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Using Copper Sulphate and Potassium Permanganate as Electron Acceptor in a Duel Chamber Microbial Fuel Cell

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***Abstract*— The energy consumption rate around the world is rising day by day. On the other hand conventional sources of energy are finished at a fast rate. There is an uncertainty about the energy security around the world. The crisis of energy can be minimized by decently utilizing the renewable sources of energy. A latest manner of renewable energy recovery is reflected by Microbial Fuel Cell (MFC). It's like a device in which electrical energy is derived directly from chemical energy. The source of this energy is the oxidation of substrate material by bacteria. Potassium ferrricyanide is the most used chemical as electron acceptor in MFC. In this paper several others chemicals are used as electron acceptor. Copper sulphate and potassium permanganate was used in the cathode to accept the electron. Potassium permanganate provided better output as electron acceptor than Copper sulphate.**

***Keywords*—*Microbial fuel cell; electron acceptor; Potassium ferrricyanide; copper sulphate; potassium permanganate*.**

I. Introduction

The need of alternative sources of energy is very acute due to the running out of conventional sources of energy in developed and developing countries [1,2]. Bangladesh gets 8208 MW of electricity from gas as of November 2016 [3]. But the amount of reserved gas is 14.16 trillion cubic feet (tcf) which will be finished within 2031 [26]. For maintaining the current growth rate of our promising economy we have to move to renewable sources. It is very much urgent to find out a sustainable clean energy source with lowest emission of carbon due to global environmental concerns [4,5]. Fuel cells have represented themselves as emerging sources of renewable energy in recent years. Microbial Fuel Cell (MFC) is one of the members of fuel cell family which draws the attention of the researchers [6]. Bacteria are separated from a terminal electron acceptor at the cathode in an MFC so that the only way for respiration isto transfer electron to the anode. Materials like glucose [7], acetate or waste water [8] are catabolized by microorganisms. Chemical energy is converted instantly to electrical energy by bacteria in Microbial Fuel Cell [9, 10, 11]. Hydrogen can be produced in Microbial Fuel Cell and it happens smoothly from the fermentation of glucose in the presence of *Clostridium butyricum*[12].

$$C_{12}H_{22}O_{11} + 13H_2O \text{ ---> } 12CO_2 + 48H^+ + 48e^- \quad (1)$$

II. Operational Principle of MFC

Organic and inorganic matters are oxidized to generate current by bacteria which is used as biocatalysts in Microbial Fuel Cell (MFC) [13]. Electrons which are produced from the substrates by bacteria are transferred to the negative terminal (anode) and go to the positive terminal (cathode) through a load. Several chemicals like neutral red, methylene blue, thionine are used as mediators to accelerate the generation of current in MFC.

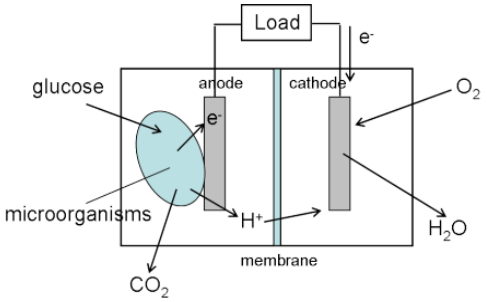

Figure 1. MFC mechanism

The above figure interprets that electrons gained from the substrate materials are transferred to the anode electrode by the bacteria present in anode chamber. Protons are also produced in oxidation reaction and passed to the cathode by proton

exchange membrane. The transport of electrons from anode chamber to cathode chamber is occurred by direct contact or by mobile electron shuttles. Finally the electrons are participating with the electron acceptor and the protons in cathode chamber [14].

