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Electrochemical Analysis and Polarization Pattern of Ekowe Clay-Pem Microbial Fuel Cell

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Abstract- ***Although fossil fuel has contributed significantly to industrial growth globally, there is need for a more sustainable alternative energy source. This study examines the electrochemical potential of microbial fuel cell (MFC) vis-à-vis cell polarization factors. Such factors include: pH, microbial community and count, external and external environmental temperatures, and proton conductivity of ion exchange membrane. The study found that change in pH and temperature of the anolyte, and proton conductivity of the proton exchange membrane (PEM) component have direct effect on the performance of microbial fuel cell in relation to power generation and wastewater clean-up. Observed initial decrease in pH of the anolyte from 6.5 to 5.5 favoured acidophiles in the microbial community and hence increased the voltage output. However, increase in pH equally increased the voltage output more significantly up to 9.5, an indication that the consortium is predominantly alkaliphiles. Change in internal and external environmental temperature equally affected the cell operation and useful life resulting in cell polarization. However, lagging of the cell external wall with cotton wool and aluminum foil controlled the temperature and hence stabilized the output. Electrochemical impedance spectroscopy (EIS) analysis of the PEM indicates that increasing the temperature of preparation of Ekowe clay increased its proton conductivity in MFC and hence increased the cell stability and useful life. This clearly suggests that MFC power output and polarization could be kept in check by controlling critical internal and external process factors.***

Index Terms- ***Microbial Fuel Cell, Proton Exchange Membrane, Bioenergy, Remediation, Cell Polarization***

I. INTRODUCTION

The need to diversify global economy has triggered wide-spread interest in microbial fuel cell (MFC) as a means of harnessing metabolic activity of microorganisms to generate electricity (Ghasemi et al., 2015; AlSayed et al., 2020). MFC is a hybrid biolo-electrochemical system with potential for wastewater clean-up taing place simultaneously with bio-electricity generation (Naha et al., 2023). MFC is made up of three basic components: the anode and cathode chambers, and the proton exchange membrane (PEM). Wastewater containing organic matter such as decomposing biomass, is fed into the anaerobic anode compartment where it undergoes biological degradation (Bazina *et al*., 2023). Metabolic activity of microorganisms on the organic matter releases electrons and protons in the anode chamber (Obileke *et al*., 2021). Electrons produced are transferred from the pili of microorganisms to the anode electrode. The anode materials provide nutrients to support the growth and multiplication of mcroorganisms. Study has shown that electricity was generated from MFC using Phragmitesaustralis (Reed plant) grown in the anode compartment (Shilpa et al., 2021). Electricity generation is achieved via flow of electrons through an external circuit. The cathode chamber is the aerobic reacting chamber containing oxidizing agent which reduces oxygen, thus completing the circuit.

Like voltaic and wet cells, microbial fuel cell (MFC) operation experiences gradual polarization due largely to direct effect of change in operating process variables such as overpotential at the electrode, anolyte pH (Puig and Colprim, 2010), temperature (Li *et al.,* 2013), type of microorganisms (Rismani-Yazdi et al., 2007), presence of redox mediators (Aldrovandi *et al*., 2009), anolyte concentration (Ghoreyshi *et al*., 2011), proton exchange membrane material (Liu and Logan, 2004), catholyte chemical potential (Mohan *et al.,* 2008), among others. All these factors affect electron transfer and power generation in MFCs. pH is an indicator of the level of acidity or alkalinity of the anolyte medium. Change in pH has a direct effect on the state, attachment, stratification and functioning of the microbes present in wastewater (Li *et al*., 2021). While some microorganisms are acidophilic, others are either alkaliphilic or neutrophilic. These specific characteristics affect the rate of microbial degradation function and hence the magnitude of bioelectricity generation from the cell. The type and concentration of organic matter can equally affect acid production

and pH changes. Electrode materials and cell design could equally influence electron transfer mechanism, proton release, and pH changes. Operating conditions such as temperature, hydraulic retention time also impact microbial activity, acid production, and pH changes. These variables affect the performance of MFC since the electrochemical activity of the microbes in the anode chamber partly depends on the operating pH of the medium. Based on the operating pH of the anolyte, anaerobes are classified into; acidophilic (pH < =2.0) (e.g Archia, Eucharya, bacteria *(e.g Acetobacter aceti, Thiobacillus prosperus, T. acidophilus)*), neutrophilic (e.g *Eschericha coil*) and alkaliphilic (pH 8.5-11) (e.g *Natronomonas pharaonis*) and extremophilic (e.g *chlorophlexus aurantiacus*). A research study by Zhang *et al*. (2012) indicates that there was a significant decrease in the anodic pH from 6.23 to 4.35 over time during the operation of MFC with attendant effect of decrease in cell performance leading to gradual drop in voltage performance termed as polarization.

