REVIEW OF LITERATURE
2.1 Fuel Cell

Fuel cells are electrochemical devices that generate electricity by converting chemical energy associated with the oxidation of fuel into direct current (DC) electricity. Since no combustion reaction is associated, fuel cells do not produce any of the undesirable products normally associated with the oxidation of fossil fuels in the conventional energy conversions system. Thus fuel cells are environmentally friendly.

In the fuel cell electricity is generated by the reaction between a fuel supply and an oxidizing agent. Hydrogen acts as the fuel and oxygen as the oxidizer. The hydrogen is fed continuously to the anode (negative electrode) compartment while oxygen is fed continuously to the cathode (positive electrode) compartment which is separated by an electrolyte which serves as the ion conductor (Grant, 2003). In the anode, the hydrogen is broken down into two components: hydrogen nucleus (proton) and an electron. The fuel cell was first demonstrated by a Welsh scientist Sir William Robert Grove in 1839 although the idea was first discovered by Christian Friedrich Schonbein, a German scientist in 1838. The efficiency of a fuel cell is dependent on the amount of power drawn from it, i.e., the more power drawn, the lower the efficiency. A typical fuel cell produces a voltage from 0.6 V to 0.7 V at full rated load (Larminie and Dicks, 2000). The electron is transferred to the cathode through the electric circuit whereas the proton migrates from the anode to the cathode through the electrolyte where it binds with the proton and the oxygen to form water which is the chemical product of the fuel cell (Logan, 2008).

Different types of fuel cells are there characterized by their electrolytes and different temperature of operation such as the Proton Exchange Membrane Fuel cell (PEMFC), Phosphoric acid Fuel cell (PAFC), Solid oxide Fuel cell (SOFC), Alkaline Fuel cell (AFC), Zinc Air Fuel cell (ZAFC) and Microbial Fuel cell (MFC).

2.2 Microbial Fuel Cell

Microbial fuel cell (MFC) is a device that converts organic matter to electricity using microorganisms as the biocatalyst. The development of processes that can use bacteria to produce electricity represents a fantastic method for bioenergy production as the bacteria are
self-replicating, and thus the catalysts for organic matter oxidation are self-sustaining (Logan, 2008). Most MFCs contain two electrodes separated into one or two chambers that are operated as a completely mixed reactor. The anode is present in the fuel cell or anode chamber. In the fuel cell oxidation occurs and electrons released from the fuel substrate are passed onto the anode in the fuel cell. Electron travels into the cathode chamber by an electrical connection. The cathode is the site where reduction i.e., the gain of electrons occurs by the oxidant present in the cathodic chamber. Simultaneously the positive ions generated in the anode chamber travel into the cathode chamber generally by way of an ion permeable membrane between the two chambers which completes the electrical circuit.

The possibility of direct conversion of organic material in wastewater to bio-electricity is exciting, but fundamental understanding of the microbiology and further development of technology is required. With continuous improvements in microbial fuel cell, it may be possible to increase power generation rates and lower their production and operating cost (Logan, 2008). Thus, the combination may help in saving of millions of rupees as a cost of wastewater treatment at present.

The first observation of electrical current generated by bacteria is credited to Potter (Potter, 1911). A very few practical advances were achieved in this field even 55 years later (Lewis, 1966). In 1990s, work on MFCs began to increase (Allen and Bennetto, 1993) but the breakthrough in MFCs occurred in 1999 when it was recognized that mediators did not need to be added (Kim et al., 1999).

Iron reduction coupled with glucose oxidation can be described by the following reaction (Bilgin et al., 2005):

\[
24Fe^{3+} + C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24Fe^{2+} + 24H^+ \quad \text{......... (3)}
\]

The reduced iron is oxidized at the electrode, giving Fe (III) as follows:

\[
Fe^{2+} \rightarrow e^- + Fe^{3+} \quad \text{......... (4)}
\]

The electrons are received at the cathode by oxygen, producing water:

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad \text{......... (5)}
\]

Acidophilic organisms and systems capable of transferring electrons at a high rate to the electrodes may have significant potential for generation of electricity via microbial fuel cells.
The popularity of the MFC technology has risen exponentially during the last few years because there is a hope that MFCs will allow harvesting the energy stored in wastewater directly in the form of electricity. This should place MFCs directly in competition with anaerobic digestion (AD) as a more sustainable and environment-friendly alternative to conventional activated sludge (CAS). Loading rate plays important role in MFC operation and at higher loads, performance appears to decrease quickly (Rabaey et al., 2003). MFCs are highly efficient as a biological treatment system at low to moderate loading rates, possibly achieving high COD removal, depending on the substrate (Liu and Logan, 2004). The part of the energy bound to wastewater is diverted into electricity in an MFC results in reduced sludge accumulation as compared with CAS (Rabaey and Verstraete, 2005).

2.3 MFC configuration

Practical applications of MFCs will require that we develop a design that will not only produce high power and columbic efficiencies, but one that is also economical to mass produce based on the materials being affordable and the manufacturing process being practical to implement on a large scale. While the reactor designs that will ultimately prove to meet these requirements of power, efficiency, stability, and longevity are still being developed, studies
showed that scalable and economical systems can be developed using graphite fibre brush electrodes and tubular cathodes immersed together in a tank. However, such a reactor has yet to be built at pilot or large scale till date. Thus, the final design and the materials that will ultimately be used in a large-scale system remain unproven at this time.

Applications of microbial fuel cells (MFCs) promise energy-efficient conversion of dissolved organics and electron donors and even the generation of useful carbon neutral power (Rabaey and Verstraete, 2005). Certainly in the context of energy efficient wastewater treatment, considerable attention has been received (Rabaey et al., 2005). The process that drives them, extracellular electron transfer, has in recent years shown high versatility in the type of conversions that can be achieved (Rabaey et al., 2007). Therefore, a broader array of applications is emerging, ranging from cathode driven denitrification to anode driven sulphide removal (Clauwaert et al., 2007).

To underline their versatility beyond energy generation, MFCs should rather be designated ‘Bio-Electrochemical Systems’. In Bio-Electrochemical Systems, bacteria have been found to deploy several strategies to use electrodes as electron acceptors. Bacteria produce or use soluble components as electron carriers (Rabaey et al., 2005). A direct contact is established either through membrane-bound complexes (Bond and Lovely, 2003) or through conductive nanowires (Reguera et al., 2005; Gorby et al., 2006). Those processes have been extensively studied for electrons flowing away from bacteria but how bacteria take in electrons from insoluble donors has not been established yet, despite a rapidly increasing number of studies on biocatalyzed cathodes (He and Angenent, 2006).

