Effect of Sodium Alginate on Proton Conductivity of Cassava Starch in a Microbial Fuel Cell

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Our previous research has shown that cassava starch can function as a proton exchange membrane in a Microbial Fuel Cell, MFC. This study further examines the effect of sodium alginate, \((\text{Na}_6\text{C}_{6}\text{H}_{7}\text{O}_6)\_n\), on the proton conductivity of cassava starch in a dual chamber microbial fuel cell using two cell set-ups operating at room temperature (27±3°C). The performance of MFC-1 with unmodified pure starch PEM showed a maximum power density of 45.69mWm\(^{-2}\) with overall coulombic efficiency of 8.70% after a ten day useful life. MFC-2 containing starch PEM modified with sodium alginate produced a maximum power density of 648.51mWm\(^{-2}\), with overall coulombic efficiency of 18.93% and COD removal efficiency of 72.8% over a 20 day study period. It was thus observed that the cell whose PEM was modified with sodium alginate showed a tremendous increase of over 100% power density generated with longer useful life than in the case of the unmodified form. Hence by this way, power production in MFCs could be improved in a more sustainable manner at a cheaper operating cost.
INTRODUCTION:

Microbial fuel cells are the major types of bioelectrochemical systems (BESs) involved basically in biocatalytic conversion of organic matter into electricity. It consists of an anaerobic anode chamber and an aerobic cathode chamber (Barron et al. 2010; Bettin, 2006). The microorganisms in the anode chamber are found to interact with the electrodes using electrons, which are either removed or supplied through an electrical circuit (Pant et al., 2009; Liu and Logan, 2004). This development in biotechnology has recently gained emergent interest among researchers considering the fact that it holds much promise to provide clean energy with simultaneous waste-water treatment in a more sustainable and cost effective fashion (Frank and Nevin, 2010, Ghangrekar and Shinde, 2008). MFC operation takes advantage of the active bioconversion potentials of certain bacteria such as Geobacter sulfurreducens KN 400, which was among the first 50 bacteria capable of generating a high amount of current in a MFC (Frank and Nevin, 2010). An additional advantage of MFC operation is its accompanying waste-water treatment as bacterial oxidative activity on biodegradable organic matter has attendant COD and BOD removal potentials (Das and Mangwani , 2010; Ghangrekar and Shinde, 2006; Leropoulos et al, 2005).

MFCs have operational and functional advantages over the technologies currently used for generating energy from organic matter. First, the direct conversion of substrate energy to electricity enables high conversion efficiency. Second, MFCs operate efficiently at ambient temperature. Third, an MFC does not require gas treatment because the off-gases of MFCs are enriched in carbon dioxide and normally have no useful energy content. Fourth, MFCs do not need energy input for aeration provided the cathode is passively aerated (Abhilasha and Sharma, 2009). This further reveals that MFCs not only presents an energy solution and reduction of overdependence on fossil fuels but also presents a platform for solving global environmental issues.

However, having identified this alternative source of energy via bacteria action on oxidizable substrate (biomass), the magnitude of power output generated in MFCs as recorded in literature is low relative to other fuel cells and as such does not justify huge investment (Liu and Logan, 2004). Hence, current effort and research are geared towards discovering cheaper and economically viable components that would incidentally reduce the overall unit cost of MFCs and increase its commercial application potential.

The type and nature of Proton Exchange Membranes (PEMs) applied in a MFC can be a limiting factor in determining its overall power performance. Hence, MFC with high performance, low cost material and good scalable is necessary and preferred for commercial application (Chai et al., 2010; Min et al., 2005). Most studies have used relatively expensive Nafion-117 as proton exchange membrane (PEM) in MFCs (Liu and Logan, 2004), but cassava starch (a cheaper alternative) can also be used. The use of cassava starch as a proton exchange membrane in MFCs reduces the cost of the cell considering its low relative cost, cheap availability and low energy requirement during treatment and installation (Obasi et al., 2012).

The aim of the present study therefore was to investigate the possibility of better performance of cassava starch as a proton exchange membrane in modified forms. We therefore designed and constructed a microbial fuel cells using cassava starch as the PEM in pure and alginate-modified forms. In order to study the effect sodium alginate on the proton conductivity of the starch, we compared the power density for cell with pure unmodified starch PEM and that for cell with Starch PEM modified with sodium alginate.

