (Xia, et al., 2020).

This study investigated the effectiveness of low-cost birnessite-type MnO_2 intercalated with cobalt and added carbon (Co- MnO_2/C) catalysts in MFC air cathodes. Unlike ordinary MnO_2 , Co- MnO_2/C synthesis does not require processes such as hydrothermal synthesis and can be made by a simple oxygen reduction reaction, thus lowering the cost of making them. To further cut the cost of the electrodes, rice husk charcoal (RHC) from agricultural waste was used as the electrode material, and Sumi ink, which has been widely used in Japan for a long time, was used as the binder. Due to its porous structure, RHC is expected to become an electrode framework with the role of expanding surface area. Sumi ink is an inexpensive conductive liquid composed of carbon black, compensating for the low conductivity of MnO_2 . In addition, because Sumi ink solidifies as it dries, it is highly operable, which is thought to help promote its practical use.

2. Materials and methods

2.1. Preparation of Co- MnO_2/C catalysts

As in the previous paper, a co-intercalation of birnessite-type MnO_2 was prepared by the redox reaction of cobalt nitrate hexahydrate and potassium permanganate (Xia, et al., 2020). Specifically, the following fabrication methods were used. 0.79 g of potassium permanganate was stirred into 50 ml of purified water at 400 rpm for 30 min. 2.91 g of cobalt nitrate hexahydrate was dissolved in 100 ml of deionized water, of which 67.8 ml was added to the potassium permanganate solution. It was synthesized by stirring an aqueous solution of cobalt nitrate hexahydrate and potassium permanganate solution at 70°C for 1 hour (400 rpm). Then 0.5 g of carbon black (PG341, HOLBEIN WORKS, Ltd., Osaka, Japan) was added, and stirring continued for 3 min. Co- MnO_2/C catalyst was obtained by removing the precipitate from the synthesized solution by centrifugation and drying.

2.2. Preparation of cathode with Co- MnO_2/C catalysts

To study the effect of the catalyst in MFC, a cathode without a Co- MnO_2/C catalyst was also fabricated and compared to the cathode using Co- MnO_2/C catalyst. In addition, three types of cathodes with different amounts of the Co- MnO_2/C catalyst were prepared to check the effect of the change in the amount of Co- MnO_2/C catalyst in the cathode material on MFC. The ratios of RHC (Tokorozawa Ueki Bachi Center, Ltd., Saitama, Japan), Sumi ink (BA7-18, Kuretake Co., Ltd., Nara, Japan), and Co- MnO_2/C catalyst used in each cathode are shown in Table 1. To measure the impact of the catalyst, electrodes were fabricated without the catalyst and with three different amounts of catalyst. In order to eliminate inconsistencies in the initial conditions caused by impurities, the RHC was alkaline-etched to remove impurities.

The electrodes used in this study were the block-type electrodes proposed in the previous study (Hirose, et al., 2022). To briefly explain the fabrication method, block electrodes are fabricated by pouring an electrode solution consisting of Co- MnO_2/C catalyst, Sumi ink, and RHC into a mold and letting it dry. The material cost of the cathode with the most used catalyst (Co- MnO_2/C 0.75) was \$0.058 per 1 cm^2 .

Table 1. The ratio of Co-MnO₂/C catalysts, Sumi ink, and rice husk charcoal in cathode materials.

	Co-MnO ₂ /C catalyst (g)	Sumi ink (ml)	Rice husk charcoal (g)
Co-MnO ₂ /C 0	0	3	0.525
Co-MnO ₂ /C 0.25	0.25	3	0.525
Co-MnO ₂ /C 0.5	0.5	3	0.525
Co-MnO ₂ /C 0.75	0.75	3	0.525

2.3. MFC Preparation

The MFC used in this experiment was the type that can float in liquid (Fig. 1), for use in rivers and wastewater. Sources of wild microorganisms such as *Schwanella* and *Geobacter* were collected from soil in Japanese farmland (34°59'42.7986" N, 135°57'16.1892" E (34.9995222, 135.954497), Shiga, Japan). To culture the microorganisms, the Luria–Bertani (LB) medium was diluted with tap water (COD: 2976 mg/L), and then MFC shown in Fig. 1 was put floating on it. The anodes were block-shaped electrodes prepared using 0.65 ml of Sumi ink and 0.2 g of RHC. The MFC was always connected to a 4600 Ω resistor by an external circuit, and the output voltage at that time was periodically measured using a voltage monitoring system (USB-6210, National Instruments Corp., USA).

