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Practices and Perspectives in Sustainable Bioenergy

A Systems Thinking Approach

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Microbial Fuel Cells: A Path to Green, Renewable Energy

Kausik S. Das

Abstract Microbial fuel cells (MFCs) are clean, renewable energy sources and they generate self-sustaining clean energy through cellular respiration. MFCs do not require any external energy to operate and do not emit any excess greenhouse gases. MFCs can also be used for bioremediation by removing toxic materials by respiring a variety of metals and other harmful elements including iron and uranium. In this article, we have discussed the principles and designs of biofuel cells.

Keywords Microbial fuel cell · Bioenergy · Bioremediation · Exo-electrogenic bacteria · Redox potential

1 Introduction

Microorganisms are ubiquitous in nature and play an important role in recycling organic compounds. Electron exchange properties of microorganisms are not only a fascinating and instructive area of bio-electrochemistry, but also have the potential to impact global bio-economy in a significant manner. Current domestic, industrial and animal wastewater together contains nearly 1.5×10^{11} kilowatt-hour (kWh) (~17 GW of power) of untapped bioenergy Logan and Rabaey (2012). Moreover, an estimated 1.44×10^{16} kWh of chemical energy stored in organic matters in marine sediment is ready to be harvested (Xie et al. 2013) in the face of current annual global power demand of ~17 TW (IEA). At present, the global energy consumption depends on extraction and oxidation of concentrated fossil fuels, such as oil (32%), coal (27%) and natural gas (21%) (IEA). Our demand for energy continues to increase while our present supply of energy resources is rapidly decreasing. Moreover, energy extraction from concentrated fossil fuel has its own shortcomings: Firstly, fossil fuel resources

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on earth are rapidly dwindling and secondly hydrocarbon combustion leaves significant carbon footprint and emission of greenhouse gasses behind. A rational approach to deal with this problem is to turn our attention to sustainable green and renewable energy where resources can be replenished in a human life span. Apart from solar, wind, tidal or geothermal energy, where fluctuating natural conditions may affect the output significantly, control parameters in bioenergy generation are much more flexible and turns out to be a potential candidate to harness sustainable green energy. Although there is an abundance of biomass on earth and without affecting food production modified agricultural practices could produce more than one billion tons of biomass, which is equivalent to 600 GW of energy, the challenge is to efficiently extract energy from much less concentrated biomass, (IEA 2012, 2013a, b). Energy recovery in low-density biomass is much lower than the concentrated fossil fuels so far. One way to overcome this challenge is to use microbe driven bio-battery or microbial fuel cell technology. In the USA, nearly 5% of the energy budget is used to treat waste water in treatment plants but instead of consuming energy these waste water treatment plants have the potential to generate energy using some special microbes capable of expelling electrons to external receptors outside their bodies.

A bio-battery is able to extract energy from organic compounds more like cells in a human body. When we consume food, cells breakdown energy reach food molecules such as glucose and pull off electrons in the process. The energy captured from electrons is stored in ATP, and the spent electrons are deposited to the terminal oxidants like oxygen. For example, in metabolism of carbohydrates living creatures extract energy in reactions similar to:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O. \tag{1}$$

In a living cell or a microbe, the process is more complex and involves many enzymes and progresses via a series of redox reactions involving NADH and other intermediates.

In a bio-battery, biomolecules such as enzymes or microbes catalyze oxidation of biomass to generate electrons. The goal of a bio-battery is to design an efficient way to harvest these electrons and channel them through an external circuit before they get oxidized at the cathode. There are different choices of cathodes and structures of a microbial fuel cell. Before going into the details of a bio-battery, let us first look at how an electrochemical battery works.

