



Determination of Factors Affecting the Performance of Sediment Microbial Fuel Cells by Long-Term Electricity Generation Using Lactic Acid Bacteria–Attached Electrodes

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Abstract Sediment microbial fuel cell (SMFC) performance can be improved using electrodes fermented with and without aeration as cathodes and anodes, respectively. However, this improved performance does not exceed 60 days. In this study, the cathode water-based factors affecting SMFC performance were identified using long-term electricity generation. Meanwhile, SMFC performance (polarization) was measured in experimental conditions. In addition to the polarization measurement, the pH, electrical conductivity (EC) of the cathode water, and adenosine triphosphate (ATP) on the cathode surface were measured. Experiments were conducted with and without the overflow of cathode water. Thereafter, the scanning electron microscopy–energy dispersive X-ray (SEM–EDX) analysis of the cathodes was performed. In line with existing literature, SMFC performance began to decrease on Day 60 from the commencement of the experiments. Furthermore, the pH difference before and after Day 60 was within 0.2, indicating that the pH of the cathode water did not directly affect SMFC performance. Moreover, EC was kept low with cathode water overflow, significantly decreasing SMFC performance. Further, the SMFC performance increased with an increase in ATP, indicating that the bacterial activities on the electrode affected SMFC performance. The SEM–EDX results revealed that metal ions that were obtained from the dissolution of steelmaking slag attached to the cathode surface, indicating the crystallization of these metal ions during the experiments. These findings indicate that the crystallization on the cathode driven by long-term electricity generation inhibited bacterial activities and cathode reactions, thereby decreasing SMFC performance.

Keywords performance, pH, electrical conductivity, adenosine triphosphate, crystallization

INTRODUCTION

Microbial fuel cell technology (MFCT) is expected to offer numerous benefits for addressing social issues, such as organic waste disposal and energy scarcity, particularly in developing countries. However, its performance remains low and must be improved before being deployed, and increasing electrode performance represents one strategy for improving MFCT performance.

Regarding the improvement of electrode performance, the adsorption of bacteria or metal ions on an electrode surface is a notable strategy. Wang et al. (2009) enhanced electrode performance by activating bacteria on the electrode, thus decreasing potential losses. Meanwhile, Nishimura et al. (2018) reported that the ferric ions obtained from the dissolution of steelmaking slag (SS) improved sediment microbial fuel cell (SMFC) performance. Thus, SMFC performance can be improved using SS and lactic acid bacteria (LAB) as the anode of SMFC (Touch et al., 2020).

Thus, numerous studies are exploring the changes in the performances of carbon fiber electrodes caused by the adsorption of iron ions (Fe) obtained from the dissolutions of SS and LAB on electrode

surfaces (Touch and Hibino, 2022). Touch et al. (2024) reported the possibility of improving SMFC performance using electrodes fermented with and without aeration as the cathode and anode, respectively. However, the improved performance only lasted for approximately 60 days owing to changes in the quality of the cathode water caused by long-term electricity generation. The factors accounting for the decreased SMFC performance after 60 days are still unknown.

Hong et al. (2009) experimentally examined the effects of controllable (e.g., electrode surface area ratio, external load, spacing between electrodes) and uncontrollable factors (e.g., dissolved oxygen concentration at the cathode, electrical conductivity [EC], and temperature) on electricity generation. Furthermore, the pH of the cathode water must be considered when bacteria are attached to the cathode, and crystallization on the cathode surface must be also examined.

OBJECTIVE

This study, which was based on long-term electricity generation, was conducted to identify the effects of the cathode water factors that decrease SMFC performance. Next, the cell polarization (current-voltage relation) was measured to detect changes in SMFC performance when fermented electrodes with and without aeration were used as the cathode and anode, respectively. Subsequently, the relationship between SMFC performance with the changes in the bacterial activities on the cathode was examined. The study further investigated the effects of the cathode water quality on SMFC performance.

