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Wireless Sensors Powered by Microbial Fuel Cells

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Monitoring parameters characterizing water quality, such as temperature, pH, and concentrations of heavy metals in natural waters, is often followed by transmitting the data to remote receivers using telemetry systems. Such systems are commonly powered by batteries, which can be inconvenient at times because batteries have a limited lifetime and must be recharged or replaced periodically to ensure that sufficient energy is available to power the electronics. To avoid these inconveniences, a microbial fuel cell was designed to power electrochemical sensors and small telemetry systems to transmit the data acquired by the sensors to remote receivers. The microbial fuel cell was combined with low-power, high-efficiency electronic circuitry providing a stable power source for wireless data transmission. To generate enough power for the telemetry system, energy produced by the microbial fuel cell was stored in a capacitor and used in short bursts when needed. Since commercial electronic circuits require a minimum 3.3 V input and our cell was able to deliver a maximum of 2.1 V, a DC-DC converter was used to boost the potential. The DC-DC converter powered a transmitter, which gathered the data from the sensor and transmitted it wirelessly to a remote receiver. To demonstrate the utility of the system, temporal variations in temperature were measured, and the data were wirelessly transmitted to a remote receiver.

Introduction

Chemical sensors have become indispensable components of contemporary systems monitoring the quality of natural waters. Once a sensor is deployed and activated, a link to an external data storing device, such as a computer, is needed. The easiest way to connect these devices is to hardwire the sensor to a computer/data logger, but in many applications such a solution is not practical and wireless communication is recommended. Recent advances in chemical sensors, electronics, and wireless data transmission have made it possible to monitor water quality remotely and transmit the data wirelessly using telemetry systems; such systems have been successfully deployed and used. For example, chemical sensors combined with telemetry systems have been used to monitor heavy metals, such as copper and mercury (1-4);

organophosphate nerve agents (5); phenolic compounds (6); explosive 2,4,6-trinitrotoluene (TNT); and hydrazine (7). Although combining chemical sensors with telemetry systems is still mostly in the research phase, some sensors, such as temperature sensors, have been widely used in such configurations (8), and instruments that can measure temperature remotely are readily available from specialized vendors.

Typically, batteries are used to power chemical sensors and telemetry systems, but in some applications replacing batteries can be costly, time-consuming, and impractical. A possible solution to this problem is to use self-renewable power supplies, such as microbial fuel cells, which can operate for a long time using local resources. Extensive research toward developing reliable microbial fuel cells is focused mostly on selecting suitable organic and inorganic substances that can be used as sources of energy (9). Examples of such studies are as follows: Kim et al. oxidized organics (such as glucose) (10), Liu et al. used various organic matter in wastewater (11), and Cooney et al. and DeLong et al. used microbially produced sulfide oxidation as an anodic reaction (12, 13). While the number of possible anodic reactions in microbial fuel cells is practically limitless, the number of cathodic reactions available in microbial fuel cells is much less impressive, and often they are abiotic reactions, such as oxygen reduction (10, 11, 14–16), ferricyanide reduction (10, 17), and iron reduction (18).

Looking for possible microbial reactions to power microbial fuel cells deployed in natural waters, some researchers have considered harvesting energy from marine and freshwater sediments. Reimers et al. and Tender et al. oxidized reduced substances in the marine bottom sediments near Tuckerton, NJ and Raritan Bay, NJ using graphite electrodes; they reduced oxygen on the cathode (19, 20). Delong and Chandler proposed using microbial fuel cells deployed in the ocean to operate sensors and suggested the oxidation of microbially produced sulfide as the anodic reaction and the reduction of oxygen as the cathodic reaction (13).

The microbial fuel cell used in this study consisted of a sacrificial anode combined with the reduction of biomineralized manganese oxides (Figure 1) (21). The sacrificial anode was a commercially available slab of a magnesium alloy composed of more than 99% magnesium; the remaining 1% was other metals added to control the dissolution rate. The magnesium in the alloy dissolved according to the following reaction:

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$
 $E'_{pH=7.2} = -2.105 V_{SCE}$ (1)