Electrochemical analysis is a crucial tool for understanding the behavior and performance of microbial fuel cells. Certain electrochemical analysis techniques provide valuable insights into the performance and behavior of MFCs, including; electron transfer mechanisms, microbial activity and biofilm formation, electrode material type and surface properties, internal resistance and ohmic losses, power output (current and power densities) and wastewater treatment efficiency. MFC irregular power development pattern shown by its lack of repeatable and predictable behavior is a major concern that necessitates the development of a supporting device for energy regulation storage (Serra *et al.,* 2020).

By applying these techniques, researchers and engineers can optimize MFC design and operation, improve performance, and scale up the technology for advanced practical applications. Some common electrochemical analysis techniques used to evaluate MFCs include: Cyclic Voltammetry (CV). CV is used to study the electrochemical reactions including oxidation and reduction reactions occurring at the anode and cathode respectively. Linear Sweep Voltammetry (LSV) is also a similar technique to CV but uses a linear potential sweep instead of a cyclic one. Chronoamperometry (CA) technique measures the current response of the MFC to a potential step. Similarly, electrochemical impedance spectroscopy (EIS) is used to study the internal resistance, PEM proton conductivity, and electrochemical processes occurring within the MFC. For instance, the EIS of Ekowe clay used as a medium for proton exchange in MFC shows downward trend with increase in preparation temperature (Obasi *et al*, 2024). Tafel analysis is used to study the kinetics of the electrochemical reactions occurring at the electrodes. Due to unstable nature of biodegradation processes power production appears irregular. Polarization curves are used to study the relationship between the working voltage and current produced by the MFC over time (Simeon *et al*., 2020). Polarization is a consequence of unfavorable cell limiting factors that develop with cell operation. Power density curves are used to study the relationship between the power output and current density of the MFC.

In this study, the cell polarization pattern was monitored and controlled by lagging to mitigate the effect of change in temperature. The application of aluminum foil and cotton wool around the external walls of the reactors helped to maintain fairly constant temperature throughout the experimental period. In general, all MFC processes that cause potential losses such as ohmic, activation and concentration losses result in decreased cell performance. Polarization curves were used to characterize the cell efficiency with respect to electrical power generation (Serra *et al.,* 2020). The cell voltage generation was measured against measurable operational parameters to determine their effect on cell performance with respect to power generation and wastewater clean-up.

II. MATERIALS AND METHODS

Materials: Materials procured and assembled to produce each dual chamber MFC in this study include: Ekowe clay (EKc) , bio-and chemical reactors (PVC cylinders), flexible wires, PVC pipes, variable and standard resistors, digital multimeter (DT-830-L), human urine, Nutri-Yo Yogurt, potassium ferry cyanide, sodium chloride, phosphate

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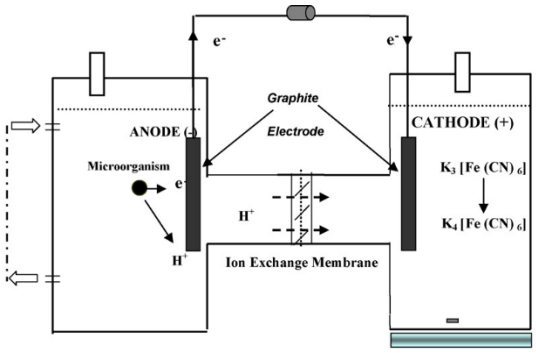
buffer (PBS), muffle furnace, thermometer, Hanna pH meter-M12151.NaCl, $C_6H_{12}O_6$.

Method: The approach employed in the design and construction of MFC (a living battery) to achieve the objective of this study was essentially experimental. The EKc-PEM MFC type of choice was the dual chambered mediatorless H-type design run on a batch mode (Figure 1). Non-mediated electron transfer (NMET) implied that no chemical mediator was applied.

