Energy Output from a Dual Chamber Anoxic Biofilm Microbial Fuel Cell Subjected to Variation in Substrate Concentration

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The energy output of a dual chamber anoxic microbial fuel cell (MFC) subjected to variation in the substrate concentration was investigated. Wastewater from a primary clarifier effluent stream was used as the MFC inoculum. The power densities and efficiencies of the respective MFC operating cycles were obtained and analysed. The microbial growth in the anodic chamber was also quantitatively described via absorbance readings. A direct correlation between the closed-loop voltage output, substrate concentration and microbes were observed. The maximum voltage output increased with increasing substrate concentration from 66.6 mV at 2.78 mM to 96.4 mV at 5.56 mM, and this correlated with an increase in the microbial cells. Further increase in substrate concentration resulted in a decrease in the closed-loop voltage output by 46 % to 51.9 mV at 27.78 mM, with maximum power densities of 10.42 mW.m^{-2}. The decrease in voltage output is attributed to substrate inhibition. Secondly, at very low pH or acidic condition, microbial activities and metabolism was inhibited.

1. Introduction

Due to rapid increase in the demand for sustainable energy in the 21st century, there has been significant interest into the development and optimisation of energy generation processes that make use of zero emission energy sources as alternatives to non-renewable fossil fuels. The exhaustion of fossil fuels due to over usage in energy generation processes has been a major contributing factor to the negative environmental impacts associated with greenhouse gas emissions into the atmosphere. It is therefore imperative that feasible alternative technologies are developed to combat the negative impact of fossil fuel exhaustion. These technologies will also create adaptability in terms of sustaining the constantly increasing energy requirements of the population (Rabaey and Verstraete, 2005). Microbial fuel cell (MFC) technology is a prospective zero emission process, which links the inherent bioenergy contained in biomass to conventional electrochemical technology (Allen and Bennetto, 1993). Electrochemically active bacteria, known as exoelectrogens (Logan and Regan, 2006), are used to catalyse the direct conversion of organic substrates into electricity (Bond and Lovley, 2003). The anoxic environment created in the anode chamber of an MFC promotes the use of the anode as the only electron acceptor in the anaerobic oxidation of bioconvertable substrates. The electrons produced as a result of the anodic oxidation reactions are transferred to the anode and thus directed through an external circuit as electrical energy (Rabaey et al, 2007).

Substantial research has been focused on the optimisation of the power output produced by MFCs utilizing various culture and subtract (Mishra et al, 2017). In term of substrate concentration, studies have also shown that local palm oil empty fruit bunch generate a maximum power of approximately 0.7 W/m^2 (Nik Mahmood et al., 2015). In a different substrate study, 0.029 W/m^2 power density was generated from cassava peels (Adekunle et al., 2016). Further studies show limitation of power density utilizing glucose as substrate (Rossi et al., 2015). There are still challenges with MFC study, including those performed by Fan et al. (2007), that the intrinsic high internal resistance of MFCs results in significant power generation losses.

Various novel MFC architectures and design specifications have been developed to reduce the internal resistance to electron flow (Torgal et al, 2015). There is, however, conspicuously minimal literature regarding the inefficiencies due to substrate concentration and the relation of these inefficiencies to the conversion of the bioenergy stored in organic substrates to electrical energy. The objective of this study is to therefore investigate

the energy output and resultant inefficiencies of MFCs with identical internal resistances due to variance in substrate concentration. A dual chamber MFC was inoculated with primary clarifier effluent from a wastewater treatment plant.

2. Material and Methods

2.1 Microbial inoculum
Wastewater was obtained from the Daspoort Waste Water Treatment Works plant in Pretoria, South Africa. The waste water was collected from the primary clarifier effluent stream and stored in a cold room at 7 °C prior to use. The microbial growth in the anode chamber was measured using a spectrophotometer and recorded as respective absorbance values to quantitatively describe the extent of microbial growth for each experimental run. The idea of isolating inoculum from a wastewater treatment work was based on experiment conducted by Di Palma et al, 2015)

2.2 Substrate and Medium
Glucose was used as an organic substrate in a wide range of concentrations (2 – 28 mM) and the subsequent voltage generation of the cell at each substrate concentration was recorded to determine the difference in cell power generation. Distilled water enriched with the following chemicals, purchased from Sigma-Aldrich, was used to ensure culture growth, increased solution conductivity and neutral pH levels. Ammonium chloride (NH_4Cl), anhydrous monosodium phosphate (NaH_2PO4), anhydrous disodium phosphate ($Na2HPO4$), potassium chloride (KCl) and dipotassium phosphate (K_2HPO4). Trace metal and vitamin solutions were also obtained from Sigma-Aldrich.