The potential of reaction 1 is given against a standard calomel electrode (SCE). Biomineralized manganese oxides are deposited by manganese-oxidizing microorganisms forming biofilms on microbially colonized surfaces in natural waters. If manganese-oxidizing biofilms are deposited on surfaces of passive metals, the potential of these metals increases in a process called ennoblement (25, 26). It has been demonstrated that biomineralized manganese oxides can affect the rates and the mechanisms of electrochemical reactions (22-24), leading to microbially influenced corrosion of metals. When corrosion coupons made of 316 L stainless steel were left immersed in a freshwater creek, the open circuit potential of the coupons increased from -50 mV to +400 mV_{SCE} (25–27). Shortly after being exposed to the creek water, the coupons were covered with biomineralized manganese oxide (MnO₂). Since the biomineralized manganese oxide was in direct electrical contact with the stainless steel, the metal exhibited the dissolution potential of MnO₂, as shown

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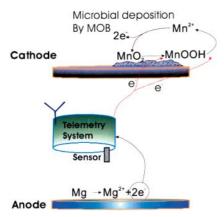


FIGURE 1. A sensor and a telemetry system powered by a microbial fuel cell. The microbial fuel cell is deployed in natural waters.

in the following reactions:

$$\label{eq:MnO2} {\rm MnO}_{2(s)} + {\rm H}^{+} + {\rm e}^{-} {\,\rightarrow\,} {\rm MnOOH}_{(s)} \quad E^{\circ} = +0.81 \; {\rm V}_{\rm SCE} \\ {E'}_{\rm pH=7.2} = +0.383 \; {\rm V}_{\rm SCE} \ \ (2)$$

$$\begin{aligned} \text{MnOOH}_{\text{(s)}} + 3\text{H}^{+} + \text{e}^{-} &\Rightarrow \text{Mn}^{2+} + 2\text{H}_{2}\text{O} \\ E^{\circ} = +1.26 \text{ V}_{\text{SCE}} \quad E'_{\text{pH}=7.2} = +0.336 \text{ V}_{\text{SCE}} \end{aligned} \tag{3}$$

The overall reaction is

$${\rm MnO_{2(s)}} + 4{\rm H^+} + 2{\rm e^-} \Longrightarrow {\rm Mn^{2+}} + 2{\rm H_2O} \quad E^{\circ} = +1.28 \; {\rm V_{SCE}} \ E'_{\rm pH=7.2} = +0.360 \; {\rm V_{SCE}} \; \; (4)$$

The potentials were calculated assuming that the concentration of $\mathrm{Mn^{2+}}$ was 1×10^{-6} M. As a result of reaction 4, manganese oxides were reduced to divalent manganese, $\mathrm{Mn^{2+}}$, by electrons released from the dissolution of magnesium. However, since the $\mathrm{Mn^{2+}}$ ions were released within the biofilm of manganese-oxidizing bacteria covering the metal surface, the manganese-oxidizing bacteria reoxidized $\mathrm{Mn^{2+}}$ ions back to manganese oxides (22), thus forming a recyclable cathodic reactant. This mechanism can lead to a particularly pervasive form of microbially influenced corrosion of stainless steel but can also be used as an efficient cathodic reaction in microbial fuel cells.

Microbial fuel cells produce only small amounts of energy, and the goal of this study was to demonstrate that by implementing an appropriate energy management program the energy generated in such fuel cells was adequate to power chemical sensors and telemetry systems such as the one shown in Figure 1.

In the microbial fuel cells described here, the magnesium anode dissolves, producing two electrons for each molecule of manganese converted to Mg²⁺. These two electrons are then used in a cathodic reaction to reduce the biomineralized manganese deposited by the manganese-oxidizing microorganisms (Figure 1). We have demonstrated that microbially deposited manganese oxides are superior cathodic reactants in microbial fuel cells (21). Having a suitable cathodic reaction, selecting an appropriate anodic reaction was the first step in the process of designing a system that could power the sensor and the telemetry system. For the application described in this paper we used a sacrificial anode made of manganese to provide the anodic reaction. The goal of the study was to demonstrate that the amount of energy produced by such devices suffices to power chemical sensors and telemetry systems; the choice of the anodic reaction was arbitrary. Before demonstrating the utility of the devices, three other challenges had to be addressed:

Challenge #1: Storing the Energy. The energy generated by the microbial fuel cell had to be accumulated and then delivered in short bursts to the sensor and to the telemetry system because microbial fuel cells could not deliver enough power to satisfy the need of the system continuously.

Challenge #2: Increasing and Controlling the Electrical Potential Generated by the Microbial Fuel Cell. Virtually all electronic components available on the market require working potentials higher than those delivered directly by microbial fuel cells. In addition, the potential of microbial fuel cells varies with time. Therefore, to power commercially available electronic components, the potential had to be increased and stabilized at an acceptable level.

