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Microbial fuel cells: performances and perspectives

Korneel Rabaey, Geert Lissens and Willy Verstraete

20.1 INTRODUCTION

Bacteria gain energy by transferring electrons from an electron donor, such as glucose or acetate, to an electron acceptor, such as oxygen. The larger the difference in potential between donor and acceptor, the larger the energetic gain for the bacterium, and generally the higher the growth yield. In a microbial fuel cell (MFC), bacteria do not directly transfer their electrons to their characteristic terminal electron acceptor, but these electrons are diverted towards an electrode, i.e. an anode. The electrons are subsequently conducted over a resistance or power user towards a cathode and thus, bacterial energy is directly converted to electrical energy (Rao *et al.* 1976). To close the cycle, protons migrate through a proton exchange membrane (Figure 20.1).

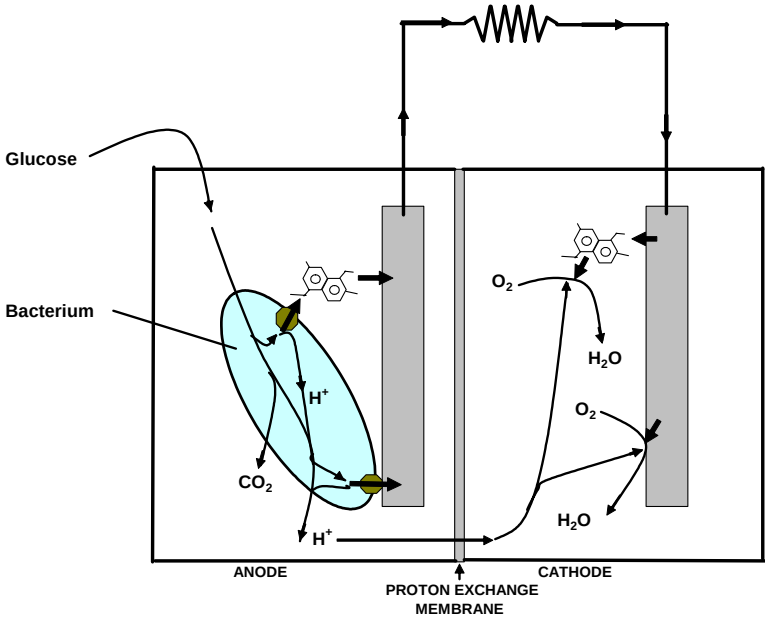

Figure 20.1. Schematic drawing of a microbial fuel cell. Electron transfer can occur through either soluble redox mediators ( ) or membrane bound complexes ( )

Simplified, a MFC can be compared to a car battery, in which the anode contains bacteria as catalyst to liberate electrons. Microbial fuel cells could be applied for the treatment of liquid waste streams. Indeed, the conventional aerobic sewage treatment faces several problems:

- Energy cost: aeration and recirculation require considerable amounts of electricity
- Footprint: the sequence of different reactors requires a considerable surface
- Investment costs: two technologies need to be installed, i.e. a system to handle the water as such, and a complex additional system to separate and handle the bio-solids
- Sludge treatment costs: the large amount of sludge formed during aerobic conversion represents a significant part of overall treatment costs
- Reliability: nitrification and phosphorus removal are sensitive processes (Verstraete and Philips 1998), sedimentation of the sludge is often a critical factor (Seka *et al.* 2001)

- Nutrient removal efficiency: influents containing distorted ratios COD/N/P often show limited potential for adequate nutrient removal

As an alternative strategy, anaerobic digestion of wastewater with concomitant methane formation has been developed (Van Lier *et al.* 2001), but up till now this strategy is not widely applied, mainly due to the low COD concentrations in the domestic sewage, which require a reactor dimension that is economically not feasible.

Microbial fuel cells might provide an answer to several of the problems traditional wastewater treatment faces, as further discussed in Chapter 20.4. Moreover, their configuration opens up possibilities for other applications, such as small scale power plants, batteries and sensors. However, for an extended period since their conception, MFCs have remained a scientific curiosity because of their limited efficiency. Several bottlenecks still exist in this technology, each needing further attention. The growing success of catalytic fuel cells has given rise to a wide variety of technological solutions for most electrochemical bottlenecks. Therefore, the MFC research focuses mainly onto the optimization of the biological compartment at this moment.

In this chapter, the technological aspects of MFCs will be assessed in relation to the current bottlenecks and advantages of the concept. Furthermore, some perspectives of MFCs in other domains of interest will be discussed.

20.2 CONVERSION OF ORGANIC MATTER TO BIOFUELS

20.2.1 Stoichiometric reactions

By means of microbiological fermentation, a whole range of biofuels and related bioproducts can be produced from organic biomass present in solid waste and wastewater (Chapters 4 to 9). Considering glucose as the principal building block of biomass, one can compare the stoichiometric reactions for the production of bio-ethanol, biogas (CO_2 and CH_4) and hydrogen gas with the overall reaction taking place in a microbial fuel cell:

Bio-ethanol:

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$

Biogas:

$$C_6H_{12}O_6 \longrightarrow 3\ CH_4 + 3\ CO_2$$

Hydrogen gas:

$$C_6H_{12}O_6 + 6\ H_2O \longrightarrow 12\ H_2 + 6\ CO_2$$

Microbial fuel cell:

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ H_2O + 6\ CO_2$$

Evidently, the total energetic yield that can be reached in practice for a particular biofuel is smaller than the theoretical yield of the above-mentioned stoichiometric reactions. Based on mass weight, the theoretical and practical yield for bio-ethanol production is clearly the highest (Table 2.1). The practical yields shown in Table 2.1 are based on average conversion efficiencies, namely 50-80% for methane (Liu *et al.* 2002), 50-90% for bio-ethanol (Bjerre *et al.* 1996) and 15-33% for hydrogen gas (Logan 2004).

Based on the calorific energy content of biogas (55.5 kJ/g methane), bio-ethanol (26.7 kJ/g ethanol) and hydrogen gas (122 kJ/g hydrogen), the energetic yields for each biofuel from glucose (15.6 kJ/g glucose) can be computed (Table 20.1). Despite the much higher calorific energy content of hydrogen gas, the practical energetic yield is about 3 times lower for hydrogen gas production from glucose (Table 20.1) than for methane (biogas) and bio-ethanol production.