III. Basic Structure

In anode chamber organic materials are used which are oxidized and produce electron, proton. Here glucose, sucrose, glucronic acid, starch etc. can be used as organic material [15]. Several chemicals are used to boost up the performance of anode chamber. These are called mediators. These include neutral red, methylene blue, thionine etc.[16]. As a mediator of electron transport from *Escherichia coli*,thionine has been used widely [17, 16]. Mediators are responsible for passing the electrons to anode electrode [18, 19]. External mediators are not demanded by the "mediator less" MFC due to the capability of the bacteria present in these MFC of doing the job of the mediator. In anode chamber co enzyme like Nicotinamide Adenine Dinucleotide Hydride (NADH) is used to transport the electron to the electron transport chain. As electrode conductive, bio compatible and chemically stable in the reactor solution material can be used. The most versatile electrode material is carbon because it is available as foam, felt, cloth, granuels, rods etc.[15]. The proton exchange membrane (PEM) is responsible for passing the protons produced in anode to the cathode. As proton exchange membrane Nafion membrane is the most used [15]. Ultrex CMI-7000 is another widely utilized PEM [20,21,22]. Zirfon [23] and Hyflon [24] are another alternative cut-rate PEM. The proton exchange membrane must be accessible to the chemicals which are used in both anode and cathode chamber.

IV. Fundamentals of Voltage Generation

Thermodynamically favourable conditions are required for the reaction to produce electricity in a microbial fuel cell. Gibbs free energy (J) can be applied to assess the reaction. Gibbs free energy is the evaluation of the maximum work which can be deduced from the reaction. It can computed as

$$\Delta G_r = \Delta G^o_r + RT\ln(\prod) \quad (2)$$

where Gibbs free energy for the specific conditions is reflected by ΔG_r (J), ΔG^o_r (J) expresses the Gibbs free energy under standard conditions normally outlined 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. From tabled energies of formation for organic compounds in water available from many sources the standard reaction Gibbs free energy is accounted. For MFC calculations, the overall cell electromotive force (emf), E_{emf} (V), outlined as the potential difference between the cathode and anode is applied to assess the reaction conveniently. This is related to the work W (J), produced by the cell or

$$W = E_{emf}\, Q = -\Delta G_r \quad (3)$$

where Q = nF is the charge transferred in the reaction, expressed in Coulomb , which is specified by the number of electrons substituted 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

$$E_{emf} = -\Delta G_r/nF \quad (4)$$

If standard conditions are provided for all reactions, $\prod = 1$, then

$$E^o_{emf} = -\Delta G^o_r/nF \quad (5)$$

Where standard cell electromotive force is reflected by E^o_{emf} (V). Hence we can apply the above equations to compute the potential of overall reaction as

$$E_{emf} = E^o_{emf} - (RT/nF)\ln(\prod) \quad (6)$$

If equation (5) is positive for a well-disposed reaction then a value of emf for the reaction is generated instantly by equation (5). Higher limit of cell voltage is provided by the computed emf. There are several losses like activation losses, bacterial metabolic losses, ohmic losses etc. those force the original potential to be lower than calculated emf [15].

V. Standard Electrode Potentials

The half-cell reactions can evaluate reactions occurring in the microbial fuel cell.

For oxidation of starch, we therefore have,

$$2C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11} \quad (7)$$

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6 \quad (8)$$

$$C_6H_{12}O_6 = CH_3CH_2OH + CO_2 \quad (9)$$

$$CH_3CH_2OH = CH_3COO^- + H^+ \quad (10)$$

$$2CH_3COO^- = CH_3CH_3 + CO_2 + 2e^- \quad (11)$$

According to Nernst equation

$$E_{An} = E^0_{An} - (RT/2F)\ln[(CH_3COO^-)^2 / (CH_3CH_3)] \quad (12)$$

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

$$Cu^{2+} + 2e^- = Cu \quad (13)$$

$$E_{cat} = E^0_{cat} - (RT/2F)\ln[(Cu)/(Cu^{2+})] \quad (14)$$

if we consider the case where Permanganate is used as the electron acceptor for the reaction, we can write

$$MnO^{4-} + 8H^+ + 5e^- = Mn^{2+} + 4H_2O \quad (15)$$

$$E_{cat} = E^0_{cat} - (RT/5F)\ln[(Mn^{2+})/(MnO^{4-})(H^+)^8] \quad (16)$$

The Cell EMF is computed as,

$$E_{emf} = E_{cat} - E_{An} \quad (17)$$ [15].

