1 Introduction

1.1 Background

Recently, increasing energy shortage and growing awareness of necessary environmental protection, harvesting low-grade waste heat as electrical power has drawn a great deal of attention.[1–4] In addition hydraulic, wind and solar radiation are typical examples of clean energy resources used as alternatives to fossil fuel resources to produce electricity. However, these energy sources are limited by climate and geographical factors. Biomass is one of the important renewable carbon sources and has been recognized as a promising energy supplier for the future.[5] Increasing demand for biofuel has encouraged researchers and politicians worldwide to find sustainable biofuel production systems in accordance with the regional conditions and needs.[6]

Microbial fuel cells (MFCs) are bioelectrochemical devices used to generate electricity from organic matter using exoelectrogenic bacteria.[7] This technology shows promise in both wastewater treatment and sustainable bioenergy conversion applications.[8]In the MFC, electrons liberated from the degradation of the electrolyte organics move through the external circuit to the cathode where oxygen is reduced and a net current/power is generated.[9]

Electricity generation during organic degradation represents a process of directly converting chemical energy within organic matters to electrical energy, which gives rise to a potential for MFC to produce electricity from organic wastewater along with wastewater treatment. The construction of an MFC and its chemical reaction on the electrodes is shown in Fig. 1.1. It can be seen in this figure that the organic reactant is oxidized to CO_2 at the anode, while the oxygen reacts in the cathode. A proton exchange membrane (PEM) is located between anode and cathode for proton exchange.

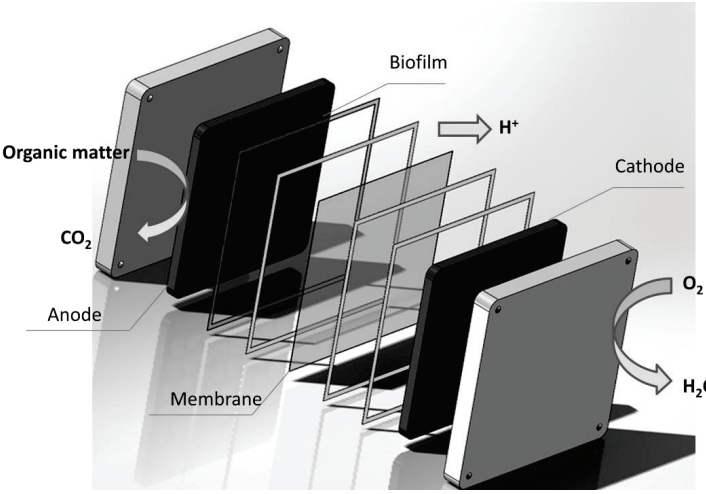

Fig. 1.1: Schematic of a typical two-chamber microbial fuel cell and its reactions

1.2 Construction of MFC

The main MFC-components are the electrodes, separated into the anodic- and cathodic-chamber. Electrons and protons are produced on the anode from the oxidation of soluble organic matters using bacteria as biocatalyst. In the cathode chamber, an electron acceptor is reduced with the electrons transferred via an external circuit and the protons diffused through the solution[10]. Chouler et al. [11] have constructed single chamber MFC, whose anode and cathode were made of carbon cloth. Three different MFCs were developed with polydimethylsiloxane (PDMS) membrane, egg shell membrane and without membrane respectively. It is observed that egg shell possesses a great potential functioning as membrane. The power density of MFC with egg shell has increased from 1 mW/m^2 to 12 mW/m^2 when the distance between the electrodes increased from 4 to 8 mm.

Liu et al.[12] have developed MFC with two chambers separated by a titanium mesh that was used as the anode current collector. Furthermore, granular activated carbon particles enriched with

exoelectrogenic biofilm are fluidized (by stirring) in the anode chamber of the MFC. The maximum power density of 951 ± 10 mW/m^2 was achieved with this construction. For further development of fluidized MFC, Ren et al.[13] have constructed a two-stage laboratory-scale MFC stack, which consisted of MFCs and an anaerobic fluidized bed membrane bioreactor (MFC-AFMBR). They found that AFMBR plays an important role in removing COD, which possessed 43.4% of total COD. This reveals that a combined MFC-AFMBR system could be used to effectively treat domestic wastewater. Thung et al.[14] have even developed a MFC without PEM, which is also defined as membrane-less microbial fuel cell (ML-MFC). In their study, they have evaluated different operational conditions of MFC, which may affect the COD removal rate of MFC. Results showed that despite the constrained power production, the highest COD removal rate has reached 96%. This suggested that ML-MFC can also be used to treat wastewater.