2 Electrochemistry of a Galvanic Cell

In a galvanic cell, energy is extracted through electrochemical reactions where oxidation-reduction takes place in two half-cells. Moreover, as oxidation occurs in one of the half-cells and reduction in the other, we can channel the electrons released in the process through an external circuit to do work. At the anode and cathode,

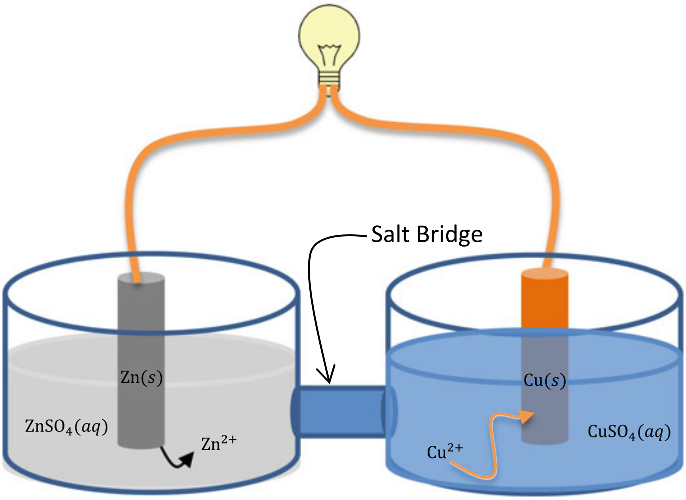

Fig. 1 A typical electrochemical cell with a salt bridge

chemical catalysts are neutralized using a salt bridge. A schematic of a standard Galvanic cell is shown in Fig. 1.

A typical cell might be constructed with two pieces of metal with different electronegativities one copper and one zinc say, each immersed in a solution containing dissolved salt of corresponding metal. It can be verified from the periodic table that copper (electronegativity 1.90) is more electronegative and has more electron affinity than zinc (electronegativity 1.65). When the copper and the zinc electrodes are connected through external circuit, zinc loses two electrons and gets oxidized to zinc cations, whereas copper ions gain these two electrons and get reduced to solid copper. These two half reactions can be written as

$$Zn(s) \rightarrow Zn^{2+} + 2e$$
$$Cu^{2+} + 2e \rightarrow Cu(s)$$

The rate of reaction can be precisely controlled by varying the external resistance connected to the electrodes. If an external source of electromotive force is connected to the circuit, the rate of reaction can be forced to proceed to non-spontaneous or even reverse direction. Current in the external circuit can be measured by an ammeter connected to the circuit. As current is a measure of amount of charge passing through the circuit, by measuring the current we can measure the amount of reactants or number of moles of reactants reduced in the process of cell reaction. For example, 1 A current flowing through a circuit means that there is 1 C of charge (1/96,467 mol of electron) flowing through the external circuit per second and determines the rate of reaction.

The electrochemical cell to operate not only needs an external electrical circuit, but the two electrolytes must be in contact with each other also. However, this type of redox reactions in two half-cells cannot continue forever. In the zinc half-cell, zinc dissolves continuously in the electrolyte to produce Zn^{2+} cations, whereas copper ions keep on receiving those excess electrons via external circuit and metallic copper is deposited on copper electrode. As a result, copper ions are neutralized and the half-cell becomes more and more negative (with sulfate anions), whereas zinc cations dissolved into aqueous solutions make the corresponding half-cell more and more positively charged. This certainly creates an imbalance and more and more work is to be needed to introduce additional Zn^{2+} ions into positively charged electrolyte or for electrons to flow into right compartment where they are needed to reduce the Cu^{2+} ions, eventually ceasing the electrons to flow from zinc to copper electrode. This type of back potential developed between the electrodes and the electrolytes is called *junction potential*. To prevent this charge separation from happening, the charge carried by the electrons through the external circuit must be compensated by some way of ion transport between the cells. This means that there should be a path for ions to cross from one cell to the other. It can be achieved by two ways: (a) two half-cells can be connected by a salt bridge, where the anions of the salt helps to neutralize the excess zinc cations and the cations of the salt helps neutralizing the sulfate anions in the aqueous solution of the copper half-cell to prevent the junction potential to develop and keep the battery running. Another way to keep the current flowing is to use a semi-permeable membrane instead of a salt bridge that prevents the electrolytes from rapid mixing, but allows ions to diffuse through.

