Chapter 11
Reactor Design for Bioelectrochemical Systems

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11.1 Introduction

Bioelectrochemical systems (BES) are novel hybrid systems which are designed to generate renewable energy from the low cost substrate in a sustainable way. Microbial fuel cells (MFCs) are the well studied application of BES systems that generate electricity from the wide variety of organic components and wastewaters. MFC mechanism deals with the microbial oxidation of organic molecules for the production of electrons and protons. The MFC design helps to build the electrochemical gradient on anode and cathode which leads for the bioelectricity generation. As whole reactions of MFCs happen at mild environmental and operating conditions and using waste organics as the substrate, it is defined as the sustainable and alternative option for global energy needs and attracted worldwide researchers into this research area. Apart from MFC, BES has other applications such as microbial electrolysis cells (MECs) for biohydrogen production, microbial desalinations cells (MDCs) for water desalination, and microbial electrosynthesis cells (MEC) for value added products formation. All these applications are designed to perform efficiently under mild operational conditions. Specific strains of bacteria or specifically enriched microbial consortia are acting as the biocatalyst for the oxidation and reduction of BES. Detailed function of the biocatalyst has been discussed in the other chapters of this book.

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Bioelectrochemical systems mechanism involves both microbial/biological and electrochemical/physical principles. So, the design of BES is quite complex than conventional fermentation reactors. Towards optimization of the reactor design various models were tried. Even though the designs are different in various studies, the design components were found to be almost similar in all the designs. Such studies were focused to achieve improved energy recovery, high electron transfer rate, efficient energy conversion, economic reactor design for scaling up, better treatment efficiency, operational easiness, etc. The present chapter is focused to bring the knowledge related to design of BES and its components at one place. The chapter is also aimed to discuss the pros and cons of different factors that are involved in design.

11.2 Components of BES

In a BES, microbes attach to the anode surface and form a living biofilm to catalyze oxidation of organic compounds such as acetate. Hence, affinity between the anode and microbe is critical for the efficiency of the BES system such as MFCs. Also, a cathode is an integral part of the MFC where the electrons reach from the anode and are reduced to complete the reaction. Plethora of materials have already been employed as the anode and cathode materials in the MFC and some of them showed excellent performances in terms of bioelectricity production and wastewater treatment. In the present chapter we discuss current status and future perspectives of electrode materials for MFCs.

11.2.1 Anode Materials

In MFCs, anode is unique with the presence of living biofilm. The metabolically generated electrons from the biofilm are transferred to the attached anode where interfacial materials dictate the electron transfer rate (Fig. 11.1). To enhance the electron transfer process and the biofilm formation, the selection of anode material is critical. The anode material should satisfy certain features to become an ideal electrode as outlined in Fig. 11.2 (Xie et al. 2015). In addition, synthesis and fabrication of anodes should be flexible and the materials should be largely available with low cost.

11.2.1.1 Nanostructured Carbon-Based Electrodes

Carbon based electrodes have received considerable attraction as anode materials in MFCs due to their outstanding conductivity, high resistance to corrosion, and excellent biocompatibility (Kalathil and Pant 2016). Traditional carbon-based

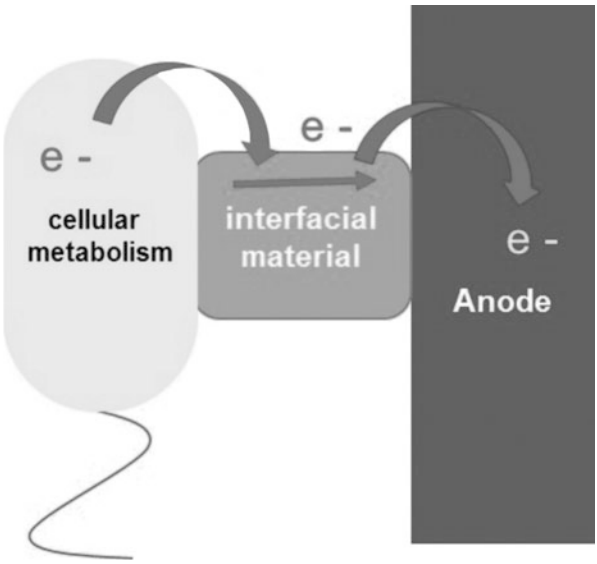

Fig. 11.1 A schematic representation for the metabolically generated electron flow to the anode in an MFC

