Design and Development of Microbial Fuel cells

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Recently, the world is facing energy crisis for non-renewable resources. So people are searching for high efficient energy transformations and way to utilize the alternate energy sources. Fuel cells are an important part in the research. The main aspects of fuel cell research is to reduce the cost and simplifying implementation conditions In recent years, people are moving towards microbiology and biotechnology to find the solution. Current review is based on studies of a form of fuel cells known as Microbial Fuel Cells (MFCs). MFCs can be the next generation of fuel cell and thus play an important role in energy conservation and alternate fuel utilization. There are different aspects of Microbial fuel Cells as well as different types of fuel cells. Microbial fuels cell can be used for different purposes such as electricity generation, Biohydrogen production, biosensors and waste water treatment.

1. Introduction

Current Prediction for the global energy has led to search for alternate resources. The non-renewable resources of energy is depleting at a faster rate in the current scenario. Hence, there is the search for high efficient energy transformations and ways to utilize the alternate renewable energy sources. Fuel cells are one of the most important topics in the research. The main aspect of fuel cell research is to reduce the cost and simplifying implementation conditions. In recent years, researchers are trying to find out the solution through biotechnology.

In the current research, an attempt is being made to devise a way to transform biomass from wastelands to portable electricity generation. Fuel cells are the most burning area of research for quite a long time. Much of the current research is focused on the development of way to convert chemical energy stored in biomass to electricity. The biomass is used as major fuel in the rural India for the cooking. The energy transformation from burning of biomass (chemical energy to heat) and that utilization of heat for different purposes is very less energy efficient. Most of the rural country has to depend on the subsidized yet scarce electricity supply. A technology using microbial fuel cells (MFCs) that can convert the energy stored in chemical bonds in organic compounds to electrical energy achieved through the enzymatic reactions by microorganisms has generated considerable interests among academic researchers in the last decades [1]. Microorganisms can be used to efficiently transform the chemical energy into electrical energy [2.3]. Microorganisms in the anodic compartment utilize the biomass for growth forming electrons and protons. These electrons can be transported out of cells using electron mediators or some microorganisms have the tendency to expel electron for reducing the substrates which can be absorbed by electrodes. The protons or H+ ion can be oxidized to water in cathode which can be done in a separate chamber or separately in the same chamber which categorize two different types of microbial fuel cell viz. Single chambered MFCs or Double chambered MFCs. Carbon dioxide is emitted as byproduct but it is the same form carbon which is fixed by plants for photosynthesis. No other byproducts are formed and the fuel cells have efficiency higher than that of conventional electricity generation devices. The separation of the oxygen or any other electron acceptors from microorganisms derives the potential difference for electricity generation and thus is an important part in designing of MFCs.

Taking a simple example of Acetate consumption typical reactions that follows

$$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 8e^- + 7H^+ \qquad (1)\ \text{Anodic Reaction}$$
$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \qquad (2)\ \text{Cathodic Reaction}$$

Based on the above reaction MFC bioreactors can efficiently generate electricity. The capacity of the reactors to use substrate determines the extent of electricity generation. The efficiency of the process depends on various factors. Optimization of these factors can solve out energy crisis in an efficient way to utilize the industrial and domestic waste to produce electricity.

2. Microorganisms in development of MFCs

Earlier it was thought only few microorganisms can be used to produce electricity. Recently, it was observed that most of the microorganisms can be utilized in MFCs. MFC concept was demonstrated as early in 1910 where *Escherichia coli* and *Saccharomyces* sp. were used to generate electricity using platinum electrodes [1]. Though not drawing much attention till early 1980s when the concept was boosted with advent of use of electron mediators to

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enhance the generation of electricity many folds. Except anodophiles, the microbes are incapable of transferring electrons directly to the anode. The outer layers of the majority of microbial species are composed of non-conductive lipid membrane, peptididoglycans and lipopolysaccharides which stops the facilitation of electron transfer to the anode[4]. The problem can be solved with mediators.

