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Fundamentals of Benthic Microbial Fuel Cells: Theory, Development and Application.

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17.1 Introduction

Recent years have been a watershed for fuel cell research, in particular for microbial fuel cells (see for example: Larminie & Dicks, 2000; Bullen et al., 2006; Logan et al., 2006; Lovley, 2006; Du et al., 2007; Rabaey et al., 2007; Schröder, 2007; Logan, 2008). While the majority of microbial fuel cell (MFC) research has focused on the performance and characteristics of laboratory reactors, benthic microbial fuel cells (BMFCs), or those that rely on a potential gradient at a sediment-water interface, have played a significant - sometimes understated- role in the evolution of MFC technology. Whereas laboratory MFCs offer a unique opportunity to examine fundamental attributes of MFC performance and microbial physiology (e.g. ohmic resistance, current density, and mechanisms of electron transfer by laboratory cultivated microbes), BMFCs offer a unique opportunity to

examine how energy moves through microbial communities, the efficiency of harvesting electricity from natural systems, and the potential role(s) that BMFCs may play in power generation or bioremediation in the natural world. Accordingly, BMFCs that have been deployed in the ocean have also furthered our understanding of marine biogeochemical processes. A comprehensive review of BMFCs would entail, by necessity, a detailed discussion of all aspects of MFC technology, and is beyond the scope of this chapter. Rather, here we provide a review of the underlying principles of BMFCs, including theoretical and geochemical considerations, aspects of material selection and system design, the trends in microbial ecology among BMFCs, and the potential that BMFCs have as practical - and commercially viable- power systems. We examine these fundamentals of BMFC development and application with the goal of illustrating how BMFCs have evolved in design, performance and application over the last decade.

17.2 Fundamental principles of sediment reduction-oxidation chemistry

In nature, reduction-oxidation gradients are typically found across sediment-water interfaces and within aquatic and terrestrial sediments (Whitfield, 1972; Reimers et al., 2001; Tender et al., 2002; Alberte et al., 2005). These gradients are the result of spatially separated microbially-mediated reduction oxidation reactions, linked to the microbial degradation of organic matter (Froelich et al., 1979). At the sediment-seawater interface, oxygen is present and microbial aerobic respiration is the dominant process. In deeper sediments where oxygen is depleted (termed suboxic sediments), other microbially mediated processes –such as nitrate, iron, and manganese reduction- are used as oxidants to support organic matter degradation. In anoxic sediments, microbial sulfate reduction, fermentation and methanogenesis

dominate, as they are most thermodynamically favored reactions in these environments. The biogeochemical zonation arises because each of the processes listed above occur in sequence according to the free energy (ΔG) yielded by the reaction, with the most energetically favorable processes occurring first. Theoretically, if all reactions were known, the difference in redox potentials between the electron-accepting and electron-donating couple (ΔE) could be characterized and related to ΔG according to:

$$\Delta E = -nF/\Delta G$$

where n is the number of electrons transferred and F is the faraday constant (96,485 coulomb mol⁻¹). From this, the theoretical redox potential difference (ΔE) between oxic seawater and anoxic sulfide-rich sediments is approximately 0.86 to 0.91 V at the conditions found *in situ* (Stumm & Morgan, 1996). In practice, observed redox potential differences in BMFCs are 0.7 to 0.8 V as measured by redox electrodes (Schulz, 2006), a consequence of environmental heterogeneity such as variations in the concentrations of redox species, *in situ* mixing of porewaters and bioturbation (mixing caused by biological processes) (Stumm & Morgan, 1996).

Based on a combination of the redox characteristics described above, the physical properties of sediments and the dynamics of natural environments, there are a special set of factors that affect the performance of BMFCs in ways that do not apply to traditional laboratory or wastewater MFCs. First, mass transport through sediments is generally slow thus limiting the availability of fuel transport to the anode (and the transport of reaction products away from the anode)(Tender et al., 2002; Nielsen et al., 2007). Electrodes may also become passivated by

electrochemical deposition (of which sulfur is one example) or by biofouling (such as biofilm formation or sedimentation on the cathode that reduces the availability of oxygen)(Reimers et al., 2006). By necessity, anodes and cathodes are spatially separated due to the scale of natural redox gradients and this separation may lead to high internal resistance with increasing sediment depth. Finally, working in underwater field settings presents a unique set of challenges that require extremely robust instrument designs that can be deployed with available resources. We will return to these considerations - and how this may influence commercialization- after describing the fundamental aspects of BMFCs below.