Challenge #3: Restarting the System. Because the energy was accumulated and delivered in short bursts (see Challenge #1), the system had two modes of operation: the sleep mode and the active mode. Each time, before entering the active mode, the system had to be restarted.

To address the first challenge, energy produced by the microbial fuel cell was stored in an ultracapacitor, which had many advantages over using rechargeable batteries, such as a charge/discharge cycle life hundreds of thousands of times greater than that of the batteries. The ultracapacitor used had a rated lifetime of 10 yrs and a very low leakage current (about 0.28 μ A/h at 25 °C).

To address the second challenge, we used a DC-DC converter. Since powering the electronic circuits used in the telemetry system required a stable potential of 3.3 V and our cell was able to deliver a maximum of 2.1 V, the DC-DC converter was used to increase the potential to the desired level and to keep it at that level. Once the potential was increased and kept at the desired level, the system controller powered the transmitter, which acquired the data from the sensor and transmitted them to a receiver, which in turn logged the data onto a computer using a serial interface.

To address the third challenge, we used a voltage comparator to monitor the voltage level of the ultracapacitor and to turn on the DC-DC converter when a charge sufficient for transmission had been accumulated. Practically, when the microbial fuel cell potential reached 1.2 V the DC-DC converter was activated to produce a 3.3 V output, which was then applied to the transmitter. After data transmission, the energy in the capacitor was depleted, causing the potential to decrease below 1.2 V. As a result, the system switched to the idle mode until the capacitor potential reached 1.2 V, which activated the system again. Selecting 1.2 V as the potential at which the system changed its operating mode was arbitrary; the lower the selected potential, the shorter the charging time for the capacitor. However, the minimum potential at which the DC–DC converter could operate was 0.9 V, so there was not much room for varying the selected potential.

The power management system described here can be used to control a variety of sensors and telemetry systems powered by microbial fuel cells. The main principle of the power management system was that the energy generated by the fuel cell was stored in the ultracapacitor and used only when the level of the stored energy was adequate to deliver enough power to operate the sensor and the telemetry system. To demonstrate the utility of the power management system, a commercially available temperature sensor, transmitter, and receiver was used to transmit the data wirelessly to a remote receiver.

Material and Methods

The Fuel Cell. The microbial fuel cell we used is shown in Figure 1. The cell was deployed in a freshwater creek, Roskie Creek in Bozeman, MT. The cathode was located near the surface and the anode at the bottom. To make the cathode, we used 316 L stainless steel electrodes (J. W. Harris, Mason,

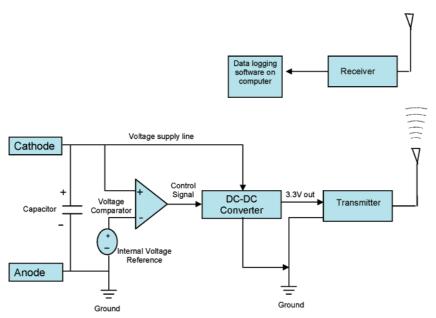


FIGURE 2. Block diagram of the telemetry system powered by the microbial fuel cell.

OH) with a 1-ft² surface area. To make sure that the cathodic reaction (which was the microbial reaction), and not the anodic reaction (which was the abiotic reaction), was limiting the current, we kept the cathode surface area constant at 1 ft² and increased the number of sacrificial anodes (surface area).

The anodes were made of a magnesium alloy (Farwest Corrosion Control Company, Gardena, CA 90248); they were cylindrical and each had a 265-cm² surface area and weighed 0.9 kg. The magnesium alloy sacrificial anodes used in this study contained aluminum 0.01% max, manganese 0.50—1.3%, copper 0.02% max, silicon 0.05% max, iron 0.03% max, nickel 0.001% max, others each 0.05% max, and the remainder, about 99%, was magnesium (specifics provided by the vendor: Farwest Corrosion Control Company, Gardena, CA 90248).

Electronics. A block diagram of the telemetry system powered by the microbial fuel cell is shown in Figure 2. All electronic components were commercially available from specialized vendors although some had to be modified to fit our needs. The capacitor used was manufactured by Maxwell Technologies (9244 Balboa Avenue, San Diego, CA 92123 http://www.maxwell.com). It was rated at 4 farad @2.5 V. The DC-DC converter was the max1797evkit manufactured by Maxim Semiconductor (120 San Gabriel Drive, Sunnyvale, CA 94086, www.maxim-ic.com) (Figure 3). The DC-DC converter provided by the vendor was modified to (1) increase the output potential to $3.3\,\mathrm{V}$ (as explained above, the potential of the fuel cell was lower than 3.3 V); (2) automatically power up the system when the capacitor voltage reached 1.2 V (when enough energy was accumulated in the system, the sensor and telemetry system operated automatically); and (3) keep the output voltage constant at 3.3 (the potential of our fuel cell varied between 1.55 and 2.2 V).

