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ORIGINAL ARTICLE

Electricity Generation by Microbail Fuel Cells

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ABSTRACT

This review article cover the literature from 1910-2006 on the development of microbial fuel cells for the generation of electrical energy by the fermentation of different organic substrates. The study of the literature showed that the researchers are currently working on two approaches for the development of microbial fuel cells *i.e.* in the *first approach* microorganisms are used as biological reactor for the fermentation of the substrates to fuel products without the use of any mediator but in the *second approach* mediators are used which increase the electron transfer rate from fuel to anode. Recently, new types of MFCs namely upflow microbial fuel cell (UMFC) and bioelectrically assisted microbial reactor (BEAMR) has been introduced by Z. He, L.T. Angenent and D. Zheng's research group for the generation of electricity. Development of the large scale MFCs namely, benthic unattended generators, wastewater, sewage and garbage fuel cells are currently underway. This is one of the most exciting and novel methodology that will overcome the problems of energy management which is the global issue today.

Key words: Chemical energy, electrical energy, benthic unattended generator, upflow microbial fuel cell, bioelectrically assisted microbial reactor, pacemaker and insulin pump.

Introduction

A number of methods and sources are currently in use for the production of the electrical energy which includes hydro-power, solar-power, wind-power, wave-power, fossil fuels, batteries and chemical fuel cells. All these technologies play a significant role in the global issue of energy management. In addition to these technologies an attractive and novel alternative for the conversion of chemical energy into electrical energy is the development of microbial fuel cells (MFCs) (Katz *et al.* 2003; Lovley 2006). A microbial fuel cell is a device that converts chemical energy to the electrical energy by the catalytic reaction of microorganisms (Allen and Bennetto 1993).

Presently, there is an unbalanced energy management due to increasing energy consumption. Mostly, the energy that we utilize is produced through the thermal or combustion processes and both have damaging effect to our environment. Due to an increasing demand of the electrical energy scientists are developing various methodologies for the generation of electrical energy by the more facile and cheaper methods. In recent years, research activity in fuel cell technology has increased remarkably. Great expectations are directed to fuel cells because of the forthcoming depletion of earth's fossil fuel resources. In addition, the MFCs offer an environmentally friendly alternative to fossil fuels (Lovley 2006; Katz *et al.* 2003).

Initially, the concept of the generation of electricity is given by M.C. Potter (Potter 1910, 1911). He stated that "the disintegration of organic compounds by microorganisms is accompanied by the liberation of electrical energy (Potter 1911). These fuel cells based on the metabolic activities of the microorganisms on the organic substrates particularly the natural sources which contain the sugars as the main component. Research to render

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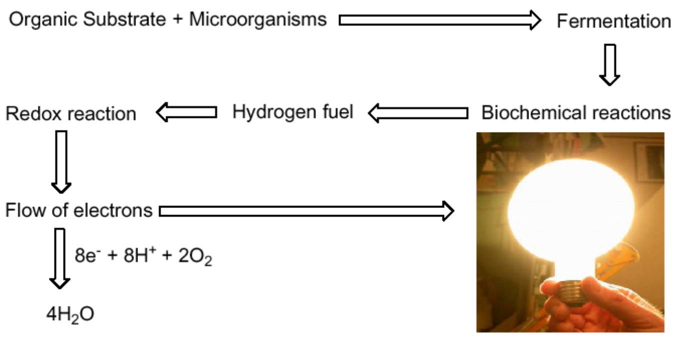
the microbial fuel cell technology is more economically feasible and applicable. A special focus on reactor configuration, power density and material cost is required (Pham *et al*. 2004). Recent studies of microbial fuel cells have greatly advanced our understanding of microbial electricity generation (Bennetto 1984, 1985, 1987, 1990). In fact, much work remains to be done to explore the chemistry and biochemistry of MFCs.

In a microbial fuel cell, different substrates such as glucose, molasses, lactose and wastewater have been used for the generation of electrical energy by their fermentation with different bacteria (Suzuki *et al*. 1978; Allen and Bennetto 1993). Various research groups are keen interested to improve the current density by more facile and efficient methods (Palmore and Whitesides 1994; Bond *et al.* 2002; Angenent *et al*. 2004; Pham *et al*. 2004). Generation of electrical energy is based on the principles of fermentation in which organic substrates undergo the biochemical reactions in the presence of microorganisms which resulted in the formation of the hydrogen fuel. The fuel so formed is finally converted into electrical energy and water through redox reaction (Scheme-1).



