

Improvement of Sediment and Water Quality with Solar Cell-Combined Sediment Microbial Fuel Cells in Oyster Farms

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Abstract- It has been reported that solar cell-combined sediment microbial fuel cell (SC-SMFC) can be an alternative method for improving sediment and water quality. This study describes the employment of SC-SMFC for improving sediment and water quality in an oyster farm. The release of hydrogen sulfide from bottom sediment is one of the factors that cause the death of oysters which should be suppressed. At 3 months after the employment of SC-SMFC, bottom water (100 mm from the seafloor) and surface sediment (-100 mm from the seafloor) were collected and analyzed. The results showed decreases in hydrogen sulfide and phosphate concentrations in the sediment, indicating the improvement of sediment quality owing to the SC-SMFC application. In addition, the quality of bottom water was also improved owing to the SC-SMFC application. For example, the dissolved oxygen concentration and redox potential of the bottom water in the system-applied area remained higher comparing with those in the control area. These findings further strengthen that SC-SMFC is a highly effective method for suppressing the release of hydrogen sulfide and phosphate from sediment, which can protect water environment from hypoxia and eutrophication.

Keywords- Solar Cell; Sediment Microbial Fuel Cell; Hydrogen Sulfide; Dissolved Oxygen; Phosphate Fixation

I. INTRODUCTION

In an oyster farm, a significant amount of organic matter deposits on the seafloor during the growth of oysters. High rates of organic matter decomposition release large amounts of reduced substances, such as hydrogen sulfide (H₂S) and nutrient salts, within bottom sediment. These substances deteriorate not only sediment quality but also bottom water quality due to diffusion [1-2]. In 2016, oyster farmers directly reported to us that 70% of oysters died during the summer season. The formation of hypoxic water owing to the oxygen consumption by bottom sediment and the release of H₂S from bottom sediment were considered to be the causes of the oyster death. Therefore, methods for suppressing the release of H₂S and lowering the oxygen consumption by bottom sediment are required.

Granulated coal ash (GCA, a by-product of coal fired power plants)-used methods have been widely used for improving bottom sediment and bottom water quality impaired by high rates of organic matter decomposition [3-4]. Kim et al. [3] reported that scattering GCA on bottom sediment could reduce the release of nutrient salts and H₂S from the bottom sediment. Yamamoto et al. [4] confirmed that scattered GCA could improve the benthic habitat environment in the surface sediment.

Recently, sediment microbial fuel cell (SMFC)-based technologies have received notable attention for improving sediment and water quality. An increasing number of studies have found a decrease in the amount and a variation in the state of the organic matter present in the sediment-applied SMFC, and a positive increase of the redox potential (ORP) of sediment when using SMFC [5-7]. SMFC is also effective in protecting against the deterioration of bottom water quality due to ion diffusion from bottom sediment [8], and in improving the benthic habitat environment in highly reduced sediment [9]. The authors proved that the oxidation of reduced substances at the anode of SMFC plays an important role in improving the water quality and the benthos inhabitation. The anode oxidation can decrease the diffusion of reduced substances from sediment into overlying water and increase the sediment ORP.

An attempt has been made [10], aimed at increasing the SMFC efficiency in improving sediment and water quality by increasing the SMFC current with addition of external power supply. The authors reported that the increasing current could obtain a higher efficiency of SMFC in sediment remediation. For instance, an increase in sediment ORP was higher when the potentiostat-combined SMFC was applied, in comparison with SMFC alone [10]. Touch et al. [11] looked into the potential of using a solar cell as the external power supply of SMFC. They reported that solar cell could be used as the external power supply of SMFC, and the SMFC efficiency was 2-fold increased after adding a solar cell.

According to the literature reviewed earlier, it is expected that solar cell-combined SMFC (SC-SMFC) can be used to remediate sediment, resulting in the improvement of bottom water quality in an oyster farm. Compared with our previous studies [11], this study aims to confirm the SC-SMFC efficiency in removing H₂S from bottom sediment and fixing phosphate (PO₄³⁻) in bottom sediment in a coastal region (field scale). Furthermore, the improving bottom water quality with regard to the

sediment remediation is also examined.