Nernst equation mentioned in equation (6) can be used for the simulation of Microbial Fuel Cell (MFC). To calculate the emf generated in our designed cells theoretically equation (5), (12), (14), (16),(17) can be used.

VI. Proposed Model with New Chemical Component

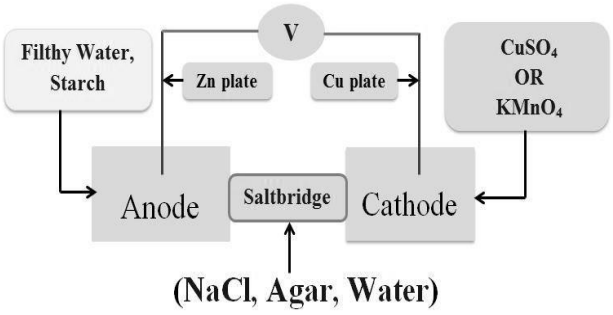

Figure 2. A substitute model of MFC

For constructing a Microbial Fuel Cell, the configuration shown in figure 1 is the most efficient model as of now. But the chemicals as well as the components which are used in that model are unavailable in this corner of the globe. The production of some of these components like Nafion membrane is limited within some of the developed nations. So it is very tough to make MFC popular as a renewable energy source in Bangladesh. It is urgent to develop a new model of Microbial Fuel Cell. Figure 2 represents a model which may be an alternative configuration of ideal model of MFC. In this configuration Nafion membrane is replaced with salt bridge. Actually salt bridge is the replacement of proton exchange membrane. The salt bridge is made of agar, sodium chloride and water. In anode chamber the co enzyme Nicotinamide Adenine Dinucleotide Hydride (NADH) is totally neglected. Also any mediators are not used. Only bacteria filled filthy water and starch as substrate are used in the anode chamber. Zinc plate is used as anode electrode whereas copper plate is chosen to do the function of cathode electrode. As electron acceptor potassium ferricyanide is widely used in cathode chamber of MFC. But it is a restricted chemical because it is poisonous to health. So we are replacing it with copper sulphate and potassium permanganate. The chemicals which are used in the model of figure 2 are quite available in any corner of Bangladesh.

VII. Experimental Setup & Data Analysis

Based on our proposed model two experimental setups had been constructed recently. One was for Copper sulphate and another one was for potassium permanganate as electron acceptor. For both the cases drain water was used as the holder of bacteria. Actually the thick muddy layer was taken from the lowest stage of the drain. The thick layer was mixed with the filthy drain water. One kg of muddy layer was mixed with 250 mL of drain water. Then 0.5 litre of liquid was used from the mixture in the anode chamber. Starch was used as organic matter whereas mediators are neglected to be used. Both cases 125 gm. starch was taken. Zn plate was served as anode electrode where cu plate did the function of cathode electrode. The salt bridge was 0.5 inch thick and 5.5 inch in length for both the set up. For developing the salt bridge 5.5 gm. agar, 27.5 gm. Sodium chloride and 275 ml of water were used. The mixture of agar, NaCl and water was heated until it became adhesive. Actually two salt bridges were constructed with same composition of chemicals. All the data's were collected under no load condition and a multimeter was used to measure the experimental findings. Figure 3 represents the diagram of set up with copper sulphate as electron acceptor whereas figure 4 reflects the diagram for potassium permanganate as electron acceptor.

Figure 3. Experimental Setup for Copper Sulphate

Figure 4. Experimental Setup for Potassium Permanganate

TABLE I. Experimental data for fig. 3

Observing internal hours	Voltage (V)	Current (mili amp)	Power (mili W)
After 2	1.046	5.78	6.046
After 8	1.034	5.42	5.604
After 16	1.011	5.32	5.379
After 24	1.009	5.28	5.328
After 32	1.003	5.38	5.396
After 40	0.972	5.59	5.433
After 48	0.931	5.19	4.832
After 56	0.931	5.11	4.757
After 64	0.834	4.97	4.145

