



Metal Ions Intercalated to Birnessite Manganese to Make High-Performance Catalyst for the Cathode of MFCs

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Abstract

Microbial fuel cells (MFCs) have garnered significant attention recently due to their dual ability to purify wastewater and sludge while generating electricity, addressing the growing energy demand. However, the practical application of MFCs is hindered by the cost and performance challenges on the cathode side. In single-chamber MFCs, the choice of cathode catalyst is crucial for enhancing output. This study explored the use of manganese oxide, a cost-effective material with diverse structures and properties, as a catalyst. Specifically, manganese oxide with a birnessite structure was utilized for its low fabrication costs and high oxygen reduction reaction (ORR) activity. The research compared the performance of manganese oxide catalysts intercalated with various metal ions, identifying the optimal metal ions for single-chamber MFCs. The experiment evaluated cobalt, nickel, and zinc as potential metal ions. Measurements of the cathode potential using a reference electrode and power density assessments were conducted to determine the most suitable configuration overall.

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Keywords

Cobalt; Sterilizing power; Microbial fuel cell; MnO₂; Birnessite

1. Introduction

Rapid scientific and technological development in recent years has required a great deal of energy. To meet this energy demand, fossil fuels have been used in large quantities (Huo & Peng, 2023). As a result, as Pang et al. (2024) suggest, the depletion of fossil fuels and the toxic substances emitted during power generation have caused global warming and water pollution. The amount of available freshwater is declining as a result, and health hazards such as infectious diseases and food poisoning are common, especially in developing countries (Boelee et al., 2019). To solve these problems, there is a need to focus on the development of renewable energies. MFC, in particular, is a technology that can reduce water pollution problems as well as energy problems.

MFCs utilize electron-producing bacteria as biocatalysts, which have the property of releasing electrons into the body when they consume organic matter under anaerobic conditions (Shimohata et al., 2023). In general, most MFCs are divided into single-chamber MFCs and double-chamber MFCs, both of which require these electron-producing bacteria as anodes. Double-chamber MFCs are used to prevent bacteria from entering the cathode chamber and to maintain anaerobic conditions in the anode chamber. However, as Daud et al. (2021) suggest, the proton exchange

membranes used to separate the chambers are costly and difficult to install. Therefore, double-chamber MFCs have many practical concerns compared to single-chamber MFCs. On the other hand, single-chamber MFCs have the problem that the cathode also forms a biofilm to create an anaerobic environment for the anode, causing a backflow of electrons and a decrease in power output. The solution to this problem is the sterilizing ability at the cathode. Even when using the same solution, it is believed that by providing the cathode with a sterilizing ability, the microorganisms around the cathode can be inactivated, and the backflow of electrons can be reduced. What is required when providing the cathode with sterilizing ability is that it should be able to exert a sterilizing effect around the cathode without adversely affecting the anodes or the surrounding environment and that it should be able to maintain its sterilizing ability over a long period.

In this study, a catalyst was employed for the cathode, and experiments were conducted in a single-chamber microbial fuel cell (MFC). The catalyst, primarily based on manganese, was synthesized through the combination of manganese, metal ions, and carbon black. The chosen metal ions exhibited favorable characteristics, including high sterilizing power and excellent conductivity. By integrating these metal ions with manganese and carbon black, the resulting catalyst demonstrated not only enhanced electrochemical performance but also the potential to improve the overall efficiency of the MFC.

2. Materials and Methods

2.1. Preparation of catalyst

The catalyst synthesis method is based on the procedure proposed by Xia et al. (2020). First, a 0.1 M aqueous solution of potassium permanganate is stirred at 400 rpm for 30 minutes. Subsequently, a 0.1 M aqueous solution of cobalt nitrate is added, and the mixture is stirred at 400 rpm and 70°C for 1 hour. Next, 1 g of carbon black is introduced, and the mixture is stirred under the same conditions for 10 minutes before being allowed to sit at room temperature for 10 minutes. The supernatant is then discarded, and the precipitate is dried at 60°C. The dried material is ground in a mortar, resulting in Co-MnO₂/C. A similar procedure is followed for the preparation of catalysts with nickel and zinc, resulting in Ni-MnO₂/C and Zn-MnO₂/C, respectively.