17.3 Principles of design and approaches to testing Benthic Microbial Fuel Cells (BMFCs)

BMFCs are electrochemical devices that generate electrical current from the natural redox gradients that commonly occur across the sediment-water interface. In general, a BMFC consists of a circuit in which inert but electrically conductive electrodes are placed in an anoxic zone (the anode) and an oxic zone (cathode). The electrodes are connected through a load such as an external resistor or potentiostat (in research applications) or a sensor system (in field demonstrations or applications). Electrons resulting from microbial metabolic activity are transferred from electron donors to the anode and flow through the load to the cathode, where they lead to the reduction of dissolved oxygen to water.

Monitoring the performance of BMFCs (with respect to power production) entails making several measurements. Typically, a voltmeter may be used to monitor cell voltage (E_{cell}) –which is the potential between anode and cathode- and a

combination of a voltmeter and reference electrode (typically a Ag/AgCl electrode in the oxic media) may be used to measure individual electrode potentials (E_{anode} and $E_{cathode}$). A potentiostat may be used to poise the cell potential at a fixed value (or, if desired, may be used to fix a single electrode potential against the reference electrode). Current (I) may be calculated according to Ohm's law if a known resistor is used, whereas the use of a potentiostat requires the investigator to directly measure current if they are interested in calculating power density. There is some debate about the merits of fixed resistance BMFCs (which results in varying electrode potentials) versus poised potential BMFCs (which results in varying current). The relative effects of varying current and potential on microbial community composition and activity have yet to be thoroughly addressed and it remains to be determined which of these approaches - if either - is better suited for commercial applications. Nevertheless, future studies should better quantify the effect of these factors on microbial processes.

BMFC investigators are often interested in determining the *efficiency* of energy transfer from endogenous fuels to the BMFC. One measure of efficiency is the current efficiency (also known as Coulombic efficiency), which is the percentage of electrons coming from oxidation of the organic matter that are harnessed by the electrode (measured as current, Bard & Faulkner, 2001). This metric provides investigators with a better understanding of how much energy in organic matter is available to –and ultimately harnessed by– the BMFC. Through the application of laboratory and *in situ* measurement techniques, investigators set out to determine the influence of electrode materials and design, as well as overall system design and deployment, to BMFC performance (discussed in detail below).

17.4 Anode material and design

In all BMFCs, the anode serves to accept electrons from biological and abiotic processes. Primarily, the anode is a solid-phase terminal electron acceptor for microbial metabolism. To insure consistent, long-term performance, the ideal BMFC anode should be impervious to biological or abiotic corrosion, passivation or degradation. To that end, different materials that have been investigated including platinum mesh (Whitfield, 1972; Reimers et al., 2001); graphite discs, plates or rods (Tender et al., 2002; Ryckelynck et al., 2005; Reimers et al., 2006; Donovan et al., 2008; Tender et al., 2008); corrosion-resistant stainless steel (Dumas et al., 2007); carbon fiber cloth (Rezaei et al., 2007; Scott et al., 2008b); glassy carbon and modified graphite (Lowy et al., 2006); as well as carbon sponge and reticulated vitreous carbon (Scott et al., 2008a).

Platinum is instinctively appealing in light of its catalytic efficiency. However, in one of the earliest studies, there was no observed increase in power production when platinum was used as an anode and cathode (relative to graphite plate, Reimers et al., 2001). While this may be due to limitations in other aspects of BMFC power production such as mass transport limitations, it may also result from chemical fouling by hydrogen sulfide (which is common in organic-rich marine sediments; Reimers et al., 2006).

A more recent study has tested the use of stainless steel as both an anode and cathode in BMFCs, in laboratory and field settings (Dumas et al., 2007). In these deployments, BMFCs with stainless steel electrodes produced power at densities of $4 \text{ mW} \cdot \text{m}^{-2}$, which is lower than those reported previously with marine BMFCs using graphite electrodes (e.g. Reimers et al., 2001, Tender et al., 2002, Bond et al., 2002, Bond et al., 2003, Holmes et al., 2004, Reimers et al., 2006).

Nevertheless, it is apparent that stainless steel is not suitable as an anode. Despite its name, stainless steel will readily corrode when kept in anoxic environments (the chromium oxide film that prevents iron oxidation is not stable in the absence of oxygen).

