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Microbial fuel cells and microbial electrolysis cells for the production of bioelectricity and biomaterials

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Today's global energy crisis requires a multifaceted solution. Bioenergy is an important part of the solution. The microbial fuel cell (MFC) technology stands out as an attractive potential technology in bioenergy. MFCs can convert energy stored in organic matter directly into bioelectricity. MFCs can also be operated in the electrolysis mode as microbial electrolysis cells to produce bioproducts such as hydrogen and ethanol. Various wastewaters containing low-grade organic carbons that are otherwise unutilized can be used as feed streams for MFCs. Despite major advances in the past decade, further improvements in MFC power output and cost reduction are needed for MFCs to be practical. This paper analysed MFC operating principles using bioenergetics and bioelectrochemistry. Several major issues were explored to improve the MFC performance. An emphasis was placed on the use of catalytic materials for MFC electrodes. Recent advances in the production of various biomaterials using MFCs were also investigated.

Keywords: microbial fuel cell, microbial electrolysis cell, bioelectrochemistry, electron transfer, wastewater treatment
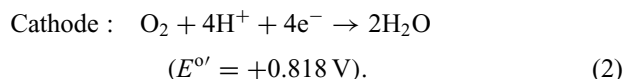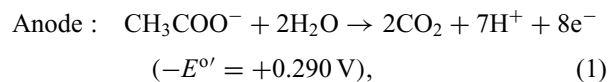
1. Introduction

The dwindling global petroleum reserve casts a shadow on the global economy and geopolitics. Many different forms of energy such as nuclear, solar, wind, geothermal and bioenergy have been proposed as possible solutions. Apparently, none of them is sufficient to tackle the energy crisis alone. They will all play their roles in relieving the energy shortage. The world economy is gradually shifting from fossil fuel-based energy to renewable energy. Renewable bioenergy, albeit a small fraction of the total energy consumption presently, is gradually gaining popularity. The microbial fuel cell (MFC) technology can be part of the bioenergy solution. Compared with other forms of bioenergy, MFCs utilize low-grade organic matter in municipal and industrial wastewaters to generate electricity directly. Intensive research in recent years is reflected by the hundreds of journal publications in this area.

Tremendous progresses have been made in the past decade in the improvement of the MFC performance. However, MFC power output still lags behind that of conventional chemical fuel cells by three to four orders of magnitude. It is not realistic for MFCs to compete with chemical fuel cells because MFCs do not use high energy-density fuels such as pure hydrogen and methanol. Nonetheless, it is still necessary to improve MFC power output furthermore so that the power generation can be meaningfully used to offset wastewater treatment or even power some appliances.

2. Bioenergetics and bioelectrochemistry of MFCs

The basic operating principle of an MFC can be explained using the classical dual-chamber MFC setup in Figure 1. Under biocatalysis, organic carbons are oxidized by the biofilm covering the anode in the anodic chamber under anaerobic condition. Reaction (1) shows the half-reaction using acetate as an example organic carbon. The oxidation occurs inside the cytoplasm of the sessile cells (i.e. biofilm cells). The electrons released by the oxidation are transferred by the sessile cells in the anodic biofilm to the anode surface. These electrons flow through an external circuit to reach the cathode in the cathodic chamber where they are used for reduction of oxygen. To maintain electroneutrality, protons migrate from the anodic chamber to the cathodic chamber to participate in Reaction (2).

$$\text{Anode}: \quad CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^-$$
$$(-E^{o\prime} = +0.290\,\text{V}), \tag{1}$$

$$\text{Cathode}: \quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$(E^{o\prime} = +0.818\,\text{V}). \tag{2}$$

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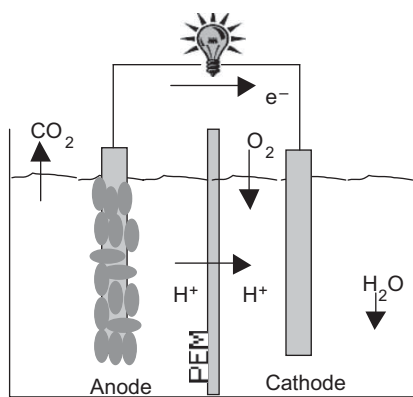
Figure 1. Classical dual-chamber MFC setup with an oxygen cathode.

The $2CO_2$/acetate (redox) couple and the $O_2/2H_2O$ couple have standard reduction potential (also known as standard redox potential or standard electrode potential) $E^{o\prime}$ values of -0.290 and $+0.818$ V, respectively.[1] In bioenergetics and bioelectrochemistry, standard conditions are defined as $25°C$, pH 7 and 1 M solutes (or 1 bar for gaseous species) for reactants and products except proton and those with fixed concentrations such as H_2O. The apostrophe in $E^{o\prime}$ indicates pH 7. The voltage reference for $E^{o\prime}$ is the Standard Hydrogen Electrode. The redox reaction of acetate oxidation combined with oxygen reduction oxidation has a cell potential of $+1.108$ V (calculated from $0.290 + 0.818$ V) under the aforementioned standard conditions. This corresponds to a standard Gibbs free energy change of reaction (at the conditions defined for $E^{o\prime}$) of $\Delta G^{o\prime} = -855$ kJ/mol acetate based on the following formula:

$$\Delta G^{o\prime} = -nF\Delta E^{o\prime} \tag{3}$$

in which n is the number of electron involved in the redox reaction (8 in this case) and F the Faraday constant (96,485 C/mol). The negative $\Delta G^{o\prime}$ value indicates that the redox reaction resulted from the combination of Reactions (1) and (2) is thermodynamically favourable with a release of 855 kJ of energy for each mole of acetate oxidized under the aforementioned standard conditions.

