

# Solar Cell-Combined Sediment Microbial Fuel Cell for Preserving Sediment and Water Environments

Narong Touch<sup>\*1</sup>, Satoshi Yamaji<sup>2</sup>, Hiroki Takata<sup>3</sup>, Tadashi Hibino<sup>4</sup>

Department of Civil and Environmental Engineering, Hiroshima University  
1-4-1 Kagamiyama, Higashihiroshima-Shi 739-8527, Hiroshima-Ken, Japan

<sup>\*1</sup>narong-cambodia@hiroshima-u.ac.jp; <sup>2</sup>m172401@hiroshima-u.ac.jp; <sup>3</sup>m175472@hiroshima-u.ac.jp;

<sup>4</sup>hibinot@hiroshima-u.ac.jp

**Abstract-**Sediment microbial fuel cell (SMFC), an electrochemistry technology, is expected to be an alternative method for improving both water and sediment environments. This study presents the development of a solar cell-combined SMFC system (SC-SMFC), and the improvement of sediment and water environments by SC-SMFC through laboratory experiments. The distributions of pH and redox potential (ORP) in sediment were formed, in which larger decreases in pH and increases in ORP were found near the anode after the SC-SMFC application. From the pH and ORP distributions, the sediment located between 0 mm and 150 mm from the anode was strongly influenced by the SC-SMFC application, which was around 2-fold higher than that influenced by the application of SMFC alone. Interestingly, the system application caused the dissociation of calcium and iron complexes. This dissociation increased the concentrations of calcium and ferric ions, leading to the fixation of phosphate in the sediment. Furthermore, different decomposition characteristics of organic matter were found in the sediments near and far from the anode. In addition, the quality of overlying water was also improved by the system application. For example, the dissolved oxygen concentration remained higher near the sediment surface. These findings validate the usefulness of SC-SMFC as an alternative method for improving both sediment and water environments concurrently.

**Keywords-** Solar Cell; Sediment Microbial Fuel Cell; Sediment Quality; Water Quality; Phosphate Fixation

## I. INTRODUCTION

With an increase of wastewater discharge in proportion to population growth, wastewater treatment plants are unable to treat the excess wastewater. As such, a significant amount is discharged into local water bodies, resulting in concomitant large accumulations of sediment in the water bodies. High rates of organic matter decomposition releases many reduced substances within sediment, such as hydrogen sulfide (H<sub>2</sub>S) and nutrient salts, deteriorating not only the sediment quality but also the bottom water quality due to diffusion [1-2]. Therefore, methods for preserving both sediment and water quality are required.

Recently, methods of using granulated coal ash (GCA, a by-product of coal thermal electric power stations), have received notable attention for improving sediment and water quality that have been impaired by high rates of organic matter decomposition [3-4]. Kim et al. [3] reported that scattering GCA on the sea bottom sediment could reduce the release of nutrient salts and H<sub>2</sub>S from the sea bottom sediment. Yamamoto et al. [4] also confirmed that GCA could improve the benthic environment in the surface sediment. However, these methods may be ineffective in water bodies over the long term, as further sediment will accumulate on the layer of remedial material.

Sediment microbial fuel cell (SMFC), an electrochemistry technology (Fig. 1), is expected to be an alternative method for improving both water and sediment environments. It has been reported that the electrons from oxidizing organic and inorganic compounds can transfer to the anode of an SMFC. This transfer is responsible for promoting anaerobic oxidation of organic matter without requiring terminal electron acceptors, such as nitrate and sulfate [5]. 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 [6-8]. However, the capacity of SMFC in remediating sediment is still low and should be improved.

An attempt has been made [9], aimed at examining changes of sediment and water quality after increasing the SMFC current with a potentiostat as an external power supply. The authors demonstrated that the increasing current could promote 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. Touch et al. [10] looked into changes of the sediment quality following electrokinetic treatments, and reported the characteristics of sediment remediation and the enrichment of microorganisms following electron recovery from the sediment.

As compared with our previous studies [9-10], one of the objectives of this study is to understand the current generation characteristics when a solar cell is combined with the SMFC system (SC-SMFC), and the effects of SC-SMFC on sediment remediation. Another objective is to evaluate the effective distance of anode on sediment remediation. This study may be useful for researchers in designing an effective SMFC system for practical uses.

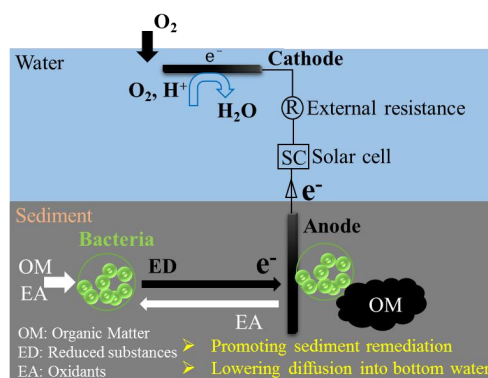


Fig. 1 Concepts of SMFC in improving sediment and water quality

## II. MATERIALS AND METHODS

### A. Experiment Methods

Figure 2 shows the diagram of apparatus used in the experiments. The apparatus was comprised of a container 685 mm in height, 575 mm in length, and 400 mm in width (New select, C-90). Sediment was filled until a given height of 100 mm from the bottom of the container. Eight sheets of 60 mm × 60 mm-carbon cloth (News Company, PL200-E) were then inserted into the sediment layer at intervals of 50 mm from the anode. This would be able to measure the potential distribution in the sediment. These carbon cloths (electrodes) were connected to an Ag/AgCl saturated KCl reference electrode (Toyo Co., TRE-7). The brush type-anode and cathode were also made from the carbon cloth. Following to Nagatsu et al. [11], the carbon cloth was heated to 500°C for 30 min to improve its performance before being used in the experiments. The heated carbon cloth was broken into fibers to create a brush-type electrode.

