Microbial Electricity

Sneha Karthikeyan
S.Y.B.Tech. (Foods)

Nisha Sahlot
S.Y.B.Tech. (Foods)

Miss Sneha Karthikeyan : I aspire to do research in my field. Since time immemorial, food has been man's basic need. With the population as well as food wastage being high in our nation, I would like to put my research efforts in this direction. This is my first attempt in writing a technical article. It gave me an opportunity to hone my writing skills in a scientific manner. I look forward to writing in the next issue as well.

Miss Nisha Mahaveer Sahlot : My carrier aims include a further study and research in food technology. Admission in this esteemed institution was a step further towards my dreams and ambitions. The achievements of students here have proved to be great inspirations for me. Writing an article for Bombay Technologist was an enriching experience, which greatly increased my knowledge.

Abstract

The dire need to produce power from renewable, non-polluting fuels has triggered the development of microbial fuel cells. In these cells, oxidation of organic substrate takes place and the electrons produced in this process are transferred to the electrode leading to generation of electric current. This has garnered an approach to harness energy from unique resources such as waste organic matter including sludge, sewage, waste biomass, etc. One such microbial fuel cell incorporates the microorganism *Rhodoferax ferrireducens*. It has the potential to oxidize glucose completely and transfer all the liberated electrons directly to the electrode in the absence of an electron shuttling redox mediator, making it more efficient than other cells belonging to the same category. Further research on microbial fuel cells will enable us to reap the benefit of this development not only for effective waste disposal but also to cope with the surmounting energy crisis. They also have profound implications in the area of waste water management. This article presents an overview of microbial fuel cells in general with its advantages, limitations and future prospects. It also describes the one using *R. ferrireducens* in particular.

Keywords: Microbial fuel cell, *R. ferrireducens*, Mediator.

1. Introduction

Batteries are the life of portable electronics in today's techno-savvy world. Despite being hugely popular, there is a plethora of problems engulfing conventional electrochemical batteries such as pollution and use of non-renewable resources. Luigi Galvani discovered electrochemistry by chance while dissecting a frog; hence calling it 'animal electricity'. Today it is sheer irony that we have come to generate electricity with the help of a microorganism. The fuel cells that operate with the aid of a microorganism are called microbial fuel cells. Before we throw more light on microbial fuel cells let us discuss about fuel cells in general.

2. Fuel Cells

Fuel cells differ from conventional galvanic cells in that its chemical reactants are stored outside the cell and do not form an integral part of the cell construction. Here the chemical reaction occurs at the electrodes which are stable conducting surfaces. Electrodes perform the function of donating and accepting electrons without being consumed in the process. As opposed to galvanic cells where working is inhibited due to consumption of electrodes; fuel cells can function unabated till electrodes wear out either mechanically or chemically by erosion. Consequently the running time of the cell is independent of its physical dimensions. Most fuel cells are hydrogen /oxygen or hydrogen/methanol cells that find extensive applications in space research.

3. Microbial Fuel Cells

A microbial fuel cell is a system which utilizes electrons produced during the metabolism of microorganisms and directs them for the generation of electric current. They are a class of biochemical fuel cells wherein the biochemical process is initiated by a living organism (bacteria). In these cells energy produced by degradation of organic matter is directly converted to electricity at temperatures near about ambient and in neutral or nearly neutral solutions. Microbial fuel cells using various types of microorganisms can operate on not only a variety of carbohydrates but also on complex substrates present in wastewaters.

