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The Next Breakthrough in Microbial Fuel Cells and Microbial Electrolysis Cells for Bioenergy and Bioproducts

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Abstract

Microbial Fuel Cells (MFCs) have demonstrated their capabilities under laboratory conditions to treat various types of wastewater with concomitant bioelectricity production. They can also be operated as Microbial Electrolysis Cells (MECs) with an external voltage to produce some bioproducts such as methane and hydrogen. Tremendous advances have been made in recent years in reactor configuration, electrode design, membrane design and multi-unit stacking. However, the MFC and MEC technologies are still far from ready for real-world applications beyond powering small sensor devices. This work discusses bioelectrochemistry principles and various bottlenecks in MFC operations. It points out that the next breakthrough may come from the use of engineered biofilms with superior performance characteristics that greatly improve electron transfer and appetite for various organic matters in wastewater streams.

Keywords: Microbial fuel cell; Microbial electrolysis cell; Biofilm; Electron transfer; Bio-electrochemistry; Wastewater treatment

Introduction

Due to an expanding global population and increasing prosperity in several large developing countries, the demand for energy is rapidly escalating. Dwindling oil reserves cast a dark shadow on the future of global economy. Coal has a more abundant supply, but it has a much bigger carbon footprint. All fossil fuels cause environmental problems and they are unsustainable. Politicians and academics alike have realized that a multifaceted approach is needed to relieve the global energy crunch by utilizing nuclear, solar, wind, geothermal and bioenergy to supplement, and eventually to replace, fossil fuels. The Microbial Fuel Cell (MFC) and Microbial Electrolysis Cell (MEC) technologies can potentially be a part of the bioenergy solution. MFCs are capable of utilizing low-grade organic carbons in various types of wastewater such as municipal and industrial wastewaters as fuels to produce bioelectricity that can offset the energy needed for wastewater treatment. Biofilms play a critical role in MFC operations. Biofilms are ubiquitous in nature. In fact, most microbes live in pure-culture biofilms or synergistic mixed-culture biofilm consortia rather than as individual planktonic cells [1]. A biofilm starts with some planktonic cells adhering to a surface. These cells undergo a phenotypical change and become sessile cells. Sessile cells secrete exopolymeric substances (EPS) consisting of polysaccharides, proteins and extracellular DNA molecules to keep the sessile cells in a biofilm community. In a mixed-culture biofilm, different types of microbes live synergistically by playing different roles. Many different types of artificial and real wastewaters have been tested for MFC applications [2]. Different wastewaters often require different biofilms for optimized organic carbon digestion. Activated sludge from wastewater treatment facilities is often used inoculum for MFC operations because it contains a large variety of anaerobes. Unlike artificial wastewater, some real wastewaters may lack ionic strength for conducting electricity internally or some nutrients for biofilm health. Thus, they are typically enriched with additional salts or nutrients. Various MFC reactor configurations and operating conditions have been reviewed by Du et al. [3].

When an external voltage is imposed on an MFC, it can be operated as an MEC to produce bioproducts such as hydrogen, methane and ethanol with much reduced energy input [4]. MFCs and MECs can be operated either in the batch mode or continuous mode for the feed stream. The intensive research efforts on MFCs in recent years have also resulted in much better understanding of bio-electrochemistry and biofilm ecology, which has benefited biosensor designs [5] and even the fundamental understanding of biocorrosion (also known as microbiologically influenced corrosion) caused by biofilms [6].

Bioelectrochemistry of MFCs

The MFC power generation concept was first demonstrated by British botanist M. C. Potter about a century ago [7]. Its research only intensified in recent years because during the current energy crisis researchers are attracted by its potential for direct electricity production from low-grade organic carbons in wastes that are otherwise not utilized. Over one thousand research papers have been published on MFCs and MECs in the past few years alone. In a typical dual-chamber MFC, an anaerobic biofilm covering the anode oxidizes the organic carbons in the substrate feed under biofilm catalysis (Figure 1). The electrons released by the oxidation reaction (Reaction 1 below with acetate as an example) in the cytoplasm of the sessile cells in the biofilm are transported through an elaborate electron transport chain across the cell wall to the anode surface. They then flow through an external circuit to the cathode. An external load is placed in the circuit to harvest the electricity. To maintain electro-neutrality in a typical MFC, protons migrate from the anodic chamber to the cathodic chamber through a

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Proton Exchange Membrane (PEM) to reach the cathode where they are used together with the incoming electrons to reduce dissolved oxygen to form water (Reaction 2).