II. MATERIALS AND METHODS

A. The Construction of SC-SMFC System and Its Installation

The SC-SMFC system comprised three anodes and three cathodes. An anode comprised nine carbon fibres-electrodes which were connected in parallel, and an electrode had a surface area of 0.09 m^2 . Note that the surface area refers to the surface area of carbon cloth (News Company, PL200-E) that was used to make the carbon fibers-electrode. The electrodes were fixed to cotton ropes at intervals of 1 m, as shown in Fig. 1a. Cu-electrical leads were used to connect from one to another electrode, and the Cu-electrical leads were also fixed to the cotton ropes. A surface area of 0.18 m^2 of the carbon cloth was broken into carbon fibers. The carbon fibers were then placed between two wooden boards to make a cathode electrode (1 m in length and 0.15 m in height), as shown in Fig. 1b. Following Nagatsu et al. [12], the carbon cloth was heated to $500 \text{ }^\circ\text{C}$ for 1 min to improve its performance before it was used as the electrode material.

The SC-SMFC system was installed at an oyster farm (Saka, Hiroshima, Japan), as shown in Fig. 2. Three anodes were fixed to PVC pipes that were inserted in bottom sediment at intervals of 5 m. The electrodes (carbon fibers) of each anode were buried in the surface sediment (-0.15 m from the seafloor) by divers after the anode fixation. On the other hand, the cathodes were suspended at water surface. The Cu-electrical leads of anodes and cathodes were connected to a data recording system. The Cu-electrical leads of anodes were fixed to cotton ropes for preventing the breaking of the Cu-electrical leads. A reference electrode (Ag/AgCl , sat. KCl) (Toyo Co., TRE-7) was fixed to the wooden board of a cathode, and suspended close to water surface.

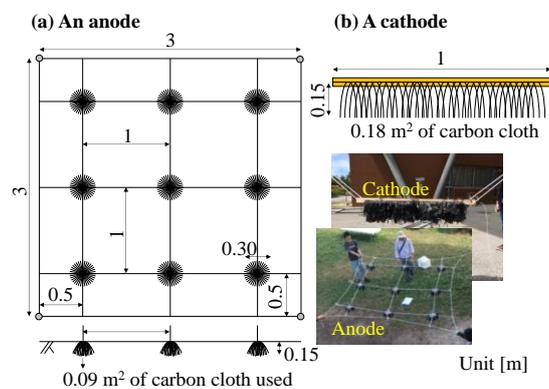


Fig. 1 Diagrams of an anode (a) and a cathode (b) of the SC-SMFC system

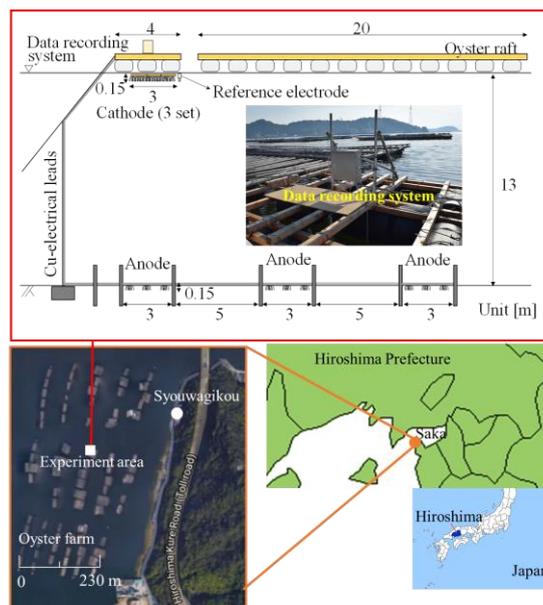


Fig. 2 Installation of the SC-SMFC system at an oyster farm (Saka, Hiroshima, Japan)

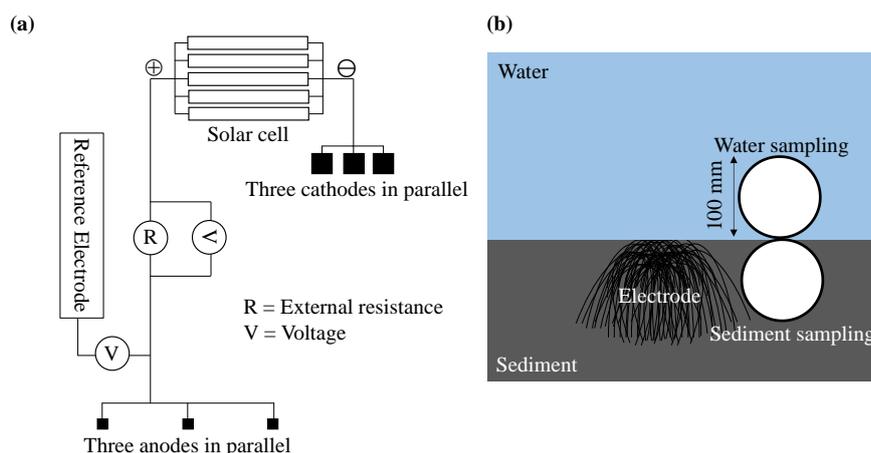


Fig. 3 Circuits for measurements of the anode potential and the system current (a) and Samplings of bottom water and bottom sediment (b)

