Sterilization and Long-Term Stability of Cobalt Intercalated MnO_2 Catalyst in the Cathode of Separator-Free Microbial Fuel Cells

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Abstract: Microbial Fuel Cells (MFCs) are a promising technology that can simultaneously address recent energy shortages and wastewater treatment problems for freshwater production. Recently, inexpensive Pt-free catalysts have been investigated to improve the cathode performance of MFCs. In this study, birnessite manganese oxide intercalated a cobalt (Co-MnO_2) catalyst to make the cathode sterilizable. The use of a bactericidal cathode is expected to improve output by suppressing electron transfer from microorganisms to the cathode, which is the cause of MFC performance degradation, and by eliminating the separator that limits proton transfer. The MFC with Co-MnO_2 catalyst on the cathode achieved a maximum power density of 110 $\mu W/cm^2$. In addition, the function of the Co-MnO_2 catalyst did not degrade for at least 158 days.

Keywords: microbial fuel cell, MnO_2, separator-free, sterilization

1. Introduction

Rapid technological development and population growth have increased energy demand and freshwater consumption. Due to the increase in energy demand, the depletion of fossil fuels, the main source of energy, and the environmental pollution caused by their use have become major issues in recent years. In addition, the increased consumption of freshwater makes it desirable not only to conserve water but also to reuse it through wastewater treatment.

Microbial Fuel Cells (MFCs) are a technology that directly converts chemical energy in wastewater into electrical energy using microorganisms called electrogenic bacteria as biocatalysts [1]. Microorganisms in the anodes break down organic matter, releasing electrons, protons and carbon dioxide. The electrons and protons pass through a separator and an external circuit to the cathode. Electrons, protons and oxygen combine at the cathode and are emitted as water [2]. This makes MFC a promising clean energy technology with few environmentally harmful by-products.

The commercialization of MFCs has been hampered by factors such as low performance and high cost. Among these factors, platinum-based catalysts have been used to improve the reaction rate at the cathode, which has a large impact on the performance of MFCs, and separators have been used to inhibit biofilm formation [3, 4]. In addition, 80% of the total cost of MFCs is spent on catalysts and membranes [5]. In other words, it is necessary to make these materials low-cost without reducing the output as an MFC to commercialize them.

Manganese oxide (MnO_2) has attracted attention due to its environmental abundance and low cost [6]. MnO_2 has a variety of crystal structures, including α-, β-, γ-, λ-, and δ- types, or birnessite-type manganese dioxide (δ-MnO_2) is composed of MnO_6 octahedra that share edges and have a high surface area, and exhibits excellent Oxygen Reduction Reaction (ORR) activity [7]. It also shows improved specific surface area, electrical conductivity, and ORR activity when intercalated with metal ions [8].

In this study, cobalt intercalated birnessite manganese dioxide (Co-MnO_2) catalysts were used as cathode catalysts in single-chamber MFCs. The advantages of using Co-MnO_2 catalysts include not only the excellent specific surface area and ORR activity but also the reduction of microbial activity on the cathode surface. In single-chamber MFCs, biofilm growth on the cathode surface reduces the power generation performance. Although biofilm formation can be inhibited by using separators, the use of cobalt, which is toxic to microorganisms, is expected to inhibit active biofilm formation while reducing costs [9]. Therefore, the effectiveness of the Co-MnO_2 catalyst is evaluated with a focus on the bactericidal performance of the cathode. The performance of the MFC was monitored over 158 days to confirm its long-term stability.

2. Materials and Methods

2.1. Synthesis of Co-MnO_2 Catalysts

A simple redox method has been proposed to prepare Co-MnO_2 catalysts [10]. Potassium permanganate, cobalt nitrate, and carbon black (PG341, Holbein Works, Ltd., Osaka, Japan) were mixed in sequence. They were prepared by a redox reaction.

2.2. Electrode Preparation

The carbon material used was Rice Husk Charcoal (RHC). RHC was mixed with 6 mM NaOH solution at 90 °C for 24 h for alkaline etching. The mixture was washed with purified water, dried in air at 60 °C for 12 h, and ground in a mortar.