2.3.1 Single chamber microbial fuel cell

Single chambered MFC are simple anode compartment where there is no definitive cathode compartment and may not contain proton exchange membranes. Porous cathodes form one side of the wall of the cathode chamber utilizing oxygen from atmosphere and letting protons diffuse through them. They are quite simple to scale up than the double chambered fuel cells and thus have found extensive utilization and research interests lately. The anodes are normal carbon electrodes but the cathodes are either porous carbon electrodes or PEM bonded with flexible carbon cloth electrodes. Cathodes are often covered with graphite in which electrolytes are poured in steady fashion which behaves as catholyte and prevent the membrane
and cathode from drying. Thus water management or better fluid management is an important issue in such single chambered fuel cells. Park and Zeikus (2003) (Fig 2.2) designed a single chambered MFC consisting of a rectangular anode chamber coupled with a porous air cathode that is exposed directly to the air. But it is found that MFC without the membrane produces lower cumbolic efficiency due to increased diffusion of oxygen into the anode. Additionally, high concentrations of hydrogen gas in the absence of oxygen in a single chamber MFC favours the growth of methanogens which can lower hydrogen recoveries and contaminate the gas with methane (Rozendal et al., 2006). Therefore, single chamber MFC suffers from low overall efficiency.

![Single chamber microbial fuel cell](image)

**Fig. 2.2: Single chamber microbial fuel cell**

According to Bruce Logan, single chamber microbial fuel cells are important because it facilitates a "continuous flow-through system," a design consistent with existing treatment systems.

### 2.3.2 Dual chamber microbial fuel cell

Dual chamber microbial fuel cells can be of a variety of shapes such as U-shape with cathode in one arm of the tube and anode being in the other arm. Both the electrodes are separated by ion selective membrane such as proton exchange membrane that permits only protons to pass through it and not to the solutions and microbes itself. The other common design of dual chamber MFC use simple H- shaped assembly with anode in one side and cathode on the other, both separated by proton exchange membrane.
Basically MFCs are of two types as mentioned above but researchers have developed another types as well that comes under broad category of single and dual chambered MFCs like U shaped MFC in which anode will be placed on bottom and cathode will be in the form of a wires to provide bigger surface area to increase in current as well overall coulomb transfer rate.

Dual chamber microbial fuel cells can also be constructed in a column with anode at the bottom and cathode at the top of the column as used by Jang et al., 2004.
2.4 Difference between the single and double chamber MFC

The basic difference between the single and double chamber MFC is

- The absence of membrane in single chamber MFC.
- In the double chamber different conditions can be maintained in each compartment.
- The rate of oxygen diffusion into the anode without an ion permeable membrane (single chamber) is 2.7 times higher than the double chamber design.
- Advantage of the single chamber MFC is the reduced set up costs, higher power output.
• The disadvantage of single chamber MFC is the low coulombic efficiency generally because of diffusion of oxygen into anode i.e. consumption of oxygen by the bacteria.

2.5 Microorganisms and Microbial Fuel Cell

Earlier it was thought only few microorganisms can be used to produce electricity. But recently it was observed that most of the microorganisms can be utilized in MFCs. MFC concept was demonstrated as early in 1910 where *Escherechia coli* and *Saccharomyces sp.* were used to generate electricity using Platinum electrodes (Potter, 1911). Marine sediment, soil, wastewater, freshwater sediment and activated sludge are all rich sources for the microorganisms (Niessen et al., 2006; Zhang et al., 2006). Microorganisms survive and grow due to the energy they generate by transferring electrons. During respiration, microorganisms liberate electrons from an electron rich substrate at a low redox potential and transfer these electrons through a number of electron transport complexes through the cell membrane where a final electron acceptor is reduced.

Respiring microorganisms can use a large variety of different electron acceptors, ranging from oxygen, nitrate, iron and manganese oxides to sulfate, but their ability to use the acceptor with the highest redox potential will increase their energy for growth (Madigen et al., 2000) and is their incentive to explore alternative electron acceptors. Microorganisms do not use the energy produced by the flow of electrons in a direct way, the flow of electrons is used to create a proton gradient across the cell membrane (Kim et al., 2003). The energy released by the inward flux of the protons through a membrane complex (ATP synthase) is used to regenerate energy carrier molecules such as adenosine triphosphates (ATP). By creating this proton gradient, the potential difference between the electron donor (i.e. the substrate at low potential) and the electron acceptor is translated into a process for the generation of energy (Logan, 2008). The higher the potential difference between the electron donor and electron acceptor, the higher the proton driven potential difference and the higher the potential amount of ATP which can be refuelled.

There are three categories of microbes that can be used in MFCs:

(a) Those that can directly transfer electrons to anode using anode as terminal electron acceptor;
(b) Those that can’t directly but use mediators to transfer electrons to anode;
(c) Those who can accept electron from cathode.
<table>
<thead>
<tr>
<th>Microorganisms</th>
<th>Substrates</th>
<th>Mediators</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Actinobacillus succinogenes</em></td>
<td>Glucose</td>
<td>Neutral red or thionin as electron mediator (Park and Zeikus 1999; Park and Zeikus, 2000)</td>
</tr>
<tr>
<td><em>Escherichia coli</em></td>
<td>Glucose, Sucrose</td>
<td>Mediators such as methylene blue needed. (Schroder et al., 2003; Ieropoulos et al., 2005, Grzebyk and Pozniak, 2005; Devasahayam and Masih, 2012)</td>
</tr>
<tr>
<td><em>Enterobacter aerogene and cloacae</em></td>
<td>Acetate and Sucrose</td>
<td>Mediator-less MFC (Masih et al., 2012a)</td>
</tr>
<tr>
<td><em>Geobacter metallireducens</em></td>
<td>Acetate</td>
<td>Mediator-less MFC (Min et al., 2005)</td>
</tr>
<tr>
<td><em>Geobacter sulfurreducens</em></td>
<td>Acetate</td>
<td>Mediator-less MFC (Bond et al., 2002; Bond and Lovely., 2003)</td>
</tr>
<tr>
<td><em>Shewanella putrefaciens</em></td>
<td>Lactate, Pruvate, Acetate, Glucose</td>
<td>Mediator-less MFC (Kim et al., 1999) but incorporating an electron mediator like Mn (IV) or NR into the anode enhanced the electricity production (Park and Zeikus, 2002)</td>
</tr>
<tr>
<td><em>Shewanella oneidensis</em></td>
<td>Lactate</td>
<td>Anthraquinone-2,6-disulfonate (AQDS) as mediator (Ringeisen et al., 2006)</td>
</tr>
<tr>
<td><em>Lactobacillus plantarum</em></td>
<td>Glucose</td>
<td>Ferric chelate complex as mediators (Vega and Fernandez, 1987)</td>
</tr>
<tr>
<td><em>Desulfovibrio desulfuricans</em></td>
<td>Sucrose</td>
<td>Sulphate/sulphides mediator (Park et al., 1997; Ieropoulos et al., 2005)</td>
</tr>
</tbody>
</table>
### Table 2.2: Details of different water samples used in MFC operations

