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Study of Electrode Structures and Redox Kinetics in Biofuel Cells

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Abstract

Selection of the anode-cathode electrodes materials and structure is one of the critical challenges of bio fuel cell application. They can affect the power density and columbic efficiency. Two types of bio fuel cell were studied , the Microbial Fuel Cell (MFC) and the Enzymatic Fuel Cell (EFC), where the electrode structure and kinetics are similar except for the rates of redox reaction. The electrochemical characteristics of the In the MFC the anode was inoculated with MRS broth containing *Lactobacillus Cesai Shirota.* Complete characterisation and optimisation of the redox kinetics will be presented. Mediators will be used to enhance electron transfer between the fuel, bacteria and electrodes to improve electrode kinetics. A fast and convenient bacterial immobilization method will be proposed as an attempt to improve the anode efficiency of a microbial fuel cell, in which bacteria will be entrapped. The electron transfer characteristics with the mediators and immobilizers shall be studied by cyclic voltammetry and SEM imaging. Enzymatic Fuel Cell is a specific type of bio fuel cell that uses enzymes as a catalyst to oxidize its fuel, instead of precious metals. Enzymatic glucose biofuel cells convert chemical energy stored in glucose into electricity. Enzymatic oxidation from complex sugar is carried out by glucose selective enzymes such as glucose oxidase (Gox) and oxygen reducing enzyme namely laccase. These reactions are highly enzyme specific and occur at relatively mild conditions (Neutral pH and ambient temperature). The specific materials and structure for the electrodes used in enzymatic fuel cell can affect the power density and columbic efficiency. This glucose EFC cell features a 3-D porous carbon anode and cathode, for high surface area for the reaction, a suitable immobilizer for the enzyme immobilization and mediators like ferrocene for optimal electron transfer. The achievable cell potential is between 0.7- 0.8V. The achieved power density is still below theoretical value. The EFC will be optimized for enzyme loading; conductive loss minimization, both electronic and ionic, direct charge transfer for improving charge transfer efficiency, and pore channel and size profile.

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Keywords: Microbial, Enzymatic, Mediators

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1. Introduction

In today's world, a lot of our energy we consume is produced by fossil fuels which have a very adverse effect on the environment. Alternative fuels such a solar and wind energy, are energy sources which don't harm our environment. One such source of energy is Fuel cells. In this study, we try to show the technical difficulties surrounding Microbial and Enzymatic Fuel cells which run on widely known sugars such as glucose found in day to day food. These electrochemical systems work on a simple redox reaction, where the fuel (Glucose) is reduced at the anode to give out hydrogen ions and electrons. The electrons are allowed to pass through an external circuit giving us an Open Circuit Voltage. The Hydrogen ions pass through membrane which is then oxidized at the cathode. We use Glucose-oxidase as the enzyme for the EFC and Lactobacillus Cesai Shirota as the bacteria in MFC. The enzyme and the bacteria oxidize glucose the give Water, Hydrogen Ions, electrons and Carbon Dioxide.

Anode: $C_6H_{12}O_6$ (electron donor) → $6H_2O + 6CO_2 + 24H^+ + 24e^-$

Cathode: $6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$

2. Materials and Methods

2.1. Fuel Cell Fabrication

A single chamber MFC and EFC with a volume of 48.105 mL were used in this study. The whole setup was made using perplex glass. The system was assembled using silicon gaskets to prevent leaks across the interface. The membrane electrode assembly (MEA) was laminated using a standard process at 80^oC.A graphite anode was used as the anode, with geometric area of $5cm^2$.The cathode is an air breathing structure with Pt-Ru on carbon as catalysts. The current collectors were Au coated on expanded metal made of SS316.

2.2. Fuel and Mediator characteristics

0.5 M glucose solution was fed into the anodic chamber of the fuel cells. The oxygen from air was used for the cathodic reaction. Methylene blue was used as a mediator for the studies. 5 mg in 1.4 ml of water was prepared and 10µl of this solution was added to the fuel cells. The concentration of the mediator as subsequently doubled.

