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# Microbial Fuel Cells for Powering Navy Devices

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# MICROBIAL FUEL CELLS FOR POWERING NAVY DEVICES

## 1. INTRODUCTION

Microbial fuel cells (MFCs) are fuel cells that generate electrical power by using microorganisms to catalyze the anode reaction [1]. In theory, they can range in scale from less than 1 W to more than 1 MW. They promise relatively high energy density (Wh/L) compared to lithium batteries and hydrogen/oxygen fuel cells and relatively high specific energy (Wh/kg) compared to lithium batteries by using non-explosive biomass-derived organic matter as fuel, such as glucose and acetate. While they promise relatively low power density (W/L) and low specific power (W/kg) owing to relatively low rates of microbe-catalyzed anode reactions, recent advancements indicate that power densities comparable to alkaline batteries are within reach [2]. They are therefore being investigated primarily for low power consuming, long duration applications such as remotely deployed sensors, for which they may prove superior to existing power supplies when fully developed. MFCs for such applications are estimated here to be at technology readiness level (TRL) 3. MFCs are also being investigated to generate electrical power from the biomass content of wastewater (i.e., sewage) in order to offset energy consumption of wastewater treatment processes. MFCs for this application are estimated to be at TRL 4.

Key factors limiting MFC development include poor performance of existing cathode oxygen reduction catalysts and ion exchange membranes in neutral pH, complex ionic electrolytes inherent to MFCs, and power required by balance of system (i.e., pumps) for delivery of reactants and removal of products. Owing to these limitations, there have not been any demonstrations to date of standalone MFCs that generate a sustained net positive power output with the exception of the Benthic Microbial Fuel Cell (BMFC). The BMFC sits on the sediment/water (benthic) interface of marine environments, where it uses organic matter naturally residing in marine sediments as its fuel and oxygen in overlying water as its oxidant [3-13]. Because of aerobic microorganisms inhabiting the benthic interface that consume organic matter supplied from below with oxygen supplied from above, the benthic interface acts as a highly effective ion exchange membrane blocking oxygen transport into sediment. Also, because mass transport of fuel and oxidant is provided by the environment through a combination of diffusion and advection, the BMFC is not subjected balance of systems limitations as are conventional MFCs. The BMFC has undergone a number of field-based research demonstrations, including powering a meteorological buoy with a radio transceiver link [8], a hydrophone with a radio transceiver link [9], an acoustic modem, [14] and a surveillance camera with a cellular link [15], and is estimated to be at TRL 6. This report describes fundamental aspects of microbial fuel cells, their state of art with respect to performance, and future prospects with respect to applications. Special emphasis is placed on BMFCs.

## 2. WHAT IS A MICROBIAL FUEL CELL?

A fuel cell is a power supply similar to a battery that converts energy released by a chemical reaction directly to electrical power. It contains two electrodes, an anode that oxidizes (removes electrons from) fuel molecules, and a cathode that reduces (adds electrons to) oxidant molecules. While a battery stores its reactants (fuel and oxidant) and products (spent fuel and spent oxidant) internally, those of a fuel cell are externally supplied and removed, enabling indefinite power generation as long as fuel and oxidant are replenished and products are withdrawn.

A microbial fuel cell (MFC) is a specific type of fuel cell in which the anode reaction is catalyzed (accelerated) by microorganisms [1]. That is, microorganisms are used that oxidize the fuel and transfer the acquired electrons to the anode much faster than the anode can oxidize the fuel itself. This enables generation of electrical power from organic matter naturally oxidized by microorganisms, such as glucose and acetate, for which conventional anode catalysts do not exist. Such fuels are abundant, renewable, relatively high in energy density (for example, the oxidation of acetate by oxygen yields 3750 Wh/L compared to 1568 Wh/L for oxidation of compressed hydrogen (700 bar) by oxygen), and are non-explosive. It also enables generation of electrical power from non-purified sources containing organic matter such as wastewater. (For an exhaustive review of the various biomass derived fuels that have been used in microbial fuel cells, see Pant et al. [16].) While there are numerous types of microorganisms that can oxidize organic matter, only a very select group can couple it to the transfer of electrons directly to anodes. It was the discovery of this ability in 2002 for *Geobacter spp.* that accelerated interest in microbial fuel cells [17].

The key benefit of using microbial catalysts in microbial fuel cells is the ability to generate electrical power directly from organic matter. The key drawback is that the rate at which microbes can catalyze anode reactions (i.e., their catalytic activity) is orders of magnitude slower than conventional catalysts. For example, while the best microbial anode catalysts can sustain on order of 0.0005 Amp/cm<sup>2</sup> of anode surface area from oxidation of acetate [18], platinum anode catalysts can sustain on order of 2 Amp/cm<sup>2</sup> from oxidation of hydrogen. Understanding what limits catalytic activity of microbial anode catalysts is a goal of many researchers that may eventually lead to rational approaches to increase power density of MFCs [18-38]. Until that time, MFCs are not envisioned for applications requiring high power density.

In the case of wastewater-fed MFCs, a primary goal of wastewater treatment is oxidation of the organic matter content of wastewater (often described by its chemical oxygen demand (COD) expressed as milligrams of oxygen required to oxidize organic matter contained in one liter of waste water). This is typically accomplished by mechanical aeration in which air is blown into wastewater to supply oxygen to microorganisms that aerobically oxidize the organic matter content, which is energy intensive [39].[40] It has been estimated that this process alone in the U.S. consumes 3% of the total electrical energy generated in the U.S.[41, 42]. As an example, the Blue Plains Wastewater Treatment Plant adjacent to the Naval Research Laboratory in Washington, DC, consumes on order of 20 MW of average power to mechanically aerate 2 billion liters of wastewater per day serving 2.5 million people. In contrast, it can be estimated that if wastewater oxidation were accomplished using MFCs, as much as 62 MW (25 W per person multiplied by 2.5 million people) could be generated at the Blue Plains Plant [41]. The prospect of generating power from wastewater is of interest to many sponsors, including the Army Research Office (ARO) and the Strategic Environmental Research and Development Program (SERDP) to minimize power consumption at forward operating bases, and the Bill and Melinda Gates Foundation to incentivize wastewater treatment in developing countries.

Figure 1 is a schematic depiction of the cross section of the most common MFC configuration, referred to as a two-chamber MFC. The MFC, typically constructed from Plexiglas, is divided into two compartments (half-cells) by an ion exchange membrane. A water-based solution containing the MFC

fuel (anolyte) is pumped into the anode half-cell containing the anode, and a water-based solution containing the MFC oxidant (catholyte) is pumped into the cathodic half-cell containing the cathode. Specific microorganisms either added from an external culture or already present in the anolyte when wastewater is used, will affix themselves to the anode surface, forming a persistent film (biofilm) that catalyzes anode oxidation of the fuel. In return, the microorganisms derive benefit from the catalytic process, extracting a small portion of the potential energy of electrons passing through them from the fuel to the anode to satisfy their own energy requirements. They all also use a small portion of the fuel as a carbon source, enabling the microbes to proliferate on the anode surface, forming the biofilm. In this way, the microbial biofilm is able to maintain itself and, as a result, its catalytic activity does not wane as does that of conventional electrode catalysts.

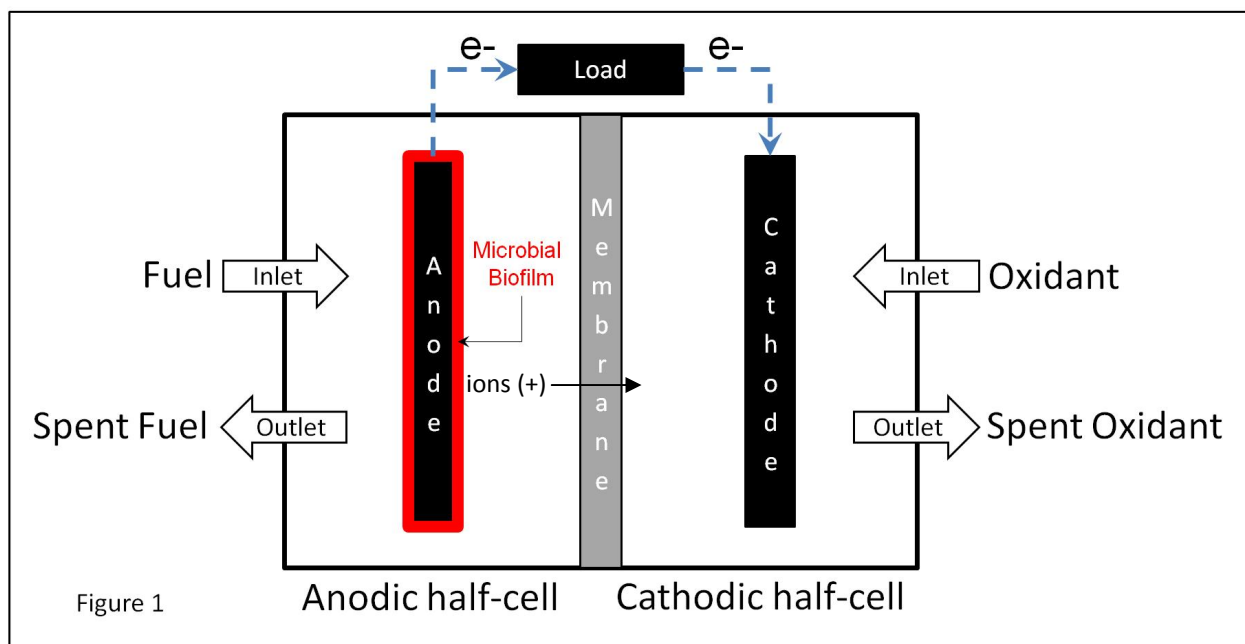
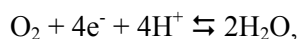


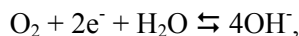
Fig. 1 – Schematic depiction of a typical two-chamber MFC

The electrons acquired by the anode from oxidation of fuel are conducted through an external circuit to the cathode, where they are consumed by reduction of the oxidant. (The external electrical circuit is indicated by blue dashed arrows in Fig. 1 that points in the direction of electron flow from the anode to the cathode.) Lacking alternatives, MFCs use the same cathode catalysts used in conventional (i.e., hydrogen-oxygen) fuel cells such as titanium. The operating conditions of MFCs (i.e., ambient temperature and neutral pH) are very different however from those of conventional fuel cells. As a consequence, the performance of these catalysts is dramatically lower in MFCs than in conventional fuel cells, resulting in MFC power densities far lower than expected based on rates of microbe catalyzed anode reactions. As such, there is growing interest in development of alternative cathode catalysts specifically for MFCs including microorganisms (so-called “biocathodes” [43-45]). For example, while it is conventionally thought that the cathode reaction of a MFC involves the four-electron reduction of oxygen forming water as occurs in hydrogen oxygen fuel cells:





it has been put forth [46] that, in light of the neutral pH conditions of MFCs, it might proceed as two-electron reduction as follows:



with implications affecting optimization of cathode materials and ion exchange membranes. As such, there is a growing need to improve understanding of the cathode reaction in MFCs.

The flow of electrons through the external circuit from the anode to the cathode constitutes an electrical current. Because the net reaction (oxidation of fuel and reduction of oxidant) is thermodynamically favorable (i.e., releases energy), this electrical current can occur spontaneously, resulting in electrical power that can be used by an electrical power consuming device comprising the external circuit represented by the load in Fig. 1. The flow of electrons, which are negatively charged, will result in accumulation of negative charge in the cathodic half-cell and positive charge in the anodic half-cell that will shut down current if not counter balanced. The role of the ion exchange membrane is to enable a net concomitant flow of positively charged ions (electrically charged atoms or molecules) from the anodic half-cell to the cathodic half-cell to compensate for charge accumulation in each half-cell due to electron flow through the external circuit. Often these ions are protons (positively charged hydrogen atoms) that are generated as a byproduct of the anode reaction and consumed by the cathode reaction. The membrane however, must exclude the flow of oxidant from the cathode half-cell into the anode half-cell. If not harmful to the microorganisms comprising the anode biofilm, the presence of oxidant in the anodic half can electrochemically short circuit a MFC, whereby the microorganisms transfer electrons directly to the oxidant, diminishing electrical current through the external circuit and reducing coulombic efficiency (ratio of amount of fuel oxidized resulting in electrical current generated per total amount of fuel oxidized in the MFC). Lacking alternatives, MFCs use the same ion exchange membranes, such as Nafion, used in conventional fuel cells. The performance of these membranes is dramatically lower in MFCs, however, owing to the complex ionic nature of MFC anolytes and catholytes, which contain trace metals that irreversibly bind into ion exchange membranes [47]. As consequence, such membranes have been shown to be a factor significantly limiting MFC power density below that expected based on rates of microbe-catalyzed anode reactions [48]. As such, there is also a pressing need to develop alternative membranes specific for MFCs. One approach currently being investigated by the author and collaborators at the University of South Carolina is the use of a porous, inert membrane colonized with benthic microorganisms to deplete oxygen as it penetrates from the cathodic half-cell to the anodic half-cell, while enabling ion flow, as occurs at the benthic interface enabling benthic microbial fuel cells to operate [49].

