Autonomous, Retrievable, Deep Sea Microbial Fuel Cell

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***Abstract*—Microbial fuel cells (MFCs) work by providing bacteria in anaerobic sediments with an electron acceptor (anode) that stimulates metabolism of organic matter. The buried anode is connected via control circuitry to a cathode exposed to oxygen in the overlying water. During metabolism, bacteria release hydrogen ions into the sediment and transfer electrons extra-cellularly to the anode that eventually reduces dissolved oxygen at the cathode, forming water. The open circuit voltage is approximately 0.8 v. The voltage between electrodes is operationally kept at 0.4 v with a potentiostat. The current is chiefly limited by the rate of microbial metabolism at the anode.**

Earlier work in shallow sediments of San Diego Bay showed that the most important environmental parameters that control fuel cell power output in San Diego Bay were total organic carbon in the sediment and seasonal water temperature. Parameters that we dismissed as unimportant were dissolved oxygen levels, light level, and initial sediment bacterial populations. Parameters whose affect we could not separate were total organic carbon and grain size.

Current MFC work includes extension of microbial fuel cell tests to the deep sea environment (>1000 m) and, in parallel, testing microbial fuel cells in the laboratory under deep sea conditions. One question we are asking is whether MFC power output from deep water sediments re-pressurized and chilled in the laboratory comparable to those measured in situ. If yes, mapping the power potential of deep sea sediments may be made much easier, requiring sediment grabs and lab tests rather than deployment and retrieval of fuel cells. Another question we are asking is whether in situ temperature and total organic carbon in the deep sea sediment can predict MFC power. If yes, then we can make use of the large collection of publicly available, deep sea oceanographic measurements to make these predictions, foregoing expensive work at sea. These regressions will be compared to those derived from shallow water measurements.

In order to meet these goals we are pursuing a field effort to (1) deploy a microbial fuel cell in progressively deeper water, (2) record in situ power and temperature over several weeks, and (3) retrieve the fuel cell along with sediment samples for analysis. We are also pursuing a laboratory effort to (1) build a matching microbial fuel cell in a pressure vessel capable of matching the pressure and temperature of deep water, (2) capable of flushing the fuel cell with oxygenated water under pressure to allow equilibrium power production, and (3) stock the pressure vessel with deep water sediment in order to take measurements analogous to those in the field. The current progress and results from this work at SPAWAR are presented.

Keywords— microbial fuel cell; deep sea; high pressure

I. INTRODUCTION

Sediment-based microbial fuel cells (MFCs) are fuel cells powered by the metabolism of organic material by facultative aerobic bacteria living in anaerobic sediments. During metabolism, organic matter is oxidized (electrons are released) and some electron acceptor is reduced (electrons are accepted). These particular bacteria (e.g., Geobacter and Shewanella sp.) are capable of taking advantage of a buried electrode, electrically linked to an oxygenated environment as an electron receptor [1,2]. While the metabolic pathways of these organisms are not well understood [3], the key feature is transport of electrons, released during intra-cellular oxidation of organic matter, to an extra-cellular electron acceptor poised by reduction of oxygen. In parallel to electron transport to oxygen, hydrogen ions are released during metabolism as well, diffuse into the sediment and overlying water column, and combine with reduced oxygen at the cathode to form water. The Office of Naval Research has encouraged development of microbial fuel cells in the marine environment at a number of academic and naval institutions. Work at SPAWAR, a navy laboratory in San Diego, involves fuel cell design and testing, applications to low power Navy sensors, and studies of important environmental parameters that affect fuel cell performance.

In a previous report [4], we found that the most important environmental parameters that control fuel cell power output in San Diego Bay were total organic carbon in the sediment and seasonal water temperature. Derived relationships between power and organic carbon, temperature and anode size, along with extensive knowledge of sediment organic carbon and seasonal water temperatures in San Diego Bay, allowed us to develop seasonal contours of power output from a benthic MFC. This study examines MFC output in sediment at greater water depth where seasonal temperature changes are more moderate, organic material in the sediment may be more refractory, and increasing pressure with water

depth may select for barophilic communities [5]. The basic question we are asking is whether in situ temperature, sediment organic carbon and perhaps pressure can be used to predict deep sea MFC power output in a manner similar to earlier shallow water studies. If yes, then we can make use of the large collection of publicly available, deep sea oceanographic measurements to make these predictions, foregoing expensive work at sea.