The circuit in Figure 3 accepts a variable or constant input voltage in the range of 0.9 V to 5.5 V and delivers a stable output at 3.3 V. The shutdown (SHDN) pin acted as an onoff switch for the output. Applying a voltage higher than 1.2 V to the SHDN pin forced the device into shutdown, and when the SHDN pin was grounded, the device was activated. The voltage level on the SHDN pin was controlled by the voltage comparator, which was built into the chip.

A voltage comparator was used to compare the external voltage level against a reference and then produce a binary

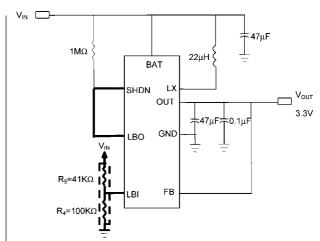


FIGURE 3. The modified DC-DC converter. The modifications are marked with a thicker line.

output indicating whether the input voltage had reached the set voltage level. The onboard comparator was activated by removing the connection between the pads of resistor R_5 and inserting resistors R_4 and R_5 , whose values depended upon the voltage chosen to activate the comparator ($V_{\rm level}$). Choosing R_4 as 100 k Ω and $V_{\rm level}$ as 1.2 V, R_5 was 41 k Ω , calculated from the following equation which was obtained from the max1797 datasheet (http://pdfserv.maxim-ic.com/en/ds/MAX1795-MAX1797.pdf):

$$R_5 = R_4 \left(\frac{V_{\text{level}}}{0.85} - 1 \right) \tag{5}$$

After resistors R_4 and R_5 were inserted onto the board, the low battery output (LBO) pin was connected to the SHDN pin, enabling the voltage comparator and thus completing the circuit. The anode and cathode of the microbial fuel cell were connected to pins $V_{\rm IN}$ and GND, respectively, and $V_{\rm OUT}$ and GND were connected to the positive and negative pins of the transmitter, respectively.

Transmitter, Receiver, and Sensor. The transmitter used was an off-the-shelf thermocouple/transmitter/receiver kit manufactured by MadgeTech, Inc. (201 Route 103 West, P.O. Box 50, Warner, NH 03278; www.madgetech.com/index.php).

It transmits at a frequency of 418 MHz and has a maximum transmission distance of 100 ft. The thermocouple used was a J-type thermocouple that could measure temperature in the range from -200 °C to 1190 °C. The transmitter was manually activated using a push-button switch when the system ran for the first time. Later on, the system restarted automatically when the fuel cell potential went above (run mode) or below 1.2 V (sleep mode). The receiver, also manufactured by MadgeTech, Inc. (RFC101), was connected directly to the serial port of a computer, and all data received were decoded using Windows-compatible software (Madge Tech data logging software version 2.00.41) by MadgeTech, Inc. All data received were date- and time-stamped and could be printed in graphical or tabular format and exported to a spreadsheet or a text file. The push-button switch was connected directly to the ground, allowing the transmitter to be activated when the DC-DC converter was turned on. When needed, the transmitter could be set to operate at predefined time intervals, for example, every 30 min. In our setup the frequency of data transmission was dependent upon the power generated by the microbial fuel cell and the energy stored in the capacitor. When there was not enough energy, data acquisition and transmission were delayed, and the system waited in idle mode, until the capacitor was charged.

Remote Measurement of the Temperature. To demonstrate that microbial fuel cells could deliver enough energy to operate the sensor and the telemetry system, the setup shown in Figure 2 was assembled to power a sensor to measure air and water temperature and to transmit the data to a remote receiver. The thermocouple, the temperature measurement unit, and the transmitter were all powered by the microbial fuel cell. To generate energy, a microbial fuel cell was assembled and deployed in a freshwater creek, Roskie Creek in Bozeman, MT. Stainless steel coupons (the cathodes) were deployed first, and we waited until their potential increased above 300 mV_{SCE}. This was followed by deploying the magnesium alloy sacrificial anode, assembling the fuel cell, and connecting it to the system shown in Figure 2. For demonstration purposes, temperature was measured, and the data were transmitted to a remote receiver. The receiver was connected to a laptop computer (IBM T41) located at a distance less than 100 ft from the transmitter. To verify that the measured and transmitted data were correct, the air temperature was also measured using a mercury thermometer, and the results were compared. Since temperature variations were negligible during the short times of the measurements, we have occasionally placed the thermocouple in a beaker filled with ice water.