Table 20.1. Energetic yields of conventional biofuels
(after Lay *et al.* 1999, Logan 2004)

• ***Methane***	• ***Bio-ethanol***	• ***Hydrogen***
Theoretical yield	*Theoretical yield*	*Theoretical yield*
(g/g glucose)	(g/g glucose)	(g/g glucose)
0.27	0.51	0.13
Yield in practice	*Yield in practice*	*Yield in practice*
(g/g glucose)	(g/g glucose)	(g/g glucose)
0.14-0.22	0.3-0.46	0.02-0.04
Energetic yield	*Energetic yield*	*Energetic yield*
(kJ/g glucose)	(kJ/g glucose)	(kJ/g glucose)
7.8-12.2	8-12.3	2.4-4.9

In a conventional biofuel process, the biochemically bound energy contained in biomass and organic waste is recovered under the form of an energy carrier that can be either a liquid fuel (bio-ethanol) or a gas (biogas and hydrogen gas). In order to effectively use the energy from the carrier liquid or gas, further physico-chemical incineration processes after the fermentation step are needed to release the energy (e.g., for electricity production) from the carrier.

In a microbial fuel cell, the biochemical energy contained in the organic matter is directly converted into electricity in what can be called a

microbiologically mediated "incineration" reaction. This implies that the overall conversion efficiencies that can be reached are potentially higher for microbial fuel cells compared to other biofuel processes.

20.2.2 Conversion efficiencies: benchmarking technology

20.2.2.1 Bio-ethanol

Compared to biogas, bio-ethanol has the main advantage that it is a liquid fuel with high performance in internal combustion engines. Despite its decreasing production cost over recent years due to the development of more efficient pretreatment methods and enzymes, bio-ethanol production even from refined materials (e.g., sugar cane or pure starch) is still not cost competitive with gasoline production. The main cost involved in the process is the need for high enzyme loadings during the simultaneous saccharification and fermentation process (Sheehan and Himmel 2001). The distillations costs have already decreased considerably and will probably further decrease in the future because of increased heat recovery (Seeman 2003).

The overall conversion efficiency from organic waste to electricity via ethanol is low (10-25%) and involves the use of an energy consuming distillation step. As a result, bio-ethanol is expected to primordially play a role in the powering of combustion engines by blending with gasoline.

20.2.2.2 Biogas

The biogas production process is a well-established technology and can undoubtedly handle the widest variety of all kinds of heterogeneous wastes. The energy content of biogas, with a calorific value of 17-25 MJ/m^3 (about 10% lower than natural gas), is usually recovered by burning the biogas in diesel stationary engines or dual-fuel engines with a thermal efficiency in the range of 30-38% (Bilcan *et al.* 2003, Henham and Makkar 1998). Smaller engines (< 200 kWh) generally have an electrical conversion efficiency of less than 25% while larger engines (> 600 kWh) can reach efficiencies up to 38%. In case hot water and steam from the engine's exhaust and cooling systems are recovered, an overall conversion efficiency of more than 80% can be reached of which 35% under the form of electricity and about 50% under the form of heat (Ross *et al.* 1996). Overall, from every kg of biodegradable waste approximately 1 kWh electricity and 2 kWh heat are produced during biogas production.

20.2.2.3 Hydrogen gas

The volumetrically based calorific yield of hydrogen gas is much lower than the calorific biogas yield because of the nearly 10-fold lower gas density of hydrogen gas compared to methane gas. Furthermore, the microbiological conversion of organics into hydrogen is relatively inefficient (15-30% efficiency) and the produced hydrogen gas is rapidly consumed by hydrogen consuming bacteria (Segers and Verstraete 1985, Liessens and Verstraete 1986). This causes also the need for much larger storage volumes of hydrogen gas compared to other biofuels. However, contrary to the low biogas to electricity conversion rate, the main advantage of hydrogen is that it can be very efficiently (90%) converted into electricity by means of chemical fuel cells. Therefore, hydrogen production from wastewater is a feasible option because the market value of hydrogen gas is nearly 20 times higher per kg of hydrogen gas compared to methane gas (Logan 2004) and because of the "negative cost" of waste and wastewater treatment. In all cases, the overall efficiency from waste to electricity via hydrogen gas remains relatively low (1 kWh for every kg of biodegradable waste) mainly due to the low efficiency in the fermentation step.

20.2.2.4 Microbial fuel cell

Based on the calorific content of glucose, a microbial fuel cell can theoretically (at 100% efficiency during fermentation) deliver 3 kWh for every kg of organic matter (dry weight) in one single fermentative step (instead of 1 kWh of electricity and 2 kWh of heat per kg in hydrogen and biogas production by employing several process steps). This means that during fermentation in MFCs, hardly any energy is released under the form of external heat, and that all the biochemical energy in the waste can potentially be converted into electricity. Recent work shows that depending on the experimental conditions employed, overall efficiencies up to 80% can be reached in practice (see chapter 20.3).

20.2.3 Current bottlenecks in conventional biofuel production

20.2.3.1 Biodegradation kinetics

Hydrolysis of complex polymers (mainly lignocellulose, proteins and lipids) by hydrolytic organisms is the first and one of the most important steps in the bioconversion of organic waste (Table 20. 2).

Table 20.2. First order kinetic rates for hydrolysis (Mata-Alvarez *et al.* 2000)

Component	Hydrolysis rates
	k values (d^{-1})
Lipids	0.005-0.010
Proteins	0.015-0.075
Carbohydrates	0.025-0.200
Food wastes	0.4
Solid wastes	0.006-0.078 (pH from 4-10)
Biowaste components	0.03-0.15 (20ºC), 0.24-0.47 (40ºC)

Despite the hydrolytic capabilities of many anaerobic bacteria by secretion of exocellular enzymes or attachment of the bacteria to the solid substrate, this step is considered to be most rate-limiting in the fermentation of organic matter and is mostly also yield-limiting in biological conversion processes (Mata-Alvarez *et al.* 2000). This is particularly true for lignocellulosic substrates due to their inherent rigid structures. As a result, the hydrolysis of most organic matter and hence their bioconversion into biofuels is normally never complete (Sanders *et al.* 2000). The lower efficiencies of anaerobic digestion in practice are a result of the presence of slowly biodegradable compounds (e.g., lignocellulose derived from plant waste) in mixed waste streams (see chapter 20.2.3). Efficiencies higher than 80% can be reached with high quality biomasses such as cellulolytic crops or carbohydrate-rich wastewaters from the food industry.