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Water Sample</th>
<th>Power Density</th>
<th>Coulombic</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical waste Water</td>
<td>24.33</td>
<td>61.11</td>
<td>VenkataMohan et al., 2008</td>
</tr>
<tr>
<td>2</td>
<td>Designed synthetic water</td>
<td>11.50</td>
<td>62.5</td>
<td>VenkataMohan et al., 2008</td>
</tr>
<tr>
<td>3</td>
<td>Primary treated municipal waste</td>
<td>180.73</td>
<td>73.5</td>
<td>Masih et al., 2011</td>
</tr>
<tr>
<td>4</td>
<td>Domestic waste</td>
<td>0.0070</td>
<td>43</td>
<td>Min et al., 2008</td>
</tr>
<tr>
<td>5</td>
<td>Musi river</td>
<td>0.00066</td>
<td>-----</td>
<td>VenkataMohan et al., 2009</td>
</tr>
<tr>
<td>6</td>
<td>Godavari river</td>
<td>0.00045</td>
<td>-----</td>
<td>VenkataMohan et al., 2009</td>
</tr>
<tr>
<td>7</td>
<td>Starch</td>
<td>0.0239</td>
<td>8</td>
<td>Lu et al., 2009</td>
</tr>
<tr>
<td>8</td>
<td>Swine</td>
<td>0.0261</td>
<td>8</td>
<td>Min et al., 2005</td>
</tr>
</tbody>
</table>

### 2.6 MFC Classification

- One type generates electricity from the addition of artificial electrons shuttles to accomplish electron transfer to the electrodes because most of the microbial cells are electrochemically inactive. The electron transfer from microbial fuel cells to the electrode is facilitated by mediators such as thionine, methyl viologen, methyl blue, humic acid, neutral red and so on (Delaney et al., 1984).

- Other type does not require this addition of exogenous chemicals and can be loosely define mediator MFC. Mediator-less microbial fuel cells do not require a mediator but uses electrochemically active bacteria to transfer electrons to the electrode (electrons are carried directly from the bacterial respiratory enzyme to the electrode) (Kim et al., 1999; Chaudhuri and Lovely, 2003). Some bacteria, which have pili on their external membrane, are able to transfer their electron production via these pili.

Among the electrochemically active bacteria are *Shewanella putrefaciens*, (Kim et al., 1999) *Aeromonas hydrophila*, and others. *Geobacteraceae sulfurreducens* (Bond and Lovely, 2003), *Geobacteraceae metalloreducens* (Min et al., 2005) are all bioelectrochemically
active and can form a biofilm on the anode surface and transfer electrons directly by conductance through the membrane and cathode acts as the final electron acceptor in the dissimilatory respiratory chain of the microbes in the biofilm.

Biofilms forming on a cathode surface may also play an important role in electron transfer between the microbes and the electrodes. *G. metalloreducens* and *G. sulfurreducens* (*Gregory et al., 2004*) or other seawater biofilms (*Bergel et al., 2005*) may all act as final electron donors. Since the cost of a mediator is eliminated, mediator-less MFCs are advantageous in waste water treatment and power generation. Cathodes can serve as electron donors for *Thiobacillus ferroxidans* suspended in a catholyte (*Prasad et al., 2006*) for an MFC system that contained microbes in both anodic and cathodic chambers.

Mediator less MFCs can be consider to have more commercial potential then MFCs that require mediators because the typical meditors are expansive and toxic to microorganism. This same principle can be used to design both a dual chamber MFCs and single chamber MFCs where the anode chamber is separated from the air cathode chamber by a gas diffusion layer allowing for a passive oxygen transfer to the cathode eliminating the need for the energy intensive air sparging of the liquid.

2.7 Electrode

The anode can be defined as the electrode at which electrons leave the cell and oxidation occurs, and the cathode as the electrode at which electrons enter the cell and reduction occurs.

2.7.1 Anode

An anode are highly conductive, on corrosive, high specific surface area, non-foulting, high porosity, inexpensive and easily made and scaled to large size the most important property is different from other biofilm reactors is that the material must be electrically conductive like carbon paper, cloth, foams, and RVC (Reticulated vitrified carbon). There are few direct comparisons on the effect of these different carbonaceous materials on power generation. Recall that if high internal resistance limits power generation, increasing anode surface area may not appreciably affect power output, making it difficult to know if one material performed better than another. In two chambered MFCs with equally-sized electrodes, it was found that an increase in power could be observed when the anode size was increased relative to the cathode only when the CEM size was substantially increased (*Oh and Logan, 2006*).
2.7.1.1 Carbon paper and Carbon cloth

It is stiff and slightly brittle but it is easily connected to a wire. It should be sealed to the wire using epoxy, with all exposed surfaces of the wire covered or sealed with epoxy as well. Copper wire can be used but it corrodes over time, either releasing copper into solution (which can be toxic to the bacteria) or causing the electrode to detach from the wire. Stainless steel or titanium wires work well in MFCs. Carbon paper is commonly available in plain and wet-proofed versions, with plain paper suggested for anode applications. Carbon cloth is more flexible and appears to have greater porosity than carbon paper (Zhao et al., 2008).

2.7.1.2 Carbon foams

Carbon foams are much thicker than the cloths, conferring more space for bacterial growth. They have not been as extensively used in MFC studies as the paper and cloth materials. (Morozan et al., 2007).

2.7.1.3 Reticulated vitrified carbon (RVC)

It has been used in several studies (He et al. 2005; He and Angenent, 2006). The conductivity of the material is excellent at 200 S/cm (5 ×10\(^{-3}\) cm). It is quite porous (97%), with different effective pore sizes specified by a manufacturer. The main disadvantage of the material is that it is quite brittle.

2.7.1.4 Graphite rods

There are a large variety of graphite materials to choose from for MFC electrodes which vary greatly in price, composition, and surface area. Graphite rods have been used in several MFC studies (Bond et al., 2002; Chaudhuri and Lovely, 2003; Liu et al., 2004; Reimers et al., 2006) as they are highly conductive and have relatively defined surface areas (low internal porosity), and they have been extensively used in electrochemical studies.

2.7.1.5 Graphite sheets

Graphite sheets can be purchased in a variety of thicknesses like pencil lead, are soft and will mark paper. These sheets are flat they are excellent surfaces to use for microscope-based analysis of electrochemically active bio films. However, graphite sheets are not porous and thus
produce less power per geometric (projected) surface area than felts or foams but there porosity can be induced by dipping them in saline solution and there active surface area can be increased by making holes in it so that more number of microbes can be attached to it (VenkataMohan et al., 2008; Masih et al., 2011).

Current densities using a graphite rod, graphite felt or graphite foam were compared and found effective (Chaudhuri and Lovely, 2003). It was found that increasing the total accessible geometrical (projected) surface area increased current generation by Rhodoferax Ferrireducens in two-chamber, poised-potential MFCs.

2.7.1.6 Graphite granule

Graphite granules are chunks of graphite that resemble pencil lead in their appearance and are available from many different sources (e.g., Graphite Sales, Inc., Chagrin Falls, OH). The first use of these materials was reported by Rabaey et al. (2005) as an anode material, but they have since been used in other packed-bed reactors as both anodes and cathodes (Aelterman et al., 2006; Heilmann and Logan, 2006; Rabaey et al., 2006).

