

Available online at www.sciencedirect.com





Journal of Power Sources 179 (2008) 571-575

www.elsevier.com/locate/jpowsour

# The first demonstration of a microbial fuel cell as a viable power supply: Powering a meteorological buoy

Short communication

Leonard M. Tender<sup>a,\*</sup>, Sam A. Gray<sup>a</sup>, Ethan Groveman<sup>b</sup>, Daniel A. Lowy<sup>c</sup>, Peter Kauffman<sup>d</sup>, Julio Melhado<sup>e</sup>, Robert C. Tyce<sup>f</sup>, Darren Flynn<sup>f</sup>, Rose Petrecca<sup>g</sup>, Joe Dobarro<sup>g</sup>

<sup>a</sup> Center for Bio/Molecular Science and Engineering, Naval Research Laboratory Code 6900, Washington, DC 20375, USA

<sup>b</sup> Millburn High School, Millburn, NJ 07041, USA

<sup>c</sup> Nova Research, Inc., Alexandria, VA 22308, USA

<sup>d</sup> Northwest Metasystems, Inc., Bainbridge Island, WA 98110, USA

<sup>e</sup> Neptune Sciences, Slidell, LA 70461, USA

<sup>f</sup> Department of Ocean Engineering, University of Rhode Island, Narragansett, RI 02882 USA <sup>g</sup> Rutgers University, Institute of Marine & Coastal Sciences, Marine Field Station, Tuckerton, NJ 08087 USA

Received 27 November 2007; received in revised form 21 December 2007; accepted 31 December 2007 Available online 17 January 2008

#### Abstract

Here we describe the first demonstration of a microbial fuel cell (MFC) as a practical alternative to batteries for a low-power consuming application. The specific application reported is a meteorological buoy (ca. 18-mW average consumption) that measures air temperature, pressure, relative humidity, and water temperature, and that is configured for real-time line-of-sight RF telemetry of data. The specific type of MFC utilized in this demonstration is the benthic microbial fuel cell (BMFC). The BMFC operates on the bottom of marine environments, where it oxidizes organic matter residing in oxygen depleted sediment with oxygen in overlying water. It is maintenance free, does not deplete (i.e., will run indefinitely), and is sufficiently powerful to operate a wide range of low-power marine-deployed scientific instruments normally powered by batteries. Two prototype BMFCs used to power the buoy are described. The first was deployed in the Potomac River in Washington, DC, USA. It had a mass of 230 kg, a volume of 1.3 m<sup>3</sup>, and sustained 24 mW (energy equivalent of ca. 16 alkaline D-cells per year at 25 °C). Although not practical due to high cost and extensive in-water manipulation required to deploy, it established the precedence that a fully functional scientific instrument could derive all of its power from a BMFC. It also provided valuable lessons for developing a second, more practical BMFC that was subsequently used to power the buoy in a salt marsh near Tuckerton, NJ, USA. The second version BMFC has a mass of 16 kg, a volume of 0.03 m<sup>3</sup>, sustains ca. 36 mW (energy equivalent of ca. 26 alkaline D-cells per year at 25 °C), and can be deployed by a single person from a small craft with minimum or no in-water manipulation. This BMFC is being further developed to reduce cost and enable greater power output by electrically connecting multiple units in parallel. Use of this BMFC powering the meteorological buoy highlights the potential impact of BMFCs to enable long term (persistent) operation of durable low-power marine instruments (up to 100 mW average power consumption) far longer than practical by batteries. © 2008 Elsevier B.V. All rights reserved.

Keywords: Benthic; Microbial; Fuel cell; Marine; Sediment

# 1. Introduction

The benthic microbial fuel cell (BMFC) consists of a noncorrosive anode (typically graphite) shallowly embedded (ca. 1–5 cm minimum depth) in marine sediment and connected through an electrical circuit (e.g., a marine scientific instru-

\* Corresponding author. Tel.: +1 202 404 6029.

E-mail address: Tender@nrl.navy.mil (L.M. Tender).

0378-7753/\$ - see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2007.12.123

ment) to a non-corrosive cathode (typically graphite) positioned in overlying water [1,2]. Substantial organic matter resides in sediments of many marine environments that is typically derived from settlement of dead phytoplankton and/or vegetative detritus [3]. In addition, in many marine environments oxidants such as oxygen and sulfate are supplied into sediment from overlying water by diffusion and by action of shear stress at the sediment–water interface resulting from motion of overlying water (e.g., tidal pumping and/or sediment re-suspension). In such environments, the combination of organic matter and supply of oxidants support microbial activity. Typically the amount of organic matter exceeds the amount of oxidant, resulting in microbial depletion of oxidants in sediment millimeters to centimeters beneath the sediment surface [4]. Under these conditions, the BMFC anode acts as a potent oxidant owing to its electrical connection through the intervening circuit and cathode to oxygen in overlying water.