20.2.3.2 Gas treatment

One of the major drawbacks of biogas and hydrogen gas production compared to microbial fuel cells is the need for further gas treatment. In fact, biogas can contain considerable amounts of H_2S (up to 2-3%) whereas hydrogen production may generate gas contaminated with volatile fatty acids and other compounds that can interfere with catalysts in chemical fuel cells. Both energy carriers therefore need further treatment before they can be valorised.

20.2.3.3 Overall conversion efficiencies

The overall conversion efficiency for waste-to-electricity conversion in conventional biofuel processes is generally of the order of 10-25% (see chapter 20.2.2). This is largely due to high thermal losses in biofuel burners after fermentation.

20.2.3.4 Post-treatment of solid residues

In conventional biofuel processes such as anaerobic digestion, post-treatment of the digested material is required for nutrient removal and further COD (chemical oxygen demand) removal from the wastewater. These post-treatments require extra energy and thus lower the efficiency of the overall biofuel process.

20.3 MICROBIAL FUEL CELLS: STATE OF THE ART

20.3.1 MFC reactor configurations

Four basic reactor configurations using bacteria can be distinguished in biofuel cells:

- *The uncoupled bioreactor MFC*: microbiological hydrogen production or methane production (with subsequent reforming) in a separate bioreactor followed by a chemical fuel cell (generally high temperature SOFC) to convert hydrogen gas into electricity (Figure 20.2 A)
- *The integrated bioreactor MFC*: microbiological hydrogen production and hydrogen to electricity conversion in a single cell (Figure 20.2 B)
- *The MFC with direct electron transfer*: microbiological electricity generation and direct electron transfer to the anode (Figure 20.2 C)
- *The MFC with mediated electron transfer*: microbiological electricity generation and electron transport towards the anode by means of electron shuttling mediators

The first two systems cannot be regarded as a real MFC since they use a chemical fuel cell to oxidize the generated gas.

In an uncoupled MFC, a biofuel (e.g. hydrogen or methane gas) is produced in a bioreactor prior to a chemical fuel cell. One of the major drawbacks of this configuration is that the conventional bottlenecks of both separate systems remain valid, mainly the low efficiencies of biological substrate to hydrogen conversion and the requirement of high fuel cell temperatures to obtain sufficient hydrogen oxidation. Moreover, the produced biofuel gas is not sufficiently pure for direct use in a fuel cell, due to contamination caused by CO, H_2S and (poly)siloxanes (see chapter 4). The second configuration (Figure 20.2, B) is basically the same as the first one, apart from the fact that the fermentation (mostly to hydrogen gas) now takes place in the fuel cell itself (Cooney *et al.* 1996, Scholz and Schroder 2003). This type of MFC commonly involves the use of expensive catalysts such as Pt to provide the most optimal environment for the conversion of hydrogen gas to electricity. The third

configuration (Figure 20.2 C) is what can be called the real MFC whereby electrons are transferred from the bacteria to the anode without the intervention of an intermediate fermentation product (Tender *et al.* 2002).

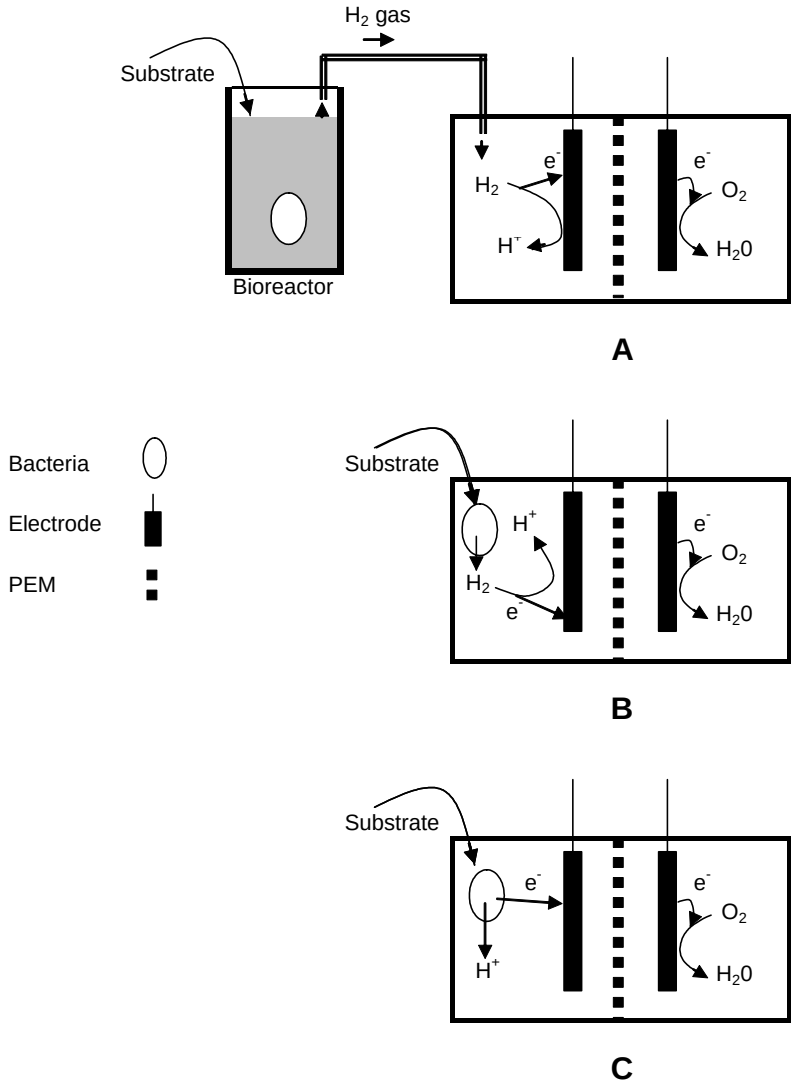

Figure 20.2. Three typical MFC configurations. A. Uncoupled bioreactor MFC in a bioreactor followed by a chemical fuel cell. B. Integrated bioreactor MFC. C. MFC with bacteria-anode interaction (after Katz *et al.* 2003)

Since micro-organisms act as a catalyst in the transfer of electrons from the substrate to the anode, the selection of a high performing microbial consortium (either pure or mixed culture) is of crucial importance in the 'real' microbial fuel cells. The electron transfer from the bacterium to the anode can proceed in a direct way from the bacterial membrane to the anode surface or indirectly by means of a mediator.