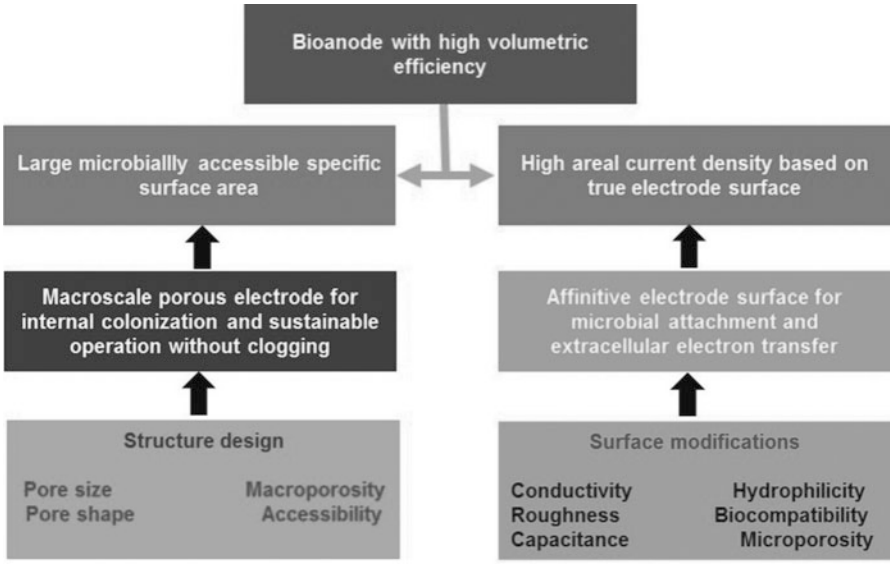

Fig. 11.2 PERT diagram for ideal characteristics of a bioanode in MFCs

electrodes such as graphite, carbon paper, carbon cloth, carbon felt and granular carbon are widely reviewed in many literature (Zhou et al. 2011). Here we focus only on nanostructured carbon materials such as carbon nanotubes, graphene, conductive polymers and metal nanoparticles.

11.2.1.2 Carbon Nanotubes

Carbon nanotube (CNT) is an attractive choice for electrode materials in MFCs due to its excellent conductivity and mechanical stability (Yazdi et al. 2016). Also, CNTs are highly biocompatible with microbes which allow biofilm growth on the CNT surface (Kalathil et al. 2013; Yazdi et al. 2016). Liu et al. (2014a) experimentally and theoretically demonstrated that CNT networks can facilitate direct extracellular electron transfer (EET) from bacterial outer membrane C-type cytochromes (OM C-Cyts) to solid electron acceptors such as electrodes. A 10-fold increase in the current production was observed with the CNT electrode as compared to a plain carbon paper with *Shewanella oneidensis* MR-1. Molecular dynamic simulation studies revealed that CNTs formed a CNT-OM C-Cyts electronic conduit to enhance the rate of EET process. The redox functional groups on the CNTs may be responsible for the formation of the electronic conduit. The study provided solid evidences on the action of CNTs in the EET process which may be helpful to fabricate CNT based electrode materials for MFCs. Erbay et al. (2015) observed that geometry of CNTs critically affects the performance of bioanodes. The study concluded that longer and loosely packed CNTs are highly suitable for the efficient EET process. Also, less amount of amorphous carbon in the CNTs facilitates microbe-electrode interactions. In another report, simple addition of CNT powders improved the performance of *Geobacter sulfurreducens* based MFC by lowering the anodic resistance and facilitating mass transfer inside the biofilm (Liang et al. 2011).

CNT hydrogel fabricated on a carbon paper improved current generation in an MFC as compared to the control (Liu et al. 2014b). The fabricated electrode provided huge surface area for the bacterial attachment and promoted direct EET due to the functional groups on CNTs. The CNT-hydrogel bioanode exhibited high stability for long term operation which is considered as one of the crucial factors for practical applications of MFCs. Many attempts have been reported for the development of micro-sized MFCs as they are highly attractive to power ultra-low-power electronics (Mink et al. 2012). A micro-sized MFC (1.25 μL) equipped with vertically grown multiwalled CNT (MWCNTs) integrated with nickel silicide (NiSi) bioanode generated a current density of 197 mA/m^2 (Mink et al. 2012). The MWCNTs provided large specific surface area for the bacterial attachment while NiSi lowered contact resistance of the modified electrode. A follow up work with a modified micro-sized MFC (75 μL) using MWCNT bioanode and air cathode performed much better than the previous work by producing a current density of 880 mA m^{-2} (Mink and Hussain 2013). However, the air cathode design allowed oxygen diffusion to the anode which deteriorated the bioanode performance. Also, the high surface area provided by the MWCNTs caused clogging of the anode with bacteria. Hence, optimization of the electrode fabrication is necessary for the long term operation of the device.

Three dimensional (3D) porous CNT bioanode showed its promising candidacy for the electrode development by producing remarkable current output as compared

to traditional electrodes such as carbon cloth (Erbay et al. 2015; Xie et al. 2011). 3D structures allow the bacteria to grow at both interior and exterior of the electrode which in turn enhance the electrochemical activities of the attached biofilm. Katuri et al. (2011) fabricated 3DMWCNT/Chitosan hybrid bioanode by ice-segregation method as a bioanode for an MFC seeded with *G. sulfurreducens*. The modified bioanode showed excellent performance with a maximum current density of 24.5 A m^{-2} by providing high conductive surface area and better mass transfer for the biofilm activity. Doping of CNTs with elements is found to be a promising strategy to improve bioanode performance (Ci et al. 2012). For instance, CNTs doped with nitrogen showed better performance over bare CNTs and carbon cloth (Ci et al. 2012). The nitrogen doping increased active sites in the bioanode and marginally lowered the internal resistance caused by the electrode.

