International Journal of Scientific Research and Engineering Development-– Volume 1 Issue 2,Nov-Dec2018

Available at www.ijsred.com

RESEARCH ARTICLE OPEN ACCESS

A Study of Soil Based Microbial Fuel Cells

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Abstract :

The performance of microbial fuel cells can be enhanced by several factors including its resistance to impact. This resistance is determined from both the proton mass and the weak cathode caused by the oxygen reduction reaction. This is due to the protons in the aqueous phase of the transport rate being very slow and remaining in the hollow fiber reactor. This helps to improve the proton transfer as well as minimize the resistance. Cathodic oxygen also assists in the reduction reaction and the concentration of dissolved oxygen works toward a unipolar response relationship. This means that when placed along with a cathode, they can improve the aerobic performance of microbial fuel cells. It also matters which additives are placed within the MFC. Adding fertilizer and molasses increased MFC performance by an average of 45 and 38% respectively while table salt decreased electric production by 23% over a period of several weeks.

Keywords :- Microbial fuel cells, electron acceptors, cellular respiration, oxidation reduction reactions, ion exchange membranes, molasses, fertilizer, salt

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Introduction

A Microbial fuel cell (MFC) is a bio-electric device that is able to harness the natural biological functions of micro-organisms to produce electrical power. It relies on a small biofilm of bacteria to attach itself to the anode catalyst. The chemical energy created from the microbes absorbing sugars and other nutrients is then converted directly into electricity through the biological device. The system works by recovering electrons produced during microbial metabolism and channels them for generation of electrical current. It functions similarly to a battery that converts chemical energy into electricity through an electro-chemical process. A battery is basically a self-contained cell that consists of three main parts: (1) anode, (the negative terminal); (2) cathode, (the positive terminal); and (3) electrolyte, which is the ionic conduction medium that allows the ions to travel from anode to cathode. Electrons flow from anode through external load to the cathode to close the circuit and generating electricity in the process. In a microbial fuel cell, the oxidation reactions are catalyzed by microbes. When the catalyst is an enzyme, the cell is considered to be an enzymatic fuel cell. While both microorganisms and enzymes catalyze oxidative reactions that takes place at the anode, only enzymes (sometime coupled with inorganic catalysts) are used in the cathode (Mahadevan et al., 2014). These fuel cells use basic organic materials including sugars and alcohols and achieve their best electrical production in a mild temperature environment where biological activity is optimal.

Fuel cells function in much the same way as a battery in that they convert fuel to electricity by electrochemical means. However, unlike a battery, a fuel cell does not require recharging since it produces energy as long as fuel is supplied. Hydrogen fuel is fed into the anode of the fuel cell, and air enters the cell through the cathode. The hydrogen atoms then become divided into protons and electrons, promoted by a catalyst. The protons pass through the electrolyte, whereas the electrons create a separate current that can be used before they return to the cathode to react with the hydrogen and oxygen, forming water (Singh and Songera, 2012). The scientific convention defines a positive current as one that flows from the positive to the negative terminal, which is opposite to the direction of electron flow.

MFC's must be capable of performing oxidization at the anode either continuously or intermittently using a renewable source or else the system is considered to be a bio-battery. The MFC has a number of advantages when compared to chemical fuel cells and batteries. This is the reason the research has been increasing over the past decade or so. First of all, the catalyst for the MFC is essentially free, since the bacteria can be grown almost anywhere. When considering a chemical fuel cell, the catalyst is responsible for a substantial portion of the total cost. The bacteria must also be versatile, so a MFC can be used with many different types of fuel. In addition, many species of bacteria have been tested were found to be well adapted to both their current environmental conditions and various changes, which means they could theoretically survive under extreme conditions of pH, temperature and salinity (Niessen et al., 2004). Another benefit of MFCs is that the catalyst is produced by live cells, so it has the ability to repair and heal itself. There are around 50 species of Shewanella bacteria that have been able to produce current when placed in a MFC (Corma et al., 2010). It is believed that the voltage produced can be increased through by changing the design of the fuel cell, and by using microbiology to develop the best possible bacteria.

MFCs can be divided into three different types (A, B and C). In type A fuel cells, artificial redox mediators are added to the culture in the anodic fuel cell compartment. These mediators penetrate the bacterial cells and transport the electrons to the anode. Type B fuel cells use metal-reducing bacteria, such as members of the families Geobacteraceae or Shewanellaceae, which exhibit special cytochromes bound to their membrane. These are capable of transferring electrons to the electrodes directly. Finally, type C fuel cells oxidize fermentation products (hydrogen, methanol, etc.) on electrocatalytic electrodes, that is, electrodes that have been chemically modified to oxidize such metabolites.

MFC have many applications including the water or sludge in the organic matter degradation, microbial metabolism of organic compounds, and the production of an electronic current in several types of soil. Several studies have found that Fes 10-reducing bacteria has been one of the chief producers of electrochemical activity.

Background

The first discovery that bacteria could generate electric current was made by Potter (1911) who created an electrical current from E. coli. In his studies of how microorganisms degrade organic compounds, he discovered that electrical energy was also produced. Potter had the idea of trying to harvest this newfound source of energy for human use. He was able to construct a primitive microbial fuel cell, but not enough was known about the metabolism of bacteria for the design to be improved upon. The topic was further advanced with the creation of several microbial half fuel cells that were connected in series to produce 35 volts and only having a 2 mA current (Cohen, 1931). A study by DelDuca et al. (1963) used hydrogen produced by the fermentation of glucose by Clostridium butyricum as the reactant at the anode by hydrogen and air to create a microbial fuel cell. Though the cell functioned, it was unreliable owing to the fluctuation of the amounts of hydrogen produced by the micro-organisms. That issue was solved by Suzuki et al. (1976) who immobilized the Clostridium butyricum by using a polyacrylamide gel.

After that there was no further study on the topic until the late 1980’s when M. J. Allen and H. Peter Bennetto from Kings College in London revolutionized the original microbial fuel cell design. They were able to combine advancements in the understanding of the electron transport chain with significant upgrades in technology to produce the basic design that is still used in MFCs today. However, their goal of MFCs being implemented in third world countries has yet to be achieved because of the complexities of simplifying the design enough to allow poor rural farmers to build them. In 1999, Kim et al. developed a mediatorless microbial fuel cell which enhanced the MFC's commercial prospects, by eliminating the requirement of costly mediator chemicals for transporting electrons. This was accomplished by the discovery of certain species of bacteria that were naturally electrochemically active.

Over the last several years, MFCs have been given more prominence as a cheap renewable source of energy and studies have seen exponential growth. Logan et al., (2006) innovated new terminology and measurement methods. This led to state of further improvements in MFC casings (Du et al., 2007). The next big discovery was the creation of MFCs that could handle conventional anaerobic digestion (Pham et al., 2006). Other studies have started to explore the practical implementation of MFCs into BES's (bioelectrochemical systems). (Rozendal et al., 2008) explored improving the bioanode performance in BES's and (Pham et al., 2009b) found a way to reduce the amount of cathodic limitations required by MFC's. Debabov (2008) discovered the mechanism of external electron transfer from the two main bacteria that were in use at the time Geobacter sulfurreducens and Shewanella oneidensis. Logan (2009) discovered the power densities for MFCs and then normalized them to minimize the electrode-projected surface areas necessary.

The first experiments that combined multiple MFCs was conducted using six individual MFC units made of robust cation exchange membrane and granular graphite anode and a hexacyanoferrate coated graphite rod as cathode (Aelterman et al., 2006). Their work was followed by Wang and Han (2009) which combined a stack of four MFC units inside a Plexiglas container using a reticulated vitreous carbon anode and a platinum on carbon (Pt/C) coated air diffusive cathode. All of the current research seems to show that the internal resistance will be minimized when the MFCs get connected in a parallel configuration. Another common theme was the use of a PEM membrane except for Fan et al. (2007) which substituted J-cloth due to the high cost of the membrane. Xu et al. (2012) was able to prove that the PEM deteriorates over time due to membrane fouling, which leads to decrease in performance of the MFC. Due to the high cost of Pt/C coating, Zhang et al. (2009) invented a new type of air cathode using activated carbon bonded with PTFE, wrapped around a Ni mesh to act as a current collector.

The earliest approaches of scaling up an MFC were either connecting multiple MFCs in series for additive Voltage output [(Aelterman et al., 2006), (Shin et al., 2006)] or increasing surface area of the electrodes [(Logan et al., 2007), (Kim et al., 2002), (Zhang et al., 2013)]. So far increasing the electrode surface area has shown better electric production under conditions where the size of electrode surface is sufficient to affect the power density. Dewan et al. (2008) studied the relationship between the surface area of the anode and the current limiting electrode in a MFC to find the power density generated. The current limiting condition of the study was created by utilizing cathodes that had surface area significantly higher than anode surface area. That lead to the discovery that the power density would vary directly in proportion to the negative natural logarithm of the anode surface area. This meant that as long as surface area of a current limiting electrode increased, it lead to the maximum power density decreasing.

MFCs can be stacked together in series or in parallel to achieve higher voltage or current. However, stacking multiple MFCs together in series can also create problems, such as voltage reversal, contact voltage losses, and erratic operation (Liu et al., 2008). If the size of the MFCs is significantly increased the electrode spacing can easily be altered, thus affecting power density through changes in the areas specific internal resistance. (Dheilly et al., 2008) found that by monitoring microbial adhesion and biofilm growth using electrochemical impedancemetry, (Rozendal et al., 2008) observed that the microbes internal resistance will decrease with biofilm detachment. (Ghosh et al., 2008) observed that a single anode cannot contribute to higher current output solely by itself. Their research was also able to successfully scaling up a MFC through utilizing multiple pairs of electrodes. (Vargas et al., 2013) managed to increase the total surface area of anode by placing five anodes in the anode chamber and connecting them in parallel circuit while only using a single cathode. Their objective was to increase power output by increasing current output with simultaneous decrease in the internal resistance range while substrate was fed hourly so as to make it a fed batch system. (Logan and Regan, 2006) have predicted that the MFC bioelectrochemical systems will eventually be limited by the capabilities of the electrochemically active micro-organisms. The main issue faced during the researching and manufacturing of microbial fuel cells comes essentially down to the optimal method for moving the electrons from the electron transport chain to the anode. When B.H. Kim encountered this problem in the late 1990s, he discovered that certain species of bacteria were already electrochemically active and thus didn’t require the use of a mediator molecule to transport electrons to the electrodes. This led to a new type of microbial fuel cell being developed that eliminated the use of the expensive and sometimes toxic mediators. The current trend of research appears to be working towards optimizing electrode materials, types and combinations of bacteria, and electron transfer.

Microbial fuel cell design

MFC designs have been generally been classified into two general groups: mediated and unmediated. The first MFCs would employ a mediator which is a chemical that transfers electrons from the electrochemically active bacteria (EAB) in the cell to the anode. (Roller et al., 1984) discovered the redox cycle which is given in the equations below. Essentially, the mediator acts as an oxidizing agent in the presence of sugar or other food source. After the first reaction is complete the mediator become a reducing agent. It then will shed some of its extra electrons to go back to being an oxidizing agent which is good for electric generation.

$$C_6H_{12}O_6 + Mediator_{(o)} \rightarrow Product + Mediator_{(r)}$$

$$Mediator_{(r)} \rightarrow Mediator_{(o)} + electrons$$

Some of the most popular mediators that have been used include: methyl viologin, thionine, humic acid, methyle blue and neutral red. The disadvantages of using this type are that the mediators are often expensive and toxic which creates difficulty in their handling (Acharya and Aithal, 2017). Figure 1 shows the different groups of mediators that have been used in MFCs thus far. Mediators have the following requirements for to be considered viable candidates: 1) Their molecules need the ability to form redox couples. 2) They need to be stable in both reduced and oxidized forms. 3) They should not be biologically degradable. 4) They should not be toxic to the biological species (Mahadevan et al., 2014). In actuality, mediators have commonly contributed to fuel cell performance issues due to degradation and toxicity to the biological medium.

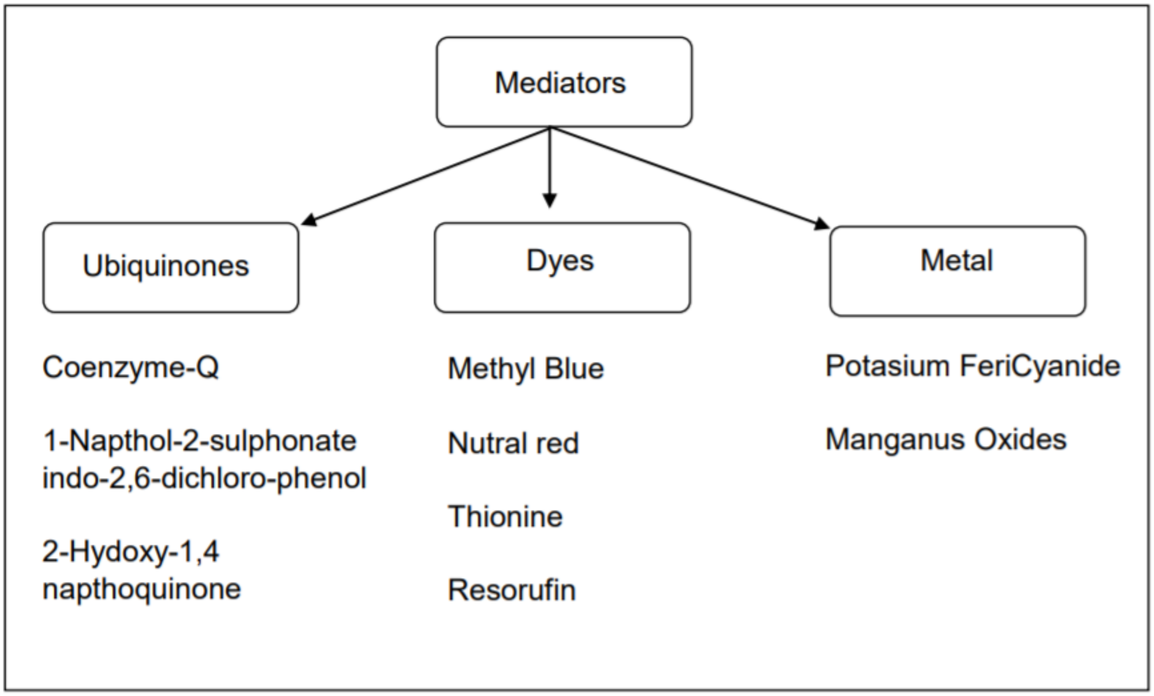

Figure 1. Mediators used in Microbial Fuel Cells.

Unmediated MFCs designs came out in the 1970s. These newer MFCs were able to use bacteria that typically had higher levels of electrochemically active redox proteins and cytochromes on their outer membranes so they could directly transfer their electrons to the anode. Unmediated fuel cells are very popular with wastewater fuels as they are able to obtain energy directly from microscopic aquatic plants such as algae. These specific types of fuel cells are known as plant microbial fuel cells. The power that is obtained from these organisms is a variant that will be able to maximize additional ecological advantages (Min et al., 2005). A new design that came out recently is soil based where the soil functions as a high nutrient anodic media. In this system the anode is placed at a particular depth within the soil and the cathode is placed at the top of the soil and it is exposed to air. This is very beneficial due to how soil naturally contains many diverse microbes, including the electrogenic bacteria needed for MFCs as well as full of complex sugars and other nutrients that have accumulated from plant and animal material decay to act as a fuel source. There are some advantages over the combustion process in that the oxidation and reduction reactions occur on the anode and cathode separately (Liao et al., 2018). This is advantageous because it requires anaerobic anode conditions to restrict the EAB from oxygen and acts to maximize the electricity generation from other terminal acceptors. The aerobic microbes found in the soil also will act as an oxygen filter, similar to the expensive chemical materials needed for mediated MFC systems, which force the redox potential of the soil to decrease with greater depth. The newest design is one that uses a phototrophic biofilm for the anode that contains at least one photosynthesis capable microorganism (Acharya and Aithal, 2017).

(Mahadevan et al., 2014) determined that all MFC designs could essentially be divided into five categories: 1) Uncoupled bioreactor MFC, 2) Integrated bioreactor MFC, 3) MFC with mediated electron transfer, 4) MFC with direct electron transfer, 5) Mediator-less and membrane-less microfluidic MFC. The bioreactor MFCs are designed to capture the hydrogen that is biologically generated and then uses the hydrogen in a proton exchange membrane fuel cell system. There is a slight difference between the two as the uncouple bioreactor MFCs have a separate compartment where organisms produce the hydrogen which is then fed into a hydrogen fuel cell while the integrated bioreactor MFCs have the hydrogen production and the electricity generation both take place in the same chamber. These bioreactor MFCs use different types of bacteria and algae that are able to generate hydrogen under anaerobic conditions including: Escherichia Coli, Enterobactor and C. Butyricum (Fraiwan et al.,2014). The issue with these MFCs is that the electrical production efficiency has been in the neighborhood of 10% and often the measured values have been slightly less. One reason for this is that the enzyme interactions (such as hydrogenases) with H_2 produce hydrogenases instead of pure hydrogen gas (Fraiwan et al.,2014). The other known reason lies with H_2 mixing with other gases such as CO and H_2S as that created impurities (Mahadevan et al., 2014).

The third and fourth categories are the mediated and non-mediated MFC designs discussed previously. The final category is a newly designed MFC that eliminates use of mediators and cation exchange membrane. This is done through miniaturization of MFC using microfluidic technology which is capable of achieving high energy efficiency and durability (Mahadevan et al., 2014). This type would possess a huge advantage over conventional MFCs by eliminating the need for membranes as a result of co-laminar flow of fuel and oxidant streams that extemporaneously separate anode and cathode in the cell (Wang & Su, 2013).

In soil based MFCs the design is typically for the anode is kept at the bottom of the configuration while the cathode is place on top. This allows a biofilm of billions of microbes to slowly form on the anode surface over time. The biofilm performs its function by consuming the available sugars and nutrients to generate highly reduced biomolecules. The biomolecules are the waste product and will transfer their excess electrons to the anode. Fuel is then supplied on the anode side where an oxidation reaction produces electrons and H+ ions, while an oxidizer is supplied on the cathode side resulting in a reduction reaction (Carter, 2007).

Cyclic Voltammetry

Bacteria can reduce activation losses by increasing their extracellularly oriented mediation capacity. There are three possible methods that can accomplish this: direct membrane complex mediated electron transfer, mobile redox shuttle mediated electron transfer, and electron transfer through conductive pili or nanowires. These methods will be discussed further in a later section. Cyclic voltammetry (CV) is a rapid and proven method that is able to determine whether the bacteria is using mobile redox shuttles to transfer the electrons, or if it is passing the electrons directly using compounds that can penetrate through the membrane (Rabaey et al., 2005) CV functions by placing a reference electrode inside the anode chamber of the MFC close to the anode and then the counter electrode or platinum wire is preferably placed in the cathode chamber, but placing the counter electrode in the anode chamber will generate good results as well. A potentiostat is then used to obtain a scan of potential. (Park et al., 2001) found that a scan rate of 25 mV/s was the optimal value for evaluating bacterial suspensions.

However, (Rabaey et al., 2004) found that there is a huge difference when performing an analysis of mediators in biofilms, and the scan rate needed to be decreased to 10 mV/s in a few cases even lower. This decrease is necessary due to its ability to affect the accuracy of peak discrimination as the peaks had a tendency to increase in width over time.

Redox Mediation

The extent of the redox mediation and the midpoint potentials can be determined through analysis of several different items: the MFC derived culture within its medium, the MFC culture after centrifugation and resuspension in physiological solution; and the supernatant of the centrifuged MFC culture (Logan et al., 2006). If a peak is found for both of the derived culture of the medium and within the physiological solution, it demonstrates a shuttle that is associated with the membrane. If a peak is found in found for both of the derived culture of the medium and within the supernatant of the centrifuged culture, then that indicates that a mobile, suspended shuttle is present. The size of the peaks determined by the voltammogram through convolution analysis does not fully show to the extent of the membrane associated electron transfer and the mobile shuttle mediated electron transfer (Reguera et al., 2005). This is caused by the restricted accessibility of the membrane associated shuttles for oxidation/reduction by the working electrode.

Anode

The anode is the place where the electroactive biofilm is created and the bioelectrochemical reactions take place. When bacteria consume an organic substrate like sugar under aerobic conditions, the products of cellular respiration are carbon dioxide and water. However, when placed in an environment void of oxygen, cellular respiration will instead produce carbon dioxide, protons and electrons. It is therefore necessary to impart an anaerobic environment in the anode chamber of the MFC. It is also essential for the anode to be made of the proper materials in order to obtain reliable MFC performance. The optimal anode configuration would have high conductivity, high specific surface area and porosity, low cost, biocompatibility, and good stability. Figure 2 displays how the anode fits in relative to the rest of the MFC design. There are several ways to improve the performance of the anode including upgrading the material used, increasing the porosity or surface roughness of the material, or making modifications to the anode itself.

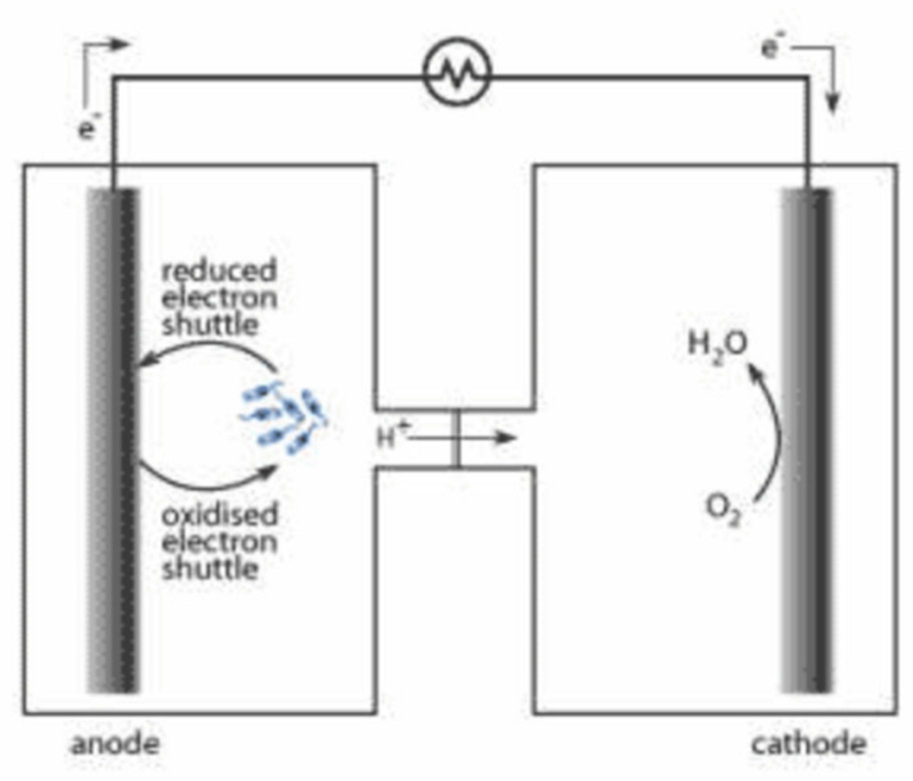

Figure 2. Typical MFC design.