3 Electron Transfer at an Electrode

Electron transfer during the oxidation or reduction process at an electrode may occur in a single step or as a succession of multiple steps. Electron transfer in an electrode takes place within a very thin solid-liquid interfacial region at the electrode surface where the electrode is in contact with the electrolyte. The structure of electrolyte within a nanometer of the metal electrode surface is known as electrical double layer. The molecular structure of the electrical double layer determines the nature of the interfacial electric field and in turn determines the reaction behavior in all electrochemical processes. Velasco-Velez et al. (2014) have explored the structure of the electrical double layer at a bare gold electrode and observed that with no applied potential and at positive potentials, the layer is highly structured (resembling ice) with few dangling hydrogen bonds. However, at negative potentials, the layer was more like bulk water, and half of the water molecules lie flat on the surface. The net oxidation or reduction process taking place at an electrode is normally referred to an *electrode reaction*. Electron transfer between electroactive species, i.e., the materials that receive or loose electrons, inside electrical double layers involves quantum mechanical tunneling. This process involves at least four steps: Firstly, hydrated cation enters electrical double layer from the bulk electrolyte solution.

Secondly, hydration sphere of cation is distorted by the electron gas at the metal surface. Thirdly, adsorbed cation gets dehydrated and ready to accept electrons and finally the water molecules break free from the former hydration shell.

4 Microbial Fuel Cell

Microbial fuel cells (MFCs) are bio-electrical devices that harness the natural metabolisms of microbes to produce electrical power, (Bennetto et al. 1985; Bennetto 1990; Allen and Bennetto 1993; Liu and Logan 2004a; Liu et al. 2004b; Logan and Regan 2006; Logan 2009; Logan and Rabaey 2012). Traditional fuel cells like hydrogen fuel cells require energy to generate hydrogen, whereas an MFC requires no external energy source, does not produce any additional greenhouse gasses, depends on the bio-degradability and is self-sustained. All these added advantages over traditional fuel cells make MFCs a potential candidate for sustainable green energy source. Within a MFC, microbes consume sugars and other nutrients in their surrounding environment and release a portion of the energy contained within that food in the form of electricity. Similar to a chemical fuel cells, MFCs offer an option to generate electricity from electron donors oxidized at the anode and electrons pass through an external load to a cathode where they combine with protons and a chemical catholyte such as O_2 is reduced. However, chemical catalysts in galvanic cells are replaced by exoelectrogens, a species of microorganisms that oxidize and transfer electrons to an electrode (Benneto et al. 1985; Chaudhuri and Lovley 2003; Logan et al. 2006). MFCs are typically designed as a two-chamber system with the bacteria in the anode chamber separated from the cathode chamber by a polymeric proton exchange membrane (PEM). Most MFCs use aqueous cathodes where water is bubbled with air to provide dissolved oxygen to electrode.

In the typical two-chamber MFC shown in Fig. 2 exo-electrogenic bacteria present in anode biofilm oxidizes fuel generating CO_2, electrons and protons. Electrons are transferred through an external circuit whereas protons travel from the anodic to cathode chamber through the PEM. At the cathode, protons recombine with electrons in the presence of oxygen to produce water.

It is observed that in a single chamber MFC in absence of PEM power density of generated electricity increases significantly (Liu and logan 2004a). Their construction the MFC consisted of an anode and cathode placed on opposite sides in a plastic (Plexiglas) cylindrical chamber 4 cm long by 3 cm in diameter (empty bed volume of 28 mL; anode surface area per volume of 25 m^2/m^3). The anode was made with carbon paper, and the cathode was manufactured by bonding a PEM directly with the carbon cloth cathode containing Pt catalyst. Using this architecture an order of magnitude higher power generation (146 mW/m^2) in comparison for other complex materials such as anaerobic sediments (16–28 mW/m^2), a high-starch content wastewater (19–20 mW/m^2), or domestic wastewaters (24 mW/m^2) with domestic wastewater can be achieved.