3.1 History

The concept of using microorganisms in fuel cells first came into picture at the end of the 20th century. In the year 1912 M. C. Potter, a professor of botany in the University of Durham was successful in generating electricity from Escherichia coli. However it was Barnet Cohen in 1931 who increased the awareness about the subject when he created a number of microbial half fuel cells capable of producing over 35 volts though only with a current of 2mA when connected in series. This was followed by the work of Delduca et al (Ref.11) who used hydrogen gas evolved during fermentation of glucose by Clostridium butyricium as the reactant at the anode of a hydrogen and air fuel cell. This cell was further developed by Suzuki et al (Ref.10) in 1976. Despite poor understanding about the functioning of microbial fuel cells even till 1970, these works gave an impetus to the research and development of microbial fuel cells which was carried on by M.J. Allen and H.Peter Bennetto. Bennetto's work enabled a better understanding of microbial fuel cell operation and he envisioned them as a cost effective method of electricity generation. It is now established that electricity can be produced directly from the degradation of organic matter with the aid of a microbial fuel cell, however the biochemical mechanisms of this processes are yet to be deciphered. Though work on microbial fuel cells has been going on for quite some time, it is only recently that microbial fuel cells with an enhanced output has been developed, opening new vistas for its practical application.

3.2 Construction of a Microbial Fuel Cell

A microbial fuel cell consists of an anode a cathode a proton or cation exchange membrane and an external circuit. The anodic chamber consists of bacteria growing under anaerobic conditions. The cathode is maintained under aerobic conditions. The two chambers are joined by a bridge containing a polymeric proton exchange membrane which allows protons but not (ideally) the substrate or oxygen to diffuse between the chambers. (Ref. 4)

3.3 Principle of Working

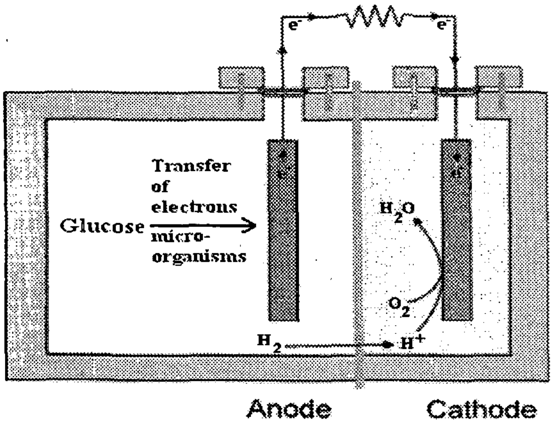

Fig.1: Microbial Fuel Cell (Ref. 8)

Bacteria residing in the anodic chamber of microbial fuel cell convert substrates such as glucose, acetate and even waste water into carbon dioxide, protons and electrons. These bacteria placed in the anaerobic anode chamber attach to the electrode. In aerobic conditions they would have used oxygen/nitrate as the final electron acceptor to produce water. But due to the non-availability of oxygen, they have no alternative but to transfer the electrons obtained from oxidation of substrate to the electrode. (Ref. Fig.1). The electrons released from the substrate during this process further require extracellular electron transport towards the anode. This can be mediated through any of the following three pathways:

- Membrane associated electron transfer.
- Mobile, soluble redox shuttle assisted electron transfer.
- Nanowires or electrically conductive bacterial appendages.

These electrons then flow through the eternal circuit with a load or a resistor to the cathode. On the other hand water is produced at the cathode due to the combination of oxygen electrons and protons. A potential difference of about 0.5V is maintained between the two electrodes and this leads to generation of power.

3.4 Factors Affecting the Performance of Microbial Fuel Cells

Both biological and electrochemical processes govern the output of microbial fuel cells.[9]

3.4.1 Substrate Conversion Rate

It depends on the number of bacterial cells, the mixing and mass transfer phenomena in the reactor, the bacterial kinetics, the biomass organic loading rate (g substrate per g biomass present per day) and the efficiency of proton exchange membrane and the potential of the microbial fuel cell.

3.4.2 Overpotentials at the Anode

The open circuit potential of microbial fuel cells is generally observed to be in the range of 750mV to a maximum of 790mV. Factors governing the overpotentials are the electrode surface, the electrochemical characteristics of the electrode, the electrode potential and the kinetics along with the electron transfer mechanism and the current of the microbial fuel cells.