2.3 Electrodes and MFC construction materials
The electrode material used was plain graphite rods obtained from the Carbon Materials research group at the University of Pretoria. The acrylic plexiglass sheets used to construct the MFC, including the adhesive glue (Magma-Bond C1), was obtained by the University of Pretoria.

2.4 MFC Configuration and operation
A dual chamber MFC design was chosen due to its simplicity and the ease of access to the required materials. As per the literature, it was of major concern to minimize the internal resistance of the cell and therefore an adjusted 'H-type' reactor design was proposed. Figure 1 depicts the top and side views of a single chamber in the cell design, noting that both the anode and cathode chambers are identical. The design allows for the electrodes to be positioned near one another in relation to the PEM. The flanges on each chamber are necessary for the joining of the two chambers. The interface between the two chambers was waterproofed by smearing petroleum jelly on each interface and then applying the PTFE sealant tape.
The membrane was inserted into the cell design as shown and the two chambers were then clamped together tightly at the flanges. The electrodes are 2 cm apart when installed. The electrodes were constructed from two graphite rods bound together by copper wire. Rubber tubing was attached to the gas product outlet ports and the ends placed in beakers filled with distilled water to ensure there was no oxygen leakage into the anode chamber via these ports. Rubber tubing was also attached to the sampling port, with the opposite end being connected to a syringe. Rubber tubing connected to an oxygen supply was connected to a port on the cathode chamber and passed down into the base of the chamber. Every orifice in the anode chamber, except for the sampling port which was sealed with a rubber stopper, was sealed with silicone sealant.

2.5 Experimental Run
All experimental runs were operated in a sequential batch process mode at constant at 30 °C. Two dual chambered MFCs designed having a total empty volume of 1,800 mL (12 cm x 12 cm x 12.5 cm) per cell. The two chambers of each cell were separated by a proton exchange membrane (Nafion 117, Dupont Co., Delaware, USA), having an exposed surface area of 12.57 cm^2. Each chamber was filled up with 1600 ml of respective medium and a varied initial glucose concentration, depending on the experimental run being performed. Experimental runs were performed at glucose concentrations of 0.5, 1, 2.5 and 5 g/L, with the initial run of 1 g.L^{-1} being replicated by both MFCs. A concentrated solution of the relevant glucose concentration was mixed with the media solution. Prior to inoculation, the anode chamber was purge with nitrogen gas to ensure an anoxic environment. The anode chamber was inoculated with the primary clarifier wastewater (10% vol\vol). The cathode chamber was continuously purge with 99 % oxygen to ensure oxygen availability at the cathode.
A digital multimeter with data logging capability (UNI-T, model UT61C) was connected over the resistor and subsequently recorded the voltage output of the cell every 16 min over the time span of the experimental run, storing this data on a PC. The recorded voltage output values (V) were used in conjunction with the resistance to calculate the current (I) and power (P) produced by the cell.
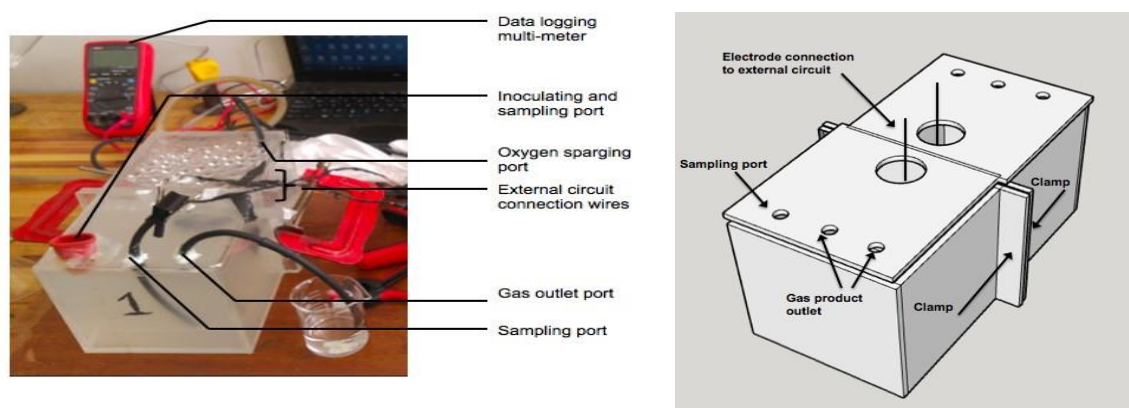
Figure 1: Fully assembled MFC with visible electrode connection

