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IONIC SALTS ENHANCE THE PERFORMANCE OF MICROBIAL FUEL CELL

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ISSN 0976-3104



ABSTRACT

Background: World is currently facing energy crisis due to the rapid exhaustion of the fossil fuel based energy sources, and are also major cause of Greenhouse Gas emissions which are known to be the cause of detrimental global warming, thus the current surge in search of alternative energy such as biofuels. Microbial fuel cells (MFCs) are biofuels based on electrochemical process that use microorganisms to generate current by direct or mediated electron transfer to electrodes. Despite the promise of MFC as future alternative energy, it suffers some setbacks including high production cost, low voltage generation. Improving the performance of MFC, require our comprehensive understanding of operational parameters of the fuel cell. In this study, the influence of different types of ionic salts (KCl, NaCl, NaOH and KOH) bridges on MFC performance operated using wastewater samples was studied. **Methods:** A two chambered microbial fuel cell was constructed, and the ionic salts bridge was fabricated 5g of salt in 0.02g/ml nutrient agar to form the bridge. **Results:** The results recorded shows that highest MFC power density (10.12 mW/m²) was found in MFC with KCl salt bridge and lowest (1.32mW/m²) was observed in MFC operated with NaOH salt bridge. In the same vain, corresponding maximum voltage (447mV) and lowest (110mV) were observed in MFC operated with salt bridges of KCl and NaOH, respectively. **Conclusion:** The study has demonstrated the importance of salt bridge optimization which is central in improving MFC performance, increased yield and production cost reduction for wider deployment.

INTRODUCTION

One The current global energy crisis due to the rapid exhaustion of the fossil fuel based energy sources and production instability, insecurity with coupled with emission of greenhouse gas has called for legislations and directives such as the Kyoto Protocol with the goal of reducing greenhouse gas emissions by at least 18% below the 1990 levels by the year [1]. The current logarithmic global population growth has incurred increase in industrial activities consequently, warranting the recent surge in energy consumption thus, resulting in environmental pollution and economic difficulties as well as epileptic power supply. Additionally, the current insecurity that exists in the oil producing nations has resulted in dwindling gas supply to power stations due to vandalism of the oil pipelines. This warranted the renewed research interests on sources of alternative energy [2-4]. On this note, advances in renewable energy research have led to the production of clean and sustainable energy such as biofuels from microalgae [5, 6], and biofuel from biomass [7]. Other research scenario, studied the technology involve in reactor design for biofuel production, specifically biodiesel [8].

Ever since the reported electron shuttling ability of some bacteria by MC Potter in 1911[9], research on the electrogenesis of certain bacteria using waste and renewable biomass has gained impetus [10, 11]. Bioelectricity is a renewable bioenergy produced from biofuel microbial cells thus described as microbial fuel cell (MFC). This particular fuel cell is a bio electrochemical system that has the ability to harness electrons produced from metabolic activities of microorganisms, thus generating electrical current [12]. Typical MFC consists of anode and cathode compartments separated by a proton exchange membrane in a double-chambered setup [10]. Nafion™ and Zirfon are some examples of proprietary proton exchange membranes commonly used in MFC. The system functions when microbes in the anodic chamber oxidize the added substrate and generate electrons and protons via bioredox reaction, thus producing carbon dioxide as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the biomass originally comes from the atmosphere. The electrons are absorbed by the anode and are transported to the cathode through an external circuit, whereas the generated protons cross the proton exchange membrane, and enter the cathode chamber where they combine with oxygen to form water [13]. The generation of electric current is made possible by keeping microbes separated from oxygen or any other end terminal other than the anode and this requires anaerobic anodic chamber. The most obvious use of the MFC is to generate electricity. They can be utilized in rural and urban sectors [14]. Though the electricity produced in fuel cells is not that efficient in small scale but large scale can be efficient, especially when coupled with water treatment process. Low power wireless systems can also be powered using MFC [15]. There has been reported study of using MFCs utilizing body glucose as carbon source to power medical implants [16-18]. In developed countries, MFCs are used in wastewater treatment and most beneficial is that with the treatment, one can actually harness the electricity as well. It produces lesser solid waste from the process, and the electricity produced can be used in aerating the sludge so it can be a self-powered treatment facility. This reduces the cost of electricity generation. Unlike conventional water treatment process, the MFCs combined process is reported to completely break down most of the acetate to carbon dioxide and water [19].