Conductive allotropes of carbon, including graphite, amorphous, and glassy carbon, are typically impervious to biological degradation and are effective as electrodes in BMFCs. Indeed, the number of BMFC studies that employed graphite or other conductive carbon electrodes are many (for review, see Lovley et al., 2006). In general, graphite sheet, plates and rods have been used as anodes because of the material's strength, inertness, and commercial availability (Reimers et al., 2001; Tender et al., 2002; Bond et al., 2003). While carbon allotropes bear a superficial similarity, they have different physical and electrical properties, including resistivity. To understand the effect of carbon allotrope composition, as well as form factor, on power production in BMFCs, Scott et al., (2008a) tested the performance of carbon sponge, carbon cloth, carbon fiber, and reticulated vitreous carbon (RVC) as anodes (with graphite cloth as a cathode). Similar open circuit voltages (up to 0.7V) were observed for most cells, though carbon sponge produced the highest power density at $55 \text{ mW} \cdot \text{m}^{-2}$, nearly twice that of carbon cloth (Scott et al., 2008a). Notably, mass transport at both the anode and cathode was found to be the limiting factor in all treatments.

In a further effort to improve upon BMFC performance by alleviating limitations in surface reactions, investigators have modified graphite to examine the effects of surface treatments such as doping with manganese, nickel, iron and compounds previously shown to be effective as electron shuttles in laboratory MFCs (Lowy et al., 2006). They typically observed a five-fold increases in power density in treated anodes over the course of the incubation, though it remains to be

determined whether this improvement in performance is sustained during long-term incubations.

As mentioned, seafloor BMFC electrodes have shown signs of passivation by elemental sulfur deposits on the anode (Reimers et al., 2006). This is largely due to the abiotic oxidation of hydrogen sulfide (which is the byproduct of microbial sulfate reduction in marine sediments) at the anode surface. It has been suggested that anodes can be electrically poised at potentials that would “strip” sulfur from the anodes, though it has yet to be determined if this is feasible in long-term deployments. Regardless of anode material, the issue of passivation is one that must be addressed prior to long-term use or commercialization.

17.5 Cathode materials and design

The function of a BMFC cathode is to donate electrons to available acceptors, thus enabling the continuous flow of current from the anode. In most cases the terminal electron acceptor at the cathode is dissolved oxygen in the surrounding seawater (though other electron acceptors are possible, and are discussed elsewhere in this volume). Indeed, cathodes are as important as anodes in terms of BMFC design, as they can limit MFC power production (Fornero et al., 2008). In general, BMFCs have typically employed the same carbon-based electrode materials that are used at the anode. At the cathode, platinum is effective in catalyzing the formation of water from oxygen and protons (proton equivalents), which could alleviate cathode limitation. However, its high cost has limited its utility in BMFCs, though platinum-doped graphite is an effective cathode that costs a fraction of platinum mesh or sheet and may prove useful in long-term deployments (Logan et al., 2006). Furthermore, in a recent study, Scott et al., (2008b) conducted

a systematic comparison of 10 different cathode materials, with and without catalysts such as Fe-Co tetramethoxyphenyl porphyrin (FeCoTMPP) and platinum. Surprisingly, the investigators found that the FeCoTMPP cathode supported power densities twice that of untreated carbon cloth. As mentioned, platinum is poisoned by hydrogen sulfide, so its utility in sulfur-rich systems may be limited. In practice, it is easier to reduce cathode limitation in BMFCs as cathodes are typically not subject to the spatial constraints of anodes, such as being buried or placed within a chamber. Thus, cathodes can be of much greater size. However, research on cathode performance in BMFCs is particularly sparse, and future research should aim to better characterize the microbial ecology, catalytic properties and overall performance of BMFC cathodes. Several research groups have designed BMFCs with stainless steel cathodes (Dumas et al., 2007; Donovan et al., 2008). In the work by Dumas, et al., the investigators decoupled the anode and cathode in laboratory BMFC experiments, and showed that the cathode was able to sustain driven current densities up to 140 mA m^{-2} (at +0.05V versus Ag/AgCl), suggesting that stainless steel cathodes are potentially useful as BMFC applications (though their observed current densities are likely to be an order of magnitude greater than what might be observed in field deployments).

17.6 Performance and practical considerations of BMFC designs

BMFCs, like all MFCs, are influenced by a variety of factors, including electrode properties, internal resistivity, environmental geochemistry, and microbial ecology. BMFC research has, in general, approached these matters via field experiments and laboratory simulations of field deployments, wherein one or more variables were manipulated to assess the influence on system performance over

time. In the sections above, we have briefly reviewed the effect of anode and cathode materials and treatments specifically in the context of BMFCs. Here we present a brief summary of key field deployments, and key changes in design and implementation that yielded improvements in performance.