When a BMFC is deployed in anoxic sediment a biofilm spontaneously forms on the anode surface. In most marine environments tested so far, the anode biofilm is enriched in at least two types of sedimentary microorganisms [5]. The first, in the family Geobacteracea (most similar to Desulfuromonas acetoxidans) is known to couple oxidation of acetate in sediment porewater with reduction of insoluble mineral oxidants. These microorganisms utilize the anode as an inexhaustible oxidant. They proliferate on the anode surface, oxidize acetate, and exploit their ability to reduce insoluble oxidants to directly transfer electrons to the anode without reliance on added electron-transfer mediators [7]. Their source of acetate is fermentation of organic matter (e.g., glucose, cellulose) by other anaerobic microorganisms in sediment (e.g., clostridium). The second type of microorganisms enriched on the anode are Desulfobulbus or Desulfucapsa genera and, which have been shown to oxidize elemental sulfur to sulfate [8], the former generated at the anode by oxidation of sedimentary sulfide. By oxidizing sulfur, these microorganisms remove a potentially fouling precipitate from the anode surface. The combined activity of these microorganisms and continuous replenishment of fuel by diffusion, convection, and shear stress ensure that anodes of BMFCs may operate indefinitely [6–9].

The electrons acquired at the anode flow through the external circuit to the cathode. A biofilm also spontaneously forms on the cathode surface that catalyzes oxygen reduction [6-9]. The net BMFC reaction, consumption of glucose with oxygen and formation of carbon dioxide and water is thermodynamically favorable enabling power to be expended in the external circuit. This favorability manifests as an open circuit voltage (cathode potential – anode potential) of ca. 0.75 V.

A key feature the BMFC is longevity (persistence), which is attributed to constant supply of fuel and oxidant by environmental processes, constant rejuvenation of its microbial electrode catalysts, and ability of these microbial catalysts to exchange electrons with their electrodes without reliance on exogenous (added) electron-transfer mediators and to completely oxidize acetate to carbon dioxide so as to accumulate deletorius byproducts [9]. This last feature has been subsequently exploited to demonstrate self-maintaining desk-top microbial fuel cells utilizing anode biofilms of Geobacteracea as catalysts [10].

There are a number of properties of BMFCs that are important to note. (1) The BMFC is a true microbial fuel cell. That is, the anode reaction is catalyzed by microorganisms [11,12]. It does not utilize a sacrificial anode as did a recently described application of a manganese/oxygen galvanic (freshwater) battery reported as a microbial fuel cell (MFC) [13]. (2) The BMFC appears best suited for sediments containing sufficient organic matter to exhibit a redox gradient across the benthic interface [2] resulting in a BMFC open circuit voltage. Such sediments are a common feature of the continental margins. The redox gradient results from depletion of oxygen by aerobic microorganisms at sediment-water interface, and generation of reductants (e.g., sulfide) by anaerobically microorganisms below the sediment surface. The presence of a redox gradient indicates sufficient fuel and microbial activity for power generation and isolates the anode from oxygen in overlying water. Recent results support the hypothesis that BMFCs may operate in sandy (i.e., low organic content) sediment if configured to capture transient organic matter [14]. (3) Thus far, we and others have demonstrated BMFC prototypes in the field that have continually operated without depletion in power for at least 2 years. (4) The operating voltage of a BMFC is very low, maximum power is typically at 0.35 V (current-voltage plots have been previously reported) [1,2]. Because BMFCs are open to the environment, they cannot be connected in series to supply higher voltage. Furthermore, a BMFC cannot directly supply short bursts of high current typically required by marine scientific instruments. To overcome these limitations, a specialized voltage conditioner is used to regulate power output of a BMFC and transform the output to an electronically useful voltage (e.g., 6, 9, 12 V, etc.). The transformed voltage is then used to recharge a battery or capacitor, which buffers the steady power output of the BMFC from the duty cycle of the instrument it powers.

