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Electrochemical Control of Methane Emission from Lake Sediment Using Microbial Fuel Cells

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Recently, a significant amount of attention has been focused on greenhouse gases in order to help satisfy the ever-increasing demand for global warming prevention technology and environmental control.[1-3] In the context of global warming, several trace gases, such as methane (CH_4), nitrous oxide (N_2O), and ammonia (NH_3), are drawing attention because of their radiative and chemical effects in the atmosphere.[4] Among the trace gases, methane is known to be 20-25 times more effective per molecule than CO_2 as a greenhouse gas.[5] Therefore, the prevention of methane emission from the environment has the potential to play an important role in climate change. In general, methane is produced when organic material decomposes under anoxic conditions in the presence of CO_2 as inorganic electron acceptor, notably from bacterial decay of waste and sewage, fermentative digestion by ruminants, and bacterial degradation of organic matter in wetlands.[2,3] Methanogenesis is the terminal step in microbial organic matter decomposition, and it can be found in a wide variety of anaerobic environments.[6] Although the methanogens are known to be quite susceptible to abrupt changes in cultural environments, such as heat or air exposure or acid/base treatment, they are potentially ubiquitous in anoxic ecosystems containing organic matter. Therefore, the control of methane emission from various ecosystems has been the focus of increased attention, as the methane concentration is increasing at a faster rate than that of carbon dioxide.[3]

A number of methods for mitigating methane emissions from various environments, including wetlands, have been developed. To reduce the CH_4 generation in conventional lake or swamp sediments, a variety of methods have been proposed, including ultrasonication, O_2 feeding, heat treatment, and acid/base treatment of the sediment.[7] Other possible practical mitigation options are water management, soil amendments, organic matter management, different tillage practices, rotation, and cultivar selection.[8] The direct addition of external inorganic electron acceptors such as SO_4^{2-}, Fe^{3+}, or Mn^{4+} to the wetland has also been suggested.[9] In this method, the addition of external inorganic electron acceptors decreased the methane emission rate from the wetland by decreasing the metabolic activity of the methanogens through metabolic competition of the methanogens with other microorganisms.[9,10] However, according to an experimental result on these external electron acceptors, considerably high concentrations of the inorganic acceptors (about 2-20 Mg per ha of wetland) were required to suppress the methane emission from a given environment.

Recently, sediment microbial fuel cells (SMFCs) have been successfully operated in lake and marine environments.[11] In a previous study, an SMFC using lake sediment as an electron donor for electrochemically active bacteria was examined, and it was determined that this method could be used to successfully reduce the organic matter content of the sediment.[12] It has been found that consortia of bacteria are responsible for providing electrical power to SMFCs *via* transfer of electrons from the oxidized organic matter to an anode. Experimental research has also demonstrated that the high Coulombic yield (*i.e.*, high electrical current) from a microbial fuel cell (MFC), which is based on the rapid oxidation of organic matter under low external resistance, can suppress methanogenesis.[6,13,14] These experimental results indicate that the electrochemical control of methanogenesis using an SMFC is possible, although the application of SMFCs in a practical environment has not yet been studied.

In the present study, we demonstrate the electrochemical control of methane emission from a hypereutrophic lake using an SMFC system capable of electrical current generation. This study was divided into two parts. First, using SMFCs that were installed in the lake sediment, the polarization characteristics and power density from the SMFCs were measured. Second, the methane emission rate from the lake in the presence of SMFCs connected to different external resistors was estimated. To the best of the authors' knowledge, this is the first report concerning the application of SMFCs to electrochemically control methane emission from an actual hypereutrophic lake.

Experimental Procedures

Construction of SMFCs. A total of two SMFCs were

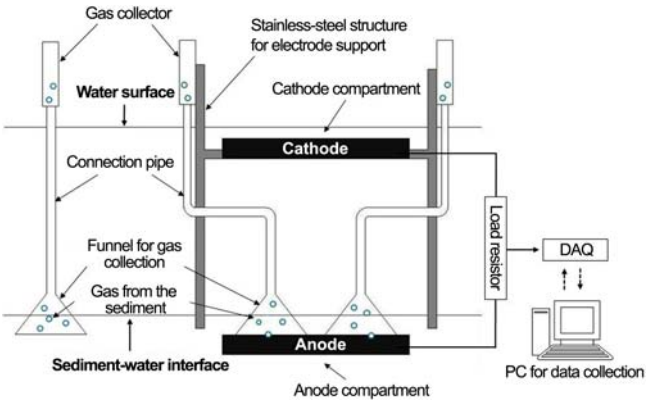

Figure 1. Schematic diagram of the SMFC system used in the study.