In the earliest BMFC studies, investigators deployed solid graphite plates as anodes and cathodes, burying the anodes at arbitrary depths within sediments, and suspending the cathodes in the overlying seawater on non-conductive frames. In these early deployments, investigators were largely focused on examining differences in power production among sites, or in relation the bulk sediment properties (Reimers et al., 2001; Tender et al., 2002). For example, in Tender et al (2002), the investigators deployed 48 cm-diameter graphite plates as anodes and cathodes, which yielded average power densities of 25 to 28 mW • m⁻² of seafloor over a three month deployment (Tender et al., 2002). While the graphite plates provided good surface area, their aspect often made them difficult to deploy in marine sediments. In particular, anodes had to be well buried to avoid shorting by wave action or bioturbation (where marine animals irrigate the sediments with oxygen-rich seawater, thereby short-circuiting the electrode and ceasing power production). Tender and colleagues, however, have recently built a larger scale system called the Benthic Unattended Generator, or B.U.G., that uses large graphite plates to generate sufficient power for submarine sensors (Lovley, 2006; Tender et al., 2008). To date, these systems have been less susceptible to the problems associated with earlier deployments perhaps because of an advantage of size. However, the size of these electrode arrays can require significant infrastructure for deployment, to insure that the arrays are properly anchored in the sediments.

To test a different anode and cathode configuration, Reimers et al (2006) deployed a 1 m x 9 cm solid graphite rod in hydrocarbon seep sediments, coupled to

a titanium-wound graphite brush cathode that was suspended approx. 1 meter above the sediment seawater interface. This BMFC yielded power densities of $34 \text{ mW} \cdot \text{m}^{-2}$ of anode, roughly three times higher than power densities obtained with similar electrode materials in coastal sediments (Ryckelynck et al., 2005). This particular anode and cathode configuration made for easier deployment by the remotely operated submersible in the deep ocean sediments. The improved performance, however, was largely attributable to the differences in porewater chemistry found at hydrocarbon seeps, including higher organic carbon and sulfide concentrations.

While the graphite rod facilitated deployment in sediments, the primary disadvantage came from its relatively limited surface area. Inspired by sediment benthic chambers (e.g. Smith & Teal, 1973), Nielsen et al. (2007) developed a chambered BMFC design in which the anode is contained in a semi-enclosed chamber that is either pushed into or set atop the sediments. The chamber design has several advantages over previous BMFCs, including the ability to use high surface area electrodes (e.g. carbon-fiber brushes) and the ability to enhance mass transport either mechanically or through natural advection (Nielsen et al., 2007, 2008). These advantages yielded greater power densities and –to date– longer-term performance. In Nielsen et al (2007), a chambered BMFC produced power densities more than an order of magnitude greater (with peak power densities of 380 mW/m^{-2}) than those achieved by previous BMFCs. All chambered BMFCs were found to generate current continuously for over 200 days. It should be noted that the highest power densities were achieved by occasionally pumping on the chamber. The cost of pumping a chambered BMFC system using BMFC-derived power remains to be determined. Chambered BMFCs have also been subject to failure due to scouring of sediments by strong bottom currents, or bioturbation, that results in oxygenation of the anode chamber.

Another effort to improve power production by BMFCs involved alleviating cathode limitation by rotating the cathode (He et al., 2007). This had the effect of increasing oxygen availability to the cathode, and therefore improving the cathode reaction rate (this method also incurs an energetic cost). This resulted in a higher power density ($49\text{mW} \cdot \text{m}^{-2}$), nearly 70% greater than the non-rotating BMFC control. Interestingly, the data suggest that the increased oxygenation also had an adverse effect on the anode potential (possibly due to irrigation of the underlying sediment). This in turn constrained maximum power density. The authors suggest that future experiments should aim to address this issue, and determine an optimum level of rotation for maximal power production.

There has also been an effort to examine the efficacy of substrate enhancement in BMFCs. Razaei and Logan (2007) examined the influence of supplementing a BMFC with chitin and cellulose. Chitin in particular is common in marine sediments and, along with keratin and cellulose, is among the more common of recalcitrant carbon compounds in both marine and terrestrial settings. The authors observed maximal power densities from 64 to $83\text{mW} \cdot \text{m}^{-2}$ for chitin and cellulose, respectively (though cellulose-stimulated power production rapidly declined). Given the availability of chitin and cellulose from industrial processing, the authors consider the benefits of supplementing BMFCs with sufficient chitin or cellulose to sustain and stimulate prolonged power production. While this is a compelling idea, it remains to be determined how much chitin or cellulose would be needed to sustain power production for longer-term deployments, as both of these compounds may be catabolized by free-living microbial phylotypes that do not contribute power to the BMFC. Further studies should examine the utility of chitin or cellulose supplementation *in situ*.

