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Microbial fuel cells: A green technology for power generation

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ABSTRACT

Environmental protection and energy crisis are two recent challenges to us. Future economic growth crucially depends on the long-term availability of energy from sources that are affordable, accessible and eco-friendly. Bio electrochemical systems (BESs) have recently emerged as an exciting technology. In a BES, bacteria interact with electrode using electrons, which are either removed or supplied through an electrical circuit. The most described type of BES is Microbial Fuel Cells (MFCs). MFCs are devices that use bacteria as the catalyst to oxidize organic and inorganic matters. Electrons produced by bacteria from their substrates are transferred to the anode and flow to the cathode linked by a conductive material containing a resistor. The anodes of an MFCs behave as bacteria's typical electron acceptor and thus, the movement of the electrons to the cathode of the MFC through a resistor, generate electricity. The construction and analysis of MFCs require knowledge of different scientific and engineering fields, ranging from microbiology and electrochemistry to materials and environmental engineering. In this paper, we are providing review of the different materials, methods used to construct MFCs and techniques used to analyze the performance.

Keywords: Environment, Energy crisis, Bacteria, MFC, Electricity.

INTRODUCTION

Alternative sources of energy are in high demand because developed as well as developing countries are facing serious energy crisis [4,5]. High energy requirement of conventional sewage treatment systems are demanding for the alternative treatment technology, which will be cost effective and require less energy for its efficient operation. In addition, due to global environmental concerns and energy insecurity, there is emergent interest to find out sustainable and clean energy source with minimal or zero use of hydrocarbons [7,10]. Bio electrochemical systems (BESs) have recently emerged as an exciting technology. In a BES, bacteria interact with electrode using electrons, which are either removed or supplied through an electrical circuit. The most described type of BES is Microbial Fuel Cells (MFCs). Bacteria can be used in fuel cell to catalyze the conversion of organic matter, present in the wastewater, into electricity [6,12].

Microbial Fuel Cell

Microbial fuel cells (MFCs) are devices that use bacteria as the catalysts to oxidize organic and inorganic matter and generate current [9]. Electrons produced by the bacteria from these substrates are transferred to the anode (negative terminal) and flow to the cathode (positive terminal) linked by a conductive material containing a resistor or operated under a load. Electrons can be transferred to the anode by electron mediators or shuttles by direct membrane associated electron transfer or by so-called nanowires produced by the bacteria or perhaps by other as yet undiscovered means. Chemical mediators such as neutral red or anthraquinone-2,6-disulfonate (AQDS) can be added to the system to allow electricity production by bacteria unable to otherwise use the electrode. If no exogenous mediators are added to the system, the MFC is classified as a “mediator-less” MFC even though the mechanism of electron transfer may not be known [8].

Microbially catalyzed electron liberation at the anode and subsequent electron consumption at the cathode, when both processes are sustainable, are the defining characteristics of an MFC. Using a sacrificial anode consisting of a slab of Mg alloy does not qualify the system as an MFC because no bacteria are needed for catalyzing the oxidation of the fuel[16]. Systems that use enzymes or catalysts not directly produced in situ by the bacteria in a sustainable manner are considered here as enzymatic biofuel cells and are well reviewed elsewhere [3].

MFCs operated using mixed cultures currently achieve substantially greater power densities than those with pure cultures [14]. In one recent test, however, an MFC showed high power generation using a pure culture but the same device was not tested using acclimated mixed cultures and the cells were grown externally to the device [8]. Community analysis of the microorganisms that exist in MFCs has so far revealed a great diversity in composition [8,15]. We believe that many new types of bacteria will be discovered which are capable of anodophilic electron transfer (electron transfer to an anode) or even interspecies electron transfer (electrons transferred between bacteria in any form). We can produce clean energy by using MFC for wastewater treatment. The benefits of using MFC for wastewater treatment include: clean, safe, quiet performance, low emissions, high efficiency and direct electricity recovery.

MFCs are being constructed using a variety of materials and in an ever increasing diversity of configurations. These systems are operated under a range of conditions that include differences in temperature, pH, electron acceptor, electrode surface areas, reactor size and operation time. Potentials are reported with different reference states and sometimes only under a single load (resistor). The ranges of conditions and in some cases a lack of important data like the internal types of MFCs, provide information on construction materials.