1.3 Microorganisms on the surface of the anode

The bacterium, which is used for the anode, is usually exoelectrogen. An exoelectrogen normally refers to a microorganism that has the ability to transfer electrons extracellularly. Electrons exocytosed in this fashion are produced following ATP production using an electron transport chain (ETC) during oxidative phosphorylation. Convention at cellular respiration requires a final electron acceptor to receive these electrons. A typical example of exoelectrogen is shown in Fig. 1.2, whose priority is that it can directly transfer electrons to a chemical or material that is not the immediate electron acceptor.[15] In this mechanism, electrons from microbial carriers are transported onto the electrode surface either by a microorganism's (Schewanella oneidensis, Geothrix ferementans) own mediator which in turn facilitate extracellular electron transfer or by added mediators. The mediators provide a platform for the microorganisms to generate electrochemically active reduced products.

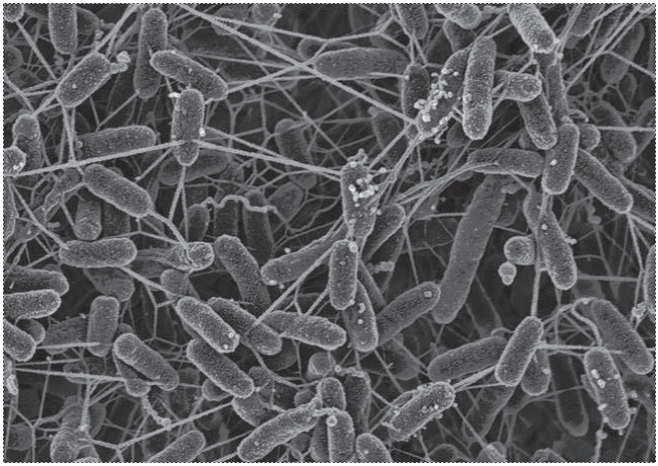

Fig. 1.2 Exoelectrogen with nanowires for transferring electrons

Many researches were conducted, which were focused on the study of bacteria on the anode. Li et al.[16] have used a polymerase chain reaction (PCR) and denaturing gradient gel electrophoresis (DGGE) technology to analyze the bacteria on the surface of the anode. In their study, three different bacteria strains were prepared for experiments, which were clostridium acetobutylicum, anerobic sludge from Luofang wastewater factory, Shenzhen and broth from turmeric wastewater. It is found by PCR-DGGE that 9 different predominant floras on anode were found after operation of MFC. Comparing with other 6 floras, three of the predominant floras produced significantly higher voltage. It has been demonstrated that these three floras possessed a high homology with impure β- proteobacterium. Sun et al. have[17] used two types of wastewater to investigate its influence on the microbial community of the anode. In their study, synthesized wastewater with glucose as main component was used as wastewater A, while wastewater from an anaerobic reactor was used as wastewater B. Results indicated that the predominant flora of wastewater A composed of mainly high G + C Gram-positive bacteria and γ-proteobacteria. Nevertheless, the predominant flora of wastewater B was composed mainly of low G + C Gram-positive bacteria and ε-proteobacteria.

Lin et al.[18] have found by DGGE analysis that the mode of operation (batch and continuous mode), COD concentration and the setup of microorganisms could even influence the structure of the microbial community in the MFC.