Generally, bacterial membranes are considered as negatively charged in neutral solution (Kalathil and Pant 2016). Owing to this negatively charged membranes, bacteria prefer to attach on positively charged solid surfaces. This factor inspired the researchers to create advanced bioanodes with positively charged surfaces. For example, a positively charged mesoporous-polysulfone supported single walled CNT (SWCNT) bioanode developed dense biofilm by attracting negatively charged *Shewanella* cells (Nguyen et al. 2013). The formation of dense biofilm caused enhanced current production and wastewater treatment. Also pretreatment of CNTs with acid can also create positively charged surface to enhance the charge based attraction between the anode and bacterial cells.

11.2.1.3 Graphene

Graphene is a two dimensional (2D) nanomaterial which possesses high electrical conductivity, good mechanical stability and excellent biocompatibility (Filip and Tkac 2014). Graphene also possesses higher specific surface area as compared to other carbon-based nanostructures. Owing to these properties, graphene has been largely employed in various energy devices including MFCs as an efficient electrode material (Filip and Tkac 2014). Graphene-based MFCs usually exhibit enhanced performance over activated carbon and CNT based MFCs (Yuan and He 2015). The first study of grapheme-based bioanode was reported a few years before (Zhang et al. 2011) using an *E. coli* seeded MFC. The graphene was anchored on a stainless steel mesh and utilized as the bioanode. The modified anode exhibited an enhanced current generation over the control, stainless steel mesh anode. The improved performance was mainly because of the high surface area of the anode that allowed large amount of biofilm formation. A vacuum stripped graphene scaffold bioanode showed 78 times higher current generation over the control carbon cloth in an MFC with *Pseudomonas aeruginosa* as biocatalysts (He et al. 2012). *P. aeruginosa* usually secretes exogenous mediators such as phenazine during its metabolism (Rabaey et al. 2005).

Graphene can stimulate phenazine production to accelerate mediated EET in *P. aeruginosa* (Liu et al. 2012). Moreover, the modified vacuum stripped graphene

electrode showed large surface area and enhanced charge transfer rate. Similarly, a graphene deposited carbon cloth improved the performance of *P. aeruginosa* MFC due to the stimulating effect of graphene on the production of phenazine (Liu et al. 2012). Xie et al. (2012) proposed a graphene sponge decorated on a stainless steel mesh as a low cost bioanode material for the MFC. The synergic contributions of both the graphene sponge and the stainless steel in terms of electrical conductivity, and high specific surface area greatly improved the MFC performance with a maximum current density of 1.32 A m^{-2}. 3D graphene sponge fabricated bioanode using ice template method produced a maximum power density of 427 W m^{-3} which was much higher than that of a carbon felt fabricated MFC (Chen et al. 2014). The modified 3D bioanode allowed efficient mass transport for attached biofilm. Recently, a miniaturized MFC (50 μL) produced a current density of 15.51 A m^{-2} with a 3D graphene bioanode which is the highest current generation from an MFC till date (Ren et al. 2016). This outstanding current generation shows that 3D graphene can be an effective bioanode material to extend the practical application of MFCs.

11.2.1.4 Conductive Polymers

Conductive polymers show excellent conductivity, biocompatibility, high chemical stability and easiness for synthesis and processing which make them widely used electrode materials in MFCs (Kalathil and Pant 2016). Polypyrrole (PPy) is the most studied conductive polymer till date (Balint et al. 2014). PPy possesses high stability in water and reasonably high conductivity. Also, it can be easily synthesized and surface properties such as porosity can be easily tuned for various applications. Zhao et al. (2015) developed a PPy nanotube membrane bioanode by a reactive self-degraded template method. The modified bioanode produced six times higher current as compared to the control in a *Shewanella* MFC. Electrochemical impedance spectroscopy (EIS) analysis confirmed that the PPy-nanotubes greatly reduced the charge transfer resistance of the electrode that facilitated the EET process. Also, SEM images depicted coverage of biofilms on the entire PPy nanotube anode while the control carbon paper anode didn't show much biofilm formation on its surface. This indicated that the modified bioanode improved the bacterial adhesion by providing large active surface area and functional groups. A bioanode fabricated with PPy hydrogel decorated on CNTs showed enhanced current production in an MFC seeded with mixed bacterial culture by reducing internal resistance and facilitating EET (Tang et al. 2015). The porous and hydrophilic nature of the modified bioanode allowed to develop thick biofilm and unhindered mass transport for efficient metabolic activities of the attached microbes. Anthraquinone-2,6-disulphonic (AQDS) is considered as an efficient mediator in the EET process (Adachi et al. 2008). PPy deposited with AQDS acted as an excellent bioanode in *Shewanella decolorationis* S12 MFC by producing 13-fold higher current density than the control bioanode (Feng et al. 2010). The

synergetic effects of PPy and AQQDS greatly improved charge transfer rate and avoided mass transfer limitations.