Figure.1 shows that bacteria in the anode compartment transfers electrons obtained from an electron donor (glucose) to the anode electrode. This occurs either through direct contact, nanowires or mobile electron shuttles. During electron production protons are also produced in excess. These protons migrate through the cation exchange membrane (CEM) into the cathode chamber. The electrons flow from the anode through an external resistance (or load) to the cathode where they react with the final electron acceptor (oxygen) and protons [15].

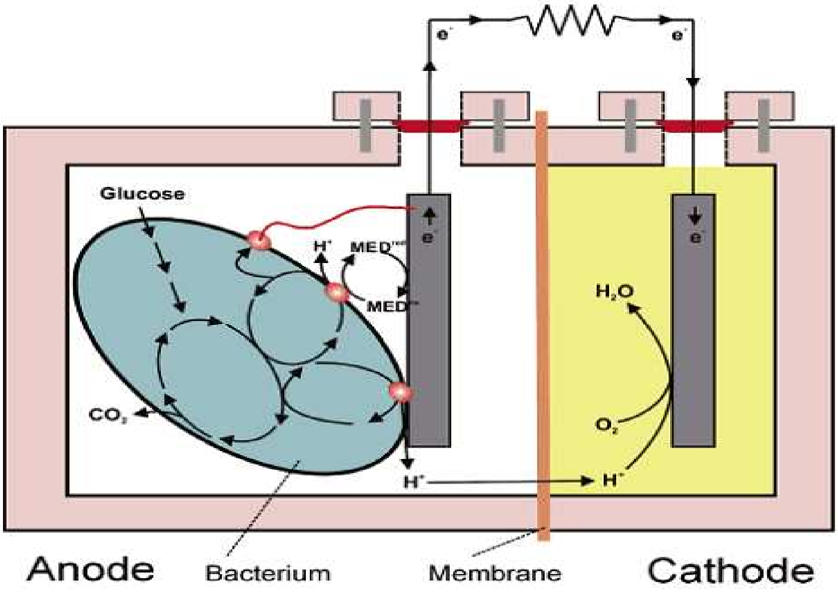

Figure. 1: Operating principles of a MFC

Microbial Fuel Cell Development

MFCs technologies represent the newest approach for generating electricity– bioelectricity generation by using bacteria. While the first observation of electrical current generated by bacterial is generally credited to Potter in 1911, very few practical advances were achieved in this field even 55 years later [9]. However, in the past three to four years there has been resurgence in microbial fuel cell research. Advances have included the development of what could be the first microbial fuel cell that can generate more conventional power sources for its designated application. Significant efforts have been undertaken for developing better systems for harvesting electricity from organic wastes and the discovery of microorganisms with enhanced capacities for sustained, efficient electricity production.

Biological optimization implies the selection of suitable bacterial consortia and the bacterial adaptation to the optimized reactor conditions. Although, the selection of the bacterial inoculum will largely determine the rate of enrichment, it does not determine the structural outcome of this procedure. Based on a mixed anaerobic–aerobic sludge inoculum and using glucose as feed, seven-fold increase in bacterial substrate to electricity conversion rates were observed after three months of microbial adaptation and selection [13,14]. Much faster increase in electricity production was noted when larger anode surfaces were available for bacterial growth [15].

Microbial Fuel Cell Design

A widely used, inexpensive design is a two chamber MFC built in a traditional "H" shape, consisting usually of two bottles connected by a tube containing a separator which is usually a cation exchange membrane (CEM) such as Nafion or Ultrex or a plain salt bridge in Figure.2a and Figure.2b [11,14]. The key to this design is to choose a membrane that allows protons to pass between the chambers (the CEM is also called a proton exchange membrane, PEM) but optimally not the substrate or electron acceptor in the cathode chamber (typically oxygen).