Anodic reaction $CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^-$ ($-E^{o\prime}=+290$ mV) (1)

Cathodic reaction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E^{o\prime}=+818$ mV) (2)

$E^{o\prime}$ is defined as the reduction potential (also known as redox potential) at 25°C, pH 7, 1 M concentration for solutes (or 1 bar partial pressure for gases) except H^+. $E^{o\prime}=-414$ mV for $2H^+/H_2$ [8], instead of 0 mV for the Standard Hydrogen Electrode (SHE) because SHE requires $[H^+]=1$ M (i.e., pH 7) while $E^{o\prime}$ requires $[H^+]=10^{-7}$ M. Table 1 lists some $E^{o\prime}$ values (vs. SHE) that are commonly used for anodic and cathodic reactions in MFCs and MECs. The theoretical cell potential for the redox reaction combining Reactions 1 and 2 is 1108 mV at the conditions defined for $E^{o\prime}$. The cell potential at actual operating temperature and concentrations/pressures will deviate from this value based on the Nernst equation. In reality, an MFC utilizing Reactions (1) and (2) will have a much lower open circuit potential due to various losses.

Bottlenecks in MFCs and possible solutions

So far, MFCs and MECs have been mostly operated in laboratory investigations. Only a few pilot-scale tests have been conducted and the results are unsatisfactory [2]. Significant hurdles must be overcome before these technologies become practical. There are several bottlenecks in MFC operations that can be lumped into two general categories: charge transfer (i.e., reaction kinetics) resistance and mass transfer resistance. Various overpotentials must be overcome. They include activation over potential, reaction over potential and concentration over potential. One of the key problems in MFCs is an elaborate electron transport chain is needed to transfer electrons released from organic carbon oxidation across the cell wall to the anode. This is because electrons do not "swim" in water. Thus, planktonic cells cannot transfer the electrons. The electrons rely on a biofilm to transport them to the anode. This means Reaction 1 has to happen in an electrogenic biofilm that is attached to an anode surface. This is a huge drawback to start with because organic carbons are not digested in the bulk liquid, unlike suspension cultures in typical non-electrochemical bioreactors such as anaerobic digesters including

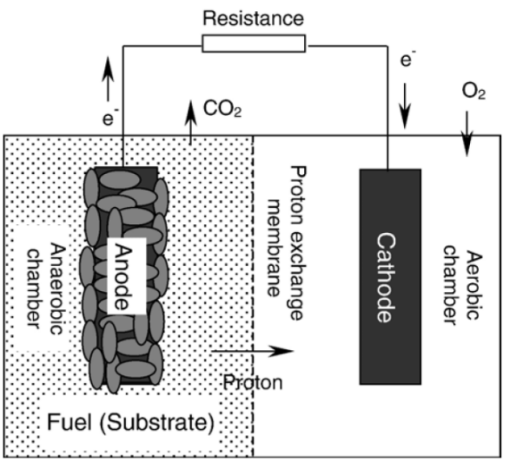

Figure 1: Classical dual-chamber MFC with a bioanode and an oxygen cathode (figure reprinted from [3] with permission from Elsevier).

Redox Couple	n	$E^{o\prime}$ (mV)
$2CO_2$ + 2acetate/hexose	8	−670
CO_2 + acetate/pyruvate	2	−660
CO_2 + acetate/lactate	4	−430
CO_2/formate	2	−432
$2H^+/H_2$	2	−414
$6CO_2$/hexose	24	−410
acetate/ethanol	4	−390
CO_2/methanol	6	−370
$4CO_2$/succinate	12	−312
$7CO_2$/benzoate	30	−300
$2CO_2$/acetate	8	−290
2acetate/butyrate	4	−290
CO_2 + acetate/glycerol	6	−290
$4CO_2$/butyrate	20	−280
$3CO_2$/propionate	7	−280
$6CO_2$/hexane	8	−250
CO_2/CH_4	8	−244
SO_4^{2-}/HS^-	8	−217
glycine/acetate+NH_3	2	−10
fumarate/succinate	2	+33
NO_2^-/NH_3	6	+330
NO_3^-/NH_3	8	+360
NO_3^-/NO_2^-	2	+430
$2NO_3^-/N_2$	10	+760
$O_2/2H_2O$	4	+818
$H_2O_2/2H_2O$	2	+1350

