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Characterization of direct methanol fuel cell (DMFC) applications with H_2SO_4 modified chitosan membrane

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A B S T R A C T

Chitosan (Chs) flakes were prepared from chitin materials that were extracted from the exoskeleton of Cape rock lobsters in South Africa. The Chs flakes were prepared into membranes and the Chs membranes were modified by cross-linking with H_2SO_4. The cross-linked Chs membranes were characterized for the application in direct methanol fuel cells. The Chs membrane characteristics such as water uptake, thermal stability, proton resistance and methanol permeability were compared to that of high performance conventional Nafion 117 membranes. Under the temperature range studied 20–60 °C, the membrane water uptake for Chs was found to be higher than that of Nafion. Thermal analysis revealed that Chs membranes could withstand temperature as high as 230 °C whereas Nafion 117 membranes were stable to 320 °C under nitrogen. Nafion 117 membranes were found to exhibit high proton resistance of 284 $s\,cm^{-1}$ than Chs membranes of 204 $s\,cm^{-1}$. The proton fluxes across the membranes were 2.73 $mol\,cm^{-2}\,s^{-1}$ for Chs- and 1.12 $mol\,cm^{-2}\,s^{-1}$ Nafion membranes. Methanol (MeOH) permeability through Chs membrane was less, $1.4 \times 10^{-6}\,cm^2\,s^{-1}$ for Chs membranes and $3.9 \times 10^{-6}\,cm^2\,s^{-1}$ for Nafion 117 membranes at 20 °C. Chs and Nafion membranes were fabricated into membrane electrode assemblies (MAE) and their performances measure in a free-breathing commercial single cell DMFC. The Nafion membranes showed a better performance as the power density determined for Nafion membranes of 0.0075 $W\,cm^{-2}$ was 2.7 times higher than in the case of Chs MEA.

1. Introduction

The growing concerns regarding the environmental degradation caused by the emissions from combustion engines using fossil fuel has led to increasing development of fuel cells as an alternative energy sources. Notable among the fuel cells is direct methanol fuel cell (DMFC), which has received much attention in recent years for its promising qualities. Some of its identified qualities are low pollution emission, existing infrastructure and propensity to be operated at low temperature. In a DMFC, methanol is oxidized at the anode in the presence of water to form protons, electrons and carbon dioxide. While the electrons move through the external circuit in the form of electric current, the protons are transported through the proton electrolyte membrane (PEM) to the cathode where they are reduced in the presence of oxygen to form water. A suitable efficient fuel cell is tied to good characteristics of the membrane as good conductor of proton and provision of a suitable catalyst site for electrochemical reaction.

The most widely used fuel cell membrane is the standard polymer electrolyte membrane known as Nafion 117 [1], having the structured shown in Fig. 1. Nafion has a polytetrafluoroethylene (PTFE) chain as a backbone, with flexible perfluoropolyalkylether (PFPAE) as side chains. The PFPAE side chains are terminated with sulfonate groups which provide the cationic exchange capacity. Although, Nafion membranes show good characteristics of thermal stability, high current densities, and high proton conductivity, it still suffers from a number of disadvantages. For example, Nafion membrane is quite expensive and it has a high rate of methanol cross over from anode to cathode in DMFC. Since methanol is used as fuel in DMFC, its transport from anode to cathode reduces fuel utilisation and causes a mixed potential in cathode. It will also polarize the cathode electrode thereby reducing the efficiency of the cell [2].

Recently, researchers have focused on the use of other membrane materials as possible replacement for Nafion membrane that can lower methanol permeation. Among many polymer electrolyte membranes studied, Chs membranes have shown a better performance for applications of low temperature fuel cells.

Chs is a biopolymeric material that is prepared from chitin by deacetylation as given in Fig. 2. Chitin is largely found in the exoskeletons of crustaceans such as crabs, lobsters krill and crayfish. Chitin, also known as acetyl-glucoseamine and Chs known as glucoseamine have acetyl and amine groups attached to C-2 positions, respectively. The amine ($-NH_2$) groups in Chs are reactive to

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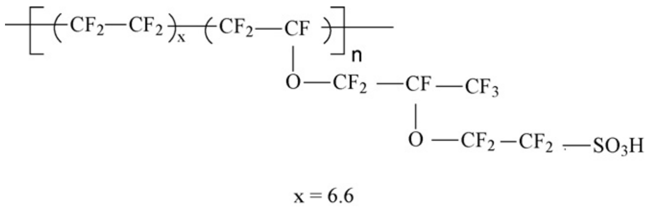

Fig. 1. The chemical structure of Nafion 117 membrane.

functional group that allows for both physical and chemical modifications. In acetic acid, Chs dissolves into gel solution that allows for physical modifications to form gel beads and membranes. Cross-linking is used as a chemical modification to render Chs insoluble in acid media [3], and to ensure good mechanical and chemical stable membrane. Several cross-linking agents such as glyoxal [4], glutaraldehyde [5] and sulfuric acid have been proposed because the sulfate group allows for better proton conductivity [6].