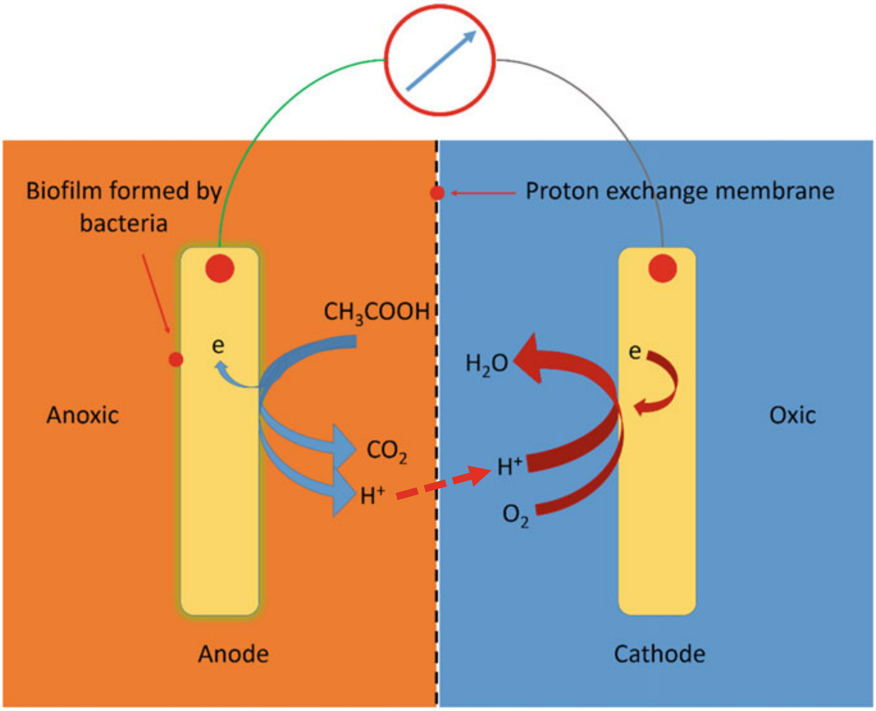

Fig. 2 A typical two-chamber microbial fuel cell with aqueous cathode

Voltage produced by a microbial fuel cell is primarily dependent on the two electrode environments (Rabaey and Verstraete 2005). The microbes form a community and grow on the surface of the anode of the MFCs. In the process of respiration, the biomolecules get reduced and decrease the overall potential of the anode, often steeling between −0.1 and −0.4 V versus a standard hydrogen electrode (SHE). On the other hand, the cathode is generally placed in a more oxygen-rich environment and the dissolved oxygen increases the electrical potential of the cathode, often ranging between 0.4 and 0.8 V versus SHE. The voltage of a MFC is thus the difference between the potential of the cathode and that of the anode and can reach the maximum theoretical limit of 1.2 V [0.8 V – (−0.4 V)]. Typical redox gradients with respect to SHE can be found in *Brock Biology of Microorganisms 13th edition* (Madigan et al. 2010).

5 Electron Transfer Mechanism at the Anode

At the anode when microbes form a colony they start to metabolize sugar and other nutrients, which act as fuel to the microorganisms. The process of metabolism generates highly reduced biomolecules with extra electrons attached to them. These extra electrons are then transferred to the anode generally in one of the following three ways (Fig. 3):

(1) Electrons can be transferred directly from the microbe's wall to the anode,
(2) Mediator assisted electron shuttling from the biomolecule to the anode and
(3) Electron transfer through microbial nanowires or conductive appendages grown by the microbes (Gorby et al. 2006). A schematic of networks of nanowires in microbes can be seen in Fig. 4.

Sometimes electrons are carried directly from the respiratory enzyme to the electrode when the microbe cells expose the redox active proteins on the surface of the electrode. Many strains of bacteria can release electrons from a terminal oxidase