3.4.3 Overpotentials at the Cathode

Considerable potential losses occur at the cathode similar to those observed at the anode. In order to compensate for these losses, hexacyanoferrate solutions have been used in microbial fuel cells. Since hexacyanoferrate is not completely re- oxidized by oxygen in the air it tends to function as an electron acceptor instead of a mediator. For long term power production microbial fuel cell cathodes should be preferably open air cathodes.

3.4.4 Internal Resistance of the Microbial Fuel Cell

This includes the resistance of the electrolyte between the electrodes as well as that of the proton exchange membrane. The distance between the anode and cathode should be minimal for optimum performance. Adequate mixing can minimize the resistance-related losses which are greatly influenced by proton migration[9].

3.5 Performance Optimization of Microbial Fuel Cells

- Biological optimization can be achieved by selection of suitable bacterial consortia and their adaptation to the optimized reactor conditions. A seven-fold increase in the rate of conversion of substrate to electricity was observed by utilizing a mixed anaerobic-aerobic sludge innoculum and glucose as the feed within three months of microbial adaptation and selection[9].

- To be sustainable, biofilm forming species of microorganisms which either utilize the electrode directly for growing or transfer the electrons through the biofilm to the electrode by using electron shuttling redox mediators are used.
- Incorporating soluble redox mediators in the microbial fuel cells consistently increases the efficiency of electron transfer process. Till now the selection of these mediators has been empirical and usually low mediator potentials are favoured. Combination of suitable microorganism and substrate needs more of experimentation due to absence of a detailed understanding of the electron transfer mechanism in microorganisms.
- Power output can be enhanced by improving the cell design or the electrode material for instance the use of manganese modified kaolin electrodes. Using conductive materials with coatings such as polyaniline for the electrode have been recently proven to boost current densities in microbial fuel cells by more than an order of magnitude[9].
- Increasing the surface area of anode leads to the availability of larger surface for the biofilm and low current density which in turn decreases the activation overpotential.
- The power output is most significantly influenced by decreasing the activation over potential and the internal resistance.

3.6 Types of Microbial Fuel Cells

There are three types of microbial fuel cells, based on the mode of electron transfer.

3.6.1 Type A

Artificial redox mediators capable of penetrating bacterial cells are added to the culture solution within the anodic fuel cell compartment. These mediators transport the electrons produced to the anode. Despite showing high current densities this cell necessitates the use of synthetic and generally toxic redox mediators which are non-reusable.

3.6.2 Type B

Metal reducing bacteria such as members of the Geobactereaceae and Shewanellaceae are incorporated. They partly exhibit special membrane bound cytochromes which can transfer electrons directly to the electrodes. These cells can be operated in natural environments such as sediments. However due to low growth rate of bacteria the current densities are very low.

3.6.3 Type C

Oxidation of fermentation product such as hydrogen and methanol is carried out in these cells. Since the surfaces of gold, platinum or carbon electrodes are unsuitable for these reactions, use of electrocatalytic electrodes is a must. These are chemically modified electrodes capable of efficiently oxidizing such metabolites. In spite of producing highest current densities and making use of easily available microorganisms, electrocatalytic electrodes require surface modifiers making the cell expensive.

3.7 Metabolism

The involvement of respiratory pathways in microbial fuel cells was first studied by Kim *et al* (Ref) in 2004. They established that inhibitors of the respiratory pathway were also successful in inhibiting current generation in microbial fuel cells. The high energy efficiency in microbial fuel cells is attributed to the oxidative phosphorylation which is commonly observed in the microbes used in a microbial fuel cell.

E.g. *Pseudomonas aeruginosa, Enterococcus faecium, Rhodoferax ferrireducens*

In microbial fuel cells methane production has been oft-observed which proves that bacteria do not fully use the anode. The fermentation products can be further oxidized at low potentials by anaerobic bacteria (Geobacter species) which are capable of extracting electrons from acetate in a microbial fuel cell.