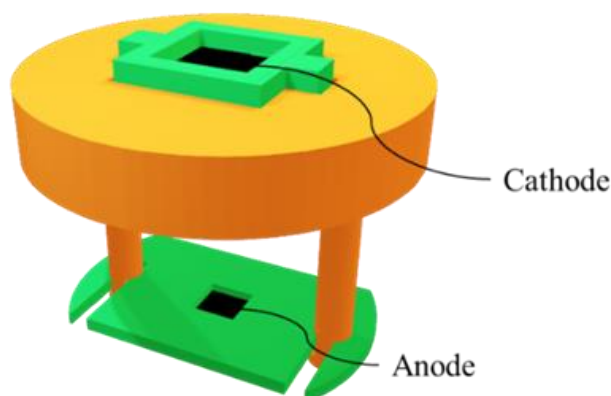


Figure 1 Schematic of a float-type microbial fuel cell.

The MFC was placed indoors with a median temperature of 25°C and a variation of ±2°C. Tap water was inoculated periodically to prevent the water level of the LB solution from changing due to evaporation.

3. Experimental Results and Discussion

3.1. The surface of Co-MnO₂/C catalytic cathode

Comparing SEM images of the surface of the cathode with and without the Co-MnO₂/C catalyst (Fig. 2), it was confirmed that the surface of the cathode with the Co-MnO₂/C catalyst was more porous. This comparison shows that the catalyst improves the surface area of the cathode. This may be because the MnO₆ layers are stacked by intercalation of cobalt, resulting in the formation of a three-dimensional structure. The increase in surface area is expected to improve the ORR performance of the cathode.

3.2. Electrochemical performance evaluation

Cyclic voltammetry (CV) was used to evaluate the effect of the catalyst on ORR performance. CV was measured in a potassium ferricyanide mixture using an Ag/AgCl reference electrode, a Pt counter electrode, and a carbon sheet working electrode coated with catalyst and Sumi ink. The analysis was performed at a scan rate of 50 mV/s and a

potential range of -1 V to 1 V. According to Fig. 3, the ORR current of Co-MnO₂/C 0.75 at potential -0.23 V is -27.75 mA. This is 17.3 times larger than that of Co-MnO₂/C 0 (-1.60 mA). It is clear that Co-MnO₂/C 0.75 is also larger than Co-MnO₂/C 0 in terms of ORR peak current. This indicates that the catalyst improves the ORR performance due to the increased surface area. The comparison of Co-MnO₂/C 0.25, Co-MnO₂/C 0.5, and Co-MnO₂/C 0.75 also confirms that the higher the concentration of the catalyst, the higher the catalytic activity.