17.6 Microbial ecology of BMFCs

In contrast to wastewater or other laboratory MFCs, there is no reliable or repeatable procedure for inoculating field deployed BMFCs; they are populated by the indigenous microbial species (or phylotypes) found in the environment. Even if laboratory microbial phylotypes could be inoculated onto field-deployed BMFCs, it remains unclear if they would remain a dominant member of the electrode community, or if they would be subject to competition and predation along with the indigenous microbes. In either case, microorganisms play two distinct roles in the generation of power by BMFCs. First, the redox gradients that are naturally found in marine sediments are established and maintained by microbially-mediated oxidation (or remineralization) of organic matter (for review see Froelich et al., 1979; Nealson, 1997; Jørgensen, 2006). In absence of these microbial processes, there would be no electrochemical potential, no voltage differential between anode and cathode, and as such BMFCs would not function. Second, electrode-hosted microorganisms play the primary role in facilitating the transfer of electrons between the electrodes (anode or cathode) and the indigenous oxidants or reductants. There are, in principal, two modes of electron transfer from microbes to solid-state oxidants: direct electron transfer (DET) and mediated electron transfer (MET). As these have been extensively reviewed herein and elsewhere (e.g. Schröder 2007 and Logan 2008), we will simply note that both of these mechanisms have been observed in BMFC-hosted microbial communities. However, the degree to which these mechanisms are differentially responsible for power production in BMFCs, as well as the extent to which these mechanisms are found within microbial communities, remains unknown.

Since the earliest experiments, most BMFC studies have examined, to varying degrees, the diversity of microbes associated with BMFC anodes. In general, BMFC studies have implicated two major phylogenetic groups in power production; the delta- and gamma-proteobacteria (e.g. Tender et al., 2002; Bond et al., 2002; Holmes et al., 2004; Reimers et al., 2006; Nielsen et al., 2008). Delta-proteobacteria are ubiquitous in marine sediments, many of which are involved in sulfate reduction via the oxidation of organic matter or hydrogen (Lovley et al., 2006 and references therein). Bond and colleagues (2002) observed that over two-thirds of the clones recovered in a 16s rRNA gene library (constructed from a BMFC anode) were allied to the genus *Desulfuromonas*. Indeed, power production in an MFC inoculated with pure cultures of *Desulfuromonas acetoxidans* as well as *Geobacter metallireducens* yielded power densities comparable to those observed *in situ*. *D. acetoxidans* is a sulfur-reducing organism and can use elemental sulfur or L-malate and fumarate as electron acceptors. This organism expresses cytochromes used to reduce metals such as Fe(III) and Mn(IV), which may be involved in direct electron transfer to MFC anodes. *G. sulfurreducens* may also employ direct electron transfer in power production, though the precise mechanism remains the subject of discussion (Reguera et al., 2006). In general, *Geobacter* species are known for their ability to oxidize acetate to CO₂ with solid-state oxidants –including MFC anodes–serving as the sole electron acceptor (Bond et al., 2002; Bond & Lovley, 2003). Comparing power production in laboratory MFCs to field deployed MFCs, however, may be problematic. Lab cultures are typically supplemented with refined organic acids and are not subject to the variations in conditions that are found *in situ*. Nevertheless, the dominance of the delta-proteobacteria, and the independent observation that cultivated strains are capable of generating electricity, clearly establish their role in power production.

A later study by Ryckelynck et al (2005), examining the geochemical impacts of BMFCs, found evidence for a mediated electron transfer in which dissolved and mineral forms of reduced sulfur were oxidized to S^0 at the anode. Ryckelynck and colleagues suggested that sulfur cycling plays a significant role in power production in marine BMFCs (analogous to an engineered system described by Habermann et al. 1991 in which microbiologically generated sulfide was oxidized abiotically at an anode). Also, the isolation of sulfur disproportionating organisms allied to *Desulfobulbus* and *Desulfocapsa* spp. from buried anodes suggests that S^0 deposited on the anode serves as a substrate for regeneration of sulfate and sulfide (Holmes et al., 2004).