1.4 Power generation using MFC

Power output by MFCs has increased considerably over the last decade due to several scientific and technical advances.[19] Unlike enzyme fuel cells in which enzymes are used as biocatalysts,[20] Booki Min et al.[21] have designed a flat plate MFC (FPMFC) to operate as a plug flow reactor combining with a PEM system. They found that the average power density of a MFC operated with domestic wastewater was 72.1 mW/m^2 at a liquid flow rate of 0.39 mL/min. Power generation was sustained at high rates with several organic substrates (all at up to 1000 mg COD/L), including glucose (212 mW/m^2), acetate (286 mW/m^2), butyrate (220 mW/m^2), dextran (150 mW/m^2), and starch (242 mW/m^2). Sona Kazemi et al. have studied the continuous operation of flat plate MFC (FPMFC). A great stability was observed and it resulted in a power density of 44 W/m^3.[22] Yang et al.[23] has established an algae biofilm microbial fuel cell (ABMFC). Results showed that the ABMFC has produced the highest power density of 62.93 mW/m^2, which is 18% higher than ordinary MFC.

There are three main factors that can affect the power generation of MFCs for a given water composition, which are namely anode, membrane and cathode. To improve the performance of the anode, it is necessary to investigate its surface and structure. Logan et al.[24] have developed graphite brush anodes, which were highly conductive, noncorrosive and possessed a high surface area. They constructed a cube (C-MFC) and a bottle (B-MFC) air-cathode MFCs. Results showed that power production in C-MFCs containing brush electrodes at 9600 m^2/m^3 reactor volume reached a maximum power density of 2400 mW/m^2, while the maximum coulombic efficiency (CE) reached the value of 60%. Zhang et al.[25] have used a novel anode, fabricated by electrodepositing manganese dioxide (MnO_2) on carbon felt to improve MFC's power production.

Comparing to a graphite felt anode, the anode capacitance has been improved by 46 times by using this type of anode. Furthermore, The maximum power density of the MFC with the MnO_2-coated anode reached 3580 ± 130 mW/m^2, 24.7% higher than that with the bare carbon felt anode (2870 mW/m^2). It is also found that the electrodeposition time also plays an important role in performance of the anode. Three different electrodeposition times (60 min, 20 min and 5 min) were compared, which were donated as ED60, ED20 and ED5 respectively. Results showed that the power density decreased in the order: ED60-MFC (3580 mW/m^2) > ED20-MFC (3000 mW/m^2) > ED5-MFC (2750 mW/m^2).

It has been shown that the oxygen reduction reaction (ORR) at the cathode is one of the main limiting factors for further improving the output of MFCs.[26,27] An improvement in the cathodic process can lead to a considerable power density increase in MFCs.[28] One of the solutions is to add catalyst on the surface of the cathode. Pt is a typical example. Pt-based catalysts are the best ORR catalysts, however, because of its high cost, it is necessary to study environmental friendly catalysts with lower price. Rossi et al. [29] have investigated the effect of metal-organic framework (MOF) on activated carbon (AC) to improve the performance of the cathode. In their study, Cathodes with the Fe–N–C/AC catalyst were synthetized. During the longterm performance, a power density of 2.78 ± 0.08 W/m^2, was achieved by using MOF catalysts on AC initially. Although the power density decreased by 26% after 8 weeks, it is still 41% higher than that of an AC cathode without MOF. Waston et al.[30] have studied different precursor materials (coal, peat, coconut shell, hardwood and phenolic resin) for AC as catalyst for the cathode. Results showed that cathodes using the coal-derived AC had the highest power densities in MFCs (1620 ± 10 mW/m^2). Furthermore, the peat-based AC performed similarly in MFC tests (1610 ± 100 mW/m^2) and had the best catalyst performance, with an onset potential of E_{onset} = 0.17 V, and n = 3.6 electrons used for oxygen reduction. Gajda et al.[31] have developed Fe-N-C catalyst to improve the performance of air cathode. Results showed that the maximum power density has reached 1300 mW/m^2 when using iron aminoantipyrine (Fe-AAPyr) as cathode catalyst.