2.3. Microbial Fuel Cell

Lactobacillus Cesai Shirota culture preparation, collection: The bacteria were first collected in test tubes from sample of Yakult and diluted using saline water (5 microliters). After auto-claving for a period of 5hours this diluted solution was allowed to incubate in a MRS broth- agar plate for 48 hours. 5 colonies of this particular sample were then added to100mlof MRS Broth. The MRS Broth with bacteria was allowed to incubate for 48hours in an incubator. After the incubation, 7 ml of Broth was added to the fuel cell.

2.4. Enzymatic Fuel Cell

Glucose Oxidase from Aspergillus Niger was used as the oxidizing enzyme.10 µl of 7mg in 1.4 ml of Glucose Oxidase in H2O and 10 ml of 0.5 M glucose solution was fed into the anodic chamber.

2.5. Fuel Cell Studies

Electrochemical Impedance Spectroscopy (EIS) was studied to obtain the interface characteristics. Open circuit voltage was recorded continuously every few hours. Cyclic voltammetry (CV) was performed on the MFC and

before the addition of the broth, and after the addition of broth, and also after the addition of glucose solution. Cyclic Voltammetry was done before the addition of the feed, after adding distilled water, and after the addition of enzyme and glucose solution in the EFC.

3. Results and Discussion

Open Circuit voltage (OCP) is the voltage when no load is connected to the fuel cell. Through these OCP, the stability of the fuel cell can be determined. As the temperature of the experiments weren't controlled, the stability might vary due to the evaporation of fuel in cell.

Figure 1 and Figure 2 represent the open circuit voltage (OCP) of the microbial fuel cell. In figure 1, we notice a significant increase in the OCP over time especially after the 2 hour marks. This rapid increase and subsequent stabilization of the OCP indicates the growth and immobilization of bacteria on the anode. As the bacteria becomes active, the proton transfer through the membrane increases and thereby producing a higher OCP. In Figure 2, which represents the OCP of the MFC with Methylene Blue (MB), has a higher average OCP than MFC with MB. This increase in OCP is due the MB, a mediator. MB aids in the process of proton exchange.