Anode material

Several metals including: stainless steel, titanium, copper, nickel, and gold, and carbon materials, such as carbon cloth/paper, carbon graphite brush, and biomass-derived porous carbon, have been used for the anode in MFCs [(Dong et al., 2012), (Ter Heijne et al., 2008), (Baudler et al., 2015), (Zhang et al., 2013)]. Among these materials, the carbonaceous anodes are regarded as the most cost-effective and promising for the large-scale application of the MFCs. Carbon materials such as carbon cloth, paper, graphite, and carbon felt are very popular choices for anode materials due to their high conductivity and biocompatibility. Carbon cloth and paper are both planar and porous, yet also fragile and expensive so they are primarily reserved for lab-scale testing. Carbon felt and reticulated vitreous carbon have been found to be porous materials that have the capability to provide many inner spaces for bacteria growth as well as channels for substrate supply and proton removal (Yuan and Kim, 2008). The disadvantages of carbon felt are the low electrical conductivity of the carbon felt produces high ohmic resistance readings, and the cost of reticulated vitreous carbon is too high for either soil based MFC's or wastewater treatment applications.

Another popular anode material is Granular activated carbon (GAC) because of its good biocompatibility and low cost. GAC is a commonly used packing material in water and wastewater treatment processes and it is durable material with a high surface area of 1000 m^2/g (Jiang and Lee, 2009). This higher surface area provides considerable improvement with bacterial adhesion and electrical conductivity. However, while the specific surface area of the GAC-based anode is quite high, the area accessible to the bacteria acclimation is relatively low because most of the pores in GAC are small pores with a diameter of less than 50 nm. The issue of contention has been performance of carbon-based anodes and how it has not yet been able to meet the expected output required which has severely limited the application and industrialization of MFC. This has led researchers to look for other alternatives. (Lu et al., 2016) still believe it is possible to improve the performance of carbon-based anodes for MFC and suggest three strategies including: improving biocompatibility of anode, providing sufficient space for exoelectrogens (Bacteria that can transfer electrons extracellularly), and facilitating electron transfer between bacteria and electrode. This is beneficial to electrical production due to the fact that aerobic bacteria use oxygen as their final electron acceptor and anaerobic bacteria use other soluble compounds as their final electron acceptor. Exoelectrogens are a special class of bacteria that can either use a strong oxidizing agent or solid conductor as a final electron acceptor.

The graphite brush electrode is one of the newer designed anodes for use in a MFC. The graphite brush was designed to have a maximum power density of 2400 mW/m^2, which was about 4 times higher than anodes that use carbon paper 600 and have a maximum power density of mW/m^2 (Logan et al., 2007). A graphite brush is made by folding and twisting a titanium wire to create a series of loops into which graphite fiber bundles are crimped to form a spiral structure (Liu et al., 2013). The titanium metal is used due to its high electrical conductivity. The very small diameter of the graphite fibers acts to provide a highly open porous structure for necessary for improving bacterial acclimation. Graphite brushes have become increasingly used as MFC anodes and the only issue that remains is reducing their overall cost (Li et al., 2018).

Another material group that can improve MFC anode performance are 3D materials that are designed with large surface areas. There have been several 3D nanomaterial-based anodes that have already been created including: chitosan/vacuum-stripped graphene scaffold, 3D chitosan–carbon nanotube scaffolds, polyaniline hybridized 3D graphene, carbon nanotube (CNT)/polyaniline (PANI) nanocomposite, PANI/graphene-coated nickel foams, 3D carbon nanotube-textiles, porous carbon nanofiber aerogels, graphene-sponges, and graphene-coated nickel foams (Li et al., 2018). (Katuri et al., 2011) fabricated a multiwall carbon nanotube (MWCNT)/chitosan 3D composite anode by ice segregation-induced self-assembly (ISISA) and was able to create a maximum current density of 24.5 A/m^2. Chitosan or vacuum-stripped graphene scaffold and 3D chitosan–carbon nanotube scaffolds prepared using ISISA also produced greater amounts of current density when compares to carbon cloth or felt (Marsili et al., 2008). This was due to the vacuum-stripped graphene powder that was embedded on the chitosan layers acted to increase the surface roughness of the layers. This acted to create a larger graphene surface area for bacteria adhesion. Vacuum-stripped graphene powder also contains additional mesopores and micropores within the anode. These mesopores and micropores then contribute to a larger internal surface area that is accessible to endogenous mediators for the electron transfer between bacteria and anode, leading to increased biofilm activity. (He et al., 2012) discovered that MFCs that were made of vacuum-stripped graphene powder within the anodes produced a power output than was 78 times higher than the power output produced by anodes made of conventional carbon cloth. The reason for this is that the 3D porous anodes generally contain a hierarchical structure which encourages the efficient diffusion of electron mediators and substrate as well as bacterial adhesion to the interior of the 3D electrode.

One big category for anode material is using biomass for the fabrication of the MFC anodes. Biomass that has been tried already includes: chestnut shells (Chen et al., 2018), pomelo peels (Chen et al., 2012), natural loofah sponges (Yuan et al., 2013), and bamboo (Zhang et al., 2014). The biomass is prepared by carbonization at a temperature above 800 °C and that causes the inherent pore structure of the biomass to solidify and evolve into macropores. These macropores are typically cross-linked and will need a rather high conductivity to work as a high performance anode. (Chen et al., 2012) used the reticulated carbon foam derived from pomelo peels in the creation of their MFC anode to produce a maximum current density of 4.0 mA/cm^2 which was 2.5 times higher than what graphite felt has produced. (Zhang et al., 2014) found that carbonized dry bamboo branches was a good material for a higher performing anode due to how the internal structure of bamboo enhanced the biofilm. The bamboo was kept as a hollow tube with an inner diameter of 2 mm and was found to contain a range of macropores from 15 to 100 um. A chestnut shell-derived porous carbon anode was also found to produce a maximum power density of 23.6 W/m^3 which was over twice as high as the maximum power density ever produced by a carbon cloth anode (10.4 W/m^3) (Chen et al., 2018). Other biomass material that was used to create anodes that were less successful include: corn stems, king mushrooms, and wild mushrooms (Karthikeyan et al., 2015). (Lu et al., 2016) created a high-performance flexible anode derived from carbonized silk cocoons that was able to achieve a 2.5-fold maximum power density greater than that of carbon cloth anodes. This increase was likely caused by their hierarchical 3D, pseudographitic microstructure, good biocompatibility, and high capacitance. As these examples have shown the use of natural and recyclable materials have the potential to greatly reduce the cost of electrode materials and improve anode performance. The issues that would need to be addressed are that the biomass that is available will vary by location, the anodes would need a lot of design and testing before a final product could be produced, and there may not be enough biomass to meet the demand for the number of MFC that are needed. Other issues that need to be addressed are that the structure of these biomass materials are difficult to control and there may also be limitations in the MFC design that may cause conflicts.

Surface roughness also greatly affects bacterial adhesion and current density of electrively active bacteria (EAB). (Katuri et al., 2011) was able to induce biofilms to grow on polished glassy carbon anodes with particle sized grits of 5 um to yield a minimal current density for the oxidation of acetate as the bacterial size was reduced to approach the surface roughness features. This current density limit observed for these biofilms on a flat surface was found to approach 0.9 A/m^2. This contrasts with recent model of EAB electron transfer created by Torres et al. (2010), which provided an estimate of a maximum current density of 0.24 A/m^2 for a monolayer of EAB. The initial parameters were a 2 to 3 mm thickness of bacteria closely packed together and vertically aligned. (Katuri et al., 2010) theorize that the differences between these two limits could correspond to the formation of multiple bacterial layers within a biofilm capable of electron transfer to the electrode but further study is needed.

Anode materials can also be modified to improve MFC performance by a number of ways including: increasing the bacterial affinity for the anode surface, providing an extra supporting and conductive surface, and facilitating the extracellular electron transfer (EET) between bacteria and the electrode. The modifications can be classified into the following types: 1) decorating with carbon nanomaterials, 2) modification using a conducting polymer, and 3) chemical/electrochemical anode modifications (Chen et al., 2018). The most commonly used nanomaterials for anode modifications are carbon nanotubes (CNTs), carbon nanospheres, and graphene. CNTs are cylindrically-shaped carbon materials with a large surface area that helps to enhance the microbial adhesion and electron transfer between the bacteria and anode surface. (Ren et al., 2015) found that an anode with horizontally aligned spin-spray layer-by-layer CNT showed a smaller sheet resistance and induced a thicker biofilm than the other unmodified samples. A maximum power density of 3320 W/m^3 was obtained by using the anode in a miniaturized MFC which was more than 8.5 times more than values previously found by prior-art MFCs using 2D and 3D nanostructured electrodes. (Hindatu et al., 2017) discovered that the addition of nitrogen-doped CNT led to increased EET from the c-cytochrome located on the outer membrane of the bacteria to the electrode and also maximized the contact area between the bacteria and the electrode. This shows great potential especially when combined with graphene which is a unique carbon nanomaterial with 2D lattice made of sp2 hybridized carbon atoms (Chen et al., 2018). (Liu et al., 2012) found that decorating the electrode with graphene can create an electrically conductive surface similar to that of CNT-coated materials while considerably reducing the electrode cost. It was also discovered that a graphene-modified anode improved the power density by 2.7 times and the energy conversion efficiency by 3 times over the control samples. (Zhang et al., 2011) was able to create a graphene-modified SSM anode that produced a maximum power density of 2668 mW/m^3, which was 18 times larger than the unmodified SSM anode. Conducting polymers, such as polyaniline and polypyrrole, have been widely used to modify the electrode due to their high conductivity and durability in MFC-relevant conditions (Chen et al., 2018). Polyaniline carries positive charges in neutral environments which makes it desirable for enhancing the adhesion of the negatively charged bacteria. (Wang et al., 2014) was able to create a polyaniline-coated anode that decreased the start-up time of MFCs from 140 to 78 hours through the enhancing of the bacterial cell attachment. This was made possible by the conducting polymer which acted to facilitate the EET between the bacteria and the anode. (Chen et al., 2013) modified one anode by using both polypyrrole and graphene oxide composites with an electro-polymerization process to obtain an 8 times higher maximum power density when compared to MFCs that used unmodified anode. (Gnana et al., 2014) found that the increase was much less when using a reduced graphene oxide/polypyrrole composite modified carbon cloth anode as only produced a 3 times higher maximum power density than that of unmodified carbon cloth. It is believed that this is due to the increased electron transfer efficiency and the increased contact area between the bacteria and the anode as compared to the cloth. With chemical and electrochemical modifications, functional groups can be introduced onto the electrode surfaces, leading to a change in the physicochemical properties of the electrodes and creating a larger electrocatalytically active area, increased surface charges on the electrode, and a faster EET rate (Chen et al., 2018). Chemical and electrochemical modifications of the anode also can be effective methods for improving the anode performance due to the enhanced bacterial cell attachment and the facilitated EET rate from the bacteria to the anode surface. Chemical modification of the anode is usually carried out by either directly soaking the electrode in strong acid or treating the carbon materials in ammonia at 600–800 °C (Feng et al., 2010). (Cheng et al., 2013) achieved a 48% increase in power production and a 50% decrease in the start-up time by previously treating the carbon cloth in ammonia at 700 °C. The disadvantage of this method of chemical modification is that it usually requires toxic chemicals and high temperatures, both of which act to increase the cost of MFCs. Anode modification can also be achieved by electrochemical oxidation in different electrolytes, such as NH_4NO_3, $(NH_4)_2SO_4$, HNO_3, and H_2SO_4 (Zhou et al., 2012). (Zhang et al., 2014) found that electrolyzing the carbon cloth in nitric acid followed by soaking in aqueous ammonia could produce a 58% higher maximum power density compared to the untreated control.

Cathode

The design and fabrication of the cathode is a major challenge in designing a MFC. In the MFC electricity is generated via oxidation of biodegradable organic matter in the presence of active biocatalyst which generates both electrons and protons from the broken down matter (Tardast et al., 2012). The generated electrons are transferred by anode to cathode through an external circuit. It is the desired function of the cathode to eliminate the protons through having them diffuse and react with oxygen to liberate water molecules. (Li et al., 2009) found that high performance could be reached by using aqueous cathodes using soluble electron acceptors with a high electrode potential such as potassium ferricyanide, and potassium peroxodisulfate. However, the downside of using one of those soluble electron acceptors lies in the fact that the electron acceptors must be replaced after depletion. That would add additional costs for the treatment of wastewater and soil secondary pollution. (Zhang et al., 2011) specify that air-cathodes that use oxygen as the electron acceptor should be applied as they have shown promising results in practical applications due to their high electrode potential and the fact that oxygen is typically easy to come by. The main components of an air-cathode include: 1) oxygen reduction reaction (ORR) catalysts which reduce the ORR overpotential, 2) ionomer binders which facilitate proton conduction in catalyst layers (CLs), and tightly deposit the ORR catalysts, 3) a hydrophobic layer that permits air supply to the ORR catalysts and prevents water leakage, and 4) electrode supports that provide mechanical support to CLs and aid in collecting the electrons. Oxygen is the most common electron acceptor used in the cathode due to its high oxidation potential and the fact that it yields a clean product of water after reduction. However, it was found that the process of supplying oxygen to the cathode compartment is energy consuming (Strik et al., 2010). Another issue is that although the oxygen in the air can be used directly by using an air cathode, there are difficulties in the area where the cathode and air surface intersect (Heijne et al., 2007). These reasons made the cathode design more expensive and were major disadvantages in the case for making oxygen the permanent electron acceptor.

(Laxmipriya et al., 2018) found that in their MFC design that there was little difference in pH between anodic and cathodic chambers and were theoretically able to say that there would be no pH shift when reaction rates of protons, electrons and oxygen given off at the cathode are equal. There is a possibility that the buffer compensated the slow proton transport and improvement in proton availability for cathodic reaction.

Oxygen reduction reaction

The oxygen reduction reaction is very important reaction in daily activities such as biological respiration and energy conversion by fuel cells. ORR in aqueous solutions occurs mainly through two pathways: the direct 4 electron reduction pathway from O_2 to H_2O, and the 2 electron reduction pathway from O_2 to hydrogen peroxide (H_2O_2) (Zhang, 2008). In non-aqueous aprotic solvents and/or in alkaline solutions, the 1 electron reduction pathway from O_2 to superoxide (O_2^-) can also occur. These reactions are shown in Table 1 with the electric potential that each reaction produces. The mechanism of these oxidation reduction reactions are very complicated and often require the addition of other intermediates. The electric potential produced can also vary depending on the natures of the electrode material, catalyst, and electrolyte. In fuel cell processes, the 4 electron direct pathway is the most desirable pathway due to the four-electron route possessing a much lower energy loss and an ability of direct reduction of O_2 without oxidative intermediates (Fan et al., 2017). The 2 electron reduction pathway is used for industrial H_2O_2 production. The 1 electron reduction pathway is of importance in the exploration of the ORR mechanism.

Table 1. Electric Potential Produced by ORR Reactions.

Electrolyte	**ORR reactions**	**Electric potential produced (V)**
Acidic aqueous solution	$O_2 + 4H^+ + 4e^- \rightarrow H_2O$ $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.229 0.70 1.76
Alkaline aqueous solution	$O_2 + H_2O + 4e^- \rightarrow 4OH^-$ $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ $HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.401 –0.065 0.867
Non-aqueous aprotic solvents	$O_2 + e^- \rightarrow O_2^-$ $O_2^- + e^- \rightarrow O_2^{2-}$	Solvent Dependant Solvent Dependant

ORR catalysts

Normally, ORR kinetics occur very slowly. The natural rate would not provide enough current for a MFC so the ORR kinetics needs a cathode ORR catalyst to speed up the reaction time. Right now platinum (Pt)-based materials are the most optimal catalysts. (Cheng et al., 2006) discovered that the Pt loading of a typical MFC air-cathode needs to be approximately 0.5 mg/cm^2 to obtain optimal electric production. However due to the high cost and scarcity of platinum, pure Pt-based catalysts are too expensive for use in microbial fuel cells. There has been extensive research over the past several decades on creating catalysts from other materials, including non-noble metal catalysts. These catalysts include noble metals and alloys, carbon materials, quinone and derivatives, transition metal macrocyclic compounds, transition metal chalcogenides, and transition metal carbides (Dong et al., 2017). The most popular catalysts are made of carbon based materials including activated carbon (AC) and biomass-derived carbons. These groups were studied and some of these carbon based materials have produced similar or slightly higher ORR activity when compared to the Pt cathodes [(Yang et al., 2017), (Watson et al., 2013), (Sun et al., 2016), (Cheng and Logan, 2007), (Lepage et al., 2012)]. (Watson et al., 2013) discovered that an air-cathode using the coal-derived AC catalyst produced a higher current density than a Pt/C hybrid. (Watson et al., 2013) was able to compare the ORR activity of the catalysts with those derived from peat, coconut shell, hardwood, and phenolic resin, and found that the ORR activity of the catalysts was dependent on the precursors. This discovery then prompted other types of plant biomass (plant moss, rice straw, bamboo, sludge, and microalgae) to be studies as precursors for the carbonaceous

ORR catalysts [(Liu et al., 2015), (Yang et al., 2017), (Zhou et al., 2016), (Zhang et al., 2009)]. (Sun et al., 2016) used a cornstalk base to derive a nitrogen-doped carbonaceous catalyst to facilitate ORR and obtained a maximum power density of 1122 mW/m^2. (Zhou et al., 2016) developed a carbon nanoparticle coated porous ORR catalyst that was derived from plant moss and achieved a maximum power density of 703 mW/m^2. Animal biomass including: eggs, blood bones, urea, and animal liver have also been applied as precursors for ORR catalysts (Li et al., 2018). (Wang et al., 2015) synthesized non-precious tremella-like mesoporous carbon as the ORR catalyst using carbonized egg white as the carbon source. (Wu et al., 2016) furthered this research by creating an ORR catalyst based on co-doped mesoporous carbon microspheres from the ecofriendly biomass of eggs without the introduction of extrinsic dopants. Microalgae, such as Chlorella spp., with a high nitrogen content between 4–8% have been proposed as the precursor for a cost-efficient ORR catalyst in MFCs (Li et al., 2018). (Fan et al., 2017) found that a catalyst that is created using Chlorella pyrenoidosa can achieve a higher power generation of over 2000 mW/m^2 than the best Pt/C catalyst that is produced currently. Another popular choice is sludge which is usually an unwanted byproduct of wastewater treatment as it can also be used as the precursor for the ORR catalyst due to high N and metal levels. (Deng et al. 2017) found that N, P, and Fe heteroatom-doped hierarchical carbon catalysts with honeycomb-like interconnected macro-mesoporous frameworks could be obtained by direct pyrolysis of livestock sewage sludge. Their research showed that a maximum power density of 1273 mW/m^2 could be obtained when that catalyst is applied in MFCs which is very close to what can be obtained from commercial Pt/C (1294 mW/m^2).

Binders

In most catalysts, a binder is made up of synthetic material, such as silica and alumina and a natural clay, such as kaolin or kaolinite. These materials are needed to provide the catalyst the required mechanical strength and resistance towards attrition loss. (Choudhary et al., 1999) found that most binders are not chemically inert to zeolites, particularly at high temperatures, and are also not catalytically inactive. Zeolites are microporous minerals made of aluminosilicate that are typically used as industrial strength adsorbents and catalysts. Binders are necessary to hold the catalysts in close contact with the current collector and to establish favorable mass transport conditions including ionic conductivity with water and gas permeability (Ivanov et al., 2017). It is essential the binder hold everything together within the designed 3D architecture of the electrode assembly. Nafion is often used as a catalyst binder due to its long history in fuel cell applications, its high performance in many types of electrochemical cells, and its wide availability. However, Nafion is much more expensive relative to other polymers, and thus it is desirable to develop MFCs that are able to use less expensive binders (Sleutels et al., 2012). (Saito et al., 2011) found that when using oxygen reduction catalysts in MFCs, binders that were composed of hydrophilic polymers showed better oxygen reduction rates. Their best performing binder had a high water uptake of 50% using polystyreneb-poly(ethylene oxide), but unfortunately this block copolymer binder was also found to be too expensive for MFC applications. (Navessin et al., 2005) explored hydrogen fuel cells, where the only positively charged species are protons, and found that increasing the ion exchange capacity (IEC) of the binder would improve performance. However, when attempted using a MFC with phosphate buffers, it was found that increasing the IEC by sulfonating Radel to facilitate cation transport resulted in decreased cathode performance (Saito et al., 2010). Several less expensive polymers, such as polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS) and polyvinylidene fluoride (PVDF), have been explored as alternatives to Nafion. (Dong et al., 2012) discovered that using the air-cathode with AC as the ORR catalyst and PTFE as the binder showed a higher performance than that just used Nafion because of the improved oxygen supply.

The catalyst layer (CL) preparation process using PTFE as the binder can also have a significant impact on MFC performance. A 35% higher performance was obtained by avoiding sintering during CL preparation due to the fact that sintering reduced the pore area and the porosity of CL and led to a deteriorated oxygen supply to the CL (Dong et al., 2013). Sintering is the process of compacting and forming a solid mass of material by heat or pressure without melting it to the point of liquefaction. (Yang et al., 2014) developed a new method to create inexpensive air-cathodes using PVDF as the binder. The PVDF-based cathode was found to be feasible in MFC operation because a cheap, but more research and development is needed so that higher voltage outputs can be realized. (Cheng and Wu, 2013) theorized that the binder content in the air-cathode must have an optimum value due to the fact that high binder loading acts to increase the ohmic resistance of the electrode because the binders usually act as an electrical insulator, while a low binder loading can lead to the detachment of catalyst powder from the catalyst layer. (Popat et al., 2014) found that the binders were usually hydrophobic and would obstruct the H^+ and OH^- flow towards the CL, contributing to an additional cathodic potential loss of the air-cathode in MFCs.

Electrode Supports

Electrode supports are essentially the material that surrounds the electrode wire. The most common electrode supports for the cathode are carbon cloth, paper, and graphite paper. The graphite paper is manufactured by having the catalyst ink be coated on the water-facing side and the waterproofed layer is applied on the air-facing side (Liu et al., 2005). Carbon cloth and paper are the most widely used when creating both anodes and air-cathodes. However the one area where this has a downside due to the friability and the high cost of materials is for wastewater treatment. Other materials including: nickel foam, nickel mesh, and stainless steel mesh have been used as alternatives to carbon cloth and graphite paper due to their high electrical conductivity and their high stability in MFCs. (Zhang et al., 2009) developed an air-cathode which presses a catalyst layer (CL) onto the nickel mesh. This acts as a cathode support and current collector to help avoid the need for carbon cloth and reduces the cost of the air-cathode. (Cheng and Wu, 2013) used nickel foam as the current collector for their air-cathode design. Their results showed that the nickel foam cathode MFC produces a power density of 1190 mW/m^2, which was close to the1320 mW/m^2 generated from a typical carbon cloth cathode MFC. This was impressive in that the cost of a nickel foam activated carbon cathode is 1/30 of that of carbon cloth cathode. While the benefits of high corrosion resistance and electrical conductivity are very desirable, pure metallic nickel is too expensive for large scale MFC applications. This led to several studies being undertaken with the goal to reduce the cost of cathode fabrication even further. (Dong et al., 2012) tried stainless steel mesh (SSM) instead of nickel foam and mesh for the cathode. The advantages of SSM are that it is corrosion resistant, with high electrical conductivity, and low cost, making it a better choice than nickel mesh and foam. The SSM can even be enhanced as a cathode support and current collector by pressing CL and a gas diffusion layer (GDL) on its two sides, respectively (Ivanov et al., 2017). (Li et al., 2014) optimized the opening size of SSM in an activated carbon air-cathode and found that a cathode using SSM with 40 M had a better performance due to the lower internal resistance. SSM is becoming one of the most widely used cathode supports for the air-cathode of MFCs.