The Nernst equation can be used to calculate the reduction potentials under non-standard conditions. For example, Equation (4) can be used to calculate the reduction potential at pH 7 for $2CO_2$/acetate at a temperature different from $25°C$, an acetate concentration different from 1 M and a CO_2 partial pressure different from 1 bar.

$$E^\prime \, (2CO_2/\text{acetate}) = -0.290 \, \text{V} - \frac{RT}{8F} \cdot \ln \frac{[\text{CH}_3\text{COO}^-]}{\text{p}_{CO_2}^2}, \tag{4}$$

$E^\prime$ can deviate from $E^{o\prime}$ significantly. Thus, the actual cell potential for acetate oxidation coupled with oxygen reduction may be different from the aforementioned cell potential of $+1.108$ V. The actual MFC voltage is much lower than this value even under the aforementioned

standard conditions because of various losses such as activation overpotential, reaction overpotential and concentration overpotential. Thus, the actual amount of electricity harvested from the MFC's external load is much lower than 855 kJ/mol acetate. The lost energy is wasted and released as unrecoverable low-grade heat, or used by the biofilm for growth or maintenance energy.

The very negative $\Delta G^{o\prime} = -855$ kJ/mol value does not mean that acetate oxidation will proceed at an appreciable rate because the redox reaction has to overcome the activation energy barrier. The anodic biofilm plays the role of biocatalysis to move acetate oxidation forward. Unlike ionic species such as H^+, electrons cannot freely migrate in an aqueous environment. This means that acetate oxidation in a planktonic cell's cytoplasm cannot get rid of the electrons in the absence of a local electron acceptor (oxidant) in the cytoplasm. The anodic chamber of an MFC is deliberately kept free of an utilizable oxidant to force the anodic biofilm to use the anode as the electron acceptor. Only electrogenic sessile cells in the anodic biofilm can use the anode as the electron acceptor by transporting the intracellularly released electrons to the anode via an elaborate electron transfer chain.

When an electron donor such as acetate and other organic carbons and an oxidant such as O_2, sulphate, nitrate diffuse into the cytoplasm, local oxidation and reduction reactions can proceed without extracellular electron transfer. This means that most cells do not need to be electrogenic for their survival because they have an exogenous electron acceptor available for respiration or they can produce their own electron acceptors as in the anaerobic fermentation. Only, a small fraction of microbes have developed the ability for electrogenesis.

There are two basic categories for electron transfer: (1) direct electron transfer (DET), and (2) mediated electron transfer (MET).[2] In DET, cell wall membrane-bound proteins (e.g. *c*-cytochrome) transfer electrons. This requires the direct contact of the cell wall with an electrode surface. Conductive pili (also known as conductive nanowires) are formed by some electrogens to link the cell wall to an electrode surface for electron transfer over a very short distance. If there is hyperpilation to network several layers of cells, much more cells can directly participate in electron transfer. Recently, it was discovered that electrons transfer over a centimetre long distance was possible for some bacteria using conductive filaments that are 200 nm in diameter, much thicker than conductive pili.[3] Thus, a biofilm with a massive number of sessile cells directly contributing to electron transfer in a thick biofilm may be discovered or engineered for greatly improved MFC power output.

Some electrogenic cells are incapable of DET. However, they can transfer electrons when redox-active mediators are present.[2] These mediators undergo redox cycles to transfer electrons. These mediators are either exogenous or endogenous (primary and secondary metabolites).[4] The exogenous mediators include thionine, methylene

Table 1. Some electrogenic microbes used in the MFC anodic biofilms.

Microbe	Anode	Electron transfer	Power or current density	References
Acinetobacter johnsonii NIUx72	Porous carbon cloth	MET	$46.35\,mW/m^2$	[16]
Clostridium butyricum	Woven graphite	MET	$1.3\,mA/m^2$	[11]
Cupriavidus basilensis	Graphite electrode	MET	$902\,mA/m^2$	[17]
P. aeruginosa	Graphite block	MET	$392\,\mu W/m^2$	[18]
E. coli K12	Carbon cloth	MET	$9.8\,mW/m^2$	[19]
Exiguobacterium acetylicum NIU-K4	Porous carbon cloth	MET	$28.3\,mA/m^2$	[20]
Proteus hauseri ZMd44	Porous carbon cloth	MET	$43.09\,mW/m^2$	[16]
Bacillus subtilis	Carbon cloth	MET	$1.066\,mW/cm^2$	[21]
E. coli	Titanium platinised mesh	MET	$502\,mW/m^2$	[22]
Shewanella oneidensis MR-1	Gold electrode	MET/DET	$3.77 \pm 0.02\,mW/m^2$, $16.47 \pm 0.04\,mA/m^2$	[23,24]
Candida melibiosica 2491	Carbon felt	MET/DET	$260 \pm 8\,mW/m^2$	[25,26]
Saccharomyces cerevisiae	Carbon paper	DET	–	[25]
Desulfuromonas acetoxidans	–	DET	–	[27]
Geobacter metallireducens	–		–	
G. sulfurreducens	Carbon paper	DET	$7\,mW/m^2$	[28]
Hasenula anomala	Graphite + PANI + platinum	DET	$2.9\,W/m^3$	[29]
Klebsiella pneumoniae	$Ni/\beta\text{-}Mo_2C$-carbon felt	DET	$4.67\,W/m^3$	[30]
C. butyricum EG3	Graphite felt	DET	$88\,mA/m^2$	[31]
Thermincola ferriacetica Z-0001	Graphite block	DET	$146\,mW/m^2$, $400\,mA/m^2$	[32]

blue, neutral red, 2-hydroxy-1,4-naphthoquinone, quinines, phenothiazines, Fe(III) ethylenediaminetetraacetic acid, phenazines, phenoxazines, etc.[5–8] When they are added to the anolyte, they transfer electrons from the sessile cells in the anodic biofilm to the anode through redox cycles.[9] Unfortunately, these chemicals are usually too expensive for practical MFC applications. They also cause environmental problems because of their recalcitrance and toxicity.[7]