Alternatively, biofuel cells exist that use enzymes, which are immobilised on the anode surface. These fuel cells can not be regarded as MFCs sensu strictu. Due to the high costs involved in enzyme production, enzymatic fuel cells are only suitable for miniaturised small-scale applications. As a result, dimensions and corresponding power outputs are significantly smaller. Commonly used enzymes are glucose-oxidase and dehydrogenases (Katz *et al.* 1999, Kim *et al.* 2003, Palmore *et al.* 1998, Pizzariello *et al.* 2002).

20.3.2 Mediating compounds

Both transfer through bacterial contact with the electrode and through soluble shuttles can be regarded as mediated. In the first case, a bacterial redox enzyme, immobilized in the cell wall, provides the electron transfer. Examples of such bacteria are *Geobacter sulfurreducens* (Bond and Lovley 2003) and *Rhodoferax ferrireducens* (Chaudhuri and Lovley 2003). These organisms have been reported to form biofilms onto the electrode surface.

When a soluble mediator is used, the electrons are shuttled by mediator molecules between the redox enzyme(s) of the bacteria and the electrode surface, thereby facilitating electron transport (Figure 20.3) (Roller *et al.* 1984). Mediators are typically redox molecules (e.g. ubiquinones, dyes and metal complexes) that can form reversible redox couples, are stable in both oxidized and reduced form, are not biologically degraded and are not toxic towards the microbial consortium (Park and Zeikus 2003, Willner *et al.* 1998).

Although externally supplied mediators can considerably enhance the electron transfer efficiency, they are generally too expensive to apply in practice and they can exhibit toxic effects or can be degraded over longer time periods (Delaney *et al.* 1984, Gil *et al.* 2003). Alternatively, it has been demonstrated that electrochemically active bacteria enriched in a MFC can produce mediator compounds *in situ* (Rabaey *et al.* 2004a). Relative to the feasibility of practical applications of MFCs, this overview only focuses on non mediator amended MFCs.

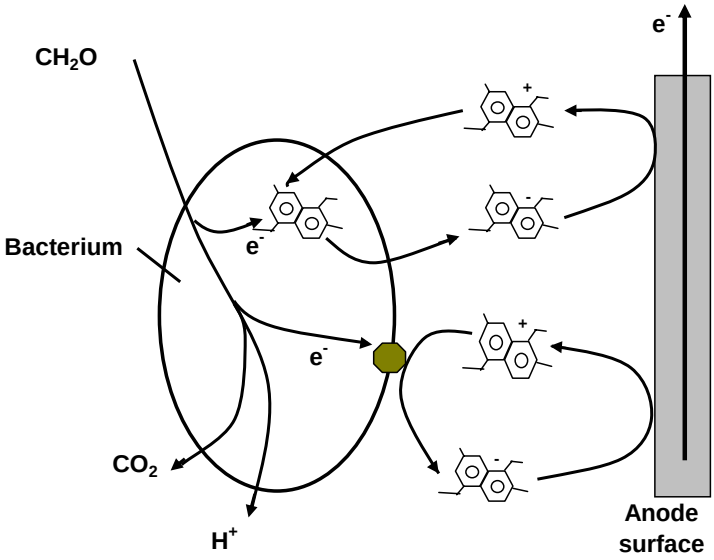

Figure 20.3. Schematic overview of the working principle of a mediator in a MFC. Soluble redox mediators ( ) can be transported into the bacteria for reduction, or reduction can occur at the bacterial surface through membrane bound complexes ( )

20.3.3 Micro-organisms

20.3.3.1 Axenic bacterial cultures

Some bacterial species in MFCs, of which metal-reducing bacterial are the most important, have recently been reported to directly transfer electrons to the anode (Table 20.3). Metal-reducing bacteria are commonly found in sediments, where they use insoluble electron acceptors such as Fe (III) and Mn (IV). Specific cytochromes at the outside of the cell membrane make *Shewanella putrefaciens* electrochemically active (Kim *et al.* 2002) in case it is grown under anaerobic conditions. The same holds true for bacteria of the family *Geobacteraceae*, which have been reported to form a biofilm on the anode surface in MFCs and to transfer the electrons from acetate with high efficiency (Bond and Lovley 2003).

Table 20.3. Overview of metal reducing bacteria applied in MFCs

Organism	References
Shewanella putrefaciens	Bond and Lovley 2003, Kim *et al.* 1999a, Kim *et al.* 1999b, Kim *et al.* 2002, Schroder *et al.* 2003
Geobacter sulfurreducens	Bond and Lovley 2003
Geobacter metallireducens	Bond *et al.* 2002
Desulfuromonas acetoxidans	Bond *et al.* 2002
Rhodoferax ferrireducens	Chaudhuri and Lovley 2003

Rhodoferax species isolated from an anoxic sediment were able to efficiently transfer electrons to a graphite anode using glucose as a sole carbon source (Chaudhuri and Lovley 2003). Remarkably, this bacterium is the first reported strain that can completely mineralize glucose to CO_2 while concomitantly generating electricity at 90% efficiency (Chaudhuri and Lovley 2003). In terms of performance, current densities in the order of 0.2-0.6 mA and a total power density of 1-17 mW/m^2 graphite surface have been reported for *Shewanella putrefaciens*, *Geobacter sulfurreducens* and *Rhodoferax ferrireducens* at conventional (woven) graphite electrodes (Bond and Lovley 2003, Chaudhuri and Lovley 2003, Kim *et al.* 2002) (Table 20.4). However, in case woven graphite in the *Rhodoferax* study was replaced by highly porous graphite electrodes, the current and power output was increased up to 74 mA/m^2 and 33 mW/m^2, respectively.