In addition to PPy, polyaniline (PANI) has also received considerable attention as bioanode materials in MFCs. PANI is a conducting polymer that has been widely employed in computer displays, tissue engineering, biosensors and fuel cells due to its ease of synthesis, pseudo-capacitance, stability, low cost and biocompatibility (Balint et al. 2014). Ding et al. (2012) proposed an interesting approach to control EET process by PANI-nanowire array fabricated bioanode. PANI showed multiple oxidation levels according to different applied potential. It stayed mostly in reduced state when the applied potential was −0.3 V vs. Ag/AgCl. At this potential, the EET from cells to the electrode was completely hindered due to thermodynamic barrier. At the same time, the EET from cells to electrode was enhanced at an applied potential of −0.2 V (vs. Ag/AgCl) as PANI stayed mostly in the oxidized state at this applied potential. This finding demonstrated that the EET process is highly sensitive to the applied potential and the EET can be controlled by altering external potential. A bioanode fabricated by the deposition of PANI on inorganic networks such as TiO_2 delivered high current output (1495 mW m^{-2}) in an *E. coli* MFC (Qiao et al. 2007). The main drawback of this study is that it used *E. coli* as the biocatalyst which needs mediator for the EET process and the mediator dependent MFC is not feasible for practical applications.

11.2.1.5 Metal Nanoparticles

As stated above, carbon-based materials are commonly employed as bioanode materials in MFCs. However, these materials possess a significant drawback in terms of electric conductivity which is two to three orders of magnitude below that of most metals (Baudler et al. 2015). Hence, application of metal-based bioanodes may be a suitable approach for the improved MFC. Various metal nanoparticles including noble metals (e.g. Au and Pd) and non-noble metals (e.g. Ni, Cu and Ti) have been widely employed as bioanode materials in MFCs.

Generally electrogenic bacteria are unable to form dense biofilm on the bare Au surfaces (Crittenden et al. 2006). However, deposition of Au on the surfaces of carbon-based electrodes proved to be an effective strategy to improve the performance of electrogenic bacteria such as *Shewanella oneidensis* MR-1 (Sun et al. 2010). A Au-sputtered carbon paper bioanode increased the performance of MFC inoculated with *S. oneidensis* MR-1 (Sun et al. 2010). The sputtered electrode showed improved electrochemical performances as compared to the control carbon paper which may be attributed to the enhanced MFC performance. Guo et al. (2012) constructed a bioanode by decorating Au nanoparticles on a carbon paper using layer-by-layer assembly method. The modified bioanode greatly enhanced MFC performance over the bare carbon paper. Here, Au layer on the modified electrode provided large active surface area and high conductivity for the efficient EET process. Several microbes are capable to produce metal nanoparticles when they are exposed to metal ions (Kalathil et al. 2011). A sulphate reducing bacterium,

Desulfovibrio desulfuricans formed membrane bound Pd-nano-assemblies after the exposure to Pd^{2+} ions (Wu et al. 2011). The membrane bound Pd networks facilitated electron transfer between the cells and electrode as a result of their higher electrical conductivity. Doping of bacteria with nanomaterials has shown to be an effective approach to accelerate EET processes in MFCs. For instance, doping of *Shewanella* with iron oxide/sulphide and nickel nanoparticles stimulated the EET rate as a result of enhanced bacterial electrical conductivity (Jiang et al. 2014).

It is generally believed that Cu and Ag are not biocompatible with bacteria (Grass et al. 2011). However, a recent report claimed that the antibacterial nature of these metals are not valid for electogenic bacteria (Baudler et al. 2015). Cu and Ag were utilized for the fabrication of bioanodes in MFCs. The bioanode modified with Cu and Ag produced maximum current density of 1.5 mA cm^{-2} and 1.1 mA cm^{-2}, respectively (Baudler et al. 2015). These current densities are comparable with benchmark, graphite bioanode (1 mA cm^{-2}). The similar performances of these expensive materials with carbon-based bioanodes raise a critical question that why expensive materials are employed for bioanodes as their performances are not better than the low cost carbon materials.

Titanium (Ti) has several advantages over conventional carbon and metal electrodes such as high biocompatibility, corrosion resistance and good dimensional stability (Zhou et al. 2016). However, Ti is not widely used as bioanodes in MFCs possibly due to poor electrical connection between bacterial cells and Ti. Zhou et al. (2016) proposed a possible solution to employ Ti as a bioanode by creating an oxide layer on the metal surface through heating. The oxide layer promoted the electron transfer between the cells and electrode by providing good electrocatalytic activities. Stainless steel is a material of choice for bioanode materials in MFCs as compared to conventional carbon-based materials. Stainless steel is a good conductive material with high mechanical strength and very stable at even severe experimental conditions. Also, the stainless steel is a cost-effective electrode with high resistance to corrosion that makes it as a first choice for the long-term operation. A systematic study conducted by Pocaznoi et al. (2012) has demonstrated that stainless steel can be an effective bioanode for MFCs as compared to carbon-based electrodes. The stainless steel anode produced a current density of 20.6 A m^{-2} while a graphite electrode delivered only 9.5 A m^{-2}. A major disadvantage of the stainless steel is its relatively smaller surface area as compared to traditional carbonaceous materials such as carbon cloth. To overcome this issue, a bioanode fabricated with stainless steel foam was employed in MFCs by producing a maximum current density of 80 A m^{-2} which was much higher than that of a plain stainless steel and carbon cloth (Ketep et al. 2014). Here, the foam structure provided a 3D porous structure for the efficient biofilm formation and mass transport. Several pretreatment processes have been proposed to improve the efficiency of stainless steel bioanodes. Heat treatment is a fruitful strategy to improve surface properties of the stainless steel (Guo et al. 2015).