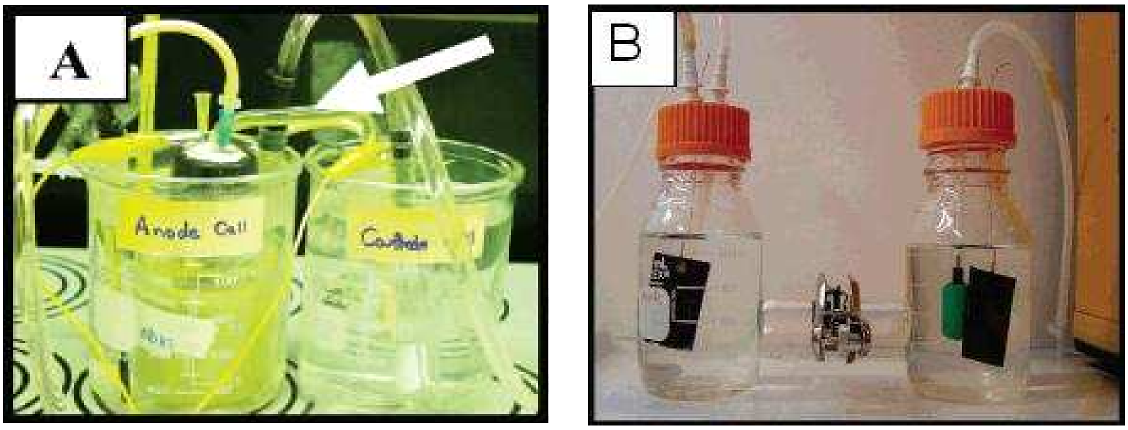

Figure.(2a): Easily constructed system containing a salt [11]; Figure. (2b): Two-chamber H-type system showing anode and cathode chambers equipped for gas sparging [9]

In the H-configuration, the membrane is clamped in the middle of the tubes connecting the bottle (Figure.2b). An inexpensive way to join the bottles is to use a glass tube that is heated and bent into a U-shape, filled with agar and salt (to serve the same function as a cation exchange membrane) and inserted through the lid of each bottle (Figure.2a). The salt bridge MFC, however, produces little power due the high internal resistance. H-shape systems are acceptable for basic parameter research, such as examining power production using new materials or types of microbial communities that arise during the degradation of specific compounds but they typically produce low power densities.

The amount of power that is generated in these systems is affected by the surface area of the cathode relative to that of the anode and the surface of the membrane. The power density produced by these systems is typically limited by high internal resistance and electrode-based losses. When comparing power produced by these systems, it makes the most sense to compare them on the basis of equally sized anodes, cathodes and membranes. Using ferricyanide as the electron acceptor in the cathode chamber increases the power density due to the availability of a good electron acceptor at high concentrations. Ferricyanide increased power by 1.5 to 1.8 times compared to a Pt-catalyst cathode and dissolved oxygen (H-design reactor with a Nafion CEM) [2,8].

Figure.3. Graphite Rod

The highest power densities so far reported for MFC systems have been low internal resistance systems with ferricyanide at the cathode [15]. While ferricyanide is an excellent catholyte in terms of system performance, it must be chemically regenerated and its use is not sustainable in practice. Thus, the use of ferricyanide is restricted to fundamental laboratory studies.

Sediment MFCs

By placing one electrode into a marine sediment rich in organic matter and sulfides and the other in the overlying oxic water, electricity can be generated at sufficient levels to power some marine devices. Protons conducted by the seawater can produce a power density of up to 28 mW/m^2. Graphite disks can be used for the electrodes, although platinum mesh electrodes have also been used. “Bottle brush” cathodes used for seawater batteries may hold the most promise for long-term operation of unattended systems as these electrodes provide a high surface area and are made of non corrosive materials. Sediments have also been placed into H-tube configured two-chamber systems to allow investigation of the bacterial community.

Modifications for Hydrogen Production

By “assisting” the potential generated by the bacteria at the anode with a small potential by an external power source (>0.25 V), it is possible to generate hydrogen at the cathode. These reactors called bioelectrochemically assisted microbial reactors (BEAMRs) or biocatalyzed electrolysis systems. These are not true fuel cells, however, as they are operated to produce hydrogen, not electricity. Through modifications of the MFC designs described above (to contain a second chamber for capturing the hydrogen gas), it should be possible to develop many new systems for hydrogen production.

material of construction of MFC

Anode: Anodic materials must be conductive, biocompatible and chemically stable in the reactor solution. Metal anodes consisting of non-corrosive stainless steel mesh can be utilized but copper is not useful due to the toxicity of even trace copper ions to bacteria. The most versatile electrode material is carbon, available as compact graphite plates, rods or granules, as fibrous material (felt, cloth, paper, fibers, foam) and as glassy carbon.