2.7.1.7 Graphite fibers and brushes

The highest specific surface areas and porosities form anodes can be achieved using graphite fiber brush electrodes (Logan et al., 2007). These brushes can be made from carbon fibers produced by different manufacturers using conventional industrial brush machines. The core of the wire can be made from non-corrosive metal.

2.7.2 Cathode

The design of the cathode is the single greatest challenge for making an MFC a useful and scalable technology. The chemical reaction that occurs at the cathode is difficult to engineer as the electrons, protons and oxygen must all meet at a catalyst in a tri-phase reaction (solid catalyst, air, and water). The catalyst must be on a conductive surface, but it must be exposed to both water and air so that protons and electrons in these different phases can reach the same point.
2.7.2.1 Carbon cathodes with Pt catalysts

The most commonly used material for a cathode is commercially available carbon paper pre-loaded with a Pt catalyst on one side, available from different manufacturers (e.g., E-Tek, USA, 0.35 mg-Pt/cm²). When used in the MFC, the side containing the catalyst faces the water, with the uncoated side facing air. Catalyst binders, when the catalyst is applied to carbon it must be held there using a material that allows transfer of protons, electrons and oxygen. Nafion is therefore typically used due to its high proton conductivity and oxygen permeability. Other materials such as polytetrafluoroethylene suspension (PTFE) can also be used (Cheng et al., 2006) prepared Pt-based cathodes.

2.7.2.2 Carbon cathodes with non-Pt catalysts

Park and Zeikus (2002) first experimented with non-precious-metal, carbon-based air cathodes in MFCs. They made ferric (Fe³⁺) cathodes by forming plates out of ferric sulfate (3% w/w), fine graphite (60%), kaolin (36%, as a binder), and nickel chloride (1%) and baking at 1100°C for 12 h under N₂ gas. These iron cathodes produced up to 3.8 times as much power as plain woven graphite cathodes, but they were not compared to Pt-based cathodes of similar dimensions (Park and Zeikus, 2003). Cathode performance equal to that of Pt-based carbon cathodes has now been achieved using transition-metal carbon cathodes, thus eliminating the need for precious metals in MFCs. Zhao et al., (2005) showed in electrochemical tests that two different transition metal catalysts, iron phthalocyanine (FePc) or cobalt tetra methoxy phenylporphyrin (cotmpp), could produce power at levels comparable to or better than those achieved with Pt-based cathodes at current densities.

2.7.2.3 Plain carbon cathodes

The efficiency of a catalyst is often assessed by comparing current or power densities to those with plain carbon electrodes of the same surface area. An oxygen reduction still proceeds in the absence of the catalyst, but the rate is reduced. In general, current and power are reduced by a factor of 10 or more with plain carbon materials. However, if the cathode surface area is substantially increased, it is possible to achieve much higher power densities. Reimers et al. (2006) tested sediment MFC that had 1-m long carbon brush cathodes the use of carbon brush cathodes was first tested by Hasvold et al., 1997 with magnesium alloy anodes.
2.7.2.4 Tubular carbon-coated cathodes

MFCs require high surface areas and porosities typical of wastewater reactors. One new approach to wastewater treatment has been to use tubular ultrafiltration membranes, providing high surface areas for filtering the treated water. Based on that idea of high surface areas provided by these membranes, Zuo et al. (2007) developed a tubular cathode by applying a conductive graphite paint material to a hydrophilic tubular ultrafiltration membrane (polysulfone membrane on a composite polyester carrier) that had an inner diameter of 14.4 mm (B0125, X-FLOW) and wall thickness of 0.6 mm. The tubes were coated on the air-facing side with a proprietary graphite paint to make the tube electrically conductive.

Apart from the same material even can be used in both anode and cathode and even without plating material will provide sufficient electron flow by applying holes in electrodes (Masih et al., 2011)

2.8 Membrane and separators

In MFC, a membrane is an essential component of the system as it separator and provides a method for conducting protons between two gases. The membrane is therefore referred to as a proton exchange membrane. Liu and Logan (2004) showed that an MFC lacking a membrane produced more power than an MFC with the membrane (Nafion) bonded to the cathode, indicating that the membrane can adversely effect power generation (Fig. 2.6).

2.8.1 Cation exchange membranes

The most commonly used cation exchange membrane (CEM) is Nafion 117 (Dupont Corp.) available from Ion Power, Inc and there the code (117) is indicate the thickness of membrane (0.019 cm) This membrane was developed for use in an HFC and thus was optimized to create a stable and conductive environment for high proton concentrations under conditions where the water content is carefully controlled. However, this material becomes completely saturated with water in an MFC, producing a pH reflective of the solution properties. Thus, it
does not function according to its intended purpose in an MFC as it cannot operate under its designed conditions.

Fig. 2.6: Different types of membranes, (a): Cation exchange membrane (CMI-7000); (b): anion exchange membrane (AMI 7001); (c): Nafion 117 membrane

A CEM membrane (CMI-7000) made by Membrane International Inc., NJ, has been used in several MFC studies, mostly those with ferricyanide as the catholytes (Rabaey et al., 2003; He et al., 2005; Rabaey et al., 2005; Masih et al., 2011, Devasahayam and Masih, 2012). This membrane is much thicker and stiffer than the Nafion 117 (0.046 cm) and in general appears to be structurally stronger. There are many manufacturers of CEMs which could be used in MFCs, but these have not been compared for their performance in MFC applications.

Nafion is also referred to as a PEM on the basis that it is designed to transfer protons (H\(^+\)), but in an MFC it preferentially conducts other positively charged species (Na\(^+\), K\(^+\), NH\(_4\)\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) that are present at typically 10\(^5\) times higher concentrations than protons in solution (Rozendal et al., 2006).

2.8.2 Anion exchange membranes

Kim et al. (2007) recognized that protons can also be effectively transported by chemicals used as a pH buffer, such as phosphate anions. So, they used an anion exchange membrane (AEM; AMI-7001, Membranes International, Inc.) as the separator in two-chambered MFC tests. The higher power was produced using the AEM than with two different CEMs (Nafion and the CMI-7000). The phosphate ion transferred across the membrane and that pH was better maintained in the anode chamber that was shown by monitoring the phosphate concentrations on one side of membrane in the chambers.
2.8.3 Bipolar membrane

A bipolar membrane consists of an anion and a cation membrane joined in series. As voltage develops rather than protons passing the membrane water is split, resulting in the transport of anions (OH\textsuperscript{-}) to the anode and cations (H\textsuperscript{+}) to the cathode to balance charge. The energy needed for the water splitting reaction is claimed to be small because water is split into ionic species, H\textsuperscript{+} and OH\textsuperscript{-}. There also examined power output in a MFC with a salt bridge instead of a membrane system. The low power output was directly attributed to the higher internal resistance of the salt bridge system compared to that of the membrane system based on measurements using impedance spectroscopy. In both systems, it was observed that oxygen diffusion from the cathode chamber into the anode chamber was a factor in power generation (Min et al., 2005). Ter Heijne et al. (2006) developed an MFC based on using a ferric iron catholyte. Using a bipolar membrane, they were able to maintain the low pH in the cathode chamber and near-neutral pH in the anode chamber.