A preheating of stainless steel at 600 °C for 5 min created an iron oxide layer on the surface that dramatically increased electrochemical interactions of the biofilm

and bioanode (Guo et al. 2015). The formation of iron oxide layer protected the electrode from corrosion. The heat treated stainless electrode produced a high current density of 1.5 mA cm^{-2} by showing its promising candidacy for the low cost and scalable bioanodes for MFCs. Similarly, flame oxidation of stainless steel produced iron oxide layer on the surface which was confirmed by X-ray diffraction spectroscopy (Yamashita et al. 2016). The flame oxidized electrode exhibited enhanced current generation over the controls (untreated stainless steel and carbon cloth). Bacterial community analysis showed high abundance of *Geobacter* on the flame oxidized electrode than the controls. The stimulated *Geobacter* growth on the modified electrode could result in high current generation in the MFC. The study revealed that the bioanode materials dictate the bacterial population in the electrode attached biofilm.

11.2.2 Cathode Materials

Cathode materials are the integral parts of MFCs and they critically affect the overall performance of the system. Low durability and high cost of the cathodes hinder the practical applications of MFCs. Oxygen reduction reaction (ORR) is usually occurring at the cathode by supplying oxygen from air. ORR follows either $2e^-$ or $4e^-$ reaction pathway by producing H_2O_2 or H_2O. However, H_2O ($4e^-$) pathway is more preferable due to the large consumption of electrons. Major obstacles that prevent the cathodic performances are high overpotential and catalyst poisoning that lead to kinetic losses in ORR. Here we discuss ORR based MFC cathodes by providing their current status and future perspectives. MFC cathodes are generally categorized as chemical and biological cathodes.

11.2.2.1 Chemical Cathodes

Carbon-based materials are commonly employed as MFC cathodes due to the low cost, high stability, good biocompatibility and large surface area. However, they suffer from poor reduction activities and need to be improved greatly to establish well-performing MFCs. Deposition of Pt catalysts on the carbon materials shows highest cathodic performance. But, the high cost of Pt catalyst prevents its practical applications and hence low cost materials should be investigated for the cost-effective electrodes. Anchoring of metal oxide nanoparticles on carbon supports is a promising approach for the development of low cost cathodes. For instance, Mn_2O_3 and Fe_2O_3 cathodes exhibited good ORR performances comparable with Pt cathodes (Martin et al. 2011). Santoro et al. (2015) developed an iron-aminoantipyrine (Fe-AAPyr) cathode for ORR in a single chamber MFC. The Fe-AAPyr cathode showed better performance than that of Pt and activated carbon cathodes. A biofilm formation was detected on the Fe-AAPyr cathode after long-term operation of the MFC. Usually the biofilm formation deteriorates the

performance of cathode by blocking catalytic active sites. Interestingly, the Fe-AAPyr cathode didn't exhibit any decrease in the performance even after the biofilm formation due to the long exposure to the wastewater. On the other hand, biofilm formation on the Pt cathode showed significant decrease in the ORR activity possibly due to the catalyst inactivation. These observations clearly show that the Fe-AAPyr is highly stable for long-term operation of MFCs without affecting its ORR activity under severe conditions of wastewater.

11.2.2.2 Biocathodes

Some aerobic bacteria have ability for ORR which is sometimes higher than that of conventional abiotic cathode catalysts (Kim et al. 2015). Biocathode represents a microbially catalyzed cathode which can perform reduction reactions such as ORR in MFC cathodes. It has several advantages over abiotic catalysts such as low cost, sustainability, and resistance to sulphide poisoning. Also, the biocathode has higher affinity for oxygen than Pt and usually aerobic bacteria can respire oxygen at maximum capacity with a dissolved oxygen concentration as low as 0.12 mg L^{-1} (Kim et al. 2015). Similar to bioanodes, carbon-based materials such as carbon cloth, carbon paper and graphite felt are commonly used as biocathode materials. Stainless steel is also proved to be a good candidate for biocathode formation. Mixed culture microbial consortia and pure cultures are employed to develop biocathodes (Butti et al. 2016). Zhang et al. (2012) systematically studied the role of cathode materials in the formation of MFC biocathodes by employing graphite felt, carbon paper and stainless steel mesh cathodes. The cathodes were inoculated using an anaerobic sludge. The graphite felt-biocathode showed maximum ORR activity over carbon paper and stainless steel mesh biocathodes. Increasing specific surface area for the microbial attachment is an effective way to accelerate the performance of biocathodes. Additions of graphite granules, activated carbon granules and activated carbon powder into cathode chambers enhanced MFC performance by providing high surface area for the biofilm formation that improved ORR activities of biocathodes (Tursun et al. 2016). Also, the improved biocathodes significantly reduced internal resistance of the MFC systems.