Figure 2 is a schematic depiction of the most common alternative MFC configuration, referred to as a single-chamber MFC, a membraneless MFC, or an air cathode MFC [1, 50-52]. Here, a permeable cathode (typically comprised of a carbon cloth) is used to cover the open end of the anodic chamber. The outer surface of the cathode is coated with a sealant (oxygen diffusion layer typically comprised of polytetrafluoroethylene (PTFE)) intended to keep liquid from leaking out of the MFC through the cathode while simultaneously allowing oxygen to diffuse into the cathode from air on the opposite side. While alleviating limitations due to membranes, such MFCs exhibit other limitations. Most notable is lower coulombic efficiency owing to incomplete reduction of oxygen diffusing through the cathode resulting in relatively high rates of oxygen intrusion into the anodic chamber compared to two-chamber MFCs. In addition, the design of air cathodes is very challenging wherein in order for each surface element of the cathode to be catalytically active it must simultaneously be exposed to protons and water molecules originating from inside the MFC and oxygen originating from outside the MFC.

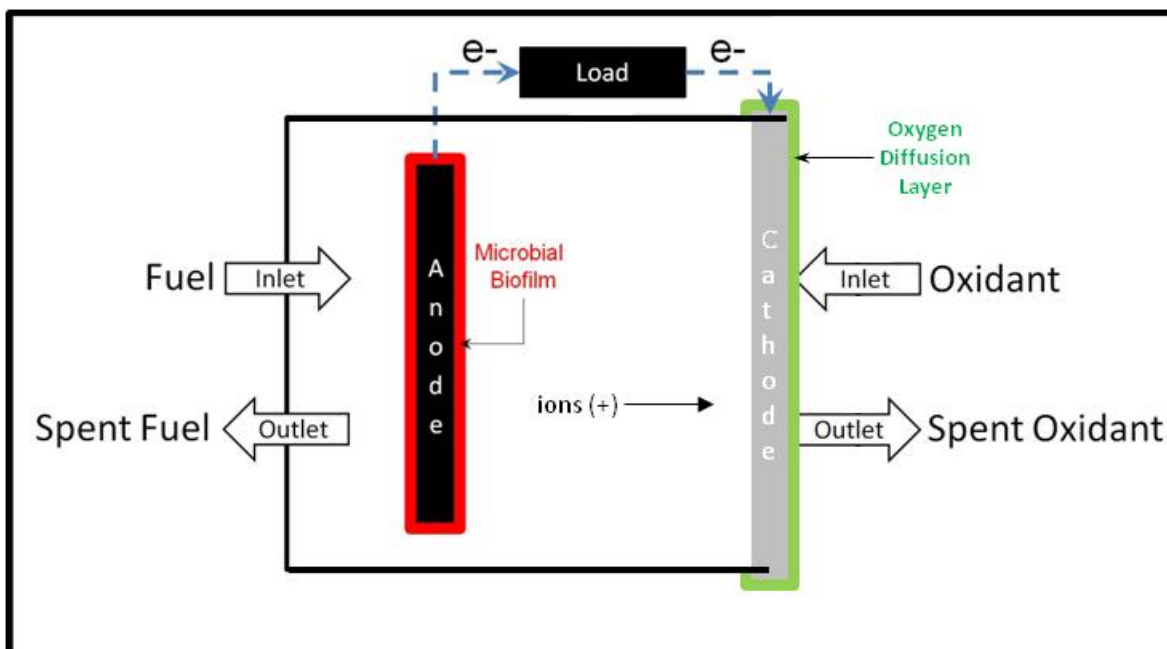
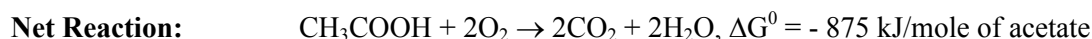


Fig. 2 – Schematic depiction of a typical single-chamber MFC

### 3. ENERGY, VOLTAGE, CURRENT, AND POWER

A common MFC uses acetate as the fuel, either added to water or as found in wastewater, and oxygen as the oxidant. The net MFC reaction is described by the following chemical equation:



This reaction is the result of two coupled half-reactions, the oxidation of acetate occurring at the anode, and the reduction of oxygen occurring at the cathode:



where the oxidation of each molecule of acetate ( $\text{CH}_3\text{COOH}$ ), in which eight electrons ( $\text{e}^-$ ) and eight protons ( $\text{H}^+$ ) are generated, requires the reduction of two molecules of oxygen ( $\text{O}_2$ ), in which eight electrons and eight protons are consumed, forming two molecules of carbon dioxide ( $\text{CO}_2$ ) and two molecules of water ( $\text{H}_2\text{O}$ ). The net reaction liberates 875 kJ (243 Wh) of energy per mole of acetate consumed when performed with 100% efficiency. This equates to a theoretical upper limit of energy density and specific energy for an acetate-oxygen MFC, assuming oxygen consumed is from the environment and that the mass and volume of the MFC is negligible compared to that of the fuel stock, of 4050 Wh/kg and 3750 Wh/L when the fuel stock is solid acetate and 1000 Wh/kg and 1375 Wh/L when the fuel stock is acetate saturated water (5 molar at 20 C). By comparison, energy density and specific energy of state of art lithium batteries is 1200 Wh/kg and 500 Wh/L, hence the promise of very high energy density of MFCs when fully developed that would be suitable for a number of Navy applications without the risk of explosion.

Like other fuel cells and batteries, the performance of an MFC is characterized by its voltage (V): the amount of energy imparted to the load per electron flowing through the load; current (I): the rate at which electrons flow through the load; and power (P): the rate at which energy is imparted to the load (P where power is the product of current and voltage ( $P = I \times V$ )). As in the case of fuel cells and batteries, voltage and current are interdependent. The maximum voltage that can be generated by a MFC, referred to as the open circuit voltage ( $V_{oc}$ ), occurs when the resistance of the load is very high such that essentially no current flows through the load. The open circuit voltage is related to the free energy of the net reaction ( $\Delta G^0$ ) of the MFC by the following equation:

$$V_{oc} = -\Delta G^0/nF,$$

where  $n$  is the number of electrons released per molecule of fuel oxidized (eight in the case of acetate) and  $F$  is the Faraday constant (96,487 coulombs/mole of electrons) yielding 1.13 V for an acetate and oxygen consuming MFC. Since no current flows through the load at open circuit, no power is imparted to the load at open circuit. The importance of  $V_{oc}$  in characterizing a MFC is that it represents that upper limit of voltage (energy per electron) that a given MFC can deliver based on the specific net reaction occurring (i.e., the fuel and oxidant used). Conversely, when the MFC is at closed circuit such that resistance of the load is very small, then as much current flows through the load as can be generated by the MFC (referred to as limiting current,  $I_L$ ). However, since no voltage is generated because the anode and cathode are effectively shorted together, no power is imparted to the MFC. Starting at open circuit, as current is increased from zero by systematically decreasing the resistance of the load, the voltage will decrease from its open circuit value, resulting in maximum power occurring at an intermediate load resistance between open and closed circuit characterized by an intermediate voltage and current. Such a measurement is referred to as a polarization analysis, and the resulting voltage vs. current and power vs. current polarization plots, analogous to those used to study battery and fuel cell performance, provide a significant amount of information about the specific MFC being analyzed.

Figure 3 depicts simulated voltage vs. current plots (black curves) and corresponding power vs. current polarization plots (red curves) for three related MFCs. Here,  $j$  is current density (current normalized by volume of the MFC),  $j_L$  is the limiting current density (maximum current density the MFC can achieve at closed circuit for which voltage is 0),  $V$  is voltage,  $V_{OC}$  is the open circuit voltage (maximum voltage the MFC can achieve at open circuit for which current density is 0),  $W$  is power density normalized by volume of the MFC), and  $W_L$  is the limiting power density (product of open circuit potential and limiting current density). Curves labeled A correspond to those expected for a MFC that is limited in performance by the anode, achieved in practice by using a very small anode relative to the membrane and to the cathode [21]. Most notable is the shark fin shape of the power vs. current polarization plot (red), in which the maximum power density occurs when current density is very close to the closed circuit current. Curves labeled B correspond to those expected for the same MFC when there is non-negligible resistance to ion flow due to poor membrane performance, resulting in downward curvature of the power vs. current polarization plot, reduced power density, and maximum power density occurring at lower current density than in the case of A. Curves labeled C correspond to those expected for the same MFC when there is significant resistance to ion flow due to very poor membrane performance, resulting in a semicircular power density vs. current density polarization (as typically observed for real MFCs), where maximum power density is considerably lower than in the two other cases.

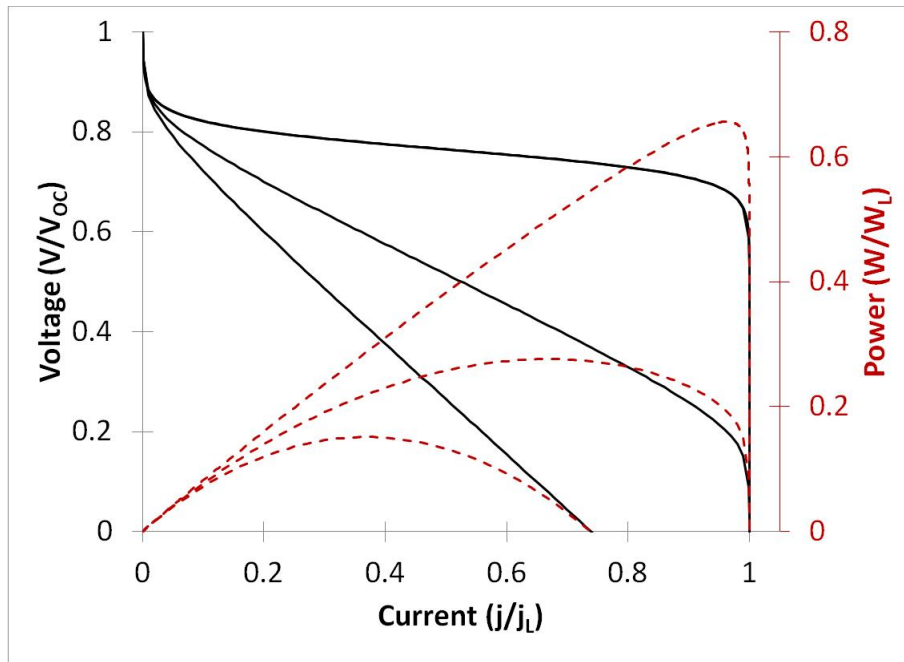


Fig. 3 – Simulated voltage vs current and power vs current polarization plots for a two-chamber MFC in which membrane resistance to ion flow is progressively increased

Tables 1 and 2 highlight the main challenge facing microbial fuels with respect to becoming worthwhile power supplies for Navy applications, namely low maximum power density compared to mature (batteries) and maturing (hydrogen/oxygen fuel cells) power supplies, and how microbial fuel cells might eventually compete against these power supplies based on the high energy density and specific energy of biomass derived fuels (represented here as acetate). In Table 1, energy density refers to the rated energy content of the power supply per unit volume and specific energy refers to the rated energy content of the power supply per unit mass where rated energy content is the integral of power output over time until the power supply is depleted. It is important to note that, in the case of batteries, energy density and specific energy are both dependent on current. That is, drawing more current from a battery or fuel cell reduces the total energy that the battery can deliver over time before depleting, reducing its energy density and specific energy. Other conditions also affect the energy that a battery can deliver such as temperature and age. As such, the values listed here are ballpark.