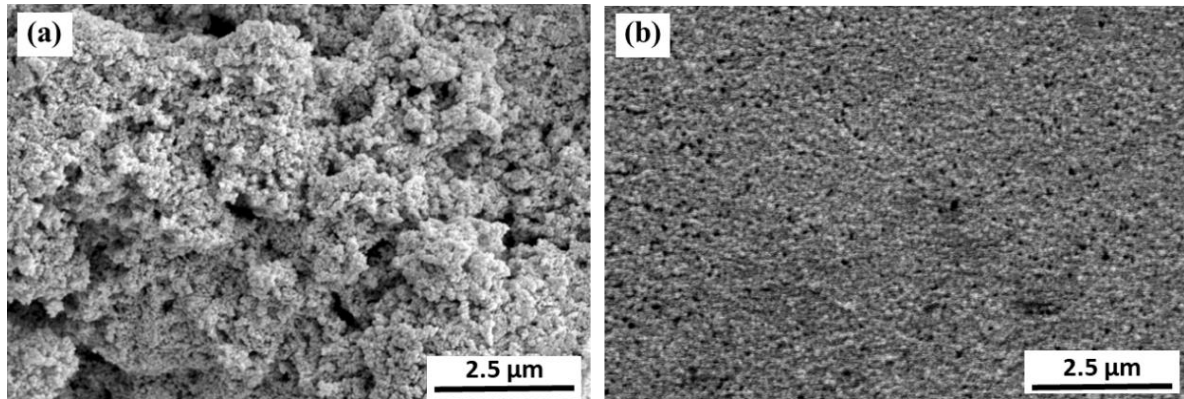


Figure 2 SEM images of cathode surfaces with (a) and without (b) catalyst.

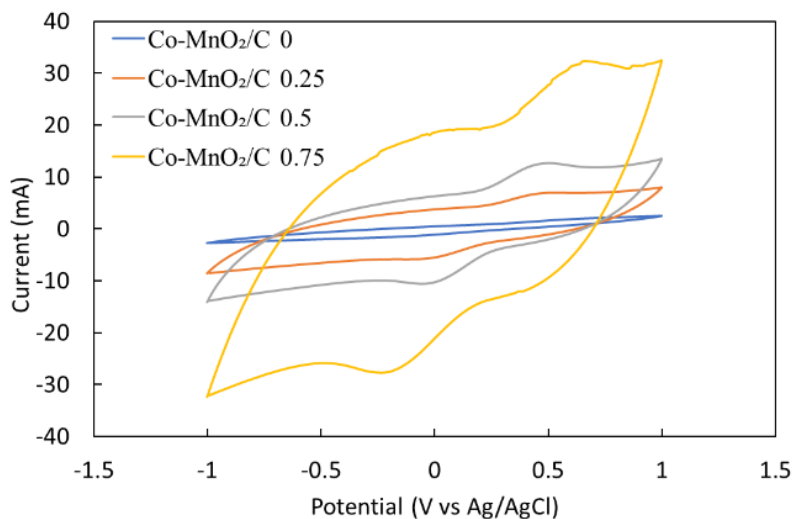


Figure 3 Cyclic voltammetry at different catalyst concentrations.

3.3. Evaluation of Microbial Fuel Cell Performance

Fig. 4 shows the voltage of the MFC monitored over a 90-day period. After each month, the LB solution was replaced to replenish organic matter. The use of the catalyst improved the maximum voltage by 71.2% compared to the case without the catalyst (Co-MnO₂/C 0: 271 mV, Co-MnO₂/C 0.75: 464 mV). It was also found that the higher the amount of catalyst occupying the cathode material, the higher the voltage of the MFC. These reasons are thought to be due to the more catalysts used, the better the ORR performance of the cathode. In addition, this time shift of voltage showed that the MFC generates electricity stably without any deterioration in catalytic performance for at least 90 days.

The current density-power density plots shown in Fig. 5 were obtained from the respective stable voltage values when the external resistance connected to the MFC was changed from 4,600Ω to 200Ω. A digital multimeter (MS8233D, Crenova) was used to measure the voltage. The maximum power density of Co-MnO₂/C 0,75 (107.3 μW/cm²) was obtained 5.8 times higher than the maximum power density of Co-MnO₂/C 0 (18.5 μW/cm²). This result may be due to the catalyst improving the ORR activity of the cathode. In addition, with the change in catalyst concentrations, the maximum power density increased by up to 271% (from 28.9 μW/cm² to 107.3 μW/cm²).