A deep sea (>1000 m) free vehicle that supports one or more MFCs and returns to the surface via acoustic release is described. The vehicle is designed to capture and return sediment samples (unpressurized) from around the MFC anode, as well as reference sediments not subjected to MFC energy harvesting. A parallel laboratory effort also is presented where in situ pressure and temperature conditions of the deep sea can be mimicked in a flow-through pressure vessel that accommodates a MFC. Sediment returned from the deep sea after retrieval of the free vehicle or from other oceanographic studies of opportunity is used in the laboratory tests. The purpose of the laboratory tests is to determine whether laboratory MFC measurements of deep sea sediment can be used in lieu of difficult in situ measurements, or whether the temporary depressurization and warming of deep water sediment introduces an unacceptable bias to these measurements in the lab. Preliminary data from both efforts is presented.

II. METHODS AND APPROACH

A. Deep Sea Free Vehicle

Fig. 1 shows a schematic of the free vehicle, which supports one to three MFCs. The MFC electrodes and recording electronics were constructed by Peter Kauffman (Northwest Metasystems, Seattle, WA) and have been described earlier [4]. Measured parameters include: (1) the voltage difference between the anode and cathode (set by the potentiostat, typically at 0.385V), (2) the current flowing between the anode and cathode, and (3) the voltage difference between the anode and a Ag□AgCl reference electrode. The latter measurement is indicative of the state of the electrodes. A self-recording thermistor (Hobo data logger from Onset Computers, Bourne, MA) is often included in the pressure case. They are the same design as used in shallower water studies. Essentially, three polycarbonate tubes with closing covers are attached to an aluminum cylinder and suspended below a ballast platform. The tubes can support MFC anodes that are forced into the sediment when the vehicle lands on the bottom. Three floatation spheres provide buoyancy to bring the MFCs and partially submerged tubes to the surface when the ballast is automatically released. The tubes have closing covers to retain sediment and are a version of those found on a sediment corer (Tim Marrs, Ocean Instruments, San Diego CA), modified to close when the aluminum cylinder separates from the ballast platform (Fig. 2). The vehicle typically descends with a net weight of 70 kg and ascends with a net buoyancy of 70 kg. Descent and ascent rates are approximately 1 m/s. At the surface, a pressure-triggered strobe, GPS and radio transmitter package designed by Kevin Hardy (Global Ocean Design, San Diego, CA) inside one of the floats aids in recovery. Fig. 3 shows the vehicle on recovery after a month-long deployment at 1000 m with full sediment tubes.

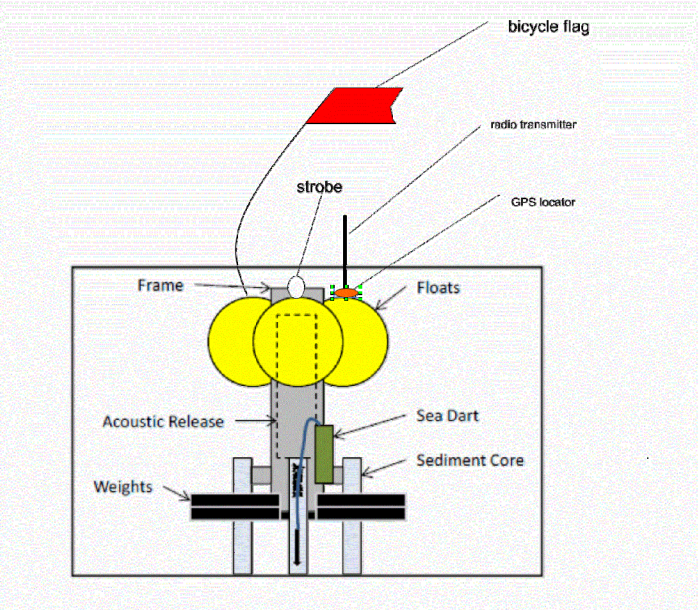

Fig. 1. Schematic of free vehicle that buries MFC anodes in sediment, records MFC power, collects sediment samples, and returns to the surface after dumping ballast via an acoustic release.