Scheme. 1: General pathway for the generation of electricity by fermentation.

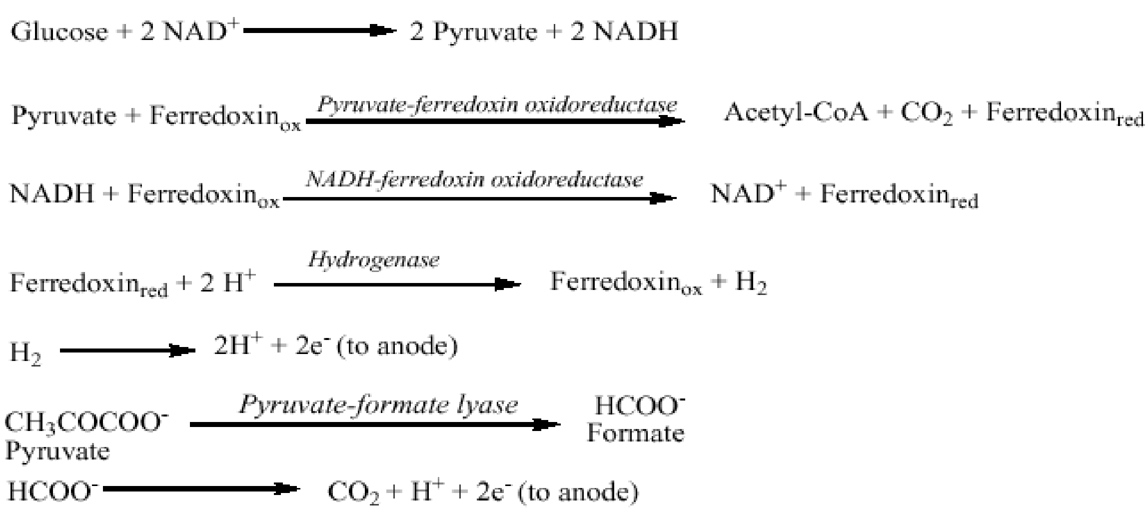
Types of Microbial Fuel Cell:

Mediator-less Microbial Fuel Cells:

This type of microbial fuel cells is reported by Kim and his co-workers (Kim *et al*. 1999a, 1999b, 2002). A mediator-less microbial fuel cell does not required a mediator but uses electrochemically active bacteria to transfer electrons to the electrode (Tanisho *et al*. 1989; Gradskov *et al*. 2001; Chaudhuri and Lovley 2003; Pham *et al*. 2004). *Shewanella putrefaciens, Aeromonas hydrophila* and some others are the electrochemically active bacteria (Kim *et al*. 1999a; Coung *et al*. 2003). In the process of the development of microbial fuel cells, the pure and mixed cultures of microorganisms have been used which are found to be active in hydrogen production under aerobic and anaerobic conditions. In addition, various bacteria such as *Escherichia coli, Enterobacter aerogenes, Clostridium butyricum, Clostridium acetobutylicum, Clostridium perfringens* have been found to be active in hydrogen production under anaerobic conditions (Lewis 1966; Raeburn and Rabinowitz 1971; Akiba *et al*. 1987; Ardeleanu *et al*.1983).

The conversion of carbohydrate to hydrogen is achieved by a multi-enzyme system. In bacteria the route is believed to involve glucose conversion to 2 mole of pyruvate and 2 mole of NADH by Embden-Meyerhof pathway (Scheme-2). The pyruvate is then oxidized through a pyruvateferredoxin oxidoreductase producing acetyl-CoA, CO_2 and reduced ferredoxin. NADH-ferredoxin oxidoreductase oxidizes NADH and reduces ferredoxin. The reduced ferredoxin is reoxidized by the hydrogenase to form hydrogen. The pyruvate so produced during the biochemical pathway can be alternatively oxidized to formate through a pyruvate-formate lyase which oxidized at the anode (Karube *et al*. 1977; Katz 2003).

Microbial cells producing H_2 gas during fermentation have been immobilized directly in the anodic compartment of a H_2/O_2 fuel cell (Karube *et al*. 1977; Tanisho *et al*. 1989). A rolled Pt-electrode was introduced into a suspension of *Clostridium butyricum* and the suspension was polymerized with acrylamide to form a gel (Karube *et al*. 1977). The fermentation was conducted directly at the anode surface, supplying the anode with the hydrogen fuel. In this case some additional by-products of the fermentation process (hydrogen = 0.60 mole, formic acid = 0.20 mole, acetic acid = 0.60 mole, lactic acid = 0.15 mole) could also be utilized as additional fuel components (Karube *et al*. 1977).