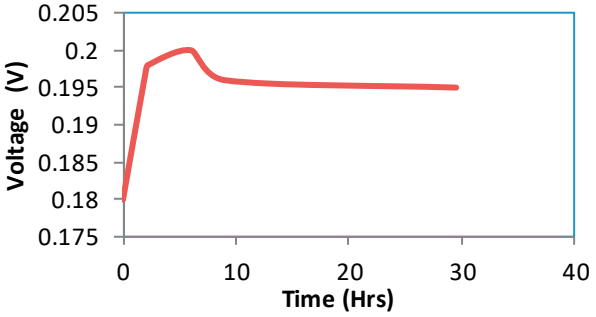

Fig. 1. OCP of Microbial Fuel cell

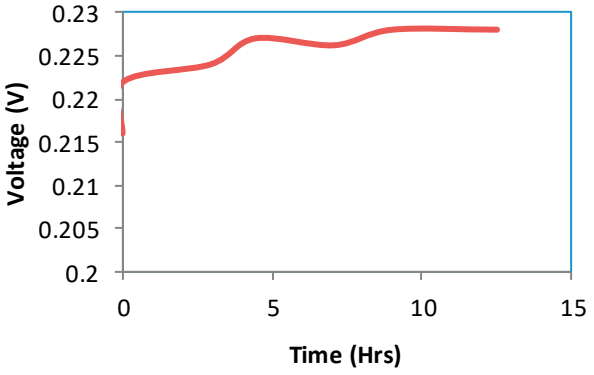

Fig. 2. OCP of MFC with Methylene Blue

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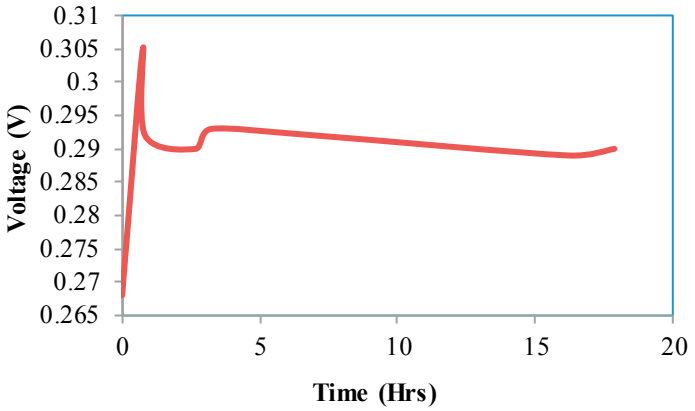

Fig. 3. OCP over time of the MFC with increased concentration of Methylene Blue.

The concentration of Methylene Blue was doubled. By doubling the concentration of Methylene Blue, we notice a higher OCP than Figure 1 and 2. This shows that more proton exchange occurs than in normal MFC and MFC with MB. As more proton exchange occurs, the OCP increases.

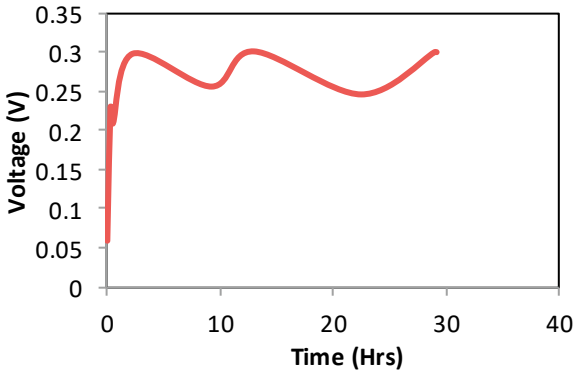

Fig. 4. OCP of Enzymatic Fuel Cell

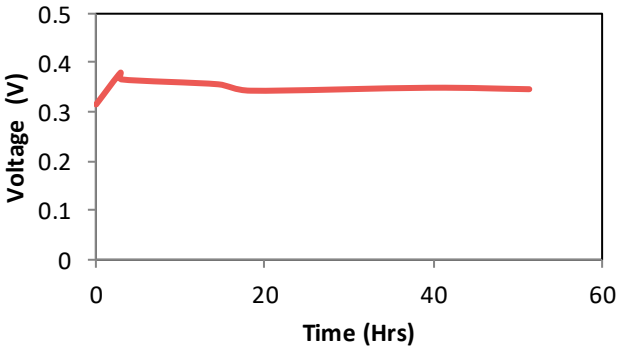

Fig. 5. OCP of EFC with MB

Figure 4 and 5 presents the OCP of the Enzymatic Fuel Cell (EFC) as a function of time. The OCP of the EFC in both the cases were measured for at least 30 hours. As per figure 1, we see that it doesn't take much time for the enzyme immobilize onto the anode. We notice in figure 2 that OCP of EFC with MB is higher than that of EFC without MB. This shows that increased proton transfer through the nafion membrane resulting to a higher OCP.

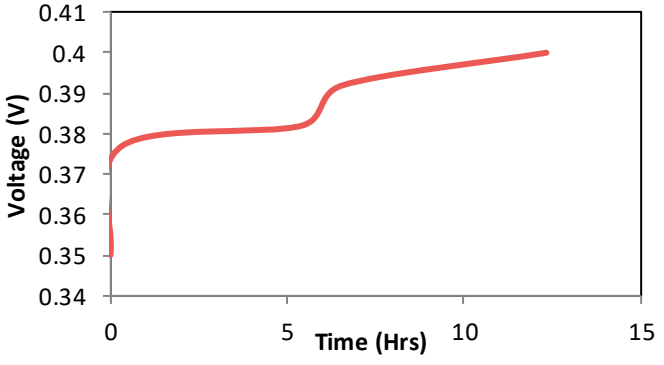

Fig. 6. OCP of EFC with 2X Conc. of MB

Figure 6, shows the OCP varying with time. The OCP was observed for almost 13 hours. By doubling the concentration of MB, we notice a higher OCP with time. The OCP rapidly increases after the 6 hour mark, depicting that more proton transfer is occurring along the membrane. From this we can conclude that in both EFC and MFC mediators (MB) play a crucial role in increasing the OCP.