These studies clearly illustrate the role of the delta-proteobacteria and sulfur cycling in power production. However, in Reimers et al (2006), the investigators found tremendous microbial diversity along the length of a one-meter sediment-hosted anode. When the electrodes were under load, nearly 65 distinct microbial phylotypes were enriched on the anode. This appears to confound prior studies in which delta-proteobacteria were dominant (Bond et al., 2003; Holmes et al., 2004). Notably, there were key differences in this study that likely resulted in the increased microbial diversity. In Reimers et al., the BMFC anode was deployed down to a depth of one meter within a hydrocarbon seep, thus transecting distinct geochemical milieus that were not found in the previous deployments. Furthermore, the investigators examined nearly 2000 sequences –compared to 60 sequences per deployment analyzed by Bond et al., 2002- which provided significantly more depth in phylogenetic diversity. Finally, the investigators analyzed the distribution of these microbial phylotypes along the length of the anode, and found that delta-proteobacteria were clearly dominant in the upper 20 cm of the anode (which is consistent with previous studies by Bond et al., 2002, 2003; and Holmes et al 2004).

At deeper horizons, however, where sulfate is depleted, no delta-proteobacteria were observed, and the investigators recovered microbial phylotypes that have not been seen in previous libraries. In some cases, dominant phylotypes (such as an epsilon-proteobacteria allied to *Arcobacter nitrofigilis*) were found at densities 3 to 4 orders of magnitude greater on the anode than in the surrounding sediment (as determined via quantitative PCR; unpublished data). Their enrichment on the MFC suggests they are capable of extracellular electron transfer. However, these observations are circumstantial, as the direct role of these phylotypes in power production was not established.

Several earlier BMFC studies set out to examine the effect of biofilm formation on cathode performance. These investigators observed that electron transfer in a BMFC appears to be enhanced by cathode-hosted microbial biofilms, which may contain bacteria that effectively use the cathode as an electron donor (Gregory et al., 2004; Bergel et al., 2005; Rhoads et al., 2005). While this suggests that microbial phylotypes on the cathode also have an influential role on power production, there is limited information on the microbial diversity associated with BMFC cathodes. Reimers et al (2006) found high representation of gamma-proteobacteria allied to *Pseudomonas fluorescens* –nearly 50%– in libraries constructed from cathode biofilms. In light of previous studies showing that Pseudomonads are capable of electron transfer via quinones (Newman & Kolter, 2000; Hernandez et al., 2004), it is likely that *P. fluorescens* was involved in electron transfer, though again the details of their role in power production are unknown.

It is apparent that power production in BMFCs is governed by a complex series of ecological, geochemical and electrochemical interactions. The data on BMFC microbial ecology has informed us of the major groups that appear to be

involved in power production. However, our understanding of which groups are primarily responsible to contributing to –or deterring from– power production is limited. The molecular microbiological approaches used in all these previous studies are primarily descriptive. These studies underscore the need for further quantitative investigations of microbial ecology in laboratory and field-deployed BMFCs (as in White et al, 2009), and future studies should aim to use quantitative molecular approaches (e.g. qPCR or fluorescent in situ hybridization) to advance our understanding of how quantitative changes in microbiological factors influence system performance.

17.7 Factors governing power output

Ultimately, the electron source for BMFCs is organic matter stored in sediments. Energy is liberated through spatially separated redox half-reactions that occur at the anode and cathode. The net reaction is, therefore, the oxidation of organic carbon by oxygen. While there is a wide range of potential electron donors for BMFCs (that is not adequately described by the bulk label of “sediment organic matter”), the general model is that complex organic matter undergoes microbially-mediated hydrolysis and is separated into fractions including long-chain fatty acids, aromatic compounds, fermentable sugars and amino acids (Lovley, 2006). The latter two fractions are further processed through microbial fermentation and produce organic acids such as acetate, lactate, propionate, butyrate, succinate and formate. These products, in turn, are known to support the growth of dissimilatory metal reducing bacteria capable of extracellular electron transfer (e.g. *Geobacter spp.*). Fermentation products may also fuel sulfate reduction resulting in dissolved sulfide

and/or solid phase iron sulfide minerals, which are electrochemically active and can donate electrons to an anode (Ryckelynck et al., 2005).