4. Introduction to Microbial Fuel Cell Using *Rhodoferax Ferrireducens*

One of the most advanced and efficient microbial fuel cell is the one using the microorganism *Rhodoferax ferrireducens*. It has the ability to completely oxidize the substrate and transfer all the electrons liberated to the electrode in the absence of a mediator.

4.1 *Rhodoferax Ferrireducens*

R. ferrireducens was isolated from anoxic subsurface sediments of Oyster Bay, Virginia, USA as a dissimilatory Fe (III)-reducing microorganism. Temperatures in the range of 4°C to 30°C favour its growth, the optimum being 25°C. Sediment from a variety of depths and locations at a site in Oyster Bay was collected. Strictly anaerobic conditions were maintained throughout. The culture medium was a defined fresh water medium using 10mM lactate as electron donor and 100mM/l poorly crystalline Fe (III) oxide as the sole electron acceptor. Around 10ml of medium was dispensed in anaerobic pressure tubes and bubbled with nitrogen/carbon dioxide (80:20 v/v) to remove dissolved oxygen. The final pH was around 6.7. The culture was initiated with a 1gm sediment innoculum. The culture was incubated at 20°C in the dark. Cells that grew in this medium were short, straight, motile rods, approximately 3 to 5μm long and 1μm wide. All cells had a single polar flagellum. Cells stained Gram-negative during the entire course of culturing.

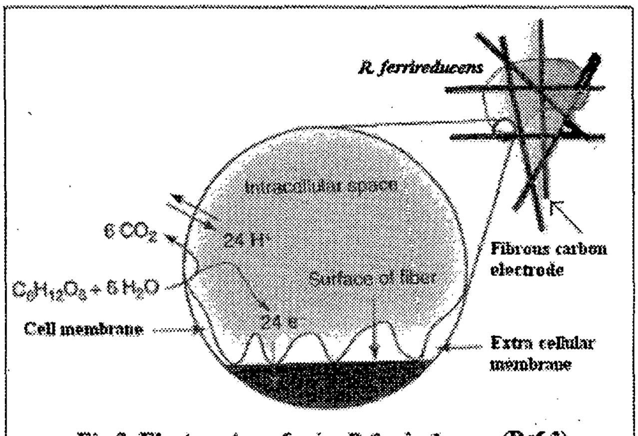

Fig.2: Electron transfer in *R.ferrireduceus* (Ref.3)

These cells can oxidize glucose coupled with Fe (III) reduction which can be represented by the reaction:

$C_6H_{12}O_6 + 6H_2O + 24Fe(III) \rightarrow 6CO_2 + 24Fe(II) + 24H+$ (Refer Fig. 2)

This is the first microorganism that completely oxidizes sugars coupled to Fe (III) reduction at circumneutral pH. Energy produced during this reaction is partly utilized for the growth of the microorganism[2].

4.2 Microbial Fuel Cell With *Rhodoferax Ferrireducens*

The cell is a two-chambered glass vessel connected with a cation-selective membrane and makes use of graphite rods or finely woven graphite felt as electrodes. The liquid volume in each chamber is about 210ml. The anodic chamber is flushed with N_2/CO_2 to maintain anaerobic conditions and to keep pH balance of growth medium constant. The cathode chamber contains 30mM Tris buffer and is continuously flushed with sterile water saturated air. *R. ferrireducens* oxidizes glucose completely to CO_2 and transfers the electrons produced to the anode in the absence of a mediator with 83% efficiency. Reckoning that the microorganism for its own growth consumes some amount of glucose, this is a significant result[2].