KEY WORDS

Biofuel, Bioelectricity, MFC, MEC, BES, Microbial fuel cell

Received: 25 Jan 2021
Accepted: 23 May 2021
Published: 12 June 2021

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The microbial fuel cell is now seen as a cost effective development solution for developing countries. Reports from international organizations argue that renewable energy is on its way to become more affordable than fossil fuels [13]. Whilst significant literature is available on the power produced in MFC, its low power generation and high production cost remained major causes of concern hence, limiting its large-scale applications [12]. For example, Nafion membranes are well studied for their application in MFCs [20]. Nafion is reported to exhibit high ionic conductivity (10^{-2} S cm⁻¹), unfortunately very costly at estimated \$ 780/m² [21]. Although new proton exchange membranes were introduced into the market, but still not cost effective, and this is major consideration. Another cost effective alternate method for proton transfer is the use of salt bridge which connects the anode and cathode chambers and is made of agar and ionic salt.

Previously, we have reported on the enhancement of microbial fuel cell performance by anode nanocomposite modification [12]. In the same vein, this research investigated the effect of ionic salts in agar salt bridge on the enhancement of electro-generation of MFC. It is expected that the research will portray the importance of salt bridge optimization on improve the efficiency of MFC.

MATERIALS AND METHODS

Materials

Ionic salts used (NaCl, KCl, NaOH and KOH) were purchased from Sigma Aldrich Germany and were of analytical grades. PVC pipes and plastic containers were purchased from utility store.

Methods

Sample collection

Samples of municipal wastewater effluent were collected from different location within Dutse metropolis, Jigawa State, Nigeria in a sample container and were taken to the Microbiology laboratory, Federal University Dutse.

Fabrication of salt bridge

A fixed concentration (2M) of salt (NaCl, KCl, NaOH or KOH) was used in the bridge unless stated otherwise. The salt bridge was prepared by dissolving the respective ionic salt each in preheated 10% agar in 300ml deionized water and allow to stand over time to have viscous molten agar, thereafter, it was cast into pvc pipes (15 cm length; 5cm diameter) and allowed to solidified. The salt-agar casted pvc pipe was used as a connecting horizontal bridge between the anode and cathode chambers [Fig. 1]. Based on the type of the ionic salt used, salt bridges prepared using NaCl, KCl, NaOH, and KOH were herein designated as MFC1, MFC2, MFC3, and MFC4, respectively.



Fig. 1: A double chambered MFC consisting of an anaerobic chamber (anode; left) and aerobic chamber (cathode; right) connected by pvc pipe salt bridge.

Electrode preparation

Rectangular iron mesh with total surface area of 32cm² was used as electrode and copper wires were attached to the mesh using a soldering iron to make the electrodes and their connector to external circuit.

MFC construction and operation

Transparent plastic container of 5L capacity and 4L working volume was used as the anode and cathode chambers, respectively [Fig. 1]. A circular hole was made on the side of the two plastic large enough for the salt bridge to fit in. The salt bridge was inserted on both holes made at the side of the chambers and sealed with epoxy glue. A single hole was bored on the cover lid of the anode chamber for the electrode connector, where two holes were bored on the cover lid of the cathode chamber for electrode and aeration Spurger tube. Wastewater sample was poured into the anode chamber and electrode was inserted. On the other hand, distilled water as poured into the cathode chamber and the cathode electrode inserted too and covered. The spurgung tube was inserted into the cathode chamber and Oxygen was spurgung into the cathode chamber