Electrodes were prepared according to the existing ones [11]. The solution of Co-MnO_2 catalyst (0.75 g), rice husk charcoal (0.525 g) as carbon material, and carbon ink (Bokuju, 3 ml) as a binder were mixed as Co-MnO_2 catalyst electrode, and RHC (0.9 g) and Bokuju (3.5 ml) were mixed as a normal electrode. Normal electrodes were used as anodes. However, when the Co-MnO_2 catalyst was used as the anode for comparison, copper, which has only bactericidal properties, was used to maintain the performance of the cathode. Copper powder (0.5 g) and Bokuju (15 ml) were mixed at 800 rpm for 3 h to form a binder.

When a separator was used for the cathode, ceramic clay (Bijutsu Shuppan Educational Co. Ltd., Tokyo) was used as the separator. The ceramic clay was cut to the same size as the electrodes and 2 mm thick. After molding, it was further left in the air at 25 °C for two days to dry completely. Then it was sintered at 900 °C for 1 h.

2.3. Structure of MFC

The structure of the MFC was a single chamber, as shown in Fig. 1, and the chamber was filled with Lysogeny Broth (LB) solution (COD: 2976 mg/L). The microbial source was wild microorganisms collected from Japanese paddy soils. The cathode floated on the surface of the solution, and the anode was placed in the solution. When a separator was used for the cathode, a ceramic separator was attached to the bottom of the cathode.

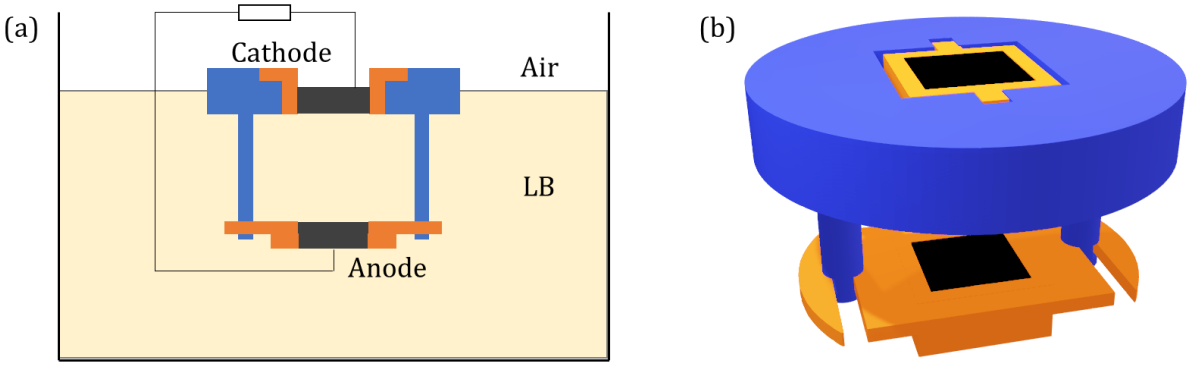

Fig. 1. Diagrams of (a) FMFC setup diagram and (b) Float model.

2.4. Evaluation of MFC Operation

A 4600 Ω resistor was always connected between the anode and cathode and kept in a discharged state. The experiments were conducted in a controlled indoor environment at 25 ± 1 °C. The water level of the solution fluctuated because of evaporation and was maintained by adding tap water daily.

To evaluate the effect of the separator, the Co-MnO_2 catalyst was used for the cathode and compared with and without the separator. The effect of the Co-MnO_2 catalyst on the cathode performance was evaluated by comparing the cathodic performance with and without the Co-MnO_2 catalyst. The Co-MnO_2 catalyst was also compared with and without the Co-MnO_2 catalyst on the anode to confirm the sterilizing performance of the Co-MnO_2 catalyst.

The power density and electrode potential were used in the evaluation: the voltage across the external resistance, which was varied from 4600 Ω to 200 Ω, was measured, and the resistance and voltage results were used to calculate the power and current. The power and current densities were obtained by dividing the power and current by the effective area of the anode. An Ag/AgCl electrode was used as a reference electrode to measure the electrode potential.

2.5. Observation of Cathode Surface

After MFC operation, SEM (S-4300, Hitachi, Ltd.) was used to observe the cathode surface. After MFC operation, the cathode was removed and stored overnight in rubbing alcohol. The cathode surface was dehydrated with ethanol and coated with gold by sputtering.