Some microbes such as *Pseudomonas aeruginosa*, *Shewanella putrefaciens* and *Escherichia coli* can utilize primary and secondary metabolites to transfer electrons.[10–12] Examples of primary metabolites include molecular hydrogen (H_2), hydrogen sulphide (H_2S), ammonia and alcohols.[11] Secondary metabolites include phenazine derivatives such as pyocyanine and 2-amino-3-carboxy-1,4-naphthoquinone.[8] These metabolites serve as electron mediators for electron transfer between the anodic biofilm and the anode. Bacterial strains can be manipulated to increase the secretion of endogenous mediators effectively to improve the electron transfer rate and MFC performance.[13,14]

Microbial community structures in anodic biofilms are important for MFC performances. Different microbial species perform different functions in a biofilm community. For example, sulphur-oxidizing bacteria (*Pseudomonas sp. and Rhodobacter sp.*) can oxidize hydrogen sulphide, sulphur, sulphite, etc. while sulphate-reducing bacteria can reduce the sulphate.[15] Microbial community structures also play an important role in biofilm electron transfer. For example, the two types of bacteria can achieve electron transfer from the sulphide oxidation between the biofilm and the anode.[15] A bacterial species in a synergistic biofilm can also enhance electron transfer contribution by secreting endogenous mediators.

Apart from the requirement for electrogenesis, biofilms must be able to digest organic carbons efficiently. Various biofilms have been tested for MFC uses. Table 1 shows a list of some of them. Among many key bottlenecks in the MFC performance are the electron transfer and the rate of digestion of organic carbons by biofilms. Some researchers have proposed the concept of 'super-bug' biofilms through mutation and genetic engineering to produce robust biofilms that are voracious for digestion of various organic carbons and are super electrogenic with multiple layers of cells contributing to electricity generation.[2] MFCs powered by super-bugs do not need costly complicated reactor designs. A simplistic membrane-less tubular reactor that requires super-bugs to make convective axial flow possible was proposed by Zhou et al.[2]

3. Anode modifications for improved biofilm attachment and electron transfer

Intensive research has been carried out in recent years on anode modifications aimed at enhanced biofilm attachment and electron donation by the anodic biofilm. Some of the modification methods are more practical than others due to lower costs. MFC experiments strongly suggest that anode material and micro-structure significantly impact biofilm attachment and electron transfer between the anodic biofilm and the anode surface (electron acceptor). Various materials have been used for anodes in MFC research. They include Pt, corrosion resistant stainless steel, carbon cloth, carbon paper, graphite granules and graphite felt. Pt (or Pt black) suffers from the formation of a PtO layer at the electrode surface that reduces its performance. To improve the performance of a Pt electrode, a polyaniline (PANI) coating was used. Compared with an uncoated Pt black anode,

this anode modification improved the current density from 0.84 to 1.45 mA/cm^2.[33] The use of Pt is feasible only for laboratory investigations due to its prohibitively high cost. Niessen et al. [34,35] found that fluorinated PANIs poly(2-fluoroaniline) and poly(2,3,5,6-tetrafluoroaniline) are better anode modifiers than PANI. Because these modifiers have molecular structures that resemble electron mediators, they may function as mediators that improve electron transfer.[33]

For carbon anodes, several different approaches including chemical and physical methods have been used for anode modifications. Park and Zeikus [36,37] reported that neutral red-woven graphite and Mn(IV) graphite anodes achieved current densities 100 times higher than using unmodified graphite anodes due to their catalytic abilities. Fe$_3$O$_4$, Fe$_3$O$_4$ and Ni^{2+} modifications also improved the MFC performance substantially.[38] Modification of graphite anodes by quinone/quinoid groups led to a three-fold increase in power density according to Scott et al.[39] A carbon felt anode modified with a conductive film containing a polypyrrole (Ppy)/anthraquinone-2,6-disulfonate (AQDS) was found to increase the anode surface area and its bio-compatibility for biofilm adhesion. An MFC bioreactor with its anode and cathode both modified with Ppy/AQDS yielded a maximum power density of 823 mW/cm^2, a magnitude larger than that with unmodified electrodes.[40]

Using the electrochemical oxidation method, Zhou et al. [41] tried nitric acid, ammonium nitrate and ammonium persulfate separately for carbon-mesh anode modifications. They resulted in enhanced MFC performance with the best performance from the nitric acid treatment. The treatment showed a maximum power density of 792 mW/m^2 in comparison with 552 mW/m^2 without modification. The modification also improved the reactor's Coulombic efficiency (CE) from 14% to 24%. In an MFC, CE reflects the fraction of the energy released by organic carbon oxidation that is harvested by the external load as electrical energy. The rest is lost due to consumption by the microbes and various overpotentials such as activation overpotential and concentration overpotential.

Activated carbon fibre felt electrodes were modified with nitric acid and ethylenediamine, respectively, by Zhu et al.,[42] who reported a maximum power density of 0.207 and 0.164 W/m^2, respectively, in comparison with 0.130 W/m^2 without modification. HSO$_4^-$-doped PANI can also be used to modify anodes. Lai et al. [43] treated a carbon cloth anode by electrochemical polymerization of aniline in a 5% H$_2$SO$_4$ solution. This modification led to a maximum power density of 5.16 W/m^3, 2.66 times larger than that without modification. Furthermore, the MFC internal resistance and start-up time after nitric acid treatment were 65.5% lower and 33.3% shorter, respectively. Recently, He et al. [44] reported a method for the surface modification of carbon paper anodes by plasma ion implantation that led to the improvement of the MFC performance.