This research was successfully carried out at the chemical Engineering Laboratory of the University of Port Harcourt, Choba Rivers State, Nigeria, July, 2012.

MATERIALS AND METHODS:

Starch PEM MFC construction

The MFC-1 and -2 used in this study have similar configurations but differ only in the nature, strength and design of the proton exchange membrane, PEM component. One used unimproved cassava starch PEM while the second used cassava starch PEM modified with sodium alginate, (NaC6H11O7)n. Both cells were the dual chamber type, each consisting of anode and cathode chambers. Each chamber was a transparent cylindrical plastic container of height 14.5cm and diameter 13.5cm (empty bed volume of 1.55l). A 14.5 cm long cylindrical PVC pipe that forms the starch PEM casing was bonded at 4cm from the base of each chamber end to end. The anode and cathode electrodes were the graphite rods of total surface area 0.00118m², each extracted from 1.5volts dry cell the tips of which had been soldered to copper wires (Barua and Dek, 2010; Obasi et al., 2012). The anode chamber contained swine house effluent (high organic content) (Scott and Murano, 2007), inoculated with an adopted consortium from mangrove forest, while the cathode chamber was filled with a solution of potassium ferricyanide, K3Fe(CN)6 (aq) containing 32.93gdm⁻³ of the salt. The potentials generated were recorded using a digital multimeter. The experimental set-up for the dual chambered MFC is as shown in Figure 3.

The Anode chamber
A consortium of bacteria present in soil solution obtained from mangrove forest located at Borikiri River bank were used to inoculate the MFCs in order to effect an increased rate of initial bacterial action for more effective electron production and recovery (Kim et al., 2002). A high strength swine house effluent collected from BA-01, effluent gathering basin at Concordial Farm, Barariya, Tai Local Government Area of Rivers state was used as the substrate. The effluent had a pH of 7.2 (stabilized with a phosphate buffer solution (KH$_2$PO$_4$ + K$_2$HPO$_4$) to sustain the growth of microorganism. The total Chemical Oxygen Demand (COD) of 3800mg/l and Biochemical Oxygen Demand (BOD) of 1200mg/l were determined using standard method (APHA 1985). No mediator was used in the chamber. The experiments were conducted at room temperature (27±3°C). The can was kept air tight with epoxy steel gum under aseptic anaerobic microbiological condition.

The Cathode Chamber

The cathode chamber of the MFC was filled with fully aerated potassium ferricyanide solution as the catholyte. An opening left at the surface of the lid allowed continuous sparging of air to keep the chamber fully in contact with air (oxygen) throughout the experiment.

The Proton Exchange Membrane

Cassava starch had been shown to be a good proton conductor in MFCs. This is based on the fact that its chemical structure contains cyanide ion (CN$^-$) which presents electrostatic potential surface that exerts electrical pressure on positive charges such as protons (H$^+$). This property is further enhanced by its water holding property, gel strength, low solubility index (3.5%) (Daramola and Osanyinlusi, 2006). The cyanides are bonded to starch polysaccharide molecules in the form of cyanogenic glycosides which has the potential to form ligands with positive ions (protons). However, these properties had been improved via modification with sodium alginate, (NaCa$_6$H$_7$O$_6$)$_n$. Being an insoluble matter with proven ability to undergo lyophilization (absorb water from other substances easily and expand), sodium alginate maintains the strength, stability and enhance the durability of the cassava starch gel. Besides, it is also able to immobilize enzymes by inclusion and encapsulation thereby stopping bacteria from eating up the starch. The calcium chloride, CaCl$_2$ mixed with the alginate caused rapid gelatinization by electrostatic cross-linking and hence improved the electrical conductivity of the solid medium (starch).