For experiments aimed at optimizing nickel quantities, the catalysts were prepared so that the molar mass of nickel nitrate was 20%, 40%, and 130% of the molar mass of potassium permanganate.

2.2. Fabrication of electrodes

Rice husk smoked charcoal (RHC), which was alkaline-etched and ground in a mortar, was utilized as the carbon material. Sumi ink served as a binder. Anodes were prepared by mixing RHC (0.9 g) and Sumi ink (3.5 ml) and then pouring the mixture into an electrode mold. The cathode was prepared by mixing Co-MnO₂/C (0.75 g), RHC (0.525 g), and Sumi ink (3.25 ml) and pouring the mixture into the electrode mold. The same proportions were used to prepare for Ni-MnO₂/C and Zn-MnO₂/C. The cathodes without a catalyst were prepared in the same manner as the anodes, serving as a control for comparison with the catalyst.

2.3. MFC model

The MFC consisted of a single chamber, as shown in Figure 1, and was filled with 600 ml of Lysogeny Broth (LB) solution (COD: 2976 mg/L). The microbial source comprised wild microorganisms collected from the soil within Ritsumeikan University, Kusatsu, Shiga, Japan. The cathode was designed with one surface immersed in the solution and another exposed to air, functioning as an air cathode, while the anode was fully submerged in the solution. The two anodes were connected in parallel. Each electrode had an area of 2 x 2 cm², and the distance between the anode and cathode was approximately 3 cm.

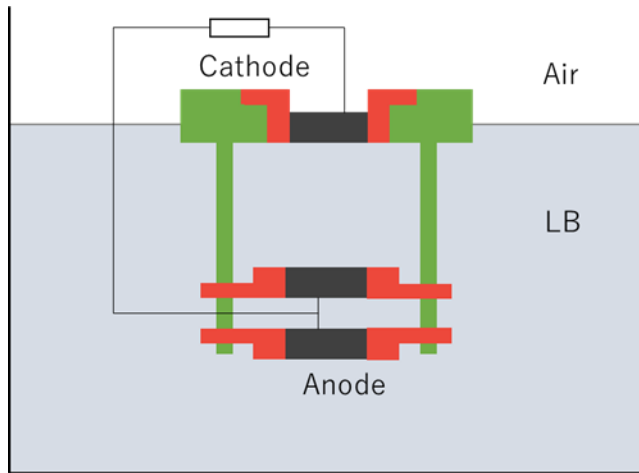


Figure 1: MFC structure.(by author)

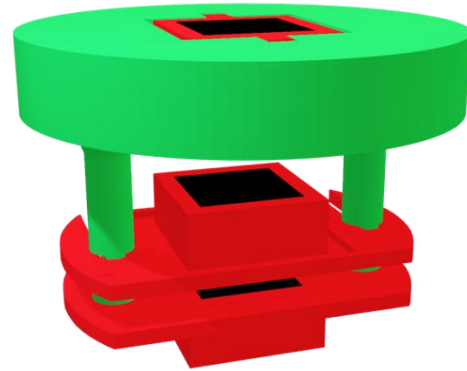


Figure 2: MFC float mode.(by author)

2.4. MFC operation and evaluation

The performance of the catalysts was evaluated by measuring electrode potential changes during the experiment. The electrode potentials versus an Ag/AgCl reference electrode were measured and compared to assess the characteristics of each catalyst material. The overall performance of the MFC was evaluated by measuring the power density. To measure the power density, the external resistance was varied from 4.6 k Ω to 100 Ω , and then the power and current were calculated from the voltage measured across each resistance and then normalized by the effective area of the anode to determine the power and current densities.