A new technology for electrode modification is the coating of carbon nanotube (CNT) on a substrate such as carbon cloth anodes.[45] An anode modified with 20% (w/w) CNT doped with PANI composites was used in an MFC with an *E. coli* anodic biofilm, resulting in a maximum power density of 42 mW/m^2.[46] CNT's cyto-toxicity is a major concern.[47] Instead of using CNT, Zhang et al. [48] used a graphene-modified anode. It achieved a maximum power density of 2.67 W/m^2 that was around 17–18 times higher than those using stainless steel mesh (SSM) and polytetrafluoroethylene-modified SSM. More recently, a two-stage carbon-cloth anode modification with graphene oxide and PANI nano-fibres conducted by Hou et al. [49] led to a maximum power density of 0.139 W/m^2, reflecting a three-fold improvement. The nanostructured PANI-coated mesoporous TiO$_2$ [50] and hierarchically porous chitosan/vacuum-stripped grapheme [51] were also found to be good anode modifications that improved the MFC performance.

4. Novel catalytic materials for cathodes

In an MFC with an air cathode, oxygen reduction rate can be a bottleneck of the MFC performance because it needs catalysis. Pt is the most popular catalyst for the cathode in lab tests due to its excellent electro-catalytic ability for oxygen reduction.[52] To reduce cost, Pt coating is often used. It has been reported that the MFC performance did not change significantly when Pt loading decreased from 2 to 0.1 mg/cm^2.[53,54] However, Pt coating is still prohibitively expensive in large-scale practical applications.[55] Pt also suffers from sulphide poisoning by dissolved H$_2$S that is often present in wastewater. Thus, it is imperative to explore other catalytic materials.

4.1. Metal catalytic cathodes

The cathodic reaction efficiency depends on the electron acceptor concentration and species, electrode structure and catalytic ability.[56] The oxygen reduction reaction is very low when a plain carbon or graphite is used.[57] With catalysis, the reaction's activation energy decreases and thus the reaction rate is increased. For example, Pt modification of a plain carbon cathode can increase MFC current output by 2–3 times.[58] There is a trend in MFC research to use non-precious metal catalysts to reduce costs. Table 2 lists some novel catalysts. Pyrolysed iron (II) phthalocyanine and cobalt tetramethoxyphenylporphyrin are often used as the cathode catalysts,[55,59] and their MFC performances were found similar to that using platinum. These inexpensive materials are promising alternatives.[53]

Lead dioxide (PbO$_2$) modified cathodes have been shown to increase MFC power density by 2–4 times compared with Pt cathodes.[64] However, lead leached from the cathode during MFC wastewater treatment causes environmental pollution. These cathodes can be fabricated using

Table 2. The performance of novel catalysts the open circuit voltage (OCV) (mV) and the maximum power density (mW/m^2) compared with that of Pt.

Type of catalyst	Cathode	Reactor structure	OCV/Pt	P_{max}/Pt	References
α-MnO$_2$	Carbon fibre cloth	Cube MFC	549/627	125/268	[60]
β-MnO$_2$			565/627	172/268	
γ-MnO$_2$			506/627	88/268	
β-MnO$_2$		Tube MFC	710	3.77 (W/m^3)	
MnO$_x$/C	Carbon cloth	Dual-chamber	714/781	161/193	[61]
C/Pt-Fe	SSM	Single-chamber	–	1098/1030	[62]
Co/Fe/N/CNT	Carbon cloth	Single-chamber	760	751/498	[63]
Co/Fe/N/graphite		Single-chamber	–	618/498	
PbO$_2$	Titanium sheeting	Dual-chamber	1000/800	78/45	[64]
Co-OMS-2	Carbon cloth	Single-chamber	147/149	180/198	[65]
Cu-OMS-2			116/149	165/198	
Ce-OMS-2			31/149	35/198	
CoTMPP	Carbon cloth	Single-chamber	–	369/360[a]	[54]
CoTMPP	Carbon paper	Single-chamber	786/889	483/593	[66]
MnPc			–	353/593	
FePc			801/889	634/593	
FePcVC			876/889	530/593	
FePc	Graphite foils	Dual-chamber	1070	13.9 (W/m^3)	[59]
CoTMPP			1100	14.3(W/m^3)	
Ppy/C	Carbon cloth	Single-chamber	–	402/576	[67]
CoNPc	Carbon paper	Dual-chamber	633/660	64.7/81.3	[68]

[a]The average power density.

a titanium base with a butanol or Nafion binder to alleviate the problem [52]. Another good cathode catalyst is manganese dioxide (MnO$_2$) because of its good oxygen reduction catalytic performance, low cost and easy electrode fabrication.[60,69]

4.2. Carbonaceous cathodes

Carbonaceous materials including carbon paper, carbon cloth, carbon mesh, graphite plate, granular graphite, CNT may be used for cathodes in MFCs.[70] Using carbon cloth, a very common electrode material, as the cathode, a maximum power density of 15.2 W/m^3 was achieved.[71] CNT-coated sponge electrodes were found to have much smaller internal resistance, more uniform macroporous structure and better stability. The CNT-coated sponge electrode achieved a higher MFC power density than

the less inexpensive carbon-cloth cathode using domestic wastewater as the substrate.[72] Granular-graphite particles with nanoscale pores achieved a maximum power density of 50 W/m^3.[73,74] It was found that the activated carbon cathode reached a power density of 220 mW/m^2, much better than the 124 mW/m^2 for granular-graphite particles.[75,76]

4.3. Metal cathodes

Corrosion resistant SSM is a common metal used in cathodes. It is more durable than carbon paper and carbon cloth. A stainless steel cathode coated with poly(dimethylsiloxane) as a diffusion layer achieved a maximum power density of 1.61 W/m^2, comparable to carbon cloth's power density of 1.64 W/m^2.[77,78] A cathode using a membrane assembly with SSM as the supported

Table 3. Costs of some anodic and the cathodic materials.

