Decomposition of Organic Matter in Steelmaking Slag-Used Sediment Microbial Fuel Cells

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Abstract- Sediment microbial fuel cells (SMFCs) have received notable attention for improving water and sediment quality. However, their low performance must be improved. Adding steelmaking slag (SS) to littoral sediment reportedly improved the SMFC performance. However, the decomposition of the organic matter in sediment that fueled SS-used SMFC (SS-SMFC) has not been revealed. The present study examines changes in the state of organic matter present in paddy soil that fueled SS-SMFC. Furthermore, the effects of a series connection of a solar cell with SS-SMFC (SC-SMFC) on changes in the state of organic matter are also examined. Increasing the electrical current of the SMFC and the alkalinity of the paddy soil by SS better facilitated the decomposition of organic matter. Relative to SS-SMFC, SC-SMFC (generating the periodic current) better facilitated the decomposition of organic matter. However, SS-SMFC (generating continuous current) better improved the redox conditions of the paddy soil than SC-SMFC. The generated electrical current decomposed the organic matter which burns at high temperature, thereby increasing the amount of organic matter that burns at lower temperature. A similar trend was observed among SMFC, SS-SMFC, and SC-SMFC. It can be said that this effect is independent of the current characteristic (continuous or periodic).

Keywords- Sediment Microbial Fuel Cell; Steelmaking Slag; Organic Matter; Decomposition, Loss on Ignition

LIST OF ABBREVIATIONS

SMFC: sediment microbial fuel cell
SS: steelmaking slag
SC: solar cell (1.5 V, 500 mA)
SS-SMFC: SMFC that the anode chamber is filled by SS
SC-SMFC: a series connection of SC with SS-SMFC
ORP: redox potential
LOI: loss on ignition at X °C
OMxy: organic matter that burns in the temperature range of X-Y °C

I. INTRODUCTION

Recently, sediment microbial fuel cells (SMFCs) have received notable attention for improving water and sediment quality. Numerous studies have reported that SMFCs decrease the amount and change the organic matter-state present in sediment and increase the redox potential (ORP) of the sediment [1-3]. Furthermore, SMFCs prevent the deterioration of water quality caused by ion diffusion from sediment [4]. Touch et al. [5] showed that SMFCs effectively remove hydrogen sulfide from sediment and fix the phosphate in sediment. They proved that the oxidation of reduced substances at the SMFC anode improve the sediment quality, in turn improving the benthos habitat in highly reduced sediment [6]. Accordingly, SMFCs have been installed in the sediment deposited near a sewage outlet and at an oyster farm to improve the quality of the sediment and water at these sites [7,8]. However, the performance of SMFCs remains low and must be improved. In previous studies, the SMFC performance has been improved by adding mediators to the sediment [9] and by activating organisms on the electrode [10].

Interestingly, Nishimura et al. [11] reported that adding steelmaking slag (SS) to littoral sediment could improve the SMFC performance. However, the decomposition of organic matter in the SS-supplemented sediment that used in SMFC has not been revealed. Hence, this study is aiming at revealing the decomposition of organic matter of the SS-supplemented sediment that fuels an SMFC. Particularly, paddy soil is used to fuel an SS-used SMFC (SS-SMFC: the SMFC that the anode chamber is filled by SS), and changes in the state of organic matter in the paddy soil that fueled SS-SMFC are investigated in laboratory experiments.

Moreover, it was also reported that a series connection of a solar cell with SMFC better improved water quality than SMFC [4]. However, to the best of our knowledge, no report has been published on the effects of the solar cell connection on the changes of organic matter-state in SS-SMFC. Thus, another objective of this study is to examine the changes of the organic matter-state when a solar cell is connected to SS-SMFC in series (SC-SMFC), in comparison with SS-SMFC.