Table 1 – Comparison of Performance of Microbial Fuel Cells to State-of-the-Art Lithium Batteries and Hydrogen/Oxygen Fuel Cells

|                         | Alkaline Battery [53] | Lithium Battery [54] | H <sub>2</sub> /O <sub>2</sub> Fuel Cell [55] | MFC                                     |
|-------------------------|-----------------------|----------------------|---|---|
| Energy Density (Wh/L)   | 430                   | 1200                 |   |   |
| Specific Energy (Wh/Kg) | 170                   | 500                  |   |   |
| Power Density (W/L)     | 27                    | 160                  | 180   | 2.9 [2]; 0.5 [56]; 0.13 [57]; 0.08 [52] |
| Specific Power (W/Kg)   | 9                     | 60                   | 300   |   |

Table 2 – Comparison of Energy Density and Specific Energy of Hydrogen, Acetate, and Domestic Wastewater

|                         | 700 bar H <sub>2</sub> [58] | Pure Acetate [59] | 5 M Acetate [60]* | Domestic Waste Water [41] |
|-------------------------|-----------------------------|-------------------|-------------------|---------------------------|
| Energy Density (Wh/L)   | 1575                        | 3750              | 1375              | 3                         |
| Specific Energy (Wh/Kg) | 34,440                      | 4050              | 1000              | 3                         |

Terms in [] refer to references.

\* Calculated free energy of oxidation acetate with oxygen as occurs in a MFC, assuming fuel stock is solid acetate in case of solid acetate, and acetate saturated water at 20C in case of 5 M acetate

In Table 1, power density refers to the rated power output of each type of power supply per unit mass and specific power refers to the rated power output of the power supply per unit volume. Based on Table 1, it is clear that lithium batteries outperform alkaline batteries based on these parameters. It is also clear that hydrogen/oxygen fuel cells have a relatively high specific power (rated power they can deliver normalized to the empty weight of the power supply), making them potentially competitive for Navy applications in which low weight is at a premium, such as unmanned air vehicles.

Table 1 also contains representative literature values for power density of current state-of-the-art microbial fuel cells (specific power is not yet a reported parameter of microbial fuel cells). These values do not reflect power required to operate pumps required for delivery of reactants into and removal products out of the microbial fuel cells. Moreover, these power densities are considerably lower than that expected based solely on the maximum rate routinely observed for microbial catalyzed anode oxidation of biomass (i.e., 0.0005 A/cm<sup>2</sup> for acetate oxidation catalyzed by *Geobacter sulfurreducens* at a smooth planar anode [18, 31, 32]), emphasizing the possibility that higher power density MFCs may eventually be developed that power the balance of system, as do hydrogen/oxygen fuel cells, and that generate a worthwhile power density.

In the case of the microbial fuel cell that demonstrated 2.9 W/L (volume of 30 cm<sup>3</sup>) [2], it used a wastewater derived inoculum to supply the necessary microorganisms. Such inocula typically contain *G. sulfurreducens* and are often as catalytically active as pure culture *G. sulfurreducens* with respect to catalyzing anode oxidation of acetate. The relatively high power density of this MFC (excluding energy consumption of pumps) was achieved by using membrane with a relatively high ionic permeability. While the membrane also allowed oxygen to diffuse from the cathode half-cell into the anode half-cell, it used an oxygen-tolerant inoculum (pure culture *G. sulfurreducens* is not oxygen tolerate). The tradeoff in such a configuration typically is that an appreciable portion of the fuel is oxidized directly by oxygen in the anodic half-cell, resulting in diminished coulombic efficiency. In this case, however, the coulombic

efficiency was reasonably high (83.5%), due apparently to a combination of geometry and materials used. Moreover, this MFC used carbon cloth anodes, which provide a higher fuel mass transport accessible surface area than smooth graphite plates. Examination of the power vs. voltage (polarization plot) of this MFC [2] indicates that it was still limited in power generation by ion conductivity of the membrane (evident by the semicircular shape of the dependency), suggesting that while the membrane has higher ion permeability than those traditionally used in MFCs (i.e., Nafion), even higher power (higher power density) may have further been achieved if a higher ion permeable membrane was available within the limit that oxygen intrusion into the anodic half-cell does not disproportionately decrease coulombic efficiency.

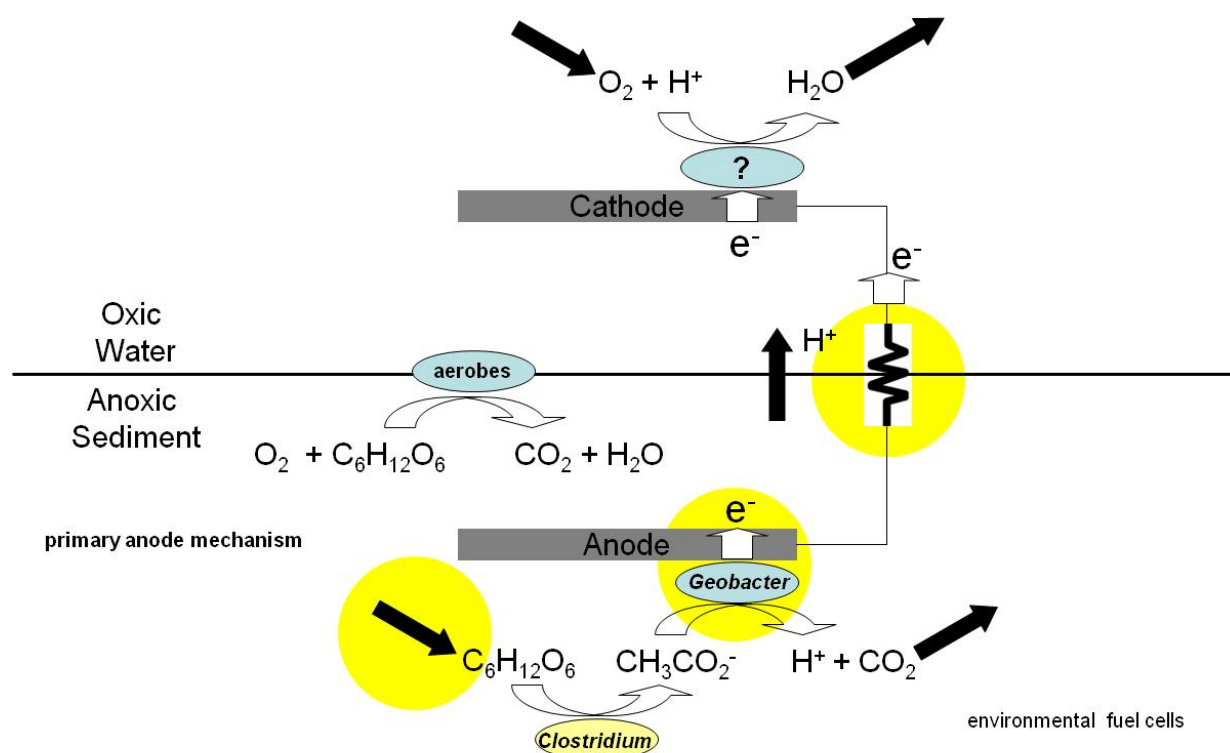
In the case of the microbial fuel cell that demonstrated 0.5 W/L [56], it used *Shewanella oneidensis* and a very high surface area reticulated vitreous carbon anode (i.e., three-dimensional, porous), providing a very high anode surface area to microbial fuel cell volume ratio [15]. While *S. oneidensis* is not known to grow thick, highly catalytic biofilms [28], the assumed thinness of the biofilm may have contributed to the ability to benefit from the high surface area of the anode, resulting in the high overall power density, whereby anode pores were less susceptible to clogging than if *G. sulfurreducens* was used, which is known to form very thick catalytically active biofilms [48]. Moreover, the very small volume of this microbial fuel cell may have enhanced efficiency of mass transport with respect to maximizing the ratio of the anode surface area that has access to fuel vs. the total anode surface area. The general trend for microbial fuel cells is that power density declines considerably with increasing volume, resulting in liter-sized MFCs with power densities that are less than 0.01 W/L [61-65]. Understanding what determines the scaling laws for microbial fuel cells is an important issue that needs to be addressed in order to transition MFCs to the Fleet.

Table 2 lists the calculated energy density and specific energy of hydrogen and of acetate (a representative microbial fuel cell fuel) when oxidized by oxygen in each type of fuel cell. The listed values are useful when considering applications in which the fuel stock (a tank of pressured hydrogen gas or of acetate saturated water) is the dominant mass and/or volume component of the system. Here it can be seen that, in theory, microbial fuel cells may eventually compete against hydrogen fuel cells based on energy density. Table 2 also reveals the very high specific energy of compressed hydrogen gas, and combined with the high specific power of hydrogen/oxygen fuel cells, makes hydrogen/oxygen fuel cells a prime choice for applications where low weight is a premium, such as unmanned air vehicles. In these comparisons, however, it is important to note that both lithium batteries and hydrogen gas are considered explosion hazards, and Navy applications requiring lithium batteries or hydrogen gas require extensive safety evaluation and costly certification before approval for use by an acquisition program. Finally, Table 2 lists the energy density and specific energy of domestic wastewater. While neither is exceedingly high, wastewater is abundant (the Blue Plains Advanced Waste Water Treatment Plant adjacent to the Naval Research Laboratory in Washington, DC, for example, processes on average 2 billion liters of wastewater per day). Wastewater is a viable fuel source for microbial fuel cells [1, 66-70] that is already under mass transport, enabling the possibility of wastewater treatment that results in power generation instead of power consumption. It is important to note that a variation of the wastewater-fed MFC gaining attention in the research literature is the wastewater-fed microbial electrolysis cell (MEC). Identical in form to the wastewater-fed MFC, the wastewater-fed MEC uses power externally applied to the external circuit to couple oxidation of organic matter in wastewater at the anode (as occurs in MFCs) with reduction of the protons at the cathode forming hydrogen gas [55, 71]. The appeal of wastewater-fed MECs is ability to generate hydrogen gas from wastewater, useful, for example, to operate hydrogen fuel cell-powered cars, while simultaneously oxidizing the organic matter content of wastewater, which is an essential component of wastewater treatment. Moreover, the energy consumed per equivalent of hydrogen gas generated from wastewater is significantly less than for conventional electrolysis cells, in which water is oxidized at the anode, forming oxygen and protons, owing to the greater free energy (i.e., greater amount of energy liberated) of oxidation of organic matter vs. water.

## 4. THE BENTHIC MICROBIAL FUEL CELL

### 4.1 Background

The Benthic Microbial Fuel Cell is distinct for being the only type of microbial fuel thus far demonstrated to sustain a net positive power output. The BMFC generates electrical power by oxidizing organic matter (fuel) residing in sediment pore water with oxygen (oxidant) in overlying water. It consists of a noncorrosive anode (typically consisting of but not limited to graphite) embedded in marine sediment connected by an external electrical circuit to a noncorrosive cathode (also typically consisting of but not limited to graphite) positioned in overlying water. Figure 4 is a schematic representation of the BMFC concept. An electric-power consuming device (such as a marine deployed Navy sensor) can comprise the external circuit indicated by the resistor.



*Nature Biotechnology* 20, 821-825 (2002); *Science* 295, 483-485 (2002); *Environmental Science and Technology* 35, 92-195 . 35,192-19; US Patent 6,913,854

Fig. 4 – Schematic depiction of the Benthic Microbial Fuel Cell

In many marine environments, substantial organic matter resides in sediment porewater. Typically, this organic matter is derived primarily from settlement of dead phytoplankton from overlying water and/or erosion of adjacent land. Likewise, in many marine environments, oxidants such as oxygen and sulfate are supplied into sediment porewater by diffusion from overlying water and by mechanisms driven by motion of overlying water (i.e., advection, for example tidal pumping, or resuspension). In such environments, the combination of organic matter and oxidants support microbial activity within the

sediment. Typically, the amount of organic matter far exceeds the amount of oxidant resulting in microbial depletion of oxidants in sediment. As a result, the BMFC anode acts as a potent oxidant owing to its electrical connection through the intervening circuit and cathode to oxygen, a potent oxidant, in overlying water (Fig. 4). When a BMFC is deployed and the anode embedded into sediment, a biofilm spontaneously forms on the anode enriched in sedimentary mineral-reducing microorganisms, which are able to directly use the anode as oxidant. These microorganisms are thought to catalyze oxidation of sedimentary acetate with coupled electron transfer to the anode [5]. The acetate consumed at the anode is generated by fermentation of glucose by other microorganisms in the sediment represented by clostridium in Fig. 4. The products of the anode reaction are carbon dioxide, protons, and electrons. The carbon dioxide diffuses away from the anode and its ultimate fate is not yet been determined. The protons diffuse away from the anode through sediment and overlying water to the cathode where they are consumed. The electrons flow through the external circuit to the cathode. A biofilm spontaneously formed on the cathode catalyzes oxidation of the cathode with coupled reduction of oxygen [45] (i.e., the electrons liberated at the anode which flowed through the external circuit to the cathode are transferred from the cathode to oxygen in overlying water) and reaction of the anode generated protons to form water.