2.9 Role of substrate in MFC

The production of current in an MFC is directly linked to the ability of bacteria to oxidize a substrate and transfer electrons resulting from this oxidation to the cathode electrode. The current and power density (PD), columbic efficiency (CE) and pollutants removal efficiencies differ between the various studies according to the experimental conditions (initial wastewater composition, concentration, and MFC set up conditions). Since there different types of substrate that provide energy to the microbes and help them to degrade organic matter while producing electricity. Substrate choice may be of two types: fermentable substrate and non fermentable substrate. Study showed that fermentable substrates are less efficient than non fermentable substrate while used in same set up of MFC (Masih et al., 2011; Masih et al., 2012a; Devasahayam and Masih, 2012).

2.9.1 Sucrose

Sucrose was used as a fuel in a thionine-mediated microbial fuel cell containing Proteus vulgaris serving as the biocatalyst in the anode compartment. In study sucrose of 0.4% concentration in various water samples and pure microbial cultures of Enterobacter cloacae,
Enterobacter aerogene and E.coli has been used and showed voltage in the range of 700 mV (Masih et al., 2011; Masih et al., 2012b; Devasahayam and Masih, 2012). The measured yields show that under suitable conditions the substrate may be oxidized quantitatively to electricity and carbon dioxide (Bennetto et al., 1985). Since this process is carried out in an anaerobic condition, carbon dioxide, protons and electrons are produced as below:

Anodic reaction:

\[
C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^- \quad (6)
\]

Cathodic reaction:

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (7)
\]

2.9.2 Cellulose

Cellulose is the most abundant biopolymer, and there is great interest in using this chemical as a substrate in an MFC. However, use of a particulate substrate in an MFC has not been well investigated. Cellulosic materials are desirable feedstocks for alternative fuels and energy carriers such as ethanol, biodiesel, or hydrogen since they are renewable and abundant (Mielenz, 2001; Powlson et al., 2005; Ni et al., 2006). Cellulose must first be hydrolyzed to a soluble substrate that can be taken up by the cell. In previous MFC tests this has required the use of enzymes to hydrolyze.

Since cellulose is substrates that cannot be directly utilized by bacteria it has to be converted to monosaccharides. Microbes utilizing cellulose should be having cellolytic and exoelectrogenic activities. Ren et al., 2007 used a culture of the cellulose fermentor Clostridium cellulolyticum and the exoelectrogen Geobacter sulfurreducens to generate electricity in an MFC fed with cellulose (Rezaei et al., 2009). Recently raw corn stover has been used for electricity generation but its power generation capacity was found to be much lesser than that in the case of glucose (Wang et al., 2009).

2.9.3 Acetate

Acetate is a mild acid and simple substrate and it is extensively used as carbon source to induce electro active bacteria (Bond et al., 2002; Masih et al., 2012a,b). In order to benchmark
new MFC components, reactor designs or operational conditions, acetate is commonly used as a substrate because of its inertness towards alternative microbial conversions (fermentations and methanogenesis) at room temperature (Aelterman, 2009).

Further, acetate is the end product of several metabolic pathways for higher order carbon sources. Very recently, Chae et al. (2009) compared the performance of four different substrates in terms of CE and power output. Acetate-fed MFC showed the highest CE (92%) (Masih et al., 2012a), followed by butyrate (43.0%), propionate (36.0%) and glucose (15.0%).

Also, when acetate was compared with various wastewater samples as substrate in MFC, the MFC based on acetate-induced consortia achieved more than 2-fold maximum electric power, and one half of optimal external load resistance compared to the MFC based on consortia induced by a protein-rich wastewater (Liu et al., 2009; Masih et al., 2011). When acetate is used as a substrate the reactions occurring at the anode and cathode are as follows:

Anodic reaction:

\[
\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8e^- + 7\text{H}^+ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
rods, carbon felt or foam electrodes) was produced with a two-chamber system. Coulombic efficiency was 83% with a poised potential working electrode and was 81% using ferricyanide at the cathode. Fructose, sucrose, and xylose also produced power (Choudhary and Lovely, 2003).

The possibility of various reactions occurring in anode and cathode chambers of MFCs with glucose as substrate considering complete oxidation are depicted in the following equations.

\[
\text{Anode} : \quad C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (10)
\]

\[
\text{Aerated catholyte} : \quad nO_2 + H^+ + e^- \rightarrow H_2O \quad (11)
\]

\[
\text{Ferricyanide catholyte} : \quad 4\text{Fe(CN)}_6^{3-} + 4e^- \rightarrow 4\text{Fe(CN)}_6^{4-} \quad (12)
\]

\[
O_2 + 4[\text{Fe(CN)}_6]^{3+} + 4H_+ \rightarrow [\text{Fe(CN)}_6]^{2+} + 2H_2O \quad (13)
\]

A reactor inoculated with a river sediment using a low concentration of glucose and glutamate produced an *Alphaproteobacteria-dominated* community (Phung et al., 2004). Aelterman et al. (2006) examined the microbial community that developed over time in a six-stack MFC fed glucose and using ferricyanide at the cathode. Zhang et al. (2007) also used ferricyanide in a two-bottle type of MFC, producing 50 mW/m² with a glucose substrate, and 70 mW/m² with acetate. However, the finding of a coulombic efficiency of 96.8% by *Geobacter sulfurreducens* seems unreasonably large, suggesting that either substrate had been accumulated in the bacteria (Freguia et al., 2007). Devasahayam and Masih, 2012 used glucose with pure culture of *E.coli* and yamuna river samples in dual chambered MFC and showed maximum voltage of 779 mV and 463 mV respectively.

2.9.5 Synthetic wastewater

Synthetic wastewaters of much defined chemical composition and pH have been also used. The wastewater was prepared by mixing Na₂HPO₄, NaH₂PO₄, KH₂PO₄, CuSO₄, MnSO₄, MgSO₄, and ZnSO₄ etc. (VenkataMohan et al., 2008) has used different wastewater at different loading rates to achieve performances.

Logan et al., 2009 have done an experiment in which they have used two different synthetic wastewaters with the same organic pollutants (glucose and peptone) and same loading rates. One was fed with readily biodegradable substrate and other with slowly degradable substrate. The results of such experiments showed that MFC with slowly degradable waste was
more efficient in terms of electricity generation probably because of production of intermediates that favors electricity generation.

2.9.6 Dye wastewater

Sun et al., 2009 have reported that electricity generation was affected by higher concentrations of ABRX3 an azo dye. The probable reason for this was due to competition between the azo dye and anode for the electrons from carbon sources.