3. Results and Discussion

3.1. Evaluation of the bactericidal ability of catalysts at the cathode

Figure 3 shows the cathode electrode potential of each catalyst when used as a cathode. Without a Catalyst, the electrode potential drops immediately after the start of the experiment, indicating very rapid biofilm formation. After about two weeks, the electrode potential of Zn-MnO₂/C also drops to the same level, indicating that zinc has a short-term bactericidal capacity that disappears after one to two weeks. The bactericidal properties of zinc, confirmed by Chen et al. (2021) in other fields, are thus validated in the context of MFCs by this experiment.

However, this short-term effect makes Zn-MnO₂/C unsuitable for single-chamber MFCs, which require sustained sterilizing power. Although Co-MnO₂/C demonstrated longer-term bactericidal efficacy, its performance was inferior to that of Ni-MnO₂/C. Therefore, based on these results, Ni-MnO₂/C exhibits the best sterilizing performance and maintains a stable electrode potential at the cathode of MFCs.

3.2. The effects of cathode catalysts on anodes

Figure 4 illustrates the anode electrode potentials for the same experiments as in the previous section. The figure presents data for each cathode material while keeping the anode materials consistent across experiments. The stability period, defined as the period between 13 and 27 days, is of particular interest. During this period, the electrode potential remains relatively stable when catalysts other than Ni-MnO₂/C are used for the cathode. This indicates that the anodes are minimally affected by these catalysts. However, when Ni-MnO₂/C is utilized, a slightly higher electrode potential is observed despite the anode materials being the same as in other MFCs. This phenomenon suggests that nickel ions leaching from the Ni-MnO₂/C cathode exhibit a bactericidal effect on microorganisms in proximity to the anode. Considering the anode-cathode distance is approximately 3 cm, the observed effect at this distance implies potential negative impacts on the anode and the surrounding environment. Consequently, this poses a significant challenge for practical applications. Nevertheless, it is worth noting that Ni-MnO₂/C was prepared in this experiment with reference to the existing Co-MnO₂/C. Therefore, it is possible that the mixing ratio of nickel may need to be adjusted to mitigate the bactericidal effects while maintaining the desired electrochemical

performance. Also, with zinc, the electrode potential is high for a short time, even at the anode, so it is possible that the ions leaked out and decreased, which is one of the reasons for the short-term sterilizing power.

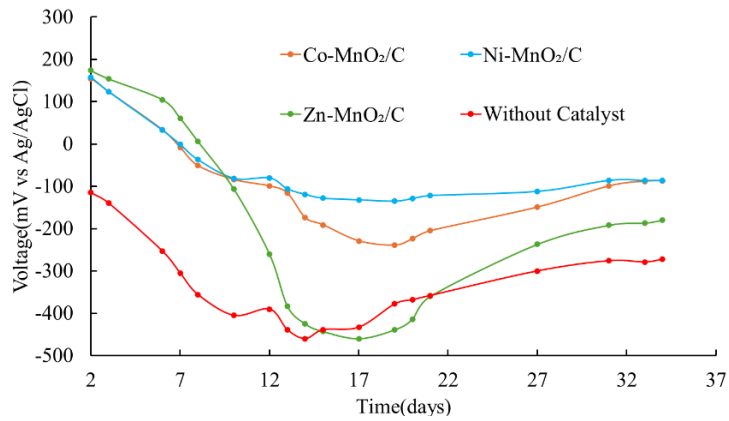


Figure 3: Cathode electrode potential for each catalyst compared with the Ag/AgCl reference electrode.(by author)