B. The System Operations and Analyses

After installing the anodes and the cathodes, the anodes were connected in parallel, and the terminal of the paralleled-anodes was then connected to the positive terminal of five paralleled-solar cells (Tamiya, 1.5 V-500 mA). Similarly, the terminal of the paralleled-cathodes was connected to the negative terminal of the paralleled-solar cells. Again, the addition of the solar cells into the SMFC system, i.e. SC-SMFC, was carried out to increase the electrical current of the system. An external resistance was loaded between the anodes and the solar cells to control the system current.

The paralleled-anodes were also connected to the reference electrode to measure the anode potential (Fig. 3a). To measure the system current, the voltage of the two ends of the external resistance was recorded. The current was calculated using the recorded voltage based on 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 voltage was recorded every 30 min using a voltage recorder (T&D Corp., VR-71).

The field experiment started from June 19, 2017; then bottom sediment and bottom water samplings (Fig. 3b) were conducted on September 22, 2017 to evaluate the potential of SC-SMFC in improving sediment and water quality. For understanding the effects of SC-SMFC application, the bottom sediment and the bottom water located 100 m from the area of SC-SMFC application were also collected and analyzed. After sampling bottom water from the sea bottom, the pH, ORP, and dissolved oxygen (DO) concentration were immediately measured by inserting a pH/ORP meter (Horiba, D-50) and a DO meter (WTW, FDO925) into the bottom water directly. And then, the bottom sediment and the bottom water were sealed and transported to the laboratory for measuring the concentration of ions present in the bottom water and the sediment pore water. The ion concentration was measured using a digital water quality analyzer (Kyoritsu Chemical-Check Lab. Corp., A9000). Here, double measurements of a sample were conducted, and the average value was used in discussion.

The pH and ORP of the sediment were measured by directly inserting the pH/ORP meter into the sediment within 15 min. The sediment was then placed in 50 mL-centrifuge tubes. The tubes were centrifuged at a speed of 6000 rpm for 10 min to extract the sediment pore water (AS ONE, CN2060). This rotation speed was chosen in order to directly measure the pore water quality without filtration. The filtration of pore water may largely influence on the sediment pore water quality. Finally, the concentrations of several major ions, such as H_2S and nutrient salts, present in the pore water were measured using the digital water quality analyzer. Note that no pre-treatment of the bottom water and the sediment pore water was conducted.

III. RESULTS AND DISCUSSION

A. Improvement of the Reduction Level of Sediment by the SC-SMFC Application

The reduction level of sediment is commonly evaluated on the basis of the sediment ORP. However, the sediment ORP cannot be continuously recorded using an available ORP meter over several months at in-situ. Instead, the anode potential is used to understand the reduction level of the sediment in this study. Figure 4 shows the temporal changes of the anode potential during the application of SC-SMFC. From the experiment started until July 13, 2017, electrons were transferred from the sediment with a maximum current (I_{max}) of 160 mA. Later, the maximum current was increased to 250 mA. As known, a solar cell only works during the daytime, the minimum anode potential (P_{min} , the anode potential during the night time) refers to the anode potential without electron transfer, i.e. the reduction level of sediment.

During $I_{max}=160$ mA, P_{min} temporally decreased and reached -0.55 V on July 12, 2017. Generally, the oxidation of electron donors (some of reduced substances) causes an increase of electron acceptors (oxidants). This increases the sediment ORP, as following the Nernst equation. Details on the increasing sediment ORP by electricity generation can be also found in the reports by Touch et al. [13], Choi et al. [14], and Sturm et al. [15]. Thus, the decrease in P_{min} during the SC-SMFC application