After the installation of the brush type-anode in the sediment, tap water was poured into the container. The brush type-cathode was then suspended near water surface. The anode and cathode were connected to a solar cell (Tamiya, 1.5 V-500 mA) in order to increase the electrical current of the system. An external resistance was loaded between the anode and the solar cell for controlling the electrical current.

### B. Material Used in the Experiments

The sediment used in the experiments was collected from the riverbank of a tidal river (Eba, Hiroshima, Japan). This site is strongly influenced by wastewater discharge. Sediment was collected near the wastewater outlet. Approximately 30 cm of surface sediment was collected from the deposited sediment on the riverbank using a scope. The sediment was placed in a clean plastic bucket and transported to the laboratory. The sediment was stored at a room temperature of  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ , and was homogenized by mixing before use. As noted earlier, tap water was used as the cathode layer.

0.135 m<sup>2</sup> of the burned carbon cloth (not carbon fibers) was used to form the brush type-anode that was buried in the sediment. The surface area of the brush type-cathode was the same as that of the anode.

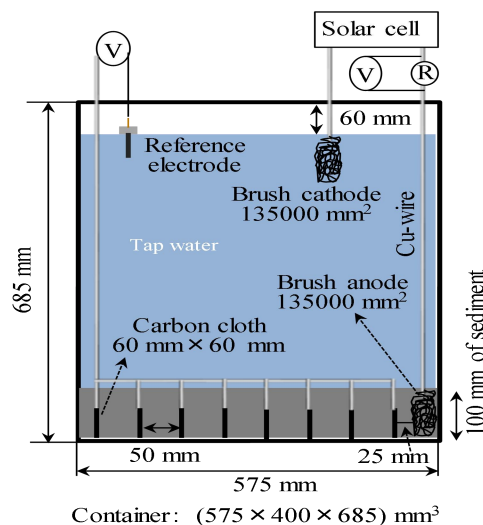


Fig. 2 Diagram of the apparatus used in the experiments

TABLE 1 THE INITIAL QUALITY OF THE SEDIMENT AND TAP WATER USED IN THE EXPERIMENTS

Parameter	Unit	Sediment	Tap water
pH		7.24	7.50
Redox potential (ORP)	mV vs. Ag/AgCl saturated KCl	-425	640
Electrical conductivity (EC)	mS/m	4480	9.53
Dissolved oxygen (DO) concentration	mg/L	N/A	8.72
Ammonium (NH <sub>4</sub> <sup>+</sup> ) concentration	mg/L	27.92	N/A
Phosphate (PO <sub>4</sub> <sup>3-</sup> ) concentration	mg/L	7.08	N/A
Manganese (Mn) concentration	mg/L	2.02	N/A
Total iron (Fe) concentration	mg/L	0.08	N/A
Ferric (Fe <sup>2+</sup> ) concentration	mg/L	0.08	N/A
Hydrogen sulfide (H <sub>2</sub> S) concentration	mg/L	26.50	N/A
Sulfate (SO <sub>4</sub> <sup>2-</sup> ) concentration	mg/L	1450	N/A

### C. Measurement Procedures

The quality of the collected sediment was analyzed before being used in the experiments. The pH and redox potential (ORP) of the sediment were measured by inserting pH/ORP meters (Horiba, D-50) into the sediment directly. 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 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 pore water quality. Finally, the concentrations of several major ions, such as hydrogen sulfide and nutrient salts, present in the pore water were measured using a digital water quality analyzer (Kyoritsu Chemical-Check Lab. Corp., A9000). No pre-treatment of samples was conducted. The initial quality of the sediment and tap water is listed in TABLE 1. Electrical conductivity (EC) was measured using an EC meter (Horiba, D-74), and the dissolved oxygen (DO) concentration was measured using a DO meter (WTW, FDO925). These meters were inserted into the samples directly. To determine the characteristics of organic matter, the thermal analysis (TG/DTA) was conducted using a Shimadzu-DTG 60H analyzer, in which around 30 mg of freeze-dried sediments was heated with a speed of 5°C/min.

The anode and cathode were connected to the solar cell using a plastic-coated Cu wire. An external resistance of 205.4  $\Omega$  was loaded between the solar cell and the anode for controlling the circuit current. This external resistance was chosen to set an initial anode potential of 200 mV vs. Ag/AgCl saturated KCl based on the results reported by Wang et al.[12] and Touch et al. [9] who showed that a positive potential of 200 mV could increase the electrochemical activity of the anodic biological community during start-up.

The voltage of the two ends of the external resistance was recorded every minute using a voltage logger (Graphtec, GL840-M). 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  $R_{ex}$  ( $\Omega$ ) is the external resistance. Both the (60 mm  $\times$  60 mm)-electrodes and the reference electrode were also connected to the voltage logger for measuring the potential distribution in the sediment layer.

The experiment was conducted for over 6 months. At the end of the experiment, water (cathode layer) and sediment (anode layer) quality were analyzed. The water was collected at intervals of 50 mm from the water surface to the sediment surface. The collected water was then placed in a clean plastic bucket, and then the pH, ORP, EC, DO, and concentrations of Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> were measured. The Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> concentrations were measured using Horiba-laqua twin electrodes. It should be noted here that the average value of duplicate samples was used. After removing all the water above the sediment, the sediment was collected at intervals of 50 mm from the anode. The sediment analysis procedures were similar to those noted above.

## III. RESULTS AND DISCUSSION

### A. Characteristics of Current Produced by SC-SMFC

The first objective of this study was to understand the characteristics of currents produced when a solar cell is used as an external power supply in SMFC. In other words, the ability of the solar cell in providing a stable variation of current generation is determined. Figure 3 depicts the current density produced by SC-SMFC over the experiment period.

As known, the solar cell only works during the daytime (no electrical current during the night time), and its current varies according to sunlight intensity. During the first ten days, the maximum current density was in the range of 50–54 mA/m<sup>2</sup>, and then it increased to reach a maximum of 60–63 mA/m<sup>2</sup> between days 23 and 80. The current density then slowly decreased from day 80, and reached a minimum of 46 mA/m<sup>2</sup> on day 127.