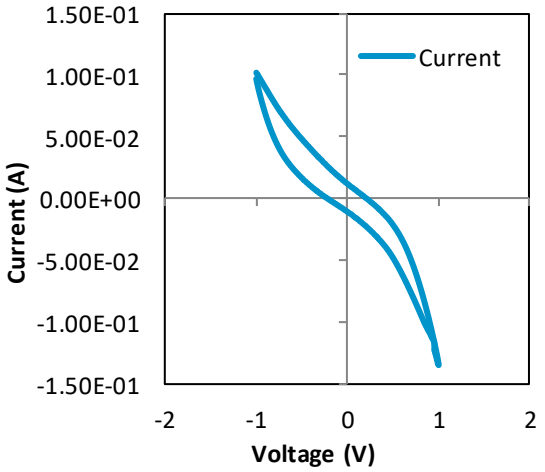

Fig. 7. Cyclic Voltammetry of EFC Before the Addition of Feed

Cyclic Voltammetry is a characteristic experiment for fuel cells. The cyclic voltammetry was performed before the addition of the enzyme, after the addition of enzyme and again before and after the addition of MB. From figure 7, it is evident that there are no redox peaks and the cell behaves as a capacitor. The absence of redox peaks proves that no electrochemical activity is taking place in the cell.

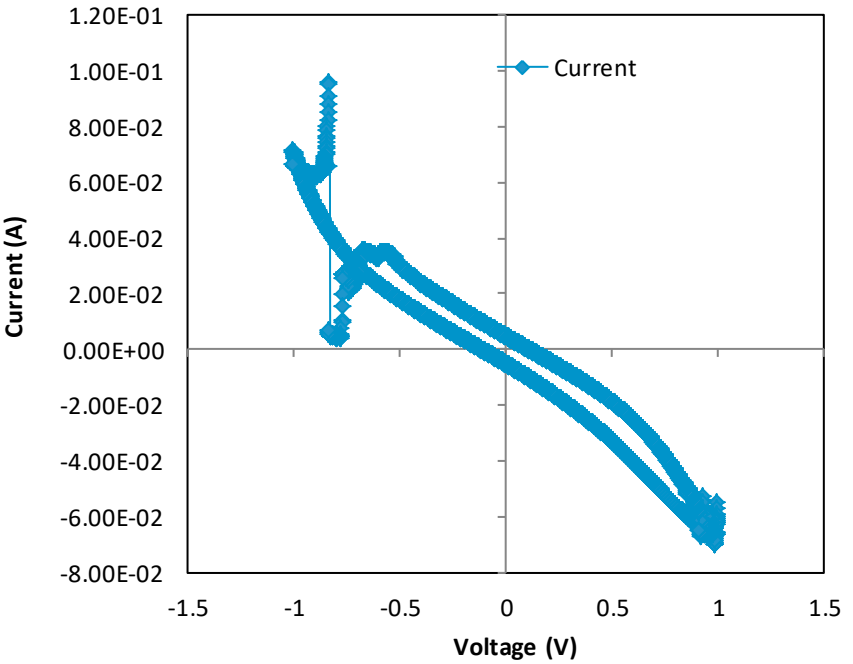

Fig. 8. Cyclic Voltammetry After the addition of Feed

Figure 8 represents the cyclic voltammetry taken after the addition of Enzyme with Glucose. Figure 8 clearly shows the presence of electrochemical activity because of the redox peak at 0.7V. The electrochemical activity shows that dissociation of glucose occurs by the enzyme to form protons and electrons which lead to the formation of current. A current of 0.1A has been produced in this case.