#### 2. Experimental

## 2.1. Buoy

The buoy consisted of a 15-cm-diameter, 45-cm tall cylindrical oceanographic enclosure and ca. 90-cm diameter ring float configured with a hollow twisted cable mooring line. A custom made power conditioner (Northwest Metasystems, Inc.) within the enclosure regulated the discharge voltage of the BMFCs used to power the buoy to 0.35 V in order to maximize power output, transformed the voltage of the output power to 6 V, and continually charged a 1 F capacitor. The power conditioner (an early version) was ca. 85% efficient at 0.35 V input and 100 mA, as determined on the benchtop using a programmable power supply. The capacitor in turn, powered a set of conventional low-power air and water temperature sensors, and air pressure and relative humidity sensors, assembled on a circuit board installed in the buoy housing. The total continuous power draw of the sensor board was 5 mW. A low-power line-of-site RF transceiver (AC4868-250, 860 MHz, Aerocomm, Inc.) installed on the buoy was also powered by the capacitor. The capacitor served to buffer the BMFC from short bursts (1 s) of high power (3 W) required by the transceiver to transmit data. As data transmission drew charge from the capacitor, the capacitor was replenished by the BMFC between transmissions. Voltage of the capacitor just before data transmission was included in the dataset to monitor performance of the BMFC. Data transmission every 5 min resulted in an average power consumption of the buoy of 18 mW, which includes the efficiency of the power conditioner and 5 min duty cycle of RF transmitter.

## 2.2. First version BMFC

The first version BMFC was comprised of seven subunits connected in parallel. Each subunit consisted of two graphite plates (GS10 grade, Graphite Engineering, Inc.), each 61-cm  $\times 61$ cm  $\times 2.5$ -cm in size, affixed to the top and bottom of a plastic milk crate by means of heavy duty cable ties. A pattern of 2.54-cm diameter holes were milled through each electrode to ease embedment of the anodes, when pressed into the sediment. Affixed to each electrode were 45-cm long, 14-guage marine insulated electrical leads terminated with wet pluggable connectors. These leads were affixed to the electrodes by exposing a ca. 5-cm length of conductor, twisting it around the shank of a titanium bolt, driving the bolt into a snug hole drilled into the electrode, pressing the conductor between the underside on the bolt head and the graphite surface, and sealing the connection with water insulating epoxy.

When deployed in the Potomac River (mean water depth 1–3 m feet depending on the tide), the BMFC subunits sat on the river bottom with the bottom electrodes (anodes) covered by ca. 5-cm of sediment, and the top electrodes (cathodes) exposed to overlying water (water depth ranged between 1 and 3 m). The seven subunits were separated at a distance of ca. 30–45 cm. All the cathodes were electrically connected together and all the anodes were electrically connected together, using wet pluggable connectors to create a single large BMFC. Electrical leads within the hollow woven-cable buoy mooring line (to minimize entanglement when the buoy rotates) terminated with wet pluggable connectors were used to electrically connect the BMFC to the power conditioner in the buoy enclosure.

## 2.3. Second version BMFC

The anode of the second version BMFC consisted of 12 graphite plates arranged in a vertical array with a 2.5-cm pitch. The graphite plates were affixed to the underside of a fiberglass top plate using fiberglass angle stock. Each graphite plate measured 30.5 cm by 30.5 cm by 0.32 cm, while the fiberglass plate measured 30.5-cm by 30.5-cm by 2.5-cm. Titanium strips affixed to each graphite plate with titanium hardware electrically connected all the graphite plates to a single node to which an insulated electrical lead terminated with a wet pluggable connector was affixed. The cathode of the second version BMFC consisted of a 1-m long graphite bottle brush electrode positioned in overlying water to which an insulated electrical lead terminated with a wet pluggable connector was affixed. This is the same cathode used in Simrad Maritime galvanic seawater batteries (SWB) [purchased from the Norwegian Defense Research Establishment], which is a proven and durable technology [15,16]. It is comprised of 4-in. lengths of graphite yarn pinched between a pair of twisted stainless steel wires. The yarn is comprised of ca. 3000 7-µm diameter graphite fibers and heat treated to separate the fibers, which increases catalytic activity for seawater oxygen reduction. In the case of a SWB, graphite bottle cathodes are mated with a high-current density sacrificial anode also exposed to seawater, which acts as the electrolyte. In oxygen-saturated seawater, graphite bottle brush cathodes can sustain ca. 0.21 W per meter-length [17] and as long as oxygen is supplied by diffusion or flow, they demonstrate continuous activity decades after deployment.