The cell experimental set-up involved a step-by-step systematic approach aimed to guarantee process reproducibility. The anode and cathode chambers were cylindrical plastic bio- and chemical reactors of equal volumes, each lagged with cotton wool and aluminum foil to maintain a relatively stable temperature throughout the experimentation period. The dimensions of each reactor were: diameter (0.12m), depth (0.17m) which gave a working volume (v = 0.0013m^3). Each reactor was placed adjacent to each other on a flat surface. The chambers were kept at 0.08m distance from each other. A hole of diameter 0.054m (1inch) was bored on each of the walls of each reactor at approximately half way up the height of each. A 1-inch diameter PVC pipe of length 0.08m was cut and placed end-to-end on the curved surface area of the two cylindrical tank reactors to fit into the holes. The two ends of the membrane pipe were fitted with rubber gasket and sealed properly with PVC gum to the external walls of the reactors to prevent leakage. An amount of water equivalent to the volume of each reactor was poured into each chamber. This was allowed to stand for about four hours to rule out any possibility of leakage. A selected proton exchange membrane (PEM) (Ekowe clay mixed with 5% carrageenan) paste was charged into the connecting pipe. Both ends were thereafter sealed with cellophane or gum to limit water access and so keep the water content of the PEM fairly constant. The PEM (salt bridge), which ideally and selectively allows the exchange of protons (H^+) from the anode chamber into the cathode chamber, not oxygen or the substrate materials.

Schematic diagram



Experimental set-up

Fig. 1 Schematic and Experimental set-up of a dual chamber microbial fuel cell

A circular hole was created at the centre of each circular lid that would just be enough to pass a carbon rod. A graphite carbon rod was inserted through each of the holes and sealed properly. The anode chamber was filled up with the required human urine proteinated with nutri-yo yogurt and the lid sealed properly to avoid oxygen or air access. Study shows the microbial composition of yogurt consists of *Lactobacillus delbrueckii subsp*., *Bulgaricus* and *Streptococcus* thermophiles which primarily functions to ferment milk to produce lactic acid (Farinde *et al.,* 2009). Yogurt proteination was aimed at making it more bioavailable, reduce toxicity to enhance microbial activity.

With the aid of a syringe and needle, the anode chamber was inoculated with an activated sludge solution (2ml). A solution of an oxidizing agent that serve as electron sink (0.1M $K_3Fe(CN)_6$ was prepared and poured into the cathode chamber. The cathode chamber was kept fully aerated. The projected part of each carbon rod made direct contact with the liquid

content of each chamber/ reactor. Two flexible wires each of length 10cm was soldered onto the terminal of each graphite carbon electrode. 100Ω external resistor was connected between the two free ends of the wires. Each end of the wires was connected at intervals of 24 hours to the terminals of a digital multimeter to read-off the open-circuit potentials and current generated by the cell. Each batch-operated cell set-up was run for 30 days.

The study specified and fabricated a dual chamber microbial fuel cell using stabilized Ekowe clay as a medium of proton exchange. A careful assembly of individual components for each cell unit: a bio-reactor (Anode chamber), a chemical-reactor (Cathode chamber), an Ekowe clay proton exchange membrane (PEM), 100 Ohms resistor, flexible wires, multimeter. Urine mixed with nutri-yo yogurt was fed into the bio-reactor. A mixture of 5g each of NaCl and $C_6H_{12}O_6$ (glucose carbon source) was added. 0.1M Potassium ferry cyanide solution in the chemical reactor served as the cathode. A 24-hourly periodic laboratory test indicated a downward trend in wastewater parameter changes.

III. RESULTS AND DISCUSSION

Polarization in a microbial fuel cell (MFC) refers to the loss of voltage due to various internal and external factors. Here are some common causes of polarization in MFCs: Activation polarization occurs due to the energy required for microbial metabolism, electron transfer, and electrochemical reactions. Ohmic polarization is caused by the internal resistance of the MFC, including the resistance of the electrodes, electrolyte, and connections. Concentration Polarization: This occurs when the reactants (e.g., organic matter) are depleted at the anode, or the products (e.g., electrons) accumulate at the cathode. Mass Transport Limitations: Insufficient mass transport of reactants, products, or microorganisms can lead to polarization. Electrode Material and Design: The type and design of electrodes can affect the polarization behavior of MFCs. Microbial Community and Biofilm: The composition and activity of the microbial community, as well as the formation of biofilms, can influence polarization. Operating Conditions: Factors such as temperature, pH, and hydraulic retention time can impact polarization.