Microbial fuel cell with *R. ferrireducens* was examined under true fuel cell conditions in which the anode chamber with the culture was anaerobic, but the sterile cathode chamber was aerobic with potassium ferricyanide. As glucose was consumed current was produced and growth of *R. ferrireducens* was observed. The current increases in the beginning and becomes constant at a certain maximum value for sometime after which it drops owing to the exhaustion of glucose supply. When the medium in the anode chamber was removed and replaced with fresh glucose solution; current production rapidly returned to the maximum levels observed before replacement of the medium.(Refer fig. 3) This immediate redemption of current accompanying the replacement of medium suggests that microbial cells attached to the electrode surface are mainly responsible for current production. It is the bio-film of *R. ferrireducens* on the surface of the electrode that is responsible for the voltage and current generated and not the organism in solution. Consequently, the increase in surface area of the graphite electrode available for the microorganism increases the power output. E.g.: Current is increased approximately threefold when graphite felt having higher surface area is used to construct the anode and the cathode instead of a graphite rod. Thus simply optimizing the surface increases power production.

Since electron transfer to the anode provides energy for the growth of the microbe, question arises as to whether the cell will continue working after periods in which there is no electron transfer that is no current flow. In order to determine this, the anode and cathode were disconnected for 36h. On reestablishing the connection, power production was resumed at the previously observed levels (Ref. fig 3). These observations lead to the conclusion that microbial fuel cell with *R. ferrireducens* has many favourable characteristics of secondary

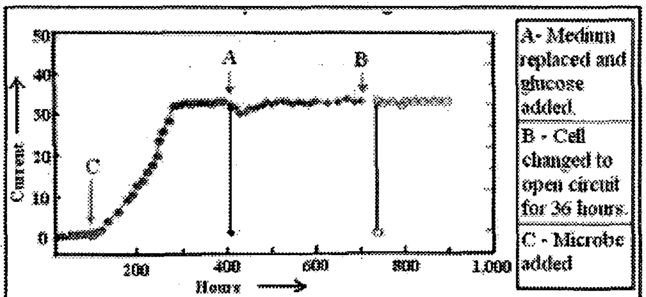

Fig.3: Graph of current on Y-axis in mA with time on X-axis before and after replacement of glucose (Ref.2)

storage batteries. These features include:

1. Rechargeability to almost the maximum level observed before discharging.
2. No drastic diminishing of capacity on charge/discharge cycling.
3. Ability to accept fast recharge.
4. Stable, long term power production.
5. Low capacity loss under open circuit conditions as well as prolonged storage under idle conditions.

4.3 *R Ferrireducens* V/S Other Microorganisms In Microbial Fuel Cells

4.3.1 Majority of the microorganisms capable of reducing Fe (III) and transferring the electrons to the electrode can oxidize only simple organic substrates (e.g. acetate) in the absence of fermentative microorganisms. On the other hand *R. ferrireducens* is capable of oxidizing a wide range of substrates such as glucose, fructose, sucrose, or xylose, with Fe (III) serving as sole electron acceptor.

4.3.2 *R. ferrireducens* completely oxidizes glucose liberating all the 24 electrons present whereas the application of other microbial fuel cells is limited due to incomplete oxidation of glucose.

4.3.3 In most of the microbial fuel cells, direct electron transfer from the microorganism to the anode is very inefficient due to the selective permeability of cell wall and cell membrane. As a result the inclusion of redox mediators that shuttle the electrons from the microorganisms to the anode is essential. These can be organic dyes, inorganic complexes and organometallics. Many of them are chemically unstable or cytotoxic at high concentrations and hence not effective for long term performance. The overall voltage and power produced by the microbial fuel cell is reduced, depending on the redox potential of the mediator.

4.3.4 *R. ferrireducens* possesses mechanisms for attaching to the electrode surface and transporting reducing equivalents across the cell membrane thereby eliminating the need for a redox mediator.

5. Advantages of Microbial Fuel Cells over Conventional Methods of Energy Generation from Organic Matter

1. Microbial fuel cells achieve efficient and direct conversion of organic substrate to electricity.

2. The capacity of microbial fuel cells to operate at ambient or even low temperatures sets them apart from all present methods of bio-energy production.
3. The gasses emitted by microbial fuel cells do not require treatment since they are high in carbon dioxide and do not possess potential energy content.
4. Microbial fuel cells have a broad spectrum of applications as they can be installed in locations lacking electrical infrastructures and they also enable us to think beyond the present sources of fuel we use to meet our energy needs.