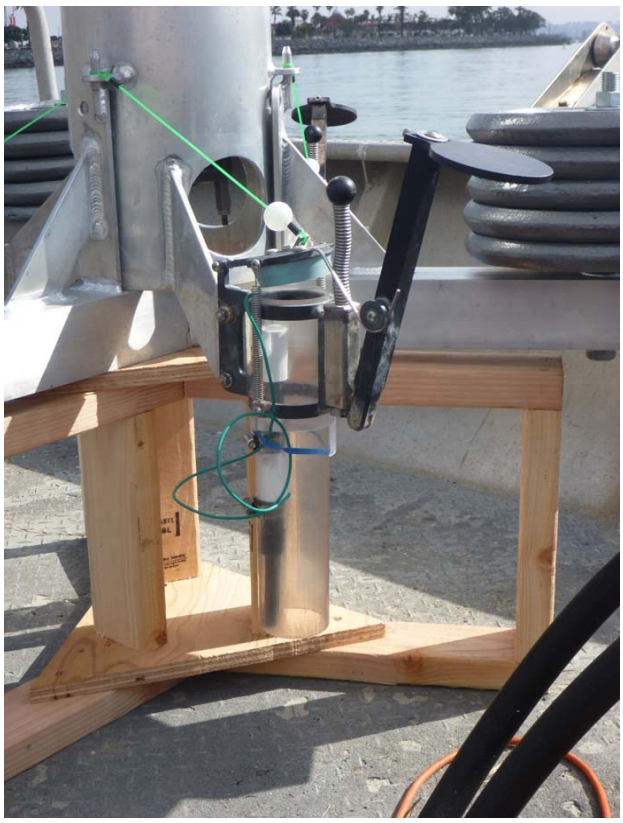

Fig. 2. Sediment retaining tube with open covers and MFC anode. Ascent of cylinder away from ballast platform releases covers to close via springs.

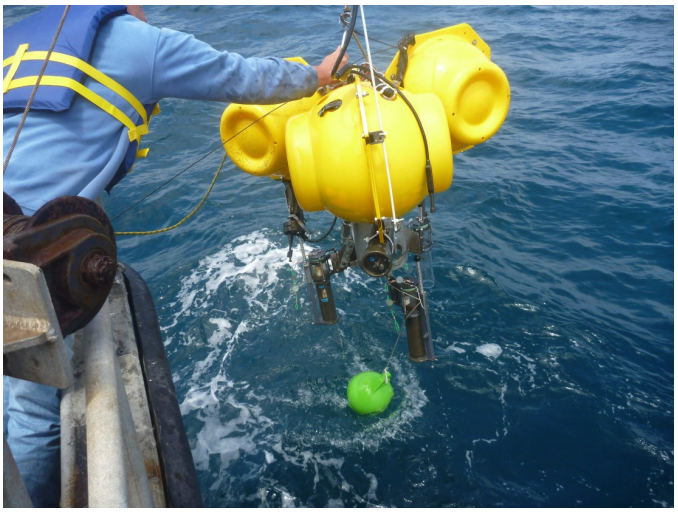

Fig. 3. Recovery of Microbial Fuel Cell vehicle with full sediment tubes.

B. *Laboratory Microbial Fuel Cell in Pressure Vessel*

Fig. 4 shows a schematic of the laboratory setup. The pressure vessel necessarily requires a continuous supply of oxygenated seawater to maintain the flow of electrons from the anode in the sediment to oxygen in the overlying water via the cathode. The anode, cathode and recording electronics are the same as those deployed during in situ measurements. A high pressure pump maintains a steady flow rate while an adjustable valve maintains pressures up to 700 bar. The pump, valve and water bath controlling pressure vessel temperature are computer controlled. Typical flow rates are 15 ml/min, empirically determined to maintain a cathode voltage of approximately 0.35 v relative to a Ag□AgCl reference electrode, comparable to what would be measured in oxygen-saturated seawater.