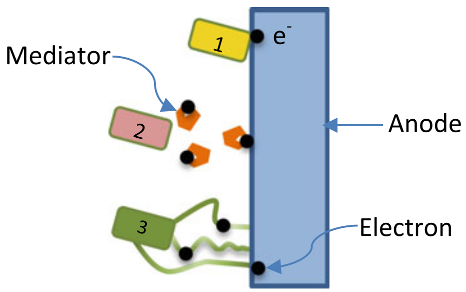

Fig. 3 Electron transfer mechanism from the microbes to the anode

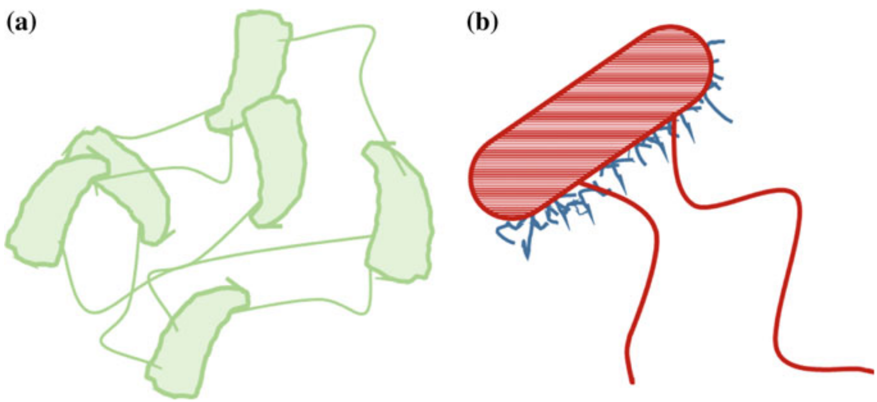

Fig. 4 **a** Electrically conductive nanowires extend many times the length of the bacteria *Shewanella oneidensis*. **b** *Geobacter* sp. with the pili

in the respiratory chain to Fe_{III} outside the cell, producing soluble Fe_{II}. Some electrochemically active bacteria such as *Aeromonas hydrophila* and *Shewanella putrefaciens* (Kim et al. 1999) can thus directly transfer electrons from the microbe to the electrode and these bacteria that can transfer electrons extracellularly, are called exoelectrogens.

Electron transfer through microbial nanowires was also observed when the fermentative bacterium *Pelotomaculum thermopropionicum* is linked to the methanogen *Methanothermobacter thermautotrophicus* by an electrically conductive appendage. This is a direct evidence for interspecies electron transfer (Gorby et al. 2006). However, recent studies have revealed that some of the bacterial nanowires were not made of pili, hair-like appendages that are common on single-celled organisms rather the wires are actually formed from the bacteria's outer membranes. For example *Shewanella oneidensis* soil bacteria extends its outer membrane in the shape of a long tube and its cell membranes have proteins embedded in them called cytochromes, which can pass electrons to one another (Pirbadian et al. 2014). The mechanism used by *Shewanella* spp. to transfer electrons outside the cell is still not clearly understood and most likely there is no single mechanism for the electron transfer. *Shewanella* spp. not only have outer membrane cytochromes for direct electron transfer by contact, but also they can extrude electrically conductive nanowires (Gorby et al. 2006).

Most of the microbial cells are electrochemically inactive. Between a microbe and electrodes, electron transfer is often facilitated by mediator chemicals. Commonly used mediators like neutral red, humic acid, thionine, methyl blue etc. are expensive and often toxic and thus detrimental to scale up the process (Delaney et al. 1984; Lithgow et al. 1986). *S. oneidensis* also produces flavins that can function as electron shuttles (Von Canstein et al. 2008).

6 Mud-Based MFC

A natural microbial fuel cell can be constructed using readily available soil. A mud-based microbial fuel cell adheres to the same basic principles of MFCs whereby mud acts as a source of exo-electrogenic bacteria, nutrient-rich anodic fuel and the proton exchange membrane. Microbes, including *Geobactor* and *Schewanela,* are ubiquitous in soil. Moreover, soil is naturally rich in complex sugars and other nutrients accumulated over millions of years of decayed plants, leaves and animal wastes. It also acts a natural proton exchange membrane as the oxygen consuming aerobic microbes present in the soil acts as an oxygen filter. Microbes present in the mud act as catalysts to break down sugars and complex nutrients thereby releasing a portion of their energy contained within those molecules in the form of electrical energy (Fig. 5).