Scheme. 2: Embden-Meyerhof pathway for the conversion of glucose to hydrogen fuel.

Mediator Microbial Fuel Cells:

Most of the microorganisms are electrochemically inactive. The electron transfer from microbial cells to the electrode is facilitated by mediators such as thionine, methyl viologen, humic acid etc (Lithgow *et al*. 1986; Vega and Fernandez 1987; Kreysa and Krämer 1989; Kim *et al*. 1999a-c; Yamazaki *et al*. 2002; Jang *et al*. 2004). Once the fuel is produced, the electrons obtained from the oxidized fuel are not immediately transported to the anode since the electron transfer rate would be too slow. To improve the electron transfer rate, an initially oxidized redox mediator is used to extract electrons. The electrons are then transferred to the anode and the mediator is once again oxidized (Kim *et al.* 2000).

Mediator microbial fuel cells are based on the metabolic activities of the microorganisms on the substrates such as glucose, sucrose and wastewater in the presence of electron transfer mediators (Davis and Yarbrough 1962; Bennetto *et al.* 1985; Lithgow *et al*. 1986; Vega and Fernandez 1987; Park *et al.* 1997; Park and Zeikus 2000; Park *et al.* 2000; Rabaey *et al.* 2003). It is because the contact of the microbial cells with an electrode usually results in a very minute electron transfer across the membrane of the microbes. These electron carriers are able to generate anodic current in the presence of terminal electron acceptors (under anaerobic conditions) which is the exceptional example (Kim *et al.* 1999a, 1999b).

A number of organic and organometallic compounds have been tested in combination with bacteria to test the efficiency of mediated electron transport from the internal bacterial metabolites to the anode of a biofuel cell. Thionine has been used extensively as a mediator of electron transport from *Proteus vulgaris* and from *Escherichia coli* (Davis and Yarbrough 1962; Ardeleanu *et al.* 1983; Bennetto *et al.* 1983, 1984; Roller *et al.* 1984; Vega and Fernandez 1987; Kim *et al.* 2000; Park and Zeikus 2000). Monitoring and control of bacterial fuel cell system is investigated by using color analysis of the biofilm reactor which converts substrate to electroactive substances in the presence of mediators (Halme *et al.* 1998).

Connecting several microbial fuel cell units in series or parallel can increase voltage and current. Six individual continous MFC units in a stacked configuration produced a maximum hourly average power output of 258 Wm^{-3} by using a hexacyanoferrate cathode. The connection of the six MFC units in series and parallel enabled an increase of voltage (2.02 V at 228 W m^{-3}) and the current (255 Am at 248 W m^{-3}) (Aelterman, *et al.* 2006). The electricity generation and energy conversion rate depends upon the size and the structure of the microbial fuel cells (Zhang and Halme 1997).

There are many microorganisms producing metabolically reduced sulfur-containing compounds (e.g. S^{2-}, H^S-, SO_4^{2-}). Sulfate reducing bacteria (e.g. *Desulfovibrio desulfuricans*) form a specialized group of anaerobic microbes that use sulfate (SO_4^{2-}) as a terminal electron acceptor for respiration. These microorganisms yield S2-while using a substrate (e. g. lactate) as a source of electrons (Scheme-3). This microbiological oxidation of lactate with the formation of sulfide has been used to derive an anodic process in biofuel cells. The metabolically produced sulfide was oxidized directly at electrode, providing an anodic reaction that produces sulfate or thiosulfate. Sulphate reducers produce sulphide which can abiotically react with the anode yielding two electron and sulphur (Habermann and Pommer 1991; Cooney *et al.* 1996; Lovley 2006).