PEM-1 (Pure unmodified starch)

The native cassava starch obtained as a wet solid (14% moisture content) was placed in a tray dryer set at 27°C operating with a linear increase in temperature with time and heated to a maximum temperature of 100°C for 1 hour. 85g of pure dry starch was measured using the top loading digital balance and mixed with 75.0cm$^3$ of distilled water in a vessel. 5cm$^3$ of 0.5M NaOH and 25cm$^3$ of 2.5M CaCl$_2$ solutions were added to 10g of sodium alginate (NaCa$_6$H$_7$O$_6$)$_n$ powder in a beaker and stirred thoroughly to obtain a voluminous gelatinous precipitate. The mixture was then carefully poured into the vessel containing a mixture of starch and water and the entire system whirled several times to ensure proper mixing. The system was then heated with about 5g of activated carbon for 10 minutes while vigorous stirring/kneading continued until a homogenous jelly, soft paste was obtained. This hot modified starch was immediately charged into a 14.5 cm long PVC pipe and

![Figure 1: Flow chart for the preparation of pure starch PEM-1](image)

PEM-2

170g of dry native cassava starch powder was weighed out using top loading digital balance and mixed with 150cm$^3$ of distilled water in a vessel. 5cm$^3$ of 0.5M NaOH and 25cm$^3$ of 2.5M CaCl$_2$ solutions were added to 10g of sodium alginate (NaCa$_6$H$_7$O$_6$)$_n$ powder in a beaker and stirred thoroughly to obtain a voluminous gelatinous precipitate. The mixture was then carefully poured into the vessel containing a mixture of starch and water and the entire system whirled several times to ensure proper mixing. The system was then heated with about 5g of activated carbon for 10 minutes while vigorous stirring/kneading continued until a homogenous jelly, soft paste was obtained. This hot modified starch was immediately charged into a 14.5 cm long PVC pipe and
allowed to cool and get fitted to the inner wall of the pipe. The PEM-2 was then ready for use in MFC-2.

Wet starch
↓
Drying
(tray dryer set at 100°C, 1hr)
↓
Agitation (Mix-1)
(Mixture of CaCl₂+NaOH)
↓
Mix-2
(Mix-1 + (NaC₆H₇O₆)n)
↓
Mix-2+starch + activated carbon
↓
Stirring/Heating (10 minutes)
↓
Hot starch paste
(Ready for use as PEM-2)

**Figure 2:** Flow chart for the preparation of alginate-modified starch PEM-2

**ANALYTICAL CALCULATIONS**

Current (I) and open circuit potential (OCP) (V) measurements were recorded every 24 h using digital multimeter (DT-830B). For polarization, current generation from the two cells was monitored simultaneously during the study period and readings were noted after stabilization of voltage (Mohan et al.; 2007). The values of currents and voltages were converted to power density P (mW/m²) according to the equation, P=IV/A, where I (mA) is the current, V (v) is the voltage, and A (m²) the surface area of the projected anode. Current density (mA/m²) was calculated by dividing the current obtained by the surface area of the projected anode.

Power density as expressed was normalized to the projected surface area of the graphite anode (m²). Power density P was analyzed according to Equation (1) (Momo and Nyeayor, 2010; Rabaey and Verstraete, 2005).

\[
P = \frac{Current\ (mA) \times Volts\ (v)}{Surface\ area\ of\ projected\ anode\ (m^2)} \quad (1)
\]

And current density C, expressed as:

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

The coulombic efficiencies were calculated using the Equations 3 and 4 (Liu et al, 2005):

\[
E_c = \frac{C_p}{C_n} \times 100\% \quad (3)
\]

Where \(C_p\) = total coulomb calculated by integrating the current over time, \(C_n\) = theoretical amount of coulombs that can be produced from the cell.

\[
C_n = \frac{F B_i S_w}{M_i} \quad (4)
\]

Where \(F\) = Faraday's constant (96,485 Coulombs/mol-electron), \(B_i\) = moles of electrons/mole of substrate, \(S_w\) = substrate concentration and \(M_i\) = molecular weight of the substrate (basically carbohydrate).

The performance of the cell was evaluated by estimating the COD and voltage removal efficiency and power generation. The COD removal efficiency was calculated using equation (5) (Mohan et al, 2007)

\[
\xi = \frac{C_{so} - C_s}{C_{so}} \times 100\% \quad (5)
\]

Where \(\xi\) = COD removal efficiency, \(C_{so}\) = initial COD concentration (mg/l), and \(C_s\) = COD concentration at time t.