Cathode oxygen reduction

Oxygen is usually used in the microbial fuel cell cathode reaction as the electron acceptor. () have discovered that the oxygen reduction reaction weakens microbial fuel cell optimum operation and lowers the constraints. The most commonly used electrode material is graphite, but it is less than ideal for the oxygen reduction reaction catalyst, due to it having more than 6.69 mg/L of dissolved oxygen saturation value. This value is found by approximating the substance in saturated water vapor while the dissolved oxygen concentration is lowered to 80%. In order to improve the catalytic activity, usually platinum-modified graphite electrodes are applied instead. This could make the saturation level of dissolved oxygen increase by 2.0 mg/L, and the resultant current is 3 to 4 times higher than using graphite electrodes, but its large-scale applications are limited by cost constraints. One solution is the use of a cathode regulator to increase the oxygen with ferrocyanide being the driving force.

In the chemical fuel cells, researchers () have examined a variety of materials and their mixtures to replace the expensive platinum cathode. These materials include copper, gold, tungsten and manganese, using the redox properties of their respective cathode and oxygen in the electron transfer between the indirect. Pant et al, (2010) also studied using a 3-valent iron as microbial fuel cell cathode for performance. However, it was found that in general as a microbial fuel cell cathode catalyst most of them were not as good as platinum due to its high efficiency. The most important criteria for the effectiveness as a cathode catalyst is the affinity for oxygen, which shows the affinity for the cathodic reaction of dissolved oxygen saturation concentration (K).

Ion exchange membranes

Currently the bioelectrochemical system of a MFC finds itself limited mostly by the non-biological part of the cell design. This stems from the performance of ion exchange membranes. Ion exchange membranes act to separate the biological anode from the cathode reactions, and also transport the ions through the membrane in order to maintain electroneutrality in the system. Ideally it is desired to have the reactions within the cathode consume an equal number of protons and electrons so that only any excess protons are transported through the ion exchange membrane. This way electroneutrality can be maintained without having to adjust the pH in the cathode. Bioelectrochemical systems on that feed on wastewater typically apply cation exchange membranes (CEMs). There are two studies that have shown that there are also cation species other than protons are responsible for the transport of positive charge through the membrane (Rozendal et al., 2006; Zhao et al., 2006). This occurs mainly due to the fact that in wastewater the concentrations of other cations (Na, K, NH_4) are sometimes found to be up to 105 times higher than the concentration of protons (Rozendal et al., 2008). This can cause an issue due to these other cation species causing a pH increase at the cathode, which can negatively affects MFC performance. In the double-chamber MFCs (DCMFCs), the membrane is usually used to separate the anode and cathode chamber. This prevents the crossover of oxygen and substrate while allowing ion transfer between the anode and cathode chamber. The ion exchange membranes that have previously been used in MFCs include: anion exchange membrane (AEM), cation exchange membrane (CEM), proton exchange membrane (PEM), bipolar membranes, and polymer/composite membranes. So far they have only as a method to separate electrode chambers and decrease oxygen diffusion into the anode chamber (Zu et al., 2008).

Cation exchange Membrane

Many CEMs, including Nafion, Hyflons, Zirfons, and Ultrexs CMI 7000, are used in dual chamber microbial fuel cells (DCMFCs). Nafions are the most commonly used material in CEM MFCs because of their good proton conductivity. This conductivity comes from the negatively charged hydrophilic sulfonate groups that are attached to the hydrophobic fluorocarbon backbone (Mauritz and Moore, 2004). In general it is the thinner membranes that contain lower ohmic resistance and are able to generate higher performance. (Rabaey and Verstraete, 2005) showed that MFCs with a thinner Nafion 112 membrane had an average power density of 31.32 mW/m^2 which was much higher than 9.95 mW/m^2 produced by MFCs using a thicker Nafion 117 membrane. (Pant et al.,2010) studied how different membrane types affected MFC performance and found that an MFC with Ultrexs CMI 7000 had a comparable performance to that with the Nafion membrane, but had a lower oxygen mass transfer coefficient ($2.8 X 10^{-4}$ cm/s) compared to one with Zirfons ($1.9 X 10^{-3}$ cm/s).

Anion exchange membrane

Anion-exchange membranes have been explored for application in low temperature chemical fuel cells by Poynton et al. (2010), but they also have the potential for use in microbial fuel cells. These membranes possess desirable characteristics such as low oxygen permeability and low ionic resistance. AEMs, such as AFN, AM-1, and ACS, are also widely used in MFCs. AFN had the lowest membrane resistance among these AEMs, resulting in the increased production of electricity (Kazemi et al., 2012). However, AM-1 and ACS have a lower oxygen mass transfer coefficient compared with AFN. (Elangovan and Dharmalingam, 2017) found that the anion exchange membrane eliminates pH splitting more effectively than a cation exchange membrane but implied that the additional amount of substrate crossover from anode to cathode is a real disadvantage. The undesirable effects that would stem from that include biofilm growth on cathode surfaces and reduced performance. Bacteria and other organic substrates form a primary biofilm layer on a membrane surface facing toward the anode chamber (Pandit et al., 2012). This means that an excessive oxygen crossover would lead to the formation of a secondary biofilm layer. (Kim et al., 2012) found that absorption of oxygen by aerobic bacteria in the biofilm causes a negative oxygen gradient in the anode side and thos them allows oxygen diffusion from the cathode chamber toward the anode

Proton exchange membrane

Proton exchange membranes are the most frequently used separators in microbial fuel cells. This is due to their moderately high conductivity to cations and low internal resistance compared to other separators. The role of proton transportation in MFC performance makes PEMs one of the most important components in the cell. The performance of PEMs is determined by the rate of proton transport from anode to cathode. Another special requirement is preventing the flow of oxygen, substances, and minerals in either direction. Poor proton transferability is one of the most substantial deficiencies in PEMs, which remains significant despite PEMs various positive traits like composition, internal resistance and conductivity. PEMs have some disadvantages in that they are expensive (up to 40% of the cost of a completed MFC) and have a greatet tendency for chemical or biological fouling which increases the internal resistance and leads to a decrease in efficiency and electric production. The cathode can also be affected by the higher transfer rate of cations to protons.

Nafion, an invention of DuPont is a sulfonated tetrafluorethylene copolymer that consists of a hydrophobic fluorocarbon back-bone (–CF–CF–) to which hydrophilic sulfate groups (SO_3) are attached. Nafion shows high conductivity to various cations because of the presence of these negatively charged sulfonate groups. (Min et al., 2005) evaluated the performance of a PEM and a salt bridge in a two chambered MFC and found that the power density of the MFC using the PEM was close to 3.91 mW/m^2 which was almost double the power density generated by the salt bridge MFC (2.2 mW/m^2). It was discovered that higher internal resistance was found to be the cause of the lower power output in the salt bridge system compared to the one using Nafion. This means that the internal resistance was a critical factor in the amount of power density that is produced. (Grzebyk and Pozniak, 2005) pretreated interpolymercation exchange membranes with polyethylene/poly(styrene-co-divinylbene) and then enhanced the mixture by sulfonation with a solution of chlorosulfonic acid in 1,2-dichloreoethane. The MFC in the study used a different membrane which had a relatively low performance compared to Nafion. Their MFC only achieved the maximum voltage of 67 mV but did obtain a total internal resistance of 830Ω by using graphite electrodes with an effective surface area of 17 cm^2 for both the anode and cathode. (Park and Zeikus, 2000) created a compartmented MFC using porcelain septum made from kaolin instead of using Nafion. It was found that the maximum current produced was 14 mA, the potential was 0.45 V, the current density was 1750 mA/m^2 and the power density was 788 mW/m^2 using sewage sludge as a biocatalyst, a Fe^{3+} based graphite as a cathode and a Mn^{4+} based graphite as an anode. The kaolin septum produced similar results as the Nafion without displaying any obvious performance issues.

Ultrex CMI 7000, a product of Membranes Inc. USA, is a CEM which is often used as a PEM in MFCs. CMI 7000 has a gel polystyrene and divinyl benzene cross-link structure containing large amounts of sulphoric acid groups which make it a strong acid polymer membrane (Rahimnejad et al., 2014). (Harnisch et al., 2008) found that the CMI 7000 cation conductivity was similar to Nafion with the bonus of better mechanical durability but there was a tradeoff of higher Ohmic resistance. A few other less expensive CEMs have been used as PEMs in MFCs, including Zirfon by (Pant et al., 2010) and Hyflon (Ieropoulos et a., 2010). Hyflon is a short side chain perfluoropolymer membrane made by Solvay-Solexis in Italy which was found to have higher conductivity levels and more chemical stability than to Nafion, but again suffers from higher levels of internal resistance. Zirfon is a macroporous organo-mineral material that is made up of 85% hydrophilic ZrO_2 powder and 15% polysulfone (Rahimnejad et al., 2014). Zirfon's high rate of oxygen permeability is harmful to its anodic reactions, but it has a lower resistance than Nafion. (Rozendalet et al., 2006) found that there should be cation, rather than proton, migration across Nafion membranes electrochemically. This was necessary to address operational problems from using Nafion in cases where only cations were present, and the results showed that only the membranes with 100% selective protons to be ideal for use in MFCs. (Zhao et al., 2006) found that porphyrin-modified cathodes could be implemented with Nafion membranes to help stabilize the pH gradients with the additional benefit of enhanced cation transportation in a neutral pH media across Nafion membranes.

The effect of PEMs in MFC performance is commonly determined according to generated power density and coulombic efficiency. Nafion is the commonly used membrane in MFCs, but there are still a number of problems associated with the use of Nafion including oxygen transfer rate, cation transport and accumulation rather than protons, membrane fouling and substrate loss. Moreover, additional problems can also be attributed to the effect of PEMs including internal resistance and pH change in MFCs. Recent developments in PEM performance are attributed to two categories including utilization of other types of membranes and improvements in Nafion by pre□treatment methods.

Oxygen transfer rate

Oxygen transfer rate is an intrinsic property of a PEM which often affects it's the performance of MFCs. This is due to the anode bacteria requiring completely anaerobic conditions. The issue is that air diffusion can cause negative effects on MFCs in terms of loss of coulombic efficiency (CE) due to aerobic bacterial respiration (Rahimnejad et al., 2014). CE is defined as the ratio of produced coulombs in reaction to the total theoretical coulombs of a substrate. (Min et al., 2005) found that there are a number of factors that can affect the operation of MFCs including the utilization of PEMs or salt bridges. A Nafion membrane with a cross-sectional area of 2.1 cm^2 was used with the dissolved oxygen on the cathode side of the membrane saturated to (7.76×10^3 mg/ cm^2). This configuration was able to obtain a maximum rate of oxygen diffusion into the anode chamber of 0.014 mg/h and an effective diffusion coefficient of 1.4×10^4 cm/s. That was much higher that what was previously produced other common PEMs (CMI-7000) or size selective membranes (UF membrane) where the diffusion coefficient for these membranes was around 0.9×10^4 cm/s and 0.4×10^4cm/s.

Nafion has so far been found to be the most permeable membrane to oxygen. (Chae et al., 2007) found that the dissolved oxygen in the anode chamber increased from 0.38 to 1.36 mg/l within 655 min due to oxygen transfer across the Nafion membrane and estimated the oxygen mass transfer coefficient for Nafion to be 2.80×10^4cm/s. (Kim et al., 2007) discovered that the oxygen diffusion coefficient often resides in the range of 1 to 6×10^6 cm^2/s. In this case the higher value shows the rate of Nafion penetrability to oxygen which acts to reduce the performance of MFCs, either by damaging anaerobic bacteria or through the loss of substrate due to aerobic bacterial respiration. (Liu and Logan, 2004) found that up to 28% of the glucose added to a MFC was consumed by aerobic bacterial respiration and lost due to oxygen diffusion through the Nafion membrane. (Chae et al., 2007) used sparged nitrogen gas in the anode chamber of an MFC as a work around and evaluated the power generated in comparison to the non-sparged MFC. Sparging is a process where a chemically inert gas is bubbled to increase the gas liquid interface. They reported that the sparged nitrogen gas MFC had a much higher power output than due to the continuous removal of diffused oxygen from the cathode compartment. The power density of the N_2 sparged MFC (29.4 mW/m^2) was found to be about 3 times higher than that of the non-sparged MFC (10.3 mW/m^2) and the CE values were 20.3% and 12.8%, respectively. (Bond and Lovley, 2003) believe maintaining aeration at a minimum level would prevent excessive transfer of oxygen across PEMs.

Oxygen transfer depends on the membrane type as well as MFC operating conditions. It has also been found to be an effective parameter of the MFC's performance.

Membrane fouling

Membrane fouling is caused by biofilm formation and buildup on a PEM over a long period of MFC operation. PEM biofouling in double chambered MFCs is a real disadvantage due to the fact that when a PEM is fouled, it needs to be replaced with a new one or recovered in order to maintain its production of electricity (Ter Heijne et al., 2006). However, the high cost of PEMs is a major drawback, especially when looking for practical MFC applications in the future. This could make the operating costs increase to go along with a potential decrease in MFC performance. Currently, there have been only a few research studies on PEM biofouling and its effect on ion transport, MFC performance, and electrical resistance (Rahimnejad et al., 2014). Unlike the fouling that occurs in membrane filtration processes or in membrane bioreactors, the PEM fouling process in MFCs is very specific due to the fact that physical, chemical and biological interactions between the contaminants and the PEM occur simultaneously. (Choi et al, 2011) studied the alteration of Nafion after membrane fouling and found that the decrease in membrane conductivity after fouling was primarily due to the replacement of protons in the binding sites of the PEM by other cations, rather than the biofilm attached on the membrane. It was also discovered that intermolecular bridging by metal ions between sulfonate groups and organic foulants had an important role in microbial adhesion and biofilm formation (Bellona et al., 2004). Electrostatic interactions between the surface charge of the PEM and the charged groups of foulants caused their deposition on to the membrane, which increased the electrical resistance.

The foulants can either be organic or biofoulants, such as extracellular polymeric substances that participate in the formation of microbial aggregates. Soluble microbial products were thought to be more effective in preventing membrane biofouling (Li and Elimelech, 2004). The cations are attracted to the intermolecular bridging between organic foulants and the fouling layer once a membrane is fouled (Bond and Lovley, 2003). This means the accumulation of bacteria, biofoulants, and cations will create a dense biofilm on the PEM surface, which will increase electrical resistance. The desirable location for biofilm formation is on the anode and not on the PEM. However, the membrane resistance has little influence on the total internal resistance of the MFC. (Oh and Logan, 2004) found that a small increase in the membrane internal resistance would not have an important influence on the performance of the MFC.

This means that the decline of the MFC's performance after the membrane fouling would be due to other factors in addition to the increase in membrane resistance. (Choi et al., 2011) investigated the biofouling effect on MFC performance by comparing the voltage produced from MFCs using three different membranes: a biofouled membrane, a physically cleaned membrane, and a fresh Nafion membrane. The biofouled membrane produced a 13.5% increase in cell voltage after it was cleaned and the biofilm was removed. It also produced a 29.5% increase in power density, but the increase in CE was limited to 4%. (Choi et al., 2011) found that when a Nafion membrane was pre-stored in deionized water to disconcert the cation occupation, this produced increases of 16.7% for maximum cell voltage, 36.3% for power density, and 31.5% for CE which is significantly higher than the biofouled Nafion membrane. What essentially is happening is that after an MFC with fresh Nafion is operated, the Nafion becomes biofouled over time due to the biofoulants and cation occupation. This then leads to a decrease in ion exchange capacity and a decrease in MFC performance is expected. (Rahimnejad et al., 2014) theorize that the cation occupation of the sulfonate functional group has a higher influence on the electrical resistance of Nafion than biofouling. This means that a regularly scheduled chemical cleansing of the PEM is essential and can be done either by removing biofilms or by regenerating the functional group of the PEM rather than simply removing the biofilm from the PEM.

Polymer/composite membrane

Polymer/composite membranes, such as sulfonated polyether ether ketone (SPEEK) membranes and disulfonated poly (arylene ether sulfone) (BPSH) membranes, are sometimes used as alternatives to the Nafion membrane in MFCs. This is due to a high proton conductivity and a low oxygen mass transfer coefficient of the SPEEK membrane which can be obtained by sulfonating the native PEEK membranes (Zaidi et al., 2000). (Leong et al., 2013) found that MFCs with a BPSH membrane had a higher performance than those with Nafion. This was caused by the lower ohimic resistance and the lower amount of biofouling activity on the membrane resulting from the higher proton conductivity and the higher hydrophilicity of the BPSH membrane. Although these ion exchange membranes are able to prevent the crossover of oxygen and the substrate, their main disadvantage is the pH imbalance created between the anode and cathode chambers (Li et al., 2018). This was found to be caused by the limited cation or anion transfer across the membranes which led to both anode chamber acidification and cathode chamber alkalization (Kazemi et al., 2012). Anode chamber acidification and cathode alkalization leads to the inhibition of microbial activity, deterioration of the cathode catalyst activity, and a reduction in whole cell performance.

Bipolar membrane

The bipolar membrane was invented by (Heijne et al., 2006) as a solution to the issue they were facing when previously using ferric iron with a cation exchange membrane. Ferrous iron oxidation has been shown to operate efficiently at a high rate (Ebrahimi et al., 2005). The MFC could not maintain the low catholyte pH required to keep ferric iron soluble. This was due to the fact that cation exchange membranes transport other cations than protons as well, which can cause a pH rise in the cathodic compartment as previously discovered by (Rozendal et al., 2006). This pH rise caused extensive iron precipitation that damaged the membrane of their MFC. Further analysis showed that the pH drop in the anodic compartment and the pH increase in the cathodic compartment were due to migration of protons and other cations through the cation exchange membrane. The problem was that other cations besides protons were able migrate through the cation exchange membrane that was being used when there were higher concentrations. It then became necessary to devise an MFC with a catholyte pH below 2.5 to keep ferric iron soluble without external acid dosing. To achieve this, a bipolar membrane was used instead of the commonly used cation exchange membrane. A diagram of their setup is shown in Figure 3. A bipolar membrane consists of cation and anion exchange sections joined together in series (Heijne et al., 2006). One function controls the bipolar membrane is water dissociation by way of electrodialysis. When an electric field is added, water will split into H^+ and OH^- at the membrane junction. This reaction then causes both proton migration through the cation exchange membrane and hydroxide migration through the anion exchange membrane.

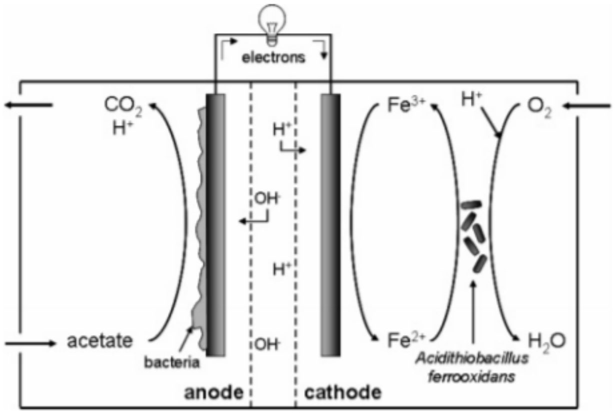

Figure 3. Design of a MF with a bipolar membrane.

The bipolar membrane was found to essential because it provided the cathodic compartment with protons and the anodic compartment with hydroxides as a result of water dissociation. The low catholyte pH was able to be maintained in this way without using any additional acid. By using the bipolar membrane (Heijne et al., 2006) was able to increase the power density from 0.5 to 0.86 W/m^2, which was the highest power density found during the research. Current density was also increased from 3.4 to 4.5 A/m^2 while the cell voltage was held stable at 190 mV. The voltage across the polar membrane is typically defined as the potential difference between the cathode reference electrode and the anode reference electrode. Ohmic losses will increase as the distance between the membrane and the electrodes increases. The measured voltage across the membrane will then consist of both ohmic losses and a true voltage across the membrane. Ohmic losses will be discussed in a future section.

Other membranes

To overcome the many problems plaguing ion exchange membranes including: pH imbalance between the anode and cathode chambers, high costs, and high internal resistance there have been many different porous membranes or separators that have been proposed. Ultrafiltration membranes, microfiltration membranes, nylon and glass fiber filters, J-cloths, and polyether sulfone resin have been studied as separators for MFCs [(Kim et al., 2007), (Sun et al., 2009), (Yang et al., 2017)]. (Fan et al., 2007) used J-cloth as the separator on the water facing side of the air cathode of an MFC. The CE was significantly improved from 35% to 71% due to the significant reduction of oxygen diffusion in the J-cloth itself. Separators with a large pore size typically produce higher performance due to lower internal resistance. (Zhang et al., 2010) used nylon filters with different pore sizes as separators in MFCs and was able to show that the power generation increased from 769 mW/m^2 to 941 mW/m^2 when the pore size was increased from 10mm to 160 mm. Porous membranes usually have a low internal resistance, compared to the ion exchange membranes, due to their porous structure that benefits the ion transfer between the anode and the cathode (Li et al., 2018). Thus, the application of these porous membranes or separators can effectively prevent the diffusion of oxygen from the cathode to the anode, improve the CE, and alleviate the pH imbalance.

Membrane application

(Kim et al., 2007) showed that placing a CEM, AEM, or Nafion membrane between the electrodes would only minimally affect the internal resistance (84-88 Ω), on the basis of a comparison to the same reactor without a membrane (84 Ω). The study also found that the power density generated using an AEM membrane (610 mW/m^2), was slightly larger than the power density obtained using either a CEM (480 mW/m^2) or Nafion (514 mW/m^2) membrane which was theorized to be due to the increased amount of charge transfer by negatively charged phosphate groups. Although AEM and CEM membranes have been applied as separators in MFCs, their performance as cathodes has not been studied yet (Zuo et al., 2008). (Zou et al., 2007) have researched the use of UF membranes as both a separator and as the supporting material for a tubular cathode in MFCs. However, their UF membrane studies have all shown a large increase in internal resistance and thus have produced lower power densities than many of the other materials that were also tested. Their results showed that the ion exchange membranes are better suited for MFC applications than UF membranes.

Potentiostat

Potentiostats are used to obtain a more detailed understanding of the bio-electrochemical reactions contained within the MFC system. Potentiostats have the ability to control either the potential or the current of an electrode in order to study how that electrode responds electrochemically under that specific condition. The potentiostat is typically operated in a three-electrode-setup consisting of a working electrode (anode or cathode), a reference electrode, and a counter electrode (He et al., 2006). Some studies have setup the potentiostat using a two-electrode setup either to obtain polarization curves or to determine the ohmic resistance using the current interrupt technique. In the two-electrode setup, the working electrode connector is connected to the cathode and both the counter electrode and reference electrode connectors are connected to the anode. In MFC experiments, this instrument is often used for voltammetry tests in where the potential of the working electrode is varied using certain scan rates (Logan et al., 2006).