The increasing current observed from day 17 was partly due to the increase in electrode performance. This is hardly distinguishable from the reports by Sacco et al. [6] and Song et al. [13], who demonstrated that electron transfer processes forming on the anode surface produce a rapid increase in current between days 7 and 10. On the other hand, the decreasing current from day 80 was due to the lack of substrates near the anode. Bond et al. [14] and Sacco et al. [6] reported a drop in

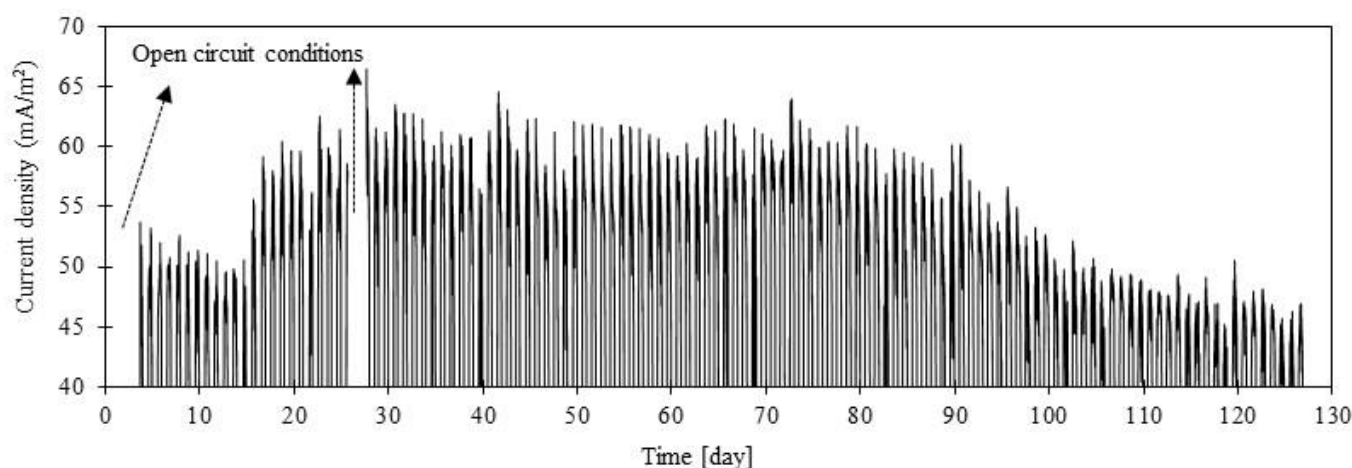


Fig. 3 Current density produced by SC-SMFC over the experiment period. The current density was measured with an error of  $\pm 0.07 \text{ mA/m}^2$

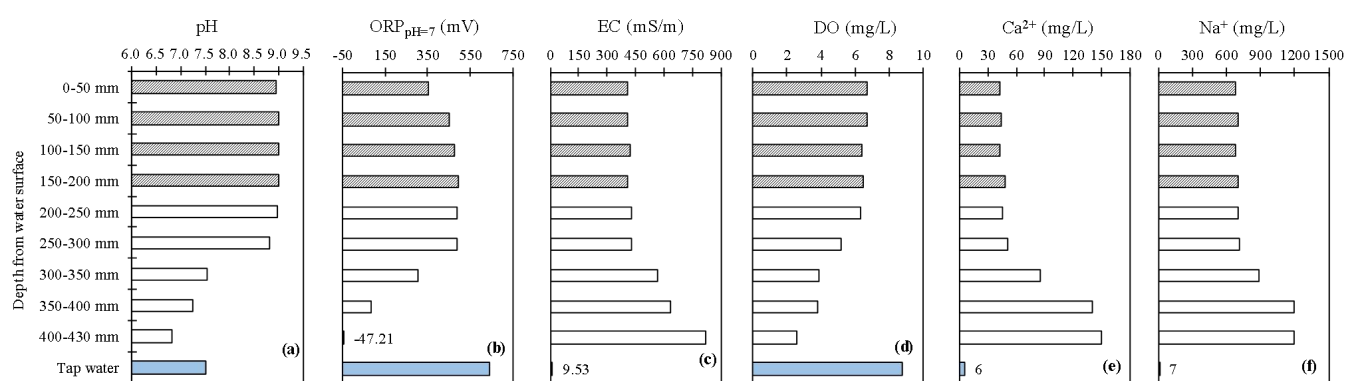


Fig. 4 Changes in water quality by SC-SMFC at the end of the experiment. pH, ORP, EC, DO,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$  were measured with an error of  $\pm 0.04$  ( $n=2$ ),  $\pm 3 \text{ mV}$  ( $n=2$ ),  $\pm 1 \text{ mS/m}$  ( $n=2$ ),  $\pm 0.1 \text{ mg/L}$  ( $n=2$ ),  $\pm 1 \text{ mg/L}$  ( $n=2$ ), and  $\pm 20 \text{ mg/L}$  ( $n=2$ ), respectively.

current that they attributed to the shortage of substrates near the anode that are used in the microbial metabolism.

The important point that should be noted here is that the variance of current density was about  $2 \text{ mA/m}^2$ , which is very small compared to the maximum current produced. It can thus be said that the solar cell can provide a stable power supply.

### B. Changes in Water Quality by SC-SMFC

As noted earlier, diffusion of reduced substances from the sediment diminishes the water quality of bottom water, for example, by decreasing DO concentration and ORP. When the cathode is installed near water surface, the deterioration of bottom water quality is reduced through electricity generation. This is because the electrons from oxidizing reduced substances at the anode can be transferred to the cathode and react with oxygen in the surface water that is continuously supplied from the air.

Figure 4 shows the profile of some parameters of water quality at the end of experiment. As ORP is a function of pH, the modified ORP at  $\text{pH}=7$  ( $\text{ORP}_{\text{pH}=7}$ ) was used instead of the measured ORP. Furthermore, the cathode region was in a range of 0–200 mm from the water surface.