2.9.6 Brewery wastewater

Because of the food derived nature of organic matter and lack of inhibitory substances in the brewery it is considered to be a good source of electricity. Other properties of brewery wastewater such as high carbohydrate content and low ammonium nitrogen concentration make it an ideal substrate for MFC operation. However maximum power produced by brewery wastewater was lower than that obtained with the domestic wastewater. This may be because of differences in the conductivities of two solutions. Wen et al., 2009 has suggested that important factors affecting the performance of brewery wastewater MFC are reaction kinetic loss and mass transport loss.

2.9.7 Sunlight

A solar powered MFC was described by Cho et al. (2008) in which only Rhodobacter sphaeroides (fed on succinate) was used as the anodic bacterium. The power output (790 mW/m²) in this case was dependent on both light and the nature of the nitrogen source. The plant MFCs in rice paddy fields have been reported to produce electricity by rhizosphere populations oxidizing organic carbon delivered to the rhizosphere (Kaku et al., 2008). Similar proof of principle was also demonstrated using reed mannagrass (Glyceria maxima) and maximum power of 67 mW/m² anode surface was achieved (Strik et al., 2008a). Another type of phototrophic MFC, a photosynthetic algal MFC was investigated (Strik et al., 2008b) which produced a maximum power of 110 mW/m² surface area of photobioreactor. The organic matter produced in the algal photobioreactor via photosynthesis was supplied to a MFC for electricity generation.

2.9.8 Starch processing wastewater

Starch processing wastewater (SPW) contains a relatively high content of carbohydrates (2300–3500 mg/L), sugars (0.65–1.18%), protein (0.12–0.15%) and starch (1500–2600 mg/L),
representing an important energy-rich resource, which can be potentially converted to a wide variety of useful products (Jin et al., 1998) and was used as a fuel to enrich a microbial consortium generating electricity and current generation (0.044 mA/cm²) was coupled to a fall in COD from over 1700 mg/L to 50 mg/L in 6 weeks (Kim et al., 2004). Lu et al. (2009) operated a MFC with SPW containing 4900 mg/L of COD over four cycles and obtained a maximum voltage output and power density of 490.8 mV and 239.4 mW/m² in the third cycle. However, the CE was only 7%. They attributed this low CE to oxygen diffusion to the anode compartment resulting in oxidization of other electron acceptors, biomass production and fermentation.

2.9.9 Inorganic and other substrates

Apart from these above mentioned substrates, some other substrates have also been explored. Electricity generation with anodic sulfide oxidation was reported (Rabaey et al., 2006) with a PD of 39 mW/ m².

Huang and Logan (2008) reported the effectiveness of electricity production with paper recycling plant wastewater using MFC and obtained a maximum PD of 672 mW/m² after amending the wastewater with phosphate buffer. However, with unamended wastewater, the power output was only 144 mW/m² mainly due to low solution conductivity. The large amount of wastewater produced in integrated biorefineries is also a potential source of energy (Kaparaju et al., 2009). Recently the use of MFCs to remove the fermentation inhibitors in cellulosic biorefineries including furfural, 5-hydroxymethylfurfural, vanillic acid, 4-hydroxybenzaldehyde and 4 hydroxyacetophenone while simultaneously producing electricity was demonstrated (Borole et al., 2009).

Some views that can be drawn are

1. Substrates being used in both MFCs have grown in complexity and strength (higher organic loading rate). A complex substrate helps in establishing a diverse and electrochemically active microbial community in the system while a simple substrate is easier to degrade and improves the electric and hydrogen output of the system.

2. The output of these systems (electric current and electric power) is still some way from large-scale applications. More technological advancements in terms of material, costs and substrates being used are necessary to bring these systems at a level where they can be commercially exploited.
3. Several new substrates hitherto exploited can be brought as substrates under the MFC set ups. These may include the wastewaters from molasses based distilleries rich in organic matter and produced in large volumes, wastewater from large number of biorefineries, wastewaters from pharmaceutical industry with recalcitrant pollutants, waste plant biomass (agriculture residue) which is burnt at this moment, etc.

4. The integration of MFCs with existing separation, conversion and treatment technologies is probably the best option where in the effluent from one stream can be used as a feed for the other one.

Table 2.3: Different substrates used in microbial fuel cells (MFCs) and the maximum current produced

<table>
<thead>
<tr>
<th>Type of substrate</th>
<th>Conc.</th>
<th>Source inoculum</th>
<th>Type of MFC (with electrode surface area)</th>
<th>Current density (mA/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>1 g/L</td>
<td>Pre-acclimated bacteria from MFC</td>
<td>Cube shaped one-chamber</td>
<td>0.8</td>
<td>Logan et al., 2007</td>
</tr>
<tr>
<td>Cellulose particles</td>
<td>4 g/L</td>
<td>Pure culture of Enterobacter</td>
<td>U-tube MFC with carbon cloth</td>
<td>0.02</td>
<td>Rezaei et al., 2009</td>
</tr>
<tr>
<td>Glucose</td>
<td>6.7 mM</td>
<td>Mixed bacterial culture</td>
<td>One-chamber air-cathode</td>
<td>0.70</td>
<td>Catal et al., 2008</td>
</tr>
<tr>
<td>Lactate</td>
<td>18 mM</td>
<td>Pure culture of S. oneidensis MR-</td>
<td>Two-chambered MFC with graphite felt</td>
<td>0.005</td>
<td>Manohar and Mansfeld, 2009</td>
</tr>
<tr>
<td>Starch</td>
<td>10 g/L</td>
<td>Pure culture of Clostridium butyricum</td>
<td>Two chambered MFC with woven graphite</td>
<td>1.3</td>
<td>Niessen et al., 2004</td>
</tr>
<tr>
<td>Sucrose</td>
<td>2674 mg/L</td>
<td>Anaerobic sludge from septicTank</td>
<td>Two-chambered mediator-less MFC with stainless steel mesh as anode</td>
<td>0.19</td>
<td>Behera and Ghangrekar, 2009</td>
</tr>
</tbody>
</table>

2.10 Working mode of MFCs operation

MFCs can be operated in batch or continuous mode. A batch mode involves setting up the MFC with desired substrate and allowing it to completion, followed by the manual addition of more substrate. A continuous flow system that uses pumps to add more substrate and remove
wastes without manual interference. While operating a non mediated MFC in continuous mode rather than batch, the power output decreased from 479W/m² to 49W/m². Although it causes a decrease in power output, continuous flow MFCs has broader possible application because they require less maintenance (Rabaey et al., 2005).

The Continuous Flow Systems (CFS) is designed to easy treatment of a continuous stream of wastewater. The unit is fully automated with the only operator intervention required being the refilling of the flocculant and disposable media. Continuous process units range from 5 gpm to 40 gpm. Additional options are available for increased flocculation with pre-ozonation, water purification with post-ozonation and increased efficiency of de-watering and drier cakes (Rabaey et al., 2003). The system has a monitoring system that sounds an alarm when restocking of media is required or when the treatment process is interrupted. Proven results for reduced TDS/TSS levels lower residual heavy metals and lower cost per gallon treated using this approach (Logan, 2008).