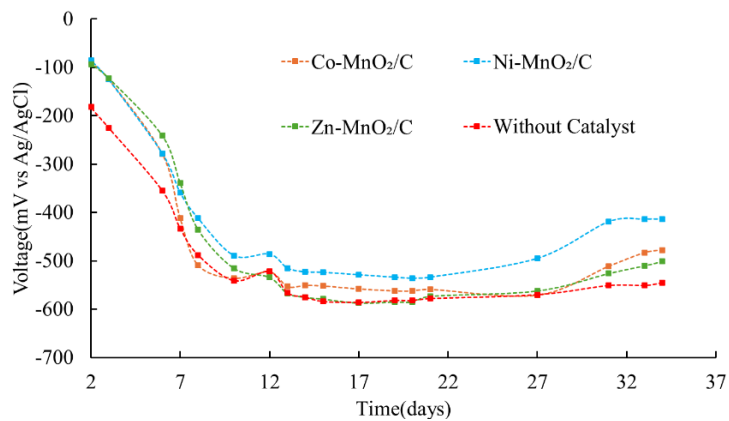


Figure 4: Anode electrode potential for each catalyst compared with the Ag/AgCl reference electrode.(by author)

3.3. Evaluation of the effects of nickel on anodes

In the previous section, it was noted that catalysts using nickel harm the environment. However, the method used to produce this catalyst was optimized for the use of cobalt and not nickel. In this experiment, a comparison was made between a catalyst with a very high nickel content (Ni:130%) and a catalyst with a reduced nickel content (Ni:20%) to confirm that the results presented in the previous section were due to the sterilizing power and to see how the sterilizing power and the catalytic capacity would change. In both cases, the catalyst was used as the cathode, and smoked charcoal and ink as the anodes.

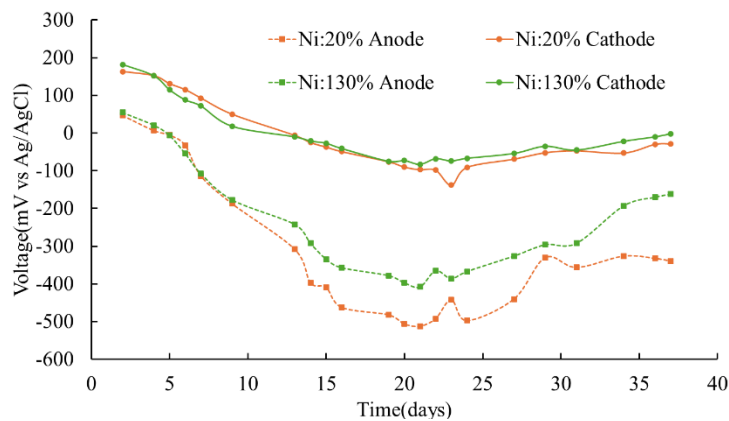


Figure 5: Electrode potential for varying amounts of nickel.(by author)

In Figure 5, the solid line shows the electrode potential of the cathode with each catalyst, and the dashed line shows the electrode potential of the anode. Focusing first on the electrode potential of the cathode, both show the same electrode potential, which was not affected by a significant reduction in the amount of nickel in the case of the nickel catalyst. Therefore, it is conceivable that a lower amount of nickel could be better when optimizing the nickel. On the other hand, focusing on the electrode potential of the anode, the electrode potential with less nickel was smaller than the one with more nickel. It can be confirmed that this is due to the fact that when too much nickel is synthesized, the nickel that is not incorporated into the structure leaches into the solution and has a negative effect on the anodes. This has a negative impact on the surrounding organisms, so it can be said to be bad for the environment.

3.4. Optimisation of nickel quantities

Figure 6 shows the power density curves for nickel in the experiments up to this point; the Ni:40% represents the ratio with manganese as well as the others and is similar to the Ni-MnO₂/C shown in sections 1 and 2. The results show that Ni:40% has the highest maximum power density and the best properties as a cathode catalyst for use in MFCs. However, even with Ni:20%, the difference with Ni:40% is only 6%, so it is possible to reduce the cost without much change in performance. For Ni:130%, it was found that if too much was used during synthesis, it might not be able to fit into the structure properly and would flow out during the experiment.