Overpotential in microbial fuel cell is the extra voltage required to drive an electrochemical reaction above its theoretical equilibrium potential resulting in excess energy requirement for the process. Overpotential is a major factor affecting the performance of the cell. Activation Overpotential: occurs due to generation of voltage used to overcome the activation barrier of the anodic reaction due to activity of microorganisms. There is a tendency for voltage drop referred to as Ohmic overpotential from the effect of internal resistance of the anolyte and the electrodes.
Concentration overpotential is the voltage drop due to the concentration gradients of reactants and products at the anodic biofilm which can hinder the reaction rate.

MFC development has been established around the optimization of power generation and energy efficiency (He *et al.*, 2007; Huang and Logan, 2008). Energy output can be recorded as current and voltage alongside computation of current density and power density which is graphically represented as polarization curve. The trend of the power curve is essentially dependent on the hydraulic retention time of the bioreaction process.

3.1 Electrical analysis models

Power density: MFC power density is the relationship between the produced power and the anode surface area or chamber volume. This parameter is used to compare power production efficiency of different MFCs systems (Franks and Nevin, 2010). Power density depends majorly on the electrode used as its surface has great influence on bacteria attachment and activity. The power density P, (mW/m^2 or mW/m^3) was calculated using the expression in Equation (1).

$$C = \frac{Current\ \ produced\ \ (mA)}{Surface\ \ area\ \ of\ projected\ \ anode\ \ (m^2)} \quad (1)$$

Current density: The current density is normally recorded as current produced per unit surface area of projected anode. This helps in the measurement of the effectiveness of the MFC unit based on current generation. The expression for the current density is as presented in Equation (2) (Huaining, 2009)

$$C = \frac{Current\ \ produced\ \ (mA)}{Surface\ \ area\ \ of\ projected\ \ \ anode\ \ (m^2)} \quad (2)$$

3.2 Polarization factors

Concentration overpotential: Change in concentration of substrate, microorganism, and electrolyte is crucial for stable and efficient MFC operation and optimal performance (Ullah and Zeshan, 2020). The initial spike in cell output could be attributed to high substrate concentration which led to enhanced microbial growth and activity, increased electron transfer rates, and hence improved power density output. At 5ml of 0.1M NaCl added to the anolyte there was an increase in power output. This may be due to improved conductivity and ionic strength of the solution due to increase in charge density, which could have enhanced electron transfer to the anode (Miyahara et al., 2015). Care was equally taken not to increase salt concentration beyond moderate levels (>10 g/L) so as not to decrease power output due to inhibition of microbial growth and activity, as well as the increased osmotic stress and electrochemical losses. Overpotential due to effect of concentration and half-reactions at the anode evidently set in cell polarization due to depletion of charge-carriers (negative ions – electrons) coupled with the formation of hydrogen bubbles thus resulting in electrical impedance and *ohmic loss* at the electrode. This loss incidentally slows down the rate at which the charged carriers would reach the electrode. Equally, the release of CO_2, CH_4, H_2S, and NH_3 from anaerobic microbial activity contributes to electrical impedance at the anode surface and eventual potential drop. On the overall, the Ohmic power loss at the anode is therefore caused by the difference between the concentration of the charge-carriers at the electrode surface and the bulk solution (electrolyte). Also, initial high microorganism concentration could have led to enhanced biofilm formation and electron transfer, and improved power density. Excess proton (H^+) when librated into the anolyte has a tendency of decreasing the pH of the medium. This increase in pH consequently lowers the activity of the micro-organisms especially the alkaliphiles and neutrophiles, whose activity is usually hampered by an acidic medium as explained by the ractions:

$$2H^+ + 2e^- \rightarrow H_2$$

$$H_2O + CO_2 \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+$$

$$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O$$

Polarization curves

MFC polarization occurs due to processes that characterize fuel cells as evident in the decline in the cell power performance. Polarization sets in in MFC due to several limiting factors such as Ohmic, activation and concentration over potentials (Rahimnejad *et al*., 2014). It is a way of quantifying the behavior or performance of microbial fuel cell. The MFC polarization curve (Figures 2 and3) is a graphical representation of the cell voltages recorded and its correlation with the density of current (I_d) as calculated using Equation (3). This curve is used in the analysis and characterization of the MFC (Huaining, 2009). The curve data is collated from the record of MFC system parameter and computed based on Ohms law. The parameters of current and the corresponding voltages are used to produce V-I data and the V-I plot. Also used for MFC performance analysis is a plot of current and power density as calculated using Equations (3) and (4) against time on the same graph.