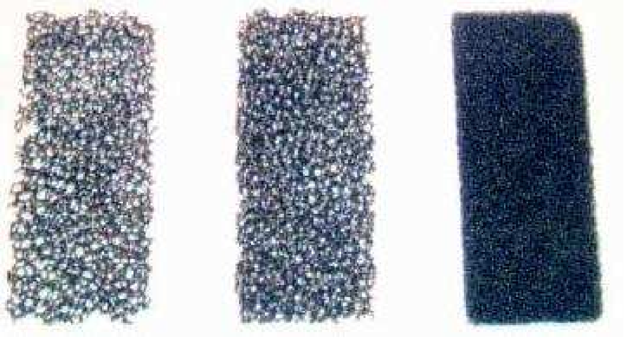

Figure.4. Reticulated Vitreous Carbon (RVC) with different pore sizes (10, 20, and 45 pores per inch)

Figure.5. (a) Graphite Plate (b) Carbon Paper

The simplest materials for anode electrodes are graphite plate (Figure. 5a) or rods (Figure. 3) as they are relatively inexpensive, easy to handle and have unambiguous surface area. Much larger surface areas are achieved with graphite felt electrodes which can have high surface areas. All the indicated surface area will not necessarily be available to bacteria. Carbon fiber, paper (Figure 5b), foam and cloth (Toray) have been extensively used as electrodes. Reticulated vitrified carbon (RVC) (Figure. 4) has been used in several studies. It is quite porous (97%) with different effective pore sizes specified by a manufacturer. The main disadvantage of the material is that it is quite brittle. It has been shown that current increases with overall internal surface area in the order carbon felt > carbon foam > graphite [9].

Cathode: Due to its good performance, ferricyanide ($K_3[Fe(CN)_6]$) is very popular as an experimental electron acceptor in microbial fuel cells [13]. The greatest advantage of ferricyanide is the low over-potential using a plain carbon cathode (Figure. 6), resulting in a cathode working potential close to its open circuit potential. The greatest disadvantage, however, is the insufficient reoxidation by oxygen, which requires the catholyte to be regularly replaced [15]. In addition, the long term performance of the system can be affected by diffusion of ferricyanide across the CEM and into the anode chamber. Oxygen is the most suitable electron acceptor for an MFC due to its high oxidation potential, availability, low cost (it is free), sustainability and the lack of a chemical waste product (water is formed as the only end product). The choice of the cathode material greatly affects performance and is varied based on application.

Figure.6. (a) Plain carbon cloth (b) carbon cloth coated with Pt catalyst on one side that typically faces the liquid (c) carbon cloth with a diffusion layer applied that typically faces the air (d) Square cathode used in two-chamber systems that is suspended in the water

Figure.7. Cation exchange membrane (CMI- 7000); anion exchange membrane (AMI-7001); Nafion 117 membrane

Membrane: The majority of MFC designs require the separation of the anode and the cathode compartments by a CEM. Exceptions are naturally separated systems such as sediment MFCs or specially designed single-compartment MFCs. The most commonly used CEM is Nafion. Alternatives to Nafion, such as Ultrex CMI-7000 also are well suited for MFC applications and are considerably more cost-effective than Nafion. When a CEM is used in an MFC, it is important to recognize that it may be permeable to chemicals such as oxygen, ferricyanide, other ions, or organic matter used as the substrate. The market for ion exchange membranes is constantly growing, and more systematic studies are necessary to evaluate the effect of the membrane on performance and long-term stability [9].

Fundamentals of voltage generation in MFCs

Thermodynamics and the Electromotive Force: Electricity is generated in an MFC only if the overall reaction is thermodynamically favorable. The reaction can be evaluated in terms of Gibbs free energy expressed in units of Joules (J), which is a measure of the maximal work that can be derived from the reaction calculated as

$$\Delta G_r=\Delta G^o_r+RT\ln(\prod) \qquad (1)$$

where ΔG_r (J) is the Gibbs free energy for the specific conditions, ΔG^o_r (J) is the Gibbs free energy under standard conditions usually defined as 298.15 K, 1 bar pressure and 1 M concentration for all species, R (8.31447 J mol^{-1} K^{-1}) is the universal gas constant, T (K) is the absolute temperature and $\prod$ (dimensionless) is the reaction quotient calculated as the activities of the products divided by those of the reactants. The standard reaction Gibbs free energy is calculated from tabulated energies of formation for organic compounds in water available from many sources [1].