More advanced measurements can be taken when the potentiostat is equipped with a frequency response analyzer (FRA). The FRA allows the potentiostat to observe electrochemical impedance spectroscopy measurements (EIS). The way that EIS works is that a sinusoidal signal with small amplitude gets superimposed on the applied potential of the working electrode. By varying the frequency of the sinusoidal signal over a wide range (typically 10^{-4} to 10^{6} Hz) and plotting the measured electrode impedance, detailed information can be obtained about the electrochemical system (Bard and Faulkner, 2001). EIS can also be used to measure the ohmic and internal resistance of an MFC (He et al., 2006), as well as to provide additional insight into the operation of an MFC. (Rabaey, and Verstraete, 2005) found that the interpretation of EIS data can be rather complex. EIS techniques will be discussed further in later section.

Oxidation and reduction reactions

The oxidation of sediment organic matter coupled to the reduction of Fe(III) and Mn(IV) oxides is catalyzed by a consortia of microorganisms. Some microorganisms break down the complex assemblage of organic matter to produce fermentation products, such as acetate, and other potential electron donors for Geobacteraceae, such as aromatic compounds and long-chain fatty acids. The Geobacteraceae can then oxidize these compounds with the reduction of Fe(III) or Mn(IV) (Lovely and Phillips, 1986). It is theorized that in a soil based microbial food chain, with anodes substituting for the Fe(III) and Mn(IV) that Geobacteraceae would naturally use, would be able to dramatically improve electron transfer.

Obtaining power density

There are two types of power density that can be referred to with a MFC: surface specific power density and volumetric power density (Liao et al., 2018). Surface specific power density is the power output normalized by the electrode surface area on either the anode or cathode surfaces. This gives a measure of how the anode and cathode are performing. If the MFC design also contains a membrane or separator the surface specific power density could also be calculated based on the membrane or separator surface area. Thus for a given MFC there could potentially be three different values for the surface specific power density. Volumetric power density is used to evaluate the power output of the entire MFC system. The calculation uses the power output normalized by the reactor volume (Li et al., 2018).

One of the issues with a MFC is that the presence of a high resistance will often limit the maximum power density. This means that optimum composition of the microbial fuel cell necessary to obtain the upper range of the power levels still remain unknown. Several groups of studies have shown that adding microbial flora and fuel to an ongoing microbial fuel cell can produce an increase of up to ten times the maximum power density. It has been observed that the performance of microbial fuel cells and reactors are influenced from a number of factors including super-potential and resistance. Chemical fuel cells are a special class of microbial fuel cells that are able to produce more than 10 times the power density (Rismani-Yazdi et al., 2008). This is due to the presence of a micro-device within the chemical fuels cell that enables the changing of various system parameters to increase its resistance, such as water and organic nitrogen demand, anode catalyst and reactor configuration. Thus, the reactor should be optimized geometry with respect to the electrolyte to reduce both the resistance and the catalytic potential of the microorganisms.

The production of electricity is highly influenced by both light photons as well as the environment temperature. The increase in the sunlight was found to increase the production of electrons. (Acharya and Aithal, 2017) found that the optimum temperature for the maximum production of the electrons was 40◦ Celsius. (Laxmipriya et al., 2018) discovered that the addition of NaCl served to enhance the conductivity of both the anode and cathode equally which led to increasing the ionic strength of the MFC and increasing its power output. Theoretically, the maximum or reversible voltage that can be generated from an MFC is restricted by the laws of thermodynamics and can be calculated using the Nernst equation:

$$E_{mef} = E^{o} - \frac{RT}{nF} ln \frac{[products]^{p}}{[reactants]^{r}}$$

where E_{mef} is the maximum electromotive force

E^o is the standard cell electromotive force,

R is the Ideal gas constant (8.31 $\frac{J}{mol\,K}$)

T is the absolute temperature (K)

N is the transferred electron number

F is Faraday's constant (96,485 $\frac{C}{mol}$)

Polarization curves

In actuality, the open current voltage (OCV) and the operation voltage of an MFC are always lower than the reversible voltage that is predicted by the above equation. OCV is defined as the cell voltage that can be measured after a period time with no current in the system. The OCV has been found to be substantially lower than the cell reversible voltage, due to various potential losses. To analyze the source of voltage losses, a polarization curve is created. Figure 3 shows an example polarization curve. The polarization curve is necessary to evaluate the performance for any fuel cell. This is accomplished by determining the appropriate external resistance which is the best fit for the designed MFC. (Watson and Logan, 2011) found that estimates of the amount of power that can be produced in an MFC are a function of the technique used to obtain polarization data. The internal resistance of MFCs can be found using electrochemical impedance spectroscopy (EIS). EIS tests work by on a potentiostat by applying a sinusoidal signal with small amplitude on the working electrode. By changing the sinusoidal signal frequency over a wide range (typically from 100 kHz to 0.01 Hz), impedance spectra can be obtained for the MFC system. A Nyquist curve is plotted using the impedance spectra as the real impedance (Zre) versus imaginary impedance (Zim). Linear sweep voltammetry (LSV) is currently the commonly used technique to obtain polarization data, but (Velasquez-Orta et al., 2009) found that high scan rates can overestimate power production by a considerable amount. An alternate approach is to vary the circuit resistance at fixed time intervals, ranging from 10s to 24h (Liu et al., 2008). There have been a few studies comparing the different techniques [(Menicucci et al., 2006), (Aelterman et al., 2006), (Zuo et al., 2009)]. (Velasquez-Orta et al., 2009) found that power production with scan rates higher than 0.1 mV/s produced higher power densities than those where the circuit resistance was varied.

As shown in Figure 4, the polarization curve can be divided into three distinct sections. In the initial section of the curve there is a rapid reduction of OCV at very small current densities. As the current density increases, the voltage decrease becomes approximately linear in nature. When the current density level becomes sufficiently high the voltage drop intensifies. (Li et al., 2018) theorize that the voltage losses are mainly caused by electrode overpotentials in the anode and cathode which are current dependent. This overpotential is essentially the energy lost due to the slowness of electrochemical reactions at the anode and the cathode electrodes and will change with current density. (Liao et al., 2018) believe that electrode overpotentials are caused by losses in three regions of the MFC circuit: activation losses, ohmic losses, and mass transport losses.

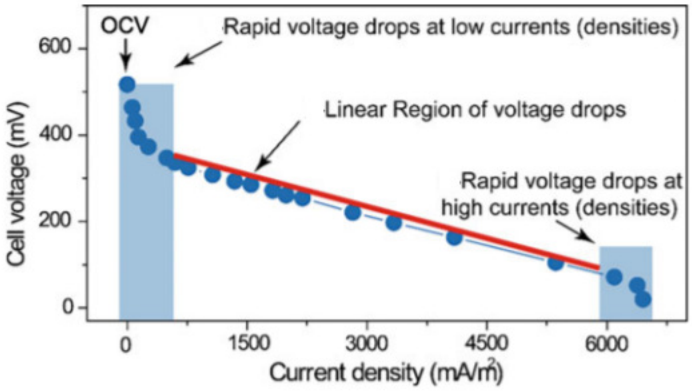

Figure 4. Polarization curve for a MFC.

Activation losses are defined as the energy lost from the following sources: oxidation and reduction reactions, transferring electrons from the bacteria to the anode surface by the conductive material on the cell surface. These activation losses could be reduced by enhancing the electron transfer between anode and bacteria, using highly efficient cathode catalysts, and improving the anode biofilm metabolism activity for substrate oxidation (Logan, 2008). Ohmic losses are caused by several forms of resistance including: ion conduction in both the solution and membrane, the flow of electrons through the electrodes and wires, and their connection points. The ohmic losses could be minimized by decreasing the electrode spacing, removing the membrane, using a membrane with a high ion conductivity, increasing the solution conductivity, improving the electrode conductivity, and ensuring a good connection between the electrodes and connection wires (Liao et al., 2018). Mass transport losses arise from the insufficient transport of protons and electrons on the journey to and from the electrode. The best case for loss reduction in this case resides at the anode, where it has been found that ensuring a sufficient substrate supply and proton removal has proven to be the most effective approach (Li et al., 2018). One issue that does appear is that as the proton removal within the biofilm becomes limited it can lower lowers the local pH of the biofilm and thus restrict the biofilm activity. There could also be an issue within the cathode where the limited proton supply for the ORR would increase the pH level and lead to lower cathode potential and decreased performance (Li et al., 2018).

Internal Resistance

The internal resistance (R_{in}) of a fuel cell is defined as the sum of the solution resistance (R_s), polarization resistance (R_p), ohmic resistance, charge-transfer resistance, and mass-transfer resistance. A multitude of factors affect the internal resistance of the cathode including: MFC configuration, solution conductivity, the distance between electrodes, and the nature and type of membrane (Elangovan and Dharmalingam, 2017).

Hydrogen production

(Coates and Wrighton, 2009) discovered that microbial fuel cells also have to capability to produce hydrogen for use as an alternative fuel. To create this hydrogen production, the MFC needs to be supplemented by an external power source to overcome the energy barrier required for turning all of the organic material into carbon dioxide and hydrogen gas. This can be accomplished by converting the MFC design to maximize hydrogen production by keeping both chambers anaerobic. Researchers at Penn State in 2005 found that an additional amount of hydrogen would be produced by supplementing the MFC with a constant 0.25 volts of electricity during the process. Hydrogen bubbles form at the cathode and can then be collected for use as fuel source. Although electricity is used instead of generated as in normal MFCs, this method of producing hydrogen is very efficient due to more than 90% of the protons and electrons generated by the bacteria at the anode being turned into hydrogen gas (Logan, 2008). Other more conventional methods for production of hydrogen require up to 10 times the amount of energy as an adapted MFC, making the MFC the most efficient and environmentally safe method to generate hydrogen for use as fuel (Rabaey and Verstraete, 2005).

Rate-limiting factors of microbial fuel cells

As with the case of other fuel cells, microbial fuel cell performance is judged by the current, power density, and fuel oxidation rate that are measured. The factors that affect the fuel oxidation rate include: catalytic activity of the anode, fuel-proliferation, spread of electrons and protons, and consumption. Potential variables that could be altered to improve voltage output include: soil and water sources, nutritive additions to the soil and water mixture, the size and shape of the container, the anode and cathode graphite felt material, and configuration of the wires connecting the anode and cathode to the circuit.

Cellular Respiration

All life species on Earth need to harness energy that comes in the form of electrons to remain alive. Most organisms get their electrons from consuming sugars. In a series of chemical reactions that happen inside their cells, the electrons are released, and ultimately flow into oxygen (Kato et al., 2012). That flow of electrons is what powers their bodies. This means that the challenge for all creatures is the same. Any organism from a single-celled bacterium to a blue whale needs to find a source of electrons and also a place to dump them to complete the circuit. Microbes obtain the energy needed for their life functions from the energy produced by the oxidation of the food source. A fraction of the free energy produced is used by the microbes for their catabolic activities and the rest may be utilized to generate electricity. This means that if a sustainable MFC with a long life span is desired, it is necessary for the microorganism to balance out the amount of energy consumed for its vitality and that being converted into electrical energy. Microbes use two metabolic pathways for energy conversion called respiration and fermentation. In the respiratory or oxidative pathway, the Gibbs free energy is utilized by the microbes for their respiration where the electrons circulate around a respiratory chain and finally exits the microbial cell via membrane-bound electron acceptors. Cellular respiration is the process of oxidizing a fuel source such as glucose to the final products of carbon dioxide and water. In the process, the cellular chemistry takes glucose apart, bond-by-bond, extracting its bond energy at each step. The equation for the respiration of glucose is given below. The respiration of a mole of glucose releases 686 kcal of energy. This value represents the difference between the energy needed to break the bonds of both the reactants glucose and oxygen and the energy liberated when the bonds of both the products H_2O and CO_2 form.

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

The energy released is stored in the form of adenosine triphosphate (ATP) which can be consumed by the microbe. ATP has its energy stored by having its third phosphate group weakly bonded to the rest of the molecule allowing it to be easily broken. This encourages stronger bonds to form and transfers the difference in energy to the cell. Most of the ATP produced by aerobic cellular respiration is made by oxidative phosphorylation. This works by the energy released in the consumption of pyruvate being used to create a chemiosmotic potential by pumping protons across a membrane. This potential is then used to drive ATP synthase and produce ATP from ADP and a phosphate group. It is often theorized that a maximum of 38 ATP molecules can be created by the oxidation of a single glucose molecule during cellular respiration (2 from glycolysis, 2 from the Krebs cycle, and about 34 from the electron transport system). In actuality this maximum yield is never quite reached due to losses from leaky membranes as well as the cost of moving pyruvate and ADP into the mitochondria's matrix so typically the maximum output is near 29 to 30 ATP per glucose.

There are three main steps of cellular respiration: 1) Glycolysis, 2) the citric acid cycle, where most of the NADH is made, 3) Oxidative phosphorylation, where most ATP of the is made from electrons carried by NADH. In some simple cells glycolysis is the only step in cellular respiration, Glycolysis is essentially the splitting of glucose, a six-carbon sugar, into two three-carbon pyruvic acid molecules. This process requires the energy stored in two molecules of ATP to be spent but in the later stages of glycolysis, four ATPs are produced and two electrons are transferred to the electron-carrier Nicotinamide adenine dinucleotide (NAD+). The net gain of the reaction is two ATPs and 2 NADH molecules. The two pyruvic acid molecules are then shuttled into the mitochondria, where they are converted to two molecules called acetyl coenzyme A (Acetyl CoA) for further breakdown.

Nicotinamide adenine dinucleotide

NADH is a crucial coenzyme in making ATP. The molecule acts as a shuttle for electrons during cellular respiration. It exists in two forms in the cell: NAD+ and NADH. NAD+ is the oxidized form which is able to accept electrons from another molecule. After it takes extra electrons, a negative charge is developed. It then has to pick up extra hydrogens atom from the surrounding environment to stay neutral which gives the reduced form of NADH. NADH, along with another molecule flavin adenine dinucleotide (FADH2) will ultimately transport the electrons to the mitochondria, where the cell can harvest energy stored in the electrons.

Acetyl CoA

Acetyl CoA is created by the joining of acetic acid with the coenzyme A. CoA is itself composed of two main parts, a long general protein-like chain and that is connected to adenosine diphosphate (ADP) which is one of the molecules used for energy storage. The most important part of the compound lies at the end of the protein chain, which terminates in a sulph-hydryl (-SH) group (Alberts et al., 2002). This group is highly reactive, and links to carboxylic acid molecules via a thioester bond. The thioester bond is very high energy bond and has a lot of resonance donation from the sulfur being much larger than the oxygen, hydrogen, and carbon molecules which makes it very unstable. This means that the acetyl group can be easily transferred to other molecules which lets acetyl-CoA be used as a universal intermediate. This provides the C_2 fragment for numerous biochemical syntheses. CoA is an extremely important biological molecule which is right at the hub of carbohydrate metabolism. This process is called the Citric Acid Cycle because C_2 gets oxidized to carbon dioxide. The cycle also produces hydrogen atoms, which then continue in another series of biochemical reactions to produce ATP and water. ATP is able to store energy in the form of phosphate bonds for later use. In the citric acid cycle one molecule of acetyl-CoA can generate up to 12 ATPs. When the acetyl is released, CoA is regenerated, which returns to the citric acid cycle to start up another reaction.

If the C_2 unit is not able to be oxidized to CO_2 so that the energy can be used immediately, another possibility is that it can be used to build important biological molecules. Acetyl-CoA also has the capability to originate the synthesis of fatty acids from carbohydrates. Fatty acids have carboxylic acid groups (-COOH) at one end, and a long alkane/alkene chain at the other (Alberts et al., 2002). Examples include linoleic acid (a constituent of margarine), palmitic acid (from palm trees, and used as a constituent of na*palm* in WW2) and butyric acid (found in butter). Three of these fatty acids then join together with one molecule of glycerol to make triglyceride or triacylglycerol which forms the main constituent of vegetable oil and animal fats. The three fatty acids RCOOH, R'COOH and R"COOH can be all different, all the same, or only two the same, but what they have in common is that they were all synthesized using acetyl-CoA (Alberts et al., 2002). The chain lengths of the fatty acids in naturally occurring triglycerides can be from 5 to 28 carbon atoms. The natural fatty acids found in plants and animals are typically composed only of even numbers of carbon atoms, due to the way they are bio-synthesized from C_2 units using acetyl-CoA while bacteria possess the ability to synthesize odd chain and branched chain fatty acids. Therefore, the fat from ruminant animals contains significant proportions of branched chain fatty acids, due to the action of bacteria in the gut. Acetyl-CoA is also used in the synthesis of isoprenoid molecules, esters and amides such as acetylcholine (an important neurotransmitter), and some steroids such as cholesterol.

Citric acid cycle

The citric acid cycle, however, occurs in the matrix of cell mitochondria. Each step in the cycle is catalyzed by a specific enzyme. The two-carbon acetyl group of acetyl CoA is added to the four-carbon oxaloacetate to form the six-carbon citrate. The conjugate acid of citrate is citric acid, hence the name citric acid cycle. Oxaloacetate is regenerated at the end of the cycle so that the cycle may continue. Citrate loses a molecule of water and another is added. In the process, citric acid is converted to its isomer isocitrate. Isocitrate then loses a molecule of carbon dioxide and is oxidized forming the five-carbon alpha ketoglutarate and NAD+ is reduced to NADH in the process. The next step has alpha ketoglutarate be converted to the 4-carbon succinyl CoA. Another carbon dioxide molecule is removed and another NAD+ is reduced to NADH. CoA then removed from the succinyl CoA molecule and is replaced by a phosphate group. The phosphate group is then removed and attached to guanosine diphosphate (GDP) thereby forming guanosine triphosphate (GTP) (Alberts et al., 2002). Like ATP, GTP is an energy-yielding molecule and is used to generate ATP when it donates a phosphate group to ADP. The final product from the removal of CoA from succinyl CoA is succinate. Succinate is then oxidized and fumarate is formed. Flavin adenine dinucleotide (FAD) is reduced and forms FADH2 in the process (Alberts et al., 2002). A water molecule is then added and bonds between the carbons in fumarate are rearranged forming malate. Malate is oxidized forming oxaloacetate, the beginning substrate in the cycle. NAD+ is reduced to NADH in the process. Then net result of the citric acid cycle is that one molecule of acetyl CoA is able to generate 1 ATP, 3 NADH, 1 FADH2, 2 CO2, and 3 H+. Since two acetyl CoA molecules are generated from the two pyruvic acid molecules produced in glycolysis, the total number of these molecules yielded in the citric acid cycle is doubled to 2 ATP, 6 NADH, 2 FADH2, 4 CO2, and 6 H+. Two additional NADH molecules are also generated in the conversion of pyruvic acid to acetyl CoA prior to the start of the cycle. The NADH and FADH2 molecules produced in the citric acid cycle are passed along to the final phase of cellular respiration called the electron transport chain. Here NADH and FADH2 undergo oxidative phosphorylation to generate more ATP.

Mitochondria

Mitochondria are considered the power producers of eukaryotic cells. These organelles generate power by converting energy into forms that are usable by the cell. Located in the cytoplasm, mitochondria are the source of cellular respiration to produce energy required to perform cellular processes such as cell division, growth, and cell death. Mitochondria have a distinctive oblong or oval shape and are bounded by a double membrane. Each of these membranes is a phospholipid bilayer with embedded proteins (Alberts et al., 2002). The outermost membrane is smooth while the inner membrane has many folds called cristae which enhance the productivity of cellular respiration by increasing the available surface area. Within the inner mitochondrial membrane are series of protein complexes and electron carrier molecules, which form the electron transport chain (ETC). The ETC represents the third stage of aerobic cellular respiration and the stage where the vast majority of ATP molecules are generated. The double membranes divide the mitochondrion into two distinct parts: the intermembrane space and the mitochondrial matrix. The mitochondrial matrix contains mitochondrial DNA (mtDNA), ribosomes, and enzymes (Alberts et al., 2002). Several of the steps in cellular respiration, including the Citric Acid Cycle and oxidative phosphorylation occur in the matrix due to its high concentration of enzymes. The intermembrane space is defined as the narrow space between the outer membrane and the inner membrane, while the mitochondrial matrix is the area that is completely enclosed by the innermost membrane.

Oxidative phosphorylation

Oxidative phosphorylation is the process where the remaining ATP are obtained by passing electrons through a series of chemical reactions to oxygen which acts as the final electron acceptor. These reactions take place in specialized protein complexes located in the inner membrane of the mitochondria of eukaryotic organisms and on the inner part of the cell membrane of prokaryotic organisms (Alberts et al., 2002). Eukaryotic organisms are organisms that contain a cell nucleus. The energy of the electrons is harvested and used to generate an electrochemical gradient across the inner mitochondrial membrane. The potential energy of this gradient is used to generate ATP.

The electron transport chain is the last step of aerobic respiration and is the only part of metabolism that uses atmospheric oxygen. Electron transport is a series of chemical reactions that resembles a bucket brigade in that electrons are passed rapidly from one component to the next, to the endpoint of the chain where oxygen is the final electron acceptor and water is produced (Alberts et al., 2002). There are four complexes composed of proteins that are used and they labeled I through IV in Figure 5. The aggregation of these four complexes, together with associated mobile, accessory electron carriers, is called the electron transport chain. The electron transport chain is present in multiple copies in the inner mitochondrial membrane of eukaryotes and in the plasma membrane of prokaryotes. In each transfer of an electron through the electron transport chain, the electron loses energy, but with some transfers, the energy is stored as potential energy by using it to pump hydrogen ions across the inner mitochondrial membrane into the intermembrane space, creating an electrochemical gradient (Alberts et al., 2002).

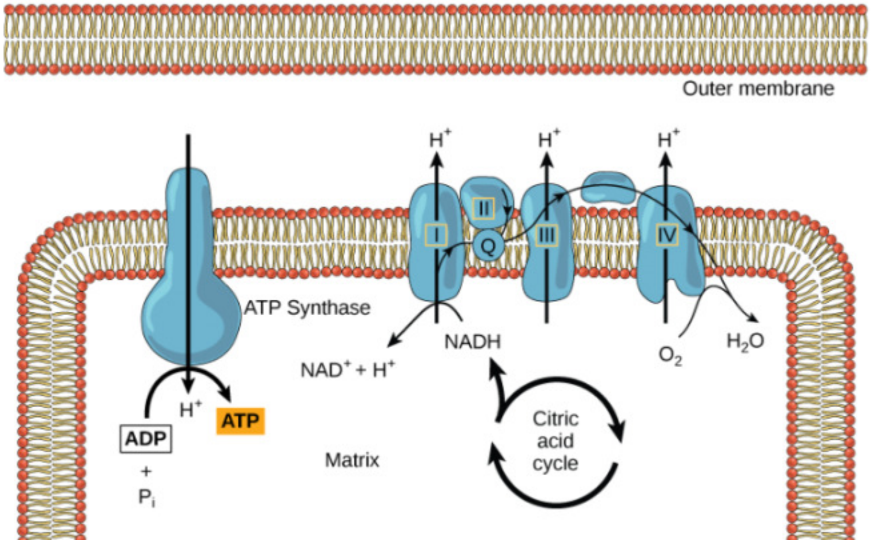

Figure 5. Electron transport chain within the mitochondria.