METHODOLOGY

Experimental Materials and Procedures

The carbon fiber electrodes were pretreated following the method of Touch et al. (2024). Briefly, tap water (3 L), SS (layer height = 20 mm), a commercially available lactic-fermenting beverage (10 mL), and bamboo powder (3 g) were added in cylindrical bottles. For the case with aeration, an air stone was placed on the SS layer and the carbon fiber electrodes were positioned 90 mm from the bottom of the bottle. Further, carbon cloth (News Company, PL200-E) was employed as the electrode material; it was preheated for 1 h at 500°C to improve its performance (Nagatsu et al., 2014). The heated carbon cloth (width and length = 100 mm) was separated into fibers to form a brush-type electrode.

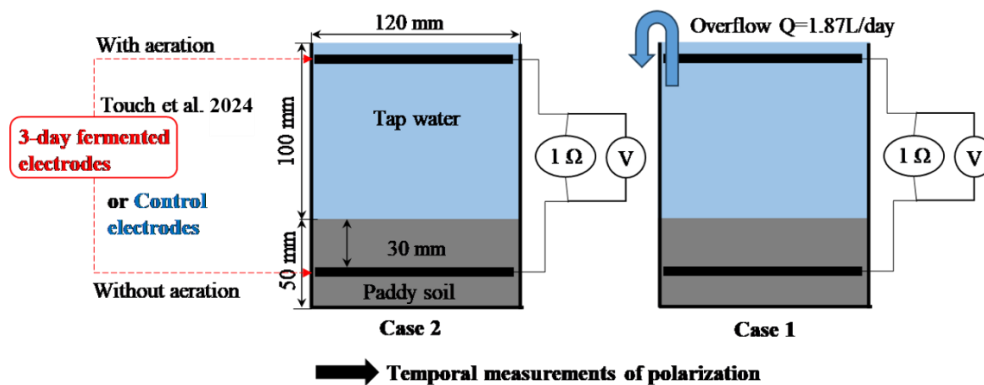


Fig. 1 Experimental procedures

The fermented electrodes with and without aeration, which were extracted from the bottles on Day 3, were utilized as the cathode and anode of SMFC, respectively, to examine the long-term performance of the cell in electricity generation (Fig. 1). Two cases were established: one with cathode water overflow (Case 1) and the other without it (Case 2). Henceforth we used Cases 2-1 and 2-2 to denote cases where the control and fermented electrodes were utilized in Case 2,

respectively. Similarly, Cases 1-1 and 1-2 denote when the control and fermented electrodes were utilized in Case 1, respectively.

By comparing Cases 2-1 and 2-2, we examined the changes in SMFC performance with the changes in the cathode water quality and determined the effects of the fermented electrodes on SMFC performance. By comparing Cases 1 and 2, we elucidated the effects of an overflow (lowering changes in the cathode water quality) on SMFC performance.

Operations and Measurements

The experiments were conducted for 97 days, as schematically shown in Fig. 1. To generate the electrical current, we loaded an external resistance of 1 Ω between the anode and cathode. The polarizations were measured several times during the electricity-generation experiments to examine the changes in SMFC performance. During the measurement, an external resistance of 1–9.1 k Ω was loaded between the anode and cathode. The cell voltage was recorded after 1 min of loading each external resistance and used to calculate the current by Ohm's law: $I = U/R_{ex}$, where U [V] is the voltage, I [A] is the current, and R_{ex} [Ω] is the external resistance. The power, P [W], was calculated using $P = IU$. Next, the current and power densities were obtained by dividing these values by the surface area of the electrode, i.e., 0.01 m². The maximum current density was also determined from the polarization.

The pH, EC of the cathode water, and the adenosine triphosphate (ATP) on the cathode surface were measured on the day of polarization measurement. The pH and EC were measured using a pH/EC meter (Horiba, D-74) while ATP was measured using a lumitester (Kikkoman, Lumitester-Smart). After the experiments, we performed scanning electron microscopy–energy dispersive X-ray (SEM–EDX) to analyze the adsorbed crystalline compounds on the cathode.

RESULTS AND DISCUSSION

Temporal Changes in Sediment Microbial Fuel Cell Performance

Figures 2a and 2b show the comparison of the SMFC performances (power and current density) in both Cases 1 and 2. The maximum power density (P_{max}) and current density (I_{max}) of SMFCs with the fermented electrodes (Cases 1-2 and 2-2) were higher than those with the control electrodes (Cases 1-1 and 2-1). Average 1.7- and 1.5-fold increases were observed in P_{max} (Fig. 2a) and I_{max} (Fig. 2b), respectively, when the fermented electrodes were used. However, it started decreasing from Day 60. These findings agree with those of Touch et al. (2024). Interestingly, inducing cathode water overflow (Case 1) produced lower P_{max} and I_{max} than the absence of overflow (Case 2), and the reasons for this will be discussed in the next section.