3. Results and Discussion

3.1. Evaluation of the Effect of the Separator on the Cathode

Fig. 2 shows the power density curves comparing the effect of the Co-MnO_2 catalyst or the separator on the cathode. Under conditions with a separator attached to the cathode, the power density was 420% higher with the Co-MnO_2 catalyst (28.6 μW/cm^2) than without the Co-MnO_2 catalyst (5.5 μW/cm^2). When the separator is installed, no biofilm is formed on the cathode, so the sterilizing power is not included in the comparison. This result indicates a high catalytic activity of the Co-MnO_2 catalyst in the cathodic reaction.

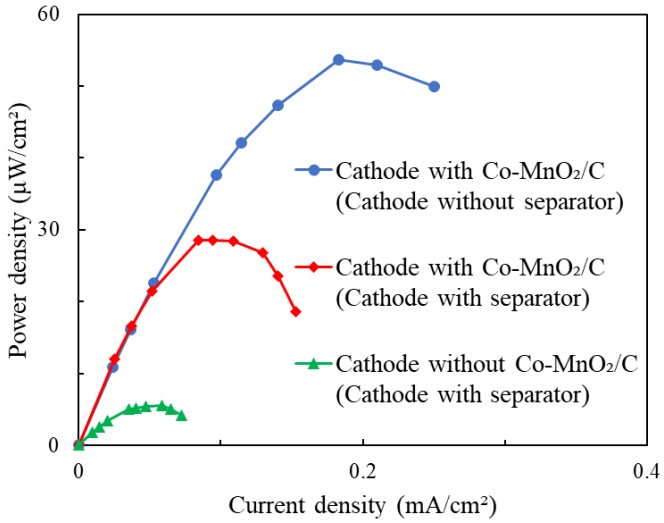

Fig. 2. Power density curves for MFCs with and without Co-MnO_2 catalyst and separator in the cathode.

The power density was 88% higher when the Co-MnO_2 catalyst was used in the cathode without the separator (53.7 μW/cm^2) than when the separator and Co-MnO_2 catalyst were used together (28.6 μW/cm^2). In addition, the internal resistance without the separator (400 Ω) was 33% lower than with the separator (600 Ω). These results indicate that the separator limits the proton transfer and may be the rate-limiting step in the cathodic reaction, which means that a separator is not necessary when using a Co-MnO_2 catalyst for the cathode.

3.2. Observation of Cathode Surface

Fig. 3 is an SEM image of the cathode surface when only the Co-MnO_2 catalyst is used for the cathode. This SEM image shows that the cathode surface is covered with microorganisms. The output density without the separator is higher than with the separator despite the biofilm formation, indicating that the Co-MnO_2 catalyst's bactericidal action has a large impact on the performance of the MFC.

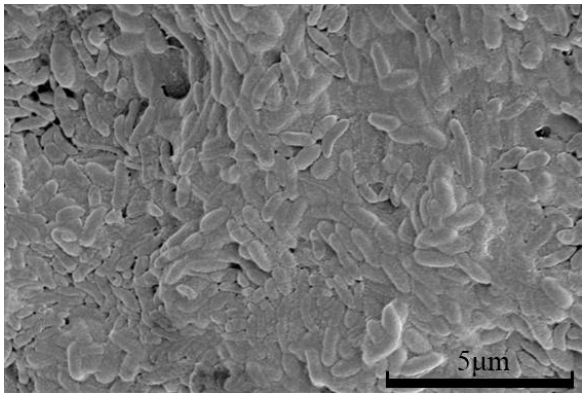

Fig. 3. SEM image of Co-MnO_2 catalyst cathode.

3.3. Evaluation of the Effect of Co-MnO_2 Catalyst on Power Density

Fig. 4 shows the power density curves comparing the effect of the Co-MnO_2 catalyst at the cathode or anode. At the cathode, the power density was 464 % higher with the Co-MnO_2 catalyst (110 μW/cm^2) than without (19.5 μW/cm^2). This result suggests that the use of the Co-MnO_2 catalyst in the cathode is effective in increasing the power density of the MFC, similar to the results when a separator is used. On the other hand, the use of the Co-MnO_2 catalyst at the anode resulted in an 86 % decrease in power density compared to the

case without catalyst. This result indicates that the Co-MnO_2 catalyst has effective sterilizing power at the cathode.