A key issue of the BMFC is that the operating voltage is very low, typically 0.35 V when generating maximum power. Furthermore, multiple BMFCs cannot be electrically connected in series to increase voltage as in the case of batteries owing to its lack of an isolating enclosure (although connecting multiple BMFCs in parallel to increase current works well). This requires power conditioning electronics in order to operate Navy sensors typically requiring 3, 6, 9, 12 V, etc., which have been successfully developed [8, 72, 73]. The low raw voltage output of BMFC also requires that attention be paid to ohmic loss due to resistance of the electrodes themselves and of the electrical leads.

A key feature the BMFC is longevity (persistence), which is attributed to 1) constant supply of fuel and oxidant (i.e., mass transport) by environmental processes (e.g., diffusion, tidal pumping, sediment resuspension); 2) aerobic microorganisms inhabiting the sediment/water (benthic) interface that inhibit oxygen penetration into sediment by depleting oxygen as it enters sediment, while allowing other chemical species such as protons to flow through, thereby acting as an effective de facto ion exchange membrane; 3) constant rejuvenation of its microbial electrode catalysts; and 4) ability of these microbial catalysts to exchange electrons with their electrodes without reliance on exogenous (added) electron-transfer mediators. The ability to provide power far longer than any existing portable marine power supply to persistently operate marine deployed sensors is the key reason why BMFCs are being developed by the Navy.

Multiple lines of evidence indicate that power output of a BMFC is limited by mass transport of fuel to the anode, attributed to diffusion of fuel through sediment porewater and to advection of sediment porewater through sediment driven by hydrodynamic processes such as tides and storm fronts. This is made most evident by the ability to increase BMFC power output by artificially increasing the fuel mass transport rate [13], the relatively high power output observed for a BMFC deployed at a cold seep where the fuel mass transport rate is naturally very high [6], and diurnal fluctuation in power output that correlates with tides often observed for BMFCs deployed in coastal environments [4, 8, 12]. Moreover, in the laboratory, under conditions when current is not mass transport limited (i.e., three-electrode configuration, flowing and stirred media, and excess acetate), a *G. sulfurreducens* biofilm-modified graphite anode can sustain on order of 0.0005 A/cm<sup>2</sup> of anode geometric surface area [18], whereas BMFC anodes can sustain on order of only 0.000001 A/cm<sup>2</sup> depending on the location [4]. In addition, after sitting at open circuit for a considerable period of time (i.e., not generating power), when discharged, a BMFC will initially generate orders of magnitude higher current, which will decay over time to steady state value [74] consistent with generation of depletion zone of fuel that develops around the anode as it is more quickly consumed than it can be replenished (i.e., mass transport limitation), and also consistent with high ion permeability of the benthic interface enabling the transient high current.



The general design solution to increase the net rate of a mass transport rate limited electrode reaction when the reactor is very large compared to the electrode, as in the case of a BMFC anode embedded in marine sediment at the bottom of a bay for example, is to increase the geometric surface area (GSA) of the electrode ( $GSA = 2 \times \text{length} \times \text{width}$  for a planar electrode of negligible thickness) to capture a larger flux of reactant. Very large anodes, however, are difficult to transport and stow, and require extensive effort to embed into sediment. Moreover, BMFCs operate at low voltage, typically 0.35 V, making them highly susceptible to voltage loss and thus power loss due to resistance to current flow through the electrodes and electrical leads used to connect the electrodes to the external circuit (i.e., ohmic losses), ultimately limiting anode size. (As mentioned earlier, multiple BMFCs cannot be connected in series to generate higher voltages because all the anodes would share a common anodic half-cell and the cathodes would share a common cathodic half-cell.)

Nearly all BMFCs demonstrated to date use cathodes consisting of carbon fiber bottle-brush electrodes [6, 8, 9, 12], comprised of bundles of carbon fiber wool-like bristles twisted between a pair of titanium or stainless steel core wires that act as structural members and current collectors, originally developed as cathodes for galvanic seawater batteries [75, 76]. These cathodes are compact, lightweight, durable, have favorable chemical and microbial properties, are easy to position in water just above the embedded anode, and are sufficiently effective at reducing oxygen in seawater without reliance on platinum catalysts owing to their very high surface area.

First-generation BMFCs used anodes fabricated from solid graphite, typically plates, owing to their favorable chemical and microbial properties that were embedded into sediment horizontally to the sediment/water interface [4, 77]. Such BMFCs generate maximum sustained power that, to a first approximation, scales linearly with geometric surface area of the anode on the order of 0.01 W per square meter depending on the location deployed. In order to generate a useful amount of power on the order 0.1 to 1.0 W to operate Navy marine-deployed sensors requires large scale anodes comprised of many plates that must be embedded into sediment. In one example demonstrated by Frank McNeilly and colleagues at the NUWC, Newport, RI, in FY09 [77, 78], a BMFC equipped with a cathode comprised of 16 bottle-brush cathodes and an anode comprised of 39 graphite discs, each 55.8 cm diameter  $\times$  1.3 cm thickness (0.25 m<sup>2</sup> foot print area (FPA), 0.5 m<sup>2</sup> GSA, and 3.1 L volume for each disc; 9.6 m<sup>2</sup> FPA, 19.2 m<sup>2</sup> GSA, and 97 L for the entire anode array) sustained approximately 0.1 W, corresponding to 0.012 W/m<sup>2</sup> FPA, 0.01 W/m<sup>2</sup> GSA, and 0.0001 W/L based on the anode array. While useful for demonstrating the concept, this BMFC highlights the impractical nature of such BMFCs owing to the unduly large anode that must be transported, stowed, and embedded in sediment to generate a worthwhile amount of power. A similar BMFC comprised of an array of matching anode and cathode plates was deployed by the author in FY06 in the Potomac River in Washington, DC, that was configured to power a meteorological buoy with an RF link for real-time data transmission, emphasizing the ability to integrate BMFCs with a real system [8]. A promising design variation for a planar anode-based BMFC is the one being developed by Chadwick and colleagues at SPAWAR, San Diego, in which the anode consists of graphite fiber cloth (1-m wide  $\times$  12-m long  $\times$  0.02-cm thick) [79]. As is shown in Fig. 5, the anode is rolled up when not in use, and deployed by an embedment plough pulled by a small boat, which unrolls the anode and embeds it parallel to and beneath the sediment surface. Such a “magic carpet BMFC” was recently shown to generate 0.09 W in the San Diego Bay [79]. While the anode is very compact in the stowed configuration (approximately 2 liters based on the estimated 5-cm. diameter of the rolled-up anode), yielding 0.0075 W/m<sup>2</sup> FPA, 0.0034 m<sup>2</sup> GSA, and 0.045 W/L, the volume of the embedment sled in its present configuration (estimated here as 500 liters), greatly reduces the overall power density of this BMFC. Regardless, this BMFC is the only design thus far demonstrated not to rely on divers or ROVs for deployment. Moreover, ignoring the volume of the embedment sled, which can be reused to deploy multiple anodes, and assuming the stowed volume of the entire BMFC including the cathode (a 1-m-long graphite fiber bottle-brush electrode) is 5 liters, the resulting power density is 0.018 W/L. Over a year of operation (8760 h), the equivalent energy density of this BMFC would be 158 Wh/L ( $[0.018 \text{ W/L}] \times$

[8760 h/y]). Comparison to the typical energy density of alkaline batteries (430 Wh/L; see Table 1) indicates that this BMFC would need to operate for at least 2.7 years (i.e., the breakeven point) with alkaline batteries ( $[0.018 \text{ W/L}] \times [2.7 \text{ y}] \times [8760 \text{ h/y}] = 430 \text{ Wh/L}$ ) to be competitive with alkaline batteries based on power density, and more like 1.35 years based on 50% packing efficiency of alkaline batteries into oceanographic enclosures taking into consideration volume of the canisters. The low power density per GSA may result from ohmic loss owing to the length of the anode, which has non-negligible resistance over which current is conducted. The large benthic footprint area occupied by the anode (BFA = length  $\times$  width) of this type of BMFC anode when scaled up requires that a large unobstructed area of the benthic interface be disrupted to embed the anode (e.g., 167 m<sup>2</sup> BFA to achieve 1 W, not taking into account ohmic losses), and may make the anode prone to being exhumed by storms or fishing trawls (a major hazard for oceanographic sensors deployed in coastal environments [80]). At the most recent Office of Naval Research Microbial Fuel Cell Program Review (July 25, 2013, Arlington, VA) however, Bart Chadwick indicated that the occurrence of such failures can be minimized by embedding the anode sufficiently deep. Regardless, carbon fiber fabric is a significantly more durable BMFC anode material compared to solid graphite, which is prone to shattering during transport and deployment. If the power density per GSA of the anode can be improved, possibly by incorporation of current collectors such as titanium threads woven into the fabric (Chadwick and colleagues are working on this now), the resulting higher power density per unit anode volume and per unit BFA may make this type of BMFC a viable alternative to batteries. At the same program review, Chadwick and colleagues reported on a larger scale version of their BMFC design (40 m<sup>2</sup> FPA) that sustained 0.250 W in the San Diego Bay. Regardless, carbon fiber fabric is a significantly more durable BMFC anode material compared to solid graphite, which is prone to shattering during transport and deployment. If the power density per GSA of the anode can be improved, possibly by incorporation of current collectors such as titanium threads woven into the fabric, the resulting higher power density per unit anode volume and per unit BFA may make this type of BMFC a viable alternative to batteries.



Fig. 5 – Photographs depicting “magic carpet” BMFC (provided by B. Chadwick, SPAWAR, San Diego). Left: embedment sled loaded with a rolled up carbon cloth anode. Right: deployment testing on beach, anode unrolled and buried beneath sand as sled is pulled forward. Sled detaches from anode and can be retrieved and reused.

An alternative configuration to those described above using planer anodes deployed parallel to the sediment surface are so called “cube” anodes comprised of parallel graphite plates inserted vertically into sediment, as shown in Fig. 6 [8, 9]. Typically, the plates are on the order of 30.5-cm-tall  $\times$  30.5-cm-wide  $\times$  0.32-cm-thick and are arranged in an array with the plates aligned parallel to one another on a 2.5-cm-pitch (0.09 m<sup>2</sup> FPA, 2.2 m<sup>2</sup> GSA, and 28.3 L for an entire array), and are embedded such that the top of the array is an inch or so below the sediment surface (such thin plates proved too fragile for future demonstrations).

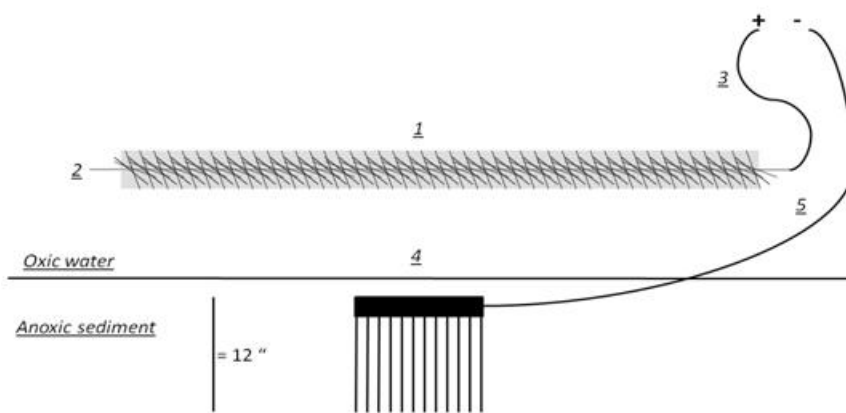


Fig. 6 – Schematic depiction of the cube anode based BMFC: 1) graphite bottle-brush cathode, 2) twisted core wire current collector of the cathode, 3) cathode electrical lead, and 4) benthic (sediment/water) marine interface.