As can be seen in Fig. 4a, the pH of tap water was 7.5. This decreased to 6.8 near the sediment surface and increased to 8.9 in the cathode region. The decreasing pH near the sediment surface was partly due to the proton diffusion from the sediment, while the increasing pH was partly due to the cathode reactions (i.e., oxygen reduction,  $4e^- + \text{O}_2 + 2\text{H}^+ \rightleftharpoons 2\text{OH}^-$ ). In the cathode region, no pH gradient was formed, but a higher pH was observed below the cathode region. It can be said that the water below the cathode region is also influenced by the diffusion of hydroxyl ions from the cathode region.

The EC of tap water was  $9.53 \text{ mS/m}$  and increased to  $818 \text{ mS/m}$  near the sediment surface due to the ion diffusion from the sediment (Fig. 4c). A concentration gradient is often formed by diffusion. Our result, however, showed no concentration gradient between 0 and 300 mm depth from the water surface (the cathode region). This may be partly due to the precipitation of metal ions resulting from the increase in pH (the adsorption between metal ions and other ions). It can be also confirmed from Figs. 4e and 4f that the concentrations of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  were low between 0 and 300 mm depth from the water surface.

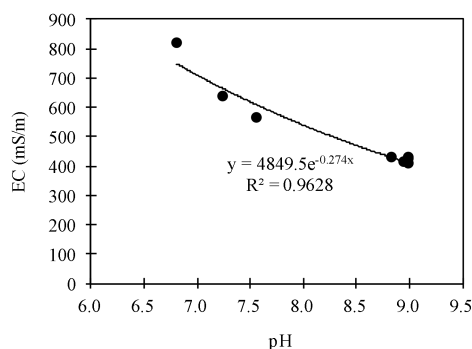


Fig. 5 Relationship between pH and electrical conductivity (EC)

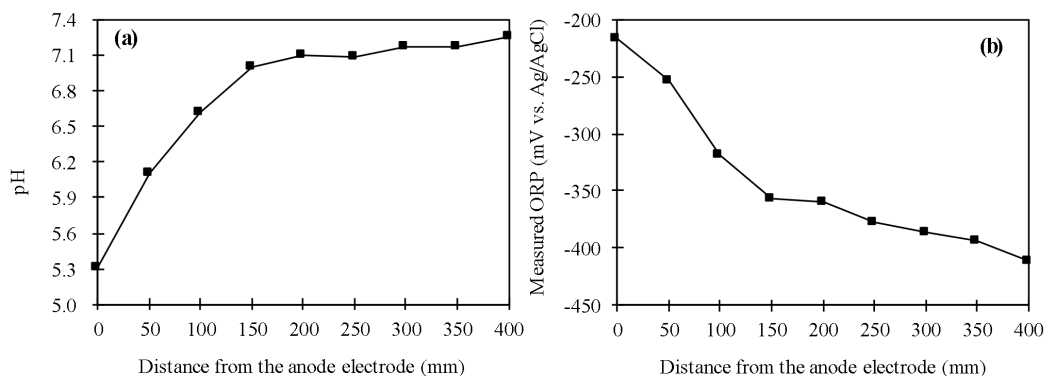


Fig. 6 Distributions of pH and measured ORP in the sediment at the end of the experiment. 0 refers to the anode of SC-SMFC

The relationship between pH and EC (Fig. 5) showed a strong negative correlation between the increasing pH and the decreasing EC ( $R^2 = 96\%$ ), suggesting the precipitation of metal ions resulted from the increase of pH.

Diffused substances from the sediment are not only metal ions but also reduced substances that consume dissolved oxygen in the water column, lowering the ORP of the water column. The  $ORP_{pH=7}$  and DO concentration of tap water were 640 mV and 8.72 mg/L and decreased to  $-47$  mV and 2.58 mg/L near the sediment surface, respectively. According to our previous report [9], the  $ORP_{pH=7}$  of overlying water (50 mm from the sediment surface) was almost the same as that of the sediment (lower than  $-350$  mV) in the cases without electricity generation.

In the cases with electricity generation, the  $ORP_{pH=7}$  of overlying water was in a range of  $-25$  to  $-230$  mV, corresponding to the period of electricity generation [9]. The  $ORP_{pH=7}$  in this present study was in the same order of magnitude ( $-47$  mV, Fig. 4b), indicating that electricity generation by SC-SMFC can improve water quality when a cathode is suspended near the water surface. As electrons in the sediment were transferred through the electrodes to consume oxygen near the water surface, the DO concentration near the sediment surface remained higher than 2.5 mg/L, as shown in Fig. 4d. The most remarkable finding to emerge from the results is that SC-SMFC can reduce the deterioration of bottom water quality caused by deposited sediments.

### C. Effective Distance of the Anode

Since the effective distance of the anode of an SC-SMFC is required for designing SC-SMFC in the field, the effective distance was examined. Many approaches exist for examining the effective distance, however, the widely used parameters, pH and ORP, were used in this study. The reason behind choosing these parameters is that pH and ORP are directly influenced by oxidation reactions at the anode. Protons are released during the oxidation of organic and inorganic matter at the anode (for example,  $H_2S$  oxidation:  $H_2S \rightarrow S + 2H^+ + 2e^-$ ). As other cations have a higher concentration than the proton concentration in sediment, proton diffusion to overlying water is restrained, leading to the decrease in sediment pH. In addition, the oxidation of electron donors (some of reduced substances) causes an increase of electron acceptors (oxidants). This increases the sediment ORP, as following to the Nernst equation. More detailed information concerning the decreasing pH and increasing ORP in sediments by electricity generation can be also found in the reports by Touch et al. [10], Choi et al. [15], and Sturm et al. [16]. As such, the effective distance can be examined based on the decrease in pH and the increase of ORP.

