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Current Opinion in Biotechnology

Harnessing energy from marine productivity using bioelectrochemical systems

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Over the past decade, studies have shown that devices called microbial fuel cells (MFCs) can harness electricity from microbially mediated degradation of organic carbon, in both lab cultures and natural environments. Other studies have shown that MFCs can harness power from coastal and deep ocean sediments, as well as from plankton, without any fuel supplementation or microbial inoculation. The fuel for these systems is organic matter resulting from oceanic primary productivity. Models suggest that MFCs may operate for decades on endogenous organic carbon. In light of their capacity to generate power in natural milieus by tapping into biogeochemical cycles, MFCs may one day provide an efficient means of generating power (or high value biofuels) directly from marine productivity.

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Current Opinion in Biotechnology 2010, **21**:252–258

This review comes from a themed issue on
Energy biotechnology
Edited by Jan R van der Meer and Alexander Steinbuchel

Available online 9th April 2010

0958-1669/$ – see front matter

DOI 10.1016/j.copbio.2010.03.015

Introduction

Recent years have been a watershed for the understanding of microbially mediated metal cycling. In particular, there has been an explosion of research on microbial fuel cells (or MFCs). MFCs are systems that harvest electrons resulting from microbial metabolism [1,2]. They have been used to generate power from a variety of organic-rich matter (e.g., wastewater, compost, and sediments). There is growing interest in using MFCs for alternative energy generation, or as systems for directing and stimulating microbial processes for industry (discussed in detail later).

Some of the earliest environmental MFC deployments were in marine sediments, and recent studies have used MFCs to generate power from seawater. In light of these studies, MFCs may offer an opportunity to harness significant amounts of energy directly from natural marine biogeochemical cycles. Here we present a brief overview of how MFCs and other bioelectrochemical systems (BESs) harness energy from marine productivity, and which environmental factors govern the efficacy of this approach. We also discuss how much energy is potentially available via bioelectrochemical approaches, limitations of the current technology, and current research directions that may enable this technology to play a significant role in supporting our energy needs.

Marine primary productivity

Primary productivity is the conversion of inorganic carbon to organic carbon by biological processes, primarily photosynthesis. Nearly half the world's primary productivity occurs in the oceans [3] and current estimates suggest that 50 gigatons of carbon are produced annually [4]. Coastal regions (ocean with a water depth <200 m) have a total area of about 36×10^6 km^2, which is about 3.5 times the area of the entire United States. They account for nearly 20% of oceanic primary productivity. Sunlight is the primary source of energy for photosynthesis (providing reducing potential for carbon fixation). Though the annual mean solar power density is approximately 168 W m^{-2} [5], photosynthetic organisms capture a very small fraction of this energy (<1%; [6]). Regardless, this productivity forms the basis of the marine food web, supporting nearly all organisms in the water column and on the seafloor. Recent studies using radiocarbon isotopes have shown that ~85% of photosynthetically derived carbon is consumed by organisms in the water column, with the remainder being deposited in the underlying marine sediments [7–9]. Much of the organic carbon deposited in sediments consists of recalcitrant chitin, keratin and some lipids, and can persist for millennia. Through this deposition, marine sediments are considered among the largest global sinks of organic matter [10].

Microbial extracellular electron transfer

Fundamentally, all life relies on the movement of electrons from one compound (a reductant such as organic carbon) to another compound (the oxidant) for generating power to do work. All *animals* (multicellular organisms) use organic carbon as a reductant and, ultimately, oxygen as an oxidant. Notably, many microbes are capable of using other oxidants such as nitrate, sulfate and carbon dioxide. Recently, scientists have found that some microbes shuttle electrons from organic carbon catabolism to insoluble mineral oxides *outside* the cell [11–14].

This physiologically stunning feat, referred to as extracellular electron transfer (or EET), is enabled by a number of mechanisms that have been the subject of much investigation in recent years. Briefly, some microbes use organic redox-active molecules to shuttle electrons to insoluble mineral oxides [15,16]. Other microbes are replete with outer membrane cytochromes (membrane bound proteins) that can shuttle electrons to the mineral oxides [17]. Recently, microbes have been found to produce 'nanowires', or conductive filamentous structures, that shuttle electrons directly to the mineral oxides over relatively long distances [18,19].

While it was originally thought that this physiological capacity was limited to a few, unique anaerobic microbes, EET has now been observed in many microbes isolated from a wide variety of environments. Microbes capable of EET have been found natively in wastewater [20–23], compost [24], soils [25–29], acid-mine drainage [30], seawater [31–40,41••], and industrial waste streams [42–47]. Strains of model microorganisms such as *Shewanella oneidensis*, *Geobacter sulfurreducens* and *Bacillus subtilis* are known to exhibit EET to varying degrees [48–50]. Ecologically, the role of EET remains hotly debated as some microbes clearly depend on EET for energy metabolism, while others may employ EET for anti-microbial warfare (anti-microbial molecules are often redox active [25,51,52]).