For MFC calculations, it is more convenient to evaluate the reaction in terms of the overall cell electromotive force (emf), E_{emf} (V), defined as the potential difference between the cathode and anode. This is related to the work W (J), produced by the cell or

$$W=E_{emf}\,Q=-\Delta G_r \qquad (2)$$

where $Q = nF$ is the charge transferred in the reaction, expressed in Coulomb , which is determined by the number of electrons exchanged in the reaction, *n* is the number of electrons per reaction mol and *F* is Faraday's constant (9.64853 ×10^4 C/mol). Combining these two equations, we have

$$E_{emf} = -\Delta G_r/nF \qquad (3)$$

If all reactions are evaluated at standard conditions, $\prod = 1$, then

$$E^o_{emf} = -\Delta G^o_r/nF \qquad (4)$$

where E^o_{emf} (V) is the standard cell electromotive force. We can therefore use the above equations to express the overall reaction in terms of the potentials as

$$E_{emf} = E^o_{emf} - (RT/nF)\ln(\prod) \qquad (5)$$

The advantage of equation (5) is that it is positive for a favorable reaction, and directly produces a value of the emf for the reaction. This calculated emf provides an upper limit for the cell voltage; the actual potential derived from the MFC will be lower due to various potential losses like (i) Ohmic losses, (ii) Activation losses, (iii) Bacterial Metabolic losses and (iv) Concentration losses.

Ohmic Losses: The ohmic losses (or ohmic polarization) in an MFC include both the resistance to the flow of electrons through the electrodes and interconnections, and the resistance to the flow of ions through the CEM (if present) and the anodic and cathodic electrolytes. Ohmic losses can be reduced by minimizing the electrode spacing, using a membrane with a low resistivity, checking thoroughly all contacts, and (if practical) increasing solution conductivity to the maximum tolerated by the bacteria.

Activation Losses: Due to the activation energy needed for an oxidation/reduction reaction, activation losses (or activation polarization) occur during the transfer of electrons from or to a compound reacting at the electrode surface. This compound can be present at the bacterial surface, as a mediator in the solution (Figure 4), or as the final electron acceptor reacting at the cathode. Activation losses often show a strong increase at low currents and steadily increase when current density increases. Low activation losses can be achieved by increasing the electrode surface area, improving electrode catalysis, increasing the operating temperature, and through the establishment of an enriched biofilm on the electrode(s).

Bacterial Metabolic Losses: To generate metabolic energy, bacteria transport electrons from a substrate at a low potential (e.g., acetate -0.296 V) through the electron transport chain to the final electron acceptor (such as oxygen or nitrate) at a higher potential. In an MFC, the anode is the final electron acceptor and its potential determines the energy gain for the bacteria. The higher the difference between the redox potential of the substrate and the anode potential, the higher the possible metabolic energy gain for the bacteria, but the lower the maximum attainable MFC voltage. To maximize the MFC voltage, therefore, the potential of the anode should be kept as low (negative) as possible. However, if the anode potential becomes too low, electron transport will be inhibited and fermentation of the substrate (if possible) may provide greater energy for the microorganisms. The impact of a low anode potential, and its possible impact on the stability of power generation, should be addressed in future studies.

Concentration Losses: Concentration losses (or concentration polarization) occur when the rate of mass transport of a species to or from the electrode limits current production. Concentration losses occur mainly at high current densities due to limited mass transfer of chemical species by diffusion to the electrode surface. At the anode concentration losses are caused by either a limited discharge of oxidized species from the electrode surface or a limited supply of reduced species toward the electrode. This increases the ratio between the oxidized and the reduced species at the electrode surface which can produce an increase in the electrode potential. At the cathode side the reverse may occur, causing a drop in cathode potential. In poorly mixed systems diffusional gradients may also arise in the bulk liquid. Mass transport limitations in the bulk fluid can limit the substrate flux to the biofilm, which is a separate type of concentration loss. By recording polarization curves, the onset of concentration losses can be determined as described below.

Standard Electrode Potentials: The reactions occurring in the MFC can be analyzed in terms of the half cell reactions, or the separate reactions occurring at the anode and the cathode. According to the IUPAC convention, standard potentials (at 298 K, 1 bar, 1 M) are reported as a reduction potential, i.e., the reaction is written as consuming electrons. For example, if acetate is oxidized by bacteria at the anode we write the reaction as

$$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O \qquad (6)$$

The standard potentials are reported relative to the normal hydrogen electrode (NHE), which has a potential of zero at standard conditions. To obtain the theoretical anode potential, E_{An}, under specific conditions, we use equation (5), with the activities of the different species assumed to be equal to their concentrations. For acetate oxidation, we therefore have

$$E_{An} = E^o_{An} – (RT/8F) \ln([CH_3COO^-]/[HCO_3^-]^2[H^+]^9) \qquad (7)$$

For the theoretical cathode potential, E_{cat}, if we consider the case where oxygen is used as the electron acceptor for the reaction, we can write