As previously mentioned, it is likely that current produced by a given BMFC results from a combination of electron donors (which in turn are found in different geochemical milieus). While factors that limit power production (P) in prototype laboratory MFCs are well described (Larminie & Dicks, 2000; Rabaey & Verstraete, 2005; Logan et al., 2006), they are not necessarily the same in BMFCs. Per Logan (2008), $P = E_{cell} \times I$, and limitations are described in terms of loss factors that affect E_{cell} , which are related to overpotentials. Current dependent overpotentials are defined as the difference between electrode potential when current is passing and the potential at zero current. Overpotentials occur at both the anode and cathode and occur as consequences of ohmic losses, activation losses, and mass transport losses. A key difference between laboratory MFCs and BMFCs is the importance and scale of mass transport losses. As mentioned, mass transport is often the main limiting factor in BMFCs due to the relatively low concentration of electron donors and the slow rate of mass transport in sediments (Tender et al., 2002; Scott et al., 2008a). However, from the data presented in these investigations, it is difficult to ascertain if power density is indeed limited by bulk transport of substrates, or by micro-scale chemical diffusion such as occurs within microbial biofilms. Nielsen et al. (2007) calculate the internal resistance of a chambered BMFC under conditions of natural and artificially enhanced mass transport. Under the natural condition the apparent internal resistance of the BMFC was far greater than when pumping eliminated mass transport limitation. In contrast, mass transport limitation is observed at different scales in laboratory and wastewater MFCs. In such systems there is little evidence that investigators have achieved maximum power based on substrate flux to the

electrodes (Logan, 2008). However, limitations arise due to transport limitations of protons through biofilms, which result in pH changes that could adversely affect bacterial physiology. Laboratory MFCs tend to be run either as batch reactor studies to investigate a particular aspect of the system or with a flow through system. In either case, the concentration of electron donors can be easily manipulated so as not to be a limiting factor. Furthermore, in laboratory MFCs ohmic losses are addressed primarily by minimizing the spacing between electrodes and by careful design of the membranes. BMFCs do not have a membrane and there is a limit to how close the electrodes can be located since the oxic and anoxic zones are spatially separated (Rezaei et al., 2007). On the other hand, the electrolyte in most BMFCs has been seawater, which has a conductivity of approximately 25 - 40 mS cm⁻² (varying as a function of temperature). Owing to the high conductivity of seawater, BMFC performance is not -in most circumstance- influenced by electrode spacing.

Calculating the Coulombic efficiency (defined above) in a laboratory MFC fed with refined fuels (e.g. acetate), is a relatively straightforward exercise, as the number of electrons available per mole of fuel via respiration to CO₂ (with the anode as a terminal electron acceptor) can be compared to the measured current to determine these efficiencies. However, in practice, the Coulombic efficiencies of MFCs varies widely from 0.7% to greater than 89% (Rabaey et al., 2003; Liu & Logan, 2004; Liu et al., 2004; He et al., 2005; Liu et al., 2005; Reimers et al., 2007). This is primarily due to differences in fuel quality, including the presence of recalcitrant carbon that likely elevates the estimate of total organic carbon while contributing very little to power production. In addition, it has been shown that other factors affect Coulombic efficiencies such as ionic strength, temperature and electrode spacing (Liu and Logan, 2004); multiple, and possibly competing, anodic reactions in seawater-based MFCs (Ryckelynck et al., 2003); and the degree to

which the particular microbial community expends energy on respiration versus growth and biosynthesis (Finkelstein et al., 2006). For example, Finkelstein et al (2006) suggested as much as 95% of energy available from organic carbon oxidation may not contribute to power production, as it is used by the anode-hosted microbial biofilm for growth and biosynthesis (though it should be noted that that other studies, e.g. Aelterman et al, 2008 have found that a greater percentage of the energy available in organic matter may be harnessed by the electrode). Similar to laboratory MFCs, BMFCs have shown a wide range of Coulombic efficiencies with an upper bound of about 65% (Nielsen, 2008). The observed differences may be due to environmental differences, or energy partitioning by the indigenous microbial community. In a BMFC, available “fuel” is particularly subject to consumption by the free-living microbial community, and as such it is difficult to determine which fraction of the available fuel is being used by the anode-hosted community. In general, the amount of potential energy stored in sediment that is available for electrical work appears to have been overestimated by previous calculations, and requires further consideration (Reimers et al., 2001; Tender et al., 2002).

17.8 Scaling and environmental variability in BMFCs

The relationship between performance and device size is currently being investigated for both laboratory MFCs and BMFCs. Dewan et al (2008) recently compiled results from 20 studies, including laboratory MFCs and field-deployed BMFCs, that clearly showed that MFCs with the largest total anode surface area had the lowest power densities. They also conducted systematic experiments and observed that power density is –to a degree- inversely proportional to the logarithm of the surface area of the anode (though we and others have observed that power

density is dependent on a great many factors such as mass transport, quality of fuel, and density and distribution of the microbial community). In sum this draws into question the validity of simply extrapolating power densities from small-scale experiments to estimate how much power might be delivered by scaling up various MFC designs. This question is central to BMFC experiments since the underlying motivation for this research is to develop useful power supplies.