Electrons from NADH and $FADH_2$ are passed to protein complexes down the electron transport chain. As they travel from one complex to another the electrons lose energy, and some of that energy is used to pump hydrogen ions from the mitochondrial matrix into the intermembrane space. In the fourth protein complex, the electrons are accepted by oxygen, the terminal acceptor. The oxygen with its extra electrons then combines with two hydrogen ions to form water. If there were no oxygen present in the mitochondrion, the electrons could not be removed from the system, and the entire electron transport chain would back up and stop. The mitochondria would be unable to generate any new ATP and the cell would ultimately die from lack of energy. In the electron transport chain, the free energy from this series of reactions just described is used to pump hydrogen ions across the membrane. The uneven distribution of H^+ ions across the membrane establishes an electrochemical gradient, owing to the H^+ ions positive charge and their higher concentration on one side of the membrane (Alberts et al., 2002). The hydrogen ions are able to diffuse through the inner membrane through an integral membrane protein called ATP synthase. This complex protein acts as a tiny generator that gets run by the force of the hydrogen ions diffusing through it. The direction of the hydrogen ions is down the electrochemical gradient from the intermembrane space, where there are many mutually repelling hydrogen ions to the matrix, where there are few. This movement acts to regenerate ATP from ADP. This flow of hydrogen ions across the membrane through ATP synthase is called chemiosmosis and it is able to generate 90 percent of the ATP made during aerobic glucose catabolism (Alberts et al., 2002). The result of the reactions is the production of ATP from the energy of the electrons removed from hydrogen atoms. These atoms were originally part of a glucose molecule. At the end of the electron transport system, the electrons are used to reduce an oxygen molecule to oxygen ions. The extra electrons on the oxygen ions attract hydrogen ions from the surrounding medium, and water is formed.

Anaerobic respiration

Anaerobic cellular respiration is similar to aerobic cellular respiration in that electrons extracted from a fuel molecule are passed through an electron transport chain, driving ATP synthesis. Some organisms use sulfate (SO_4^{2-}) as the final electron acceptor at the end of the transport chain, while others use nitrate (NO_3^-) (Alberts et al., 2002). Some prokaryotes such as bacteria and archaea that live in low-oxygen environments are forced to rely on anaerobic respiration to break down fuels. A soil based archaea called methanogens uses carbon dioxide as a terminal electron acceptor and produces methane as a byproduct. Some sulfate-reducing bacteria and archaea use sulfate as a terminal electron acceptor, producing hydrogen sulfide (H_2S) as a byproduct (Alberts et al., 2002).

Glycolysis is the first step in anaerobic respiration and it produces two ATP molecules as well as pyruvate. Pyruvate can be either used in fermentation to produce ethanol and NAD^+ or for the production of lactate and NAD^+. The production of NAD^+ is crucial because glycolysis requires it and all cellular respiration would cease when its supply was exhausted, resulting in cell death. Both glycolysis and fermentation take place in the fluid portion of the cytoplasm whereas the bulk of the energy yield of aerobic respiration takes place in the mitochondria. Pyruvic acid or pyruvate can be routed by the organism into one of three pathways: lactic acid fermentation, alcohol fermentation, or cellular anaerobic respiration. It is unfortunate that most of the energy produced by anaerobic respiration are stored in either the ethanol or lactate molecules which the cell cannot use and must excrete.

Fermentation

Fermentation is another anaerobic pathway for breaking down glucose, one that's performed by many types of organisms and cells. In fermentation, the only energy extraction pathway is glycolysis, with one or two extra reactions tacked on at the end. Fermentation and cellular respiration begin the same way, with glycolysis. In fermentation, however, the pyruvate made in glycolysis does not continue through oxidation and the citric acid cycle, and the electron transport chain does not run. Because the electron transport chain isn't functional, NADH produced during glycolysis cannot drop its electrons off there to turn back into NAD^+. The purpose of the extra reactions in fermentation, then, is to regenerate the electron carrier NAD^+. The extra reactions accomplish this by letting NADH drop its electrons off with an organic molecule (such as pyruvate, the end product of glycolysis). This drop-off allows glycolysis to keep running by ensuring a steady supply of NAD^+. There are two different types of fermentation: lactic acid fermentation and alcohol fermentation.

Lactic acid fermentation

In lactic acid fermentation, NADH transfers its electrons directly to pyruvate, generating lactate as a byproduct. It is caused by an enzyme found in most every organism called lactate dehydrogenase which catalyzes a reaction between the NADH produced from glycolysis with the pyruvate molecules to create the NAD+ necessary to begin glycolysis. Lactate is then formed as a byproduct of this reaction. The lactate produced will eventually protonate into lactic acid. Rather than attaching excess hydrogen molecules to oxygen to create water as in aerobic respiration, the hydrogen molecules are instead placed back on the middle carbon of the pyruvate molecules to create lactate. This is why lactate is also known as lactic acid, because it has two hydrogens it can easily donate in water. Lactic acid $(C_3H_6O_3)$ is considered by many as a waste product of anaerobic respiration, but in fact it acts as a storage container. Lactate goes through what is known as the Cori cycle in humans and other advanced organisms. The bacteria that make yogurt carry out lactic acid fermentation. The reactions that make up lactic acid fermentation are 100 times faster than those of cellular respiration. The disadvantages of lactic acid fermentation are that it only produces about 5.26 percent of the ATP that could be made through cellular respiration and it produces 2 molecules of lactic acid for each glucose consumed. This means that as the lactic acid builds up the cells will become more acidic. This increase in acidity can inhibit the processes that break down glucose, making it harder for the cell to produce ATP and usable energy. Figure 6 shows a summary of the process.

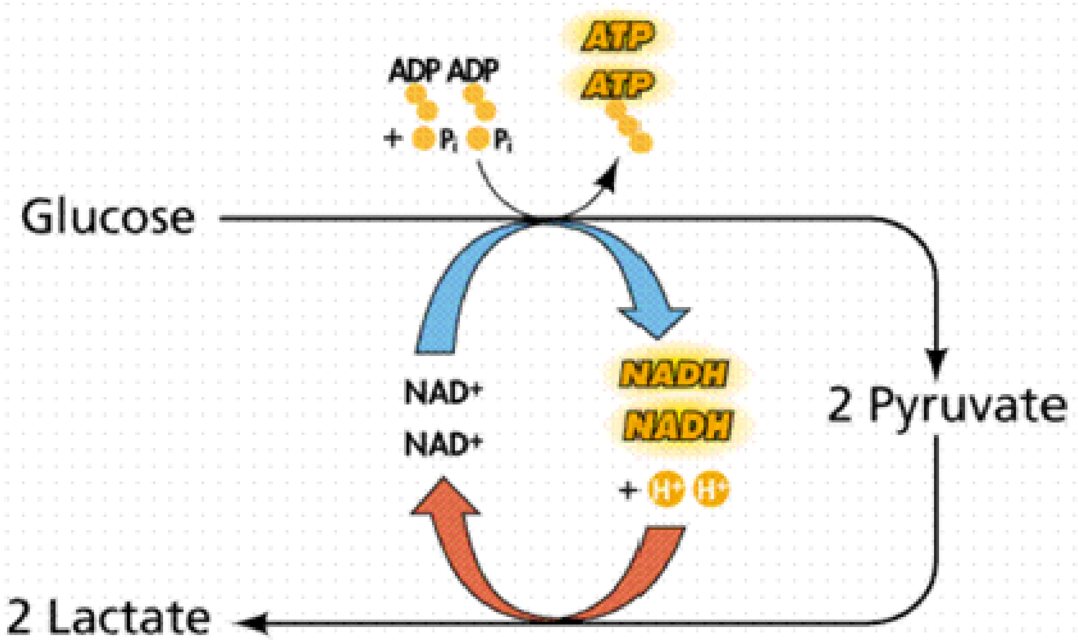

Figure 6. Lactic acid fermentation process.

Alcohol fermentation

Another possible fermentation process is alcohol fermentation, in which NADH donates its electrons to a derivative of pyruvate, producing ethanol. The process of changing from pyruvate to ethanol is a two-step process. In the first step, a carboxyl group is removed from pyruvate and released in as carbon dioxide, producing a two-carbon molecule called acetaldehyde. In the second step NADH passes its electrons to acetaldehyde, regenerating NAD^+ and forming ethanol. This process is generally done by microscopic organisms like bacteria and certain fungi like yeast. Figure 7 shows an overview of the process.

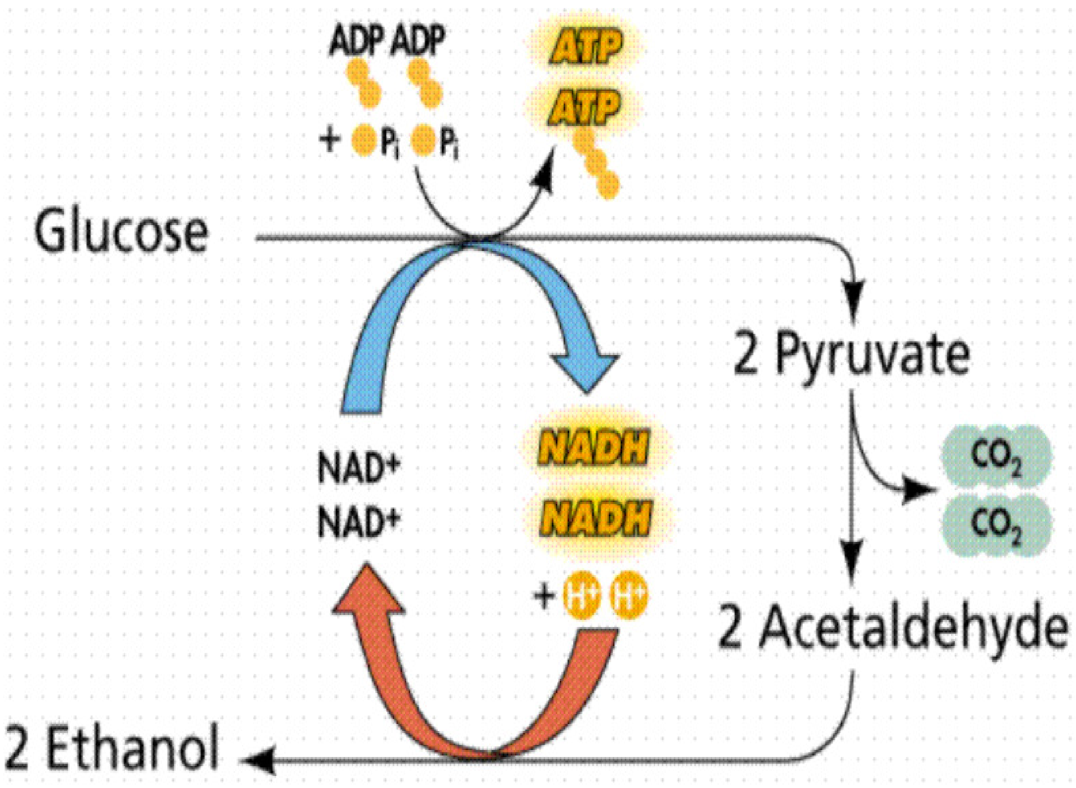

Figure 7. Alcohol fermentation process.

Facultative and obligate anaerobes

Many bacteria and archaea are facultative anaerobes which are able to switch between aerobic respiration and anaerobic pathways (fermentation or anaerobic respiration) depending on the availability of oxygen. This approach allows lets them get more ATP out of their glucose molecules when oxygen is available and still keep metabolizing and when oxygen is scarce. Other bacteria and archaea are obligate anaerobes which can only live and grow in the absence of oxygen. Oxygen is toxic to these microorganisms and injures or kills them on exposure. The Clostridium bacteria that causes botulism which is a form of food poisoning is an example of an obligate anaerobe.

Electron transfer

The microbes use their biomolecules to transfer their spare electrons to the anode. This is accomplished using three possible methods: 1) direct transfer from microbe's cell wall to the anode, 2) mediated transfer using shuttling biomolecules, 3) transfer through nanowire network which are conductive appendages grown by the microbes. Chemical mediators, such as neutral red or anthraquinone-2,6-disulfonate (AQDS), can be added to the system to allow electricity production by bacteria that are unable to function using the electrodes (Logan et al, 2006). This process works especially well under anaerobic conditions when a solution containing food for the bacteria is circulated around the cell. The optimal food should contain either of glucose or acetate, which are often contained within food waste and sewage. The bacteria metabolize food by first breaking apart the food molecules into hydrogen ions, carbon dioxide, and electrons. As shown in Figure (), bacteria use the electrons to produce energy by way of the electron transport chain. The microbial fuel cell disrupts the electron transport chain using a mediator molecule to shuttle electrons to the anode. In many ways, a microbial fuel cell is an extension of the electron transport chain where the final step of the process (the combination of oxygen, electrons, and H+ to form water) is transferred outside of the bacterial cell from which energy can be harvested.

As Figure 8 shows the electron transport chain begins with NADH. NADH is a biological transport molecule that releases a high energy electron (e-) and a proton (H+). The electron will then follow the red path through the proteins (large blobs) in the mitochondrial membrane. As the electron passes through each protein, it pumps hydrogen ions (H+) through the membrane. In a normal bacterial cell, the electron would continue along the dotted red path where it then would combine with oxygen to produce water. However, in a microbial fuel cell, the electron will only continue along the solid red path, where it is then picked up by a mediator molecule and taken to the anode.

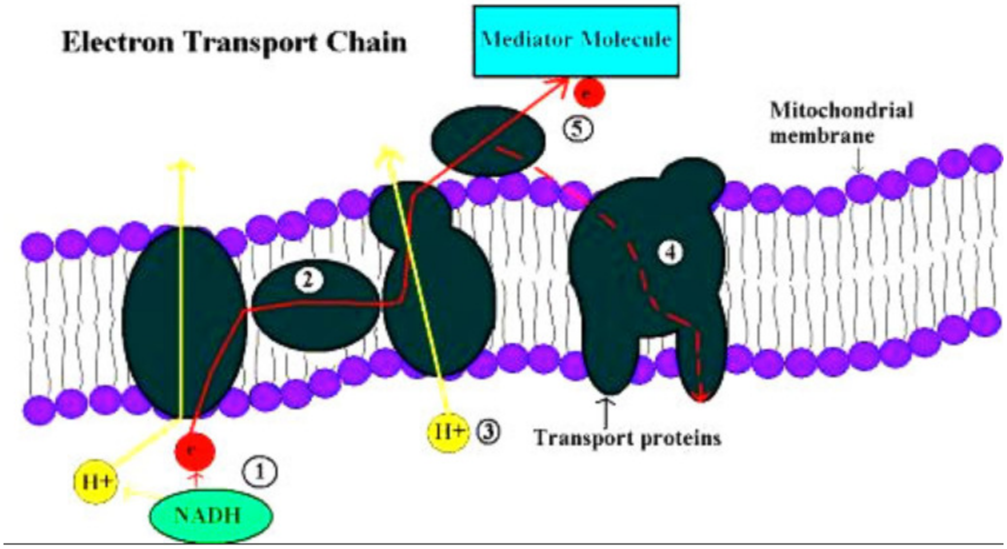

Figure 8. Electron transport chain.

Aerobic respiratory electron transport system

The end of the oxidase on the molecular oxygen affinity than any known chemical catalyst for the high. Therefore, the aerobic bacteria in the 0.1mg/L of low dissolved oxygen concentrations have the greatest ability to breathe. To this end, the study focus on that as a cathode catalyst on the aerobic bacteria. Cathode biofilm development on improving the overall performance of microbial fuel cells have a significant role. Under closed-loop conditions, the bacteria formed on the cathode is different from that formed under open-loop conditions. There is also a great difference between microbial fuel cells formed using seawater and freshwater sediment. Bergel et al, (2005) found that sea water corrosion in the formation of biofilm using coated stainless steel cathodes, the fuel cells were able to produce 0.32 w/m, without alteration of the power density.

Electron acceptors other than oxygen

The use of alternative electron acceptors has many benefits including: increasing power generation, reducing operating costs, and expanding the application scope of MFCs. (Gu et al., 2007) found that some recalcitrant compounds could be treated in the cathode as an electron acceptor. These findings suggest that MFCs can be used to control environmental pollutants.

Permanganate

Under both acidic and alkaline conditions, permanganate is reduced to manganese dioxide by receiving three electrons as shown in the equations below. This property of permanganate makes it an alternative that can be used as an electron acceptor. Under acidic conditions, permanganate is able to produce a higher power output since its oxidation potential is higher than it is in alkaline conditions. (You et al., 2006) performed experimented with using different pH values to determine how much of an effect it would have on the performance of permanganate in MFCs. (Yang and Logan, 2016) discovered that using a cathode in addition to potassium permanganate as an electron acceptor in MFCs can generate a maximum of 115.6 mw/m. The results of their research found that a power density of 115.60 mW/m^2 at a current density of 0.017 mA/cm^2 could be achieved by using permanganate as an electron acceptor, and this was 4.5 and 11.3 times higher than what was obtained from both hexachnoferrate (25.62 mW/m^2) and oxygen (10.2 mW/m^2) respectively. (You et al., 2006) created a bushing MFC using permanganate as the electron acceptor and was able to obtain a maximum power density of 3986.72 mW/m^2 at 0.59 mA/cm^2. However, there are also some disadvantages in using permanganate. One disadvantage is that permangate is similar to other soluble electron acceptors and suffers from depletion during electricity generation thus requiring a continuous liquid replacement. Since the cathode potential is primarily dependent on the pH of the solution, it needs to be controlled for stable power output. This means that it may only be applied to small scale power supplies. The advantage of permanganate is that it does not require catalysis (You et al., 2006). (Eliato et al., 2016) was able to find the best permanganate concentration in terms of electricity production. The maximum power density was achieved using 400 mM of potassium permanganate and the current density at this power density were found to be 93.13 mW/m^2 and 0.03 mA/cm^2 respectively.

$$\mathrm{Mn}O_4^- + 3e^- + 4H^+ \rightarrow \mathrm{Mn}O_2^- + 2H_2O$$

$$\mathrm{Mn}O_4^- + 2H_2O + 3e^- \rightarrow \mathrm{Mn}O_2^- + 4OH^-$$

Ferricyanide

Ferricyanide is another popular choice electron donor used in MFC applications due to its concentration not being limited to solubility like in the case of oxygen (Rhoads et al., 2005). The disadvantage of this is that the standard redox potential of ferricyanide which is shown in the equation below is not as high as that of oxygen. Some additional benefits include having a much lower overpotential, a faster reaction rate, and much higher power output (Rabaey et al., 2005). (Oh et al., 2006) discovered that applying ferricyanide with a carbon electrode produced 50–80% higher power than oxygen with Pt-carbon cathode due to increased mass transfer efficiencies and larger cathode potential. It was also found that ferrocyanide would create a power density of 25.6 mw/mZ while pure oxygen could only create a power density of 10.2 mw/mZ as electron acceptor (Aelterman et al., 2006). This becomes promising that the high power density could be enhanced up to 4.5 times its former value. This is due to microbial fuel cells using the permanganate to create a higher open-circuit potential. These results indicate that the cathode reaction also affect the microbial fuel cell applications, which is an important factor for future research.

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

Although ferricyanide provides excellent performance as an electron acceptor in terms of power generation, there are some reasons that potassium ferricyanide is not practically sustainable. It is toxic, so chemical regeneration and recycling is difficult. This means that ferricyanide is pretty much restricted to basic laboratory facilities (Logan et al., 2006). However, ferricyanide still has a role as an important cathodic electron acceptor to prove some important concepts in the laboratory due to its stability and high system performance. (Aelterman et al., 2006) conducted performance experiments with MFCs operated in series and in parallel to each other by using a hexacyanoferrate cathode, and six independent continuous MFC units to produce a maximum hourly average power output of 258 W/m^3 in the stacked configuration. Ferricyanide has also been used to compare the performance of electrode materials due to its catalytic activity. (Zain et al., 2015) analyzed three different MFC processes to remove nitrogen and carbon from wastewater including: continuous operation, continuous operation with ferricyanide, and continuous operation with oxygen. The highest current, carbon and nitrogen removal was observed in the continuously operating MFC with ferricyanide. The currents obtained were 0.833 V and 0.589 V for ferricyanide and oxygen respectively and it was also found that with ferricyanide, the carbon and nitrogen removals were 36 and 9% higher than that removed with oxygen respectively.

Nitrate

(Jia et al., 2008) found that the redox potentials of nitrate and oxygen are very close to each other so nitrate could be used as an electron acceptor in the cathode. The application of biocathodes has made nitrate usable as an electron acceptor in MFCs for denitrification and electricity generation (Schroder et al., 2003). The feasibility of nitrate as a cathodic electron acceptor in MFCs was first demonstrated by (Clauwaert et al., 2007). It was found that the denitrification by microorganisms took place in a tubular reactor without an energy input. (Lefebvre et al., 2008) investigated the idea of using the same cathodic process in a two-chambered MFC. In their study, 95.7% of nitrate was removed at the cathode by using acetate as an anodic substrate, and 73% of the total nitrogen was converted to N_2 gas through electrochemical denitrification process which has the equations shown below. However, only 0.095 V was obtained as the maximum cell potential at external resistance of 1000 Ω, which was much lower than that of oxygen reported previously. This may be due to the fact that nitrate has a relatively low redox potential (0.74 V).

$$NO_3^- + e^- + 2H^+ \rightarrow NO_2^- + H_2O$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O$$

$$NO + e^- + H^+ \rightarrow \frac{1}{2} N_2O + \frac{1}{2} H_2O$$

$$\frac{1}{2} N_2O + e^- + H^+ \rightarrow \frac{1}{2} N_2 + \frac{1}{2} H_2O$$

Persulfate

Persulfate is considered to be hazardous waste because it is an oxidizing agent. Applicability of persulfate in MFCs is possible with its standard oxidation reduction potential of 2.12 V, which is higher than many electron acceptors such as permanganate which are widely used in MFCs. The oxidation equation is given below. (Li J. et al., 2009) found that power density was doubled when $K_3Fe\ (CN)_6$ was replaced with persulfate in MFC (166.7 vs. 83.9 mW/m^2). One disadvantage of operating a MFC that uses $K_2S_2O_8^{2+}$ would be the lower cell performance compared with a MFC using $K_3Fe(CN)_6$ especially at medium to high current densities. The reason for this could be explained by the faster electron reduction kinetics of ferricyanide solution on the surface of the carbon electrode (Li J. et al., 2009).