In one case, the author demonstrated a BMFC in the field at the Rutgers University Marine Field Station (RUMFS) in FY08 that was equipped with an anode comprised of a single graphite plate cube array that sustained 0.036 W, corresponding to 0.39 W/ m<sup>2</sup> FPA, 0.016 W/ m<sup>2</sup> GSA, and 0.0013 W/L based on the anode array [81]. Moreover, 10 such BMFCs deployed side by side at the same site generated more than 0.3 W, saturating the 1-amp current input of powering monitoring electronics used at the time.

#### 4.2 The Advanced Benthic Microbial Fuel Cell (ABMFC)

One approach to increasing the power density of BMFCs is to use a graphite-fiber bottle-brush electrode for both the anode and the cathode. In order to provide necessary rigidity to the anode and prevent compaction of carbon fiber strands by direct contact with sediment, the anode carbon fiber electrode is inserted into a small diameter (e.g., 1 in.) slotted PVC tube [12]. In order to deploy, the tube-enclosed bottle-brush anode is pressed horizontally into the sediment surface.

Figure 7 is a schematic depiction of a small-scale advanced BMFC (ABMFC) tested by the author with support by Jeff Lloyd and colleagues at SPAWAR in San Diego Bay FY10 that was deployed by divers by pressing the tube horizontally into sediment [12]. Figure 8 is a portion of the time record plotted as sustained power generated by the ABMFC and the cube BMFC that was deployed alongside for comparison. Figure 9 is the same portion of the time record plotted as sustained power density (power normalized by volume of the anode).

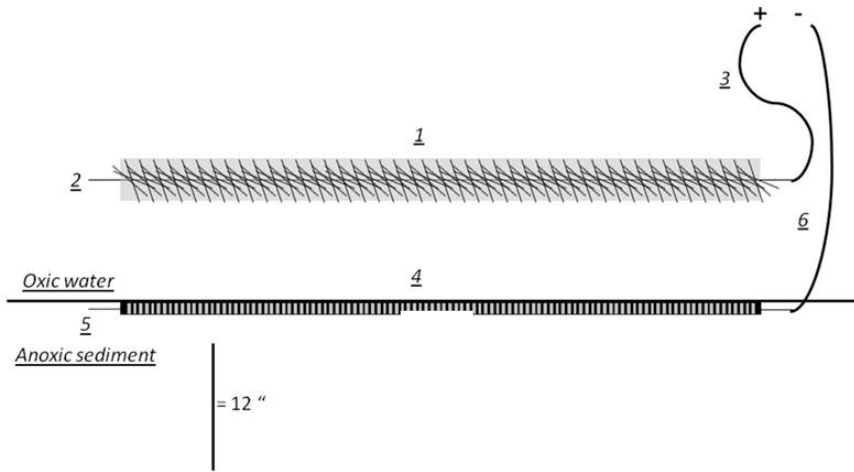


Fig. 7 – Schematic depiction of the Advanced BMFC (ABMFC): 1) graphite bottle-brush cathode; 2) twisted core wire current collector of the cathode; 3) cathode electrical lead; 4) benthic (sediment/water) marine interface; and 5) graphite bottle-brush anode housed in a slotted PVC tube.

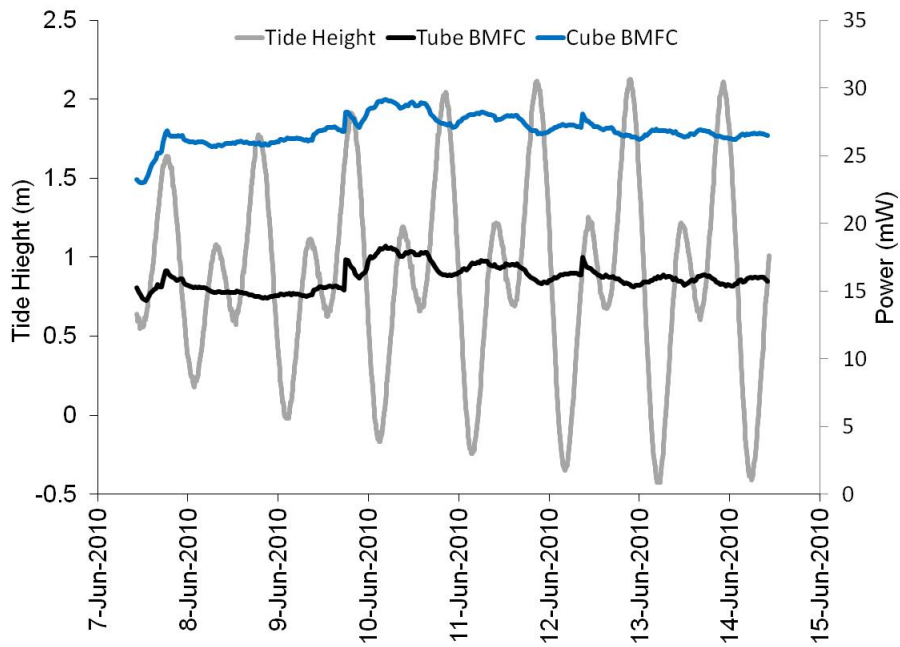


Fig. 8 – Portion of time record of power generated by the ABMFC (black) and cube-based BMFC (blue) at the San Diego Bay site.

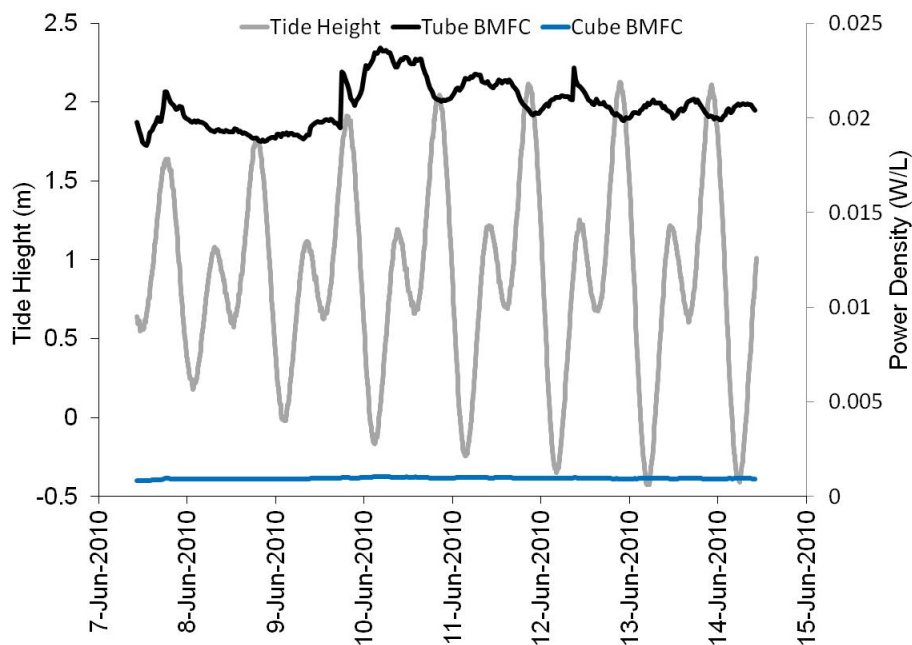


Fig. 9 – Portion of time record of power density of the ABMFC (black), cube-based BMFC (black) at the San Diego site

The ABMFC deployed in San Diego Bay during FY10 was equipped with a 1.53-m-long  $\times$  5.1-cm-diameter graphite bottle-brush anode housed in 1.53-m-long  $\times$  2.5-cm-diameter slotted PVC tube embedded inches below and parallel to the anode surface. This ABMFC generated 0.015 W at 0.35 V. This equates to a power density of 0.12 W/m<sup>2</sup> GSA (per square meter of the anode geometric (cylindrical) surface area) and 0.024 W/L (per liter of the anode (cylindrical) displacement volume) - both very high). By comparison, a BMFC deployed at the same time at the same site configured with a graphite plate anode array (12 plates, each 0.64-cm-thick  $\times$  30.5-cm-long  $\times$  30.5-cm-wide arranged in an array with 3/4-in. spacing between adjacent plates) embedded vertically into sediment such that the top of the array was inches below the sediment surface generated 0.025 W at 0.35 V (0.011 W/m<sup>2</sup> GSA based on the total GSA of the 12 plates, and 0.00083 W/L (0.0025 A/L) based on 30.5-cm  $\times$  30.5-cm  $\times$  30.5-cm displacement dimensions of the entire array – both considerably lower than the tube anode).

The results indicate 1) that the tube-enclosed anode is significantly easier to embed than graphite plate anodes and 2) that the tube-enclosed bottle-brush anode benefits from enhanced and mass transport through the anode of porewater containing organic matter and anode generated protons. The net result is a very durable, lightweight, and easier to deploy BMFC that generates approximately 20-fold higher current density based on anode volume compared to graphite cube anode-based BMFCs. Moreover, the breakeven point compared to alkaline batteries based on power density is comparable to that of the “magic carpet” BMFC described above (Fig. 5), but in a form that may be easier to deploy.

A proposed explanation for the increased power density of the ABMFC vs. that of the graphite plate array-equipped BMFC may be the relationship between the depletion zone of fuel that envelopes a BMFC anode during power production and the geometry of the anode. Following Fick’s laws of diffusion [82], consumption of an electrode reactant (such as sedimentary acetate by a BMFC anode) results in a depletion zone of thickness  $d$  that surrounds the anode in which the concentration of the reactant drops from its value in bulk media (sediment) at the outer boundary of the depletion zone (distance  $r$  normal from the electrode surface) to a lower concentration at the electrode surface due to its consumption by the

electrode. (Depletion zones associated with power generation surrounding BMFC plate anodes have been observed [4].) In the case of BMFCs, the key factor affecting  $d$  is sediment porosity whereby sandy, permeable, organic-poor sediments favor relatively large values of  $d$  while silty, impermeable; organic-rich sediments favor relatively small values of  $d$ . The current due to mass transport-limited consumption of the reactant by the electrode is proportional to the surface area of the depletion zone. In the case of a cylindrical electrode, this can be expressed as

$$i = K2\pi(r + d)l,$$

where  $K$  is the proportionality constant and  $l$  is the electrode length. The current density per unit geometric surface area of the electrode (**GSA**) can be expressed as

$$\frac{i}{GSA} = \frac{K2\pi(r+d)l}{2\pi r l} = \frac{K(r+d)}{r},$$

and the current density per unit volume of the electrode ( $V$ ) can be expressed as

$$\frac{i}{V} = \frac{K2\pi(r+d)l}{\pi r^2 l} = \frac{K2(r+d)}{r^2}.$$

A consequence of the radial geometry of a cylindrical electrode is that as the radius of the electrode ( $r$ ) is made smaller, the radius of the depletion zone ( $r + d$ ) is expected to become independent of  $r$ . As a result, the surface area of the depletion zone and, thus, current is expected to become dependent only on the anode length ( $l$ ) and not on the anode radius ( $r$ ). That is, when the radius is sufficiently small, further reducing the radius of the anode does not reduce current and, thus, power. Moreover, current density per unit surface area of the electrode and per unit volume of the electrode is expected to increase. In this way, it may be possible to configure very small volume BMFCs anodes that generate as much power as much larger anodes. The limit to the smallest value of  $r$  is that current density ( $i/GSA$ ) cannot exceed the 0.0005 A per cm<sup>2</sup> GSA limit of the biofilm-catalyzed anode reaction.

In contrast, in the case of a planar anode of width  $w$  and length  $l$  such as the magic carpet anode described above, a consequence of the linear geometry of the anode is that as the width or length is changed, the surface area of the depletion zone and, thus, current is expected to change in proportion. That is, current and, thus, power are expected to scale linearly with the electrode surface area, and current density per unit geometric surface area and per unit volume remains the same.