3. Result and Discussion

3.1 Preliminary experiment

The voltage generation for each MFC (MFC A and MFC B) over the operation cycle time with an initial glucose substrate concentration of 5.56 mM is shown in Figure 2. The experiment was conducted at neutral pH as indicated by Mahmood et al., 2017 with better MFC performance. In conjunction with the previously discussed variability of results obtained during MFC experimental research, Logan (2012) stipulates that the replication of results is essential to determine and observe the variability of the tested systems. It is noted that the initial time taken for the microbial communities to begin generating significant voltages is approximately 20 h in each respective MFC. MFC A achieved a maximum voltage output of 96.4 mV whilst MFC B achieved a maximum voltage output of 85.4 mV. There is a strong similarity between the performance of both reactors operating at the same operational conditions. The preliminary results obtained in the further experimental analysis were concluded to be viable.
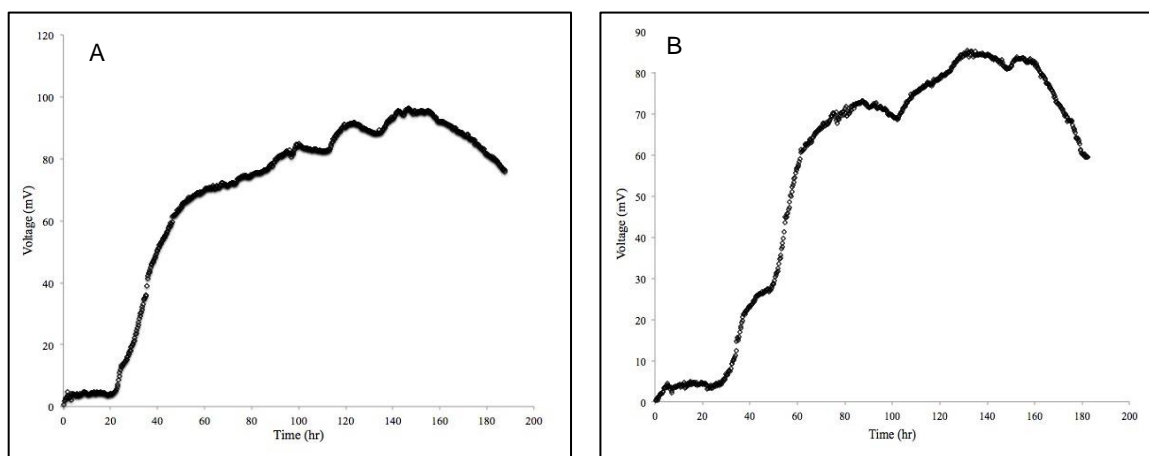

Figure 2: Voltage generation over the operation cycle time with each MFC having an initial glucose substrate concentration of 5.56 mM