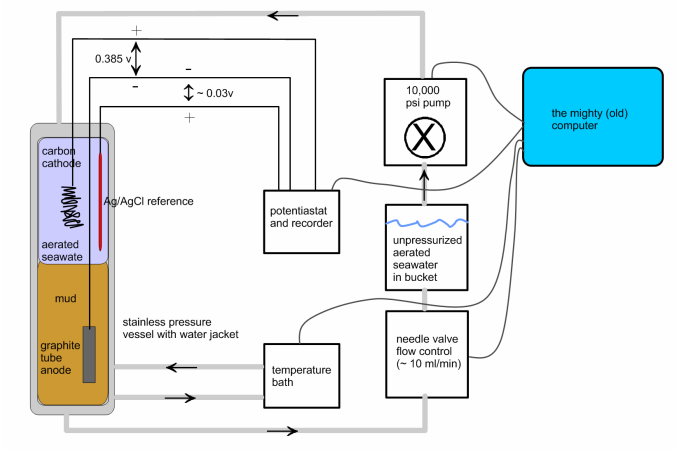

Fig 4. Laboratory MFC in pressure vessel, meant to mimic deep sea conditions of in situ measurements.

This work was generously sponsored by Dr. Linda Chrisey of Office of Naval Research and through SPAWAR internal funding.

III. RESULTS

A. *Deep Water Microbial Fuel Cells*

Deployment of the MFCs on the free vehicle was made in progressively deeper water. Fig. 5 shows the locations of the current set of data, first at 5 m in the boat channel of the Marine Corps Recruiting Depot (MCRD), then at 10 m off the bait barge in San Diego Bay, then at 100m depth (10 km offshore) and finally at 1000 m depth (24 km offshore). Deployments typically lasted three to four weeks to allow the fuel cells to reach steady state.

Fig. 6 plots power output as mW/m^2 of anode surface area. Note the log10 scale on the power axis. The power output at the 5 m location off MCRD is typical of earlier measurements at this site with the 0.5 in diameter carbon fiber tube anode we were using. The same site will produce approximately 20 mW/ m^2 anode if graphite plate or carbon fiber cloth is used.

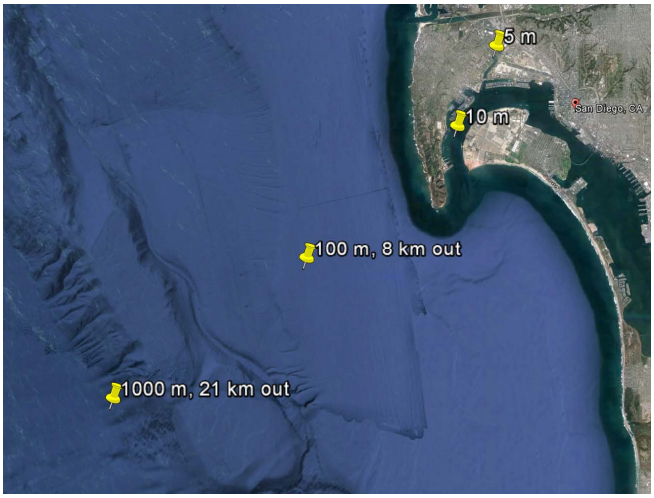

Fig.5. Microbial Fuel Cell deployment on the free vehicle off San Diego in progressively deeper water.

The carbon tube is deployed on the free vehicle because of its rigidity and strength, resulting in easy deployment into the sediment. It is unclear why the power output at 100 m was so variable over time, though there were problems during deployment when the vehicle became entangled in a tethered float used to aid in retrieval. The vehicle did not fully bury the sediment tubes, no sediment was recovered during this deployment, and use of a small cabled robot was necessary to free the vehicle from the ballast frame. The deployment to 1000 m returned all sediment traps filled with sediment, though one electronics package was crushed. We feel that the decrease in power output with depth is like caused by the decreasing ambient temperatures.