The Sequencing Batch Reactor (SBR) is an activated sludge process designed to operate under non-steady state conditions. An SBR operates in a true batch mode with aeration and sludge settlement both occurring in the same tank (Cheng et al., 2006). The major differences between SBR and conventional continuous-flow, activated sludge system is that the SBR tank carries out the functions of equalization aeration and sedimentation in a time sequence rather than in the conventional space sequence of continuous-flow systems (Logan et al., 2006).

In addition, the SBR system can be designed with the ability to treat a wide range of influent volumes whereas the continuous system is based upon a fixed influent flow rate (Cheng and Logan, 2007). Thus, there is a degree of flexibility associated with working in a time rather than in a space sequence SBRs produce sludges with good settling properties providing the influent wastewater is admitted into the aeration in a controlled manner. Controls range from a simplified float and timer based system with color graphics using either flow proportional aeration or dissolved oxygen controlled aeration to reduce aeration to reduce energy consumption and enhance the selective pressures for BOD, nutrient removal, and control of filaments (Kim et al., 2007). An appropriately designed SBR process is a unique combination of equipment and software. Working with automated control reduces the number of operator skill and attention requirement.
2.11 Effect of the external resistance in MFC

There are several different methods to evaluate the internal resistance of an MFC. These include polarization slope, power density peak, electrochemical impedance spectroscopy (EIS) using a Nyquist plot, and current interrupt methods. The microorganism oxidizing the substrate release electrons onto the anode surface and should thus be considered a current. However, this current source is not constant, but affected the amount of resistance in the system. There is not a linear relationship between voltage and current in this case. The optimal resistance to be used in each setup depends on numerous factors, including the application, substrate, inoculums, type of reactor, and any potential losses within the system (Allen and Bennetto, 1993).

The lower current production means that some electrons are consumed by mechanism other than the cathode reaction (Kim et al., 2003). Gil et al. (2003) or oxygen diffused from cathode compartment or dissolved oxygen present in the influent. At low resistance the electrons move more easily through the external circuit than at high resistance, oxidizing electron carriers of the microbes in the anode. Higher fuel oxidation by the microbes is expected with high ratio of oxidized electron carriers of the culture at a low resistance to remove organic contaminants at a high rate (Jang et al., 2004). It was observed that at lower external resistance the current production is higher and vice versa (Logan, 2008). Even for same waste water COD concentration the production of current is decreases due to increase in resistance. At same time COD concentration when resistance was increased, the production of current decreased. This shows that the resistance becomes the rate-limiting step. Even at lower resistance, low current production could be attributed to the lower electron consumption rate at the cathode than transfer rate from the external circuit. This might be due to limited supply of proton or oxygen but at this point it is not known how this is possible. It is plausible that under the conditions of limited electron disposal through the circuit with a high resistance, the electrons are consumed in the anode to reduce other electron acceptors such as sulfate and nitrate.

2.12 Electrical Parameter

2.12.1 Open circuit voltage

Open circuit voltage is the voltage measured in the absence of any resistor. By definition it is the difference of electrical potential between the two electrodes i.e. anode and cathode of a
cell in the absence of any resistor. Theoretically open circuit voltage should be almost close to the electromotive force of a cell but in practice it does not happen generally. The probable reason for this disparity between the two is the large energy losses at the cathode, which is called the over potential. Over potential is directly related to current density and generally includes:

2.12.2 Activation losses
To carry out the oxidation-reduction reaction at the electrode bacteria need to cross an energy barrier that results in large activation losses. But increasing the electrode surface area can minimize this loss. Other measures taken to overcome this loss are increasing temperature and by enrichment of biofilm on the anode surface (Logan et al., 2006).

2.12.3 Metabolic losses
Metabolic loss during MFC operations is another important electrical parameter that affects the efficiency of the working model. This is because of the large difference of redox potential between the substrate and anode (Logan et al., 2006).

2.12.4 Concentration losses
These occur at the high current density and are due to rate of mass transport of a species to or from the electrode and these losses limit the current production. (Larminie, 2000).

2.12.5 Ohmic losses
Impedence to the flow of electrons at the electrodes and interconnections and to the protons at the membrane and electrolytes is the cause of these losses. Keeping the electrodes in close proximity to each other i.e. at the closest distance and using the electrolytes of higher conductivity can overcome these losses (Hoogers, 2003).

2.12.6 Power and power density
Power can be calculated as

\[ P = \frac{E_{cell}^2}{R_{ext}} \] \hspace{1cm} (14)
where \( E_{\text{cell}} / R_{\text{ext}} \) is calculated by Ohm’s law. Thus power density is calculated as amount of power per unit surface area of the electrode. To enhance power density it is preferred to use anode with the projected surface area. Surface area of anode can be enhanced greatly by using porous electrodes. Other measures are using electrodes in sieve or brush form but in these cases it is difficult to measure surface area of each and every unit of the anode. Therefore using porous anode with defined surface area of the plate and of each pore as well is advantageous over others.

### 2.12.7 Polarization curve

In microbial fuel cells the highest voltage is achieved at open circuit condition and the voltage drop off with increasing current draw. This is known as polarization and is represented as polarization curve. In other words in polarization curve voltage is represented as function of current. ([Logan et al., 2006](#)).

The three basic regions affecting the overall polarization in a polarization curve are:

**Fig 2.7 (a) - Polarization curve- relation between power and current.**

**Fig. 2.7(b)- Polarization curve- relation between voltage and current**
2.13 Coulombic efficiency

Coulombic efficiency is the efficiency with which electrons are transferred in a system to carry out an electrochemical reaction. This is an important measure of the microbial fuel cell efficiency as it measures the number of coulombs recovered as electrical current. The coulombic efficiency is dependent on two major factors firstly it depends on microorganism carrying out the electrochemical reaction and secondly the substrate used by the bacteria to generate current (Lee et al., 2008).

Coulombic efficiency of the system is thus directly associated with the chemical oxygen demand of the anode solution at the start of the operation and at the end of the operation as well. This can be represented by simple formula:

\[(C_s-C_o)/C_s \times 100 \]  

Where \(C_s\) is the initial value of chemical oxygen demand and \(C_o\) is the final value of chemical oxygen demand.

The possible relation between the chemical oxygen demand and coulombic efficiency of the system can be cited as at the start of the process when bacteria are at rest and reaction has not commenced, the system contain maximum amount of chemicals dissolved in it. The results of experiments using wastewater as a substrate show a higher coulombic efficiency (Rabaey et al., 2003). As the reaction starts; bacteria begin to decompose the complex organic substrates into simpler form and \(CO_2\). For attainment of the maximum amount of energy derived from the system the substrate must be completely oxidized to \(CO_2\) with efficient transfer of electrons to the electrodes. In the absence of complete oxidation a significant portion of the energy may lost in the form of unoxidized substrate. The maximum coulombic efficiency obtained with complete oxidation of substrate using Geothrix fermentans is about 94%. (Bond and Lovely, 2005).