TABLE II. Experimental data for fig. 4

Observing internal hours	Voltage (V)	Current (mili amp)	Power (mili W)
After 2	1.283	1.515	1.944
After 8	1.224	1.419	1.739
After 16	1.227	1.406	1.725
After 24	1.252	1.389	1.739
After 32	1.176	1.099	1.292
After 40	1.233	1.161	1.432
After 48	1.237	1.284	1.588
After 56	1.033	1.165	1.203
After 64	1.002	1.133	1.135

VIII. Comparison With an Ideal Case

Chambers:	**Anode and cathode**
Length	3.3 cm = 33 mm
Diameter	3.9 cm = 39 mm
Projected surface area	11.94 cm^2
Membrane:	**Nafion 117**
Thickness	177.8 um = 0.1778 mm
Projected surface area	11.94 cm^2
Electrodes:	**Anode and cathode**
Thickness	0.6 cm = 6 mm
Projected surface area (large)	11.94 cm^2
Surface/ Volume ratio	10 666*

Fig 5. Specific data for MFC experiments at University of Southern California [25]

An experimental model was constructed by using Nafion 117 as a membrane at department of aerospace and mechanical engineering in University of southern California, Test data's and graph are given below [25].

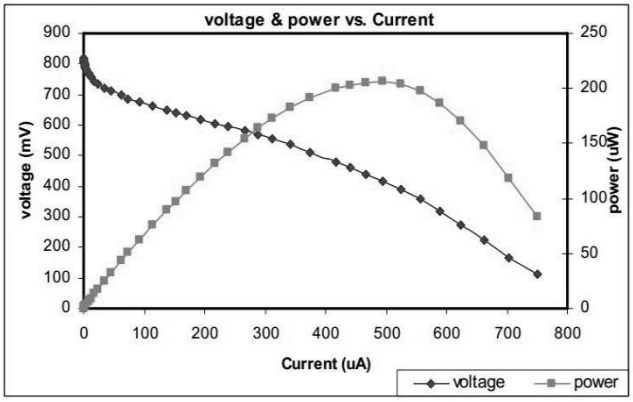

Fig. 6 Voltage and power vs current for for MFC experiments at University of Southern California [25]

With a projected electrode surface area of 11.94 cm^2 the maximum Power attained was approximately 206.4 microwatts [25].The values are given below for our experimental setup. Figure 7 shows that 1.046V was obtained as maximum voltage where figure 8 shows that 5.78 mili amperes and 6.046 mili watts were obtained as maximum current and maximum power respectively for Copper Sulphate as electron acceptor.

TABLE III. Experimental Setup Data

Chambers	**Anode & Cathode**
Length	16 cm
Diameter	6 cm
Surface Area	358 cm^2
Salt bridge Length	12.7 cm
Salt bridge Diameter	1.3 cm
Electrode Length	14.5 cm
Electrode Width	4 cm
Electrode Surface Area	58 cm^2