2.1 Use of Mediators to transfer electron:

Mediators in oxidized state are easily reduced by capturing electrons from within the membrane of microorganisms. The mediators then transfer across the membrane and release the electrons to the electrode and become oxidized again in anodic chamber and thus are reutilized. Good mediators should have following characteristics [5]: (a) It should be cell membrane permeable; (b) It should have electron affinity more than the electron carries of the electron transport chains; (c) It should possess a high electrode reaction rate; (d) It should be well soluble; (e) It should be completely non-biodegradable and non-toxic to microbes and (f) it should be of low cost. These characteristics describe the efficiency of mediators. Contrary to lower redox potential mediators being theoretically better the higher redox potential mediators for high affinity for electrons absorbing from electron carriers in cell are the best. Methylene blue, neutral red, thionine, Meldola's blue, Fe(III)EDTA are sysnthetic mediators but the problem is their toxicity which limits their use in MFCs[5,6].

Microbes are also reported to use naturally occurring compounds including microbial metabolites (Endogenous mediators) such as humic acids, anthraquinone, the oxyanions of sulphur (sulphate and thiosulphate)[7]. All of them can transfer electrons from inside the cell membrane to the anode.

2.2 Microorganisms directly transferring electrons to anode:

There are also several microorganisms reported which can transfer electrons across the membrane by themselves to anode. [8]. These microorganisms are stable and have high coulombic efficiency. *Shewanella putrefaciens* (Kim et al., 2002), *Geobacteraceae sulferreducens* (Bond and Lovley, 2003), *Geobacter metallireducens* (Min et al., 2005a) and *Rhodoferax ferrireducens* (Chaudhuri and Lovley, 2003) [9,10,11,12] are all effective and form film on the anode surface and transfer electrons directly to electrode across the membrane. These microorganisms brought a revolution in study as it reduced the use of mediators, a potential pollutant. The anode here acts as the final electron acceptor for the cell and thus effectively enhances the electricity generation. There are also reported studies on cathodophillic microorganisms such as *Thiobacillus ferrooxidans* which forms a film on cathode and the cathode acts as the electron donor. These organisms causes a potential difference in cathode driving a suitable reaction at anode by anodophillic microorgamisms to produce the electricity.[10] These double microbial chambered fuel cells have comparatively high generation and lower cost.

2.3 Function of Microorganisms:

There are three categories of microbes that can be used in MFCs: a) those who can directly transfer electrons to anode using anode as terminal electron acceptors; b) those who can't directly but use mediators to transfer electrons to anode; c) those who can accepts electron from cathode. There are two subcategories in the second which are of those who can use natural mediators and those who can't. There are lots of reported studies on microorganism that can directly transfer to anode. Marine sediments, waste water, fresh water sediments, mining dumps are the main sources of these microorganisms. Almost all of the microorganisms are metal reducing in nature. Some of them are high source of electrons. Though the use of mediators enhances the transfer in these cases too but most of the time mediators are toxic to cell and are environmental pollutants. The transport of the electrons is due to electron shuttles present in soluble form in bulk solution or transport units in the extracellular matrix. The later cases preferentially form a film on the anode. *Geobacter* sp. are a particular group of microorganisms which synthesizes ATP on dissimilarity reduction of metal oxides under anaerobic condition in soils and sediments.[10,11] The final electron acceptors are the oxides in which electrons are transported by direct contact with microorganisms. Most of the time designing anode, these metal reducing organisms are preferred. *Geobacters, Shwenella* and *Rhodoferax* behave similar to their natural condition as anode acts as metal oxides behaving as metal oxides [9,10,12]. *Clostridium butyricum* is only mediatorless microorganism which doesn't reduce metals [13]. *S. putrefaciens*, *G. sulferreducens*, *G. metallireducens* and *R. ferrireducens* , transfer electrons to the solid electrode (anode) using this system [9,10,11,12]. Some natural mediators also enhance their activity. Mediators play an important role of behaving as shuttle between anode and electron carriers inside the cell. $Mn4^{+}$, neutral red, methylene blue, humic acid and Fe(III)-EDTA are typical mediators that found some use [5,6]. Most of the time mixed cultures is preferred as they have a wide range of substrates. Mixture of electrophiles and anodophiles together use array of substrates and can be used for generation of electricity from waste water. Sulphate/sulphides mediated systems have major role in power generation [7] and most of the time sludge is rich in these compounds. Thus large scale reactors can be synthesized to use sludge and sewage sources as substrates for electricity generation.

3. Design of MFCs

There are basic components of MFCs which are important in constructions. Electrodes, wirings, glass cell and salt bridge have an important role. Salt bridge is replaced with Proton exchange membrane in PEM fuel cell. Though it enhances the cost but handling and the power generation both get enhanced, thus increasing the portability and efficiency of the system. Apart from that fuel cells can be classified in two types on the basis of number of compartments or chambers.