II. MATERIALS AND METHODS

A. Construction of the SS-SMFC

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The illustrations of SMFC, SS-SMFC, and SC-SMFC are shown in Fig. 1. The SS-SMFC was constructed in a cylindrical bottle of inner diameter 120 mm and height 150 mm. The bottle was filled with SS (diameter 5–40 mm) to a depth of 20 mm, and the anode electrode was placed on the SS layer. Another SS layer (of depth 20 mm) was placed on the anode electrode. The wet paddy soil was mixed with deionized water at a soil-to-water weight ratio of 1:2 to facilitate its pouring into the SS layer. The mixture was slowly poured into the bottle to a height of 50 mm from the bottom of the bottle. Finally, tap water was poured over the soil layer, and the cathode electrode was submerged near the water surface (Fig. 1a). In the case of SMFC, only the paddy soil was used in the anode (Fig. 1b). SC-SMFC refers to a series connection of a solar cell (Tamiya, 1.5 V-500 mA) with SS-SMFC (Fig. 1c).

The paddy soil was collected from a rice field (Ebina, Kanagawa, Japan) during the agricultural off-season. Approximately 150 mm of the surface soil was collected and transported to the laboratory. The electrode material was carbon cloth (News Company, PL200-E). Prior to use, the material was heated at 500 °C for 1 h to improve its performance, as suggested by Nagatsu et al. [12]. The heated carbon cloth (of width 150 mm and length 150 mm: surface area 22500 mm²), was separated into carbon fibers to form a brush-type anode or cathode (see photograph in Fig. 1). All the connections in the SS-SMFC and operating circuits were plastic-coated copper wire (a commercial product).

![Photographs and schematics of the experimental devices](image)

**B. Operations and Analyses**

All SMFCs and SS-SMFCs were configured in open-circuit mode (without electrical current) until their voltages stabilized at approximately 7 days. Next, an electrical current was provided by the circuits shown in Fig. 2. To generate electrical current, an external resistance of 3 Ω was loaded between the anode and cathode of the SMFC or SS-SMFC (Fig. 2a). In SC-SMFC, the solar cell was connected with the SS-SMFC in series. The anode and cathode were connected to the positive and negative terminals of the solar cell, respectively. The system current was controlled by an external resistance of 20 Ω loaded between the anode and the solar cell (Fig. 2b).

To calculate the circuit current, the voltage across the external resistance was measured every 30 min by a voltmeter (midi LOGGER GL840-M Graphitec for SMFC and SS-SMFC, VR-71 T&D Corp. for SC-SMFC). The current was calculated by Ohm’s law, namely, \( I = \frac{U}{R_{\text{ex}}} \), where \( U \) (V) is the voltage, \( I \) (A) is the current, and \( R_{\text{ex}} \) (Ω) is the external resistance. The current density was obtained by dividing the current by the surface area of the electrode (0.0225 m²).

The paddy soil was analyzed at one and three months after starting the experiment. Prior to analysis, the SS-mixed paddy soil was collected from the bottle and passed through a 5 mm-sieve to remove the SS. This sieving is unnecessary in the cases without using SS. The pH and ORP of each soil sample were measured by inserting pH/ORP meters (Horiba, D-50) directly into the soil sample.

To understand the organic matter-state present in paddy soil, loss on ignition (LOI) was used according to previous studies [13-15]. Cuppers et al. [15] reported that labile and rather simple organic matter, e.g., fatty acids, peptides, and carbohydrates, mostly burned at 290-310 °C. On the other hand, humified organic matter, e.g., the humic and fulvic acids, burned mostly at 370-390 °C and 530-540 °C. Therefore, the organic matter-state in each soil sample was determined by measuring the LOI at one and three months after generating electrical current. In this study, the organic matter-state refers to the mass ratio of each soil organic matter to the total soil organic matter, and assuming that the LOI at 600 °C is the total amount of soil organic matter.
For measuring LOI, the soil sample was first dried at 50 °C in an electric drying oven (Advantec, FS-605) for one week, and its dry weight was measured. 50 °C was chosen as the typical drying temperature for determining organic matter content. The dried paddy soil was then heated to 200, 300, and 600 °C in an electric muffle furnace (Advantec, KL-420) for 4 h. Note that the same sample burned at progressively higher temperature. This approach was borrowed from Touch et al. [16,17], who demonstrated that the LOI at these temperatures can index the organic matter-state in littoral sediments. Subsequently, the sample was weighed, and its LOI at the burning temperature was determined by comparing the weight after burning with the 50 °C-dried weight. The LOI was measured in triplicate with an error of ±0.2%.