MFCs Based on Wastewater:

Special focus on the development of microbial fuel cells by using different wastewater such as domestic wastewater, industrial wastewater and agriculture wastewater was given by a types of number of research groups (Suzuki 1978; Wang *et al*. 2003; Angenent 2004; Liu *et al.* 2005a, 2005b; Min and Logan 2004. He *et al*. 2005; Logan 2005; Min *et al.* 2005). Microbial fuel cells can simultaneously be used to generate the electricity and for the wastewater treatment (Rabaey 2006; Angenent *et al.* 2004).

$$\text{Lactate} + SO_4^{2-} + 8\,H^+ \longrightarrow S^{2-} + 4H_2O + \text{Pyruvate}$$

$$S^{2-} + 4H_2O \longrightarrow S0_4^{2-} + 8H^+ + 8e^- \text{ (to anode)}$$

$$2S^{2-} + 3H_2O \longrightarrow S_2O_3^{2-} + 6H^+ + 8e^- \text{ (to anode)}$$

Scheme. 3: Chemical reactions for the fermentation of sulphur containing compounds.

Tubular and Square Type MFCs:

The square type MFCs demonstrated a potential-dependent conversion of sulfide to sulfur. In the tubular system, upto 514 mg sulfide L^{-1} net anodic compartment (NAC) day^{-1} (241 mg L^{-1} day^{-1} total anodic compartment, TAC) was removed. The sulfide oxidation in the anodic compartment resulted in electricity generation with power outputs upto 101 mW L^{-1} NAC (47 W m^{-3} TAC) (Rabaey *et al*. 2006). A tubular, single-chambered, continuous microbial fuel cell that generates high power outputs using a granular graphite matrix as the anode and a ferricyanide solution as the cathode. The maximal power outputs obtained were 90 and 66 Wm^{-3} net anodic compartment (NAC), 48 and 38 Wm^{-3} total anodic compartment (TAC) for feed streams based on acetate and glucose, respectively, whereas 59 and 48 Wm^{-3} NAC was recorded for digester effluent and domestic wastewater, respectively. For acetate and glucose the total coulombic conversion efficiencies were 75 ± and 59 ± 4%, respectively, at loading rates of 1.1kg chemical oxygen demand m^{-3} NAC volume day^{-1} (Rabaey *et al.* 2005).

Upflow Microbial Fuel Cell (UMFC):

A new type of upflow microbial fuel cell (UMFC) was devised by a group of researcher in USA (He *et al.* 2006; Zheng *et al.* 2006). The device is fed continuously and unlike most microbial fuel cell works with chambers atop each other than beside each other. Angenet has created electricity with the UMFC, which is about the size of the thermost bottle (He *et al.* 2006; Zheng *et al.* 2006).

Bioelectrically Assisted Microbial Reactor (BEAMR):

This device demonstrates the feasibility of generating hydrogen from any biodegradable organic matter. An additional voltage of 250 mV was used in this MFC to produce hydrogen at the cathode directly from the oxidized organic matter (Liu, *et al*, 2005 a,b). More than 90% of the protons and electrons produced by the bacteria from the oxidation of acetate were recovered as hydrogen gas with an overall coulombic efficiency (total recovery of electrons from acetate) of 60-78%. This is equivalent to an overall yield of 2.9 mole H_2/mole acetate (assuming 78 % coulombic efficiency and 92 % recovery of electrons as hydrogen). This bioelectrochemically assisted microbial system, if combined with hydrogen fermentation that produces 2-3 mole H_2/mole glucose, has the potential to produce ca. 8-9 mole H_2/mole glucose at an energy cost equivalent to 1.2 mole H_2/mole glucose. Production of hydrogen by this anaerobic process is not limited to carbohydrates, as in a fermentation process, as any biodegradable dissolved organic matter can theoretically used in this process to generate hydrogen from the complete oxidation of organic matter (Liu *et al.* 2005 a,b).

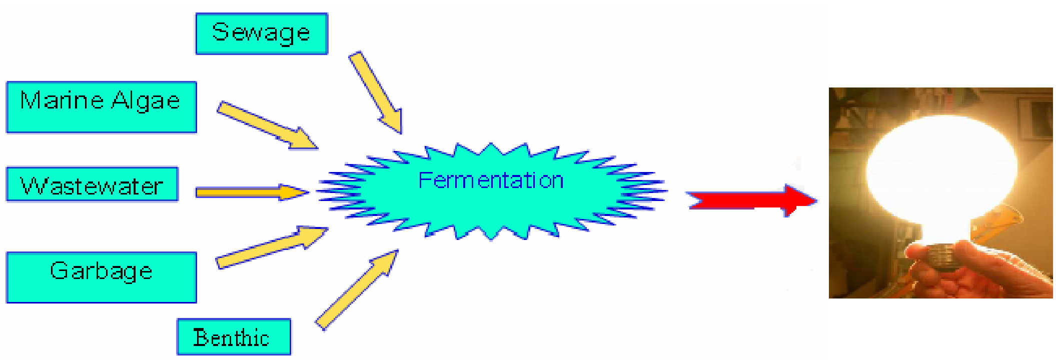
Large-scale MFCs:

Biomass and Wastewater Large-scale MFCs:

Researchers are interested to develop the large scale MFCs by the fermentation of the sewage, marine algae, garbage and wastewater using the microorganisms (Lovley 2006). Upflow microbial fuel cell (UMFC) can be scaled up considerably to someday handle the 2 million gallons of wastewater needs to churn out enough power for 900 homes. Angenent said, "We have proven that we can generate the electricity on a small scale. It will take time but we will believe that the process has potential to be used for the local electricity generation. He also added that the UMFC is a promising wastewater treatment process and has a lab-scale unit, generated electricity and purified wastewater simultaneously for more than five months" (He *et al.* 2006; Zheng *et al.* 2006).

Benthic Unattended Generators (BUGs):

During the last few years a number of research groups were able to harvest electricity from the organic matter in the bottom of the oceans (Bond *et al.* 2002; Tender *et al.* 2002; Lovley 2006). BUGs are designed for powering the electronic devices in remote locations, such as the bottom of the ocean where it would be expensive and technically difficult to routinely exchange traditional batteries (DeLong and Chandler 2002; Tender *et al.* 2002;
Lovley 2006). A complex organic matter is present in the bottom of the oceans which naturally undergo the process of fermentation by the microorganisms present in the bottom. Due to this natural fermentation chemical energy is converted into electrical energy. The artificial system is required which can accumulate the energy and use to power the monitoring devices of the oceans. This system is called Benthic Unattended Generators (BUGs) because it can run for ever without the recharging (Scheme-4).



Scheme. 4: Generation of electricity by large scale MFCs.

Advantages of MFCs:

1. Development of microbial fuel cells is an attractive alternative for the production of electricity with minimal environmental interference as compared to the currently used thermal and combustion methods.
2. Most of the portable electronic devices possessing some disadvantages such as they run out too fast, recharging is inconvenient and time consuming. MFCs potentially offer the solution to all these problems.
3. Fossil fuels that have sustained civilized society for so long, have been abused and are now rapidly becoming non-existent. It is important for us to learn that whatever the energy source of the future turn out to be, we must learn to conserve and value it by the development of MFCs.
4. It is convenient to move these MFCs from one place to another place due to their compact size and weight.

Disadvantages of MFCs:

1. Certain conditions are required for the survival of the microorganisms.
2. Presently, the current density is not enough to run the heavy machinery.
3. Most of the available mediators are expensive and toxic.

Applications of MFCs:

1. Advances in the medical sciences are leading to an increasing number of implantable electrically operated devices. These items need power supplies that will operate for extremely long duration. An important potential use of MFCs is to power the pacemaker which can control the heart beat of the cardiac patient.

The fuel cell in the pacemaker will be powered by taking the glucose from the blood stream of the patient (Katz 2003; Lovley 2006).

2. Similarly, the insulin pump in the diabatic patient can be powered by the glucose of the blood stream of the patient (Katz *et al.* 2003; Lovley 2006).
3. One of the most interesting examples of a novel device is robot named *"Gastronome"*, uses a MFC system to directly convert carbohydrate fuel to an electrical power source without combustion (Wilkinson 2000; Katz *et al.* 2003).
4. Microbial fuel cells can potentially be used to power the large number of portable devices such as laptop, digital camera, cell phones, military applications, mobile devices and to maintain the telecommunication in remote areas including outer space, weather stations and rural locations (Katz *et al.* 2003; Lovley 2006).

Conclusion:

Microbial fuel cells can be used to generate electrical energy by using any biowaste material that contains significant amount of carbohydrates, proteins and lipids etc. Mircobial catalyzed fuel cells could be the best alternative of fossil fuels to overcome global warming and energy crisis. They can play a significant role to power the biomedical devices such as pacemaker and insulin pump. There is an urgent need to give the special focus for the advanced research in this direction. The collective efforts of Chemists, Biochemists, Microbiologists, Environmental Enegineers and some other disciplines in this area of reseach can produce the fruitful result for the development of novel technology of bio-energy around the globe.

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