$$I_d = \frac{I_{gen}}{A_{anode}} \quad (3)$$

$$P_d = \frac{I_{gen} V_{gen}}{A_{anode}} \quad (4)$$

where I and V are current and voltage generated measured with digital multimeter; A is the surface area of projected anode.

MFC performance curve determines the point where the maximum (peak) power generation occurs in a

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power generation process (Simeon *et al*., 2020). The power curve presented in Figures 2 and 3 show the power performance characteristics of MFC operating with Ekowe clay PEM. The power generation in the cell during start-up was low, but increased with the progress of time to a peak value P due to exponential growth and multiplication of electrochemically active bacteria in the anolyte medium. A period of relative power stability preceded cell polarization. During polarization process, the current and voltage output gradually winds down due primarily to, activation, Ohmic, mass transfer and concentrations losses (Simeon *et al*., 2020), and increased solution resistance due to decrease in solution conductivity (Babanova *et al*., 2019). In addition to nutrient depletion, there is a gradual build-up of higher internal resistance in the cell which also contribute to voltage drop and eventual cell polarization. There was increase in the growth of biofilm on the anode surface which constitutes some form of resistance to the transfer of electron from the external layer of the biofilm onto the anode and hence hampers power generation in the cell (Wang *et al*., 2009).

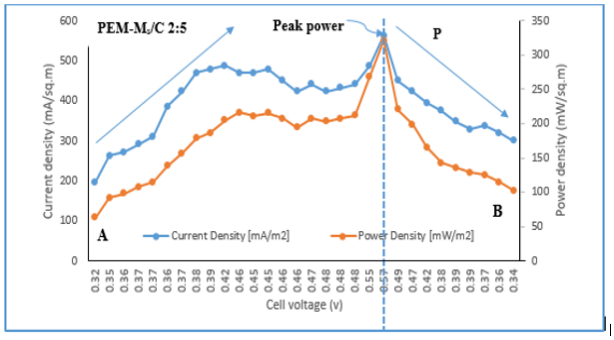

Fig. 2 Plot showing power and current densities against cell voltage

Change in anolyte temperature: The temperature of anolyte medium is one of the physical factors that wield enormous influence on the performance of MFCs as it directly affects the microbial degradation activity. In addition, power density generated is also affected by the temperature condition of the anode. Bacteria are known to be naturally facultative (sensitive to changes in environmental conditions). The rate of microbial activity and hence power generation usually increases in thermophilic anolyte conditions (50-55^{o}C) compared to psychrophilic (cold temperature) or mesophilic conditions (35-40^{o}C) (Malekmohammadi and Mirbagheri, 2021). In line with the contribution from Gadkari *et al*. (2020) there was a significant drop in the MFC power performance at higher temperatures due to drop in microbial activity. This is shown in the undulating pattern of the power curves (Figures 2 and 3). The rise and fall in environmental temperature affected the activity of microrganisms in the anode. Lagging materials applied caused a relatively stable production output over time before cell polarization due playout of other dominant factors. Hence the cell temperature need to be controlled within the upper and lower limits for optimum cell performance.

The power curve (Figure 3) showing power density as a function of cell voltage and current density for MFC without lagging material (A) and lagged cell (B). Figure 3(A) shows the initial spike in voltage up to the 10th day of cell operation. The peak power and current densities generated were 223.7mW/m^2 and 187mA/m^2 respectively. Polarization set in thereafter as shown by the steady decrease in voltage output over time. Conversely, cell in Figure 3(B) shows the effect of lagging on the microbial activity of the cell as evidenced by the relative power performance stability of the cell with time. This stability could be attributed to the reduction in voltage loss due to uniform cell biocatalytic and chemical reaction temperature thus removing the effect of concentration overpotential and unstable microbial activity.