Although these bacteria generally show high electron transfer efficiency, they have a slow growth rate, a high substrate specificity (mostly acetate or lactate) and relatively low energy transfer efficiency compared to mixed cultures (Rabaey *et al.* 2003). Furthermore, the use of a pure culture implies a continuous risk of contamination of the MFCs with undesired bacteria.

20.3.3.2 Mixed bacterial cultures

MFCs that make use of mixed bacterial cultures have some important advantages over MFCs driven by axenic cultures: higher resistance against process disturbances, higher substrate consumption rates, smaller substrate specificity and higher power output (Rabaey *et al.* 2004a, b). Mostly, the electrochemically active mixed cultures are enriched either from sediment (both marine and lake sediment) (Bond and Lovley 2003, Tender *et al.* 2002) or activated sludge from wastewater treatment plants (Bond and Lovley 2003, Kim *et al.* 2004, Lee *et al.* 2003, Park *et al.* 2001, Rabaey *et al.* 2004a, Tender *et al.* 2002). By means of molecular analysis, electrochemically active species of

Geobacteraceae, *Desulfuromonas*, *Alcaligenes faecalis*, *Enterococcus faecium*, *Pseudomonas aeruginosa*, *Proteobacteria*, *Clostridia*, *Bacteroides* and *Aeromonas* species were detected in the before-mentioned studies. Most remarkably, the study of Kim *et al.* (2004) also showed the presence of nitrogen fixing bacteria (e.g., *Azoarcus* and *Azospirillum*) amongst the electrochemically active bacterial populations. The study of Rabaey *et al.* (2004a) showed that by starting from methanogenic sludge and by continuously harvesting the anodic populations over a 5-month period using glucose as carbon source, an electrochemically active consortium can be obtained that mainly consists of facultative anaerobic bacteria (e.g. *Alcaligenes*, *Enterococcus* and *Pseudomonas* species). In this particular study, very high glucose-to-power efficiencies could be reached in the order of 80% (Table 20.4) (Rabaey *et al.* 2004a).

So far, only the study of Tender *et al.* (2002), Kim *et al.* (2004) and Liu *et al.* (2004) reported the use of complex substrates, respectively sediments on the seafloor and organics present in wastewater (latter two) to generate electricity in MFCs. Table 20.4 summarizes the most relevant facts of the main MFC studies reported so far. It should be remarked that in order to maximize the power output, experiments with varying external resistance should be performed. However, from the data derived from the references given in Table 20.4, it appears that this optimisation was not always performed.

To estimate the power per unit surface to putative power output per unit reactor volume, one can take into account that at present some 100-500 m^2 of anode surface can be installed per m^3 anodic reactor volume. Hence, the state of the art power supply ranges from approximately 1 to 1800 W per m^3 anode reactor volume installed.

To render the anode more susceptible for receiving electrons from the bacteria, electrochemically active compounds can be incorporated in the electrode material. This approach has been investigated by Park and Zeikus (2003), who incorporated dyes such as neutral red and metals such as Mn^{4+} into Fe^{3+} containing graphite anodes. In this way, the main disadvantages of mediators in solution, namely toxicity and degradation, can thus be circumvented since the mediator is not released from the electrode material and thus has a longer life time. Moreover, bacteria are still able to form a biofilm on the modified anode surface.

Table 20.4. Overview of the power output delivered by MFCs without mediator addition

Micro-organism	Substrate	Anode	Current (mA)	Power (mW/m^2)	Reference
Shewanella putrefaciens	lactate	woven graphite	0,031	0,19	Kim *et al.* 2002
Geobacter sulfurreducens	acetate	graphite	0,40	13	Bond and Lovley 2003
Rhodoferax ferrireducens	glucose	graphite	0,2	8	Chaudhuri and Lovley 2003
	glucose	woven graphite	0,57	17,4	Chaudhuri and Lovley 2003
	glucose	porous graphite	74	33	Chaudhuri and Lovley 2003
Mixed seawater culture	acetate	graphite	0,23	10	Bond *et al.* 2002
	sulphide /acetate	graphite	60	32	Tender *et al.* 2002
Mixed active sludge culture	acetate	graphite	5	-	Lee *et al.* 2003
	glucose	graphite	30	3600	Rabaey *et al.* 2003
	sewage	woven graphite	0,2	8	Kim *et al.* 2004

20.4 ADVANTAGES OF MFCs

Microbial fuel cells present several advantages, both operational and functional, in comparison to the currently used technologies for generation of energy out of organic matter or treatment of waste streams:

20.4.1 Generation of energy out of biowaste/organic matter

This feature is certainly the most 'green' aspect of microbial fuel cells. Electricity is being generated in a direct way from biowastes and organic matter. This energy can be used for operation of the waste treatment plant, or sold to the energy market. Furthermore, the generated current can be used to produce

hydrogen gas. Since waste flows are often variable, a temporary storage of the energy in the form of hydrogen, as a buffer, can be desirable.

20.4.2 Direct conversion of substrate energy to electricity

As previously reported, in anaerobic processes the yield of high value electrical energy is only one third of the input energy during the thermal combustion of the biogas. While recuperation of energy can be obtained by heat exchange, the overall effective yield still remains of the order of 30%.
A microbial fuel cell has no substantial intermediary processes. This means that if the efficiency of the MFC equals at best 30% conversion, it is the most efficient biological electricity producing process at this moment. However, this power comes at potentials of approximately 0.5 Volts per biofuel cell. Hence, significant amounts of MFCs will be needed, either in stack or separated in series, in order to reach acceptable voltages. If this is not possible, transformation will be needed, entailing additional investments and an energy loss of approximately 5 %.

Another important aspect is the fact that a fuel cell does not –as is the case for a conventional battery- need to be charged during several hours before being operational, but can operate within a very short time after feeding, unless the starvation period before use was too long too sustain active biomass.

