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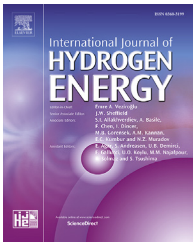

Electricity generation in microbial fuel cell systems with *Thiobacillus ferrooxidans* as the cathode microorganism

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ABSTRACT

Microbial fuel cells (MFC) are systems that enable biochemical activities of bacteria to generate the electricity. These systems are of great interest because of their designs that enable biological activity in organic wastes to be transformed into direct electrical energy. In order to increase the commercial usage of MFCs, it is necessary to increase the power output of the system. So as to improve MFC performance, used material selection, the pH value of the used bacterial medium and the choice of the appropriate substrate are very important. In this study, oxidation bacteria *Thiobacillus ferrooxidans* on the cathode and mixed culture bacteria on the anode of MFC were used. Different anode and cathode pH values were examined in MFC. Best open circuit potential result (0.8 V) was obtained at anode pH 8 and cathode pH 2 conditions. In addition, three different substrates had been used in the anode. In the conditions of acetate the most stable and high valued curve was obtained. The open circuit potential had reached 0.726 V, and power density had reached 0.88 mW/cm^2.

Introduction

Microbial fuel cells (MFCs) are seen as the technology of the future because of the appropriate systems for the use of wastewater to generate electricity. MFCs usually consist of two compartments separated by a proton exchange membrane. Used as anode and cathode compartments include aqueous solutions containing the microorganisms as biocatalyst. MFC systems have been extensively studied in single, double or triple chamber designs [1–3]. There are systems that use a proton exchange membrane or salt bridge that separates the anode and cathode compartments from each other, as well as systems that are designed without separating the anode and the cathode. Due to high proton permeability and low internal resistance, proton exchange membranes are preferred in MFC systems. *Geobacter* spp., *Shewanella* spp., *Rhodoferax ferrireducens, Aeromonas hydrophila, Pseudomonas aeruginosa, Clostridium butyricum, Shewadella oneidensis MR-1, Rhodobacter sphaeroide and Enterococcus gallinarum* are some of the commonly tested microorganisms for the power generation in MFCs [4–16].

Thiobacillus ferrooxidans is a gram negative rod-shaped bacterium, and it is suitable for the growth physiology of the inorganic mineral environment. It provides carbon by fixing atmospheric carbon dioxide and is necessarily autotrophic.

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Heterotrophic growth of the bacteria in several studies is thought to be related to a fault.

Thiobacillus ferrooxidans cultures in the absence of heterotrophic bacteria belonging to the types of *Acidiphillium* are known to be difficult to form, and these bacteria are formed as a result of a mistake, while *Thiobacillus ferrooxidans* bacteria are magnified. In another study, mixotrophic strain is obtained in iron and glucose media [17]. But in this media organic compounds prevent the bacteria's growth. It is seen usually, but not always, formic acid is used at place of carbon dioxide, as a source of carbon in *Thiobacillus ferrooxidans* strain studies. But formate concentration should be kept low by the use of the chemostat. One strain, ATCC 21834, was found to work more efficiently, especially when formic acid is exhausted [18]. *Thiobacillus ferrooxidans* has five characteristic features. The first one is that it is chemolithotrophic. *Thiobacillus ferrooxidans* uses reduced inorganic sulfur and Fe^{2+} for cellular development and energy need in the presence of atmospheric oxygen and carbon dioxide [17].

MFCs are divided into two groups, according to the mechanisms of electron transport from the bacteria to the electrode. In the MFC systems, electron carriers are also known as mediators added to the system to perform electron transfer. Mediators (most of them are toxic chemicals) are to be used in high concentration. However, this situation makes them use difficult in the large-scale systems. The use of mediatorless MFCs for the electricity production from organic waste waters is promising. By using *Shewanella, Rhodoferax,* and *Geobacteraceae* as metal reducing bacteria, and *Clostridium butyricum* species as a fermentative bacterium in the MFC, mediatorless systems can be designed. It is believed that metal reducing bacteria transfer their electrons directly to the anode by using their electrochemically active redox enzymes in their outer membranes.