Figure 6 shows the distributions of pH and measured ORP in the sediment at the end of experiment. As the anode potential varied according to the current variation, several types of oxidation reactions occurred in the sediment. Therefore, it is difficult to modify the measured ORP to  $ORP_{pH=7}$ . As such, the measured ORP was used.

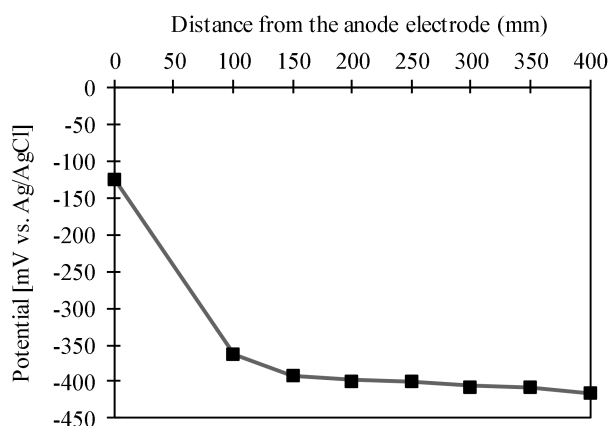


Fig. 7 Sediment potential distribution during electricity generation (at 75 days). The potential was measured with an error of  $\pm 0.001$  V

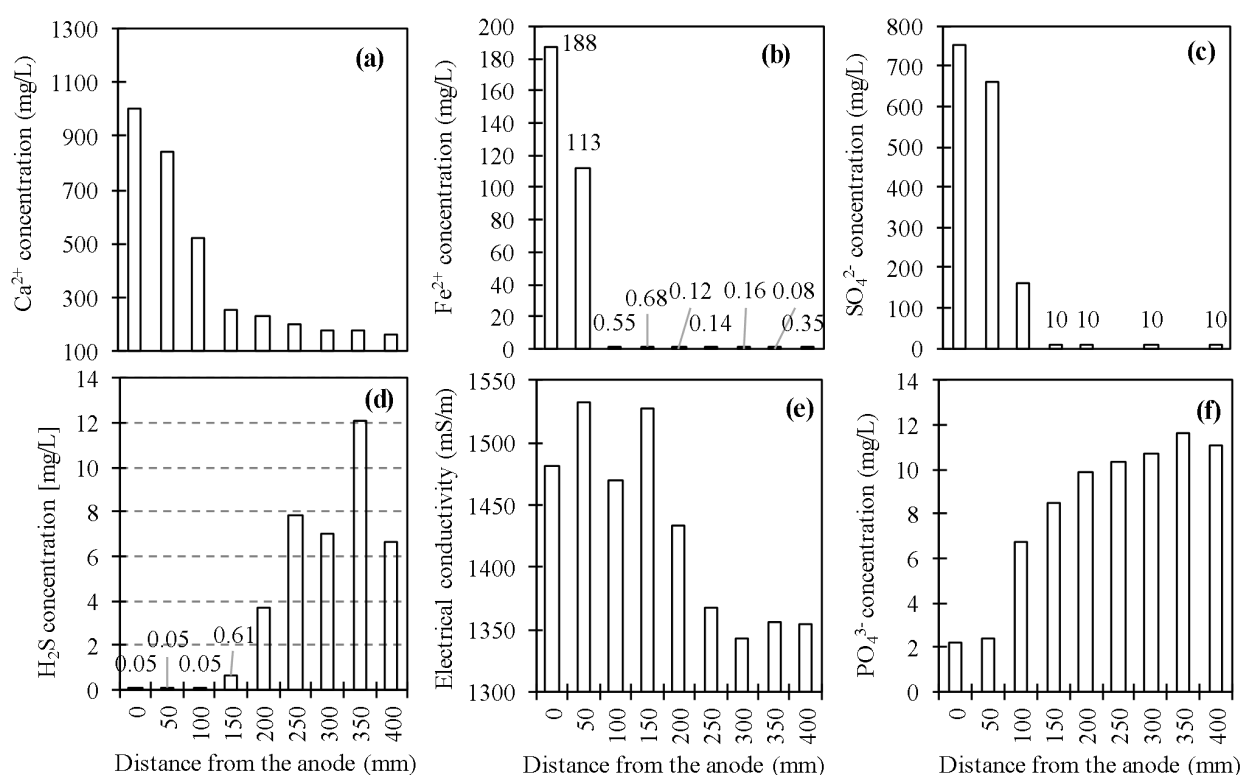


Fig. 8 Concentration distributions of some major ions in the pore water of sediments at the end of the experiment. 0 refers to the anode electrode.  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{S}$ , and  $\text{PO}_4^{3-}$  were measured with an error of  $\pm 0.01$  (n=2),  $\pm 4$  mS/m (n=2),  $\pm 0.01$  mg/L (n=2), and  $\pm 0.02$  mg/L (n=2), respectively.

The pH of the sediment located between 200 mm and 400 mm from the anode were in a range of 7.10–7.25 (Fig. 6a). The starting point of large decreases in pH was found in the sediment located 150 mm from the anode. The sediment pH decreased from 7 to 5.3 between 150 mm and 0 mm from the anode. The pH gradient between the sediments near and far from the anode caused the diffusion of protons from the anode, which partly contributed to the observed pH distribution.

These results indicated that the sediment in a range of 0–150 mm from the anode was strongly influenced by electricity generation. Similarly, Fig. 6b also showed that the starting point of large increases in the sediment ORP was found in the sediment at a distance of 150 mm from the anode. The sediment ORP increased from  $-357$  mV to  $-217$  mV between 150 mm and 0 mm from the anode. This also denotes that the sediment in a range of 0–150 mm from the anode is strongly influenced by electricity generation, which is in good agreement with the suggestion from the pH distribution.