Polarization curve presented in Figure 4 pictures the stage-wise processes that led to the cell exhaustion. This process is described by four sections of the curve, namely; the voltage drops due to fuel cross-over (A-B), rapid voltage drops (B-C), Ohmic loss (linear drop) (C-D), and concentration or mass transfer loss (fast drop) (D-E). The slope of the linear voltage drop section (C-D) due to Ohmic loss calculated from $^{dv}/_{dI}$ gives the cell total internal resistance (R_{int}) of 2.245Ω. This value was lower than the values in the range of 12.21 and 12.78Ω proposed by Manohar and Mansfeld, (2009).

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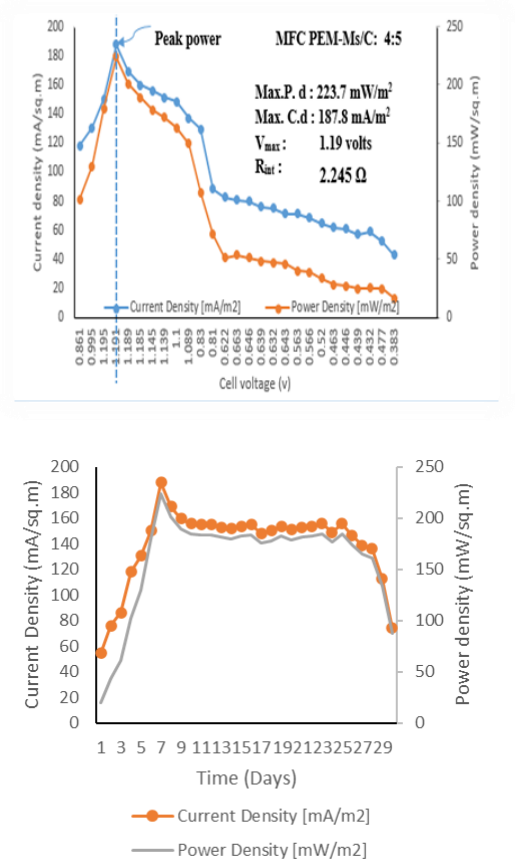

Fig 3 Plot of current and power densities against time for non-lagged cell (A) and lagged cell (B)

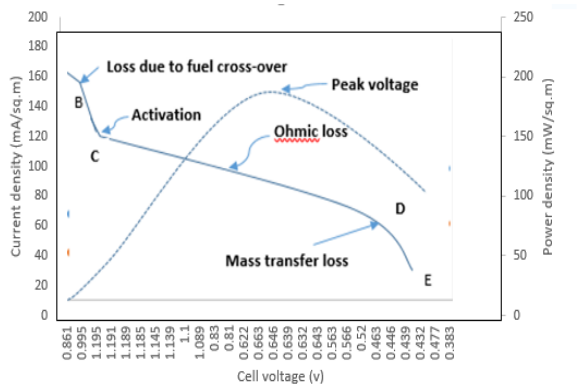

Figure 4. Polarization curve featuring activation, Ohmic and mass transfer losses.

Catholytic Reaction Effect

The catholyte used in the study was one prepared with 0.1M potassium ferrycyanide (0.1M $k_3Fe(CN)_6$ (molar mass: 329.24g/mol) solution (standard reduction potential, E^o =+0.43v), an oxidizing agent that provides ferrycyanide ion ($Fe(CN)_6^{3-}$) to accept the electrons at the cathode (Haslett, 2012). The chemicals were standardized according to the official method of analysis illustrated by Association of Official Analytical Chemists (AOAC, 2010). Upon acceptance of electron during cell operation, the ferrycyanide reduces to ferrocyanide, $Fe(CN)_6^{4-}$. It is important, however, to mention that as an alternative to ferrycyanide, potassium permanganate ($KMnO_4$) (E^o = +1.71v) could also be used in the cathode chamber as electron acceptor. Ferrycyanide with a lower electrode potential has advantage of producing higher Gibbs free energy for bacterial electrogenesis over permanganate with higher electrode potential derived from Nernst equation:

$$(\Delta G^o = E^o_{Anode} - E^o_{Cathode}).$$

According to a review by Ucar, Zhang and Angelidaki (2017), the major drawback in using ferrycyanide is that it is toxic and would need to be replaced as soon as it gets depleted due to reaction. The effect of this attribute is linked with the cell polarization. However, ferry cyanide is chosen due to its high solubility, stability, relatively low overpotential with attendant effect of faster rate of reaction which cumulatively translate to improvement in power generation in MFCs. Reduction reaction of the catholyte applied in the cathode chamber during cell operation raises the potential of the anode, though not above the potential of the solution specie. The difference in potential between the anode and the cathode is the major driving force that causes electron flow. The cathode chamber is fully aerated by passing air through an open ended plastic pipe of 0.5cm internal diameter. This is necessary so as to make oxygen, a high oxidation potential substance (Shanmuganathan *et al*., 2018) available to the cathode for reaction with reduced protons (2H) at the end of the oxygen transport chain to produce water (Barua and Deka, 2010). Graphite rod cathode was fixed firmly at the chamber lid with a non-conductive epoxy glue and suspended in the catholyte medium to provide the means of electron

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transfer into the catholyte for reduction reaction (electron sink). This was kept constant for all the cells throughout the experiments. Catholyte concentration can impact ion transport and conductivity, electrode potential and performance, and hence overall MFC efficiency.

Effect of anolyte pH

pH is an expression of the degree of acidity or alkalinity of the substrate sample in the anode chamber. The pH of a microbial fuel cell (MFC) changes over time. The direction of pH change depends on various factors. The initial decrease in pH usually observed during cell operation occurs as a result of acid production as end product of microbial metabolic activity. Microorganisms in the anode compartment break down organic matter, producing weak acids such as acetic, propionic, and butyric acids. This can lead to a decrease in pH. Also, as electrons are transferred from the microorganisms to the anode, protons (H^+) are released, contributing to a decrease in pH. The modified proton conductivity of Ekowe clay improved proton (H^+) transfer to the cathode chamber to keep the pH in check and hence stabilize the cell performance. Over time, the pH increased. This was due to alkalinity generation. As microorganisms in the cathode compartment reduce oxygen, they consume protons (H^+) and produce hydroxide ions (OH-), leading to an increase in pH. Also, the electrolyte solution in the MFC could have had a buffering capacity, which helps to neutralize pH changes over time. As shown in Figures 5, the initial pH value of 6.5 decreased to 5.5 during the first ten days and thereafter increased to 9.5 over a 30 day period. Correspondingly, the power density generated increased initially until a peak value of 223.66mW/m^2 was reached on the 10th day, thereafter the power production declined gradually with increase in pH. The power performance was better at higher pH than at lower pH (increasing acidity).

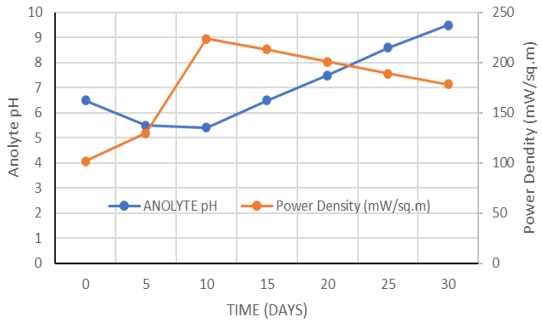

Figure 5. Plot of changes in operating pH with time during MFC operation

The drastic reduction in power performance by adjusting the pH higher than the optimum value for an MFC system with respect to power generation and COD removal have been found to impart negatively on the cell performance due to its lethal effect on the exoelectrogenic anodic bacteria (Puig and Colprim, 2010). According to the study, the power production of 0.66Wm^{-3} was achieved at pH of 9.5, while an improved power performance of 1.8Wm^{-3} and COD removal of 77% was achieved at optimum pH (close to neutral). The variation in the pH are often associated with a number of internal factors such as: release of waste product of bacterial digestion activity, release of protons (H^+) from electrochemical activity, the reaction of released protons and carbon (iv) oxide from anaerobic oxidation to produce week inorganic acid. To stabilize the solution pH, drops of aqueous acid (HCl) and alkali (NaOH) are usually added, or get the medium buffered with phosphate buffer solution (PBS), a mixture of potassium dihydroxyhotophosphate (KH_2PO_4) and dipotassium hydroxyhotophosphate (K_2HPO_4).

Research by Raghavulu *et al* (2009) indicated that the facultative nature of anaerobes directly affect the performance in MFC. Acidophiles (pH 6) are best in electrogenic performance compared to neutrophiles (pH 7) and alkaliphiles (pH 8), while substrate degradation (COD removal) is highest with neutrophiles (pH 7) followed by alkaliphilic and acidophilic conditions.