Table 1: Reduction potentials at pH 7, 25°C, 1 M solutes (1 bar gases) except H^+ [8].

methane digesters that use volume-based reactions instead of surface-based reactions. Most biofilms are not electrogenic and thus they cannot be used for the anode. Electrogenic biofilms rely on either Direct Electron Transfer (DET) or Mediated Electron Transfer (MET) methods [3]. In DET (Figure 2), sessile cells utilize cell membrane-bound redox proteins such as *c*-type cytochromes or conductive pili (also known as conductive nanowires). The former allows only a single monolayer of sessile cells for electron transfer while the latter makes it possible for several layers of sessile cells to be electrogenic via extensive pilus networking [9]. In MET, soluble redox-active compounds known as electron mediators transport the electrons from the cytoplasm where organic carbon oxidation occurs to the anode surface. These mediators can absorb and release electrons and they are recycled. Externally supplied mediators are not sustainable because of cost and potential for environmental pollution. Some microbes in a synergistic biofilm may secrete mediators locally to enhance electron transfer by themselves or other microbes in the same biofilm community.

Another bottleneck is the internal "electricity flow" in an MFC in order to maintain electro-neutrality, thus completing the circuit. In a typical MFC, proton migration from the anodic chamber through a PEM to the cathodic chamber achieves this goal. Other membranes such as anion exchange, cation exchange and charge-mosaic membranes may also be used to allow other ionic species to balance the charges [10]. The membrane partitions the anodic and cathodic chambers such that oxygen in the cathodic chamber cannot diffuse into the anodic chamber. If oxygen is leaded to the anodic chamber, it will oxidize the organic carbon in an aerobic biofilm without releasing electrons, which would reduce Coulombic efficiency because oxygen becomes the electron

acceptor rather than the cathode. Such a membrane is expensive and easily fouled. It is also a key contributor to concentration overpotential causing a large Ohmic resistance and sometimes a acidification of the anodic chamber. The dual-chamber MFC design in figure 1 is actually no longer a popular design because of its large Ohmic resistance. They are often replaced by single-chamber MFC designs that have a much shorter distance between the electrodes [3].

The cathodic reaction in an MFC is often another bottleneck. Oxygen oxidation is kinetically very slow without catalysis. Unfortunately, the catalysis usually requires costly metal catalysts such as platinum that is prohibitively expensive even if only a thin coating is used. Many research efforts have been devoted to the making of less expensive cathodes through chemical modifications and the use of novel materials [11]. To avoid using expensive cathodes, biocathodes may also be a substitute [2]. They use catalytic biofilms without a catalytic base electrode for the reduction of an oxidant. Either aerobic or anaerobic biofilm is used to cover a cathode for oxygen reduction or the reduction of a non-oxygen oxidant such as sulfate and nitrate that may come from agricultural run-offs. Just like the case for anodes, the biofilm for the cathode must also be electrogenic albeit with an opposite electron transfer direction, i.e., from electrode (cathode) to the cytoplasm of sessile cells. Thus, charge transfer resistance in the biofilm can still be a major hurdle. Low reduction potential especially in the case of sulfate reduction ($E^{o'}$=−217 mV) is another drawback. Nitrate has a much higher reduction ($E^{o'}$=+760 mV for $2NO_3^-/N_2$) (Table 1). In a wastewater stream, nitrate may come from agricultural fertilizer run-off. An MFC with an anodic biofilm and a cathodic biofilm can potentially be used to treat two different wastewater streams simultaneously.

The maximum MFC power density has increased by several orders of magnitude through intensive research in recently years. However, it is still 1,000 times below the 10^3 to 10^4 W/m^2 (anode surface area) power density achieved by chemical fuel cells [12]. Realistically, we should not compare MFCs with chemical fuel cells in power density output because MFCs are not powered by high energy-density fuels such as pure hydrogen or ethanol. Nonetheless, for practical applications beyond powering sensor devices, MFC power densities must improve much further for MFCs to be practically meaningful. Various MFC and MEC bioreactors have been developed [3]. Improvements have also been made through electrode modifications [13] and multi-reactor arrangements [2]. Unfortunately, further reactor improvements may encounter cost limitations. A high performance MFC may not find any practical use if the cost is uneconomical. One obvious way to improve power density is to increase the substrate feed rate. With a fixed reactor volume, several improvements are needed to accommodate the high fee rate: (1) The rate of the anodic biofilm digestion of organic carbons must increase; (2) the electron transfer between the anodic biofilm and the anode must be accelerated; (3) proton migration from the anodic region to the cathodic region must speed up, and (4) the cathodic reduction reaction must keep up with the electron and proton supplies. A simplistic MFC reactor proposed by Zhou et al. [2,4] contains an inexpensive membrane-less tubular reactor with an anodic zone and a cathodic zone with convective flow from the anodic zone to the cathodic zone to reduce MFC internal resistance. Oxygen back diffusion can be eliminated only if the flow rate is sufficiently high. This design is hinged on a very efficient biofilm that is capable of digesting substrates and donating the electrons to the anode fast enough to catch up with the convective flow of protons.