11.2.3 Membranes

MFCs usually employ membranes for separating anodes and cathodes. The membrane can prevent oxygen diffusion and substrate crossover between the chambers of MFC. However, the use of membranes adds huge cost to MFC design and hinders commercial applications. Also, they increase internal resistance and sometimes allow oxygen diffusion which adversely affects the MFC performance. Another major concern is membrane biofouling that diminishes the suitability of membrane-based MFCs for long-term applications. There are two types of membranes

available for MFCs namely cation exchange membranes and anion exchange membranes.

11.2.3.1 Cation Exchange Membranes

Cation exchange membranes (CEMs) such as Nafion, Hyflon, Zirfons and Ultrex CMI 7000 are generally employed as membrane separator for MFCs due to their high proton conductivity (Leong et al. 2013). Among them, Nafion is the mostly used membrane in MFCs as it is highly proton conductive because of the negatively charged hydrophilic sulphonate group. Thinner Nafion membranes are proved to be more effective for MFCs than the thicker ones as the former contribute less ohmic resistance (Jung et al. 1998). But, the thinner membranes suffer from high permeability of oxygen and substrate crossover that lower the Coulombic efficiency of the MFC system. To avoid this issue, optimization of the membrane thickness should be achieved for the better performance of MFCs. pH drop in the anode chamber is another major concern for the Nafion-based MFC (Kim et al. 2007). At the anode, the oxidation of substrate produces protons which may cause pH drop and this pH drop is significant with Nafion membranes. It is known that bacterial respiration at the anode is inhibited by low pH (Kim et al. 2007) that deteriorates the performance of MFC. Also, the Nafion membrane allows cations transport (e.g. Na^+) other than protons which causes charge imbalance between the anode and cathode.

11.2.3.2 Anion Exchange Membranes

Anion exchange membranes (AEMs) usually produce higher current generation over CEMs in MFCs. The protons generated at the anode are consumed by OH^- ions transferred from the cathode through the AEM that can largely prevent the anodic pH drop. Due to this property, the AEM lowers ion transport resistance and the cathode resistance caused by the precipitation of transported cations (Jingmei et al. 2013).

11.3 Bioelectrochemical Cell Designs

11.3.1 Dual Chamber

Dual chamber design is the first and most common design for MFCs and MECs. The design considers an anode chamber and a cathode chamber. Both the chambers are separated by a cation exchange membrane. Anode from anode chamber and cathode from cathode chamber connects externally with resistor. Dual chamber configuration was used for different designs by changing placement of each

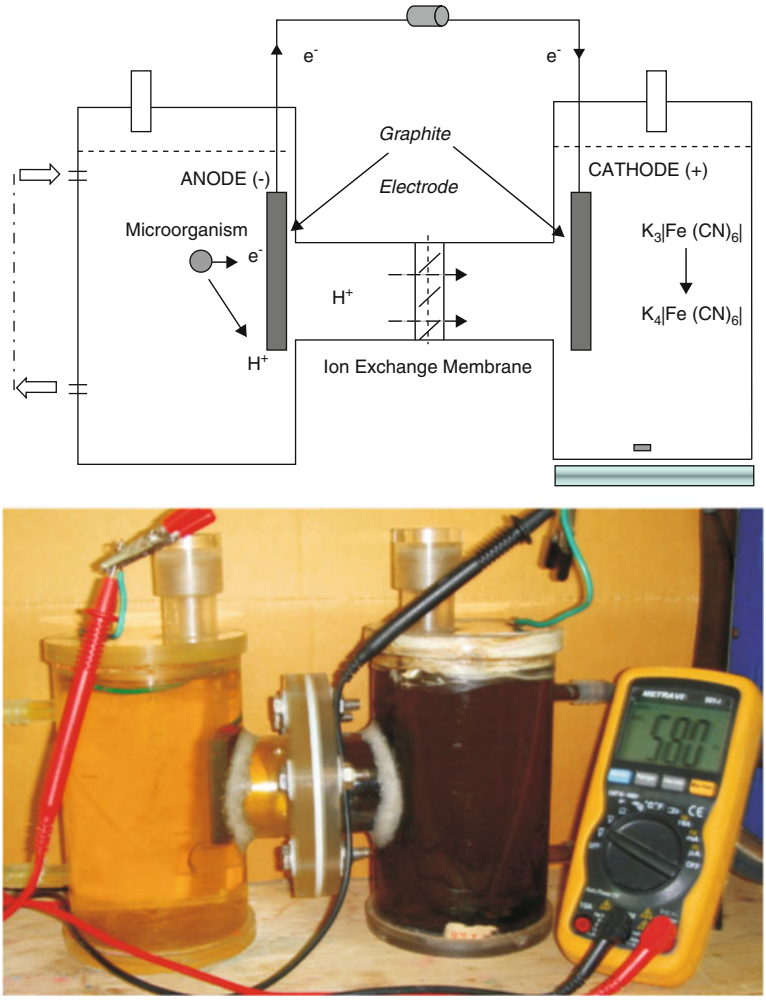

Fig. 11.3 Schematic details and photograph of H-type dual chambered MFC (Venkata Mohan et al. 2008)