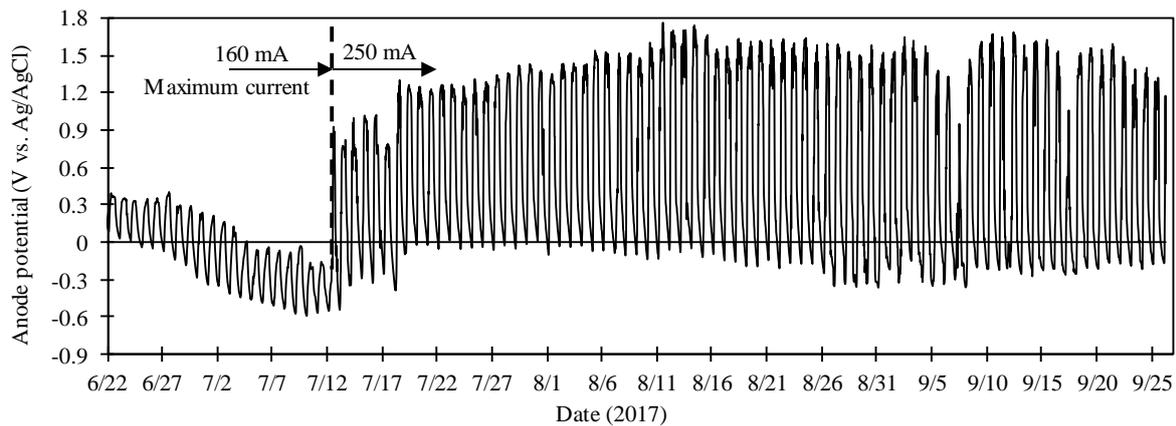


Fig. 4 Temporal changes of the anode potential during the application of SC-SMFC. The potential was measured with an error of ± 0.002 V

TABLE 1 THE SEDIMENT QUALITY IN THE AREAS WITH AND WITHOUT SC-SMFC APPLICATION

Parameter	Unit	SC-SMFC applied Sediment	Control sediment	Error
pH		7.22	7.29	± 0.03
Redox potential (ORP)	mV vs. Ag/AgCl saturated KCl	-390	-387	± 3
Ammonium (NH_4^+) concentration	mg/L	24.50	26.00	± 0.02
Phosphate (PO_4^{3-}) concentration	mg/L	2.40	6.00	± 0.04
Manganese (Mn) concentration	mg/L	<0.50	2.45	± 0.05
Hydrogen sulfide (H_2S) concentration	mg/L	6.40	37.50	± 0.02
Sulfate (SO_4^{2-}) concentration	mg/L	2150	2125	± 2

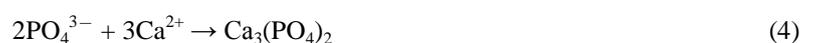
suggested the I_{max} of 160 mA was inadequate for improving the reduction level of the sediment, i.e. the amount of electron transferred < the amount of electron released.

After the increasing I_{max} to 250 mA, P_{min} temporally increased and reached 0 V on August 1, 2017. This ensured the improvement of the reduction level of sediment owing to the SC-SMFC application. P_{min} started to decrease from August 1, 2017, and reached -0.36 V on August 31, 2017. During the summer season, anaerobic decomposition of organic matter is advanced in response to an increase in temperature, leading to a decrease in the reduction level of sediment. It can be understood that the I_{max} of 250 mA is still not enough for improving the reduction level of the sediment during the summer season. The anode potential also depended on temperature. However, the potential variation due to changes in temperature is too small (10 °C-change in temperature causes only 6 mV-change in potential), so that the temperature dependence was not discussed in this study.

B. Changes in the Quality of Sediment Pore Water by the SC-SMFC Application

As noted earlier, one of our purposes was to examine the improvement of sediment quality, i.e., removal of H_2S and fixation of PO_4^{3-} , in response to the application of SC-SMFC in a coastal region (field scale). Thus, the bottom sediment near the anode (Fig. 3b) was collected and analyzed on September 22, 2017.

In a laboratory scale, it has been reported that H_2S and PO_4^{3-} concentrations decrease owing to the application of SC-SMFC [11]. The authors have reported that H_2S is removed by the oxidation of H_2S at the anode (e.g., Eq.1). On the other hand, PO_4^{3-} is removed due to the fixation of PO_4^{3-} by Fe^{2+} and Ca^{2+} ions dissociated from metal complexes during the SC-SMFC application (e.g., Eqs. 2-4).



In this study, i.e., in a field scale, decreases in H_2S and PO_4^{3-} concentrations in the sediment were also confirmed (Table 1). The H_2S concentration decreased from 37.50 to 6.40 mg/L, and PO_4^{3-} concentration decreased from 6.00 to 2.40 mg/L owing to the SC-SMFC application. These findings further strengthen that SC-SMFC is a highly effective method from improving sediment quality, i.e., removal of H_2S and fixation of PO_4^{3-} .