Microbial fuel cells and other bioelectrochemical systems

By definition, fuel cells are devices capable of converting chemical energy to electrical energy without combustion. By analogy, MFCs rely on catabolic activity of microorganisms to convert chemical energy into electrical energy [53]. This conversion is enabled by spatially separating redox half-reactions so that electrons from oxidation reactions at an anode flow through a circuit to a cathode (the site of reduction reactions). Anode-hosted microbes are typically anaerobes that oxidize reduced chemical species such as organic carbon and transfer electrons to the anode, producing current that may be used to do work (e.g., charge batteries or power a sensor). Typically, reduction of dissolved oxygen at the cathode balances the oxidation reactions at the anode (although other terminal electron acceptors have been investigated; [54–56]). Recently investigators have observed that microbes growing on the cathode may potentially use it as an electron donor [54,57]. In these systems, electrons are harvested by the microbes to regenerate reducing equivalents, which provides reducing power for synthesizing compounds such as hydrogen [57]. Our understanding of microbially mediated electrode oxidation is limited, and ongoing research is aimed at better understanding this physiological capacity.

Reports of MFCs date to the early 20th century [58], when investigators employed toxic chemical mediators to facilitate electron shuttling to the electrode. The discovery that microbes capable of EET can shuttle electrons to the anode of a microbial fuel cell [59] spawned a new surge of research on 'mediatorless' MFCs. Some of the earliest 'mediatorless' MFC studies were in marine estuarine sediments, where systems were deployed across naturally occurring redox gradients at the sediment–seawater interface [60,31–33]. Briefly, oxygen is typically present in the overlying water but is depleted in marine sediments. Anaerobic microbes in the sediments use alternative oxidants – including the MFC anode – to support organic matter degradation. Thus an anode buried in marine sediments, electrically connected to a cathode in the overlying water, generates current (a full review of benthic MFCs may be found in [61]). Investigators have consistently observed continuous, uninterrupted power generation in every organic-rich sediment, though at modest power densities (ca. 28 mW/m^2; [32]). In more recent studies, investigators developed chambered MFC systems in which the anode was enclosed in a chamber that was placed atop the sediments to achieve chemical equilibrium with the sediment porewaters [36,38••,62]. They observed significantly higher power densities for the duration of the experiment owing to improved mass transport within the chamber (ca. 140 mW/m^2; [38••]).

As mentioned, much of the energy from photosynthetic primary productivity is cycled in the water column. To investigate the feasibility of accessing this carbon for power generation, investigators conducted a series of experiments wherein they used fresh plankton as the fuel for a laboratory MFC [37••,41••]. In their experiments, roughly 80% of the organic carbon added as fresh substrate was degraded over two months of incubation. The rate of degradation was significantly greater in the active MFC versus the control MFC (in which electrodes were electrically isolated). These data underscore the capacity of MFCs to stimulate organic matter degradation. A subsequent study showed that microbes colonizing the plankton-fed MFC anodes were phylogenetically allied to those recovered from marine sediments, despite the lack of sediments in these incubations [41••]. Moreover, the observed ecological succession of bacteria during the course of the experiment suggest that varying anode potential can maximize current generation by selecting for different microbes that catabolize different pools of organic carbon. The capacity for these microbial communities to degrade nearly 80% of the organic carbon is promising, and the authors suggest that plankton-fed MFCs may be a viable means of power production. In particular, the use of plankton-enriched seawater alleviates the issue of diffusion limitation to and from sediment-hosted anodes. The authors suggest that pre-inoculated electrodes may increase coulombic efficiency by an order of magnitude since the microbial community might be able to rapidly utilize labile carbon in power production [62].