chamber and using different shapes of chambers. Even though biocatalyst and the electron generation are confined to anode chamber, cathode reaction is also equally important. So, most of the studies were used with equal volumes of anode and cathode chambers. A typical H-type MFC is depicted in Fig. 11.3. Proton exchange membrane or cation exchange membranes were used as the membrane. As the design is simple and MFC performance is efficient, this design can be considered as the model for early stage researchers.

11.3.2 Single Chamber

After dual chamber configuration, single chamber design was studied. It contains only anode chamber and the cathode electrode is exposed to air. Here, atmospheric air or oxygen supplied on to the cathode surface acts as the catholyte and involves in oxygen reduction reaction (ORR). Compared to dual chamber design, this design was less efficient for electricity generation. However, the design was considered beneficial to scale up the process, where it requires less space for construction and set-up. When wastewater treatment is also major aim from the process, this design can deliver similar performance towards treatment but less bioelectricity generation. The design is also similar to the conventional anaerobic digesters for methane generation and it has the potential to convert the existing anaerobic digesters to MFCs (Fig. 11.4).

11.3.3 Stack Designs

In the course of scaling up the MFC technology stacking up the more number of MFCs into a single operating system was done. Practically, the maximum potential of single MFC (irrespective of anolyte volume) unit that can be achieved is approximately 1.0 V, which is very less and no proper application can be run with this potential except low power electronic modules and actuators has permitted the employment of MFCs in real applications as exemplified by Gastrobot (Wilkinson 2000) and EcoBots-I and -II (Ieropoulos et al. 2003; Melhuish et al. 2006). To achieve more potential and power, multiple electrodes need to be stacked to get the higher potential (Fig. 11.5). Since not much advantage is possible towards power generation with high volumes of MFCs, multiple MFCs with small volume were designed and integrated into a single operating system. First study with stacking of MFCs was reportedly done by Ieropoulos and co-workers (2003) in which approximately 50 times higher current generation was recorded than the output produced by the large MFC. The results from this study suggest that MFC scale-up may be better achieved by connecting multiple small-sized units together rather than increasing the size of an individual unit. It was also understood that the electrochemical connection and hydraulic/fluidic connections influence the MFC scaling up.

11.4 Future Perspectives and Conclusions

Electrode materials are the key components of the MFC systems and they dictate the performance of the MFC. Currently, many materials are available for the fabrication of both the anodes and cathodes. The application of improved electrodes