The open circuit potential (OCP) (V) produced in the MFC-2 (Figures 5a, b and c), in which case the starch
PEM was modified with the alginate, during the cell operation was observed to decrease exponentially with time in the form:

\[ V = V_0 e^{-kt} \]  

(6)

Where \( V \) = voltage produced at time \( t \); \( V_0 \) = initial voltage value; \( K \) = proton conductivity of the PEM; and \( t \) = time.

Table 1: Design Criteria for a dual-chambered microbial fuel cell

<table>
<thead>
<tr>
<th>Reactor configuration</th>
<th>Dual chambered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of Cathode and anode chamber</td>
<td>1.55l</td>
</tr>
<tr>
<td>Volume of swine house effluent</td>
<td>1.55l</td>
</tr>
<tr>
<td>Anode and cathode material</td>
<td>Graphite rods.</td>
</tr>
<tr>
<td>Anode inoculums</td>
<td>Mixed anaerobic consortia</td>
</tr>
<tr>
<td>Mediator-anode</td>
<td>Nil</td>
</tr>
<tr>
<td>Mediator-cathode</td>
<td>Air</td>
</tr>
<tr>
<td>Length of projected graphite rod</td>
<td>5.0cm</td>
</tr>
<tr>
<td>Total surface area of projected electrode</td>
<td>0.001138m² (anode and cathode)</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>27±3°C</td>
</tr>
<tr>
<td>Operating pH</td>
<td>Anode (7.2), cathode (6.8).</td>
</tr>
<tr>
<td>Membrane used</td>
<td>Starch</td>
</tr>
<tr>
<td>COD</td>
<td>3,800 mg/l</td>
</tr>
<tr>
<td>BOD</td>
<td>1,200 mg/l</td>
</tr>
<tr>
<td>Starch (membrane) casing</td>
<td>1 inch diameter PVC pipe14.5cm</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSIONS:

After inoculation with the adopted consortium, the MFC-1 and 2 were operated with different designed PEMs,
varying only in physical properties, to produce electricity. Table 1 below shows a summary of the power densities produced within the first ten days and 20th day of operation.

Table 1: Summary of Power density values for MFC-1 and 2 (mW/m²) for the 1\textsuperscript{st} 10 and 20\textsuperscript{th} day

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>1\textsuperscript{st}</th>
<th>2\textsuperscript{nd}</th>
<th>3\textsuperscript{rd}</th>
<th>4\textsuperscript{th}</th>
<th>5\textsuperscript{th}</th>
<th>6\textsuperscript{th}</th>
<th>7\textsuperscript{th}</th>
<th>8\textsuperscript{th}</th>
<th>9\textsuperscript{th}</th>
<th>10\textsuperscript{th}</th>
<th>20\textsuperscript{th}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC-1</td>
<td>12.48</td>
<td>7.38</td>
<td>39.02</td>
<td>45.69</td>
<td>10.54</td>
<td>7.21</td>
<td>7.21</td>
<td>0.97</td>
<td>5.27</td>
<td>6.59</td>
<td>0.00</td>
</tr>
<tr>
<td>MFC-2</td>
<td>648.51</td>
<td>570.83</td>
<td>408.61</td>
<td>323.37</td>
<td>151.58</td>
<td>131.81</td>
<td>33.84</td>
<td>25.66</td>
<td>32.95</td>
<td>29.00</td>
<td>12.83</td>
</tr>
</tbody>
</table>

Figure 4a: Current and Voltage against Time (days) for a dual-chambered MFC-1 with pure starch PEM-1.

Figure 4b: Power density and Current density against Voltage for a dual-chambered MFC-1 with pure starch PEM-1 over 10-day period.

Figure 4c: Voltage and Power Density against Time (Days) for a dual-chambered MFC-1 with pure starch PEM over 10-day period.