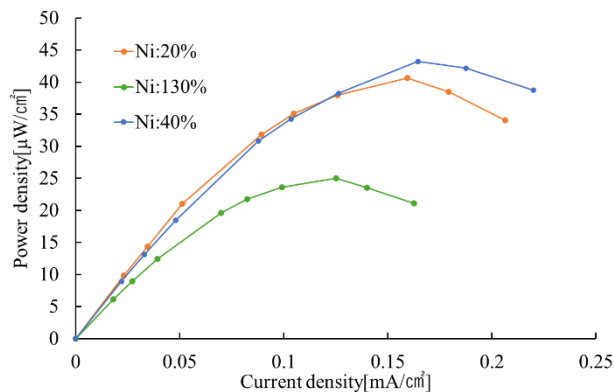


Figure 6: Power density curves for varying amounts of nickel.(by author)

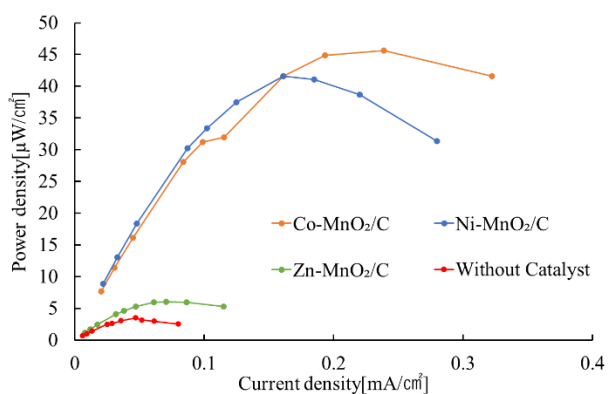


Figure 7: Power density curves for each cathode catalyst.(by author)

3.5. Evaluation of optimized cathode catalysts

Figure 7 shows the power density curves generated by the MFCs using different catalysts. When Co-MnO₂/C was used as the cathode (45.6 μW/cm²), the power density was 10% higher than when Ni-MnO₂/C was used (41.6 μW/cm²). From the shape of the graph, if the resistance of Ni-MnO₂/C is the same as that of Co-MnO₂/C, as mentioned later, the output density may be the same, or Ni-MnO₂/C may have a better value. It was also 650% higher than when Zn-MnO₂/C was used (6.02 μW/cm²). Although Zn-MnO₂/C has no sterilizing power and the voltage is low, it is thought to have a positive effect on improving conductivity because it is 70% higher than Without Catalyst. Compared to the case without catalyst (3.20 μW/cm²), it was improved by 1325%. As for the internal resistance, Co-MnO₂/C shows the best value at 200 Ω, while Ni-MnO₂/C shows a twice difference at 400 Ω. For Zn-MnO₂/C and the case without catalyst, the values were 300 Ω and 400 Ω, respectively. These results suggest that Co-MnO₂/C is the most suitable cathode catalyst for the application in MFC.

4. Discussion

In terms of sterilizing power, Ni-MnO₂/C showed outstanding performance, but considering the environmental impact, Co-MnO₂/C, which showed the next best performance, is considered more suitable. Ni-MnO₂/C's high sterilizing power may lead to environmental concerns if the nickel leaches into the surrounding environment, potentially causing pollution and health hazards. In contrast, cobalt is generally considered to have a lower environmental impact, making Co-MnO₂/C a more environmentally friendly option. The insufficient sterilizing power of Zn-MnO₂/C indicates that zinc is not suitable as a catalyst for single-chamber systems. While zinc may improve conductivity to some extent, its overall performance in terms of power output and sterilizing capability is suboptimal.

This suggests that zinc-based catalysts may not be ideal for applications where both high power output and sterilization are required. Judging from a comprehensive perspective, cobalt is the most suitable catalyst for single-chamber MFCs. Co-MnO₂/C demonstrated superior performance, showing 14% higher power output than cobalt-based catalysts reported by Simran & Patit (2022) and 185% higher power output than manganese-based catalysts documented by Dena et al. (2021).