installed at Ilgam Lake, an artificial lake in the Seoul metropolitan area (37°32'32.24" N, 27°4'35.86" E) created in 1957. The lake is small and shallow, with a surface area of about 55,661 m^2, a mean depth of about 1.5 m, and a long hydraulic retention time of approximately 288 days. This lake is recharged by rainfall and groundwater pumped from nearby subway stations. The average amounts of organic matter in the sediment as measured using the loss on ignition (LOI) and readily oxidizable organic matter (ROOM) methods were 10.4% and 3.52%, respectively.[12] Figure 1 shows a schematic diagram of the SMFC system employed in this study. Both the anode and cathode consisted of a graphite plate (1000 × 1000 × 15 mm, IG-11, Toyo Tanso Co., Ltd., Osaka, Japan). To increase the contract of an electrode, a total of 240 holes with diameters of 12 mm were drilled in both electrodes. An electrical connection was made between the anode and cathode through PVC-insulated copper wires and stainless steel screws. All contact points were completely covered with insulating epoxy (5 Minute epoxy, Devcon, IL, USA) to prevent short-circuit. The anode was buried about 10 cm below the sediment-water interface. The cathode was positioned horizontally about 80 cm above the sediment-water interface (distance between the electrodes = *ca*. 90 cm) and 5 cm below the water-air interface. For direct collection of the gas generated from the lake sediment, four funnel-type gas collectors (d = 320 mm, *ca.* 40% of the electrode surface area) were placed on the sediment-water interface (*i.e.*, on the sediment-covered anode) and connected to a gas-sample bag (232 series, SKC, USA) *via* PVC tubes. To measure any possible effect of the buried electrode (*i.e.*, anode) on the methane generation in the sediment, an auxiliary funnel type gas collector uninfluenced by the buried electrode was also installed at the sediment-water interface 1.5 m away from the SMFC.

SMFC Operation and Methane Analysis. The SMFCs were operated for 3 months in 2011 (from July to September). At the beginning of the experimental period, each SMFC was kept under open-circuit conditions. About ten days later, a connection between the anode and cathode was made *via* external load resistors, and the current generated from each SMFC was monitored with a computer-controlled data acquisition system (DAQ, model 2700 DMM, Keithley, USA).[15] The current can be calculated from the measured voltage using Ohm's law as $I = V/R$, where I represents the current in amperes, V represents the potential difference between two electrodes in volts, and R represents the resistance measured in ohms. The SMFC operations were carried out with different load resistors to evaluate the effect of the current generation on the methane emission from the sediment. The gas generated during the operation of the SMFCs was collected by the gas collector and stored in the sample bag. The current (power) density was calculated by dividing the current (power) by the apparent surface area of each electrode. The methane from the lake area was analyzed using gas chromatography, as previously described.[16] The pH, dissolved oxygen (DO) and water temperature were measured using a water quality analyzer (model D-54, Horiba, Japan). Biochemical oxygen demand (BOD) of the water samples were analyzed by the standard method.[17] All analyses were conducted at least in duplicate.

Results and Discussion

As a preliminary experiment, the methane generation in the lake was measured from April to November in 2010 (9 months) using the auxiliary gas collector. These experimental data are shown in Figure 2. In the initial stage of experiment, when the water temperature was lower than 15 °C, no significant quantities of methane were detected from the sediment. During the summer season (June to September; average water temperature 23.5 °C), however, the methane emission from the lake-bottom sediment continually increased, reaching a maximum level in August. A number of reports have shown that temperature affects both the number and activity of the methanogens in wetlands.[18,19] In the present study, the variation of the methane emission rate from the lake sediment would be a typical result of the temperature effect on the activity and number of methanogens in the sediment. In addition, it should be noted that the operation of the SMFC, which is based on the activity of the electrochemically active bacteria, is also affected by the sediment temperature.[12] In view of these observations, the summer season (*i.e.*, July to September) was selected as the

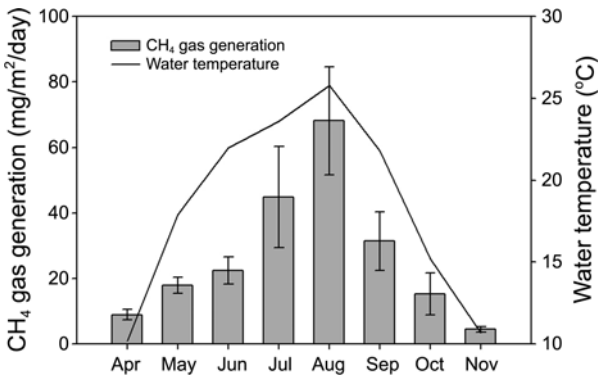

Figure 2. Methane generation rate from the lake (Apr.-Nov. 2010). This measurement was made using the auxiliary gas collector.