using electric aquarium pump at 1.6 L/min. Sugar solution (40 g/L) was added to the anode chamber to enrich the mixed bacterial consortia in the wastewater effluent sample. Then volt meter was connected to the positive and negative terminal of the microbial fuel cell to display the readings [Fig. 1]. The circuit was completed with a fixed load of 1000 Ω , and the setup was monitored at time intervals. The anodic medium was replaced if the voltage was below 60 mV. Results were recorded in milli voltage (mV) at intervals using Multi-meter (Kusam meco model R 33275 china).

Numerical calculations

Current (i) was calculated according to Ohm's law at a resistance (R) from the voltage (V) according to Eq. (1), normalized by the anode surface area as described somewhere else [20]:

$$i = \frac{V}{R} \quad \text{Eq.(1)}$$

Generally, the overall performance of an MFC is evaluated through power output and current density. The current density (CD) and power (P) were calculated according to Eq. (2) and Eq. (3), respectively

$$CD = \frac{V}{A_{an}R} \quad \text{Eq.(2)}$$

$$P = iV \quad \text{Eq.(3)}$$

But since the voltage is measured across a fixed external resistor (R), while the current (i) is calculated from Ohm's law. Thus, relating Eq. (3) to Eq. (1), power is usually calculated as presented in Eq. (4)

$$P = \frac{V^2}{R} \quad \text{Eq.(4)}$$

It has been reported that in

order to compare the power output of different MFC, the power is often normalized to some characteristic of the reactor [8]. Since anode is where the biochemical reaction occurs in MFC, the power output is usually normalized to the projected anode surface area because the anode [8]. The power density (PD) is therefore calculated on the basis of the area of the anode (A_{an}) according to Eq. (5)

$$PD = \frac{V^2}{A_{an}R} \quad \text{Eq.(5)}$$

The polarization curve was obtained by plotting the graph of the voltage obtained against the current density (mA m^{-2}).

RESULTS AND DISCUSSIONS

Type of ionic salt bridge as a function of MFC cell voltage and power density

The type of ionic salt used in agar bridge play an important role on the transport of proton (H^+) ions. The effect of type of agar salt bridge on the MFC performance was studied [Fig. 2]. Different ionic salts (KCl, NaCl, NaOH and KOH) were tested. Generally, in both salt bridges, a linear increase in voltage generation with corresponding increase in power density to a maximum level was observed over time, thereafter the MFC voltage and power density start to decrease gradually [Fig. 2]. The MFC power density was found to be substantially higher (10.12 mW/m^2) =when KCl salt bridge was used compared to that with NaCl salt bridge (9.21 mW/m^2). In the same vain, corresponding maximum voltage of 447mV and 380mV were observed in MFC operated with KCl and NaCl, respectively.

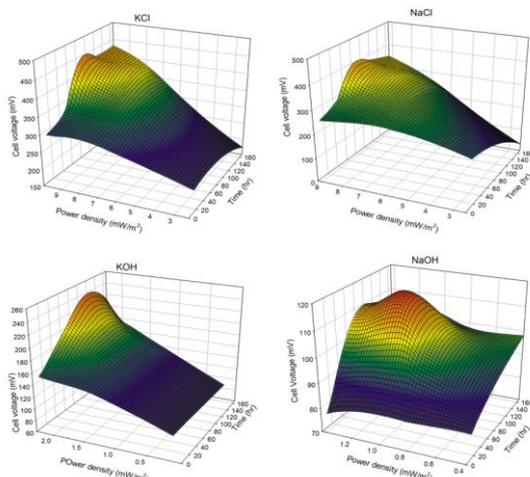


Fig. 2: Response surface plot displaying the type of ionic salt bridge as a function of Cell voltage and power density in MFC.