# 3. Results and discussion

In August 2004, the meteorological data buoy powered by the first version BMFC was deployed in the Potomac River, in Washington, DC, USA (Fig. 1). Prior to connecting the buoy, the power output of this BMFC was measured to be  $24 \pm 2 \text{ mW}$ at 0.35 V over the course of 3 months at the Potomac River site. Once connected, the BMFC-powered buoy operated from October 2004 to March 2005 (nearly 7 months) without incident until the buoy was pulled down river by an ice flow, severing electrical connection to the BMFC. Fig. 2 depicts a typical 7day time record of the transmitted meteorological data. Early BMFC prototypes were configured as the first version BMFC described here with graphite plate anodes embedded parallel to the sediment surface [1,2]. These BMFCs generated sustained maximum power that scaled linearly with geometric surface area  $(2 \times \text{length} \times \text{width when thickness} \ll \text{length and width})$  of the anode on the order of  $9-20 \text{ mW m}^{-2}$ , depending on the specific location [1,2]. The first version BMFC described here (geometric surface area =  $5.2 \text{ m}^2$  not including plate edges and hole walls,



Fig. 1. *Top*: meteorological data buoy used in demonstration on the pier of the Naval Research Laboratory in Washington, DC, being prior to deployment (mooring and RF transmitter antenna not yet configured). *Bottom*: one of the first generation BMFC subunits on pier prior to deployment. Seven subunits were electrically connected in parallel to provide sufficient power to operate buoy.



Fig. 2. Example 7-day time record of meteorological data transmitted from first generation BMFC-powered buoy.

 $6.9 \,\mathrm{m}^2$  including plate edges and hole walls) generated a very low power density of 3.5 and 4.6 W m<sup>-2</sup>, respectively. This specific deployment was the first demonstration of a BMFC operating in a fresh water environment. As in the case SWBs, BMFCs utilize the surrounding water as their electrolyte. This results in low-power density of the BMFC in fresh water environments (nearly fourfold reduction) owing to low ionic content of the river water. This relationship was determined by stepwise increasing salt content of the river water in laboratory-scale BMFCs [1,5] utilizing harvested river sediment and water [18]. This relationship results from the specific requirement of the BMFC of mass transfer of protons generated by the anode (from acetate oxidation) for consumption at the cathode (for oxygen reduction) [19] and the general requirement of all fuel cells for charge balance (i.e., each electron passing thorough the external circuit of a fuel cell requires an accompanying charge compensating ion flux trough the electrolyte between the anode and cathode). Nonetheless, the power output of this BMFC was more than sufficient to operate the buoy in the river.

Fig. 3 depicts the anode of the second Version BMFC we developed to reduce cost and simplify deployment from a pier, small boat, by ROV (remotely operated vehicle), or by diver. This BMFC was deployed in August 2006 to power the buoy in a boat basin carved into a salt marsh near Tuckerton, NJ, USA. It sustained 36 mW (Fig. 4) in the salt-water environment of the estuary. This represents a power density of ca.  $16 \text{ mW m}^{-2}$  of anode geometric surface area  $(36 \text{ mW}/2.2 \text{ m}^2)$ , which is consistent with power densities observed for BMFCs configured as in Fig. 1, deployed in the same estuary location [2]. This result indicates that although the individual plates comprising the anode are closely spaced, there is sufficient flux of fuel by environmental processes to ensure that sediment between the plates is not depleted. We are presently investigating the relationship between plate spacing, power generation, and force required for embedment in various sediment types.

Fig. 5 depicts the latest version anode array-based BMFC we are developing. Here the array consists of alternating graphite plates and graphite spacers pressed into a single unit by nylon threaded rods. Rope threaded through aligned holes enables rigging of multiple BMFCs anode arrays to provide multiple amounts of power. The materials cost for a BMFC depicted in



Fig. 3. *Top*: 12-balded graphite anode array of second generation BMFC used to power buoy on pier at Rutgers University Marine Field Station, Tuckerton, NJ. *Bottom*: testing of anode embedment by impalement.

Fig. 5 is ca. \$500 US, including the bottlebrush cathode. To sustain 0.12 W persistently in the New Jersey site, for example, would require 4 BMFCs (\$2000) and 1 power conditioner (\$500). By comparison, a deep sea power and light enclosed lead acid battery could deliver the same amount of power for only 1 year at the same total cost.



Fig. 4. Typical first 30-day time record of power generation by second generation BMFC. BMFC embedded at start of day 1. During first 2 days, open circuit voltage (i.e., no current flow) seen rising due to reestablishment of benthic redox gradient disturbed when anode embedded. Beginning of day 3, BMFC discharged alternatively between 0.35 and 0.65 V. Growth in power to ca. 0.36 W at 0.35 V attributed to establishment of a catalytically active anode biofilm.



Fig. 5. *Top*: rendering of newest version of BMFC anode array. *Bottom*: fielded version on pier prior to deployment. Here, a 1-m long graphite fiber bottle brush cathode is affixed to the underside of a small buoy (remains submerged) attached to anode array by a 30-cm tether. This configuration intended to keep cathode near anode and above sediment surface. Cinderblock used as ballast for embedment.