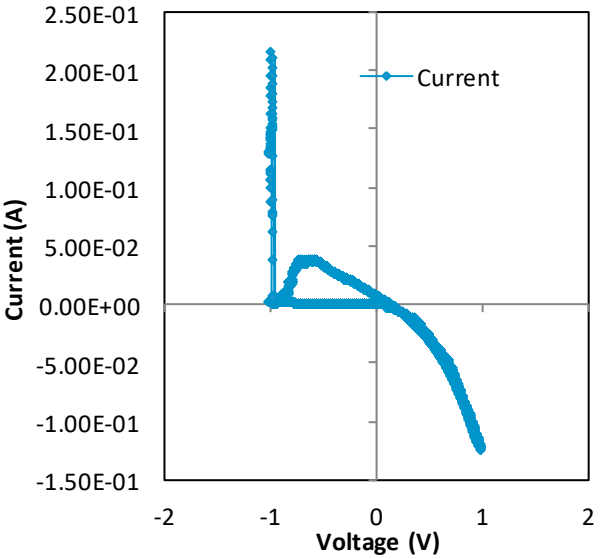

Fig 9. Cyclic Voltammetry after the addition of MB to EFC

In figure 9, we notice a drastic change in the current produced. The current produced is double the current produced when no MB was added to the EFC. The redox is peak is more evident compared to those produced in figure 7 and 8. The higher current and more definite redox peak is a result of increased proton exchange by MB.

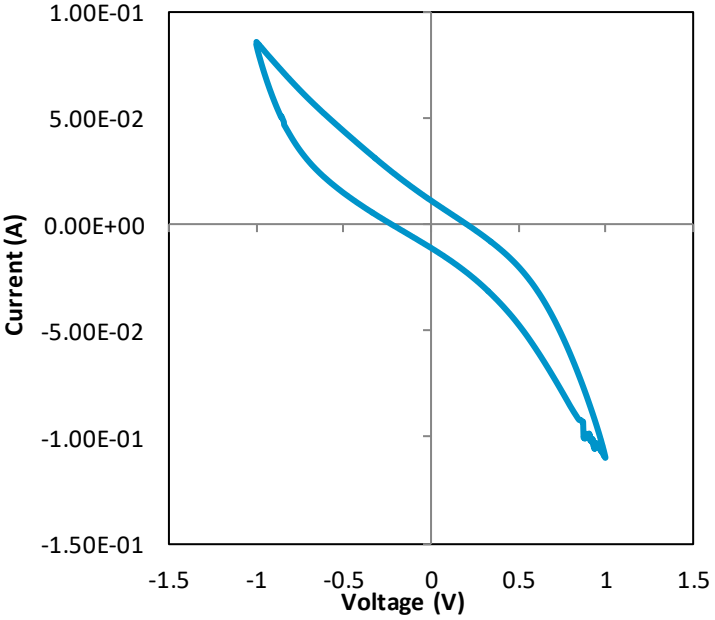

Fig. 10 Cyclic Voltammetry of MFC without Feed

From Figure 10, it is evident that before the addition of bacteria, there exists no redox peaks and the cell behaves like a capacitor. Before the addition of bacteria, the dry MFC shows a current of 0.8A.