5. Conclusion

In this study, Co-MnO₂/C emerges as the most suitable cathode catalyst for single-chamber MFCs. It not only demonstrates superior power output and efficiency but also poses a lower environmental impact compared to other catalysts. While Ni-MnO₂/C shows outstanding sterilizing power, its potential environmental hazards make Co-MnO₂/C a more viable option. Zinc-based catalysts, on the other hand, fall short in both power output and sterilizing capability, rendering them unsuitable for single-chamber systems. Overall, Co-MnO₂/C's balance of high power output, low internal resistance, environmental friendliness, and long-term stability positions it as the optimal catalyst for enhancing MFC performance.

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Ethics Approval

Not applicable.

Conflict of Interest

The authors declare there is no conflict.

References

- Huo, J., & Peng, C. (2023). Depletion of natural resources and environmental quality: Prospects of energy use, energy imports, and economic growth hindrances. *Resources Policy*, 86(A). <https://doi.org/10.1016/j.resourpol.2023.104049>
- Pang, L., & Liu, L., & Zhou, X., & Hafeez, M., & Ullah, S., & Sohail, M. T. (2024). How does natural resource depletion affect energy security risk? New insights from major energy-consuming countries. *Energy Strategy Reviews*, 54. <https://doi.org/10.1016/j.esr.2024.101460>
- Boelee, E., & Geerling, G., & Zaam, B. V. D., & Blauw, A., & Vethaak, A. D. (2019). Water and health: From environmental pressures to integrated responses. *Acta Tropica*, 193, 217-226. <https://doi.org/10.1016/j.actatropica.2019.03.011>
- Simohata, H., & Nakamoto, T., & Taguchi, K. (2023). Proposal for a practical MFC using vertical electrodes with improved air cathode function. *Energy Reports*, 9(12), 280-283. <https://doi.org/10.1016/j.egy.2023.10.004>
- Daud, S. M., & Bakar, M. H. A., & Daud, W. R. W., & Kim, B. H., & Jahim, J. M., & Muchtar, A., & Somalu, M. R., & Lee, P. H., & Abdul, P. M. (2021). Improvement of microbial fuel cell performance using novel kaolin earthenware membrane coated with a polybenzimidazole layer. *Energy Science & Engineering*, 9(12), 2342-2353. <https://doi.org/10.1002/ese3.988>
- Xia, Z., & Zhu, Y., & Zhang, W., & Hu, T., & Chen, T., & Zhang, J., & Liu, Y., & Ma, H., & Fang, H., & Li, L. (2020). Cobalt ion intercalated MnO₂/C as air cathode catalyst for rechargeable aluminum-air battery. *Journal of Alloys and Compounds*, 824. <https://doi.org/10.1016/j.jallcom.2020.153950>
- Chen, K. & Zhou, G., & Li, Q., & Tang, H., & Wang, S., & Li, P., & Gu, X., & Fan, Y. (2021). In vitro degradation, biocompatibility and antibacterial properties of pure zinc: assessing the potential of Zn as a guided bone regeneration membrane. *Journal of Materials Chemistry B*, 9, 5114-5127. <https://doi.org/10.1039/D1TB00596K>
- Dena, Z. K., & Amin, R. S., & Amani, E. F., & El-Khatib, K. M. & Mohamed, M. (2021). Bifunctional manganese oxide-silver nanocomposites anchored on graphitic mesoporous carbon to promote oxygen reduction and inhibit cathodic biofilm growth for long-term operation of microbial fuel cells fed with sewage. *Sustainable Energy Fuels*, 6, 430-439. <https://doi.org/10.1039/D1SE01479J>
- Simran, K. D., & Patit, P. K. (2022). Magnesium Cobaltite Embedded in Corncob-Derived Nitrogen-Doped Carbon as a Cathode Catalyst for Power Generation in Microbial Fuel Cells. *ACS Applied Materials & Interfaces*, 14, 42, 47633-47649. <https://doi.org/10.1021/acsami.2c12279>