In collaboration with Navy and NOAA partners, we deployed in October 2007 a BMFC-powered ultrasonic receiver in San Diego Bay, CA, that is to be configured shortly with a surface RF transceiver at the same location. This instrument is intended to enable persistent, real-time tracking of acoustically tagged green sea turtles in order to better understand their long-term behavioral patterns in a cost-effective manner. This application consumes 50 mW average power including the RF gateway. Power density of laboratory-scale BMFCs [1,5] utilizing harvested sediment collected from the deployment site  $(11 \text{ mW m}^{-2})$  indicated that the BMFC requires nine anode array subunits (100 mW output) for this application including a 100% margin for error.

#### 4. Conclusion

The BMFC is an emergent maintenance free power supply. Here we demonstrated its application. It promises persistent operation of robust marine-deployed scientific instrumentation that would normally be powered by batteries. By replacing batteries, the BMFC promises long periods of uninterrupted operation, resulting in possible scientific, logistic, and cost saving benefits [20].

## Acknowledgements

This work supported by the Naval Research Laboratory. This manuscript dedicated to Dr. Harold Bright on the occasion of his retirement from the office of Naval Research.

# References

- L.M. Tender, C.E. Reimers, H.A. Stecher III, D.E. Holmes, D.R. Bond, D.A. Lowy, K. Pilobello, S.J. Fertig, D.R. Lovley, Nature Biotechnol. 20 (2002) 821–825.
- [2] C.E. Reimers, L.M. Tender, S.J. Fertig, W. Wang, Environ. Sci. Technol. 35 (2001) 192–195.
- [3] T.F. Yan, Chemical aspects of marine sediments, in: T.F. Yan (Ed.), Chemistry of Marine Sediments, Ann Arbor Science Publishers, Ann Arbor, MI, 1977.
- [4] P.N. Froelich, G.P. Klinkhammer, L.M. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman, V. Maynard, Geochim. Cosmochim. Acta 43 (1979) 1075–1090.
- [5] D.A. Lowy, L.M. Tender, J.G. Zeikus, D.H. Park, D.R. Lovley, Biosens. Bioelectron. 21 (2006) 2058–2063.
- [6] W.S.D. Wilcock, P.C. Kauffman, J. Power Sources 66 (1996) 71-75.
- [7] C.E. Reimers, P. Girguis, H.A. Stecher III, L.M. Tender, N. Ryckelynck, P. Whaling, Geobiology 4 (2006) 123–136.
- [8] D.E. Holmes, D.R. Bond, D.R. Lovley, Appl. Environ. Microbiol. 70 (2004) 1234–1237.
- [9] D.R. Bond, D.E. Holmes, L.M. Tender, D.R. Lovley, Science 295 (2002) 285–483.
- [10] S.K. Chaudhuri, D.R. Lovley, Nat. Biotechnol. 21 (2003) 1229-1232.
- [11] B.H. Logan, B. Hamelers, R. Rozendal, U. Schrorder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Environ. Sci. Technol. 40 (2006) 5181–5192.
- [12] G.T.R. Palmore, G.M. Whitesides, in: M.E. Himmel, J.O. Baker, R.P. Overend (Eds.), Symposium on Enzymatic Conversion of Biomass For Fuels Production, Series 566, American Chemical Society, Washington, DC, 1994, pp. 271–290.
- [13] A. Shantaram, H. Beyenal H., R.P.A. Veluchamy, Z. Lewandowski, Environ. Sci. Technol. 39 (2005) 5037–5042.
- [14] A. Rusch, M. Huettel, C. Wild, C.E. Reimers, Aquat. Geochem. 12 (2006) 1–19.
- [15] O. Hasvold, T. Lian, E. Haakaas, N. Storkersen, O. Perelman, S. Cordier, J. Power Sources 136 (2004) 232–239.
- [16] T. Garshol, O. Hasvold, United States Patent 5,427,871 (1995).
- [17] SWB Kongsberg Maritime, http://www.km.kongsberg.com/KS/WEB/ NOKBG0397.nsf/f8aa365e2cee6bd2c125693f003f6ee2/942513f5a2d7a530c1256d28003d5f02/\$FILE/160049ah\_Sea\_water\_battery\_SWB\_ 1200\_lr.pdf.
- [18] J.L. Liu, D.A. Lowy, R.G. Baumann, L.M. Tender, J. Appl. Microbiol. 102 (2007) 177–183.
- [19] L.M. Tender, United States Patent Application 20,060,172,186 (2006).
- [20] E.F. DeLong, P. Chandler, Nat. Biotechnol. 20 (2002) 788-789.