III. RESULTS AND DISCUSSION

A. Temporal Changes of Current Densities in SMFC, SS-SMFC, and SC-SMFC

Fig. 3 shows the temporal changes in the current densities of SMFC, SS-SMFC, and SC-SMFC. During the experiments, the maximum current density was approximately 10 mA/m² in the SMFC, while was stable at 130 mA/m² in the SS-SMFC (13-fold higher than in the SMFC). It can be said that SS can increase the SMFC performance either paddy soil (from our results) or littoral sediment (suggested by Nishimura et al. [11]) is used.

Fig. 3 confirms that the current was continuously generated in SMFC and SS-SMFC. However, as a solar cell operates only during the sunlight, the current density in the SC-SMFC periodically fluctuated with sunlight intensity. Specifically, the current density varied from zero to approximately 350 mA/m². The maximum current density of SC-SMFC was 1.5 to 2.7-fold higher than in the SS-SMFC. Over one month, the total electrical charges in the SMFC, SS-SMFC, and SC-SMFC were approximately 15600, 354000, and 290000 C/m², respectively. As sediment remediation depends on the current characteristics [18], the changes of the organic matter-state in paddy soil are expected to differ between the SS-SMFC and SC-SMFC.

B. Temporal Changes of pH and Redox Potential (ORP) of Paddy Soil

Fig. 4 shows the temporal changes of the pH and ORP in paddy soil. After one month of current generation, the ORP of paddy soil was −174 mV (PS-1 month), increasing to −130 mV (SMFC-1 month) during the SMFC application. This suggests that the current generation increases in the ORP, consistent with Touch et al. [19] who observed the increase in ORP of littoral sediment. However, the ORP was decreased in the SS-SMFC and SC-SMFC. Following Yamaji et al. [20], who observed a decreased ORP of the littoral sediment present in the SS layer, we attribute this decrease (at least partly) to the SS added to the paddy soil.
Touch et al. [16] reported that the decomposition of organic matter decreases the pH and ORP of littoral sediment. Our results showed a lower decrease in pH and a larger decrease in ORP of paddy soil for the SMFC, SS-SMFC, and SC-SMFC than for PS (Fig. 4), indicating that current generation facilitates the decomposition of organic matter in the paddy soil. Especially, the ORP decreased to a greater extent in SC-SMFC than in SS-SMFC, indicating that more of the organic matter was decomposed in SC-SMFC than in SS-SMFC. Moreover, the higher ORP in SS-SMFC suggests an improvement of the reduced environment of the paddy soil.

In summary, the SS-SMFC effectively improved the reduced environment of the paddy soil and probably degraded the organic matter. In other words, generating continuous current (SS-SMFC) can effectively improve the ORP, whereas generating periodic current (SC-SMFC) can facilitate the organic matter decomposition. When the current is generated continuously, the soil potential is maintained at the same level. However, when connecting the solar cell with SS-SMFC in series (generating a periodic current), the current is paused during the nighttime, and the soil potential decreases. The periodic decrease of soil potential is expected to enhance the decomposition of organic matter.

C. Changes in the Organic Matter-State

Fig. 5 shows the weight-loss ratios on ignition at 200°C (LOI$_{200}$), 200–300°C (LOI$_{200}$–LOI$_{300}$), and 300–600°C (LOI$_{300}$–LOI$_{600}$) to 600°C (LOI$_{600}$). Here, LOI$_{200}$, LOI$_{300}$–LOI$_{300}$, LOI$_{400}$–LOI$_{600}$, and LOI$_{600}$ are assumed to burn off the organic matters at 200°C (OM$_{200}$), from 200 to 300°C (OM$_{200}$–OM$_{300}$), from 300 to 600°C (OM$_{300}$–OM$_{600}$), and at 600°C (OM$_{600}$), respectively. No difference was confirmed between the non-electrified paddy soil and SMFC after one month. However, relative to the non-electrified paddy soil, the (LOI$_{300}$–LOI$_{200}$)/LOI$_{600}$ increased and the (LOI$_{600}$–LOI$_{100}$)/LOI$_{600}$ decreased in SMFC after three months. This suggests that SMFC facilitates the changes of the organic matter-state in paddy soil. Relative to SS-SMFC, the LOI$_{200}$/LOI$_{600}$ increased and the (LOI$_{300}$–LOI$_{200}$)/LOI$_{600}$ decreased in SC-SMFC. Meanwhile, the (LOI$_{600}$–LOI$_{300}$)/LOI$_{600}$ was almost constant after one month of current generation (Fig. 5a). A similar trend was also confirmed after three months of current generation (Fig. 5b). This suggests that a series connection of SC with SS-SMFC facilitates the changes of the organic matter-state in paddy soil of SS-SMFC.