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (8)$$

$$E_{cat} = E^o_{cat} – (RT/4F) \ln(1/pO_2[H^+]^4) \qquad (9)$$

The cell emf is calculated a

$$E_{emf} = E_{cat} - E_{An} \qquad (10)$$

Power Density: Power is often normalized to some characteristic of the reactor in order to make it possible to compare power output of different systems. The choice of the parameter that is used for normalization depends on application, as many systems are not optimized for power production. The power output is usually normalized to the projected anode surface area because the anode is where the biological reaction occurs. The power density (P_{An}, W/m^2) is therefore calculated on the basis of the area of the anode (A_{An}) as

$$P_{An} = E^2_{cell}/(A_{An}R_{ext}) \qquad (11)$$

In many instances, however, the cathode reaction is thought to limit overall power generation or the anode consists of a material which can be difficult to express in terms of surface area (i.e., granular material). In such cases the area of the cathode (A_{Cat}) can alternatively be used to obtain a power density (P_{Cat}). The projected surface areas of all components should always be clearly stated, as well as the specific surface area (if known) and the method of its determination. To perform engineering calculations for size and costing of reactors, and as a useful comparison to chemical fuel cells, the power is normalized to the reactor volume, or

$$P_v = E^2_{cell}/(vR_{ext}) \qquad (12)$$

where P_v is the volumetric power (W/m^3) and v is the total reactor volume (i.e., the empty bed volume). The use of the total bed reactor volume is consistent with a tradition in environmental engineering to use the total reactor size as a basis for the calculation. A comparison on the basis of total reactor volume, however, is not always level when comparing two- and single-chambered reactors because there is no "second chamber" for an open air cathode. In such cases it is useful to compare reactors on the basis of the total anode compartment volume. If multiple reactors are operated in concert, for example as a series of stacked reactors, the volume used for the air-space for the cathode (or volume for the catholyte) is then included for the overall reactor volume. Thus, the volume used in the calculation should be clearly stated, and volumes of the individual chambers must always be clearly noted.

Microbial fuel cells in the future

There are many challenges remaining to full exploit the maximum power production possible by MFCs, to find ways to make the systems economical, and to create wastewater treatment systems based on MFC bioreactor. Discovery of new organisms that can directly transfer electrons to or from an electrode might be exploited to remediate polluted waters or soils while concurrently generating electrical power. More fundamental studies might lead to an understanding of which proteins and cellular structures are responsible for electron transport across the cell membrane. Perhaps the most intriguing question of all is how these microorganisms 'sense' the electron sink, be it metal oxide or electrode, when deprived of oxygen. Answers to questions such as these will have implications across many disciplines in science and engineering and hold promise for a wide range of exciting new discoveries and technologies.

MFC designs need improvements before a marketable product will be possible. Both the issues identified above and the scale-up of the process remain critical issues. Most of the designs reviewed here cannot be scaled to the level needed for a large wastewater treatment plant which requires hundreds of cubic meters of reactor volume. Either the intrinsic conversion rate of MFCs will need to be increased, or the design will need to be simplified so that a cost-effective, large-scale system can be developed. Designs that can most easily be manufactured in stacks, to produce increased voltages, will be useful as the voltage for a single cell is low.

In the long term more dilute substrates, such as domestic sewage, could be treated with MFCs, decreasing society's need to invest substantial amounts of energy in their treatment. A varied array of alternative applications could also emerge, ranging from biosensor development and sustained energy generation from the seafloor, to bio-batteries operating on various biodegradable fuels [9].

CONCLUSION

The ultimate achievement in MFCs will be when they can be used solely as a method of renewable energy production. Right now, the high costs of materials for MFCs and the relatively cheap price of fossil fuels makes it unlikely that electricity production can be competitive with existing energy production methods. However, MFCs are carbon neutral and power can be generated with cellulosic materials. Thus, advancements in power densities, reductions in materials costs, and a global need to produce power without net CO_2 emissions may one day make MFCs practical just for electricity production. It will be a great success in the field of renewable energy production if we will integrate this small production of electricity in to powerful electricity.

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