Figure 5a: Current and Voltage against Time (days) for a single dual-chambered MFC-2 with modified starch (PEM-2) over a 20 day period.
FIGURE 5b: Current density and Power density against voltage for a single dual-chambered MFC-2 with alginate-modified starch (PEM-2) over a 20 day period

FIGURE 5c: Voltage and Power Density against Time (Days) for a single dual-chambered MFC-2 with modified starch (PEM-2) over a 20 day period

MFC-1 with pure unmodified starch PEM

Figures 4a, b and c above show the power generation pattern for MFC with pure unimproved starch PEM. By using this cell, it was possible to produce as much as 45.69 mW/m² power density and corresponding current density of 35 mA/m² at the fourth day after inoculation, with swine house effluent used as the substrate (fuel). This peak power value may have resulted from the effectiveness of proton conductivity by the starch PEM.
which has direct linkage with electron recovery. This may have been made possible as a result of the net electrical pressures on the protons by the cyanide ions (CN) present in the starch molecules. However, the cell performance dropped gradually to a minimum value of 6.59mW/m² on the tenth day, after which the power production dropped to zero. This short useful life of the cell due to loss of efficiency of the PEM could have been as a result of several factors which may include: activity loss caused by increasing concentration of acidic fermentation product (such as alcohol) during bacteria activity (Mathuriya and Sharma, 2009); developed impedance on proton transfer due to high water absorption and retention; collapse of PEM mass due to bacteria and potassium ferricyanide (catholyte) gradually eating up the PEM surface; gradual build-up of hydrogen gas around the graphite anode; breaking up of intermolecular forces between starch molecules with attendant effect of oxygen diffusion through the PEM; and proton clogging in the available pores, thus leading to polarization of the cell as an overall effect.

MFC-2 with Alginate–modified starch PEM

In the second phase of the experimentation process, the cell was operated with the PEM treated with sodium alginate (BDH). Figures 5a, b and c show the pattern of power generation. The peak current and voltage of 0.6mA and 1.23v (power density - 648.51mW/m²) was observed about 3 hours of inoculation on the first day. This indicates a major power improvement suggesting a better proton transfer and subsequent increase in electron recovery due to improved PEM properties via modification. This value was however lower than the maximum power value, 3600mW/m² so far reported in literature (Liu and Logan, 2004). The cell performance later showed an exponential decrease in voltage production with time up to 20 days study period. This sustainable power generation and relative longevity could have been attributed to certain factors that are connected with the presence and properties of the alginate such as: exceptional ability of sodium alginate to lyophilize (absorb water from the starch and expand) thus maintaining the PEM strength and stability; its ability to immobilize enzymes (bacteria) by inclusion and encapsulation thereby stopping it from eating up the starch; being a gum it boosts the bonding strength of starch molecules with themselves and the walls of the pipe (Raymond, 2009; Remminghorst and Rehm, 2009), coupled with improved conductivity, gelatinization and electrostatic cross-linking due to the presence of calcium chloride in the solid matrix. The cell reached a current and voltage values of 0.02mA and 0.73 volts giving a current and power densities of 17.57mA/m² and 12.83mW/m² respectively on the 20th day.

The cell was loaded with a light-emitting diode (LED), an indicator lamp from an electronic device (remote controller) of voltage rating between 0.4v and 0.8v. The light emitted from the diode dimmed gradually by the day due to decrease in the power output over time (cell polarization process).

ELECTRON RECOVERY AND COD REMOVAL:

The products of the bio-oxidative process occurring at the anode chamber (protons and electrons) require immediate transfer to the PEM and anode respectively (Kasango and Togo, 2010; Strik et al., 2008). Hence, highly electrochemically active bacteria (for a mediatorless case), coupled with anode of high electrode potential and an effective proton conductor (PEM) are required for maximum cell performance. The effect of using a PEM and bacteria of insufficient performance is the eventual formation of hydrogen gas in the anode chamber which builds up gradually and clogs around the anode and consequently prevent electron access leading to cell low coulombic efficiency and eventual polarization.

CONCLUSION

This research work has demonstrated the feasibility of operating a simple “batch” dual chambered microbial fuel cell incorporating cassava starch PEM whose proton conductivity has been improved with sodium alginate. Thus, it has become clear that in addition to the overall cell cost reduction, addition of the alginate (owing to its advantageous physical properties) improves the performance of the PEM and promotes cell durability. However, the research does reorganize the striking relative advantages of using other precious materials such as nafion, agar-agar, polystyrene, ultrex, divinylbenzene, etc as proton exchange membranes. Hence, the cost and sustainability of power generation in MFCs can be controlled and enhanced by modifying the properties of the chosen PEM.

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