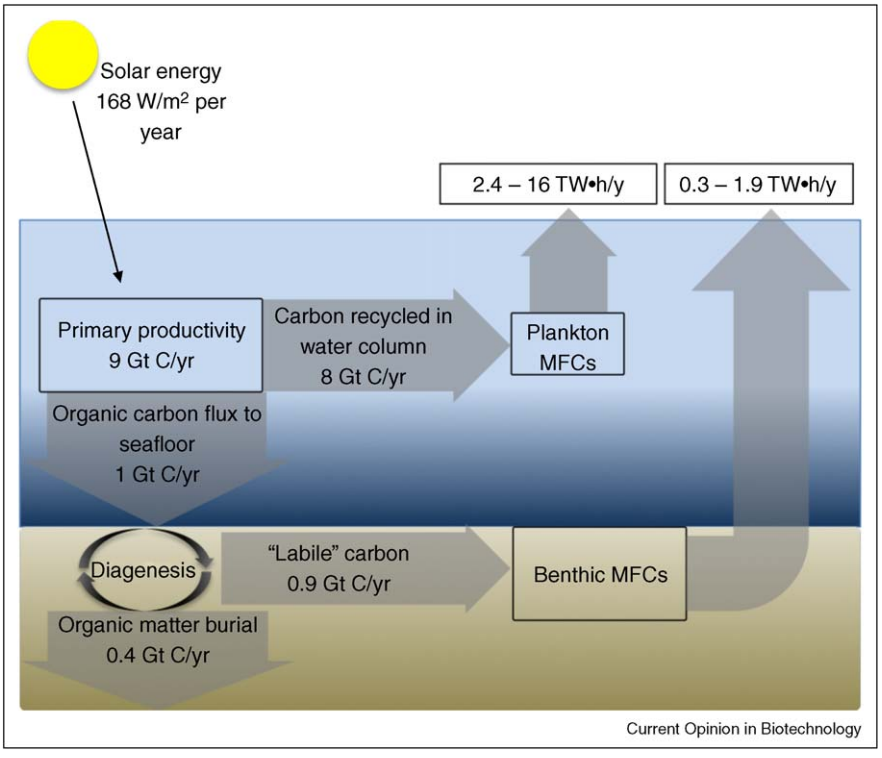
To our knowledge, the experiments by Reimers and coworkers are the only plankton MFC experiments to date. Other studies describe MFCs which use novel membrane configurations so that they could be deployed in the water column [63]. However, these experiments used *S. oneidensis* and refined substrates as fuel, so it is difficult to speculate about the performance of this system in natural settings.

Scalability of marine MFCs and factors limiting power generation

The studies described above unequivocally demonstrate that power can be harnessed from seawater and marine sediments. Investigators have alluded to the potential of environmental MFCs in harnessing significant amounts of energy from global biogeochemical cycles at a commercially viable scale. However, little research has been done in this area and no pilot scale studies have been conducted to examine the scalability and viability of this approach. Here we provide a model wherein we estimate the amount of power that may be harnessed by sediment-hosted and plankton-fed MFCs deployed to capture 1% of total productivity in coastal environments (Figure 1). 1% was chosen because the feasibility of such deployments remains unknown, and this percentage allows one to easily calculate power generation from larger systems. These calculations are based on the assumption that (A) annual production in those waters is 9 gigatons carbon per year [4], (B) 85% of the organic carbon is recycled in the water column, while 15% is exported to the sediments [64], (C) coulombic efficiencies of environmental MFCs range between 10 and 65% [37••,62], (D) the potential between anode and cathode is 0.35 V, and (E) plankton MFC operation does not adversely affect sediment MFC operation. Based on these assumptions we determined that 2.5–16 TW h/yr and 0.3–1.8 TW h/yr of energy can be harnessed from the water column and sediment MFCs respectively (Figure 1).

These estimates underscore the amount of energy that flows through just 1% of coastal marine ecosystems, but do not offer a realistic depiction of how much energy may be captured annually. Let us consider a plankton-fed MFC power plant consisting of a 3-m diameter reactor, with a 40 km path length, and a volume of approximately 340,000 m^3. If the average organic carbon concentrations in seawater is 110 μM, and coulombic efficiencies range from 10 to 65% [37••,62], and the pumping rate is 4 m^3/s, this reactor may produce between 5 and 35 MW h/yr. However, pumping this volume of water at this rate –

Figure 1



Model of energy available from MFCs via the marine carbon cycle. Solar input is based on [5], primary productivity for coastal ocean is based on [4]. Partitioning of primary productivity is 85 and 15% to the water column and sediments, respectively [7]. About 70% of the carbon that reaches the seafloor is remineralized through diagenesis (the 'labile' fraction) and about 30% is buried [8]. Energy calculations for plankton and benthic MFCs depict the theoretical maximum energy that may be harnessed from these pools of carbon, and are based on a potential of 0.35 V between anode and cathode, a yield of 4 electrons per carbon oxidized (CH_2O to CO_2) and coulombic efficiencies ranging from 10 to 65% [37••,62].

assuming no head pressure from elevation – would consume at least 650 MW h/yr (assuming a pump efficiency of 70%, and accounting for the frictional losses attributable to the pipe and electrodes using the Colebrook–White equation; [65]). Thus, when using raw seawater as the fuel it is impractical to expend energy on pumping. Alternatively, if it were possible to mechanically or biologically concentrate biomass from seawater, the power density could be increased. As in Reimers *et al.* [37••], if one could increase organic carbon concentrations by two orders of magnitude, this same reactor may produce 1.7 GW h/y.