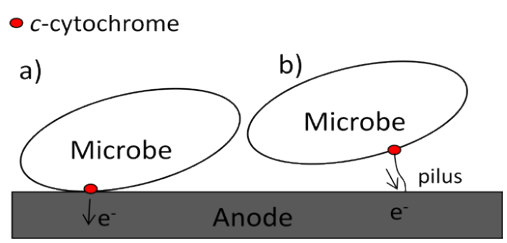

Figure 2: Two direct electron transfer methods.

The MFC technology has to compete with the anaerobic digestion technology (e.g., methane digesters) [3]. Both technologies use wastes for energy production. The former is a surface based technology while the latter is volume based that is far less capital-intensive, and is already in practical uses in rural areas of many third-world countries. In some cases, the two technologies are complimentary because MFCs deal with rather dilute wastewater while anaerobic digesters deal with solid wastes with much less water. The degradation of biomass for direct bioelectricity production by MFCs is an attractive selling point compared with production of biofuels. However, photovoltaic cells have becoming much less expensive nowadays. So far, the results from a few reported pilot-scale MFC and MEC studies suggest that they are still far from practical [2,14,15]. Clearly, a major breakthrough is needed to advance the MFC and MEC technologies beyond academic research.

Perspectives

Some recent exciting findings bring hopes for potential game-changing improvements in biofilms for MFCs. For example, a whole cell aggregate was found conductive by a group of researchers [16]. It consisted of a syntrophic coculture of *Geobacter sulfurreducens* and *Geobacter metallireducens* grown on ethanol. The researchers speculated that *c*-type cytochromes were used for electron transfer from *G. metallireducens* to *G. sulfurreducens*, thus overcoming the inability of *G. sulfurreducens* to use H_2 as an electron carrier. Interspecies electron transfer like this suggests that much more cells in a biofilm community can contribute to MFC power generations rather than just a monolayer or a few layers of sessile cells in a biofilm. Recently, Pfeffer et al. [17] discovered that conductive filaments (0.2 μm or larger in diameter) as shown in figure 3, much thicker than conductive pili, from some filamentous bacteria in marine sediments can transfer large amounts of electrons over a centimeter in distance. This is much farther than pili and mediators could achieve, making it possible for a very bulky biofilm to be electrogenic. Genes controlling biofilm dispersal and secretion of exopolymers can also be manipulated to improve biofilm performances [18].

Breakthrough advances may be made by engineering synergistic biofilms with extensive networking of sessile cells via conductive pili or filaments, reduced exopolymer secretion for better nutrient diffusion, increased secretion of endogenous electron mediators, more tenacious binding via intervention of biofilm dispersal, and elevated metabolic rates for faster substrate degradation [2,18]. An engineered biofilm consortium containing "super-bugs" may be capable of digesting a wide variety of substrates including lignocellulosics and biorefractory compounds in many kinds of wastewater. A successful biofilm must be robust enough to survive selective pressures in field operations and retains its functional microbial species over time when processing wastewater containing various native microbes. Otherwise, electrode re-inoculation will be required that would increase operating

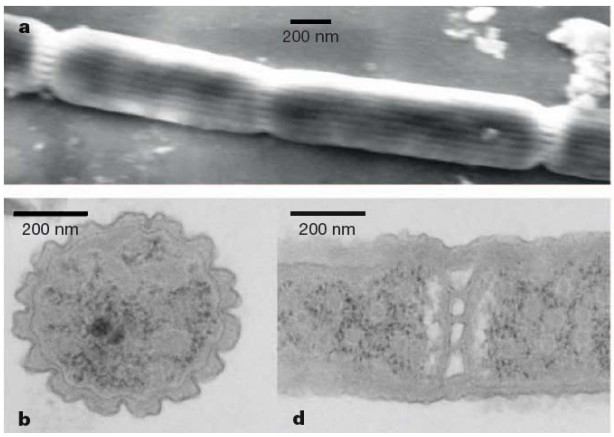

Figure 3: Conductive filaments from filamentous bacteria for electron transfer over centimeter distance in bacterial biofilm (figure reprinted from [17] with permission from Nature Publishing Group).

costs. This kind of research requires close collaborations among molecular biologists, microbiologists, biochemical engineering and environmental engineers. Powerful and efficient electrogenic biofilm consortia can make an aforementioned simplistic MFC design possible with much reduced capital and operating costs.