3.1 Double chambered fuel cells:

Both the cathode and anode are housed in different compartments or chambers connected via a proton exchange membrane (PEM) or sometimes salt bridge [14]. PEM or salt bridge mainly functions as medium for transfer of proton to make the circuit complete as shown in figure 1A. This not only completes the reaction process but also prevents anode to come in direct contact with oxygen or any other oxidizers. They are run in batches and can be used for producing higher power output and can be utilized to give power in much inaccessible conditions. It can be suitable designed to scale up to treat large volume of wastewater and other source of carbon. These particular types are called up flow mode of microbial fuel cell as shown figure 1 B. They practically fall between the classification of single chambered and double chambered microbial fuel cells. They are mediator-less and sometimes membrane-less and can be used for large scale production of electricity from the wastes [15, 16].

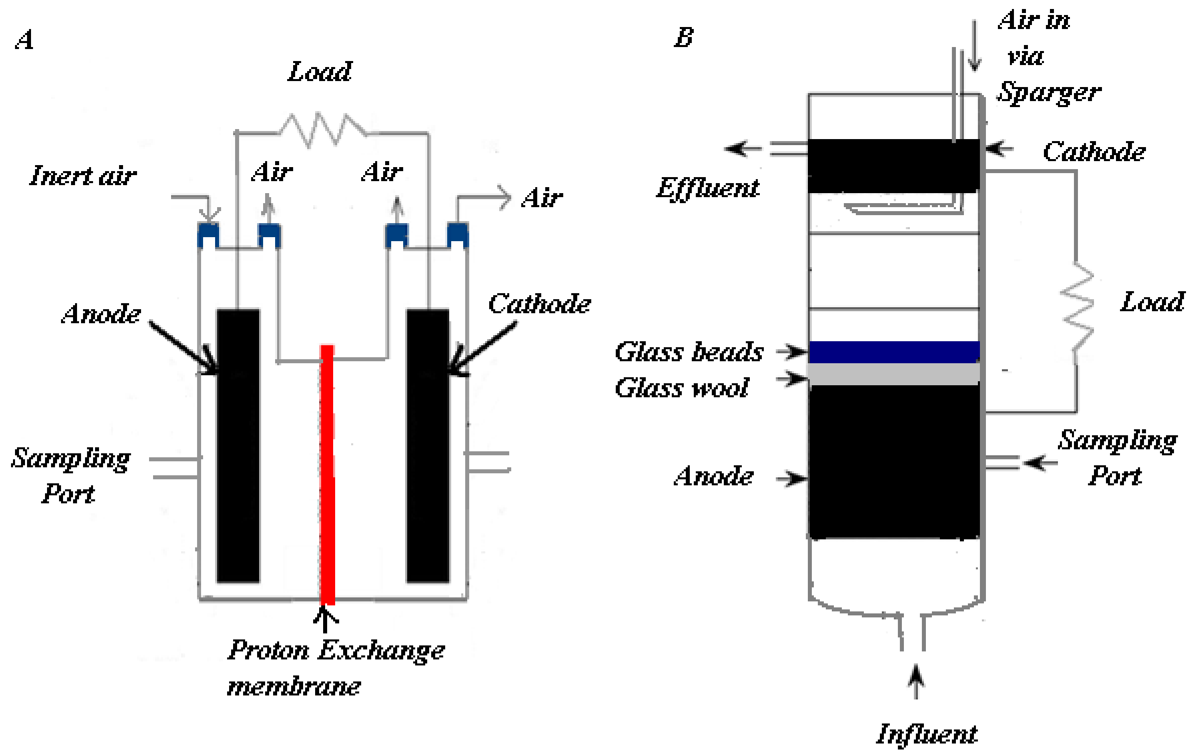

Fig 1: A) Simple design of Double chambered Microbial Fuel Cell **B)** Schematic Designs of Cylindrical Membrane-less fuel Cells (As proposed [16]).

3.2 Single Chambered Fuel cells:

They are simple anode compartment where there is no definitive cathode compartment and may not contain proton exchange membranes as shown in Figure 2 [17]. Porous cathodes form one side of the wall of the cathode chamber utilizing oxygen from atmosphere and letting protons diffuse through them. They are quite simple to scale up than the double chambered fuel cells and thus have found extensive utilization and research interests lately. The anodes are normal carbon electrodes but the cathodes are either porous carbon electrodes or PEM bonded with flexible carbon cloth electrodes. Cathodes are often covered with graphite in which electrolytes are poured in steady fashion which behaves as catholytes and prevent the membrane and cathode from drying. Thus water management or better fluid management is an important issue in such single chambered fuel cells.