TABLE 2 THE BOTTOM WATER QUALITY IN THE AREAS WITH AND WITHOUT SC-SMFC APPLICATION

Parameter	Unit	Bottom water in the area with SC-SMFC application	Bottom water in the area without SC-SMFC application	Error
pH		7.81	7.77	±0.03
Redox potential (ORP)	mV vs. Ag/AgCl sat. KCl	152	107	±3
Electrical conductivity (EC)	mS/m	4810	4820	±1
Dissolved oxygen (DO) concentration	mg/L	3.78	2.30	±0.1
Ammonium (NH ₄ ⁺) concentration	mg/L	0.30	0.40	±0.02
Phosphate (PO ₄ ³⁻) concentration	mg/L	0.20	0.30	±0.04
Manganese (Mn) concentration	mg/L	<0.50	<0.5	±0.05
Hydrogen sulfide (H ₂ S) concentration	mg/L	<0.05	<0.05	±0.02
Total iron ion (Fe) concentration	mg/L	0.12	<0.05	±0.01
Sulfate (SO ₄ ²⁻) concentration	mg/L	2350	2475	±2

C. Changes in the Quality of Bottom Water by the SC-SMFC Application

Another purpose of this study was to examine the improvement of water quality in a field scale in response to the application of SC-SMFC. Hence, bottom water (Fig. 3b) was also collected together with the sediment collection on September 22, 2017. The analyzed results of the bottom water are listed in Table 2. Again, the ORP, DO concentration, and electrical conductivity (Horiba, D-74) of the bottom water were measured at field.

As explained earlier, diffusion of reduced substances from bottom sediment diminishes the water quality of bottom water, for example, by decreasing DO concentration and ORP. This deterioration is reduced due to the application of SC-SMFC when suspending the cathode of SC-SMFC at water surface. This is because the electrons from oxidizing reduced substances at the anode can be transferred to the cathode, reacting with oxygen in the surface water that is continuously supplied from the air.

In a laboratory scale, Touch et al. [8] [11] already confirmed that the DO concentration and ORP of overlying water in the SC-SMFC applied-cases remained higher than the cases without the SC-SMFC application. Our results (Table 2) also showed a difference in either DO concentration or ORP of the bottom water between the areas with and without SC-SMFC application. The DO concentration was 3.78 mg/L in the bottom water located the SC-SMFC applied-area, which was higher than that in the area without SC-SMFC application (2.30 mg/L). Moreover, the ORP of bottom water (152 mV) remained higher in the SC-SMFC applied- area compared to that in the area without SC-SMFC application (107 mV). As shown in Table 1, H₂S present in sediment was decreased by the anode oxidation. This decrease reduces the H₂S diffusion from the sediment to bottom water, resulting in a reduction of the oxygen consumption in the bottom water. This is a reason behind the higher DO concentration in the SC-SMFC applied area. Moreover, ORP refers to the ratio of oxidants (e.g., O₂) to reductants (e.g., H₂S) according to the Nernst equation. Thus, a lower diffusion of H₂S and a higher DO concentration were considered to be the reasons behind the higher ORP in the SC-SMFC applied area.

It is surprising that the improvement of water quality by the SC-SMFC application was confirmed in a field scale. In a coastal region, bottom water moves corresponding to tidal fluctuations. This means that deteriorated water are always transported into the SC-SMFC applied area by tidal fluctuations. Our results, however, showed the improvement of bottom water quality. Although bottom water always moves, a better water quality was kept in the SC-SMFC applied area compared to the area without SC-SMFC application. This ensures that SC-SMFC is a highly effective method for sediment remediation, leading to the improvement of water quality deterioration caused by bottom sediment.

IV. CONCLUSIONS

Field experiments were conducted to examine the potential of SC-SMFC in improving sediment and water quality in an oyster farm. The results suggested that the SC-SMFC employment in bottom sediment when suspending the cathode at water surface could reduce the H₂S and PO₄³⁻ concentrations in the sediment. This in turn reduced the deterioration of bottom water quality, for example the DO concentration and ORP in the bottom water of the SC-SMFC applied area remained higher compared to those in the area without SC-SMFC application. In addition to the previous laboratory results, the findings of this study further strengthen that SC-SMFC is a highly effective method for improving sediment and water quality. It is expected that SC-SMFC can be used to remove H₂S and improve water quality in oyster farms, reducing the death of oysters due to the water quality deterioration caused by bottom sediment.

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