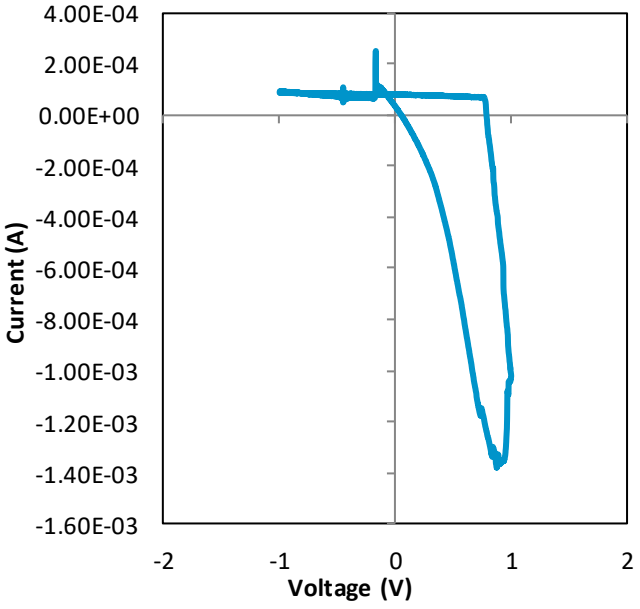

Fig. 11. Cyclic Voltammetry After the Addition of Feed and MB

Power characteristics and Stability play a key role in productivity of the Energy system. Stability, scientifically defines how long the systemcan generate power in a certain working environment. The power experiments conducted weren't temperature controlled resulting in variations of stability as evaporation of fuel takes place. Through experimentation the following results were obtained. Figure 11 depicts the cyclic voltammetry after the addition of feed and MB. From the figure it is evident that a redox peak is form, proving the presence of electrochemical activity.

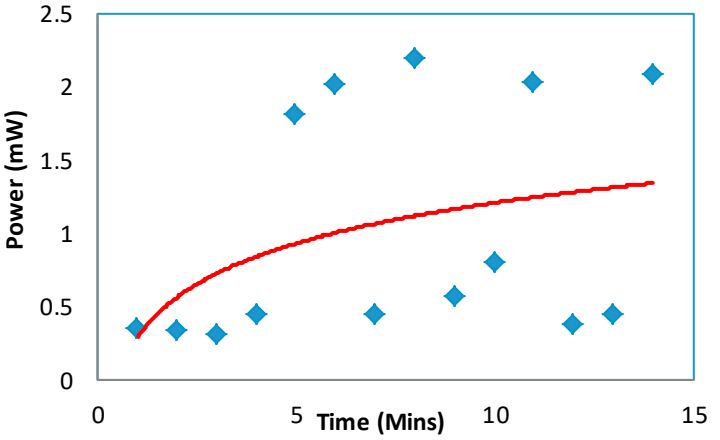

Fig. 12.Variation of EFC power with time

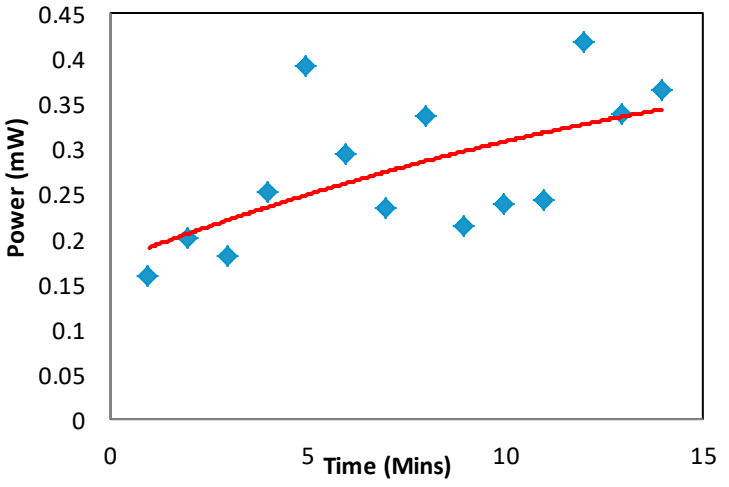

Fig. 13. Variation of MFC Power with time

4. Conclusion

The present work shows a potential method to generate electrical energy from sugars. Insight into optimizing the conditions in terms of temperature, growth of enzyme and immobilization of bacteria, was obtained A low power of around 0.35 milliwatts was obtained in the 5 cm^2 MFC and 1.5 milliwatts for the 5cm^2 EFC. This presents a very

cost effective and clean process of energy conversion.

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