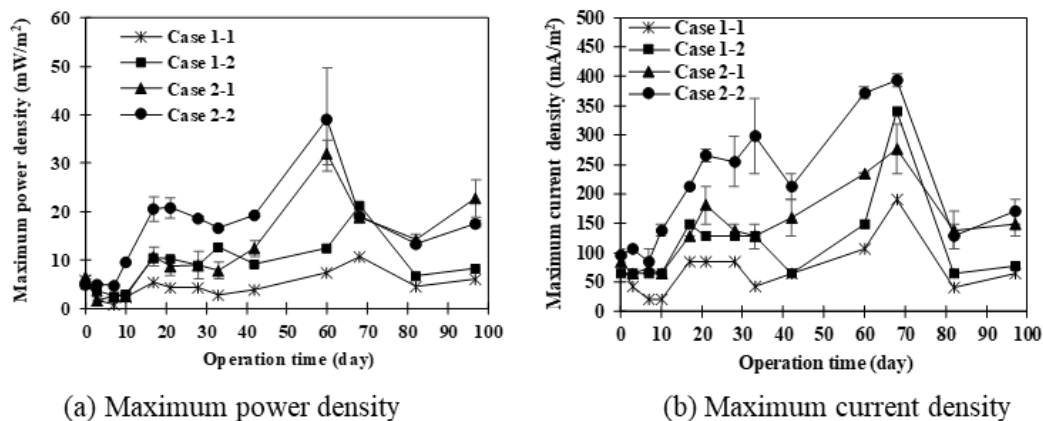


Fig. 2 Temporal variations of P_{max} and I_{max}

Temporal Changes in the pH and Electrical Conductivity

Figures 3a and 3b show that the pH and EC of the cathode water increased temporally. The diffusion of ions from paddy soils into the cathode water contributed to these increments. Additionally, the reduction of oxygen at the cathode contributed to the increase in pH. Hong et al. (2009) reported that changes in cathode water quality caused variations in SMFC performance. Likewise, in this study, we observed a relationship between SMFC performance and EC. Compared with the EC of Case 2 (without overflow), that of Case 1 (with overflow) was lower, contributing to lower power generations in Cases 1-1 and 1-2 (Fig. 2a) than in 2-1 and 2-2. Generally, a higher EC corresponds to a higher electron flow.

Considering the pH variation, we observed that the pH difference before and after Day 60 was within 0.2, indicating that pH did not directly affect the significant decrease in SMFC performance after Day 60 (Fig. 2).