Anode	Cost[a]	Cathodic	Cost	References[b]
Carbon fibre	$24–28/m^2	CoNPc	$114/m^2	[68]
Carbon cloth	$16–20/m^2	PbO$_2$	$18/m^2	[64]
Woven graphite	$8.5–15/kg	Ppy/C	$34/m^2	[67]
Graphite block	$3–5/kg	FePc/C	$74/m^2	[64]
Titanium mesh	$40–60/m^2	Ni/MnO$_2$	$0.106/m^2	[81]
Carbon felt	$24/kg	Pt/C	$447/m^2	[68]
Carbon paper	$2.8–15/kg	Cu/Ni	$13/m^2	[82]
Graphene	$10–30/g	Carpenter alloy	$210/m^2	

[a]Anodic material cost data collected from www.alibaba.com e-commerce website in June 2013.
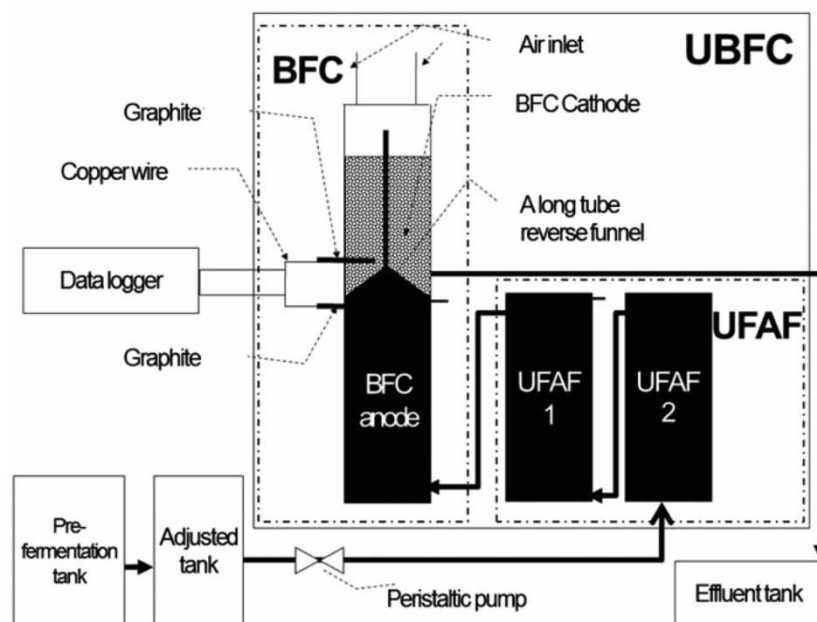[b]Sources for cathodic material cost data.

Figure 2.   UBFC reactor (figure from [89] with permission from Elsevier).

material reduced the MFC internal resistance by cutting the distance between the cathode and the proton exchange membrane (PEM). The MFC's power density was similar to that with an air-cathode using a carbon cloth.[79] A SSM coated with MnO_2/CNT yielded a power density of $2.68\,W/m^2$.[80] Table 3 shows costs of some anodic and cathodic materials.

4.4.   Cathode modifications

To enhance cathode performance, chemical, electrochemical and thermal methods have been used for cathode modifications. HNO_3, H_3PO_4, KOH, H_2O_2, etc. have been used to treat cathodes to increase the electrode surface area and nitrogen superficial groups.[83] Nitric acid activation of graphite granules accelerated non-catalytic dissolved oxygen reduction and improved an MFC's current density from 16 to $96\,A/m^3$.[84] The nitrogen-doped carbon cathode was found to possess a better nucleophilic property and a better catalytic ability. It achieved a slightly better power density ($0.22\,W/m^2$) than the Pt-cathode ($0.2\,W/m^2$).[85] Redox mediators such as thionine and AQDS have also been used to modify the cathode through electropolymerization. Thionine modification was found to greatly increase electron transfer, leading to a three-fold power density increase.[86]

5.   Some new MFC reactors for wastewater treatment

The classical dual-chamber MFC setup in Figure 1 is actually rather inefficient for practical applications.

For example, the distance between the two electrodes is too large, leading to a large internal resistance. The PEM is not only expensive, but also easily fouled. Researchers have created different designs to improve the performance and to cut cost.[87] Several new reactor designs have emerged in recent years.

Freguia et al. [88] designed a continuous-flow dual-chamber oxygen-cathode MFC for wastewater treatment. The effluent from an acetate-fed anodic chamber was fed to the cathodic chamber in a sequential anode–cathode arrangement. The anodic chamber achieved an organic substrate removal rate of 2.45 kg Chemical Oxygen Demand (COD) per cubic metre of anolyte each day. Owing to its design, the heterotrophic biomass on the cathode played a polishing role for the COD removal. The MFC had a maximal power output of $110\,W/m^3$ (catholyte volume) with a CE between 65% and 95%.