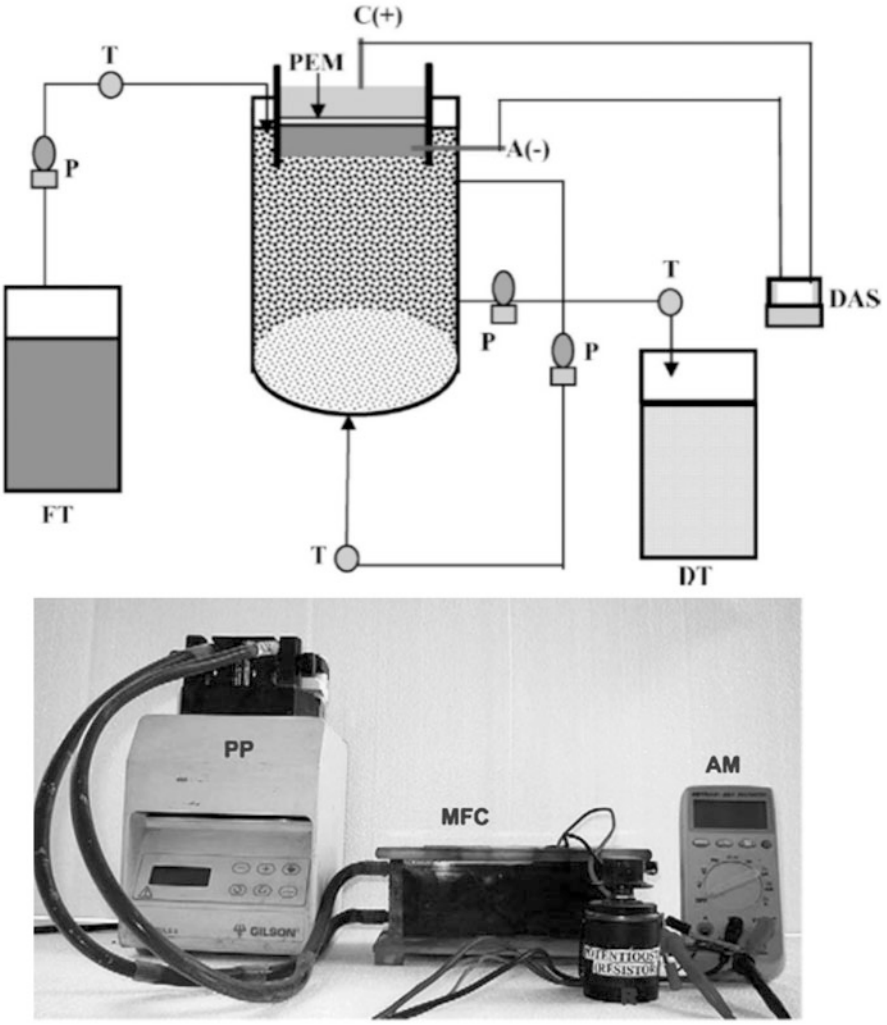

Fig. 11.4 Schematic details and photograph of single chambered MFCs used in different studies (*FT* feeding tank, *DT* decant tank, *T* pre-programmed timer, *P* peristaltic pump, *A(−)* anode, *C(+)* cathode, *PEM* proton exchange membrane, *DAS* data acquisition system, *MFC* single chambered microbial fuel cell, *PP* peristaltic pump, *AM* Multimeter, *R* variable resistor (Raghavulu et al. 2009)

significantly enhanced the MFC performance in terms of current output and wastewater treatment. However, many obstacles still need to be addressed for the practical application of these electrode materials. Even though some materials such as CNTs and graphene seem to be promising materials for the electrode development, the high cost and complicated synthesis procedures make them less attractive for the practical applications. Another major concern is the stability of the

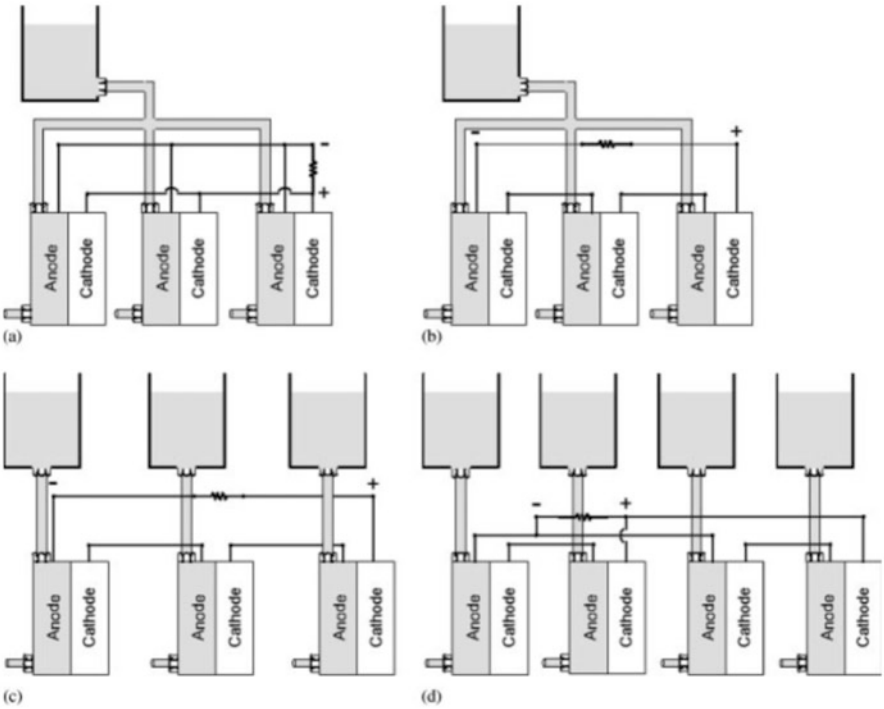

Fig. 11.5 Schematic representation of the different fluidic and electrical configurations for stacks of MFCs: (**a**) Parallel electrical connection with a common feed line; (**b**) Series electrical connection with a common feed line; (**c**) Series electrical connection but with individual feed lines; and (**d**) Series–parallel connections with individual feed lines and with an even number of MFCs (Ieropoulos et al. 2003)

electrode materials for the long-term applications. Unfortunately, most of the studies have been done for short duration with only concern on the power output by neglecting long-term stability of the materials. Hence, cost-effective and durable electrodes should be investigated to extend the MFC application in practical fields. 3D porous structures are more advisable for the electrode materials as they can allow dense biofilm formation and efficient mass transport including substrates. But, sometimes thick biofilm formation may prevent mass transfer that can create dead zones in the biofilms. Hence, a compromise on the biofilm formation and mass transport should be achieved to develop well-performing electrodes. The role of nanomaterials on the bacterial metabolism is currently largely unknown. A recent report demonstrated that CNTs can even alter bacterial respiration pathway from intracellular to extracellular (Yan et al. 2014). This observation warrants that a prior understanding on the action of nanomaterials on the bacterial metabolism is essential for the fabrication of efficient electrode materials for the MFC. The development of biocathode is a sustainable approach for the MFC cathodes. However, the

current knowledge on the biocathode mechanism is very limited and further investigations may lead to efficient biocathodes.

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