Figure 7 shows the sediment potential distribution during electricity generation (at 75 days). It should be noted here that the potential was measured using the carbon electrodes (60 mm  $\times$  60 mm) that were inserted into the sediment layer at intervals of 50 mm. The potential at 50 mm from the anode was omitted from the figure because it accidentally connected to the anode (the

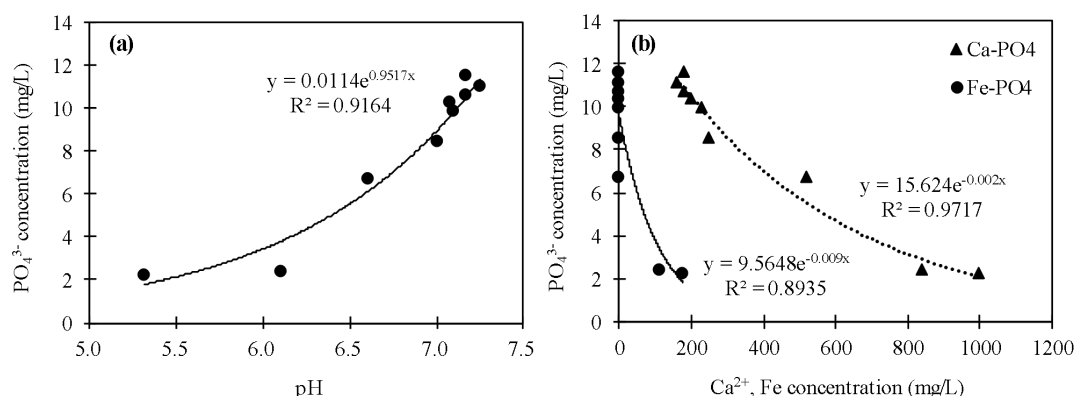


Fig. 9 Relationships among pH,  $\text{Ca}^{2+}$ , Fe, and  $\text{PO}_4^{3-}$  concentrations. The Fe ion concentration was measured with an error of  $\pm 0.02$  mg/L.

potential was the same as that of the anode). It can be confirmed from Fig. 7 that a large increase in the potential also started at 150 mm from the anode during electricity generation. This is coincident with the suggestions from the pH and ORP distributions.

In summary, our results showed that the sediment located in a range of 0–150 mm from the anode was strongly impacted by SC-SMFC. Previously, Nagatsu et al. [17] reported that the effective distance of using SMFC alone was about 75 mm. Consequently, the effective distance of SC-SMFC was 2-fold larger than that of SMFC. Thus, it can be said that the sediment remediation by SMFC can be increased through the addition of a solar cell to the SMFC system (i.e., SC-SMFC).

#### D. Changes in the Quality of Sediment Pore Water by SC-SMFC

The  $\text{Ca}^{2+}$  concentration in the sediment located 400 mm from the anode was 160 mg/L, and increased towards the anode. The starting point of large increase in the  $\text{Ca}^{2+}$  concentration was observed in the sediment located 150 mm from the anode. The sediment  $\text{Ca}^{2+}$  concentration increased from 250 to 1000 mg/L between 150 mm and 0 mm from the anode (Fig. 8a). Similarly, increasing  $\text{Fe}^{2+}$  concentration was also observed in the sediment located between 0 and 150 mm from the anode (Fig. 8b).

The  $\text{Fe}^{2+}$  concentration was 0.08 mg/L (TABLE 1), increased to 0.68 mg/L in the sediment located 150 mm from the anode, and to 188 mg/L in the sediment located in the immediate environment of the anode. The EC in the sediment located between 0 and 150 mm from the anode also increased (Fig. 8e). Based on these results, it is thought that dissociation of calcium and iron complexes occurred in the sediment during electricity generation. The reason behind the dissociation is may be partly due to the decrease in pH. In the course of sedimentation, organic matter or other ions adsorb to each other as complex molecules, depositing in the sediment. The stability of a complex molecule depends on pH, in which a decreasing pH makes a complex molecule unstable and leads to its dissociation. Hence, the decreasing pH resulting from electricity generation is considered to cause the dissociation of calcium and iron complexes.

Moreover, it was also found that  $\text{H}_2\text{S}$  concentrations largely decreased in the sediment near the anode (Fig. 8d). The  $\text{H}_2\text{S}$  concentration in the sediment that was located at over 250 mm from the anode was about 8 mg/L, decreased to 0.61 mg/L in the sediment located 150 mm from the anode, and to less than 0.05 mg/L in the sediment located between 0 and 100 mm from the anode.  $\text{H}_2\text{S}$  is one of the toxic components found in the biological environment, which should be removed from the sediment. It is thought that SC-SMFC can remove  $\text{H}_2\text{S}$  from the sediment, leading to an improvement in the biological environment. The removal of  $\text{H}_2\text{S}$  occurred due to the oxidation of  $\text{H}_2\text{S}$  at the anode (for example,  $\text{H}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^-$ ), which is in good agreement with the previous report by Ieropoulos et al. [18], who demonstrated that 70–80% of electricity generation from sediments was due to sulfate/sulfide reactions. It was also confirmed from our results that sulfate ( $\text{SO}_4^{2-}$ ) concentrations largely increased in the sediments where concomitant large decreases in  $\text{H}_2\text{S}$  concentrations were found (Fig. 8c).

Furthermore, phosphate ( $\text{PO}_4^{3-}$ ) concentrations also decreased towards the anode. The  $\text{PO}_4^{3-}$  concentration was about 9.9 mg/L, decreased to 8.5 mg/L in the sediment located 150 mm from the anode, and to 2.2 mg/L in the sediment located near the anode (Fig. 8f).  $\text{PO}_4^{3-}$  is a contributor to eutrophication when it diffuses into a water body. Thus, fixing  $\text{PO}_4^{3-}$  in the sediment is a means to protect the water environment from eutrophication. The removal of  $\text{PO}_4^{3-}$  is not directly caused by the anode oxidation. In fact, the decreasing pH resulting from anode oxidation releases  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  (dissociation of calcium and iron complexes), as discussed earlier. Hence,  $\text{PO}_4^{3-}$  is considered to be removed through the fixation of  $\text{PO}_4^{3-}$  by  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$ , for example through the formation of  $\text{Fe}_3(\text{PO}_4)_2$  and  $\text{Ca}_3(\text{PO}_4)_2$ .