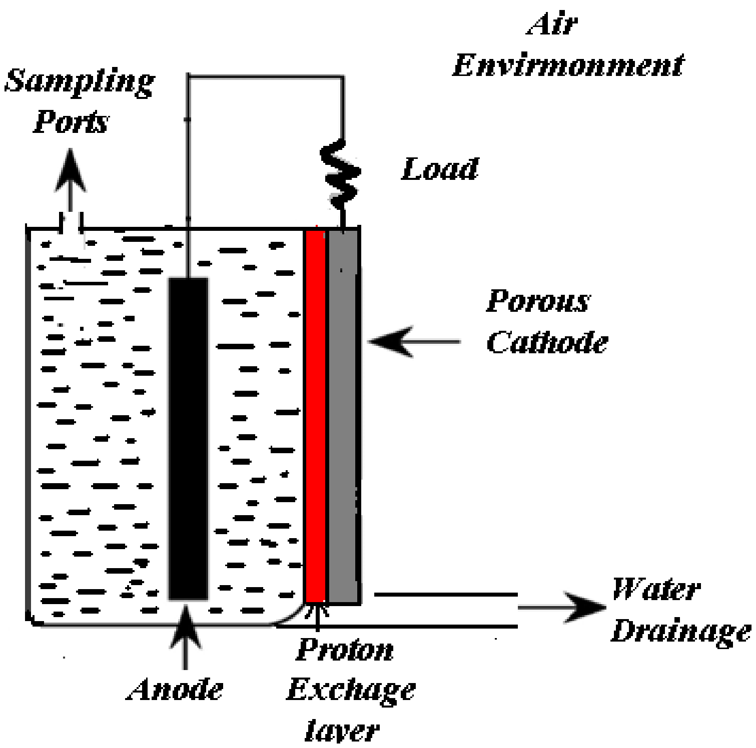

Fig 2: Schematic design of Single chambered Microbial Fuel Cell (As Proposed [17]).

3.3 Stacked Microbial fuel cells:

These are another type of construction in which fuel cells are stacked to form battery of fuel cell.[18] This type of construction doesn't affect each cell's individual Coulombic efficiency but in together it increases the output of overall battery to be comparable to normal power sources as shown in figure 3. These can be either stacked in series or stacked in parallel. Both have their own importance and are high in power efficiency and can be practically utilized as power source.

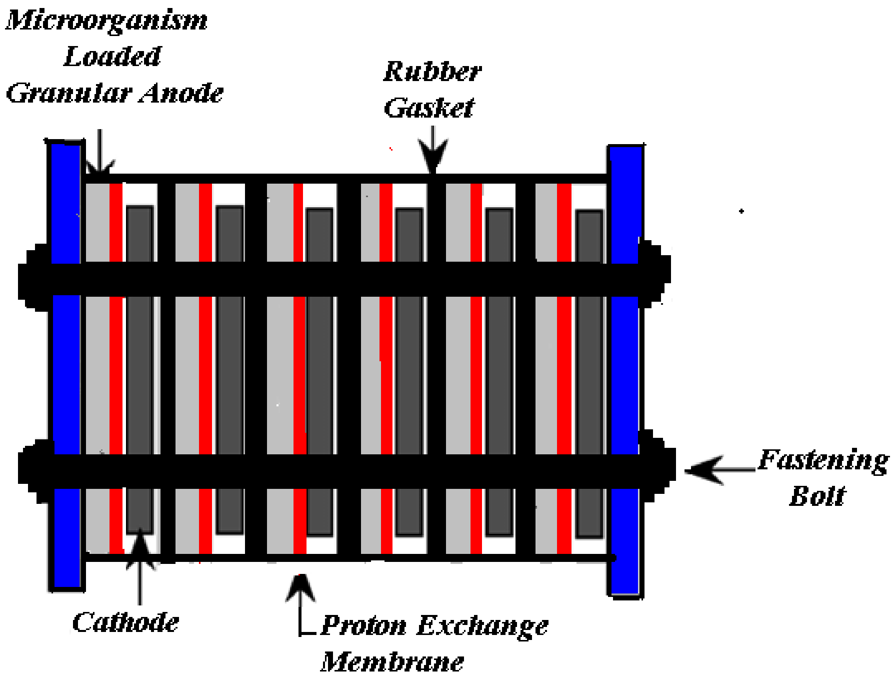

Fig. 3: Schematic Design of Stacked type Microbial Fuel Cell (As Proposed [18]).