3.2 Effects of substrate concentration on voltage output

Figure 3 a-d shows the evident that the absorbance values at higher substrate concentrations increase more rapidly while producing lower maximum voltages. At high substrate concentrations, the amount of fermentation products produced affect the anodic chamber environment and lower the pH (Fan et al., 2007). The acidity of the anodic environment inhibits the microbial metabolic reactions and thus decreases the maximum voltage output. Figure 3d depicts the lowest maximum voltage output of 51.9 mV but does not exhibit the rapid increase in absorbance as previously discussed. This observation is attributed to both the effects of increased metabolite concentration as well as substrate inhibition which decreases the rate at which the microorganisms can grow and form extracellular electron transport mechanisms.
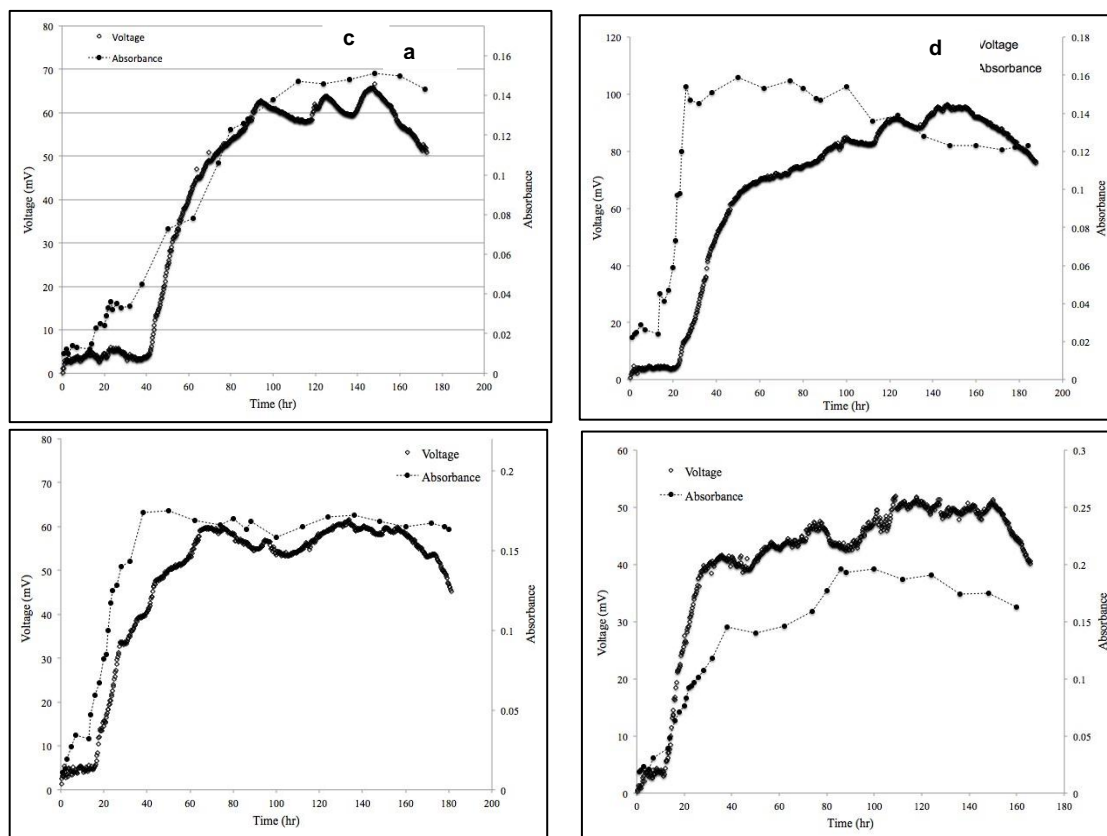
Figure 3: Voltage generation and absorbance in the anode chamber as a function of initial glucose concentration with a) 2.78 mM, b) 5.56 mM, c) 13.89 mM and d) 27.78 mM

3.3 Effects of substrate concentration on power density

Figure 4 indicate the overall effect of variation substrate concentration versus power density. At low glucose substrate concentration of 2.78 mM, low power output was observed, and this is attributed to insufficient substrate concentration to sustain microbial growth and metabolism. There was a lag phase at start off period resulting to zero power generation and power density. Though power density increases above 4.98 mW.m^{-2} after 40 h of incubation. A maximum power density of 10.43 mW.m^{-2} was seen when the glucose substrate concentration was increase to 5.56 mM whereas power density decreases to 4.26 mW.m^{-2} and 3.02 mW.m^{-2} when the glucose substrate concentration was increase to 13.89 and 27.78 mM. The decrease in power density is attributed to substrate inhibition which create unfavourable condition for the biofilm growth and metabolism.