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$$

Magnesium dioxide

(Li et al., 2010) found that manganese dioxide has the potential to be a good cathode material and catalysis for battery and alkalinine fuel cells. MnO_2/Mn^{2+} redox couple can also be used to transfer electrons from the cathode to an electron acceptor. The possibility of bio-mineralized manganese oxides was first investigated by (Rhoads et al., 2005). The reaction consists of the accumulation of manganese dioxide on the cathode surface and subsequent reduction with electrons from the anode. The reaction results in the release of manganese ions which are subsequently reoxidized to manganese dioxide by manganese-oxidizing bacteria (Lepthothrix discophora SP-6). The oxidation equations are given below. (Rhoads et al., 2005) found that the maximum power density of 126.7 mW/m^2 could be obtained using 50 Ω resistors. (Liew et al., 2015) discovered that manganese dioxide would be practical not only in the electron mediator mechanism but also as an alternative cathode catalyst to platinum due to its low cost. Their research showed that by using manganese dioxide as an alternative catalyst, a maximum volumetric anode density of 3,773 mW/m^3 could be obtained with a tube MFC. Thus, using MnO_2 instead of Pt could serve as a suitable option for real applications due to its low cost (Zhang et al., 2009).

$$MnO_2 + e^- + H^+ \rightarrow MnOOH_{(S)}$$

$$MnOOH + e^- + 3H^+ \rightarrow Mn^{2+} + 2H_2O$$

$$Mn^{2+} + 2e^- + O_2 \rightarrow MnO_2$$

Mercury

(Wang et al., 2011) found the redox potential of mercury, which is about −320 mV (Hg^{2+}), is higher than that of NADH/NAD$^+$. This means it could be accepted as an alternative electron acceptor. The benefit of this is that by using a MFC designed for mercury, the removal of mercury from the aquatic environment can be achieved simultaneously with electricity production. The possible path of removal for mercury in a water source is to precipitate Hg^{2+} in the presence of Cl^- and then generate a subsequent reduction using the electrons at the cathode. The chemical equations for these reactions are shown below. (Wang et al., 2011) was able to generate a maximum power density of 433.1 mW/m^2 using these processes and the end products were elemental Hg in the cathode surface and Hg_2CI_2 as deposits on the bottom of the cathode chamber.

$$2Hg^{2+} + 2Cl^- \rightarrow Hg_2Cl_2(s)$$

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(I) + 2Cl^-$$

Iron

Iron can be used as an electron mediator to enhance the performance in the cathode compartment. The most common redox couple used in MFCs is Fe^{+3}/Fe^{+2} (Heijne et al., 2006). Ferric iron can be reduced to ferrous iron in the cathode chamber. The relevant equations are given below. This reversible electron transfer reaction has several advantages such as fast reaction speed, high standard potentials, biological degradability, and release of some valuable compounds such as phosphate (Fischer et al., 2011). (Heijne et al., 2006) found that when this redox reaction was coupled together with a bipolar membrane and graphite electrode combination, a maximum power density of 0.86 W/m^2 at a current density of 4.5 A/m^2 could be obtained. These results also included ranges coulombic efficiency and energy recovery between 80–95% and 18–29% respectively. In order to complete the Fe^{3+}/Fe^{2+} redox cycle, an oxidative mechanism is needed. To achieve this, (Heijne et al., 2007), used an acidophilic chemolithoautotrophic microorganism called Acidithiobacillus ferrooxidans to oxidize ferrous iron and investigated the performance of the MFC with continuous ferrous iron oxidation. Oxidation of ferrous iron to ferric iron resulted in a 38% higher power output (1.2 W/m^2 and a current of 4.4 A/m^2) than that which was obtained in their previous study. Besides being an electron mediator, iron also has applications as an electron acceptor. (Fischer et al., 2011) discovered that iron in the form of $FePO_4$ could be used. $FePO_4$ is a compound found in sewage sludge, which not only has a potential as an electron acceptor due to its Fe^{3+} content, but also has a great importance due to its orthophosphate content. A MFC could reduce $FePO_4$ by delivering necessary electrons and protons. When iron cations are reduced by the electrons, iron and phosphate are separated and mobilized orthophosphate (PO_4^{3-}) is released into the solution. Released orthophosphate can be further precipitated as struvite (NH_4MgPO_4) by adding stoichiometric amounts of Mg^{2+} and NH_4^+. (Fischer et al., 2011) found that by using this method, 82% orthophosphate recovery could be achieved while also producing a varied current density ranging from 0.1 to 0.7 mA. One disadvantage of using a MFC with ferric iron is that it requires a bipolar membrane instead of a cation exchange membrane (CEM). This is due to CEMs not being suitable for pH adjustment in the cathode chamber since they carry other cations together with protons. Therefore, either a bipolar membrane or acid addition is required when ferric iron is used (Heijne et al., 2006). The main advantage using orthophosphate is that the phosphate is obtained in pure form. Thus, phosphate can be separated from iron and other toxic materials such as As, Pb, Cr. However, low pH is required to keep ferric iron soluble since ferric iron is tent to be precipitated as ferric iron hydroxides at pH values higher than 2.5 (Nguyen et al., 2016). These precipitates are reported to be harmful to membrane use.

Additionally, in order to shuttle electrons and protons to the Fe^{3+}, a cathodic mediator such as methylene blue needs to be supplied, which may hinder its wide application (Fischer et al., 2011). While iron was used as an electron acceptor, up-to-date studies show that it can also be used to prepare efficient catalysts (Santoro et al., 2016).

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

$$3e^{-} + 3H^{+} + Fe3 + PO_4 \leftrightarrow H_3PO, H_2PO_4^{-}, HPO_4^{2-}, PO_4^{3-}$$

Copper

Copper is another potential candidate as it is one of the widespread heavy metals in the soil and aquatic environment, which are mainly emitted from mining and metallurgical industries. Trace amounts of copper are an essential micronutrient to all plants and animals, but as copper levels increase it can become toxic to all life as ingested amounts build up over time (Alaoui-Sossé et al., 2004). Thus the removal of copper is of great importance. (Tao et al., 2011) designed a two compartment MFC to enhance both simultaneous copper recovery and energy production. The copper reduction equation in its basic form is shown below. (Heijne et al., 2010) was able to achieve a level of copper recovery with a MFC by using a bipolar membrane as a pH separator. Their maximum power density was 0.80 W/m^2 at a current density of 3.2 A/m^2 and over 99.88% removal efficiency was achieved with pure copper crystals being observed as the main products formed on the cathode surface and neither CuO nor Cu_2O were detected. The authors theorized that the bipolar membrane provided low pH in the cathode compartment. (Tao et al., 2011) investigated Cu^{2+} reduction in an MFC using a PEM and cupric sulfate solution as catholyte. Their maximum power density found using an initial copper concentration of 6412.5 mg Cu^{2+}/L in glucose-fed MFC was 339 mW/m^3. Their results found that extremely high copper removal efficiency of over 99% could be obtained when the initial copper concentration was 196.2 mg Cu^{2+}/L and using an 15 Ω external resistance. In order to further lower the construction cost for this process, (Tao et al., 2011) developed a lab scale membrane free buffered MFC. At an initial copper concentration of 500 mg/L, a removal efficiency of 70% was observed over a period of 144 hours (Tao et al., 2011). Because of this research, the cathodic copper reduction has become a hot commodity the field of MFC applications. (Wu et al., 2016) found that the ratio between copper reduction and electricity generation can vary greatly depending on the architectural structure and operational parameters of the reactors an electricity production can also be affected by multiple batch cycle operations with different cathode materials. (Wu et al., 2016) tested various materials as cathodes for their effectiveness in copper removal:

a carbon rod, a titanium sheet, and stainless steel woven mesh materials. Stainless steel woven mesh was found to be both the most effective and the cheapest cathode material. It was also found that the copper reduction in a MFC is most dependent on the deposition of copper on the cathode and smaller effects were power density and copper purity. However, this technology is still in an early stage of development, more developments such as cost-effective reactor design and study of the catalytic behavior of copper for oxygen reduction at the cathode are required. (Wu et al., 2016) found that with MFCs designed for copper removal the power density that could be achieved was at least 33.6 W/m^3 and could be significantly more depending on parameters such as reactor type, electron source, anode and cathode materials.

$$4Cu^{2+} + 8e^- \rightarrow 4Cu(s)$$

Chromium

The use of chromium as an electron acceptor has been explored in several studies [(Li et al., 2008), (Li et al., 2009), (Sahinkaya et al., 2016)]. Most of the studies have deal with the issue of real and synthetic wastewaters containing chromium being treated in MFCs and the goal of having chromium reduction and electricity production get accomplished simultaneously. The premise of this treatment lies in the fact that in acidic conditions Cr(IV) can be reduced to Cr(III) by the transfer of six electrons as can be seen in the chemical equation below. (Li et al., 2008) found that this reduction reaction is thermodynamically feasible with a redox potential of 1.33 V. (Wang et al., 2008) discovered a synthetic wastewater containing 200 mg Cr(IV)/L could produce a maximum power density of 150 mW/m^2 and a current density of 0.04 mA/cm^2 with the maximum open circuit voltage of 0.91 V. It was theorized that low pH was the key component which had a positive effect on Cr(VI) reduction. (Li et al., 2009) used the same process with real electroplating wastewater containing Cr(VI) and found that Cr(VI) removal was most heavily influenced by the electrode material. Graphite paper and graphite plates were used as cathode material in chrome removal with graphite paper producing better results than graphite plate in terms of power density: 1,600 and 99.5% chromium removal rate for electroplating wastewater containing 204 mg Cr(VI)/L. There was also other research looking into conventional Cr(VI) reduction for MFCs. (Li et. al., 2009) studied the Cr(VI) reduction in an MFC photoelectrochemical cell coupled system. Their findings indicated that under light irradiation, 97% Cr(IV) removal could be achieved within 26 hours when using an initial concentration of 26 mg/L. There was also a key difference in the maximum potential generated under light irradiation and dark controls which were 0.80 and 0.55 V, respectively. The study used a rutile coated cathode for waste treatment and solar energy conversion in a single unit of

MFC. These synergies between a biocatalyzed anode and a rutile coated cathode were found to increase both the power output and Cr(IV) reduction. (Wu et al., 2015) found the microbial concentration could be increased to improve chromium reduction performance in the cathode chamber. That was accomplished by enriching the exoelectrogenic biofilm in the anode compartment so the system gains the ability to use the anode as biocathode. The new method was able to increase Cr(VI) reduction efficiency by 2.9 times compared to previous methods. Other recent studies on Cr(VI) reduction were focused on self-assembled graphene biocathode applications (Song et al., 2016) and on electrode material modification (Wu X. et al., 2016). The latest research appears to be trending towards determining the best cathode material for chromium removal. (Gupta et al., 2017) explored Cr(VI) removal in an MFC operated with an alumina (AA)/nickel (Ni) nanoparticles (NPs)-dispersed carbon nanofiber electrode. Using their developed electrode, a power density of 1,540 mW/m^2 was achieved together with the complete reduction of 100 mg Cr(VI)/L at a reduction rate of 2.12 $g/(m^3\ h)$ and the columbic efficiency was 93%. (Xafenias et al., 2015) developed a MFC with abiotic cathode and was able to obtain a power density of 21.4 mW/m^2 in treating alkaline Cr(VI) wastewater, while 10 mg/L chromium reduction was achieved within 45 hours.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Triiodide

Triiodide behaves similarly to both Fe^{+3}/Fe^{+2} and copper and is based on the iodide/iodine redox couple with the capability to act as an electron mediator. Some advantages of using the iodide/iodine couple in the cathode include: no depletion of triiodide (I_3^-) in the catholyte since it can be regenerated, stability at both acidic and alkaline conditions, and it acts to demonstrate the feasibility of using carbonaceous materials as the cathode. The regeneration is usually performed through a photo-driven reaction between I^- and oxygen. After the formation of iodine, the combination of iodide anion with an iodine molecule in water forms triiodide and then the cycle is then able to continue as shown in Figure 9 (Li et al., 2010).

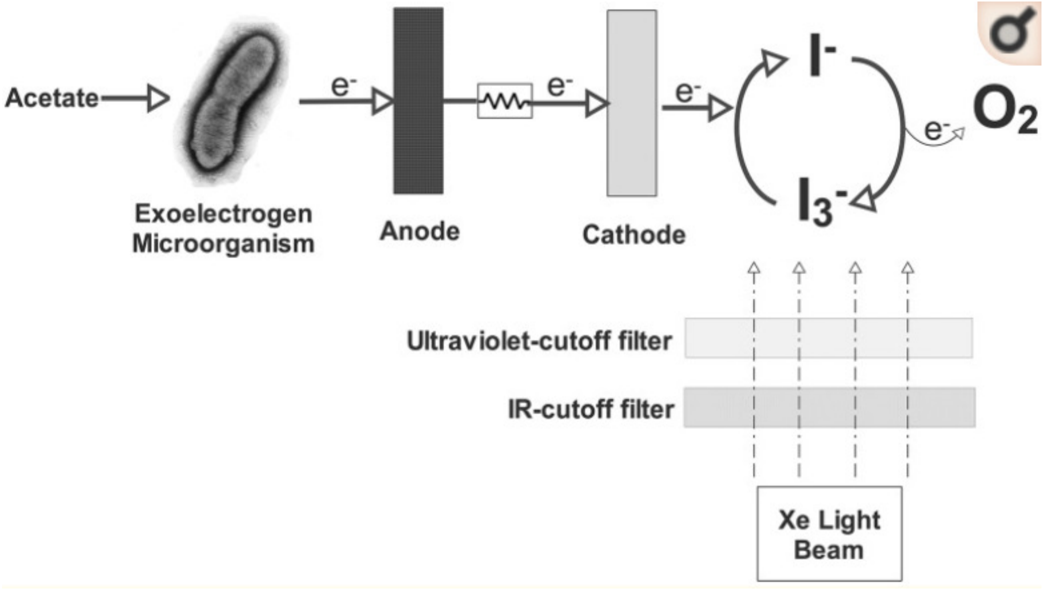

Figure 9. Process performed by MFCs using triodide in aqueous ion solution as the catholyte.

The equations for this redox reaction are shown below. The iodide/iodine redox couple makes for an easy transition to be an electron mediator in the cathode chamber. (Li et al., 2010) created a two chamber MFC that was able to demonstrate the feasibility of this redox couple as an electron acceptor or mediator. The maximum power density achieved was 484.0 mW/m^2 by using 1.2 mM I_3^- and 0.2 M KI. The trend for current studies appears to be in the application of H type MFCs which have a more efficient reactor design for high power generation that is required. One of the disadvantages of this method lies in the fact that I_3^- ion is toxic to the electrochemically active microbes that are living in the anodic chamber so that should be taken into consideration when designing MFC configurations for better performance (Li et al., 2010).

$$I_3^- + 2e^- \rightarrow 3I^-$$

$$4I^- + O_2 + 4H^+ + h\upsilon \rightarrow 2I_2 + 2H_2O$$

$$I_2 + I^- \rightarrow I_3^-$$

Carbon dioxide

The use of carbon dioxide can prove to be advantageous due to the fact that the thermodynamic reaction of CO_2 reduction has a very low redox potential and its use in the cathode compartment produces a very low voltage. This CO_2 reduction potential is –0.420 V at neutral pH. However, one issue with its use lies in the requirement that the cathode potential must be higher than the anode potential in order to generate electricity. For this reason, external energy must be supplied in order to provide CO_2 reduction. (Cao et al., 2009) discovered that CO_2 reduction driven by sunlight using a biocathode MFC. It was found that electrons could be received by the carbon dioxide when CH_2O is used as the biomass as shown in the chemical reaction equations below. This means that CO_2 reduction can occur simultaneously with biomass production. This bio-reaction allows the CO_2 sequestration.

$$HCO_3^- + 5H^+ + 4e^- \rightarrow CH_2O + 2H_2O$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$

Another method of CO_2 energy production in the cathodic chambers is to reduce carbon dioxide to methane (Villano et al., 2010). This is feasible due to the fact that both electrons and CO_2 are released during the oxidation of organic matter which means they may be utilized in the production of methane. (Villano et al., 2010) was able to refine this concept further using a two-chambered MFC. There are a few benefits in using carbon dioxide as a final electron accepter in the treatment of wastewater. First, the methanogens are protected from possible inhibitors present in the wastewater by separating the oxidation part of the organic matter from the methane production. The next advantage of this process is that it consumes less energy because there is no need to heat the cathode to maintain a set temperature (Villano et al., 2010). In addition, this process transitions well to the additional operations of anaerobic digestion and the production of methane gas. These new operations would ensure that the MFC could operate effectively at low substrate concentrations. The next group of possible electron acceptors are more of an effort to eliminate a pollutant from the environment using the MFC design.

Hydrogen Peroxide

Hydrogen peroxide, H_2O_2 also has the capability to be used as an electron acceptor due to its strong oxidizing properties. One of the main benefits is that the oxygen concentration used in the cathode section can be added to hydrogen peroxide. (Tartakovsky and Guiot, 2006) found that using of hydrogen peroxide provided additional stability for their long-run MFC operations. Their study compared the use of air against using hydrogen peroxide and found that the power density in the air-operated MFC was 7.2

mW/m^2 while the hydrogen peroxide led to an increase of 22 mW/m^2. The key essential was found to be the use of liquid hydrogen peroxide as it providesd high levels of oxygen which ensured high performance in long-run operation (Tartakovsky and Guiot, 2006). The chemical equation for this process is shown below. One seldom occurring issue happens when H_2O_2 is used to remove contaminants with hydroxyl radicals formed as a result of reaction with fenton. In this case the remaining H_2O_2 must be removed. (Zhang et al., 2015) have developed an innovative bioelectro-fenton system that uses alternative switching to operate the system in either microbial electrolysis cell (MEC) or MFC mode. In the MEC mode, methylene blue was removed with H_2O_2, while the residual H_2O_2 was removed in the cathode as an electron acceptor. Their system was able to remove 50 mg/L of methylene blue in the MEC system while 180 mg/L of residue H_2O_2 was used as an electron acceptor in MFC to produce a maximum current density of 0.49 A/m^2. The advantage gained was that H_2O_2 was effectively controlled and contaminant removal was ensured (Zhang. et al., 2015).

$$H_2O_2(aq) + 2H^+ + 2e^- \rightarrow 2H_2O(I)$$

Vanadium

Another option for the using of MFCs with pollutant removal in mind is vanadium (V) which is usually found in wastewaters of vanadium mines and pentoxide processing activities (Carpentier et al., 2003). (Zhang et al., 2009) found that vanadium has high redox potential in acidic conditions and could be successfully used in MFC. The equations for the reaction are shown below. The benefit of using vanadium is that at its reduction, both organic and inorganic compounds can be used as electron donors. (Zhang et al. 2009) used sulfide and glucose as the electron source to reduce vanadium in their study to accomplish the removal of both sulfide and vanadium in the anode and cathode chambers of their MFC. The sulfur and vanadium removal rates were found to be 84.7% and 25.3%, and a maximum power density of 572.4 mW/m^2. (Zhang et al., 2010) discovered that the initial sulfur concentration had an effect on microbial activity in that as the initial sulfide concentration increased, microbes in the anode compartment became less effective. This meant that there was a long lag time and decreased sulfide removal efficiency from 95.2% (50 mg/L) to 47.5% (200 mg/L) while average V(V) removal was 23.7% in terms of V(IV) formation using an initial V(V) concentration of 500 mg/L. V(V) is a form of vanadium oxide and is the inorganic compound with the formula V_2O_5. Because of its high oxidation state, it is both an amphoteric oxide and an oxidizing agent. V(IV) is known as vanadium dioxide and is an inorganic compound with the formula VO_2. Anodic electrolyte conductivity is another factor affecting vanadium (V) removal and electricity production. (Zhang et al., 2010) was able to increase the anode electrolyte conductivity considerably and managed to raise the sulfur and vanadium reduction rates by the increasing electron transfer rate at enhanced conductivity. Their study found that increasing anode electrolyte conductivity to 12.3 mS/cm worked to increase V(IV) generation up to 36%. Another factor theat impacted the MFC performance wasthe initial concentration of Vanadium (V). When the initial V(V) concentration is increased, the rate of V(IV) formation is also increased (Zhang et al., 2010). It was stated that the optimum initial V(V) concentration for 100 mg/L sulfide was 500 mg/L and then additonal increases in V(V) concentration only resulted in a saturation in V(IV) generation. Another interesting finding was that the Vanadium (V) removal rate increased with the decrease of pH. This may be due to acidic conditions being necessary to compensate for the slower proton transport rate through the membrane. (Zhang et al., 2010) also noted that under optimal conditions, average removal rates of sulfide and V(V) were 82.2 and 26.1% respectively, while the maximum power density was 614.1 mW/m^2. (Hao et al., 2015) obtained a power density of 543.4 mW/m^2 at the end of 12 hours of operation with a vanadium reduction of 93.6%. Their research found that V was simultaneously reduced in both anode and cathode compartments. (Zhang et al., 2015) was able to obtain a power density of 419 mW/m^2 was achieved while initial vanadium concentrations in the anode and cathode were 75 and 150 mg/L respectively in their MFC design. Their research was able to raise total vanadium removal rate to values as high as 76.8% with the final reduction product being V(IV).

Vanadium Reduction Reactions in the Anode Chamber

$$HS^- \rightarrow S^0 + H^+ + 2e^-$$

$$S^0 + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 6e^-$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$$

Vanadium Reduction Reactions in the Cathode Chamber

$$VO_2^+ + 2H^+ + e^- \rightarrow VO_2^{2+} + H_2O$$

$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$$

Uranium

Uranium is an unwanted pollutant is select areas due mostly from leachate in uranium processing. These places tend to have low but stable uranium concentrations and they can contaminate water resources, groundwater and sediment (Williams et al., 2010). One solution to this problem is to treat it in situ, with metal reducing bacteria being used together with the acetate feed (Vrionis et al., 2005). While uranium removal can be done by adsorption, biological reduction or membrane filtration, cathodic U(VI) reduction was also found to be a productive method. Williams et al. (2010) created an acetate fed-MFC system which consisted of a reference electrode in a uranium contaminated aquifer sediment and another electrode at the surface. Their MFC was found to produce up to 10 mW/m^2 power density during sulfate reduction and U(IV) removal (Williams et al., 2010). One of the biggest issues still yet to be solved is how to further treat the U(IV) with further MFC exposure. Currently the only known removal mechanism of the uranium is reductive immobilization of U(IV) by non-acetate oxidizing sulfate reducers (N'Guessan et al., 2008).

Chloroethenes

Chlorinated aliphatic hydrocarbons (CAHs), which are used as solvents and degreasing agents, pose a great risk due to their toxic and carcinogenic properties. These pollutants can be removed by some anaerobic bacteria which remove the chlorines from CAHs by degrading them with the electrons obtained from an external electron donor or externally supplied voltage (Holliger and Schraa, 1994). (Aulenta et al., 2009) discovered an alternative method of using insoluble electrodes to provide electrons to dechlorinating communities. Their research explored two different communities (mixed culture of dechlorinating bacteria and pure culture of Geobacter lovleyi) and found that in a mixed culture, dechlorination of TCE could be achieved under acetate fed conditions. The formed dechlorination products were cis-DCE (83.9%), VC (3.5 %), as well as ethene and ethane (12.6%). It was also proved that polarized carbon paper electrode could be used as the sole electron donor for the complete dechlorination of TCE with a mixed culture (Aulenta et al., 2009). This was done by supplying external electron donors to the contamination zone however it did result in some unwanted processes and accumulate byproducts. When that has the potential for occurring, it was found that using MFC with a solid electrode would be optimal since bacterial oxidation happens in the anode and no external organic matter is added to the site (Aulenta et al., 2007).