Another group of researchers developed an upflow bio-filter circuit (UBFC) by combining two upflow anaerobic filter (UFAF) units and a bio-filter circuit (BFC) as shown in Figure 2.[89] Microorganisms were immobilized on granular-activated carbon (GAC) for UFAF 1 and UFAF 2 and the BFC anode. Aerobic microorganisms were grown on GAC for the BFC cathode that was fed with air. Biodiesel wastewater was pretreated by anaerobic pre-fermentation, and then diluted with tap water (1:1 v/v) before being fed to the UBFC. Instead of a membrane, a plastic tube-funnel was placed between the anodic and cathodic chambers to prevent oxygen diffusion into the anodic chamber. Without chemical treatment or nutrient supplements, the system achieved a maximum COD removal of 15.0 g/L per day, much higher than other MFCs.
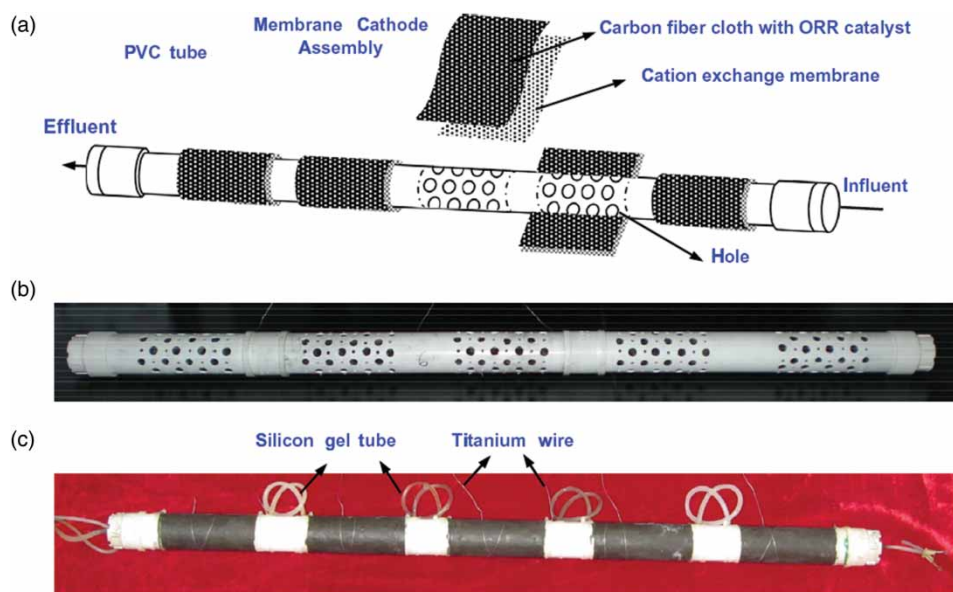
Figure 3.   MFC stack with five MFC modules (figure from [90] with permission Elsevier).

A Pt-free MFC stack shown in Figure 3 was used by Zhuang et al. [90] to treat real wastewater with concomitant electricity generation. The MFC stack was evenly divided into five cell modules. On the two ends of each cathode, disc-shaped circular clapboards placed inside the polyvinyl chloride (PVC) pipe vertically served as anodes. Carbon fibre clothes containing MnO_2 (catalyst) hot-pressed onto cation exchange membranes were wrapped around perforated pipe sections to form cathodes. A maximum power density of $176 \, W/m^2$ was achieved together with 77.1% COD removal and 80.7% NH_4^+-N removal from the wastewater.

An integrated up-flow anaerobic sludge blanket reactor–MFC–biological aerated filter (UASB–MFC–BAF) system was built by a group of researchers.[91] The UASB reactor was used for the COD removal with sulphate reduction, while the MFC unit was intended for sulphide oxidation with electricity generation. Most of the colour removal and degradation of phenol derivatives were performed by the BAF unit. With a feed of high-strength molasses $(1.26 \times 10^5 \, mg/L \, COD)$, a maximum power density of $1.41 \, W/m^2$ was obtained at a current density of $4.95 \, A/m^2$. This integrated system achieved total COD, sulphate and colour removal efficiencies of 53.2%, 52.7% and 41.1%, respectively.

Various substrates have been used in MFCs in lab tests,[92] including volatile fatty acids, alcohols, fermentable sugar and even lignocellulosic biomass. Biorefractory wastes such as dye, leachates and pharmaceutical wastewater have also been used.[53] Treatment of some azo dyes by MFCs has been extensively reviewed by Solís et al. [93] and Solanki et al.[94] Although power densities produced by the MFCs were still too low for practical applications, MFCs have the potential ability
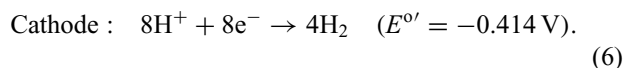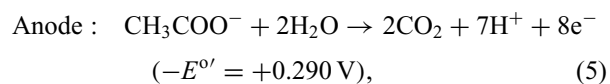
to treat various wastewaters without good efficiencies (Table 4).

6.   MFCs/MECs for production of biofuels and other bio-materials

When MFCs are operated as microbial electrolysis cells (MECs), they can be used to produce biofuels and other bio-materials. Biofuels can be accumulated to power chemical fuel cells or internal combustion engines. This means that large devices can be powered. This overcomes the drawback of low output voltage and low power density of MFCs that limit them to powering only small sensor devices.[110]

6.1.   Hydrogen

Hydrogen is a clean alternative fuel to fossil fuels. MFCs can be operated with externally imposed voltages as MECs to produce hydrogen gas.[111] Figure 4 is a schematic diagram of a dual-chamber MEC. Using acetate as the substrate in the anodic chamber, the anodic and cathodic reactions are shown as follows:

$$\text{Anode}: \quad CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^-$$
$$(-E^{o\prime} = +0.290 \, \text{V}), \tag{5}$$

$$\text{Cathode}: \quad 8H^+ + 8e^- \rightarrow 4H_2 \quad (E^{o\prime} = -0.414 \, \text{V}). \tag{6}$$

The difference between the two standard reduction potential ($E^{o\prime}$) values yields a standard cell potential of $-0.124 \, V$. This corresponds to a positive Gibbs free energy change based on Equation (3), indicating that the redox reaction combining Reactions (5) and (6) is thermodynamically unfavourable. Thus, under standard conditions defined

Table 4. Some wastewaters treatment by MFC.