20.4.3 Sludge production

In an aerobic bioconversion process, the growth yield is generally estimated to be about 0.4 g Cell Dry Weight / g Chemical Oxygen Demand removed. Due to the harvesting of electrical energy, the bacterial growth yield in a MFC is considerably lower than the yield of an aerobic process. The actual growth yield, however, depends on several parameters:

- The amount of electrons diverted towards the anode and the energy they represent. This energy (J) can be calculated as $E = P \times t = V \times I \times t$, with E energy (J), P power (W), t time (s), V voltage (V) and I current (A)
- The amount of substrate converted to volatile fatty acids that are not further converted: often, the effluent of a MFC still contains considerable amounts of VFA (Rabaey *et al.*, 2003) that need removal during post-treatment. These VFA represent an additional loss in energetic efficiency, and will yield additional sludge if the effluent is post-treated aerobically

- The amount of hydrogen formed: per equivalent of bio-hydrogen formed, two equivalents of electrons are not diverted to the anode. Hydrogen formation appears to be in competition with anodic electron transfer (Rabaey *et al.* 2004a). Normally, bio-hydrogen formation can be completely suppressed in microbial fuel cells, indicating that the anode is a more energetically feasible electron acceptor than protons, due to a higher overall redox potential.

20.4.4 Omission of gas treatment

Generally, off-gases of anaerobic processes contain high concentrations of nitrogen gas, hydrogen sulphide and carbon dioxide next to the desired hydrogen or methane gas. The off-gases of MFCs have generally no economic value, since the energy contained in the substrate was prior directed towards the anode. The separation has been done by the bacteria, draining off the energy of the compounds towards the anode in the form of electrons. The gas generated by the anode compartment can hence be discharged, provided that no large quantities of H_2S or other odorous compounds are present in the gas, and no aerosols with undesired bacteria are liberated into the environment.

20.4.5 Aeration

The cathode can be installed as a ‘membrane electrode assembly’, in which the cathode is precipitated on top of the proton exchange membrane or conductive support, and is exposed to the open air. This omits the necessity for aeration, thereby largely decreasing electricity costs. However, from a technical point of view, several aspects need additional consideration when open air cathodes are used.

First, the cathode needs to remain sufficiently moist to ensure electrical contact. Preliminary experiments by Rabaey *et al.* (unpublished data) indicated that the water formation through oxygen reduction is insufficient to keep the cathode moist. Therefore, a water recirculation needs to be installed, possibly entailing extra energy costs. Secondly, the cathode needs to contain a non-soluble redox mediator to efficiently transfer the electrons from the electrode to oxygen. Generally, platinum is being used as a catalyst, at concentrations up to 40% w/w, representing considerable costs. However, new catalysts need to be developed, which would compensate their possible lower efficiency by a significantly reduced cost and higher sustainability.

20.5 BOTTLENECKS OF MICROBIAL FUEL CELLS

20.5.1 Anode compartment: potential losses decrease MFC voltage

The direct transfer of electrons from the bacteria towards the electrode is hampered by so-called overpotentials, which can be described as transfer resistances (Larminie and Dicks 2000). These overpotentials lower the potential attained over the MFC and hence decrease the energetic efficiency (Fig. 20.4). The losses can be categorized as activation overpotentials, Ohmic losses and concentration polarization.

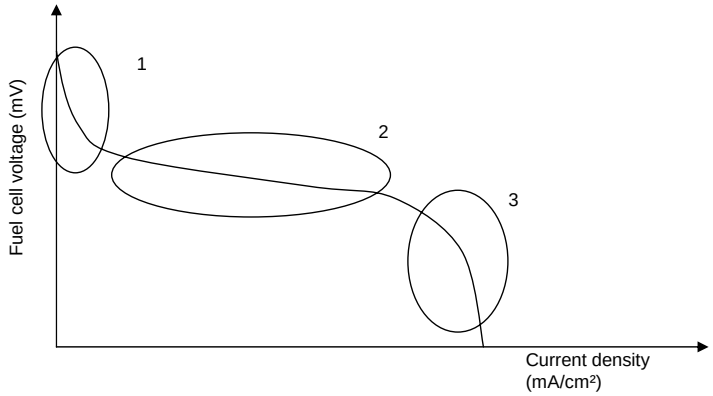

Figure 20.4. The voltage over a fuel cell as a function of the current density. Three zones can be distinguished, in which losses mainly occur through one form of the overpotentials: 1. Zone of activation losses, 2. Zone of Ohmic losses, 3. Zone of concentration polarization (after Larminie and Dicks 2000).

20.5.1.1 Activation overpotential

Either oxidizing a compound at the anode surface, or reducing a compound at the bacterial surface or in the bacterial interior surface requires certain energy to activate the oxidation reaction. This activation incurs a potential loss generally described as activation overpotential (Larminie and Dicks 2000).

The extent of the activation losses can be described by the Tafel equation (Bockris *et al.* 2000):

$$V = A \log\left(\frac{i}{i_0}\right)$$

With V the overvoltage (V), A a correlation coefficient determined by the reaction, i the current density (A) and i_0 the limit current density, the current density at which the overpotential is zero. Clearly, the activation overpotential depends on the current density and a correlation coefficient.

Activation potentials are mainly important in the zone of 0 to 1 mA/cm² and are hence most important for MFCs. The possible solutions mentioned below for activation losses are of crucial importance for MFCs. In order to decrease this activation overpotential, several solutions are possible for MFCs. They can be grouped as follows:

Increasing the operation temperature

For catalytic fuel cells, raising the temperature up to several hundreds degrees Celsius can decrease the activation losses significantly. However, the temperature range of the current MFCs does not allow the temperature increases needed (above 70°C). Only for indirect systems e.g. hydrogen production in a bioreactor with subsequent catalytic oxidation in a fuel cell higher temperatures in the fuel cell are possible.

Decreasing the activation losses at the electrode surface

- Addition of a catalyst to the electrode, which decreases the activation energy: inserting platinum into the electrode has been previously described to be successful. However, Pt is being polluted rapidly by the bacterial suspension. This can be counteracted by covering the electrode with a more robust conductive layer (Schroder *et al.* 2003). Also organic compounds can be immobilized onto the electrode surface, such as neutral red (Park and Zeikus 2000). It has to be noted that neutral red can also be used as soluble redox mediator (so it can function both as mediator and catalyst). In addition, mixtures of the catalyst into the electrode matrix have been described, such as manganese oxide in graphite-kaolin electrode matrices (Park and Zeikus 2003). The addition of these catalysts can significantly increase the MFC power output on short term.
- Increasing the roughness and specific surface of the electrode: an increase of the specific surface decreases the current density and hence the activation losses. Carbon felt mats can be a solution for short term operations (experiments of several hours). However, on the longer term (days and weeks), clogging has been repeatedly observed (Rabaey *et al.* non-published data), actually transforming the electrode surface to a

plate shaped surface. Larger structures like graphite granules are more suited for the purposes of MFC anode for several reasons (see further).