Recently, many studies [32] have focused on the effect of manganese dioxide (MnO_2) catalysts on improving the performance of the cathode in MFCs. Because of the low conductivity of MnO_2,

major benefits can be achieved by anchoring MnO_2 nanostructures over carbon supports such as graphite, activated carbon (AC), carbon nanotube (CNT) and graphite oxide (GO). The carbon support (graphite) is expected to increase the electrochemically active surface area and number of active sites to improve the performance of MnO_2 catalysts.[33] Li et al.[34] have developed manganese oxides with a cryptomelane-type octahedral molecular sieve (OMS-2) structure to replace platinum as a cathode catalyst in MFCs. They investigated undoped (ud-OSM-2) and three catalysts doped with cobalt (Co-OMS-2), copper (Cu-OMS-2), and cerium (Ce-OMS-2) to enhance their catalytic performances in granular activated carbon MFC (GACMFC). Results showed that the voltage of the Cu-OMS-2 GACMFC was 214 mV. The cell possessed a relatively high power density of 165 mW/m^2. In addition, the degradation rates of organic substrates in the OMS-2 GACMFCs were twice compared to those in the platinum GACMFCs, which enhanced their wastewater treatment efficiencies. Zhang et al. [35] have investigated the influence of different MnO_2 morphologies on the performance of the cathode. Three manganese dioxide materials, α-MnO_2, β-MnO_2, γ-MnO_2 were compared to platinum (Pt) in air-cathodes of MFCs. Results showed that the power density decreased in the order: Pt (2200 ± 8 mW/m^3) > β-MnO_2 (1300 ± 10 mW/m^3) > α-MnO_2 (920 ± 10 mW/m^3) > γ-MnO_2 (600 ± 11 mW/m^3) > without catalyst (230 ± 5 mW/m^3), showing that β-MnO_2 is an relatively ideal catalyst for MFC. It can also be used as alternative to Pt witch has a much higher price.

Another alternative catalytic material is molybdenum sulfide (MoS_2), which is a silvery black solid that occurs in nature as the mineral molybdenite. Because of its high stability, MoS_2 is usually unaffected by dilute acids and oxygen. In appearance, it is relatively similar to graphite. MoS_2 nanoparticles supported on graphite are also considered as an exciting new catalyst for hydrogen evolution on the nitrogenase enzyme[36]. However, an inherent disadvantage of this material is its low conductivity and insufficient number of active sites. Yuan et al. [37] have used MoS_2 plus CNT composite as catalyst to produce hydrogen in microbial electrolysis cell (MEC) and found that its activity is high. Hou et al. [38] have also developed a MoS_2/nitrogen-doped graphene nanosheet aerogel catalyst for hydrogen evolution in an MEC. They achieved a high output current density of 0.36 mA/cm^2. Furthermore, a hydrogen production rate of 19 m^3/day

was also obtained for the hybrid at a bias of 0.8 V. Our group [5] has also shown that the graphite/MoS_2 composite shows a much higher stability than the graphite/MnO_2 composite. Because of its simple synthetic procedure, and the low cost [39], MoS_2 is promising for future MFC studies.

1.5 Energy harvesting from MFC

Current/power generated from MFC systems is over 3 to 5 orders of magnitude lower compared to traditional hydrogen- or methanol-fueled FC [40] and therefore a smart design is necessary in order to harvest the low energy produced. Alaraj et al. [41] have used a synchronous flyback converter to harvest energy from MFCs, which has a relatively simpler configuration and improves harvesting efficiency by 37.6% compared to a diode based boost converter. Moreover, the proposed harvester was able to store 2.27 J in the output capacitor out of 4.91 J generated energy from the MFC, while the boost converter can capture only 1.67 J from 4.95 J. Boghani et al. [42] have developed a novel strategy of a MFC subsystem. Series connectivity along with maximum power point tracking (MPPT) generates increased power from individual MFCs whilst eliminating cell reversal. In the study, each MFC was connected to a MPPT device which controlled the current sourced from each MFC. They found that the application of MPPT and the connection strategy presented here can increase stack voltages and avoids the reversal of cell voltage, whilst also applying a control mechanism that facilitates peak power extraction from MFCs in real-time. Donovan et al.[43] have constructed a sediment microbial fuel cell (SMFC) using a power management system (PMS) with two DC/DC converters, and digital logic to control energy storage and use. They calculated the process efficiency of PMS. It has been measured that DC/DC1 was operated with an output current of about 1 mA at an efficiency of 70.0%, while the power efficiency of DC/DC2 was 80.6% with an input potential of 4.07 V and an output current of 500 mA. According to the values, the overall system efficiency under these operating conditions was 70.0% × 80.6% = 56.4%. Wang et al. [44] have developed a new approach and system that can actively extract energy from MFC