6. Limitations of Microbial Fuel Cells

Microbial fuel cells face the following limitations due to which their large scale application is hampered.

1. Surface area of the anode can be increased only to a limited extent as the bacteria can clog small pores rapidly. This sets a limit to the extent to which the area of the biofilm and hence the current that can be increased.
2. Microbial fuel cells still need important breakthroughs to become economically competitive.
3. The power produced by microbial fuel cells has not reached the levels produced by conventional batteries.
4. The difference between theoretical cell electromotive force and over voltage is due to overpotentials at the anode and the cathode and ohmic loss in the system.
5. The theoretical maximum voltage achievable in a microbial fuel cell is of the order of 1.1V. However the practical value is much lower. The maximum open circuit voltage (when no current flows) obtained so far is 0.8V which drops down to 0.62V under operating conditions.
6. The overpotentials of the electrode depend upon current and are generally due to

6.1 Activation losses

These losses occur during transfer of electrons to or from a compound reacting at electrode surface. Losses increase at low currents and can be minimized by increasing electrode surface area, improving electrode catalysis, increasing operating temperature, establishment of enriched biofilm on electrode.

6.2 Bacterial metabolic losses

6.3 Mass transport or concentration losses

These occur at high current densities due to limited mass transfer of chemical species to the electrode[9].

7. Applications of Microbial Fuel Cell

7.1 Waste water management

One of the most important applications of microbial fuel cells has been in wastewater treatment with simultaneous generation of electricity. If methods to increase the fraction of organic matter converted to electricity could be devised, microbial fuel cells may provide a new technology to reduce the operational cost of expensive wastewater treatment to achieve high levels of sanitation.

A single chamber microbial fuel cell containing 8 graphite electrodes (anodes) and a single air cathode was used for wastewater treatment. Current generation was controlled primarily by the efficiency of the cathode. Optimal cathode performance was obtained by allowing passive air flow rather than forced air flow. Electricity generated by the single chamber microbial fuel cell was proportional to wastewater strength. Power output was a function of circuit load in the system5.

7.2 Sediment microbial fuel cells

By placing one electrode into 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 seawater produce a power density up to $28 mW/m^2$. "Bottle brush" cathodes used for seawater batteries may hold most promise for long term operation of unattended systems. This is because they provide increased surface area and are made of non-corrosive materials.

7.3 Pilot-scale reactors:

Pilot-scale reactors can be developed at industrial locations, where a high quality and reliable influent is available, by using microbial fuel cells. Food processing wastewaters and digesters are good examples. A food processing plant producing 1500 kg/day of waste represents a potential for 950 kW of power or at 330 kW, assuming 30% efficiency.

8. Further Developments

One-compartment fuel cells have been developed which are less expensive and more practical than the two-compartment system. It produces nearly equivalent amounts of electricity as the more complex two-compartment system (Ref.6). It offers the following advantages over the two-compartment fuel cell.

1. Eliminates the need for ferricyanide solution and aeration in the cathode compartment.
2. Expensive proton selective membrane is replaced by a porcelain septum.
3. Using single compartment fuel cell with Mn-graphite anode or Fe-graphite anode can enhance the amount of electricity produced along with cost reduction. The oxidation-reduction efficiency is enhanced with a wide range of microbes as potential biocatalysts.

9. Future Aspects

The need to enhance the efficiency of microbial fuel cells to increase their large scale application opens up various avenues for further research and development. Numerous other microorganisms like *R. ferrireducens* capable of oxidizing a host of organic substrates and directly transferring the electrons to the electrode may exist. Discovery of these organisms and development of fuel cells incorporating them might be explored to purify polluted waters or soils simultaneously generating electric power.

There is a lot of ambiguity regarding the proteins and cellular structures that are responsible for direct electron transport across the cell membrane and the mechanisms by which they do so. Understanding these will have a profound impact on various streams of science and engineering such as cell-adhesion and cell-to-cell communication in cell biology[3].