Decreasing the activation losses at the bacteria

A redox mediator can be added to the anode compartment to facilitate effective electron transfer. Two effects are caused by mediators in solution: 1. Increasing physical transport of electrons from the bacteria to the bulk solution, 2. By selecting a suitable mediator, one also decreases the activation losses occurring at the level of the bacterial cells.

Hence, a good redox mediator needs to meet several requirements (Katz *et al.* 2003, Park and Zeikus 2002):

- The oxidized state of the mediator should easily access the membrane bound redox active complexes to be reduced.
- The oxidized state of the mediator should easily penetrate the bacterial membrane to reach the reductive species inside the bacterium.
- The redox potential of the mediator should fit the potential of the reductive metabolite (the mediator potential should be positive enough to provide fast electron transfer from the metabolite, but it should not be so positive as to prevent significant loss of potential).
- Neither oxidation state of the mediator should interfere with other metabolic processes (should not inhibit them or be decomposed by them).
- The reduced state of the mediator should easily escape from the cell through the bacterial membrane.
- Both oxidation states of the mediator should be chemically stable in the electrolyte solution. They should be well soluble and they should not adsorb on the bacterial cells or electrode surface.
- The electrochemical kinetics of the oxidation process of the mediator-reduced state at the electrode should be fast (electrochemically reversible).

20.5.1.2 Ohmic overpotential

Ohmic losses are caused by electrical resistances of the electrodes, the electrolyte and the membrane. They are important at higher current levels if the sum of the resistances is limited. However, the resistance over the MFC can increase rapidly by suboptimal contacts or limited conductivity and turbulence of the electrolyte. A resistance of only 15 Ω causes a potential loss of 150 mV at a current of 10 mA, a loss not to be neglected.

20.5.1.3 Concentration polarization

Concentration polarization occurs when, due to the large oxidative force of the anode, compounds are being oxidized faster at the anode than they can be transported to the surface. However, this is a problem only occurring at higher current densities and therefore not important for microbial fuel cells. Only in cases where diffusion is seriously hampered by for example a thick non-conductive biofilm, concentration polarization would be a problem.

20.5.2 Transport of charge and ions in the electrolyte: the influence of turbulence

For a good operation of the MFC, both protons and electrons need to migrate from the anode to the cathode, be it through another medium, at the highest possible rate. Diffusion is not sufficient to reach acceptable levels of current and cell potential. Moreover, lacking proton transport could decrease the pH of the anode to undesired levels for bacteria (e.g. below 5).

Therefore, turbulent conditions need to be introduced to the anode and the cathode. Both shaking and recirculation of the influent can be applied to solve this problem. Both methods cost energy, depleting the overall efficiency of the MFC system. It has to be noted that in a realistic MFC system, this will be the largest energy cost by far.

20.5.3 Membrane resistance, selectivity and O_2 permeability

The selection of a membrane, separating anode and cathode, represents a choice between two opposing interests:

- High selectivity: the higher the selectivity for protons, the better the biofuel cell will operate and the lower the resistance of the membrane
- High stability: membranes need to be robust in a colloidal and nutrient rich environment, which the bacterial suspension generally is

Nafion™ has been widely used as proton exchange membrane (PEM) for fuel cells and MFCs (Bond and Lovley 2003, Liu *et al.* 2004, Park and Zeikus, 2000), and has the large advantage of being very selective for protons. However, this membrane contains sulfonic acid groups, that are binding with ammonia present in the bacterial solution. Hence, at this moment, this membrane type scores high for selectivity but low for stability.

A second approach is the use of a more general cation exchange membrane (CEM), such as Ultrex™ (Rabaey *et al.* 2003). This type of membrane has a larger resistance and is less selective but generally shows larger stability. These

membranes have been reported to perform adequately for over three months (Rabaey *et al.,* 2004b).

One can also omit the selective membrane and use a rigid carbon electrode as separator and open air cathode (Liu and Logan 2004). This approach provides satisfying power output, although conversion efficiencies are lowered due to the increased oxygen diffusion.

The approach used will depend on the application foreseen. When clean influents will be used, the first approach can be a possibility if no ammonia is present. Probably, Nafion™ will be the material of choice for battery MFCs. When wastewater will be used, approach two and three are more feasible due to their robustness. The difference between the two approaches can be made on the basis of two determinants: efficiency (approach two provides higher coulombic and energetic efficiency) and cost (approach two is more expensive).

20.5.4 The structure of the anode

Several anode configurations are currently used, such as plate shaped plain graphite (Bond and Lovley 2003), graphite felt (Bond and Lovley 2003, Liu *et al.* 2004) and graphite granules (Rabaey *et al.* 2004b). These three possible configurations have already shown reasonable to good results, depending on the application desired. However, fine tuning still needs to be performed, based on several requirements:

- Free flow of influent and effluent through the electrode matrix, in order to supply sufficient feed, and to remove biodegradation products
- Adequate surface for growth of a biofilm, which will perform most of the electron transfer
- Sufficient support and conductive surface
- Sufficient turbulence for adequate proton diffusion towards the membrane and the cathode

20.5.5 The role of the cathode performance

As in the anode compartment, losses occur in the cathode compartment due to overpotentials. Although small current densities flow through the electrode surface, these losses need consideration. To decrease the activation overpotential, catalysts need to be added to the electrode, or a suitable mediator is needed to transfer the electrons from the cathode to oxygen. Generally, Pt is used as a catalyst in the electrode (Schroder *et al.* 2003), at concentrations up to 45% w/w, entailing a considerable cost. Another option is adding $K_3Fe(CN)_6$ to the liquid catholyte (Park *et al.* 2000), which is aerated. The use of Pt enables an

open air cathode, decreasing aeration cost (operation cost), but the investment cost is considerable. Less expensive catalysts are currently being developed, which may render the open air cathodes more feasible in terms of capex.

Theory dictates that, when the reactant concentration (oxygen in this case) is increased, this will increase the transfer efficiency (Larminie and Dicks 2000). However, in most cases, the use of pure oxygen seems not feasible for practical design reasons.