Wastewater	Species	Initial concentration	Voltage, current and/or power density	COD removal (%)	References
Chemical wastewater	Mixed culture	6200 mg/L COD	272 mV, 5.43 mA	35.4	[95]
		10,540 mg/L COD	304 mV, 6.08 mA	62.9	
Synthetic Wastewater	Mixed culture	2.64 kg COD/m^{3}d	pH 7: 226 mV, 0.84 mA, 7.43 mW/m^2	43.8	[96]
			pH 6: 297 mV, 0.82 mA, 7.83 mW/m^2	35.2	
		3.54 kg COD/m^{3}d	pH 7: 291 mV, 0.82 mA, 7.69 mW/m^2	43.2	
			pH 6: 308 mV, 0.93 mA, 8.89 mW/m^2	41.9	
Domestic wastewater	Mixed culture	3200 mg/L COD	289.61 mA/m^2, 125.4 mW/m^2	23.8	[97]
Swine wastewater	Mixed culture	1.2 kg COD/m^{3}d	About 480 mV, 60 mW/m^2	81	[98]
		4.9 kg COD/m^{3}d	610 mV, 226.3 mW/m^2	66.1	
Rice mill wastewater	Mixed culture	2200–2250 mg/L COD	pH 8: 304 mV, 48.64 mW/m^2	96.5	[99]
			pH 7: 249 mV, 32.63 mW/m^2	92.3	
			pH 6: 211 mV, 23.43 mW/m^2	89.2	
Palm oil mill effluent	Mixed culture	200 mg/L COD	622 mW/m^2, 32%CE	23	[100]
Dairy wastewater	*E. coli* (DH5-a)	1200 mg/L COD	400 ± 15 mV, 5.7 ± 0.2 W/m^3	80 ± 10	[101]
Domestic wastewater		545 mg/L COD	300 ± 10 mV, 3.2 ± 0.2 W/m^3	75 ± 7	
Pharmaceutical wastewater	Anaerobic consortia	12,000 mg/L COD	346 mV, 120 mW/m^2	85.8	[102]
Human feces wastewater	Mixed culture	450 mg/L COD	548 mV, 209 mA/m^2, 70.8 mW/m^2	88	[103]
Bad wine	*Acetobacter aceti* and *Gluconobacter roseus*	7.8 ± 0.2 g/L COD	535 mV, 7.13 A/m^3, 3.82 W/m^3, 45% CE	59	[104]
Agriculture wastewater	*S. oneidensis* MR-1	397 ± 15 mg/L COD	0.23 mA, 13 mW/m^2	64.5	[105]
Domestic wastewater		671 ± 20 mg/L COD	0.38 mA, 36 mW/m^2	73.9	
Paper wastewater		1250 ± 15 mg/L COD	0.3 mA, 28 mW/m^2	34.8	
Food/Dairy wastewater		1562 ± 20 mg/L COD	0.66 mA, 13 mW/m^2	83.0	
Alcohol distillery wastewater	*Bacteroidetes thermophiles*	9.7 ± 0.6 kg COD/m^{3}d	11.5 ± 0.3 mA, 0.36 ± 0.01 W/m^2, 81 ± 2% CE	76 ± 3	[106]
Dye wastewater	*S. oneidensis*	350 mg/L Acid Orange 7	38 mW/m^2	73.7 ± 15	[107]
Dye wastewater	Mixed culture	76.5 mg/L Reactive Blue 221	620 mV, 28 mW/m^2	84	[108]
Molasses mixed sewage wastewater	Mixed culture	9978 mg/L COD	762 mV, 382.5 mW/m^2	59	[109]

Figure 4. Schematic of an MEC.

Figure 5. Schematic for CH_4 production from CO_2 with biocathode.
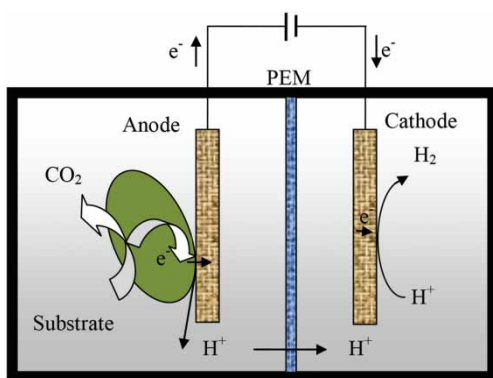
for $E^{o\prime}$, an external voltage greater than $+0.124$ V is needed between the anode and the cathode to drive the redox reaction coupling Reactions (5) and (6) forward for hydrogen production. In practical applications, due to various overpotentials and non-standard conditions, the actual external voltage is between 0.25 and 0.8 V.[112] Compared with the 1.21 V needed for the direct hydrolysis of water, this voltage is much lower.[87] The lower voltage requirement comes from the utilization of acetate as a fuel molecule. Formate ($E^{o\prime} = -0.432$ V for CO_2/formate) and lactate ($E^{o\prime} = -0.430$ V for CO_2 + acetate/lactate) [1] are both more energetic than acetate. Thus, the required voltages are even lower when they are used as fuels instead of acetate. Apart from these three common fuel molecules, many other biodegradable substrates can be used to generate electricity in MFCs or to produce hydrogen gas in MECs.[111] Many reactor design aspects such as reactor structure, electrode material, proton (or ion) exchange membrane, substrate adjustment (including ionic strength, pH) must be optimized to improve the MEC performance.[110]

6.2. Methane

Methane has been produced from biomass using anaerobic methane digesters using solid wastes or slurries. For a wastewater feed, one attractive route for methane production is to use an MEC through the following reaction in the MEC's cathodic chamber:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (E^{o\prime} = -0.244 \text{ V}). \tag{7}$$
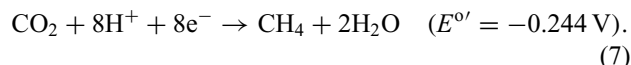
CO_2/CH_4 has a higher standard reduction potential of $E^{o\prime} = -0.244$ V than the $E^{o\prime} = -0.414$ V for $2H^+$/H_2.[1] This means a lower external voltage requirement compared with hydrogen production under the standard conditions defined for $E^{o\prime}$.