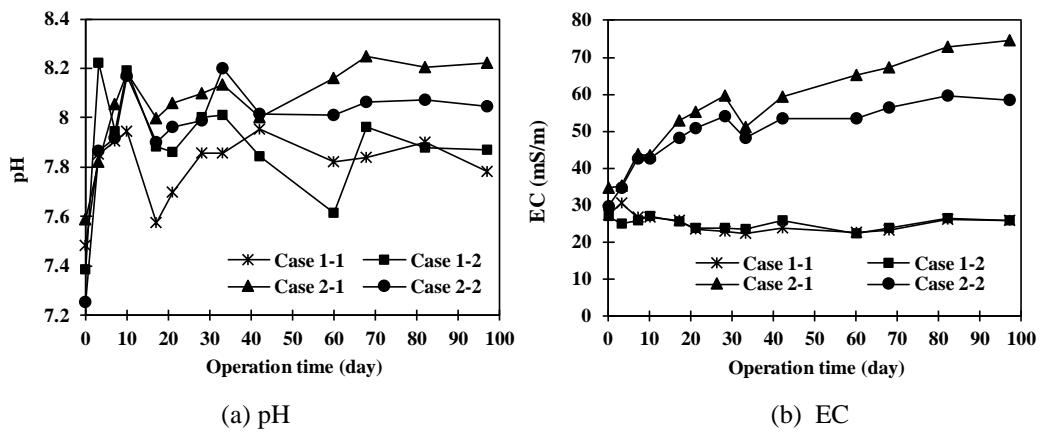


Fig. 3 Temporal changes in the cathode water pH and EC

Effects of Bacterial Activities on Sediment Microbial Fuel Cell Performance

Generally, SMFC performance depends on the cathode water quality and bacterial activities on the cathode. Figures 4a and 4b show the relationship between ATP on the cathode surface and SMFC performance. Notably, P_{max} increased with the increasing ATP within the correlation coefficient of 0.28, whereas I_{max} increased with the increasing ATP within the correlation coefficient of 0.45. Our results also confirmed that SMFC performance depends on the bacterial activities on the electrode surface, which agreed with Kang et al. (2012). This in turn confirmed that the decrease in the bacterial activities on the cathode might contribute to the decrease in SMFC performance after Day 60.

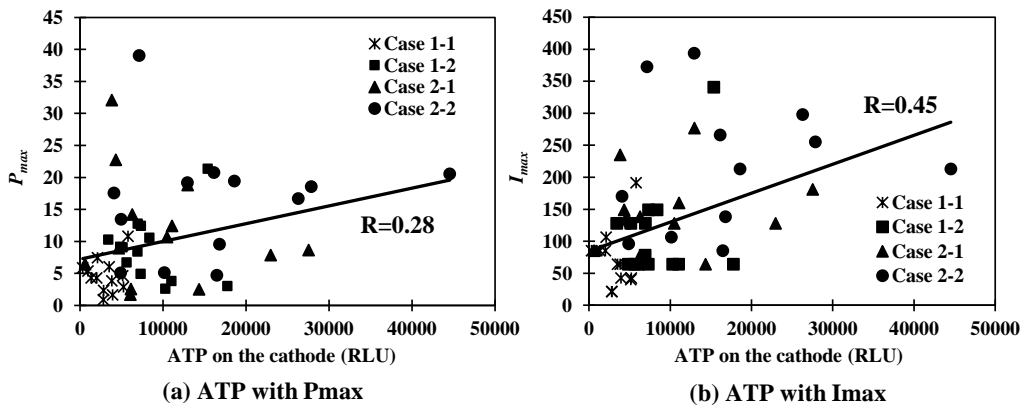


Fig. 4 Relationship between ATP on the cathode and the SMFC performance

Crystallization on the Cathode Surface

During the experiments, the appearance of white substances attached to the cathode surface was confirmed (Fig. 5). It is possible that they might affect the bacterial activities on the cathode. In Case 1-1, the formation of the substances (crystallization) was not confirmed from the SEM image, as most of the ions flowed out (Fig. 3b, EC was kept low as well as the tap water level) of the cathode chamber, causing a lack of ions for crystallization. Therefore, these substances were formed from the reaction of the cathode with ions present in the cathode water.

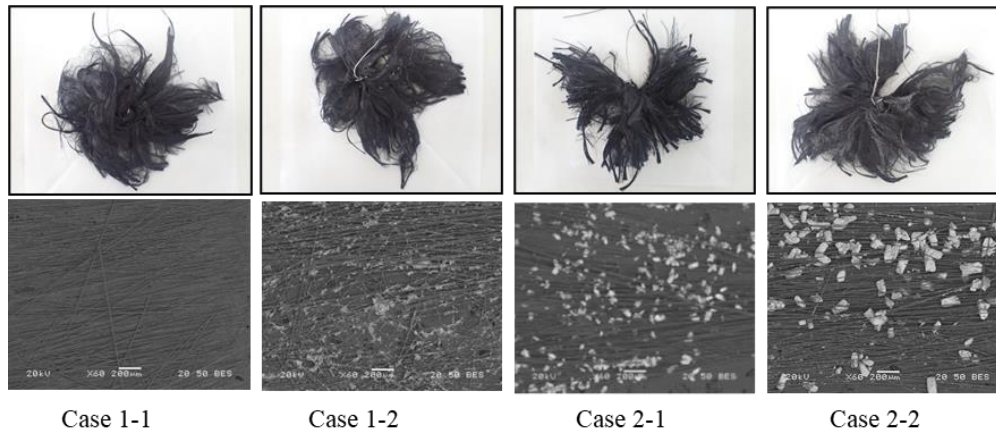


Fig. 5 SEM images of the cathodes

We also characterized the attached substances in Cases 1-2; however, they exhibited different characteristics from those of Cases 2-1 and 2-2. These substances might have been attached to the electrode during fermentation. As the amount of electricity that was generated (Fig. 2b, Case 2-2) was positively correlated to the number of these crystalline substances formed, these substances might have been obtained from the crystallization of the metal ions during cathode reactions.