On a general note, the relatively low voltage generated in MFC running on wastewater was due to increase in the amount of ions with attendant positive effect on its dielectric permittivity and change in

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medium pH. It can be recalled that these parameters affect the amount of surface charges on the particles and hence increase the rate of particle coagulation according to the following empirical Equation (8) (Bello, Hamam, and Djouani, 2014).

$$\sigma = \left[\left(\frac{2}{\pi}\right) n\varepsilon kT\right]^{\frac{1}{2}} \sinh 1.15(pH_0 - pH) \quad (8)$$

Where σ is surface charge (SC), k= boltzman constant, T= temperature, ε = relative dielectric permittivity, pH_0 = pH at point zero charge and n = ionic strength.

This equation shows that surface charge depends on the temperature and change in pH of the anolyte.

3.3 Electrochemical Impedance Spectroscopy (EIS) ANALYSIS

To investigate the effect of thermal modification of Ekowe clay at various temperatures on its capacity to function as proton conductivity of proton exchange membrane in a microbial fuel cell using electrochemical impedance spectroscopy analytical technique. EIS analysis shows a decrease in value of electrical impedance with increase in preparation temperature and hence a corresponding increase in proton conductivity (Table 1).

Table 1. Results of Electrochemical Impedance spectroscopy analysis of Ekowe clay samples at different temperatures

Sample	Impedance (Ohm g^{-1})	Proton conductivity ($S.cm^{-1}$)
Ekc $_{25^oC(room\ temperature)}$	3.1	2.3096
Ekc $_{500^oC}$	1.7	3.9283
Ekc $_{600^oC}$	1.4	4.7139
Ekc $_{700^oC}$	1.3	5.9924
Ekc $_{800^oC}$	1.0	7.1708

MFC Cost implication: Table 2 presents the summary of economic assessment of the MFC produced. The total cost of production of ten (10) units of dual chambered MFC was N76,700 at N7,670 per unit. It has been established that several unit cells in series boost the overall power generation. The low labour and annual operating costs indicate low overall production cost and increase in return on investment. This trends therefore justifies more investment in this technology to expand the frontiers of renewable energy production. Due to low energy performance of MFC currently, an efficient energy storage system could be developed to store the produced electrical charges in batteries and capacitors for higher applications. Charge storage device attached to the connections could maximally boost the power output of MFCs.

Table 2 Cost of raw materials for a unit dual chamber MFC construction

MFC reactor materials	Cost (NGN)	Initial investments associated with each component (NGN)	
		unit	Ten units (MFC)
Cylindrical bioreactors (2)	2,000	2,000	20,000
Potassium ferrycyanide (500g)	8,500	170	1,700
Phosphate buffer solution (PBS)	3,500	200	2,000
Sodium Chloride (500g)	6,000	300	3,000
Sodium bicarbonate (500g)	6,000	300	3,000
Resistance box (100 Ohms)	3,500	3,500	35,000
Flexible wires(1 rolll)	3,000	200	2,000
1” PVC (pipe) length	7,000	400	4,000
Cell electrodes (anodes and cathodes)	600	600	6,000
Initial investment capital	40,110	7,670	76,700

IV. CONCLUSION

Basically, the value of power density obtained in microbial fuel cell is a direct consequence of the circuit potential difference between the anode and the cathode. However, the theoretical amount of power that is possible during cell operation depends on the potential difference between the chemical potential energy consumed due to microbial activity of microorganism (which act as biological catalyst) at the anode and the reduction reaction in the cathode chamber. The drop in power density, referred to as cell polarization, is as a result of high internal resistance and overpotential at the electrodes. However, in order to improve the power density generation in MFC, effort should be made to ensure that (1) the absolute value of potential of the cathode is as close to that of the chemical potential of the anode reaction as possible, (2) the potential of the cathode should be as close as possible to the reaction potential of the catholyte (electron acceptor), (3) the tendency for overpotential due to gas build up and the anodic internal resistance should be kept under control, (4) the electrode applied should be made of materials with high electrical conductivity in order to reduce ohmic loss to the barest minimum, (5) due to unsteady nature of microbial decomposition activity, energy produced should be stored in supercapacitors for higher applications. The unstable nature of microbial activity usually occasioned by variation in environmental temperature was controlled by lagging. MFCs offer a promising technology for sustainable energy production, wastewater treatment, and bioremediation.

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