There are additional limitations in MFC technology that are not captured in the previous models. In addition to parasitic losses, existing data are mixed in terms of how well MFC electrodes scale up [66,67]. This makes it difficult to discern whether a large-scale MFC system with many individual electrodes is practical. Moreover, investigators have observed the deposition of elemental sulfur on the electrodes of environmental MFCs reduces performance over time [34]. Mitigating this phenomenon may add significantly to the overall operating costs, though this remains unconstrained. Biofouling may also be problematic, though to date this not been an issue in marine MFC deployments [36,38••].

Other approaches to harnessing energy from marine productivity

Recent studies have examined the performance of phototrophic MFCs, in which mixed cultures of photosynthetic microbes and EET-competent bacteria were used to provide power from photosynthesis in a reactor [68•]. Contained systems such as these could be deployed in coastal waters to convert solar energy to electricity by coupling photosynthesis to EET at the anode. While organic carbon is continuously replenished during the day, the coulombic efficiency of these systems may be diminished by photosynthetically derived oxygen accumulation over time. One solution may be to use anaerobic photosynthetic bacteria, such as purple and green sulfur bacteria, to provide organic carbon without the deleterious effects of oxygen on anaerobic processes [69]. Although the maximum theoretical efficiency of photosynthesis is 9%, which is lower than the efficiency of 17% currently achieved by commercially available photovoltaic cells [70], the ability of algae to utilize light over a wider range of wavelengths and intensities [71] may enable these systems to be more cost effective than conventional photovoltaic cells. This supposition also remains to be tested.

Given many of the aforementioned limitations of MFC power production, a number of researchers believe that the greatest potential of BESs lies in the generation of fuels and other commodities [72]. For example, investigators have developed bioelectrochemical reactors that generate hydrogen gas at the cathode [73]. In such systems, bacteria at the anode oxidize carbon substrates, generating protons and electrons as in a MFC. A potentiostat raises the potential to overcome thermodynamic limitations, stimulating the production of hydrogen. Since the protons and electrons are being derived from organic matter through biocatalysis, the voltage needed to generate H_2 is an order of magnitude lower than that needed for electrolysis of water. This system uses the equivalent of 0.2 mol hydrogen energy per mole of hydrogen produced, compared to the 1.7 mol loss typical of electrolysis [74]. In addition to hydrogen, a variety of other products have already been generated using BESs (some of which required supplemental current). This includes glutamic acid [75], propionic acid [76], succinate [77], sulfur [78], methane [79], formate [80•], and ethanol [81]. In a marine BES, biofuels and other products might be produced in a cathode chamber, coupled to microbial organic carbon degradation at an anode. However, here again there are no data on the efficiency of this approach when using marine biomass as fuel. Future studies should test the feasibility of this approach at both the laboratory and commercially relevant scales.

Future directions and considerations

Vast amounts of energy flow through marine biogeochemical cycles and may offer the opportunity to harness commercially relevant quantities of electrical energy. To date, sediment and plankton MFCs have been used to power electronic devices in the field, such as oceanographic instruments, beacons, and remotely operated vehicles [32,37••,82,38••,83], and companies are capitalizing on these efforts to commercialize these technologies. Comparatively little work has been done on the scalability and commercial utility of environmental MFCs and other BESs, and the aforementioned discussions have outlined some of the key limitations. Nevertheless, MFCs offer some significant advantages over existing conventional and alternative energy systems. Most MFCs have no moving parts and have proven to be quite reliable. In nature, they are likely to produce power for decades as they tap into open, natural biogeochemical cycles. They generate power day and night, regardless of solar intensity or wind speed. They function over a wide range of temperatures, and the naturally occurring electrode-hosted microbial communities are highly resistant to perturbations. When considered in aggregate, these attributes make MFC power generation attractive. Should advances in engineering (such as the development of appropriate, cost effective current collectors) or biology enable MFCs to produce one order of magnitude more power per unit area or volume, 'standalone' MFC power generation begins to approach economic viability. Ongoing research is targeted at improving power densities, and it is likely that advances in the coming years will attain that goal. Even so, it remains to be seen whether MFCs will become a commercially viable means of power production in a landscape of alternative energy technologies.

Acknowledgements

We would like to thank Stephanie Nielsen and Pengfei Song for editorial assistance. Thanks to the Center for Ocean Science Education and Excellence (COSEE) Ocean Systems group for fruitful discussions about concept mapping. We also wish to thank the Gordon and Betty Moore Foundation for their support (grant #1609).

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