These results suggest that the decomposition of organic matter is facilitated by the current generation, as noted in previous studies [21,22]. After three months of current generation, the decomposition of OM$_{300}$–OM$_{600}$ was facilitated, with consequent formation of OM$_{200}$ and OM$_{200}$–OM$_{300}$. As the time of current generation increased, it decomposed the organic matter that burns at increasingly higher temperatures. Consistent with this finding, Touch et al. [23,24] reported that an electrical current dissociates the organic matter from metal complexes, facilitating its decomposition in littoral sediments. In paddy soil, a similar trend of organic matter decomposition was observed among the SMFC, SS-SMFC, and SC-SMFC. Contrary to our
expectation, the trends of the changes of the organic matter-state were similar between SS-SMFC and SC-SMFC and unrelated to the current characteristics (i.e., continuous or periodic).

As shown in Fig. 5b, relative to the paddy soil, the (LOI_{soil}−LOI_{sm})/LOI_{soil} decreased in SMFC, and more decreased in SS-SMFC. It is thought that the SS facilitates the changes of the organic matter-state. This can be attributed to the higher electricity generation in SS-SMFC (354000 C/m²) than in SMFC (15600 C/m²). Generally, the decomposition increased with increasing time of electricity generation. In addition, Zhang et al. [25] reported that the alkaline treatment of adding SS into waste-activated sludge improved the performance of both sludge hydrolysis and acidification. They revealed that the alkaline treatment increases in the production of volatile fatty acids and boosts the enzyme activities. Thus, The SS addition also increases the alkalinity of the paddy soil, further enhancing the organic matter decomposition. Furthermore, small volume of the paddy soil used in SS-SMFC may also attributed to the enhancement of the changes in the organic matter-state.

Interestingly, our results also suggested that the organic matter-state was more changed in SC-SMFC than in SS-SMFC, despite the lower electricity generation in SC-SMFC (290000 C/m²) than in SS-SMFC (354000 C/m²). The lack of nighttime current in SC-SMFC might encourage the changes of the organic matter-state, probably by advancing the reduction reactions of the oxidants formed by the current generation (which decrease the anode potential). Touch et al. [18] reported that organisms limit their activity under high anode-potential conditions, thereby retarding the decomposition of organic matter in littoral sediments. The changes of the organic matter-state might also be accelerated by the wide variation of the anode potential in the series-connected solar cell and SS-SMFC. This behavior can be explained by various redox reactions induced by the variable anode potential. We concluded that connecting the solar cell to SS-SMFC in series can effectively facilitate the decomposition of organic matter.

IV. CONCLUSIONS

The changes of the organic matter-state in paddy soil which fuels an SS-SMFC were elucidated in laboratory experiments. These changes were observed under continuous current by SS-SMFC and periodic current by SC-SMFC. Large changes in the organic matter-state were observed in SS-SMFC than in SMFC. This result was attributed partly due to the increased current generation and alkalinity of paddy soil after mixing the SS. The decomposition characteristics of the organic matter were independent of the current characteristics (continuous or periodic), being similar in SS-SMFC, and SC-SMFC. The generated current decomposed the organic matter burns at higher temperature, increasing the amount of organic matter burning at low temperature. As the time of the electricity generation increased, more of the organic matter that burns at high temperature was decomposed. However, the current characteristics strongly affected the redox conditions of the paddy soil and the amount of decomposed organic matter. The SS-SMFC delivered a higher redox potential than SC-SMFC, suggesting that a continuous generation of current can effectively improve the redox conditions of the paddy soil. On the other hand, large changes in the state of organic matter was observed in SC-SMFC than in SS-SMFC, suggesting that the periodic current generation enforced by serial connection of SS-SMFC with the solar cell facilitates the decomposition of organic matter.

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