Results and Discussion

As described above, the system was assembled step by step, starting from the fuel cell. The 316 L stainless steel plates used to deposit biomineralized manganese oxides exhibited an initial potential of $-50~\text{mV}_{\text{SCE}}$, and after approximately 2-3 weeks exposure to the creek water the potential increased to almost $+400~\text{mV}_{\text{SCE}}$, which is consistent with our previous observations (21, 24) and with thermodynamic calculations. After the cathodic potential reached the desired level of +400~mV, we deployed the magnesium alloy sacrificial anodes, connected the microbial fuel cell to the circuit in Figure 2, and left it for 3 weeks. During that time, the potential of the sacrificial anode varied between $-1.6~\text{and}~-1.8~\text{V}_{\text{SCE}}$. The variations in anode potential can be ascribed to the changing chemistry of water and the attached deposits on the surface of the electrode.

To evaluate the amount of energy generated by the microbial fuel cell, its short-circuit current was measured by directly connecting the anode to the cathode. When the cell was short-circuited, the entire measured current was caused

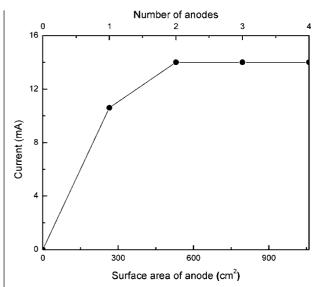


FIGURE 4. Current versus anode surface area. The current increases with increasing anode surface and reaches a plateau when the current is limited by the cathode.

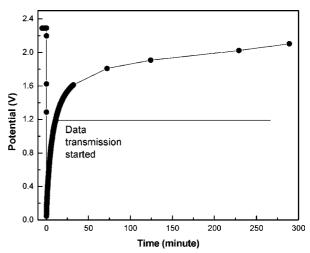


FIGURE 5. Capacitor charge curve obtained from the microbial fuel cell deployed in Roskie Creek.

by the dissolution of the sacrificial anode on one side and reduction of the biomineralized manganese oxides on the other side of the cell. As described above, the cell was designed so that the current was limited by the cathodic reaction. During the pseudo-steady state (lasting for over 10 min) the current was 14 mA, and the current density with respect to the surface of the cathodes was $3.9\,\mu\text{A/cm}^2$. The short-circuit current was almost constant for over 10 min, and then it decreased slowly, at a rate of 0.1 mA during 10 min. We explain the existence of the pseudo-steady state by the microbiology-stimulated recycling of the cathodic reactant, MnO₂.

As described above, to make sure that the cathodic reaction was limiting the current, the number of anodes (i.e. the surface area) was increased until the current reached a plateau. The plot of the measured current versus the number of sacrificial anodes is shown in Figure 4, which shows that the cell current was limited by the cathode when the anode surface area exceeded 570 cm 2 (which was equivalent to 1.8 kg of the anode).

Charging the Capacitor and Starting the System. A charge curve for the capacitor is shown in Figure 5. When the potential of the fuel cell reached 2.1 V, the capacitor was

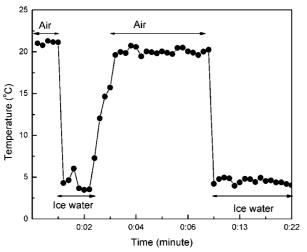


FIGURE 6. Wirelessly transferred temperature data.

connected to the circuit to measure the capacitor charge curve, shown in Figure 5. Immediately after connecting the capacitor, the potential of the cell dropped to zero because the uncharged capacitor acted like a short circuit in the system. However, over time, the potential of the system slowly increased, showing the ability of the fuel cell to charge the capacitor.

Once the capacitor was charged above 1.2 V, our telemetry system was automatically activated and transmitted the measured temperature wirelessly. The selection of 1.2 V for starting the telemetry system was arbitrary. Examples of the transmitted data are shown in Figure 6.

Example of Application: Remote Measurement of the Temperature. To test the telemetry system, the ambient air temperature was measured, followed by the thermocouple being inserted into ice water and the temperature remeasured. This cycle was repeated several times (Figure 6). During these tests the entire system was powered by the microbial fuel cell. The readouts were wirelessly transmitted from the thermocouple via the transmitter to the receiver (the computer).