In FY 11, an array of 25 ABMFCs were deployed at the Rutgers University Marine Field Station (RUMFS) in coastal New Jersey that are similar to the ABMFC deployed in the San Diego Bay with the exception that the bottle-brush anodes were 4-in.-long  $\times$  2-in.-diameter housed in 4-in.-long  $\times$  2-in.-diameter slotted PVC tubes. (Here, the effective anode diameter is 2 in.) These BMFCs were generating an average of 0.0033 W (0.0095 A) at 0.35 V (0.08 W total) (equates to a surface area power density of 0.017 W/m<sup>2</sup> GSA, a power density of 0.0013 W/L, – all lower than observed in San Diego). By comparison, a BMFC deployed at the same time at the same site equipped with a graphite plate disc anode (a single plate, 1-in.-thick  $\times$  16-in.-diameter) that was embedded horizontally into sediment such that the top of the plate was inches below the sediment surface generated 0.0048 W (0.014 A) at 0.35 V (0.0185 W/m<sup>2</sup> GSA and 0.053 A/m<sup>2</sup> GSA, and 0.0005 W/L and 0.00014 A/L based on the volume occupied by the anode). Unlike at SPAWAR, the power and current densities per geometric surface area of the tube and disc anode equipped BMFCs were nearly identical to one another. Owing to the low porosity of sediment of the New Jersey site, the comparable current and power densities may have resulted from the anode radius (2.5 cm) being considerably larger than thickness of the depletion zone

surrounding the anode, resulting in linear diffusion behavior. This is corroborated by earlier results described above in which a BMFC equipped with a cube anode identical to the one deployed at the SPAWAR site generated  $0.016 \text{ W/m}^2$  GSA ( $0.046 \text{ A/m}^2$ ) when deployed at the RUMFS site based on the total GSA of the 12 graphite plates[8]) – similar to that of the tube and disc anode equipped BMFCs now operating at the RUMFS site. Here, the depletion zone thickness appears to be so small that each of 12 plates comprising the array had its own depletion zone boundary supplying fuel to the anode. Just as in the case of the SPAWAR results, however, we contend that a considerably smaller diameter tube anode, one in which the radius is smaller than the depletion zone thickness, could have generated a higher power density per geometric surface and per volume as the 5.1-cm-diameter tube before hitting the  $5 \text{ A/m}^2$  GSA current density limit. In this case, the net power per anode length may be considerably lower, since the surface area of the outer boundary of the depletion zone would be expected to be considerably smaller as well before it becomes independent of the anode radius. Since the depletion zone thickness at the RUMFS site does appear to be very small, however, thin anodes could be deployed close together (on the order of inches) in parallel to shorten net anode length since their depletion zones should not overlap.

### 4.3 The Chambered Benthic Microbial Fuel Cell

An alternative BMFC design involves placing the anode in an inverted chamber with the open end embedded beneath the sediment such that the chamber becomes filled with sediment porewater [13, 14, 83]. The appeal of this design approach is that it may be easier to embed the chamber than the anodes themselves, and that porewater can be pumped into the chamber through the open bottom to increase mass transport and thus power. While the latter ability showed promise in the laboratory [12], it became quickly apparent that using pumps to increase mass transport in the field is not feasible because the BMFCs did not generate enough power to offset power consumed by the pumps. A more promising approach involves using flexible membrane as the chamber top with a one-way check valve intended to enable use of natural upwelling of sediment porewater to increase fuel mass transport to the anode [83]. The chambered BMFC recently reported by Clare Reimers and colleagues from Oregon State University [14] generated an average power output of  $0.011 \text{ W}$  ( $0.044 \text{ W/m}^2 \times 0.25 \text{ m}^2$  footprint area). Although impressive with respect to system integration (they powered an acoustic modem and an oxygen/temperature sensor), based on the 95-liter chamber volume (0.56-m diameter  $\times$  0.38-m height), this equates to a power density of only  $0.00012 \text{ W/L}$ . However, chambered BMFCs might prove to be the best design for bottom-mounted oceanographic sensor moorings in which the unused volume of a mooring is used as the chamber, resulting in a fully integrated BMFC-instrument sensor.

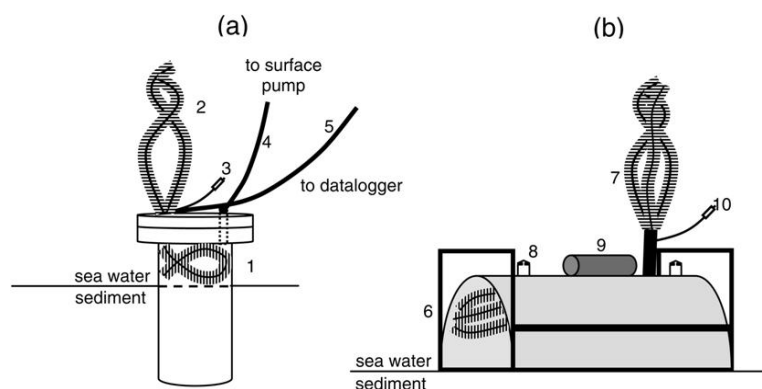


Fig. 10 – Schematic depiction of Chambered BMFC (adapted from Ref. 83). (a) Schematic of the Yaquina Bay BMFCs. Each BMFC included a 1-m-long carbon brush anode inside an anode chamber with a  $2 \times 10^{-3} \text{ m}^3$  volume (1); a 2-m-long carbon brush cathode (2); a reference electrode (3); and a sampling tube fitted to a port (4). Electrodes were connected to the data logger through 20 m of 12-gauge, three-conductor wire (5). (B) The Monterey BMFC was constructed from a piece of plastic sewer pipe and included a 3-m-long carbon brush anode (6); a 4-m-long carbon brush cathode (7); two identical check valves (8); a titanium pressure housing containing passive potentiostat and dataloggers (9); and a reference electrode (10).

#### 4.4 The Cold Seep Experiment

Thus far, the organic matter considered as the fuel source for BMFCs is that dispersed in marine sediment where the dominant mode of mass transport is diffusion. Ample sites, such as cold seeps, exist in the marine environment where organic matter at the benthic interface flows at relatively high rates. In 2004, in a series of experiments led by Clare Reimers at Oregon State University, a BMFC [6] composed of a graphite bottle-brush cathode and a graphite spike anode was deployed on a cold seep in the Monterey Canyon off the coast of California in which an ROV was used to insert the anode spike directly into the seep. The power density based on the footprint area of the spike ( $1.1 \text{ m}^2$  FPA) is the highest of any recorded to date and is attributed to the high flux of fuel-infused porewater flowing out of the seep to the anode. This result was later corroborated by a second experiment led by Clare Reimers in which a chambered BMFC was placed overtop the seep[14], resulting in a power density based on the footprint area of the chamber ( $1.1 \text{ W/m}^2$  FPA) that was the highest for any chambered BMFC not relying on an external pump. There are numerous features on the seafloor that exhibit high rates of fuel mass transport (e.g., at methane hydrate outcrops), which may constitute BMFC hotspots where very high power can be generated.

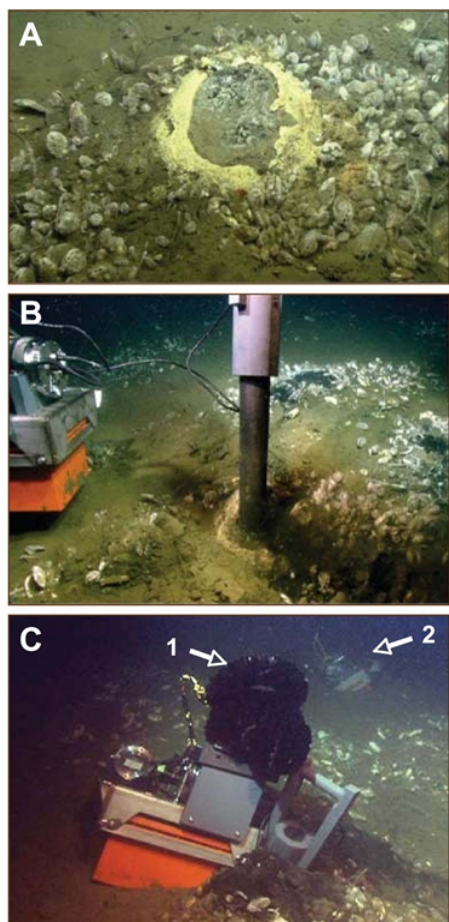


Fig. 11 – Photographs depicting BMFC at a cold seep in Monterey Canyon (adapted from Ref.). Seep ring at Extravert Cliff where FC1 was placed. (B) FC1 anode being inserted by the ROV Ventana. (C) FC2 showing cathode carbon-brushes (1 arrow) and graphite plate mounted to a PVC plate above the load housing and battery. The anode is buried to the right so that only the PVC cap and handle are visible. FC1 is in the background (2 arrow).



At the most recent Office of Naval Research Microbial Fuel Cell Program Review (July 25, 2013, Arlington, VA) Peter Girguis of Harvard University reported on a BMFC in which the anode was inserted into a hydrothermal vent that generated 1.1 W, further indicating potential to generate high amounts of power at localized sites in the marine environment characterized by high concentrations and/or rates of mass transport of BMFC fuel.

#### 4.5 Conclusion

Microbial fuel cells (MFCs) are fuel cells that generate electrical power by using microorganisms to catalyze the anode reaction [1]. MFCs enable generation of electrical power from organic matter naturally oxidized by microorganisms, such as glucose and acetate, for which conventional anode catalysts do not exist. Such fuels are abundant, renewable, relatively high in energy density and are non-explosive. It also enables generation of electrical power from non-purified sources containing organic matter such as wastewater. The key drawback of MFCs is that the rate at which microbes can catalyze anode reactions (i.e., their catalytic activity) is orders of magnitude slower than conventional catalysts. For this reason, MFCs are being investigated primarily for low power consuming, long duration applications such as remotely deployed sensors, for which they may prove superior to existing power supplies when fully developed. Key factors limiting MFC development include poor performance of existing cathode oxygen reduction catalysts and ion exchange membranes in neutral pH, complex ionic electrolytes inherent to MFCs, and power required by balance of system (i.e., pumps) for delivery of reactants and removal of products. As such, there have not been any demonstrations to date of standalone MFCs that generate a sustained net positive power output with the exception of the Benthic Microbial Fuel Cell (BMFC).

The BMFC has proven a durable source of persistent power to operate Navy in-water sensors presently powered by batteries. Table 3 provides a compilation of notable BMFC field demonstrations. Based on these demonstrations and the author's experience in designing, deploying, and evaluating BMFCs, it is clear that BMFCs must be made easier and more reliable to deploy and have a higher power density per unit volume (at least in the stowed configuration) due to space limitations of potential deployment platforms. (While batteries do not last indefinitely, they are easy to deploy, have useful energy densities, and can last years – at least long enough to satisfy most typical deployment scenarios.) This will significantly impact applications, transition to the Fleet, and enable persistent operation of robust sensors. Because BMFCs are fuel mass transport-limited, achieving this goal requires development of BMFCs that use small volume anodes with high volumetric power densities. Two design approaches seem to point in this direction: the “magic carpet” BMFC under development by Bart Chadwick and colleagues at SPAWAR, San Diego, and the Advanced BMFC under development by the author and colleagues at NRL. In addition, the chambered BMFC may prove the best option when fully integrated within the unused volume of a bottom-mount sensor mooring. Moreover, one way in which BMFCs may prove superior to conventional battery packs for long term applications is that they can be made lightweight. Large battery packs are extremely heavy requiring significant assets to deploy.

Table 3 – Compilation of Field Test BMFCs

| Reference                            | [4]                                       | [4]                                       | [8]   |
|--------------------------------------|---|---|---|
| Principal Investigator               | Reimers                                   | Tender                                    | Tender  |
| Institution                          | Rutgers University                        | NRL                                       | NRL   |
| BMFC Location                        | Yaquina Bay Estuary near Newport, OR      | Salt marsh near Tuckerton, NJ             | Potomac River, Washington, DC                   |
| BMFC TYPE                            | matching graphite plate anode and cathode | matching graphite plate anode and cathode | matching graphite plate anode and cathode       |
| Net Power Output (W)                 | 0.0051                                    | 0.0049                                    | 0.024   |
| Device Powered                       | none                                      | none                                      | Meteorological Buoy with real time RF data link |
| BMFC Anode Volume (L)                | 2.20                                      | 2.20                                      | 66.2  |
| BMFC Anode GSA (m <sup>2</sup> )     | 0.37                                      | 0.37                                      | 5.2   |
| BMFC FPA (m <sup>2</sup> )           | 0.18                                      | 0.18                                      | 2.6   |
| Power Density (W/L)                  | 0.0023                                    | 0.0022                                    | 0.00036   |
| Power Density (W/m <sup>2</sup> GSA) | 0.014                                     | 0.013                                     | 0.0046  |
| Power Density (W/m <sup>2</sup> FPA) | 0.028                                     | 0.027                                     | 0.0092  |
| Comment                              | A   | B   | C   |

**Note:** This list is not exhaustive. It does not include, for example, recently completed deployments by the author and NRL colleagues worldwide using a standardized BMFC and environmental sensor package (ADCP, CTD, O<sub>2</sub>) to correlate power with sediment type and environment. Also, it does not contain recent results by Reimers and colleagues powering an acoustic modem relay near the MARS Observatory off the coast of California (<http://www.mbari.org/mars/>).