It should also be noted that the natural environment is extremely dynamic, and not subject to control like a typical laboratory or industrial setting. Accordingly, BMFC studies should make a concerted effort to understand the degree to which natural fluctuations influence BMFC performance and spatial or temporal variability. Natural fluctuations, including temperature changes, tidal cycles, pressure variations, changes in water flow, salinity and conductivity changes and dissolved oxygen changes, can readily influence microbial physiology and ultimately BMFC performance. For example, Reimers et al (2006) observed a relationship between current (produced by the abiotic oxidation of sulfide) and temperature on the order of $1.3 \text{ mA} \cdot \text{m}^{-2}$ for every $^{\circ}\text{C}$. In estuarine environments, Nielsen and colleagues (2007) observed current oscillations, the frequency of which were consistent with tidal pumping. In the latter example, Nielsen et al determined that the total resistance in a BMFC decreases by 100Ω from high tide to low tide due to changes in seawater conductivity. Even larger relative power fluctuations were observed in the power records from chambered BMFCs deployed at cold seeps in Monterey Canyon (Nielsen et al., 2008). Curiously, these chambered BMFCs were deployed at a water depth of 960 m and the frequency of the power oscillations did not correlate with tidal changes or any measured environmental factor. The most likely explanation for the variability was variable sediment porewater seepage

and mixing with the chambers that would control the delivery of electroactive species to the anode.

In sum, significant power fluctuations appear to be a common feature of all chambered BMFC deployments regardless of where they are deployed. Regardless of the underlying cause, variable power generation affects the requirement for power management devices in that they must be able to store fluctuating levels of power for subsequent use in powering a sensor with steady or variable demands.

17.9 Commercial viability of BMFCs

As of late, there has been a surge in the development of low power sensor and monitoring systems for remote and rural applications. Such systems are widely used in both science and industry, to increase the footprint of data collection or to monitor materials and infrastructure. Examples of parameters that are of interest to both science and industry include temperature, salinity, water level, irradiance, pressure, pH, fluid flow including tidal patterns, migration patterns of fish and other animals, and pollution monitoring. Long-term monitoring requires instrumentation that is powered to collect, store and transmit data, and to date most sensor systems have relied on solar power or battery packs for extended deployments. However, solar systems are of limited long-term use above certain latitudes, and batteries, while improving in energy density and duration, are typically unable to provide power for any deployment longer than two or three years (depending upon the sensor system). With respect to oceanographic applications, batteries can typically power a sensor for about one year. For logistical and financial reasons, this limits the ability of the end user to deploy extensive sensor systems in nature. BMFCs should, in principal,

be able to meet the power requirements of a number of sensors systems that are also robust enough to operate for many years.

For the reasons described above, the practical use of electricity from BMFCs requires power management systems that satisfy three requirements (Nielsen, 2008). First, current is produced at a low voltage and must be converted to higher voltages to satisfy sensor requirements, second, modest and steady power production requires storage to satisfy variable load cycles, and third, cell voltage should be regulated to operate at the most efficient and maximum sustainable level. Recently, the development and deployment of the B.U.G. (Tender et al., 2008), has shown that small sensor systems on buoys may be powered by BMFCs. Shantaram et al. (2005) were able to power a wireless sensor and telemetry system, though their system employed a sacrificial anode that provided higher voltage, which in turn enabled the use of commercial electronics for power management (the low voltages generated by most BMFCs limits the use of commercial electronics for power management). More recently, Donovan et al (2008) developed a power management system that enabled sufficient power to be harnessed from a BMFC without a sacrificial anode, by using a capacitor to store charge, and a voltage comparator and DC-DC converter to boost the voltage to 3.3 V (sufficient to power most solid state devices). Here too, the duty cycle of the sensor was decreased to meet the performance of the BMFC. In sum, the potential for BMFCs to power sensor systems in the environment has been largely established. With respect to potential commercialization, the success of BMFCs as power systems will depend on their ability to compete – in terms of performance, cost and reliability – with conventional and alternative systems. Ultimately, this will require a concerted and thorough investigation of the aforementioned factors, from electrode material to

microbial ecology, to further optimize BMFCs for powering future sensor infrastructure.

On the whole, BMFC studies comprise a small fraction of the total body of research on microbial fuel cells. Nevertheless, BMFC research has provided critical insights into the geochemical and microbiological factors that contribute to -and may ultimately limit- power production in complex systems. Whether BMFC research grows in proportion to the field remains to be determined. However, it is likely that BMFCs will continue to be used as a testbed for those interested in understanding the intricacies of geochemical and microbial interactions in natural systems, as well as those in pursuit of developing BMFCs as reliable and cost-effective means of remote power generation.

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