This observation was found to be in good agreement with previous reports on increase in higher voltage in KCl (823mV) compared to NaCl with 713 mV [21]. It was also found to be in accord with reported observation by Parkash [7]. The observed higher performance of potassium salt over that of sodium could be attributed to the lower ionization energy of potassium, and reported higher transfer rate of K^+ (0.49) in water compared to 0.4 for Na^+ [21, 22]. Similarly, KOH and NaOH salt bridges displayed 2.29 mW/m² and 1.32 mW/m², with cell voltage of 238mV and 110 mV, respectively. When compared to chloride (Cl^-) associated salts (KCl, NaCl), the observed low MFC performance of hydroxyl (OH^-) associated salt (KOH, NaOH) could be due to fact that OH^- is a strong conjugate base thus making it a poor leaving group, thus difficult to be ionized and transport protons. For example, the PK_a for KCl is -7 and that of KOH is 15.7, which indicates the readiness of chlorine to leave compared to the hydroxyl moiety.

Effect of salt concentration in agar on MFC current density

Salt molar concentration in MFC salt bridge is critical in facilitating proton transfer due to its dissociated ions. The effect of different salt concentrations (0.5M to 7M) on MFC current density was studied (Fig. 3). Initial gradual increase in current density from 0.5M to 1M was observed in all the studied MFC samples. Highest current density occurred at 1M concentration in both salt bridges samples. However, MFC operated with KCl salt bridge was found to exhibit highest current density (2.81×10^{-2} mA/m²) and lowest current density (6.17×10^{-3} mA/m²) was produced by MFC NaOH salt bridge [Fig. 3]. Parkash [7] reported similar observation of highest MFC performance at 1M salt concentration in KCl and NaCl bridges. The researchers further observed a decrease in cell current with increase in molar concentration of the salt. In the same vein, optimum molar concentration for KCl salt bridge was reported to be 1M which delivered maximum voltage of 1056 mV [21]. In another research, 1M NaCl concentration was found to produced highest current (256 μ A) compared to 62 μ A been the lowest produced by the MFC when operated by 9M NaCl [23]. Similarly, increase in MFC performance in terms of power density with increasing salt concentration from 1% to 5%, thereafter, a gradual decrease in power and current was reported [18]. It has been reported that increasing the concentration of salt in agar bridge enhances the transfer of protons from the anode chamber to the cathode, at the same time reduces the activation loss [18]. The observed decrease in current generation while increasing the molar concentration of the salt could be due to reported microbial cells dehydration in higher salt concentrations, which resulted in slower electron and proton transfer, thus causing drastic increase in internal resistance [24].

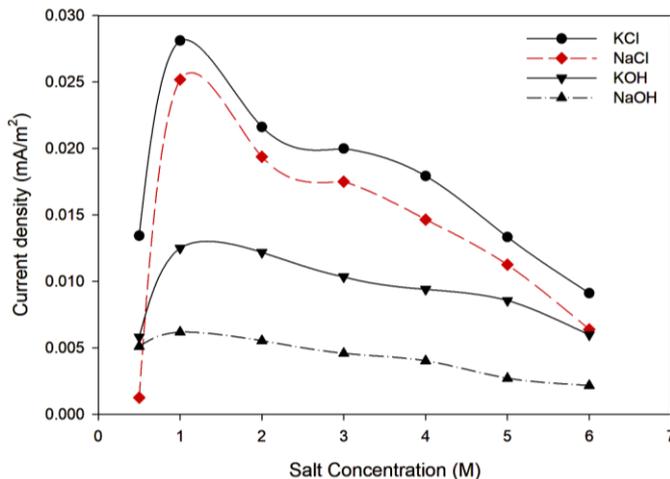


Fig. 3: Effect of salt concentration in agar on MFC current density.