*Glossary:*

GSA: geometric surface area

FPA: footprint area

*Comments:*

A: Operated for 1 year without indication of depletion in power

B: Operated for 8 months without indication of depletion in power

C: Seven separate BMFCs connected in parallel, operated for 9 months without indication of depletion in power. Low power attributed to low ionic conductivity of brackish river water compared to seawater.

Table 3 – Compilation of Field Test BMFCs, continued

| Reference                            | [8]   | [78]                                       | [12]   | [12]  |
|--------------------------------------|---|--|--|---|
| Principal Investigator               | Tender  | McNeilly                                   | Tender   | Tender  |
| Institution                          | NRL   | NUWC,<br>Newport, RI                       | NRL  | NRL   |
| BMFC Location                        | Salt marsh near Tuckerton, NJ                         | Narragansett Bay, RI                       | San Diego Bay, Near SPAWAR   | San Diego Bay, Near SPAWAR                            |
| BMFC TYPE                            | bottle-brush cathode, graphite plate cube array anode | bottle-brush cathode, graphite plate anode | Advanced BMFC: bottle-brush cathode, bottle-brush anode housed in a slotted pvc tube | bottle-brush cathode, graphite plate cube array anode |
| Net Power Output (W)                 | 0.036   | 0.10                                       | 0.015  | 0.025   |
| Device Powered                       | Meteorological Buoy with real time RF data link       | acoustic vector sensor                     | none   | none  |
| BMFC Anode Volume (L)                | 28.3  | 120.9                                      | 0.62   | 28.3  |
| BMFC Anode GSA (m <sup>2</sup> )     | 2.2   | 20.28                                      | 0.10   | 2.2   |
| BMFC FPA (m <sup>2</sup> )           | 0.09  | 10.14                                      | 0.031  | 0.09  |
| Power Density (W/L)                  | 0.00127   | 0.00083                                    | 0.024  | 0.00088   |
| Power Density (W/m <sup>2</sup> GSA) | 0.0164  | 0.0049                                     | 0.15   | 0.0114  |
| Power Density (W/m <sup>2</sup> FPA) | 0.40  | 0.01                                       | 0.48   | 0.28  |
| Comment                              | D   |  |  | E   |

*Comments:*

D: Single cube array BMFC

E: Volume, GSA, and FPA of anode based on tube dimensions

Table 3 – Compilation of Field Test BMFCs, continued

| Reference                            | [84]   | [83]  | [13]   | [72]                                      |
|--------------------------------------|--|---|--|---|
| Principal Investigator               | Chadwick   | Reimers   | Tender   | Beyenal                                   |
| Institution                          | SPAWAR, San Diego, CA  | Oregon State Univ.  | NRL  | Univ. of Washington                       |
| BMFC Location                        | San Diego Bay, Near Marine Corp Recruiting Depot                   | Yaquina Bay Estuary near Newport, OR  | Salt marsh near Tuckerton, NJ  | Palouse River, Pullman, WA                |
| BMFC TYPE                            | bottle-brush cathode, 12-m × 1-m carbon cloth "magic carpet" anode | bottle-brush cathode, bottle-brush anode housed in a chamber with open end inserted into sediment | Advanced BMFC: bottle-brush cathode, bottle-brush anode housed in a slotted pvc tube | matching graphite plate anode and cathode |
| Net Power Output (W)                 | 0.09   | 0.011   | 0.09   | 0.0018                                    |
| Device Powered                       | hydrophone   | acoustic modem and oxygen/temp sensor system  | pier mounted digital camera with cell phone data link                                | wireless sensor                           |
| BMFC Anode Volume (L)                | 2  | 95  | 61.78  | 3.76                                      |
| BMFC Anode GSA (m <sup>2</sup> )     | 12   | 0.25  | 4.86   | 0.30                                      |
| BMFC FPA (m <sup>2</sup> )           | 24   | 0.7   | 1.548  | 0.15                                      |
| Power Density (W/L)                  | 0.045  | 0.00012   | 0.00146  | 0.0005                                    |
| Power Density (W/m <sup>2</sup> GSA) | 0.0075   | 0.044   | 0.0185   | 0.006                                     |
| Power Density (W/m <sup>2</sup> FPA) | 0.00375  | 0.016   | 0.06   | 0.012                                     |
| Comment                              | F  | G   | H  |   |

*Comments:*

- F: Uses a reusable embedment sled that can be towed behind a small boat. Estimated volume of sled is 500 liters. No diver or ROV needed.
- G: Volume, GSA, and FPA of anode taken based on chamber dimensions. Variations tested with mechanical pumping of sediment porewater into chamber. Could not sustain enough power to offset power required to operate pump. Variation tested on cold seep in the Monterey Canyon off the coast of CA (1000-m depth) equipped with a unidirectional check valve. Due to local high flux of fuel into the chamber by the seep, power increased 5-fold (to 0.149 W/m<sup>2</sup> GSA). See Ref. [85] for details.
- H: In this test, 25 separate BMFCs were connected in parallel. Volume, GSA, and FPA of anode based on tube dimensions.

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## Appendix

### A CONCISE HISTORY OF MICROBIAL FUEL CELLS (ADAPTED FROM REF. A1)

#### INTRODUCTION

Dissimilatory metal-reducing bacteria (DMRB) are a class of microorganisms that inhabit many natural environments, including aquatic sediments. They possess a distinct capability wherein they can acquire energy by coupling oxidation of organic matter with reduction of insoluble oxidants such as mineral deposits. This capability requires that DMRB transfer respired electrons to the microbe outer surface where electron transfer can occur to an insoluble oxidant. This is distinct from the dominant paradigm, wherein soluble oxidants are transported into microbes for reduction during metabolism. This unique extracellular electron transfer (EET) capability of DMRB extends to reduction of electrodes on which they can proliferate and form persistent films (biofilms). It is this capability of DMRB that makes them useful as anode catalysts in microbial fuel cells. In the case of *Geobacter spp.*, which are *Deltaproteobacteria*, a group of bacteria that share many similar traits, anode biofilms can grow to be many microbes thick. In such biofilms, individual microbes contribute to a flux of electrons to the underlying electrode surface, which may be many cell-lengths away, confounding long-held notions about inability of biological systems to engage in such long-range EET.

#### FROM MUD...

The sediment bottoms of many marine environments are great repositories in which dead creatures, such as phytoplankton that inhabit overlying water, settle. The resulting accumulation of organic matter supports a diversity of sedimentary microorganisms. These microbes metabolize a portion of the organic matter to acquire energy, and in doing so, deplete sedimentary oxidants, which are less abundant. In such sediments, a curious phenomenon occurs in which the oxidants, supplied by diffusion from overlying water, are utilized by microorganisms in a depth-dependent manner in order of oxidation potential [A2]. So oxygen, a potent oxidant that liberates a high amount of energy when used by microorganisms, is preferentially consumed by aerobic microbes at the topmost sediment layer (typically millimeters to a centimeter thick depending on location) as it diffuses into sediment from overlying water, rendering the underlying sediment anoxic (oxygen depleted). However, sulfate, a weak oxidant that liberates one-ninth as much energy when used by microorganisms, is unused by microbes in the topmost sediment layer. Instead, it diffuses deeper into sediment (a few centimeters or so depending on location) where it is eventually used by microbes if other more potent oxidants were depleted higher up in the sediment. Since sulfate is a weak oxidant, the byproduct of microbial sulfate respiration, sulfide, is a potent reductant. As a result of this phenomenon, many marine sediments transition from being oxidizing to reducing over the top few millimeters to centimeters depth due to microbial activity, and when an inert electrode is stepwise inserted into such sediments from overlying (oxygenated) water, its open circuit potential will shift by as much as  $-0.8$  V [A3, A4].

With little more than this knowledge, Reimers et al. [A4] set out to create a battery for powering oceanographic sensors by embedding one electrode into marine sediment and placing the other in overlying water. It was hypothesized that the sediment-embedded electrode would act as an anode owing

to its lower potential, whereas the electrode in the overlying water would act as a cathode owing to its higher potential. The first experiments involved bench-top shoebox-sized aquaria of marine sediments and seawater and platinum electrodes, which generated miniscule current across resistive loads[A4]. The notion at the time was that the anode was oxidizing microbial-generated reductants in sediment, and the cathode was reducing oxygen in the overlying water. Indeed, non-corrosive electrodes made of graphite in seawater have been used for decades as oxygen-reducing cathodes for galvanic seawater batteries [A5, 6]. Since the net reaction proposed at the time by Reimers et al. is thermodynamically favorable (electron transfer from a reductant to an oxidant), power could be expended across a resistive load, connecting the electrodes across which the electrons flowed as long as oxygen was replenished at the cathode (the aquaria were open to the environment to keep the seawater oxygenated) and mass transport (assumed to be diffusion) supplied the anode reactants and removed the anode products. Most interesting was the observation that current increased over time to a steady-state level that could not be explained at the time [A4].

### ...TO MICROBIAL CATALYSTS

These results were followed upon immediately with experiments conducted by Bond et al.[A7], in which graphite electrodes were used for both the anode and cathode, resulting in greater current density per unit area of the anode. After generating power for some time across a resistor, the anode was removed from sediment and examined, revealing a biofilm coating adhered to the anode surface. A genetics-based analysis based on 16S rDNA sequences from microorganisms found in the biofilm was performed and, as a control, an identical experimental setup was used in which the anode and cathode were not electrically connected by a resistor (i.e., left at open circuit) that did not generate power. The results indicated that while both biofilms contained a mixture microorganisms found in sediment, the biofilm on the surface of the power-generating anode had a significantly higher abundance of *Deltaproteobacteria* than the biofilm that grew on the non power-generating anode.

The microorganism available in pure culture most similar to the organism most enriched on the power-generating anode was *Desulfuromonas acetoxidans* (*D. acetoxidans*); a dissimilatory metal-reducing bacteria (DMRB) closely related to *Geobacter spp.* prevalent in marine sediment that couples oxidation of sedimentary acetate with reduction of insoluble iron oxide mineral deposits. A bench-top two-chamber proton exchange membrane (PEM) fuel cell was then assembled using a nafion membrane, which generated power that increased over time to a steady state value following addition of *D. acetoxidans* to the anodic half-cell. Here, instead of sediment, an acetate-containing aqueous solution was used in the anodic half-cell. In the PEM fuel cell, a *D. acetoxidans* biofilm spontaneously grew on the anode surface that metabolized acetate, passing the acquired electrons (eight per equivalent of acetate oxidized) to the underlying anode. In doing so, *D. acetoxidans* was catalyzing the anode half reaction of the fuel cell, resulting in the observed power generation. In essence, *D. acetoxidans* treated the anode of the PEM fuel cell as an insoluble oxidant. Unlike in the natural environment, however, where insoluble oxidants are quickly depleted, requiring the microbes to constantly seek out fresh ones (the microbes are mobile); the anode of the PEM fuel cell is never exhausted owing to its electrical connection to the oxygenated cathode. This induced the microbes to colonize the anode, to stay put, and to proliferate (form a biofilm on the anode surface); hence, current increased as the number of microbes utilizing the anode as a metabolic electron acceptor increased.

Using the anode as an oxidant, *D. acetoxidans* can acquire approximately 0.1 V for each electron passing through to satisfy its energy requirement, which is small but adequate. [A8](This can be determined by taking the difference in redox potential of the oxidation of acetate to carbon dioxide minus the minimum anode potential for which *D. acetoxidans* can still use the anode as an electron acceptor determined by cyclic voltammetry.) The majority of the available energy, as much as 0.7 V for each electron, was left for use in the external circuit, depending upon the current, resulting in the observed power generation. During growth of the biofilm, it was determined that approximately 20% of the acetate

was used to generate biomass (carbon for proteins and membranes, comprising new microbes), which tapered off to approximately 1% for cell maintenance once the biofilm achieved its self-determined thickness.