To provide more evidences relating to the fixation of  $\text{PO}_4^{3-}$ , the relationships among  $\text{PO}_4^{3-}$ , pH,  $\text{Ca}^{2+}$ , and Fe concentrations were examined, as shown in Fig. 9. A strong correlation ( $R^2 > 91\%$ ) between pH and  $\text{PO}_4^{3-}$  concentration was found, in which

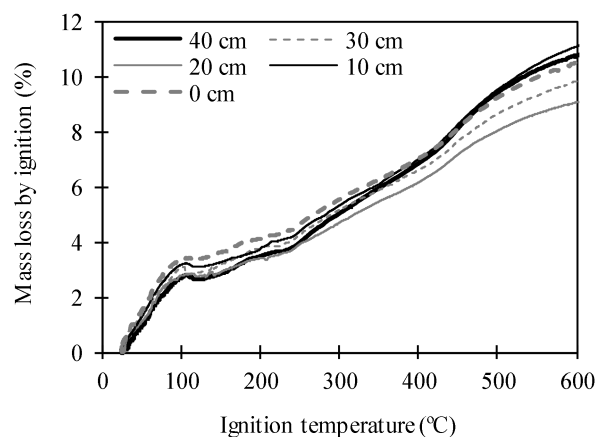


Fig. 10 Mass loss by ignition of sediments. The mass loss on ignition was measured with an error of  $\pm 0.5\%$

$\text{PO}_4^{3-}$  decreased with decreasing pH (Fig. 9a). In addition, strong colorations among  $\text{Ca}^{2+}$ , Fe, and  $\text{PO}_4^{3-}$  were also confirmed (Fig. 9b), supporting the fixation of  $\text{PO}_4^{3-}$  by Fe and  $\text{Ca}^{2+}$ . The important point to note here is that SC-SMFC can be used as a technology to fix  $\text{PO}_4^{3-}$  in the sediment, thus reducing the  $\text{PO}_4^{3-}$  diffusion from the sediment into the water body.

#### E. Decomposition Characteristics of Organic Matter

To understand the characteristics of organic matter decomposition, the mass loss by ignition of sediments were investigated (Fig. 10). Each sediment location showed a different ignition characteristic. A higher mass loss by ignition in the temperature range of 100–300°C was observed in the sediment located near the anode as compared to the sediment located 400 mm from the anode. Interestingly, the mass loss in the sediment located 200 mm from the anode, occurring in the temperature range of 300–600°C, largely decreased.

It should be noted that the variation in mass loss on ignition refers to changes in the organic matter state in sediment, in which the decrease and the increase of mass loss indicates mineralization and formation of organic matter, respectively. Based on the variation observed in the ignition characteristics, it is believed that the mineralization of organic matter burned at 300–600°C is enhanced in the sediment located 200 mm from the anode, and the organic matter burned at 100–300°C was produced in the sediment near the anode. In other words, the organic matter decomposition was enhanced by electricity generation in the sediment located at around 200 mm from the anode and was restrained near the anode. The restriction of organic matter decomposition may be partly due to the large decreases in pH.

It has been noted that the activity of anaerobic microorganisms (i.e., sulfate-reducing bacteria) decreases when pH is below 6.5 [19]. It could be confirmed from Fig. 6a that the pH of the sediment located near the anode was lower than 6.5. On the other hand, as there was no re-supply of organic matter into the sediment, the increasing organic matter burned at 100–300°C results from the dissociation of calcium and iron complexes. As noted earlier, increases in  $\text{Ca}^{2+}$  and Fe concentrations were also confirmed near the anode, thus it is thought that the organic matter that adsorbed with  $\text{Ca}^{2+}$  and Fe are dissociated from calcium and iron complexes. Organic matter present in metal complexes is generally difficult to decompose. Therefore, the dissociation of organic matter from metal complexes may be useful in enhancing sediment remediation following electricity generation.

#### IV. CONCLUSIONS

Laboratory experiments were conducted to understand the current generation characteristics, the effective distance of anode, and sediment remediation when a solar cell was combined into the system of SMFC. The results suggested that the solar cell could be used as an external power supply because it can provide a stable current variation over a long-term operation. Furthermore, the application of SC-SMFC into sediment when the cathode is suspended near the water surface could reduce the deterioration of bottom water quality, for example by lowering depletions of DO concentration and ORP. Based on the pH, ORP, and potential distributions, large variations of these parameters occurred in the sediments located between 0 mm and 150 mm from the anode, indicating that the effective distance of the anode of SC-SMFC was 150 mm, which 2-fold higher than that of using SMFC alone. The oxidation of organic and inorganic matter at the anode increased ORP and decreased the pH of the sediment. Large decreases in pH near the anode caused the dissociation of calcium and iron complexes, producing organic matter burned at 100–300°C. However, the decomposition of organic matter in the sediment located near the anode was restrained. Fortunately, the SC-SMFC application can enhance the mineralization of organic matter burned at 300–600°C in the sediment located at around 200 mm from the anode. Further, SC-SMFC can fix  $\text{PO}_4^{3-}$  in the sediment and remove  $\text{H}_2\text{S}$  from the sediment. It can be concluded that our developed SC-SMFC can be an alternative technology for improving both sediment and water environments.



## ACKNOWLEDGMENT

The authors gratefully acknowledge partially funding from the Japan Society for the Promotion of Science: Grant-in-Aid for Science Research [Grant number 16K18158] and [Grant number 16H04418]. The useful comments of anonymous reviewers are also appreciated.