4. Effects of conditions and construction on MFC operation

Electrode materials, Proton exchange membranes or salt bridge and operation conditions of anode and cathode have important effect on MFCs. The electrode material determines the diffusivity of oxygen in single chambered MFCs. If the electrodes are more porous it allows diffusion of oxygen to anode which reduces the efficiency of fuel cells. The electrode material also determines the power loss of fuel cell in terms of internal resistance [19]. The longevity of electrodes is also an important criterion. But the most important criterion is cost. Electrodes can be replaced if they are corroded or saturated and it doesn't affect the conditions much if the microbes are non-film making and are present in liquid anolyte.

Proton Exchange membranes also play an important part but they are very costly and needed proper installation procedures for limiting the dangers of clogging and drying. But they make the assembly very robust and thus usable in practical conditions [20]. The ratio of membrane surface area to system volume is critical to the system performance. Alternative membranes such as porous polymers and glass wools have been tested but are not utilized by researchers most of the time. Some researchers prepared their own polymer using Polyethylene by sulphonation with chlorosulphonic acid in 1,2 dichloroethane [21]. But none of them were as efficient as NAFION.

Operating condition such as Dissolved Oxygen (DO) content is important parameter. Anode uses low DO but Cathode uses high DO. But higher DO facilitates diffusion of more oxygen into anode compartment through the porous membrane. Oxygen saturated catholytes are found to be the optimum [22]. Increasing the DO more than that doesn't give any considerable change in efficiency of the system. Fuel or substrate concentration also plays an important role. Though higher fuels are preferable but most of the time it is inhibitory to microorganism. So a proper feed rate should be maintained in continuous systems and proper feed concentrations in batch mode of working.

5. Applications of MFCs

The most obvious use of MFCs are the source of electricity. They can be utilized in rural sector and urban sectors. Though till now the electricity generation via fuel cells is not that efficient in small scale but large scale use can be efficient. These have conversion efficiency of fuel to electricity of an order of 70% and above and are not limited to Carnot cycle. Higher electricity recovery of 80% to 97% have been reported [12,24].The best way to utilize is to store the electricity in rechargeable battery.

Low power wireless systems can also be powered with MFCs. There has been reported study of using the MFC to utilize the body glucose to power implanted medical devices [25]. Robotics has also high usage of MFCs for sustaining self sustainable autonomous robots.

Waste water treatment can be carried out and the most beneficial is that with the treatment one can actually harness the electricity as well. It produces lesser solid wastes from the process and the electricity produced can be used in aerating the sludge. So it can be a self powered treatment facility. Unlike conventional processes it can completely break down most of the acetate and carbon compounds to CO_2 and water. Some of the species used in MFCs can also utilize the sulphides and other forms of sulphur compounds. The upflow mode MFCs and Single chambered like constructions are favored because of large scale implementation [16].

There are also some reported studies on production of Biohydrogen at Cathode of MFCs. Though the process is not thermodynamically feasible but if a potential is applied to overcome the energy barrier, hydrogen can be produced at cathode instead of water. A potential as low as 110 mV can produce hydrogen which is far less that the 1210 mV required to break water to hydrogen and oxygen via electrolysis [33]. There have been studies on using the MFCs to produce sensors to detect the level of pollutants by measuring the voltage and if suitable modified can be used to measure the BOD too via measuring Coulombic yields.[26]

6. Future scope in MFC studies

The development and utilization is still in infancy of MFCs. There is a wide scope for development of MFCs as the power density is too low for deployment in automobiles and other industrial applications. The microorganism can be genetically modified to form high reducing recombinant strains producing more available electron at anode. Materials of construction can also be studied to lower the internal resistance and corrosion. The membrane is also a costly hindrance and can be suitably replaced to lower the cost and simply the mode of operation. The stacked and upflow mode of MFCs are also lower stage of development. The miniaturized form is also awaited which can be used to power up medical implants and hand held appliances. MFCs can also have utilization in defense to power up remote surveillance and communication gears to be used in unmanned stations. The implementation and operation cost can also be lowered with better designs of single chamber fuel cells and upflow mode of fuel cells to be scaled up for wastewater treatment facility.

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