The same story can be told for the power-generating anode embedded in sediment. In this case, *D. acetoxidans* observed in the biofilm was naturally residing in the sediment. Since it is able to utilize insoluble oxidants, among which are anodes, it had an advantage over other microorganisms present in sediment that could not benefit metabolically from the anode, hence its higher abundance in the biofilm of the power-generating anode. This also explains the higher current density observed in sediment when using a graphite anode, since graphite tends to have better kinetics for electron transfer reactions with biologicals such as redox proteins, which are thought to play a pivotal role in the extracellular electron transfer capability of DMRB.

In these first experiments, Reimers et al. [A4] and Bond et al. [A9] rediscovered the microbial fuel cell (MFC), which uses microbes to catalyze anode oxidation of biological fuels (such as acetate and glucose). Biological fuels are relatively high in energy (a five pound sack of sugar if oxidized with atmospheric oxygen has more than 10 times the potential energy compared to a five pound sack of lithium batteries) for which traditional, abiotic, anode catalysts do not exist. Potter [A10] established the underlying concept, the transduction of microbial metabolism to an electrical current in 1911, and Cohen demonstrated the MFC as a power-generating device in 1931 [A11]. This and subsequently demonstrated MFCs [A12, A13, A14] utilized non-DMRB microorganisms that are very adept at oxidizing organic matter but are unable to directly transfer electrons to anodes. In order to generate current, such MFCs require exogenous electron transfer mediators such as thionine and methyl viologen to accept electrons from the microbes (which tend to stay in solution), diffuse to the anode, transfer the electrons to the anode, and then diffuse back to the microbes to accept more electrons. The use of electron transfer mediators limits current density because diffusion is inherently a slow process, and as the anodic half-cell is flushed to replenish fuel and remove byproducts, new mediator needs to be added and old mediator (typically toxic) dealt with. In contrast, Reimers et al. [A4] and Bond et al. [A9] demonstrated MFCs, first in marine sediment but now termed sediment or benthic microbial fuel cells (SMFCs or BMFCs), and subsequently on the bench-top sans sediment, utilized DMRB. This obviated the need for exogenous electron transfer mediators, greatly simplifying implantation and enabling orders of magnitude higher current densities than was previously possible.

Following these experiments, the first BMFC field experiments were performed, which included a BMFC generating power at a coastal site in New Jersey continuously for nine months without indication of depletion in power before the experiment was terminated [A15]. This and subsequent longer-term experiments since performed by researchers involving BMFCs and DMRB-based bench-top MFCs revealed an important attribute of microbial anode catalysts: as living entities metabolically benefiting from the reaction they catalyze, they self-maintain themselves and therefore do not degrade over time, as long as their environment is kept hospitable. In this way, they can maintain catalytic activity indefinitely, unlike abiotic or enzyme-based anode catalysts which, while great for short-term applications, ultimately degrade [A16].

A genetics-based community analysis of the anode biofilm of the New Jersey BMFC indicated enrichment of *D. acetoxidans*, but also enrichment of microorganisms in the *Desulfobulbus* or *Desulfocapsa* genera that possess the ability to oxidize and disproportionate sulfur. In sulfide-enriched sediment such as the New Jersey site, a graphite anode can directly oxidize sulfide to sulfur without a catalyst, forming a passivating sulfur precipitate on the anode surface that can shut down current [A17]. It is thought that these microorganisms act to clear electrode-generated sulfur from the anode surface, forming sulfate and sulfite, both soluble. The enrichment of these microorganisms therefore suggests that a portion of the current generated at a BMFC anode can, in fact, result from direct oxidation of

microbially generated sedimentary reductant by the anode, as first postulated by Reimers et al. [A4]. One interesting aspect of the BMFC is the lack of a proton exchange membrane (PEM) used in microbial and non-microbial fuel cells alike to isolate the oxidant from the anode while allowing charge-compensating protons to flow between the anodic and cathodic half-cells required for electrons to flow through the external circuit. In the case of the BMFC, the top aerobic (oxygen-using) layer of marine sediment serves this purpose. At this juncture, research in the field of microbial catalyzed electrode reactions took off in many directions.

### **FROM OCEANOGRAPHIC POWER SUPPLIES...**

A number of researchers are working to develop BMFCs into power supplies for oceanographic sensors that are straightforward to deploy [A18, A19, A20, A21]. There are thousands of battery-powered sensors deployed each year that provide valuable scientific information about marine environments. The prospect of using BMFCs to power them indefinitely, or at least far longer than practical with batteries (which is on the order of months), is enticing for many reasons, including the ability to acquire long-term uninterrupted data [A22] and the reduction of the cost and logistics burden of keeping sensors running (research vessels are very expensive to be used to replace sensor batteries) [A23]. In one present form, the BMFC consists of a 60-in.-long graphite bottle-brush anode housed within a rigid but permeable 1-in. diameter tube shallowly embedded horizontally into sediment configured with a matching graphite bottle-brush cathode floating in overlying water. Such a BMFC can sustain approximately 0.015 W in the San Diego Bay, California, which is equivalent to a power density of 0.02 W/L [A24]. By comparison, commonly employed oceanographic alkaline battery packs have an energy density of approximately 100 Wh/L. This specific BMFC can therefore indefinitely sustain as much power as a comparably sized alkaline battery pack lasting approximately 5000 hours (30 weeks) before it depletes ( $0.02 \text{ W/L} \times 5000 \text{ h} = 100 \text{ Wh/L}$ ). Presently, there are 25 such BMFCs now deployed in Great Bay, NJ, where design variations are being evaluated with respect to ease of deployment, power density, and net power output. One very interesting BMFC variant uses deposition (the secretion of organic matter into sediment by vegetation such as rice plants) to augment mass transport of organic matter to the anode, resulting in substantially higher power densities than otherwise possible [A25].

A number of researchers are working to develop DMRB-based MFCs into power supplies for a wide range of applications [A26, A27, A28, A29]. Here, the enticement is the potential for high energy density without the risk of explosion. Although the use of DMRB enables higher anode current densities by orders of magnitude from oxidation of biomass-derived fuels than possible with non-DMRB, it has not translated directly into overall higher power density MFCs. One reason appears to be low ionic conductivity of ion exchange membranes, such as Nafion as typically used in hydrogen/oxygen (non-microbial) fuel cells, in complex ionic media inherent to MFCs [A30, A31]. Another appears to be low catalytic activity of MFC cathodes at neutral pH also inherent to MFCs [A30, A32]. Overcoming these limitations is a highly worthwhile materials research objective.

A number of researchers are working to develop microbial catalyzed electrode reactions into processes in which high value microbial oxidation or reduction reactions are accelerated. Such processes are termed bioelectrochemical systems (BESs), [A33, A34] which encompass MFCs (including BMFCs) as well as microbial electrolytic cells (MECs), in which external power is applied to drive such processes that are not thermodynamically favorable or at rates faster than spontaneously possible by MFCs. For example, many researchers are focusing on the use of BESs to treat wastewater [A35, A36, A37, A38]. Wastewater treatment principally comprises oxidation of the organic matter content accomplished traditionally using aerobic microorganisms—provided oxygen by mechanical aeration that is very power intensive. The use of DMRB catalyzed anode oxidation of wastewater may enable more efficient wastewater treatment when configured as MECs by enabling more efficient delivery of oxidizing equivalents to the microbes and ultimately lead to power generating wastewater treating MFCs if current densities improve. DMRBs have also been shown to reduce graphene oxide to graphene [A39], and when

implemented as a BES, such a process may lead to interesting graphene structures such as large continuous sheets on scales not yet possible by other methods.

DMRBs have also been shown to catalyze cathode reactions as well in which the microorganisms acquire electrons from the cathode. In many subsurface environments, DMRBs naturally reduce potent groundwater contaminants such as tetrachlorethene and hexavalent uranium into tractable products (i.e., bioremediation[A40]) at rates limited by the availability of electron donors. In such circumstances, MEC cathodes can act as inexhaustible sources [A41, A42] of electrons, greatly accelerating these processes [A43, A44]. Microbial catalyzed cathode reactions also show promise for electrosynthesis of fuels from carbon dioxide [A45, A46]. First demonstrations of this capability used select non-DMRBs, indicating that cathode-catalyzing phenotypes may be more widespread than previously thought.

The products of MFCs (carbon dioxide and water) are the reactants of photosynthesis, whereas the products of photosynthesis (organic matter and oxygen) are the reactants of MFCs. Based on this observation, Malik et al. [A47] demonstrated a simple bench-top BMFC-based microbial solar cell (MSC) in which photosynthetic organisms enabled power generation from sunlight in a closed system for more than 8000 hours without indication of depletion in power. In their MSC, power was correlated with sunlight intensity due to regeneration of the MFC products from MFC reactants. The understanding and optimization of MSCs represent an exciting research challenge and potential solution to the conundrum of storing solar energy, since the photosynthetically generated reactants can accumulate internally within the MSC until power is required [A48, A49]

### ...TO CONDUCTIVE NANOMATERIALS

Aside from their potential applications, DMRB biofilms that catalyze electrode reactions are fascinating as materials on their own because of their conducting properties. In the case of *Geobacter spp.*, which appear to have the highest catalytic activity (highest current density) among all known DMRB biofilms, anode biofilms can grow more than 20 cell lengths thick (approximately 20 microns). This requires that the biofilm be conductive in order to enable cells at the biofilm outer surface to transfer their respired electrons through the biofilm to the underlying electrode [A8, A50, A51, A52, A53, A54, A55]. Biofilms are ubiquitous in nature, yet it appears that only those of *Geobacter spp.* and other, closely related DMRB are sufficiently conductive to form thick, electrode catalytically active biofilms. A defining feature of DMRB is the abundance of electron-transfer proteins (e.g., multiheme *c*-type cytochromes) [A56, A57] on their surfaces, along secreted nanometer-diameter, micron-long protein filaments extending from their surfaces (aka “pili” and “nanowires”) [A58], and throughout the extracellular matrix between individual microbes [A43]. Conductivity measurements made *ex vivo* across the diameter of a single filament sheared from *Geobacter sulfurreducens* [A59] and from *Shewanella oneidensis* MR-1 [A60] (a DMRB unable to form thick biofilms) and along the length of a single MR-1 filament [A61] indicate that they are conductive (hence the term “nanowire”). As such, microbial secreted filaments may represent a new class of conductive nanomaterials that might eventually be custom tailored through synthetic biology.

The measurements described previously have led to the supposition that filaments confer conductivity to biofilms, creating a conductive mesh as they extend from cell to cell and to the electrode surface. The current-voltage dependencies resulting from these measurements have been modeled based on the hypothesis that filament conductivity results from electron incoherent multi-step hopping (e.g., “electron hopping,” “thermal hopping,” phonon-assisted tunneling) [A8, A50, A51] among the electron-transfer proteins aligned along the filaments based on theory first applied by Murray and colleagues to describe the conductive properties of redox polymers [A62]. In essence, it is hypothesized that electrons hop from electron-transfer protein to electron-transfer protein along the filaments in a bucket brigade manner between the source and drain electrodes used to make the measurements. This same mode of conductivity was invoked to model cyclic voltammetry of a *Geobacter* biofilm modified anode that was actively



catalyzing acetate oxidation [A8, A50, A51, A53, A54, A63]. In this model, the microbes themselves act as electron sources distributed throughout the biofilm; the underlying anode acts as the drain; and electron transfer proteins aligned along the filaments, on the cell surfaces, and/or within the extracellular matrix confer biofilm conductivity. One aspect of this model is that it predicts a finite biofilm thickness, as experimentally observed due to the decreasing contribution to the flux of electrons to the electrode surface by microbes, with increasing distance they occupy from the electrode surface. This same model has also been applied to describe *in situ* conductivity measurements made across a *Geobacter* biofilm spanning two electrodes [A50, A51] based on a technique developed by Malvankar et al. [A55, A64]. They contend, however, that the filaments are themselves intrinsically conductive, wherein they contain electronically delocalized domains that conduct electrons much like conducting polymers, and provide compelling evidence to support this hypothesis. This hypothesis is a very provocative, stimulating significant debate, and if true, would represent a new paradigm in electrical conduction in biological systems.

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