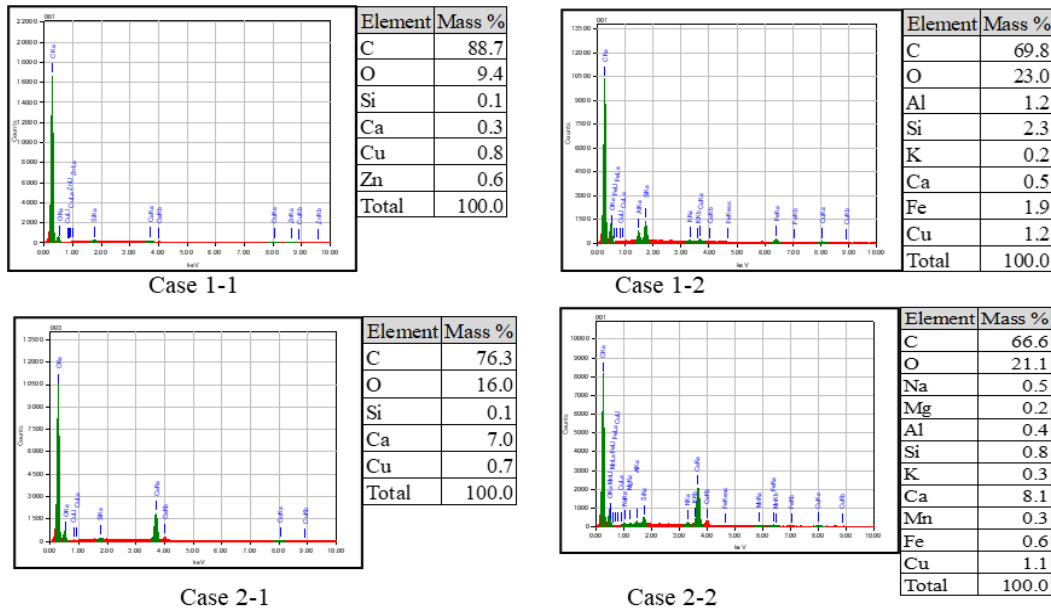


Fig. 6 Results of EDX analysis of the cathodes

The EDX results (Fig. 6) revealed that more metal ions, that is, Al, Si, Fe, Mn, and Mg ions, were attached to the fermented cathode (Cases 1-2 and 2-2) than to the control cathode (Cases 1-1 and 2-1). These metal ions are obtained from the dissolution of the steelmaking slag. The dissolution

could attach metal ions to the carbon fiber electrode through fermentation. The crystallization of these metal ions on the cathode surface might restrain the bacterial activities and chemical reactions on the cathode, thereby decreasing SMFC performance.

CONCLUSIONS

In line with existing literature, SMFC performance started decreasing on Day 60 after the commencement of the experiments. As the difference in the pH values before and after Day 60 was minimal, we concluded that the pH of the cathode water did not directly affect SMFC performance. SMFC performance decreased even though the cathode water overflowed. Notably, inducing cathode water overflow further decreased the SMFC performance. We observed a positive correlation between ATP on the cathode surface with SMFC performance. Therefore, the changes in the bacterial activities on the cathode surface might cause a decrease in SMFC performance during long-term electricity generation. The SEM–EDX results indicated that the metal ions obtained during the dissolution of steelmaking slag were adsorbed on the cathode surface, indicating the crystallization of these metal ions at the end of the experiments. Thus, during long-term electricity generation, crystallization on the cathode inhibits bacterial activities and cathode reactions, resulting in a decrease in SMFC performance.

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