2-chlorophenol

(Aulenta et al., 2009) found that when using chloroethens, a solid electrode functioning as the sole electron donor is more advantageous than using soluble electron donors directly. This is due to the application of electrodes for supporting the necessary electrons for pollutant reduction and could be further used for bioremediation of chlorinated contaminants and metals (Strycharz et al., 2010). Geobacter is one of the typical species used for this purpose. (Strycharz et al. 2010) reported that Anaeromyxobacter dehalogenans also had the ability to transfer electrons to 2-chlorophenol and finally dechlorinate it to phenol. In their study, 10 mM of acetate was initially applied as a substrate for Anaeromyxobacter dehalogenans while 80 μM 2-chlorophenol was used as an electron acceptor. The most rapid rates of dechlorination were found to be 40 uM Cl/d in 200 mL of solution. These results showed that bioremediation of contaminants with electrodes were capable of acting as an electron donor (Strycharz et al., 2010). (Akbulut et al., 2012) found that the dechlorination of 2-chlorophenol was possible. Their study had one hundred fifty micro molar 2-chlorophenol become removed using a crude laccase enzyme under optimum dechlorination conditions. There are several advantages to use solid electrodes as an electron donor for chloroethens reduction (Strycharz et al., 2010). The main reason is that electrons can be effectively transferred to microorganisms for reducing the pollutant. Using the electrode as the electron donor can also be easily applied to the site. Another reason is that by having the contaminants reacted directly with electrode, unwanted reaction can be eliminated. Contaminant metals can be easily extracted from the electrode surface where they precipitated.

Proton mass transfer

Microbial fuel cells share some similarities with chemical fuel cells in that they both contain a cation-exchange membrane. However in microbial fuel cells, it was found by Winfield et al, (2011) that the available proton mass should not be restricted. Thus a comparison of operation under similar conditions would show that microbial fuel cells produce a much higher level of anode catalytic activity. In general, microbial fuel cells can produce more energy when the soil density is increased. This is due to the microbial fuel cell cathode proton consumption rate being higher than the rate of transport through the cellular membrane due to the intrinsic chemical differences. Microbial fuel cell using a variety of inorganic compounds, in addition to things, as a fuel for the maintenance of microbial metabolism, while chemical fuel cell is a simple as fuel. Microbial fuel cells use various chemical substances in the aqueous phase decomposition of cation, required that the concentration ratio of these cations also have close to a neutral pH. If the proton concentration was significantly higher, they could interfere with transmembrane proton transport. Microbial fuel cells also required substances for gaining proton mass. Another limiting factor is the water quality as the electrolyte solution of choice.

Rozendal et al, (2008) verified the cathode chamber using a layer of the Nafion 117 membrane and was able to determine the transport cation transport effect and its impact on microbial fuel cell performance. It was found that the microbial fuel cell transported to the cathode from the anode the proton (K+, Na+, Mg+, Ca+) cations. This meant that outside the positive charge transferred the same number of electrons. Analysis of microbial fuel cell from the film shows, K + and Na + membrane sulfonate residues account for about 74%. Cation transport does not depend on the concentration gradient to complete, but rather an electrodialysis process. This means that there is no microbial fuel cell proton transport. Instead it is mainly through the neutral cation transport, rather than proton transport. This phenomenon raises a range of electrochemical and microbiological problems, which affect the efficient operation of microbial fuel cells. Acidification in the anode chamber impedes the increase in anode potential while reducing the activity of microbial catalytic anode reaction. This occurs mostly under conditions where the cathode chamber fully reduced the anodic potential leading to alkaline conditions.

Usually microbial fuel cells are designed with a close fitting arrangement to avoid having two electrodes short-circuit. The cathode current can be enhanced using salt or acid solution. (Marsili et al., 2008) found that the proliferation of protons in the aqueous phase is a relatively slow process, with a high salt concentration in the electrolyte to the membrane microbial fuel cell being essential in determining the proton diffusion rate of speed. Salts inhibit transmembrane proton transport, but the promotion of protons in the aqueous phase enhance effective diffusion. In the microbial fuel cell with a membrane, using a reduced proton diffusion solution and low-salt electrolyte can increase the anode proton transfer. (Xaio et al, 2013) found that miniature microbial fuel cell performance may be affected by the diffusion which is in turn caused by the depth of the reduction. The cathode surface of the alkali has a limited buffering capacity when compared to the cathode-electrolyte salt concentration. Thus, a low value can lead to lower cathode potential. (Chatterjee et al., 2013) discovered that using potassium permanganate as an electron acceptor would increase the cation exchange membrane and cathode. This caused the casing-type microbial fuel cell power density to be as high as 3987 mw/mZ, which the 34.5 times higher than the average microbial fuel cell value. Permanganate has been successfully used to double the microbial fuel cell resistance to 51Z. From the above results it can be seen that the proton mass is one of the microbial fuel cell’s main limiting factors. It is hoped that by increasing the cathode's internal resistance, it will lead to increases of the microbial cell performance.

Microbe adaptability

Some microbes live in low-oxygen environments such as swamps and river sediment so they are forced to use alternative electron dumps such as using metals to breathe in place of oxygen. (Lovely et al., 1987) found a species of microbe called Geobacter metallireducens along the Potamic River banks. The research showed that this new microbe was getting electrons from organic compounds, and passing them onto iron oxides. In essence the Geobacter metallireducens are breathing iron in place of oxygen. Since bacteria are not advanced enough to have lungs they must pass their electrons to metal oxides that lie outside the cell (Kato et al., 2012). This is accomplished through the use of special hair-like wires that protrude from the cell's surface. These microbial nanowires function similarly to copper wire when conducting electricity. This enables the microbes to not only generate electricity but also convert either the organic compounds from ethanol, gasoline, or oil spills into carbon dioxide, as well as change soluble radioactive metals such as plutonium and uranium into insoluble forms that are less likely to contaminate the environment.

The next year Shewanella oneidensis was discovered at Oneida Lake located in New York State (Meyers and Nealson, 1988). That lake primarily contained manganese which reacted with the oxygen in the air to form magnesium oxide. Shewanella oneidensis was found to be able to breathe oxygen when it was present, but during times when oxygen is scarce it can instead pass its electrons directly onto the manganese oxide, which would produce an electric current. Further research showed that it could also function with other metals such as iron. When first examined Shewanella appear to have long thin hair-like extensions of their outer membrane in a similar layout as Geobacter. However, further research discovered that the long filaments are only conductive when dried out in a lab environment. It was found that Shewanella are able to shuttle electrons out of their cells using transport molecules called flavins and stepping stone proteins embedded in the outer membrane called cytochromes.

There are other bacteria species that have the ability to harvest electrons directly from minerals and rocks. (Rowe et al., 2015) found six species of bacteria inside sediment samples from Catalina Harbor off the Californian coast with this ability including: Halomonas, Idiomarina, Marinobacter, and Pseudomonas of the Gammaproteobacteria family, and Thalassospira and Thioclava from the Alphaproteobacteria family. The study varied amounts of voltage sent to the soil samples to see whether the bacteria in the sediment would either accept electrons from an electrode, or discharge electrons on to it. The results showed that when no other food source was available, the bacteria would happily take electrons directly from the electrodes. In their natural habitat, the bacteria likely take their electrons directly from iron and sulphur located within the seabed (Kato et al., 2012). Some species of bacteria have been discovered with the ability to attach onto conductive materials, such as the iron-rich mineral magnetite, in order to pass electrons between each other through the magnetite. (Petersen et al., 2015) theorize that chains of magnetite can be formed to bridge the gap between the electron-donating and the electron-accepting bacteria. Desulfobulbaceae or cable bacteria exist primarily on sea floors and river beds where there is little oxygen (He et al., 2006). They have be found to be able to exist primarily by the formation of chains that are one cell in diameter. These chains are able to extend thousands of cells long up to distances of several cms which is a huge distance for a bacterium only 3 or 4 ums long (Petersen et al., 2015). The first bacterium in the chain which is located in a low oxygen environment takes electrons from sulphide or another available mineral and passes them onto the next bacterium. That bacterium then passes the electrons on to the next one, and so on up the chain until the final bacterium can finally pass the electrons onto oxygen (Poynton et al., 2010). This system is the only available method that bacteria living in seabed mud where no oxygen penetrates can access oxygen dissolved in the seawater above. Running along the chains of bacteria are ridges that connect the cells together, possibly allowing electrons to flow between them (Acharya and Aithal, 2017). Surviving on electrons alone is a smart way of coping when oxygen and food are scarce such as in locations including the bottom of the ocean or deep underground. It is a beneficial strategy where there is not quite enough energy for an organism to grow or compete, but only enough for it to exist. Bacteria species will be discussed in much more detail in future sections.

Choosing catalyst micro-organisms

One of the main features of the microbial fuel cell anode is that it can be attached to by micro-organisms and facilitate their transmission of electrons. The main key of this is to determine the microbial fuel cell produced electricity generation capacity through the study of specific micro-organisms capable of producing high rates of electron transfer. Logan et al. (2006) discovered that a MFC using activated sludge or anaerobic sludge digestion as fuel, could generate 0.6V open-circuit potential on a closed-circuit. It was found that in most cases the current did not play any significant factor and could be ignored in the grand scheme. This is essentially due to the process of getting the anode chamber to expend the supply of fuel which will typically take as long as 2 to 3 weeks. At that point the current will have gradually settled at a stable value and is no longer a factor.

(Choo et al, 2006) developed the theory that electrochemically active bacteria are taxonomically very diverse by comparing the bacteria composition of others in the literature with their mixture of glucose and glutamate which created a culture of γ-Proteobacteria (36.5%), Firmicutes (27%) and δ-Proteobacteria (15%). From this comparison they found that enrichments using different types of fuel sources led to the development of many different groups of bacteria.

Bacteroides oralis

Nam et al. (2010) performed an analysis of the small ribosomal particles (165rDNA) and was able to discover that the bacteria found on the anode was different those that were found in sludge and acted as an inoculum of the bacterial flora Bacteroides oralis. It was further discovered that there was a correlation between the top performers of many of the microbial groups that could be determined by the concentration levels of the most suitable poly-microbials. This is due to their ability to improve the digestive efficiency used under the required conditions for successful microbial fuel cells run operation.

In the enrichment process, many studies [(Liu et al., 2008), (Park et al., 2001), (Rozendal et al., 2008)] suggest starting out with a pure culture for creating the biofilm that is found on the fuel cell electrode surface. Vargas et al. (2013) found that the formation of microbial biofilm between the bacterial cells and cathode would be maximized when using insoluble Fe3O as the electron acceptor. The main cause of this phenomenon is the restoration of direct contact between the electronic transfer through the Bacteroides oralis via special pili. Some research has even indicated that some bacteria can produce a natural body of electronic flow within the microbial fuel cell.

Shewanella

Shewanella are commonly found nearly everywhere on Earth in the soil and sediments. They are able to digest many chemical compounds and elements such as uranium that are toxic to nature but are benign to humans. Shewanella oneidensis (MR-1) is the bacteria most frequently used because of its incredible ability to digest the highest variety of carbon sources and reduce the highest amounts of electron acceptors. This versatility helps the MFC to become very tolerant with regards to fuel requirements, and thus enabling the use of many different types of biomasses to provide power to the MFC (Carter, 2007). The Shewanella oneidensis MR-1 was discovered and first isolated in 1988 by Dr. Kenneth Nealson from sediments of Lake Oneida in New York. The MR-1 is popular for its ability to reduce solid substrates such as Fe and Mn oxides. It can also grow both aerobically and anaerobically, and develops quickly on defined mediums such as graphite felt (Carter, 2007). Figure 10 shows the graphite felt before exposure to Shewanella MR-1 and Figure 11 indicates the amount of growth possible after exposure. It usually uses oxygen as its electron acceptor to transport its excess electrons. However, if there is no oxygen available, the MR-1 bacteria have the ability to use various metals as electron acceptor in order to survive. It is not completely understood how this is done, but Gorby et al. (2006) theorize that by growing on the electrode surface, the bacteria can use the electrode to breathe through direct contact. Additionally, microscopic pictures such as Figure 12 have shown the existence of some type of nanowires, which have been shown to be excellent electrical conductors that link neighboring MR-1 cells together. This may be the method that bacteria which are not in direct contact with the electrode are able to emit electrons.

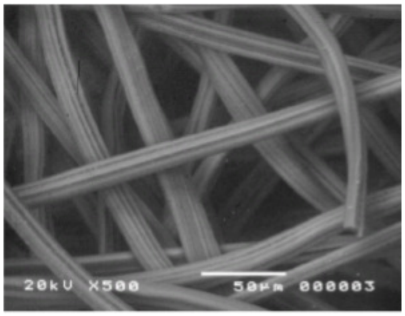

Figure 10. Graphite felt electrode without Shewanella MR-1.

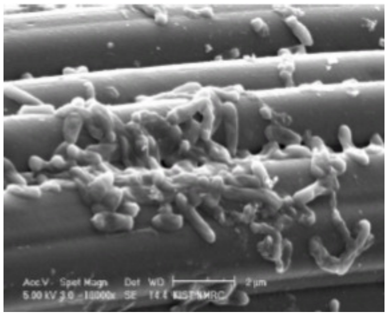

Figure 11. Graphite felt electrode with Shewanella MR-1.

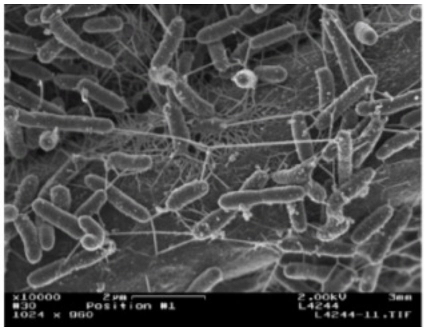

Figure 12. Shewanella MR-1 nano wires.

Geobacter

Microorganisms within the family Geobacteraceae have the ability to oxidize organic compounds using their electrodes as the sole electron acceptor for their respiration. In general, molecular analysis of the microbial community on most anode surfaces typically reveal that Geobacteraceae will make up about half of the microbe population (Tender, 2002). However, there have not been similar populations of Geobacteraceae contained either within in the sediment or on the cathode (Holmes, 2004). Geobacteracae are found mostly in freshwater sediments. In cases where salt water predominates the water table, the Desulfuromonas species has been found to dominate the anode film. Pure culture studies have shown that Geobacteraceae have the ability to completely oxidize acetate and other organic compounds into carbon dioxide using only an electrode that serves as the sole electron acceptor (Bond et al., 2002, Holmes et al., 2003). This helps the microbe to optimize energy production and support their increasing population. (Lovely et al., 2004) discovered the ability of Geobacteraceae to produce electricity is proportional to their ability to transfer electrons from the cell onto Fe(III) and Mn(IV) oxides. This was due to their insoluble and extracellular nature and propensity for electron acceptance.

Geobacter species were also found to be very adept at harvesting electricity from other organic material, such as swine waste. This is primarily due to their ability to move their tiny hairlike extensions called pili to generate additional electricity from mud and wastewater. (Lovley et al., 2005) designed a strain of Geobacter that was found to be up to eight times more efficient than other bacterial strains in electron transfer. Their design took into account that Geobacter use iron compounds much in the same way as mammals use oxygen. This lets them thrive in anaerobic environments such as the ocean floor or very deep underground so they can be applied in the bioremediation cleanup of petroleum spills. (Holmes et al., 2003) found that Geobacter were the first microorganisms found to derive energy to support growth from organic matter oxidation with an electrode serving as the sole electron acceptor and can produce the highest current densities of any pure culture. Geobacter species are often found to be the microorganisms that have the highest rate of enrichment of the electrodes harvesting electricity in the greatest number of different environments. Geobacter sulfurreducens has become the microbe of choice for studying the mechanisms for direct electron transfer from microbial biofilms to electrodes. Recent studies have demonstrated that it produces highly conductive biofilms that promote electron transfer to the electrode and releases the *c*-type cytochrome, OmcZ, which accumulates at the biofilm-electrode interface to promote electron transfer to the electrode. One of the unique abilities of Geobacter species is its ability to accept nearly all electrons even those that contain negative potential (Gregory et al., 2004). This makes it much easier to make electrical connections with graphite electrodes. (Lovley et al., 2005) found that when a negatively poised electrode was placed in a sediment inoculum, it led to a reduction of the nitrate level and also there was an increase of the Geobacter population that was found on the electrode surface. (Park et al., 2005) discovered that using pure cultures of Geobacter species would at least double the reduction of physiological electron acceptors such as nitrate and fumarate even further as the reaction was enhanced by the electrode serving as the sole electron donor. (Gregory and Lovely, 2005) expanded the scope of the MFC research to include uranium-contaminated subsurface sediments and found that when poised the electrodes facilitated the reduction of soluble U(VI) to insoluble U(IV). This was believed to occur due to the amount of U(IV) precipitated on the electrode surface. This means that the reduction of U(VI) using electrodes is a better alternative in the bioremediation of uranium-contaminated subsurface environments than the addition of organic electron donors. This is due to the fact that electrodes also provide a simple means of removing the uranium from the ground. (Gregory and Lovely, 2005) also discovered that electrodes could be used to provide electrons for the bioremediation of other contaminants, such as chlorinated solvents and perchlorate. (Rhoads et al., 2005) discovered that Manganese-oxidizing microorganisms could also function as the catalysts in a novel cathode system and were able to produce an increase in the current generated by almost two orders of magnitude over plain graphite electrodes in a microbial fuel cell. The reason for this was due to the process where the Mn(IV) that precipitated on the cathode was reduced to Mn(II). The manganese oxidizers were then able to recycle much of it back to Mn(IV) to restart the cycle.

Electron transfer to electrodes in Geobacteraceae has sometimes been studied using Geobacter sulfurreducens, due to its close relation and ability to that colonize electrodes in sediments and the fact that the complete genome sequence, genetic system, and whole-genome DNA microarrays are readily available for this microorganism (Lovely, 2006). This makes it possible to track the metabolism of G. sulfurreducens growing on electrodes by monitoring the gene transcript levels. (Bond et al., 2005) found that Geobacteraceae have a unique, eukaryotic-like citrate synthase that catalyzes a key step in acetate oxidation. Citrate synthase is pace making enzyme that provides microbes assistance for the first step of the citric acid cycle. This means that levels of transcripts for citrate synthase would increase in cells of G. sulfurreducens growing on electrodes as current production from acetate oxidation was increased. (Holmes et al., 2005) theorize there is a direct link between transcript levels and metabolism on electrodes. (Mehta et al., 2005) performed a series of gene expression and genetic studies and found that many of the key components involved in extracellular electron transfer to Fe(III) oxides, such as the outer-membrane c-type cytochromes OmcS and OmcE, were also important to the electron transfer process from the microbes to the electrodes. One key discovery stipulates that the electrically conductive pili that are essential for electron transfer to Fe(III) oxides were not necessarily required for successful electron transfer to electrodes (Holmes et al., 2003). Another route to increasing electricity production that may be possible would be to alter the central metabolism of the microbe to increase rates of respiration. (Mahadevan et al., 2006) created a genome-based in silico model of G. sulfurreducens which has been able to predict increasing respiration rates.

Rhodoferax ferrireducens

R. ferrireducens has the unique ability to directly transfer electrons to the surface of electrodes. R. ferrireducens reduces Fe(III) during the oxidation of glucose to CO_2 and quantitatively transfers electrons to graphite electrodes. It is able to grow at a range of 4 to 30^{o}C with 25^{o}C being found as its optimal temperature. Various substrates can support its growth, ranging from organic acids to sugars such as glucose or fructose. MFCs using this organism have been found to have superior performance than other previously described microbial fuel cells for several reasons. The primary reason for this is its ability to oxidize glucose at 80% electron efficiency while other strains, such as Clostridium strains, oxidize glucose at only 0.04% efficiency). In other fuel cells that use immobilized enzymes, glucose is oxidized to gluconic acid, which generates only two electrons. However, MFCs using R. ferrireducens are able to completely oxidize glucose to CO_2. R. ferrireducens also does not require the addition of toxic electron shuttling mediator compounds employed in other microbial fuel cells. The R. ferrireducens MFCs are able to provide a steady electron flow over extended periods which adds to their long term stability. These R. ferrireducens MFCs exhibit many of the desirable features of secondary storage batteries, including the ability to be recharged, no severe capacity fading, the ability to accept fast recharge, reasonable cycle life and low capacity loss under open circuit conditions. Finally, they allow the harvest of electricity from many types of organic waste matter or renewable biomass. This fact provides an advantage over other microorganisms in the family Geobacteraceae, which can also transfer electrons directly on electrodes, but which cannot metabolize sugars. (Chaudhuri and lovely, 2003) found that the R. ferrireducens MFCs performer best when grown under strict anaerobic conditions in a bicarbonate-buffered defined medium, under N_2/CO_2 (80% and 20%, respectively) at 25°C. They also found that for additional growth on Fe(III), 10 mM Fe(III) should be chelated with nitrilotriacetic acid (FE(III)-NTA) and were able to generate a current density of 31 mA/m^2 which was able to last over a period of more than 600 hours.

Other microbe species

Currently there have been several cultures studied that have been found to be capable of producing current in a MFC including: Firmicutes (Park et al., 2001), Acidobacteria (Holmes et al., 2004), four of the five classes of Proteobacteria [(Rabaey et al., 2004), (Borole et al., 2008), (Chaudhuri and Lovely, 2003)] as well as the yeast strains Saccharomyces cerevisiae (Walker and Walker, 2006) and Hansenula anomala (Prasad et al., 2007). These organisms interact with the anode through a variety of direct and indirect processes producing current to varying degrees. (Park et al., 2001) studied the benefits of using Clostridium butyricum which is a strict anaerobic Gram-positive bacteria and found that the optimum temperature was 37°C and a pH of 7.0 was necessary to stimulate growth. The major products of this glucose and Fe(O)OH metabolism were lactate, formate, butyrate, acetate, CO_2 and H_2 (Franks and Nevin, 2010). Growth was found to occur faster at the initial phase and the cell yield was higher when the medium was supplemented with Fe(O)OH. These results imply that Fe(III) ion is ideal to be utilized as an electron sink. Cyclic voltammetry showed that the Clostridium butyricum cells were naturally electrochemically active.

In freshwater environments the Geothrix species which is closely related to Geobacteraceae might be a better choice to increase electricity production (Holmes et al., 2004). This was due to the findings of (Nevin and Lovely, 2002) which found an enrichment of microorganisms closely related to Geothrix fermentans electrodes deployed in freshwater sediments. G. fermentans was previously shown to oxidize acetate and other organic substrates to carbon dioxide with Fe(III) as the sole electron acceptor (Park and Zeikus, 2000). It has been theorized that G. fermentans releases an as yet unidentified soluble electron shuttle which permits it to reduce Fe(III) oxides that it cannot directly access (Holmes et al., 2004). This means that that this organism may use a similar strategy to enhance transfer of electrons to electrodes, when faced with a different insoluble, extracellular electron acceptor. (Holmes et al, 2004) found that removing the medium surrounding the G. fermentans cultures only decreased power production by 50% and there was also significant evidence of a putative shuttling compound that could not be detected in the surrounding medium until weeks had elapsed. This result suggested that cells on the electrode surface may have a mechanism to prevent loss of the compound into the external medium. It was generally found that the current-voltage profiles of G. fermentans fuel cells contained lower total power outputs at all rates of current flow in comparison to G. sulfurreducens fuel cells (Bond and Lovely, 2003). Each individual fuel cell demonstrated variations in peak performance of up to 30% which was likely caused by differences such as the amount of biomass attached to electrodes and electrode roughness.