2.14 Applications of MFC

Until now discussion has primarily centered on the use of MFCs for either wastewater treatment or as a method of renewable energy production in the form of electricity or hydrogen. However, MFCs have been examined for two other applications that will be examined in this chapter. The
first one is using the MFC as a remote source of power. Reimers et al. (2001) first developed this new concept of a sediment MFC (SMFC) and showed that power generation could be sustained by bacteria using only the organic matter in the sediment. Since then, there have been improvements in power output through modification of the materials, but also in the development of enhanced SMFCs through augmentation of the anode with additional sources of energy. The second novel application of the MFC is as a method of bioremediation. Remediation can include both degradation of organic pollutants at the anode as well as reduction of inorganic chemicals such as nitrate or uranium at the cathode.

2.14.1 Electricity generation

MFCs are capable of converting the chemical energy stored in the chemical compounds in a biomass to electrical energy with the aid of microorganisms. MFCs themselves can serve as distributed power systems for local uses, especially in underdeveloped regions of the world. MFCs are viewed by some researchers as a perfect energy supply candidate for Gastrobots by self-feeding the biomass collected by themselves (Wilkinson, 2000). Because chemical energy from the oxidization of fuel molecules is converted directly into electricity instead of heat, the carnot cycle with a limited thermal efficiency is avoided and theoretically a much higher conversion efficiency can be achieved (70%) just like conventional chemical fuel cells. Chaudhury and Lovely (2003) reported that R. ferrireducens could generate electricity with an electron yield as high as 80%. Higher electron recovery as electricity of up to 89% was also reported (Rabaey et al., 2003).

However, MFC power generation is still very low (Tender et al., 2002; Delong and Chandler, 2002), that is the rate of electron abstraction is very low. One feasible way to solve this problem is to store the electricity in rechargeable devices and then distribute the electricity to end-users (Ieropoulos et al., 2003). Capacitors were used in their biologically inspired robots named EcoBot I to accumulate the energy generated by the MFCs and worked in a pulsed manner. MFCs are especially suitable for powering small telemetry systems and wireless sensors that have only low power requirements to transmit signals such as temperature to receivers in remote locations (Ieropoulos et al., 2005; Shantaram et al., 2005).
2.14.2 Biohydrogen generation

MFCs can be readily modified to produce hydrogen instead of electricity. Under normal operating conditions, protons released by the anodic reaction migrate to the cathode to combine with oxygen to form water. Hydrogen generation from the protons and the electrons produced by the metabolism of microbes in an MFC is thermodynamically unfavorable. Liu et al. (2005) applied an external potential to increase the cathode potential in a MFC circuit and thus overcame the thermodynamic barrier. In this mode, protons and electrons produced by the anodic reaction are combined at the cathode to form hydrogen. The required external potential for an MFC is theoretically 110 mV, much lower than the 1210 mV required for direct electrolysis of water at neutral pH because some energy comes from the biomass oxidation process in the anodic chamber. MFCs can potentially produce about 8–9 mol H₂/mol glucose compared to the typical 4 mol H₂/mol glucose achieved in conventional fermentation (Liu et al., 2005).

In biohydrogen production using MFCs, oxygen is no longer needed in the cathodic chamber. Thus, MFC efficiencies improve because oxygen leak to the anodic chamber is no longer an issue. Another advantage is that hydrogen can be accumulated and stored for later usage to overcome the inherent low power feature of the MFCs. Therefore, MFCs provide a renewable hydrogen source that can contribute to the overall hydrogen demand in a hydrogen economy (Holzman, 2005).

2.14.3 Waste water treatment

The high energy requirement of conventional sewage treatment systems are demanding for the alternative treatment technology which will be cost effective and require less energy for its efficient operation. In past two decades, high rate anaerobic processes are finding increasing application for the treatment of domestic as well as industrial wastewaters. The major advantages these systems offer over conventional aerobic treatment are no energy requirement for oxygen supply, less sludge production, and recovery of methane gas. While treating sewage, particularly in small capacity treatment plant recovery of methane may not be attractive, because most of the methane produced in the reactor is lost through effluent of the reactor. The methane concentration of about 16 mg/L (equivalent COD 64 mg/L) is expected in the effluent of the reactor due to high partial pressure of methane gas inside the reactor (Adrianus and Lettinga, 1994). Hence, while treating low strength wastewater major fraction of the methane gas may be
lost through effluents, reducing the energy recovery. In addition, due to global environmental concerns and energy insecurity, there is emergent interest to find out sustainable and clean energy source with minimal or zero use of hydrocarbons.

Until now discussion has primarily centered on the use of MFCs for either wastewater treatment or as a method of renewable energy production in the form of electricity or hydrogen. Unlike conventional processes it can completely break down most of the acetate and carbon compounds to CO$_2$ and water. Some of the species used in MFCs can also utilize the sulphides and other forms of sulphur compounds. The upflow mode MFCs and Single chambered like constructions are favoured because of large scale implementation. (Jang et al., 2004).

Despite the potential of the MFC as a method of wastewater treatment, most researchers have chosen to work with defined compounds such as glucose or acetate. Using these compounds is necessary to understand the response of the system uncomplicated by the variations in wastewater. However, most of the organic matter in waste water is protein, and the bulk of the material is poorly defined and will likely remain so. Much more work is needed on actual wastewaters in order to better understand how designs will function when given the complex and particle laden waters. We need to focus on reactor factors that govern the cost of treatment systems, such as hydraulic and solids retention times (HRTs and SRTs), the mass of biomass produced and its settleability or filterability in engineered systems, and the impact of recycle streams on system performance. More information is needed on the flow of nutrients, such as nitrogen and phosphorous in the system, and methods to control these in MFC-based systems. Pilot reactors need to be designed and tested so that we can be more realistic data on system performance. The potential for system failure due to biofouling or loss of conductivity of the medium need to be explored with materials considered for use in the system. As the MFC is inherently an anaerobic process, we need additional information on how to control the community to shift it towards electrogensis, and away from sulfate reduction and methanogenesis.

In industrial applications, it may be possible to better control the types of bacteria in a process or even use pure cultures. In all systems, we need better information on the microorganisms that can function as exoelectrogens. What are the most useful strains, and which bacteria can produce the most power for us? How can we manipulate these strains for efficient cellulose degradation and maximize hydrogen recovery in an MEC or BEAMR process? How
thick can a biofilm become before it is no longer useful as a method of electricity generation, and what signals trigger nanowire production in cells? Is there a natural evolution of bacteria in an electrogenic biofilm, and, if so, what controls that and what bacteria emerge as the “winners”? Clearly, there is much exciting work to be done on better understanding the bacteria that function within an electrogenic biofilm and that help us to harvest electricity from MFCs.