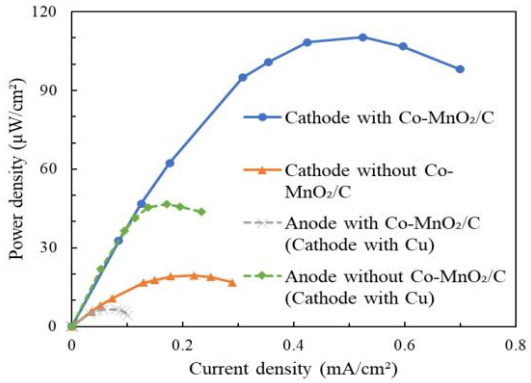

Fig. 4. Power density curves of the MFC with and without Co-MnO_2 catalyst in the cathode or anode.

3.4. Evaluation of the Bactericidal Potential of Co-MnO_2 Catalysts

According to the electrode potentials in Fig. 5, the anode potential approached positively when the Co-MnO_2 catalyst was used. This indicates that the Co-MnO_2 catalyst reduced the number of electrons received from the microbes.

The above results for power density and electrode potential suggest that the Co-MnO_2 catalyst has bactericidal power. The bactericidal power is thought to be due to cobalt. This bactericidal power is expected to prevent electrons from passing from the microorganisms to the cathode and back through the circuit, thus improving the output of the MFC (Fig. 6).

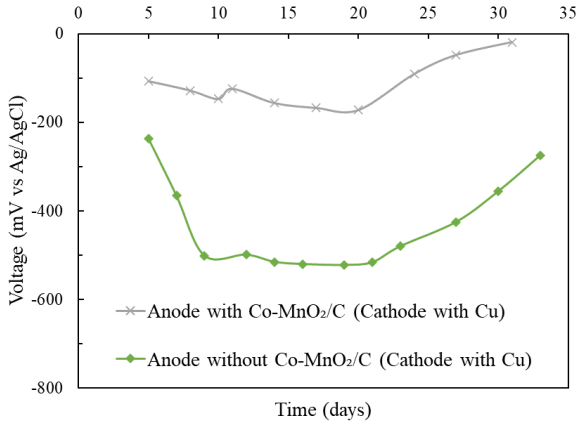

Fig. 5. Anodic potential with and without Co-MnO_2 catalyst.

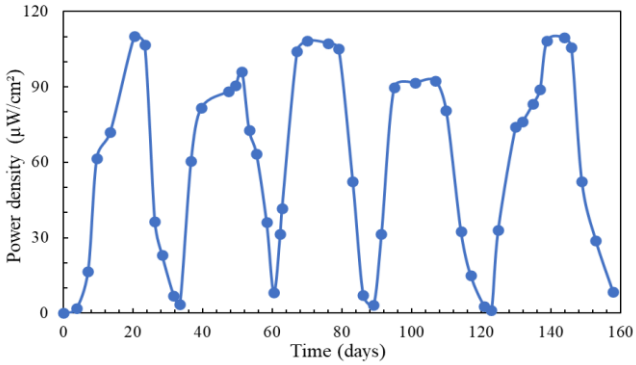

Fig. 6. Time evolution of power density of MFC with Co-MnO_2 catalyst in the cathode.

3.5. Long-Term Stability of Co-MnO_2 Catalysts

To confirm the Stability of the Co-MnO_2 catalyst function in the long term, the power density was monitored over 158 days; significant decreases in power density on days 33, 60, 89, 122, and 158 were due to depletion of the organic content in the LB solution. Output density recovered as a result of replacement with a new LB solution. Furthermore, no degradation of Co-MnO_2 catalytic function was observed for at least 158 days.

4. Conclusion

The sterilizing power, catalytic activity, and long-term stability of Co-MnO_2 catalyst were investigated in this study, and it was confirmed that Co-MnO_2 catalyst has effective sterilizing properties and catalytic activity at the cathode and does not require a separator. In addition, its sterilizing power did not degrade for at least 158 days. These results indicate that the Co-MnO_2 catalyst has potential for use in the cathode of single-chamber MFCs, and it is expected to help encourage the development of single-chamber MFCs.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Kozo Taguchi conducted the research. Kaisei Shiraki and Soichiro Hirose analyzed the data. Kaisei Shiraki and Trang Nakamoto wrote the paper and all authors had approved the final version.

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