Effect of operation time on Current generation in MFC operated with different ionic salt bridge

The effect of operation time on MFC current generation was studied using different agar-salt bridges [Fig.4]. In all the MFC tested, gradual increase in current generation with increasing time to a maximum level was observed, with salts of potassium having higher generation compared to that of sodium. The current generation was however observed to gradually decrease after the optimum time. In MFC with salt of potassium (KCl, KOH) bridges, optimum current generation of 0.45mA and 0.20mA was observed at 120hrs and 96hrs of operation, respectively. On the other hand, the performance of MFC with salts of sodium bridges (NaCl, NaOH) in terms of current generation was observed to be below that of MFC with potassium salts. In MFC with NaOH salt bridge, the current generation reach optimum level early and decline progressively [Fig. 4].

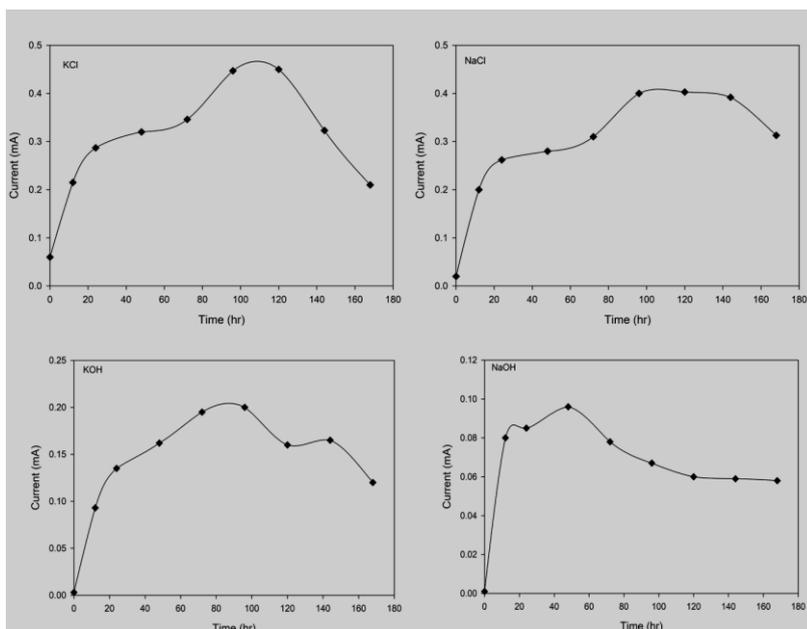


Fig. 4: Operation time as a function of cell current in MFC operated with different ionic salt bridge.

The general decrease in current generation with prolong operation time could be as a result of ohmic polarization [8]. Equally, the observed high current generation in potassium salt could be due to the same reason mentioned earlier i.e. low ionization energy and higher ion transfer of potassium in comparison to sodium. The progressive decline of current generation in MFC with NaOH could be akin to the strong conjugate nature of the hydroxyl group. Our observation of gradual decrease in current generation after attaining optimum level in MFC over time was in accord with previous literatures [7, 18, 23, 25].

CONCLUSION

In this study we analyzed the effect of different agar- salt bridges and the ionic salt concentration on the performance of a two-chamber MFC. Optimum performance was observed when the MFC was operated with 1M salt concentration in the bridge. Salt of potassium perform better compared to that of sodium probably due to lower ionization energy of the potassium. Accordingly, chloride is known to be poor conjugate base, thus ready to leave the group allowing for proton capture and its subsequent transport. Thence, ionic salts containing chloride exhibit higher performance than those with hydroxyl group. Highest power density (10.12 mW/m²) and corresponding cell voltage (447mV) were observed in MFC operated with KCl salt bridge. This study has demonstrated the importance of salt bridge in optimizing the performance of MFC.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

ACKNOWLEDGEMENTS

This work was carried out in the Department of Microbiology and Biotechnology, Federal University Dutse, Jigawa State, Nigeria.

FINANCIAL DISCLOSURE

None.

AUTHOR CONTRIBUTION

GAM: Experimental design, research execution and Statistical analyses; SFB, MM, HY, R MA, GR: Sample and data collection; ZM: Bio electrochemical and Statistical analyses

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