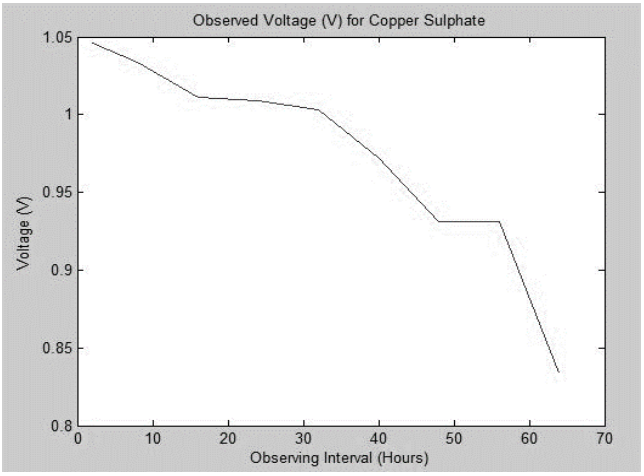

Fig 7. Obtained Voltage for Copper Sulphate

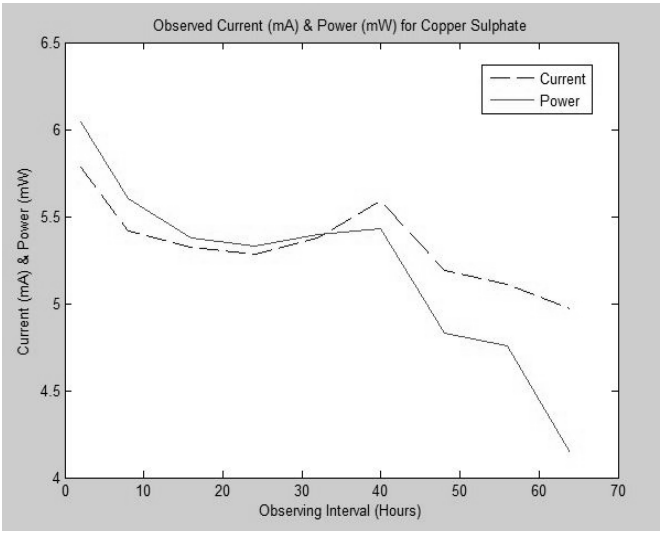

Fig 8. Obtained Current & Power for Copper Sulphate

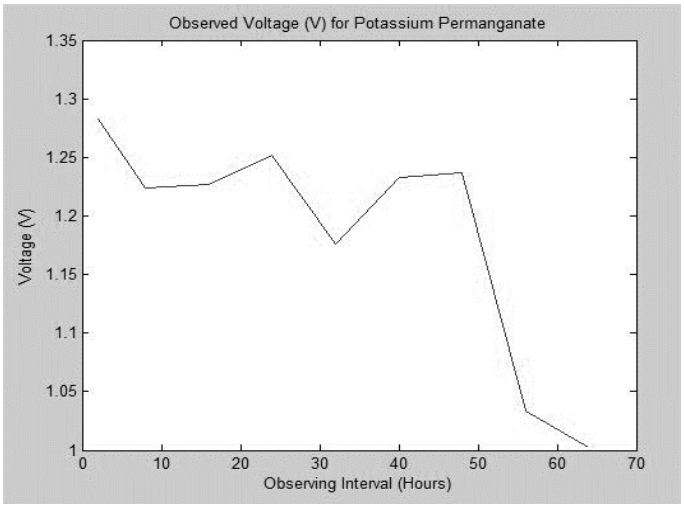

Fig 9. Obtained Voltage for Potassium Permanganate

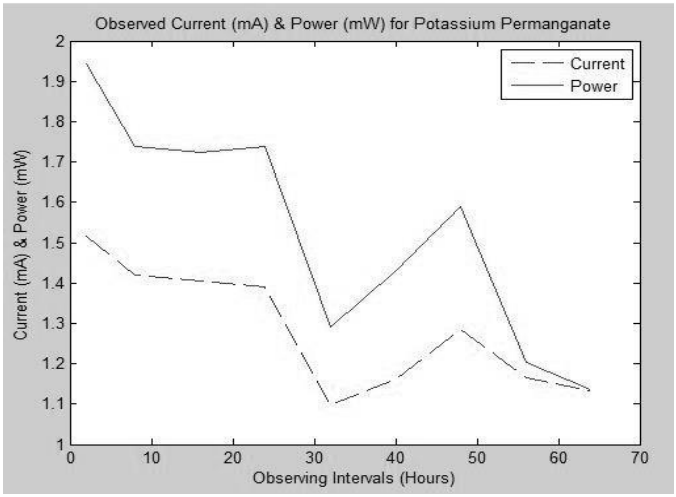

Fig 10. Obtained Current & Power for Potassium Permanganate

Figure 9 shows that 1.283V was obtained as maximum voltage where Figure 10 shows that 1.515 mili amperes and 1.944 mili watts were obtained as maximum current and maximum power respectively for Potassium Permanganate as electron acceptor.

IX. Conclusion

The reduction of conventional energy sources forces the researchers to think such kind of renewable energy source. We checked the performance of Microbial Fuel Cell for different chemicals as electron acceptor. Our observations found that its output voltage is not stable. Further research on stable output as well as on different aspects like effect of surface area of anode and cathode chamber, effect of different electrodes materials may speed up the process of making it as a mainstream renewable energy source.

Acknowledgment

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