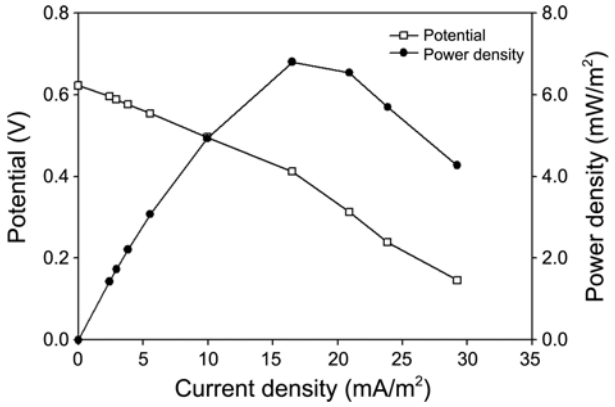

Figure 3. Polarization curves of the SMFC installed in the lake. The external resistances used in this experiment were 10, 20, 40, 50, 100, 200, 300, 400, and 500 Ω.

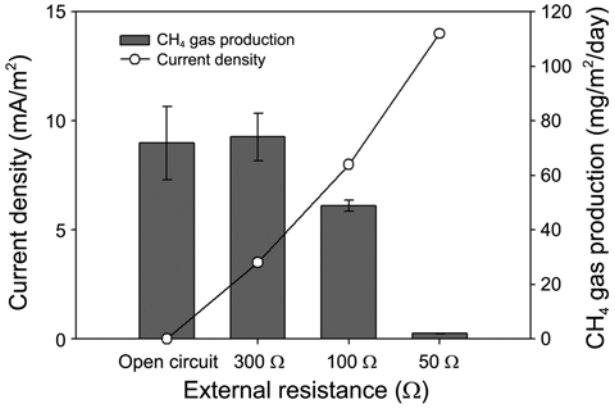

Figure 4. Effect of current density on methane generation in the lake. This experiment was performed in Aug. 2011.

most appropriate experimental period for examining the electrochemical control of methane emission from the lake using SMFCs. Average values of DO, BOD and pH of samples obtained from the water-air interface were 9 mg O_2/L , 4.26 mg/L, and 8.3, respectively.

A total of two SMFC systems were installed at the experimental site. The open-circuit potentials from both SMFCs gradually increased for 2 weeks, and they eventually achieved steady values (both *ca*. 0.62 V). When the setup of the SMFCs was completed, one SMFC system was used for the evaluation of the electrochemical characteristics, and the other SMFC system was used for evaluating the control of methane emission from the lake sediment. To estimate the electrical performance of the SMFC, the external resistance was varied from 10 Ω to 500 Ω, and the polarization characteristics of the SMFC were monitored. The results showed that the maximum power density (*ca*. 6.80 mW/m^2 anode) was obtained when a 50 Ω external resistor was used (Fig. 3). In previous research using a laboratory-operated SMFC, the methane emission from the anode compartment was inversely correlated with the current generated by the SMFC.[14] Therefore, based on the polarization curve, it can be deduced that the employment of 50 Ω of external resistance in this SMFC system would be effective for the suppression of methane emission. To verify the relationship between the power density and the methane emission from the sediment, another experiment was carried out with various external resistances. An important precaution that ensured the reproducibility of the experiment was the consideration of the organic matter concentration around the anode of the SMFC. To minimize the effect of shortages of organic matter due to the series of SMFC operations at one experimental site, a second SMFC system was set up at a different site and operated with various external resistances to control the methane emission from the lake.

Figure 4 shows the effect of the external resistance on the methane emission from the lake sediment. At the open-circuit potential, the methane emission rate (71.794 mg/m^2/day) was almost identical to that observed in a previous experiment involving an auxiliary gas collector. Therefore, this observation indicates that the potential difference between the SMFC electrodes does not affect the activity of the methanogens. When the SMFC was connected to lower resistances, a gradual decrease in the methane generation in the lake sediment was observed. In the presence of 50 Ω of external resistance, an approximately 35-fold decrease in methane emission compared to that under open-circuit operation was observed. When the lower resistances (10-40 Ω) were connected to the SMFC, almost the same methane emission rates from the lake were observed (data not shown). In this experiment, changes in the methane emission rate from the lake sediment can be attributed to the action of the anode in the sediment, that is, the oxidation of the electron donors and subsequent variations in the activity of related microorganisms.[20] Previous studies have shown that current generated by a microbial fuel cell is fully dependent on carbon oxidation (*i.e.*, metabolism) by the bacteria and that the anode of the microbial fuel cell acts as an electron acceptor for electrochemically active bacteria.[15,21] A report also showed that the enrichment of electrochemically active bacteria in sediment suppressed the activity of methanogens.[7] Therefore, the inverse correlation between decreasing methane emissions and increasing current generated by SMFCs with low levels of external resistance could be attributed to the decreased metabolic speed of the methanogens in the sediment due to the limited substrate concentration.

The authors believe that the application of SMFCs to control methane emissions from wetlands has important implications, since the greenhouse effect of methane is of great environmental concern. Further studies will be required to establish electrochemical suppression of greenhouse gas emissions under various experimental environments, including paddies, animal agricultural sites, and sewage treatment systems. In addition, to maximize the inhibition of methane emission from wetlands using electrochemical methods, the effect of temperature on the methanogens' activity will also be explored.[19] Current research in our group is focused on the optimization of SMFCs for suppressing greenhouse gases and as a renewable energy source.

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