(Rabaey et al., 2004) found that there are some bacterial species including Pseudomonas aeruginosa that can produce compounds such as phenazine pyocyanin. These compounds are then able to serve as electron shuttles between the bacterium and an electron acceptor. This would mean that the bacteria present in a mediator-less microbial fuel cell would be able to self-mediate the electron transfer toward the anode, either with compounds released into the solution or by enhanced membrane-driven electron transfer. The potential of this research would lead to the development of a bacterial consortium with increased energy efficiency and possibly determine whether membrane-bound or extracellular electron shuttles is the most prevalent factor towards increasing in energy efficiency. Denaturing gradient gel electrophoresis (DGGE) was performed to determine the levels of enrichment for each microbial species obtained during the course of the study. The band patterns on the DGGE showed that the microbial consortium within the soil was evolving constantly during this time period (Rabaey et al., 2004). It was also found that the banding patterns of the suspended and attached consortia were similar, and the similarity would further increase as the time went on. This means that the increase was likely linked to an increasing power output of the microbial fuel cells. (Rabaey et al., 2004) theorized that to identify the bacterial species required to generate good biofuel cell performance, the most dominant bands of the DGGE gel should be excised and sequenced no later than days 117 and 155 respectively.

(Lovely, 2006) found that when using sulfide-rich sediments the anodes would be heavily populated with microorganisms with 16S rRNA sequences such as the Desulfobulbus species. The likely reason for this is that sulfide has a natural tendency to react with the electrode to form S^o, the elemental form of sulfur. The Desulfobulbus species then is able oxidize the S^o back to sulfate using the anode as the electron acceptor. Most research studies have been run using Desulfobulbus propionicus (D.

propionicus). It has the ability to perform dissimilatory sulfate reduction through the incomplete oxidation of organic acids including: lactate, propionate, butyrate, and ethanol to acetate through its primary metabolism (Widdel and Pfennig, 1992). However, D. propionicus also has the capability to oxidize organic electron donors with nitrate, nitrite, or oxygen and can oxidize inorganic sulfur compounds with the reduction of O_2, nitrite, nitrate, or Mn(IV) (Dannenberg et al., 1994). (Tasaki et al., 2003) found that when an electron acceptor is not present, D. propionicuscan are able to ferment lactate, pyruvate, or ethanol to a mixture of acetate and propionate via the succinate-propionate pathway. Previous studies also discovered that cell suspensions of D. propionicus were able to reduce both Fe(III)-nitrilotriacetic acid (NTA) and crystalline Fe(III)-oxide when propionate was provided as the electron donor (Park et al., 2001). However, Fe(III) was found to not support growth in studies done by (Lovely et al., 1993). The ability to grow via reduction of Fe(III) oxides may be relevant to growing better microbes on the electricity harvesting electrodes in soils due to both the electrodes and Fe(III) oxides containing insoluble and extracellular electron acceptors.

(Prasad et al., 2007) explored the capability of the yeast cells, Hansenula anomala to perform direct electron transfer. The H. anomala was sub cultured using a medium composed of the following ingredients: d-glucose (1 g), peptone (0.5 g), malt extract (0.3 g), yeast extract (0.3 g), and phosphate buffer (100 mL). The phosphate buffer solution was created by combining KCl (1 g), NaH_2PO_4 (6 g), NaCl (2.9 g), and Na_2CO_3 (2 g) in 1 L of water. The study created a two compartment microbial fuel cell made of Perspex with Nafion (961) membrane as the separator. Three different anode materials were tested in the study: graphite, graphite felt and polyaniline (PANI)–Pt composite coated graphite electrodes and graphite was used as the cathode material. At the completion of the MFC life, each membrane was analyzed and the fraction of the species H. anomala was separated and evaluated. The analysis also found the presence of some other redox enzymes. The isolated membrane fraction was found to contain Lactate dehydrogenase (cytochrome b2), NADH-Ferricyanide reductase, NADPH-Ferricyanide reductase, and cytochrome b5 and the total protein content of each membrane fraction was found to have an average ratio of 52.35 g protein/10 uL. The study found that since H. anomala is aerobic in nature, oxygen can be an electron acceptor. Further high performance liquid chromatography (HPLC) testing found that the end products formed were gluconic acid, succinic acid and pyruvic acid. These products are generally observed in the metabolic cyle of yeasts and provide proof that glucose can be utilized as a fuel for current generation by the species H. anomala. The final finding of the study confirmed that the redox potentials present in the membrane fraction of H. anomola are favorably arranged in comparison with that of electrode material for direct electron transport without any external mediator and without any intermediate redox reaction like ferric ion reduction.

(Walker and Walker, 2006) over at Army Research Labs developed a biological fuel cell that uses ordinary dry Baker's yeast and Saccharomyces cerevisiae. One of the advantages of this setup was that neither sterilization procedures nor the maintenance of live cultures and labile enzymes were needed. (Walker and Walker, 2006) found that yeast had the ability to grow rapidly in aerobic and anaerobic conditions with simple nutritional requirements and could use a wide variety of substrates which made them ideal for a biological fuel cell. A commercial off-the-shelf (COTS) yeast preparation was found to be preferable to immobilized enzymes which were expensive, difficult to isolate, substrate specific, and more sensitive to parameters such as temperature and pH. They designed a two compartment fuel cell with platinum electrodes separated by a proton conducting membrane. One half of the cell contained yeast, Saccharomyces cerevisiae, glucose, and an electron mediator, methylene blue. The reduced mediator acted to transfer the captured electrons to an electrode, producing an electric current and re-oxidizing the methylene blue. The other half of the cell contained an electron acceptor, potassium ferricyanide, which accepted the electrons from the circuit and was reduced. Ferricyanide was chosen as the electron acceptor over an oxygen-saturated solution to prevent significant oxygen diffusion through the membrane into the anode compartment where it would oxidize the methylene blue before the methylene blue could transfer electrons to the electrode. Several different experiments were performed testing a range of temperatures, yeast concentration, glucose concentration, and level of agitation. The result of their study found that the optimum conditions for producing current were obtained with a yeast inoculum concentration of 20 mg/mL in agitated, partially oxygenated electrolyte maintained at 45 °C and containing 0.1 M glucose.

Microbial movement in soil

Bacteria and other microbes have been found to have the ability to travel through soil and other porous materials with the distance that they move being dependent on both the type of porous medium and the amount of time elapsed. Many studies of bacterial movement were done in the late 1970's into the 1980s and focused on soil. Most have been conducted in the field and the results generally show a rapid movement and high concentration of bacteria reaching receiving waters. (Gerba et al., 1975) found that coliforms had a movement range from 0.6 m in fine sandy loam to 830 m in sand-gravel. (Keswick et al., 1982) discovered that the bacteriophage T4 could move up to 1.6 km in a carbonate rock terrain area. (Stewart and Reneau, 1981) detected migration of coliforms from septic tank drainfields in both vertical and horizontal directions to monitoring wells of 152- and 305-cm depth located within 30 m of the drainfields and found that their movement in both directions varied depending on the position of the monitoring well relative to the drainfield. This was surprising and it was theorized that it was due to variations of water flow. (Palmateer et al., 1989) found that the application of liquid manure to agricultural fields resulted in rapid movement of a tracer bacterium, nalidixic acid-resistant Escherichia coli, through the soil and under drain systems leading to contamination of surface receiving waters. (Smith et al., 1985) found that the movement of microorganisms through soil could be very fast through comparing the movement of a streptomycin-resistant E. coli K12 strain and C1 tracer through soils of different texture. This biggest differential in the tests occurred in Huntington silt soil which were stored in 0.28 m columns. It was found that 90% of the E. coli applied initially moved through the column in 17 min, while only 70% of the applied C1 trace moved through within the same time. It was theorized that this rapid movement stemmed from the presence of continuous macropores. (McCoy and Hagedorn, 1979) discovered that E. coli strains within the subsurface had a maximum speed of 17 cm/min. (Skilton and Wheeler, 1988) performed research where bacteriophages were injected into an aquifer by boreholes at 366 and 122 m from a pumping well and the bacteriophages reached a maximum speed of 2.8 cm/s. The explanation normally provided from these studies is that the observed phenomena are due to preferential flow of microorganisms through macropores, cracks, fractures, worm holes and channels formed by plant roots, or animals in the soil. Preferential flow through macropores was observed by (Van Elsas et al., 1991). (White, 1985) discovered the increased effect macropores had on the transport of dissolved and suspended matter through soil. He theorized the flow along preferential paths was the cause of rapid movement of dissolved and suspended matter through soil. (Rice et al., 1988) studied the movement of solutes and herbicides that were applied on irrigated fields and discovered that the extra flow resulted in solute and herbicide movement velocities of 1.5 to 2.5 times greater than those expected based on water balance considerations. (Beven and Germann, 1982) were able to conclusively prove that the flow of water and chemicals through macropores is more rapid than that through a soil matrix. (Everts and Kanwarm, 1988) used a hydrograph separation technique to quantify the preferential and matrix flow components to a tile line. They found that preferential flow contributed less than 2% of the total water flow. However, flow of bromide and nitrate account for up to 25% of these tracer chemicals found in the tile line. This large contribution occurred because these chemicals moved through preferential paths at the applied concentrations.

Many factors have been found to impact the survival and movement of microorganisms in soil including: the physical and chemical nature of the water, atmospheric conditions, biological interactions, and the soil characteristics. These are mainly related to interactions between soil, water, microorganisms and the surrounding environment (Tim et al., 1988). The effect of these factors on movement of microorganisms in soil have been a subject of study by many researchers. (Van Elsas et al., 1991) studied the influence of soil properties on the vertical movement of a genetically-marked Pseudomonas fluorescens bacterial strain through 50 cm long soil columns of loamy sand. They added bacterial cells at the top of soil columns of 5.3 and 13% moisture content, and measured the concentration of cells translocated to various depths. They found the ratio of cell concentration in the dryer soil to that in the wetter one ranged from 68% at 20 cm depth to 98% at the soil surface. The researchers also explored the effect of soil bulk density on bacterial transport observing a higher degree of transport to lower soil layers at the lowest bulk density (1 g/cm^3) compared to higher bulk densities (1.15 and 1.3 g/cm^3). (Huysman and Verstraete, 1993) also demonstrated the strong influence of soil bulk density on bacterial transport. In their work an increase in the bulk density from 1.27 to 1.37 g/cm^3 resulted in up to a 60% decrease in the migration of bacteria in laboratory columns.

Soil texture can affect bacterial movement through soils. (Smith et al., 1985) experimented on the movement of streptomycin-resistant E. coli through both undisturbed and repacked soils of different texture. In undisturbed soils, 22% of the applied E. coli passed through a 0.28 m column of Maury silt soil while 44% of the microorganisms passed through similar columns containing the Crider silt and 79% passed through the Bruno silt loam soils. It was also found that when columns were repacked with the same soils, at least 93% of the applied E. coli were retained in the soil core. The Size and morphology of microorganisms may also affect their transport through soil. (Gerba and Bitton, 1984) discovered that when E. coli and coliphage were injected together into an aquifer, the larger E. coli were detected 150m down gradient in an observation well ahead of the smaller coliphage. The reason for this rapid movement of E. coli is still yet to be discovered. This is especially true since (Kott, 1988) studied the movement of different types of bacteria in sand columns and was able to conclusively prove that bacterial size and morphology did not affect the filtration efficiency of the sand. (Fontes et al., 1991) studied the effects of ionic strength of artificial groundwater, cell size, mineral grain size and the presence of heterogeneities within the porous media on bacterial transport. It was discovered that the grain size was the most important factor while cell size and ionic strength were about equally important, but of lesser importance than the grain size in controlling bacterial transport. (Gannon et al., 1991) studied the relationship between cell size, cell surface hydrophobicities and surface charges of 19 bacterial strains and their transport through Kendaia loam soil. They found transport was related to cell size, with bacteria that had a radius of less than 1 nm being transported in higher percentages through soil than larger ones. There was no correlation between either the transport or retention of these strains by soil and their hydrophobicities or net surface charges. They also found no relation between the presence of flagella and the extent of bacterial transport through soil. (Scholl et al., 1990) studied the influence of soil mineral composition, ionic strength and pH on bacterial attachment to aquifer materials. Their results indicated that interactions between mineral grains in the aquifer and bacterial cells influenced adhesion of cells to the mineral grains, and hence play an important role in determining the movement of bacteria through saturated porous media. (Gannon et al., 199l) studied the influence of NaC1 in the carrying solution, cell density and flow velocity on transport of Pseudomonas sp. strain KL2 through 0.3 m columns of aquifer sand under saturated conditions. When 108 bacterial cells in 0.01 M NaC1 were applied to the column at a flux of 10^{-4} m/s, only 1.5% of the applied bacteria passed through the column within 2 h of application. However, when distilled water was used as the carrying solution, 60% of the applied bacteria passed through a similar column under the same flow conditions. That meant that the movement of bacteria added to sandy aquifers may be enhanced or reduced by modifying the chemical composition of the carrying solution. The presence of plants and large living organisms may also affect the persistence and movement of microorganisms in soils. For example, bacteria in soil are subject to competition and predation from other bacteria such as streptomycetes, myxobacter and Bdellovibrio, and larger soil organisms such as protozoa and nematodes (Peterson and Ward, 1989). In some instances, the presence of such organisms may enhance mixing of microorganisms within soil. (Opperman et al., 1987) studied the effect that earth worms had on movement of cattle slurry through soil. The slurry was obtained from drainage ditches beneath the cattle shed floor. Ten worms were introduced to 17.5 cm sand columns. Their activity was found to mix the slurry with the sandy soil to a depth of 17.5 cm as indicated by the movement of coliform bacteria through the soil.

Power generation

In order for a MFC to function it is necessary to have a means of completing a circuit. In a majority of MFC designs the cathode and anode are separated by a cation selective membrane and linked together with an external wire. When an organic material that is used for fuel enters the anode chamber, the bacteria set to work oxidizing and reducing the organic matter to generate the life sustaining bodily functions that fuel their cellular growth. Protons, electrons, and carbon dioxide are produced as byproducts, with the anode serving as the electron acceptor in the bacteria's electron transport chain. The newly generated electrons are then passed from the anode to the cathode using the wire as a conductive bridge. Nearly instantaneously, protons will pass freely into the cathode chamber through the proton exchange membrane separating the two chambers. Finally either an oxidizing agent or oxygen that is present at the cathode will recombine with hydrogen and the electrons from the cathode to produce pure water, completing the circuit. A bulb or some other load can then be placed into the circuit to receive the electrons produced.

Microbial fuel cell applications in wastewater treatment

During the wastewater treatment process, microbial fuel cell can be used as an energy or power source, and in addition, some of the more stable configurations in aerobic treatment can also produce less sludge. The microbes in the aerobic treatment of organic pollutants are exposed to the availability of all the potential energy in nature. However, while inside the microbial fuel cell the growth of microorganisms that consumes this energy is only able to convert a fraction to electricity. (Scholz and Schroder, 2003) found that a good estimate is made by assuming the following conditions: (1) a redox potential of 0.32V under the electrons from the contaminants passed to adjoining nucleotides, (2) using oxygen as an electron acceptor end, (3) the energy use of the nutrients was broken down to 1/3 is for the micro-organisms internal use, and other 2/3 into electricity. This proves that micro-organisms in wastewater treatment sludge from the fuel cell can be substantial savings to address the capital. (Bezerra et al, 2008) found that in different operating conditions, glucose and water half-saturation constant (K,) the best performance of the microbes resided in a range between 79-103 mg/L and 461-719 mg/L. This means that it is possible that the optimization of microbial fuel cell can not only enhance output power, while also detecting the quality of effluents to effectively treat waste water.

Materials and Methods

In this study the MFCs were built using the Build Your MudWatt kit manufactured by Keego. Their setup is shown in Figure 13. The anodes and cathodes for each MFC were cut out of carbon based felt material and Loam +OM soil was used. Distilled water was added to the soil to control the soil moisture content at 30% during the MFC assembly. The assembly process was as followed: a 1cm layer of soil was added to the bottom of the MudWatt container and tamped down. Then the anode was placed with a wire inserted inside that sticks out of the top of the container. Another 5 cm layer of soil was then added on top of the anode and tamped down. This layer of soil also had any feed source or other additives mixed in. The cathode was then placed on top with a similar wire. The MFCs wires were then led through the top of the container and the MFCs were then sealed. Several measurements were taken daily for each MFC and were averaged.

Figure 13. MudWatt MFC container design

The MFCs were grouped according to the additive applied and each group consisted of 10 members. MFC Group 1 had a tablespoon of Miracle Grow Pearlite fertilizer mixed with the soil. MFC Group 2 had 1 tablespoon of table salt mixed in with the soil. MFC Group 3 had 1 tablespoon of Grandma's Unsulphured Molasses added. MFC Group 4 was the control group and there was nothing added to the MFC.

Results and Discussion

The results of this study are shown in Figure 14. The fertilizer additive in MFC Group 1 produced the biggest impact within the first several weeks but started to level off in later weeks. The molasses additive in Group 3 also provided a large increase in voltage production. It was disappointing to see the electrical production decrease in MFC Group 2 as other researchers had reported voltage increases with the additive. It is theorized that perhaps too much was added which affected the soil moisture content as well as the microbes and their ability to generate electricity. Table 2 displays the percentage increase above the control. Future study is needed to determine the optimal levels for each additive and possibly the idea of combining them.

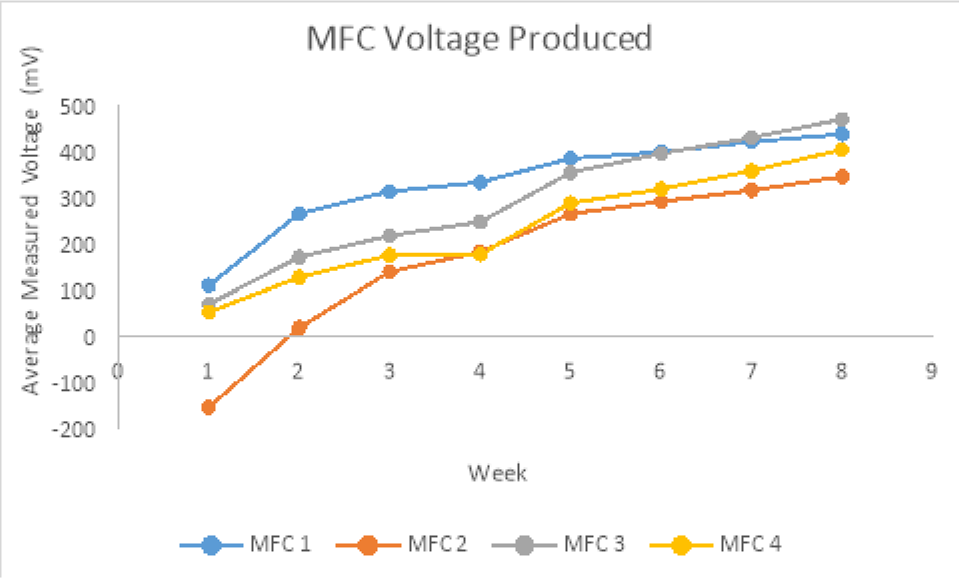

Figure 14. Voltage produced by each MFC group.

Table 2. Percent Increase of Voltage From Control

Week	MFC1	MFC2	MFC3
1	111.50	-403.31	32.75
2	109.34	-86.22	34.60

3	79.55	-20.68	24.24
4	88.96	3.01	40.05
5	33.77	-8.15	23.15
6	25.35	-8.47	24.35
7	17.61	-11.84	20.16
8	8.33	-14.59	16.33

Issues needing resolution

One problem that all fuel cells share is entailed in the crossover through the membrane of other species in addition to the H+ ions that are intended to go through. In a regular fuel cell this can be caused by either fuel that permeates through and contaminates the cathode electrode, or oxygen coming through to the anode side and reacting directly with the fuel without producing electricity. In the case of MFCs, the issue becomes that the nutrient consists of such a large molecular structure with a high molecular weight that it often cannot permeate through the membrane. Oxygen however, is still free to permeate from the cathode side through to the anode side. Once the oxygen reaches the anode side, the bacteria will utilize the oxygen instead of using the electrodes, which leads a loss of energy production.

One major hurdle in the implementation of MFCs is in the creation of high-performance and cost-effective anodes and cathodes. Many alternative materials have already been tried for anodes and cathodes in MFCs: carbon brushes, loofah sponge-derived porous carbon, graphene aerogels, and carbon nanomaterials. It has been found so far that porous materials have produced a higher level of voltage than carbon, cloth, and paper materials mostly because of the greater electrode surface accessible to electroactive bacteria. However, their high price and the complex production process often are not yet met with enough benefits and performance improvement to make it economically feasible. A low-cost and high-performance cathode is especially important for MFC performance due to interactions with the air within the container. Gosh et al. (2014) found that MFCs that use carbonaceous materials as the ORR catalysts can deliver similar or greater performance than that of the Pt/C cathode, while the cost can be reduced by at least one order of magnitude. However, there is the issue of fabricating and doping the carbon materials which usually requires toxic chemicals, sophisticated preparation routines, and specialized equipment (Li et al., 2018). Preparation of these catalysts can have a negative environmental impact. Although there has been significant progress in the design of MFCs recent years, most innovations were based on lab-size MFCs ranging from microliters to milliliters. Therefore, these results cannot be directly applied to large-scale reactors. (Lin et al., 2011) found that the low power densities observed in MFCs were mainly caused by poor electron transfer from bacteria to electrode.

The reason why the size of MFCs has limitations is primarily due to the fact that electron transport only occurs on the bacteria layer that is directly contact with the electrodes (Picioreanu et al., 2007). While MFCs were successfully designed for large scale batch processing of waste water streams, it is believed that their greatest potential lies in small scale devices where the surface to volume ratio is high. More research is needed to find the optimal flow rate of reactants that would increase the voltage output of an MFC. Advances in microfluidics will allow engineers to make increasingly smaller MFC devices that can take advantage of this high surface to volume ratio. Research into advanced microfluidics, bacterial strains, more robust separator membranes, and efficient electrodes are the key to unlocking the potential of MFCs.

Conclusion

The performance of microbial fuel cells is enhanced by its resistance to impact. Such resistance is based upon both the proton mass and the weak cathode caused by the oxygen reduction reaction. Protons in the aqueous phase of the transport rate are known to be very slow and remain in the hollow fiber reactor. This helps to improve the proton transfer as well as minimize the resistance. Cathodic oxygen also assists in the reduction reaction and the concentration of dissolved oxygen works toward a unipolar response relationship. This means that when placed along with a cathode, they can improve the aerobic performance of fuel cells. It also matters what additives are placed within the MFC. Adding fertelizer and moleses increased MFC performance by an average of 45 and 38% respectively while table salt decreased electric production by 30%. Appropriate aggregation of concentrated cathode micro-organisms can be further enhanced by using oxygen reduction kinetics. As the microbial fuel cell operating conditions improve with a moderate resource-efficient and pollution-free, environment, the current micro-devices have the potential for application for use in biochemical oxygen demand sensors.

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