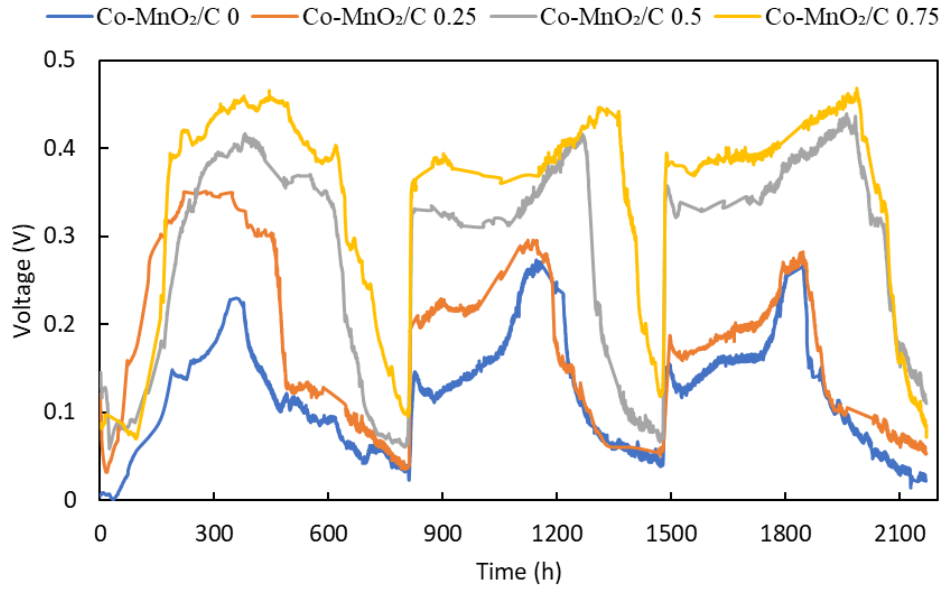


Figure 4 Time shift of the voltage of MFC when an external resistor of 4,600 Ω is connected.

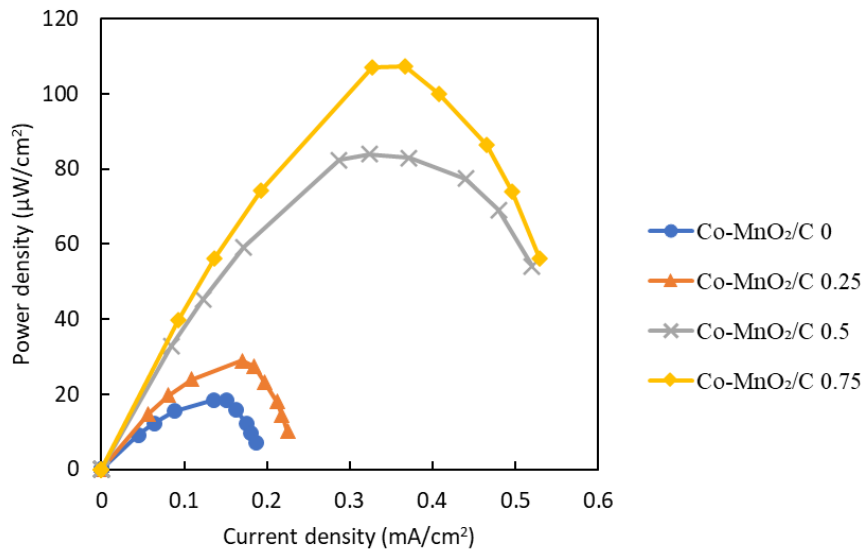


Figure 5 Current density-power density at day 78 of MFCs with different catalyst concentrations.

4. Conclusion

In this research, the cathode fabricated with low-cost Sumi ink and Co-MnO₂/C catalyst prepared by intercalating cobalt with birnessite-type MnO₂ was investigated for use as air cathodes for MFC. Using the Co-MnO₂/C catalyst increased the specific surface area and improved ORR performance at the cathode, resulting in a 5.8-fold increase in MFC power density. Because the Sumi ink becomes solid after drying, it holds the catalyst well, resulting in output from the MFC for at least 90 days. Furthermore, the output of the MFC varied with the amount of catalyst used.

In addition, the use of rice husk charcoal from agricultural waste and inexpensive Sumi ink made it possible to produce this product at the cost of \$0.058 per 1 cm². Since Co-MnO₂/C catalysts are fabricated by a simple redox reaction, they are not difficult to mass produce. Therefore, the proposed cathode material is expected to facilitate the practical application of MFCs.

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The authors declare that there is no competing interest.

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