The purple squares and regression line in Fig. 7 are a reproduction of a figure in Price and Sowers [6], depicting in situ metabolic activity of microorganisms from sediment samples off Nova Scotia and in the Arctic Ocean as a function of temperature. The black vertical lines in Fig. 7

represent the electrical currents as a proxy for microbial metabolism. The red dots are the mean values for each water depth and the linear regression is the dashed line. The regression line is based on >21000 data points ($r^2 = 0.72$).The slopes (E) and temperature coefficients (Q_{10}) are remarkably similar.

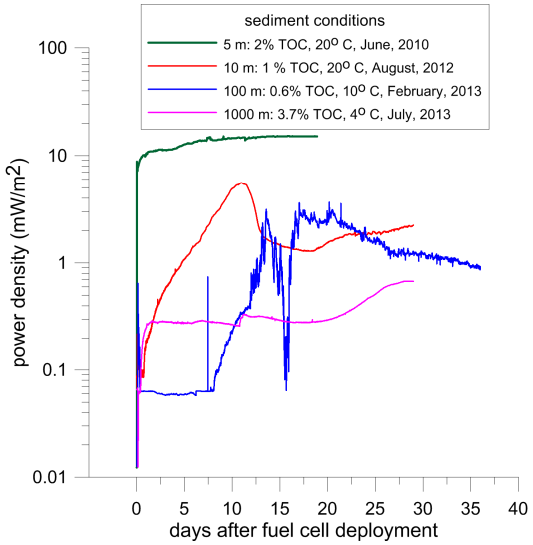

Fig 6. MFC output at various depths and temperatures.

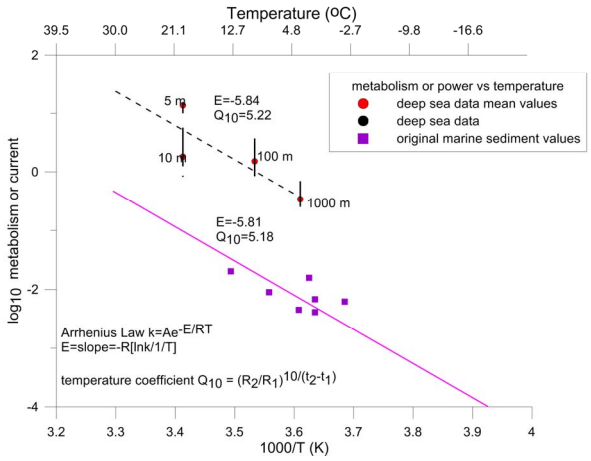

Fig 7. Arrhenius plot of metabolic activity and MFC output versus temperature. Upper regression line and data from Fig 6.

B. *Pressurized Vessel Microbial Fuel Cells*

Fig. 8 plots MFC output from shallow (5 m) sediment collected off MCRD in San Diego Bay at a variety of pressures. Fig. 9 plots the subsequent power from MCRD sediment under a range of temperatures while the pressure was held at 500 bar. Fig. 10 plots temperature sensitivity of MCRD sediment. The dramatic power drop seen in Fig. 9, in light of Fig. 8, we believe is due to temperature. On restoring ambient pressure and temperature in the pressure vessel, power output has fully recovered to earlier levels. Unpublished data from our lab, using a different electrode scheme, has shown that the power output from 1000 m sediment collected off the Monterey Canyon (courtesy Clare Reimers, OSU and Peter Girguis, Harvard) is similarly affected by temperature when held at 100 bar. Unpublished data of the output power response to temperature from sediment collected at 5809 m from the Philippine Sea (courtesy Doug Bartlett, UCSD) and held at 580 bar, surprisingly show very little response to temperature. Current efforts consist of testing the 100 m and 1000 m deep sediment under various temperature and pressure regimes in the flow-through pressure vessel system.