reactors at any operating point without using any resistors. Results showed that within 18-h test, the energy gained from the MPPC was 76.8 J, 76 times higher than the charge pump (1.0 J) that was commonly used in MFC studies, while the coulombic efficiency obtained from the MPPC was also 21 times higher than that of the charge pump. Furthermore, different numbers (3, 6, 9, and 12) of capacitors during 18-h harvesting were characterized. For 12-capacitor condition, the voltage has not reached the saturated level even after 16 h. The energy storage in the 6, 9, and 12-capacitor conditions was 47.0, 65.6, and 76.8 J, respectively, and the corresponded voltage after 18 h was 2.8, 2.7, and 2.5 V, respectively. Zhang et al. [45] have compared the capacitor-transformer-converter type PMS with pump-capacitor-converter type PMS. They found that the capacitor-transformer-converter type PMS can accommodate lower input voltages, but the charge pump-capacitor-converter type PMS has a slightly higher power efficiency. Furthermore, the charging speed of the capacitor-transformer-converter type PMS is not limited by the charge pump as in the charge pump-capacitor-converter type PMS, resulting in a shorter charging/discharging cycle.

1.6 MFC for real wastewater, manure and urine treatment

Recently, MFCs have been used treating real wastewater, manure and urine. Heidrich et al.[46] have developed MFCs reactors, which can be operated at low temperature without specialized inocula. By treating real wastewater, they have obtained the maximum COD removal rate and Coulombic efficiency of 90% and 25% respectively. Liu et al.[47] have used MFC to treat pharmaceutical wastewater with the initial COD value of 200 mg/L. They obtained the COD removal rate between 92% and 94%. Nikhil et al.[48] have treated pharmaceutical wastewater with much higher COD value comparing to Liu et al. By using the MFC system with total volume of 1 L and surface area of 70 cm^2, they obtained the maximum removal rate of 85%. Qin et al.[49] have used MFC to treat human urine with the COD value of 1448 mg/L. The maximum COD removal rate of 89.1% was achieved by using MFC system with total volume of 75 mL and

surface area of 75 cm^2. Shen et al.[50] have used MFC system with total volume of 600 mL to treat daily manure. The maximum COD removal rate of 75% was achieved in their study. Cerrilo et al.[51] have treated cattle manure with initial COD value of 1500 mg/L and achieved COD removal rate of 84.72%.

1.7 MFC scale up

Scaling up MFCs is challenging based on the need to use inexpensive and non-precious metal materials and to achieve good performance. The use of carbon fiber brushes provides a route to make low-cost anodes, [52–54] and several different cathodes have been constructed without precious metals using AC as a catalyst [55,56]. Liang et al.[57] have developed a 1000 L modularized MFC system, which was operated for more than one year to test its treating ablility for wastewater. Results showed that the concentration of effluent from MFC system remains less than 50 mg/L, while the COD removal rate possessed the value between 70% and 90%. Babauta et al.[58] have scaled up benthic microbial fuel cells (BMFC). They found that by using an in-line flyback converter, the input voltage of BMFC can be held within a relatively optimal range between 0.35 and 0.5 V. When two converters were used, 16 mW of MFC power can be delivered to battery with the efficiency of 77%. In order to improve the performance of MFCs, many works have focused on electrode modification, such as electrochemical treatment [55], metal oxide doping [56] and polymer modification [59].

Alexis et al.[60] have reported a novel membraneless stack design using ceramic plates, with fully submerged anodes and partially submerged cathodes in the same urine solution. In their research, they constructed self-stratifying urine column MFCs (SSC-MFC) with different scales. Comparing to the smaller cells, the larger cells possessed the dimension increase factor of 6. Results showed that the larger MFCs possessed the power density of 12.596 mW/m^2, which is only slightly lower than that of smaller cells (13.836 mW/m^2). This reveals that this SSC-MFC scaling up approach was successful in converting chemical energy in urine into electricity.