Limitations of the System. It is important to estimate how long the entire system—the microbial fuel cell, the sensor, and the telemetry system—may last. This may be estimated by predicting the lifetime of the components.

The lifetime of the cathodic side of the fuel cell, 316 L stainless steel, should not be the limiting factor. Assuming that the lifetime of the fuel cell is limited by the lifetime of the anode, it can be calculated from the current required to power the telemetry system and the temperature sensor. Using data available from the manufacturer of the telemetry system and the sacrificial anodes, we estimate that approximately 0.015 A is required to measure temperature and transmit data every 8 s. The ampere-hour rating of the anodes varies with environmental conditions; a 0.9-kg (265-cm² initial surface area) magnesium anode can be rated at about 1000 ampere-hour (Farwest Corrosion Control Company, Gardena, CA 90248). Based on that, the lifetime of the microbial fuel cell is estimated as the following: lifetime (h) with 0.9 kg of anode = 1000Ah/(0.015A) = 66666 h = 7.61 years. If needed, this can be doubled or tripled just by increasing the numbers

The calculated lifetime depending on the number of the anodes and the current needed to operate the system is hypothetical, and the actual lifetime may vary depending on environmental conditions. For example, one unknown factor is the rate of corrosion of the sacrificial anodes; this can be evaluated by running long-term tests. However, the lifetime

of the anode in this fuel cell can still be controlled by increasing the surface area of the anode.

The lifetimes of the telemetry system and the temperature sensor are limited by the lifetime of the capacitor, which is listed by the vendor as 10 years. Also, the telemetry system and temperature system may break down before the capacitor loses its ability to charge and discharge or the anode may dissolve directly. Altogether, if carefully designed and protected when deployed, the system can last for years.

Rechargeable batteries were considered instead of the capacitor, and it was concluded that using rechargeable batteries might shorten the lifetime of the system because capacitors have a longer lifetime and can sustain a higher number of charge/discharge cycles than rechargeable batteries (28). If we used a dry cell battery or a car battery to power the sensor and the telemetry system, it would lose its charge with time and could not be used for a long time without recharging; the lifetimes of these batteries are controlled by their maintenance requirements, number of charge/discharge cycles, and leakage currents.

Another limitation of microbial fuel cells is that they cannot operate at extremely low temperatures because microbial reactions slow at low temperatures. Currently, we do not know how the system behaves at low temperatures: this will require long-term testing. However, it is expected that when the temperature returns to a higher value, the rates of microbial reactions will increase and the system will recover. We tested our system for over 1 year in the laboratory and in the field, stopping it artificially to estimate the effect of interrupted power generation: the system recharged the capacitor and started to transfer data again every time the conditions of normal operation were restored.

Microbial fuel cells offer many advantages over batteries as power sources because they generate limitless amounts of energy and require no recharging. The main problem with using microbial cells is the small amount of power produced by the cell, which may not be enough to run a sensor and a transmitter continuously. To some extent this problem can be solved by increasing the surface area of the electrodes. If it is not possible to increase the surface area, the system can be operated less frequently using a suitable power management program: the data are transferred only when enough energy has been accumulated. Another advantage of microbial fuel cells over batteries is that even when exposed to extreme conditions microbial fuel cells can spontaneously recover once these conditions are removed. It is well-known that regular batteries lose their efficiency permanently at very low temperatures and do not recover when the temperature returns to normal (28). The obvious disadvantages of solar batteries are as follows: (1) inconsistency of energy generation due to the daily and seasonal variation in the illumination and (2) difficulties in powering sensors deposited at locations with low or nonexistent illumination, such as the sea floor.

The obvious disadvantage of microbial fuel cells is the susceptibility of microbial reactions to temperature variations, and we are currently testing the possibility of using microbial fuel cells deployed under ice cover in natural waters.

Several studies have shown the possibility of harvesting energy from the environment using microbial fuel cells, such as harvesting energy from marine sediments (13). Our study is the first attempt to use microbial fuel cells to power a sensor and a telemetry system that transmits the measured data wirelessly. Although in this paper for demonstration purposes we measured temperature, it is possible to use microbial fuel cells, and using different anodic reactions, to power other types of sensors, such as pH and dissolved oxygen sensors, which are our future research goals.

Acknowledgments

The authors gratefully acknowledge the financial support provided by grant N-00014-02-1-0567 from the U.S. Office of Naval Research.

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Received for review December 7, 2004. Revised manuscript received May 5, 2005. Accepted May 10, 2005.

ES0480668