References

1. Costerton JW (2007) The biofilm primer. Springer Series on Biofilms 1.
2. Zhou M, Wang H, Hassett DJ, Gu T (2013) Recent advances in Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs) for wastewater treatment, bioenergy and bioproducts. J Chem Technol Biotechnol 88: 508-518.
3. Du Z, Li H, Gu T (2007) A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. Biotechnol Adv 25: 464-482.
4. Zhou M, Jin T, Wu Z, Chi M, Gu T (2012) Microbial Fuel Cells for Bioenergy and Bioproducts. In Sustainable Bioenergy and Bioproducts. Springer 131-171.
5. Stein NE, Hamelers HVM, Buisman CNJ (2012) The effect of different control mechanisms on the sensitivity and recovery time of a microbial fuel cell based biosensor. Sensors Actuators B: Chemical 171-172: 816-821.
6. Gu T (2012) New Understandings of Biocorrosion Mechanisms and their Classifications. J Microbial Biochem Technol 4: iii-vi.
7. Potter MC (1915) Electrical Effects Accompanying the Decomposition of Organic Compounds. II. Ionisation of the Gases Produced during Fermentation. Proc R Soc Lond Ser 91: 465-480.
8. Thauer RK, Stackebrandt E, Hamilton WA (2007) Energy metabolism and phylogenetic diversity of sulphate-reducing bacteria. Cambridge University Press, UK 1-38.
9. Reguera G, Nevin KP, Nicoll JS, Covalla SF, Woodard TL, et al. (2006) Biofilm and nanowire production leads to increased current in Geobacter sulfurreducens fuel cells. Appl Environ Microbiol 72: 7345-7348.
10. Rozendal RA, Sleutels TH, Hamelers HV, Buisman CJ (2008) Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater. Water Sci Technol 57: 1757-1762.
11. Jin T, Luo J, Yang J, Zhou L, Zhao Y, et al. (2012) Coupling of anodic and cathodic modification for increased power generation in microbial fuel cells. J Power Sources 219: 358-363.
12. Tong M, Du Z, Gu T (2012) Converting low-grade biomass to produce energy using bio-fuel cells. In: Zhou Y (Eds.) Eco- and Renewable Energy Materials. Springer, Berlin-New York, USA 73-97.
13. Zhang L, Liu C, Zhuang L, Li W, Zhou S, et al. (2009) Manganese dioxide as an alternative cathodic catalyst to platinum in microbial fuel cells. Biosens Bioelectron 24: 2825-2829.
14. Cusick RD, Bryan B, Parker DS, Merrill MD, Mehanna M, et al. (2011) Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater. Appl Microbiol Biotechnol 89: 2053-2063.
15. Logan BE (2010) Scaling up microbial fuel cells and other bioelectrochemical systems. Appl Microbiol Biotechnol 85: 1665-1671.
16. Summers ZM, Fogarty HE, Leang C, Franks AE, Malvankar NS, et al. (2010) Direct exchange of electrons within aggregates of an evolved syntrophic coculture of anaerobic bacteria. Science 330: 1413-1415.
17. Pfeffer C, Larsen S, Song J, Dong M, Besenbacher F, et al. (2012) Filamentous bacteria transport electrons over centimetre distances. 491: 218-221.
18. Guo K, Hassett DJ, and Gu T (2012) Advances in Microbial Fuel Cells for Potential Energy Production from Organic Feed Streams. In Microbial Biotechnology: Energy and Environment, CAB International, Oxon, United Kingdom 162-189.

Zhou M, Gu T (2013) The Next Breakthrough in Microbial Fuel Cells and Microbial Electrolysis Cells for Bioenergy and Bioproducts. J Microb Biochem Technol S12: 003. doi:10.4172/1948-5948.S12-003

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