Many different substrates are used in MFCs which are the most important factor affecting biofilm formation by bacteria. At the same time, the substrate used greatly affects power density, coulombic efficiency and system performance [19] [20]. In the MFC systems, carbohydrates such as glucose, fructose, xylose, sucrose, maltose and trehalose [21] [22], organic acids such as acetate, propionate, butyrate, lactate, succinate and malate [23–25], alcohols such as ethanol and methanol [26] and inorganic compounds such as sulfate [27] are some of the materials used as substrate [20].

The amount of power generated by the MFCs usually varies according to the vaccination, types of food, and the reactor. Generated power rate in the MFCs is 1–3600 mW/m^2 [28]. Iron sulfate in the nutrient water of the microbiological cathode compartment serves as an electron acceptor. As far as the cathode compartment solution is refreshed by microorganisms, it remains clean. One of the used metal oxidation bacteria is *Thiobacillus ferrooxidans*. It was observed [29], that with graphite as electrode and *Thiobacillus ferrooxidans* as redox bacteria, the open circuit potential at the cathode reached 0.74 V. With current density of 23 A/m^3 power density had reached 6.61 W/m^3. In another study, 4.4 A/m^2 current density and 1.2 W/m^2 power density values were reached by using *Thiobacillus ferrooxidans* [30]. This result is 38% higher than that one obtained in a study, where iron oxidation mechanism was not used.

Using acetate as substrate at the anode, we have the following net reaction in MFCs:

$$CH_3COO^- + 2O_2 \rightarrow 2HCO_3^- + H^+ \qquad (1)$$

In our study, an MFC system was assembled by using *Thiobacillus ferrooxidans* as the cathode microorganism, and its electrochemical performance was measured. In MFC systems pH value, microorganism and substrate selection are very important parameters. The aim of this study is optimize these parameters for obtain maximum power density by using *Thiobacillus ferrooxidans* as cathode microorganism and, using the most common and high yielding nutrients as substrate at anode.

Experimental

Experimental setup

I3C1–coded Freudenberg commercial carbon electrodes were coated with thin film Pt catalyst to increase electric conductivity and used as anodes and cathodes. Carbon electrodes were cut into squares of 25 cm^2. Nafion 115, selected as a proton exchange membrane, was kept in a 0.1 M H_2SO_4 solution for activation for 12 h, then washed with deionized water and dried. Anodes and cathodes were placed on both sides of the selected Nafion 115 membrane. The formed membrane-electrode layers were then converted to membrane electrode assembly (MEA) by hot pressing.

3 μl 5% nafion solution was applied as a binder to the catalyst layers. Hot press conditions are; the MEA was heated to 117 °C and 20 bar pressure was applied for 5 min in this temperature. Then the temperature application was stopped and MEA was allowed to become cooler under pressure.

Assembled MFC's outer chamber is made of plexiglass. Internal volume of the fuel cell is 100 cm^3. This volume is divided into two equal parts, which include anode and cathode. The cell design is given in Fig. 1a. After placing MEA between anode and cathode, teflon seals providing sealing were used, and two compartments were combined with the help of bolts. After the system installation, iron oxidation reactor was added to the cathode compartment, as in Fig. 1b.

The anode and cathode were connected to each other with Pt current collector wires. Sulfonated polyurethane foam pieces were added to the iron oxidation reactor in order to obtain large surface area for the biofilm formation. Ag/AgCl electrodes were used as reference electrodes during the electrochemical measurements. During the tests, oxygen gas was supplied to the cathode compartment permanently.

Solution circulation between the cathode and reactor was provided with a peristaltic pump. The experiments were done at room temperature. pH values of the anode and cathode and open circuit potentials were being measured every day. Electrochemical measurements were made with the help of computer and commercial software for CHI Model 800B potentiostat.

Anode microorganism media

15 mL of the homogenized mixed culture of anaerobic microorganisms were used in the anode compartment. By using