3.4 Cathodic Fouling

Figure 5 depicts the fouling which occurred on the surface of the PEM which was exposed to the cathode chamber. The blue colouration of the membrane is due to the copper, which was attached to the cathode, being oxidised by the sparged oxygen and thus existing as copper oxide ions in the electrolyte solution. The copper oxide ions therefore contributed to the inefficiency of the cell as the proton exchange capability of the PEM was decreased by the fouling. This is an image of the PEM membrane after the conclusion of a MFC operation cycle. The blurred image is a result of a flash being used to enhance the blue tinge observed on the PEM. The blue tinge is attributed to the oxidation of copper in the cathode chamber to copper oxide.
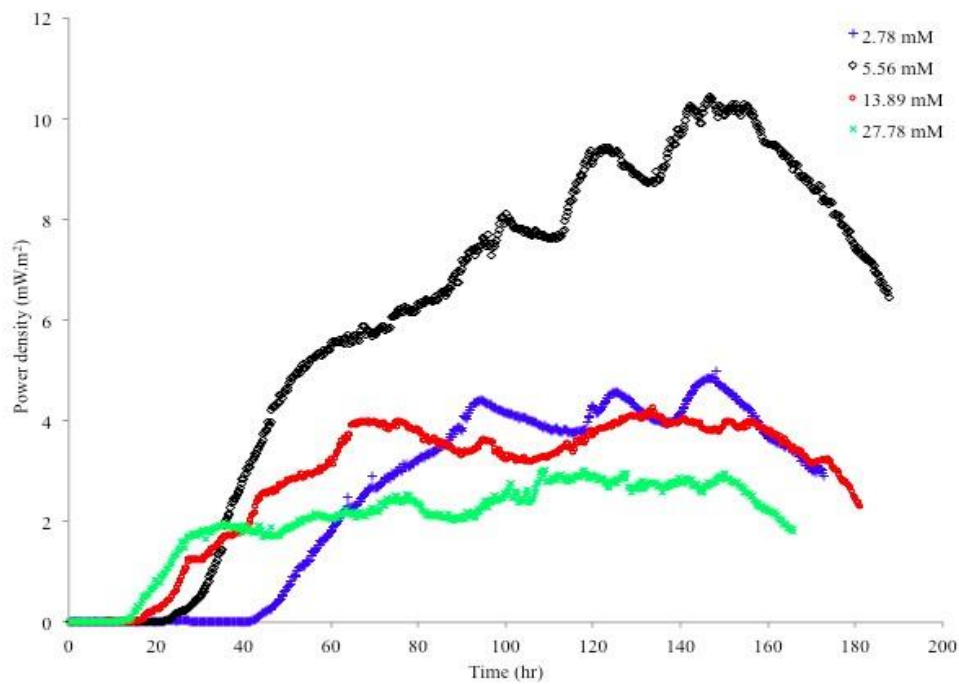
Figure 4: Power density over the operating cycle time for varied glucose substrate concentrations
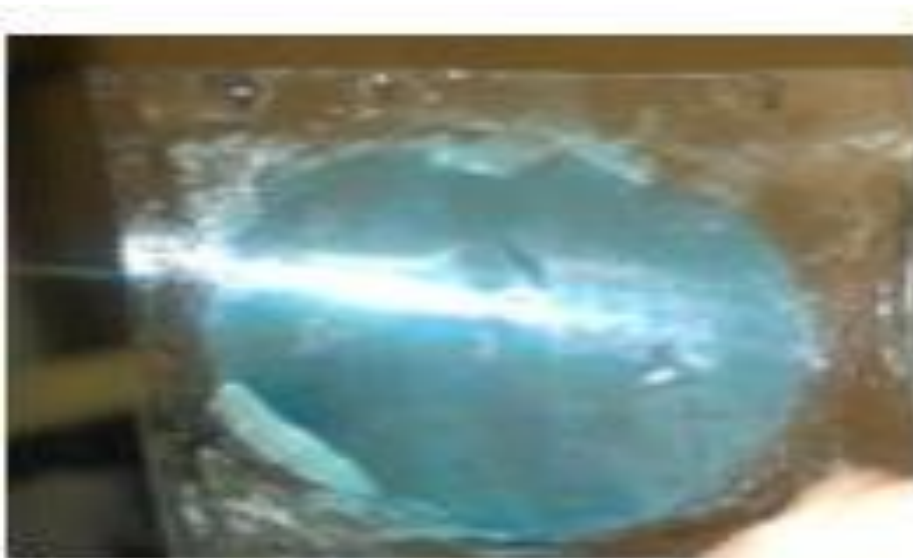

Figure 5: Fouled PEM after an operation cycle in an MFC

4. Conclusions

It is concluded that there are a multitude of inefficiencies and thus energy losses associated with substrate variation in dual chamber MFCs. The increase in glucose substrate concentration resulted in a maximum power density of 10.43 mW.m^{-2} at 5.56 mM glucose. Subsequent increases in substrate concentration led to maximum power density losses of up to 46 %, which are associated with an increase in the fermentation metabolites produced in the bioconsumption of the substrate. As a consequence of experimentally analysing the substrate variance effects, the batch procedure which was utilised did not allow for sufficient biofilm formation. A fed-batch analysis of the substrate concentration effects should be analysed in order to gain maximum insight into the

substrate concentration effects. The experimental setup used in the fed-batch analysis should ensure that copper is not exposed to the cathodic electrolyte or anolyte medium. This will reduce fouling and contamination of the PEM and media and hence increase the efficiencies of the MFC.

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