10. Conclusion

The storehouse of energy in carbohydrates found in sludge, sewage and waste biomass from agricultural, municipal and industrial sources may directly and efficiently be converted into electrical energy, thanks to the development of microbial fuel cells. This technology has come a long way in overcoming numerous technical and economical hurdles involved in the conventional energy generation from carbohydrates. (E.g. the conversion to ethanol and hydrogen) Bacteria being self-producing and self-renewing biocatalysts are convenient, cost reducing alternatives to conventional metal-metal catalyzed fuel cells.

Although microbial fuel cells might take sometime to catch up with physico-chemical electrical batteries which are established in the commercial race, further research and development in this arena will transform them into the powerhouses of future[2].

11. References

Journals

1. Roller S. D., Delaney G. M. *et al* 'Electron-Transfer Coupling in Microbial Fuel Cells: Performance of microbial fuel cells containing selected Microorganism-Mediator-Substrate combinations.'*J. Chem. Technol. Biotechnol.*, **34B** (No.1), (March 1984) **13-27.**
2. Chaudhuri S.K.and Lovley D.R., 'Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells', *Nat. Biotechnol.*, 21 (No.9), (Sept 2003) **1229-1232.**
3. G.Tayhas and R.Palmore, 'Bioelectric Power Generation', *Trends in Biotechnol.* 22(No.1), (Jan 2004) **99-100.**
4. B.E.Logan, 'Extracting hydrogen and electricity from renewable sources', *Environmental Sci & Technol,* 38 (No.9), (May 1, 2004) **160A-167A.**
5. Liu H., Ramnarayanan R.,Logan, 'Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell', *Environmental Sci. & Technol,* 38 (No.7), (April 1,2004) **2281-2285.**
6. Park D.H., Zeikus J.G., 'Improved Fuel Cell & Electrode Designs for Producing Electricity from Microbial Degradation', *Biotechnol. & Bioeng.*, 81 (No.1), (Jan 5, 2003) **348-355.**
7. D.R.Lovley, Phillips J.P., 'Novel Method of Microbial Energy Metabolism: Organic Carbon oxidation Coupled to Dissimilatory Reduction of Iron or Manganese', *App. & Environ. Microbiology,* 54 (No.5), (May 1988) **1472-1480.**
8. Wikipedia homepage http://en.wikipedia.org/wiki/Microbial_fuel_cell (accessed December 2007)
9. Korneel Rabaey and Willy Verstraete, 'Microbial Fuel Cells: novel biotechnology for energy generation', *Trends in Biotechnology,*23,(No.1)(Jan 2005) **291-298.**
10. Karube I., T. Matasunga,S.Suzuki,S.Tsuru 'Biochemical Cells utilizing immobilized cells of *Clostridium butyricum*' *Biotechnol. & Bioeng.* 19, (1977) **1727-1733.**
11. Delduca M.G.,Friscoe, J.M.Zurilla, 'Developments in Industrial Microbiology', *American Institute of Biological Sciences*',9,(1962) **81-89.**
12. B. Logan, B. Hammelers, R. Rozendal, U. Schroder, J. Keller, S. Freguia, P. Alterman, W. Verstraete, K. Rabaey 'Microbial Fuel Cells-Methodology and Technology', *Environmental Sci. & Tech.*, 40,(2006) **5181-5792.**
13. Allen,R.M and Bennetto,H.P 'Microbial Fuel Cells-Electricity production from carbohydrates',*Applied Biochem. & Biotech.*39/40,(1993) **27-40.**

Book References

1. R.W. Glazebrook, F.Jones, *An Introduction to Fuel Cells,* Keith R.Williams, Elsevier Publishing Co., Amsterdam-London-New York, 1966.
2. J.O.M. Bockris, S.Srinivasan, *Fuel Cells: Their Electrochemistry,* Mc-Graw Hill Book Co., New York, 1969.