For a mud-based fuel cell to function two electrodes— anode and cathode separated by a proton exchange membrane is needed. Similar to a galvanic cell discussed earlier, a proton exchange membrane (PEM) ensures that very small ions such as

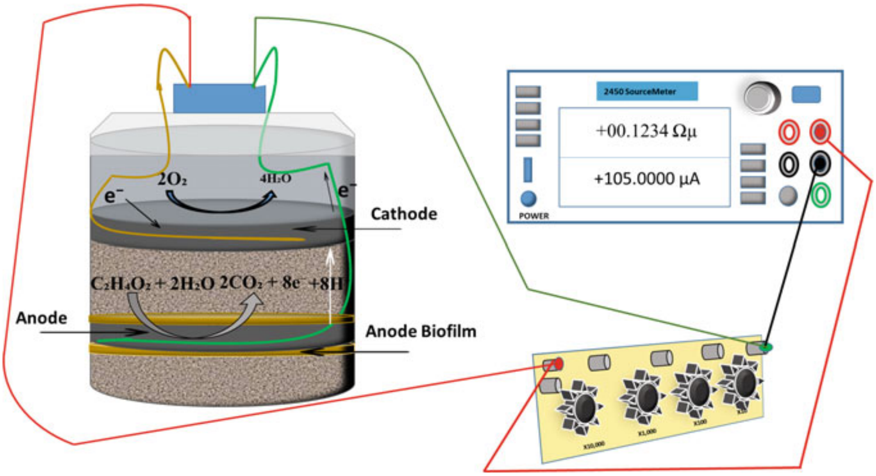

Fig. 5 Schematic of a mud-based MFC (MudWatt)

protons pass through although larger ions such as oxygen is blocked by this membrane. In a mud-based MFC, mud is not only a source of microbes and nutrients, but also it acts as an effective PEM. Inside a MudWatt, an **anode** is placed under the mud. In this anoxic environment, microbes metabolize sugars and other nutrients in the surrounding environment releasing electrons using **anaerobic respiration**. Bacteria multiply over time to cover the anode with a biofilm. Similar to a galvanic cell, the anode acts as the electron acceptor for **exo-electrogenic bacteria**, such as *Shewanella* and *Geobacter*. The other electrode, the cathode is normally placed in an oxic environment where electrons from the anode travel through an external circuit before reacting with oxygen and hydrogen to produce clean water. Thus, this set up not only generates electricity from microbes but also it can be used for bioremediation of waste water to regenerate clean water. Mud-based MFCs are also used to power sensors on the sea and river beds as microbes continue to generate electricity so long as there is a supply of nutrients and other conditions are fulfilled.

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Glossary

Aerobic Metabolism in presence of oxygen.

Anaerobic Metabolism in absence of oxygen.

Anode The electrode where electrons are collected (−).

Bioremediation Using microbes to breakdown environmental through natural biological processes.

Cathode The electrode at which electrons are released (+).

Cellular respiration The chemical process in which cells break down nutrients and sugars and release energy.

Electricity The net motion of charged particles (such as electrons) under a potential difference.

Electrogenic bacteria Organisms that can transfer electrons to extracellular electron acceptors outside their bodies (e.g., an anode).

Electrons Negatively charged fundamental particles.

Galvanic cell An electrochemical cell that uses spontaneous chemical reactions to generate electricity.

Redox Potential A measure of electron affinity or electronegativity of substances.

Redox reaction A reaction that involves electron transfer between two reacting substances.

Metabolism A process by which complex foods are broken down by chemical reactions to yield energy.

Microbe Short form of microorganism.

Microbial fuel cell A fuel cell that uses bacteria to produce electrons and a potential difference.

Review Questions

1. What is the difference between aerobic and anaerobic metabolism?
2. Electrogenic bacteria give off electrons when they respire. In an MFC, what are the transfer mechanisms of the electron from the microbe to the anode?
3. Globally, how much solar energy is captured by plants, algae and cyanobacteria through photosynthesis each year?
4. What is the net annual primary production of terrestrial plants?
5. What is the global sustainable bioenergy production potential? Is this figure significant in the current global energy demand?
6. What biomass materials are identified as bioenergy feedstocks?
7. What are biomass logistics? Name the typical operations of biomass logistics.
8. Explain the general logistics of switchgrass production for bioethanol.
9. What equipment is commonly used for collecting and densifying woody biomass in the field?
10. What techniques have been tested to pre-process lignocellulosic materials for bioethanol generation?

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