## REFERENCES

- [1] W. R. Martin, "Chemical Processes in Estuarine Sediments," In: John HS, Karl KT, Steve AP (eds.) *Encycl Ocean Sci.*, Elsevier, pp. 539-550, 2009.
- [2] J. J. Wright, K. M. Konwar, and S. J. Hallam, "Microbial ecology of expanding oxygen minimum zones," *Nat Rev Microbiol.*, vol. 10, pp. 381-394, 2012.
- [3] K. H. Kim, T. Hibino, T. Yamamoto, S. Hayakawa, Y. Mito, K. Nakamoto, and I. C. Lee, "Field experiments on remediation of coastal sediments using granulated coal ash," *Mar. Pollut. Bull.*, vol. 83, no. 1, pp. 132-137, 2014.
- [4] T. Yamamoto, K. H. Kim, K. Shirono, "A pilot study on remediation of sediments enriched by oyster farming wastes using granulated coal ash," *Mar. Pollut. Bull.*, vol. 90, pp. 54-59, 2015.
- [5] S. T. Oh, J. R. Kim, G. C. Premier, T. H. Lee, C. Kim, and W. T. Sloan, "Sustainable wastewater treatment: How might microbial fuel cells contribute," *Biotechnol. Adv.*, vol. 28, pp. 871-881, 2010.
- [6] N. J. Sacco, E. L. M. Figuerola, G. Pataccini, M. C. Bonetto, L. Erijman, and E. Cortón, "Performance of planar and cylindrical carbon electrodes at sedimentary microbial fuel cells," *Bioresour. Technol.*, vol. 126, pp. 328-335, 2012.
- [7] N. Touch, T. Hibino, Y. Nagatsu, and K. Tachiuchi, "Characteristics of electricity generation and biodegradation in tidal river sludge-used microbial fuel cells," *Bioresour. Technol.*, vol. 158, pp. 225-230, 2014.
- [8] T. K. Sajana, M. M., Ghangrekar, and A. Mitra, "Application of sediment microbial fuel cell for in situ reclamation of aquaculture pond water quality," *Aquacult. Eng.*, vol. 57, pp.101-107, 2013.
- [9] N. Touch, N. Kinjo, K. Tachiuchi, S. Nakashita, and T. Hibino, "Development of a method for improving reduced environment of the sludge deposited in estuarine regions," *J. Jpn. Soc. Civ. Eng. Ser. B1 (Hydraul. Eng.)*, vol. 71, pp. 697-702, 2015. (in Japanese)
- [10] N. Touch, T. Hibino, S. Nakashita, and K. Nakamoto, "Variation in properties of the sediment following electrokinetic treatments," *Environ Technol.*, vol. 38, no. 3, pp.277-284, 2017.
- [11] Y. Nagatsu, K. Tachiuchi, N. Touch, and T. Hibino, "Factors for improving the performance of sediment microbial fuel cell," *J. Jpn. Soc. Civ. Eng. Ser. B2 (Coast. Eng.)*, vol. 70, no. 2, pp. 1066-1070, 2014. (in Japanese)
- [12] X. Wang, Y. Feng, N. Ren, H. Wang, H. Lee, N. Li, and Q. Zhao, "Accelerated start-up of two-chambered microbial fuel cells: Effect of anodic positive poised potential," *Electrochem. Acta*, vol. 54, no. 3, pp. 1109-1114, 2009.
- [13] T. S. Song, and H. L. Jiang, "Effects of sediment pretreatment on the performance of sediment microbial fuel cells," *Bioresour. Technol.*, vol. 102, pp. 10465-10470, 2011.
- [14] D. R. Bond, D. E. Holmes, L. M. Tender, and D. R. Lovley, "Electrode-reducing microorganisms that harvest energy from marine sediments," *Science*, vol. 295, pp. 483-485, 2002.
- [15] J. H. Choi, S. Maruthamuthu, H. G. Lee, T. H. Ha, J. H. Bae, and A. N. Alshawabkeh, "Removal of phosphate from agricultural soil by electrokinetic remediation with iron electrode," *J. Appl. Electrochem.*, vol. 40, pp. 1101-1111, 2010.
- [16] G. Sturm, H. Weigand, C. Marb, W. Weiß, and B. Huwe, "Electrokinetic phosphorus recovery from packed beds of sewage sludge ash: yield and energy demand," *J. Appl. Electrochem.*, vol. 40, pp. 1069-1078, 2010.
- [17] Y. Nagatsu, N. Touch, T. Nakaoka, and T. Hibino, "Influenced distance of anode electrode on sediment remediation in a sediment microbial fuel cell," in *Proc. MFC4*, Cairns (Australia) 2013, pp. 186-187.
- [18] I. Ieropoulos, J. Greenman, C. Melhuish, and J. Hart, "Energy accumulation and improved performance in microbial fuel cells," *J. Power Sources*, vol. 145, pp. 253-256, 2005.
- [19] S. Al-Zuhair, M. H. El-Naas, and H. Al-Hassani, "Sulfate inhibition effect on sulfate reducing bacteria," *J. Biochem. Tech.*, vol. 1, pp. 39-44, 2008.



**Narong Touch** is an assistant professor at the Department of Civil and Environmental Engineering, Hiroshima University (Hiroshima, Japan). He received his Bachelor, Master, and Doctor degrees in Engineering from Hiroshima University in 2008, 2010, and 2013, respectively. He was a Research Fellowship for Young Scientists of Japan Society for the Promotion of Science during 2010–2013.

He has been involved in the development and application of environmental materials, for example the development and application of granulated coal ash for water purification and sediment remediation. His other research interests are resource recovery, specifically converting sediment into natural resources, recovering electricity from sediment through sediment microbial fuel cells, and developing electrochemistry technologies for sediment and wastewater treatments.

In addition to his research activities, he is a research supervisor of students in Bachelor and Master courses, belong to Coastal Engineering Laboratory, Hiroshima University. He is a member of Japan Society of Civil Engineers, and a reviewer of international journals. He has been granted three awards from international conference communities, two awards from Hiroshima University, one award from Japan Society of Civil Engineers, and one award from the mayor of Osaka City (Osaka, Japan).