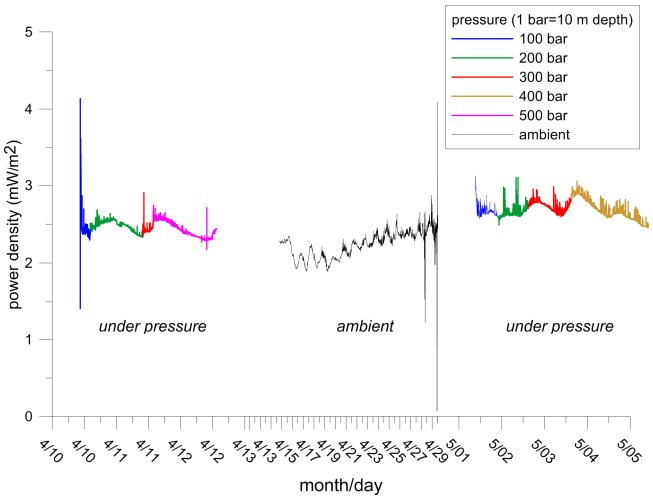

Fig 8. Effects of various pressure regimes on MFC output from MCRD sediment at ambient (~20 °C) temperature.

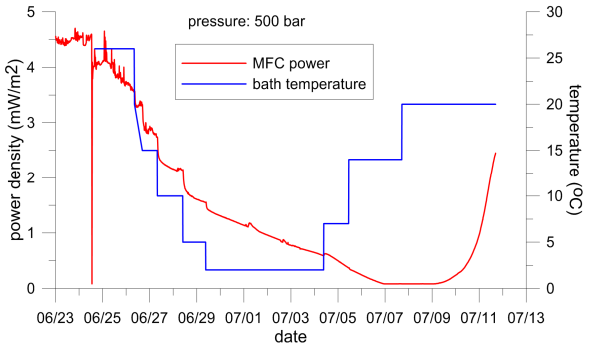

Fig 9. Effect of temperature on MFC output from MCRD sediment at 500 bar.

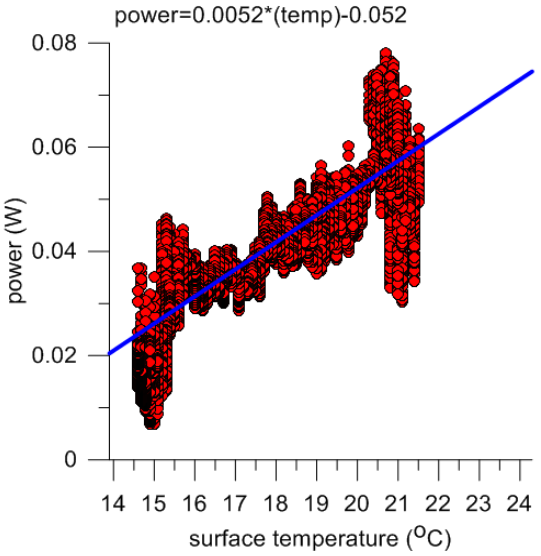

Fig 10. Effect of temperature on MFC output from MCRD sediments in situ.

IV. DISCUSSION AND FUTURE DIRECTIONS

We have developed a deep water-deployable MFC vehicle that can take in situ measurements for a month at a time and return with sediment samples for laboratory testing and chemical analysis. We have developed a flow-through pressure vessel system that can mimic deep water conditions to approximately 6500 m that supports a MFC identical to that deployed in the field. From data collected, we see a progressive decrease in MFC output with depth from 5 m to 1000 m off southern California. The laboratory studies indicate that temperature may be the primary culprit, though the amount and quality of the sediment organic fraction may be important, as well as the permeability of the sediment which controls diffusion of organic material to microbes on the anode. As water depth increases away from the coast, organic material takes longer to settle to the bottom, probably allowing the more labile fraction to be stripped by microbes in the water column [7]. Sediment grain size also tends to become smaller with depth, impeding diffusion [8]. In gyre waters with low surface productivity, the small amount of organic material reaching the bottom may not be sufficient to drive sediments anoxic [9, 10, 11], and hence are unsuitable for MFCs.

We plan to continue in situ measurements in deeper (>4000 m) waters off Puerto Rico or Guam. We plan to make the MFC vehicle more robust by putting all the electronics within the glass floats. We hope to continue testing sediment collected at depth from cooperating research surveys. We hope to better characterize the retrieved sediment in the lab, relative to the quantity and quality of organic matter, grain size, and microbial population from reference and anode-impacted sediment collected in the sediment tubes. We will continue this work through collaboration with Naval Research Laboratory and a number of universities.

V. ACKNOWLEDGMENT

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VI. REFERENCES

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