Figure 5 shows that the MEC reactor captures CO_2 and converts it into a fuel by using the energy from biomass degradation and the external electricity supply.
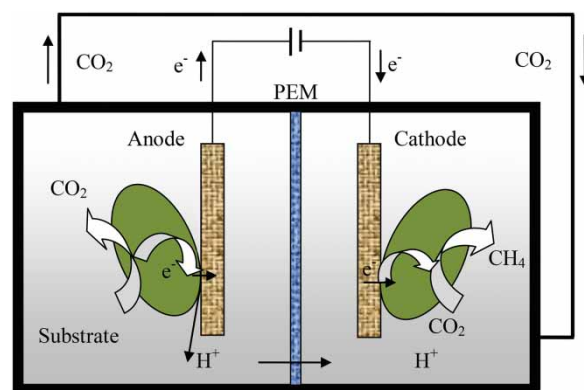
This kind of MEC reactor can use substrates at low concentrations at ambient temperature with CEs greater than 80%.[113,114] This new technology can supplement the already mature methane digester technology because the former uses wastewaters while the latter solid wastes.

6.3. Bioethanol

Bioethanol has been produced from corn for use as a transportation fuel. There is a major push to produce bioethanol from cellulosic biomass. In an anaerobic digester with mixed culture microbes, volatile fatty acids can be reduced by hydrogen that serves as the electron donor.[115] Instead of using hydrogen, bioelectrochemical ethanol production is achieved using a cathode as the electron donor in the following cathodic reaction [116]:

$$CH_3COO^- + 5H^+ + 4e^- \rightarrow CH_3CH_2OH + H_2O$$
$$(E^{o\prime} = -0.390 \text{ V}). \tag{8}$$
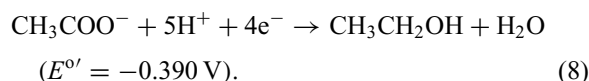
An applied cathode potential of -0.55 V is needed to move the acetate reduction forward.[116] Methyl viologen used as a mediator doubled ethanol concentration in lab tests.[116] In their experiment, Steinbusch et al. found that about 93% of the electrical energy was recovered in ethanol, reduced methyl viologen, hydrogen and other products on the first day. Apart from ethanol, other alcohols such as propanol and butanol can also be produced bioelectrochemically in MECs.[117]

6.4. Polyhydroxyalkanoates

Recently, the synthesis of polyhydroxyalkanoates (PHA) in a bioelectrochemical system was reported by Srikanth et al.[118] They produced PHA in the cathodic chamber and treated wastewater in the anodic chamber simultaneously. PHA was synthesized by microorganisms under a microaerophilic microenvironment (low DO concentrations which suppressed the microbial growth and the microbial assimilation activities).[118,119] In their MFC

system, 19% of dry cell weight PHA was produced after 48 h. The substrate removal efficiencies were 76.5% in the cathodic chamber and 59.6% in the anodic chamber, respectively. A power density of 15.2 mW/m² was achieved after 144 h.[118]

6.5. Other bio-materials

Formic acid is an important commodity chemical. In an MEC's cathodic chamber, formate is formed from the following reaction:

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \quad (E^{o\prime} = -0.432\,V). \quad (9)$$
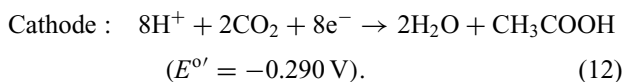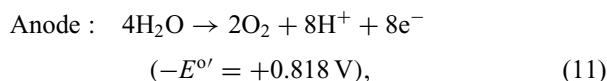
An external MFC can be used to supply the required voltage needed to drive the MEC.[120] *Geobacter sulfurreducens* in a biocathode's biofilm can reduce fumarate to form succinate [121]:

$$Fumarate + 2H^+ + 2e^- \rightarrow Succinate \quad (E^{o\prime} = +0.033\,V). \quad (10)$$
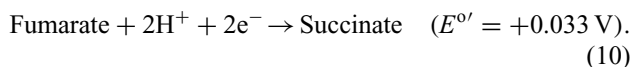
The $E^{o\prime} = +0.033\,V$ value is far more favourable (far more positive) that those for $2H^+/H_2$ ($-0.414\,V$),[1] CO_2/formate, and $2CO_2$/acetate under the standard conditions defined for $E^{o\prime}$. When acetate oxidation in Reaction (1) is coupled with fumarate reduction, the standard cell potential is $+0.323\,V$. If overpotentials are smaller than this value, no externally imposed voltage is needed to drive forward the redox reaction of acetate oxidation coupled with fumarate reduction. In such a situation, the reactor is not strictly an MEC, but rather an MFC.

Nevin et al. [122] found that acetogenic *Sporomusa ovate* converted CO_2 and water to acetate with the help of an imposed external voltage in the following reactions:

$$Anode: \quad 4H_2O \rightarrow 2O_2 + 8H^+ + 8e^-$$
$$(-E^{o\prime} = +0.818\,V), \quad (11)$$
$$Cathode: \quad 8H^+ + 2CO_2 + 8e^- \rightarrow 2H_2O + CH_3COOH$$
$$(E^{o\prime} = -0.290\,V). \quad (12)$$

A small amount of 2-oxobutyrate was also produced during acetatproduction.

7. Summary

The green MFC technology is a potentially attractive technology to tackle two important issues in our modern society: energy shortage and wastewater pollution. MFC research is highly multidisciplinary involving bioelectrochemistry, microbiology, molecular biology, chemical engineering and environmental engineering among others. Despite the advances made in the past decade, significant hurdles remain before the MFC technology is ready for the practical deployment in wastewater treatment or power generation beyond powering small sensors. MFC power

densities are still too low and MFC reactor construction and operation costs too high. New electrode materials and designs discussed in this work have proven to enhance the MFC performance considerably. This work discussed the bioenergetics of MFCs, electrode modifications and reviewed several new MFC reactors created by researchers to process various wastewaters in lab tests. When MFCs are operated as MECs, various biofuels such as hydrogen, methane and ethanol can be produced. Using MECs, biofuels can be accumulated to power devices that cannot be powered by low voltage and low power density MFCs.

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