20.5.6 Upscaling problems

Several aspects needed for an efficient MFC are hampering upscaling:

- The influent needs to reach the whole anode matrix sufficiently
- Protons need rapid diffusion towards the membrane
- Sufficient electrical contact needs to be established between bacteria in suspension and the anode
- Sufficient voltage needs to be reached over the MFC to have a useful power
- Instatement of an aeration device should be avoided

To overcome these bottlenecks, several techniques can be copied from conventional fuel cells, such as the use of fuel cell stacks, constructed from several plate shaped fuel cells (Larminie and Dicks 2000).

20.6 FUTURE APPLICATIONS OF MICROBIAL FUEL CELLS

Microbial fuel cells have still some way to go to reach large scale commercialisation. The largest reactors reported thus far had an anode internal volume of 0.388 L (Liu *et al.* 2004). Two types of implementation into practice offer perspectives within a reasonable time scale: MFCs for treatment of wastewater and MFCs converting renewable biomass in batteries.

20.6.1 MFCs for wastewater treatment

Consider a conventional WWTP designed for 30,000 IE, receiving a daily influent flow of 5,400 m^3. At a biodegradable chemical oxygen demand (bCOD) concentration of 500 mg/L, this represents an influx of organic matter of 2,700 kg dry weight per day. The amount of sludge formed, at a nominal yield of 0.4 g cell dry weight per g bCOD converted (Verstraete and Van Vaerenberg 1986) will be 1,080 kg per day. This needs to be disposed off at a cost which can rise up to €500 per ton dry matter (Weemaes and Verstraete 2001). The other costs

contained in the operational costs are the aeration costs and pump costs for recirculation and processing.

If a MFC is used with an open air cathode, no aeration is needed. The putative energy of the input organic matter amounts to 8,950 kWh per day. The costs for sludge processing will be lower, since no aerobic cell yields can be attained. For methanogenesis, the cell yield is about 0.05 g CDW / g substrate; for MFC the yield can be estimated somewhere in between aerobic and methanogenic conditions. At an energetic efficiency of 35%, which should be attainable on large scale, approximately 3,150 kWh per day of useful energy will be produced. This comparison does not take into account the capital cost of both systems. However, if the capital cost is of the same order, the comparison illustrates a significant difference in operational costs. Hence, if large scale MFCs can be built at an acceptable price, this will be a viable technology.

20.6.2 Renewable biomass conversion

Conventional batteries have several drawbacks:

- They need to be charged for several hours in order to be used
- They are environmentally unfriendly due to the heavy metal content
- One needs electricity to power them up

Therefore, much research is performed with respect to the development of fuel cells that can use hydrogen, methanol or ethanol to power portable applications. At this moment, several fuel cell types based on hydrogen and methanol work appropriately, and applications already exist for e.g. portable computers. However, the question can be raised whether this energy generation is really sustainable. Furthermore, the customer may not like to carry hydrogen gas (even captured within a metal hydrid matrix) or methanol.

Microbial fuel cells can operate on a large variety of substrates that are readily available, even in any supermarket. Substrates such as plain sugar and starch are easy to store, contain more energy than any other feed type per unit of volume, and are easy to dose. Furthermore, they have a more ‘green’ image than e.g. methanol. Moreover, MFCs can be developed that are environmentally friendly in terms of material composition.

If the development of MFCs leads to a product that has a reasonable (read: usable) power output per unit of MFC volume, it will be a viable product. A customer will accept a larger battery, and a larger feeding tank, provided the feeding is easy to perform and has a green and safe label.

20.7 EMERGING OPPORTUNITIES

20.7.1 Body fluid batteries

In the future, the amount of low-power devices implanted in the human body will significantly expand. These devices need long term, stable power provision. To provide this power, a MFC can be used. Two possibilities exist: enzymatic and microbial fuel cells. In enzymatic fuel cells, the potential difference is created by the use of two electrodes with different enzymatic reactions, creating a potential difference based on the reaction redox potential (Pizzariello *et al.* 2002).

Also micro-organisms can be used, such as *Saccharomyces cerevisiae* (Chiao *et al.* 2003). Micro-organisms have the advantage of providing a more long term stability than enzymes immobilized onto a surface.

20.7.2 Electricity from photosynthesis

Plants produce, as a product of photosynthesis, sucrose and other low-molecular carbohydrates. These carbohydrates are transported through the stem during certain periods of the year. These plant saps can be harvested and the possibility exists to use this flow as a feed for MFCs that would be installed in a stationary way. Some plant saps such as maple syrup have already been tested and yielded a conversion efficiency of up to 50% (Rabaey *et al.* 2004b). The minerals remaining after the MFC could be recycled to the trees or the plants. This way, a forest could function as a continuous, green power providing system that converts directly light energy into electricity.

20.7.3 Bio-sensors

Bacteria show lower metabolic activity when inhibited by toxic compounds. This will cause a lower electron transfer towards an electrode. Bio-sensors could be constructed, in which bacteria are immobilized onto an electrode and protected behind a membrane. If a toxic component diffuses through the membrane, this can be measured by the change in potential over the sensor. Such sensors could be extremely useful as indicators of toxicants in rivers, at the entrance of wastewater treatment plants, to detect pollution or illegal dumping, or to perform research on polluted sites (Meyer *et al.* 2002, Chang *et al.* 2004).

20.7.4 Sediment electricity

MFCs can be used to generate electricity based on the potential difference generated by bacteria between sediment and the aqueous phase above (Tender *et al.* 2002). Two anode reactions appear to occur: oxidation of sulphide present in the sediment, which is formed through bacterial oxidation of organic carbon, and oxidation of organic matter by bacteria growing onto the anode. The potential for energy generation from the seafloor is large, although the accessibility will often pose a problem.

20.8 CONCLUSIONS

Microbial fuel cells do hold promise towards sustainable energy generation in the near future. Many bottlenecks yet exist, which pose a challenge that will take a multidisciplinary approach and intensive research. As shown in this chapter, a multitude of solutions exists to answer these (mainly) technical problems. Aside from the main goal of bioreactors producing electricity in an elegant way, several serendipities of this technology emerge, applicable within a broad range of life sciences.

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