There has been a limited study that provides information specifically concerning the fabrication of Chs membrane electrode assemblies. In this study, Chs membranes would be prepared, characterized and fabricated into MEA, and the performance will be measured and compared to Nafion MEA.

2. Methods

2.1. Materials

Chs flakes were prepared from Cape rock lobsters [7]. Nafion 117 membranes (non-electroplated) were purchased from Ion-Power (USA). The following reagents were obtained from Sigma–Aldrich: acetic acid anhydride, sulfuric acid (99.8%), hydrochloric acid (32%), sodium hydroxide pellets, potassium bromide, methanol (99%) and hydrogen peroxide (30%).

The degree of deacetylation (DDA) of Chs was 82 mol%, determined using the method described by Roberts [8]. The molecular weights of Chs were determined to be 940 (±4%) kg mol^{-1} by size exclusion chromatography (SEC) according to the method described by Osifo et al. [7].

2.2. Membrane preparation

Chs flakes weighing between 1 and 2 g were dissolved in 100 ml of aqueous acetic acid (1%, v/v) for 24 h. The solution was filtered to remove impurities. The filtered solution was then cast on a Petri-dish under atmospheric conditions and left to de-gas overnight. After degassing, the Petri-dish containing the Chs solution was transferred to a drying oven which was controlled at 55 °C for 24 h. Upon removal from the oven, the membranes were cross-linked in a solution of 0.5 M H_2SO_4 for 24 h. Chitosan cross-linking reaction with sulfuric acid is given in Fig. 3. The transparent dried membranes were washed with distilled water and later immersed in 2 M aqueous solution of sodium hydroxide (NaOH) for 2 min to remove the residual acid (neutralization) from the membranes. The membranes were then washed in de-ionized water until a neutral pH was reached. Nafion 117 membranes were pre-treated by boiling them separately in 3% H_2O_2 in de-ionized water for over 1 h. The membranes were further treated separately in 0.5 M H_2SO_4 de-ionized water for 1 h. Pre-treatment was done to activate Nafion 117 membrane's hydrophilic sites. Pre-treated membranes were continuously rinsed in de-ionized water until a neutral pH was reached. The thickness of the membranes was measured with an Electronic Digital Caliper (0–150 mm) and their thickness ranged between 0.18 and 0.20 mm.

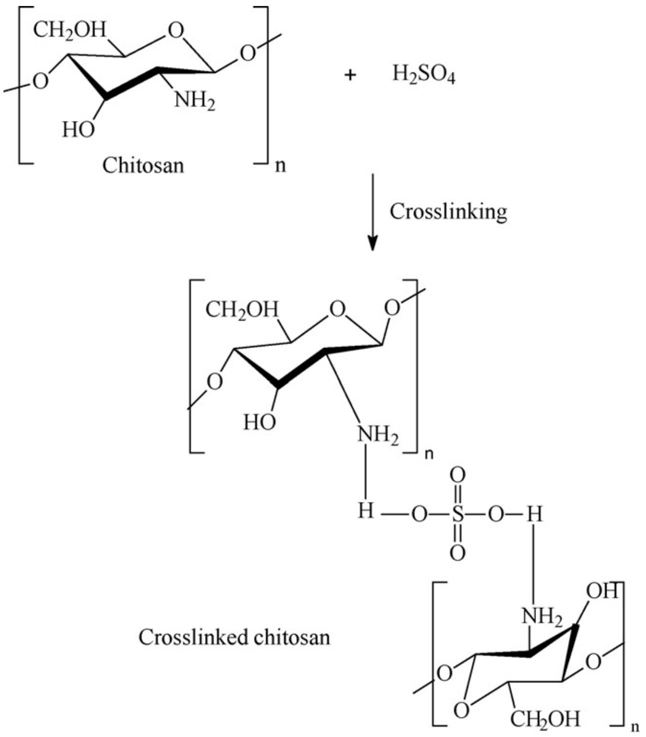

Fig. 3. Cross-linking reaction of chitosan with sulfuric acid.

2.3. Membrane water uptake

The membrane water uptake was determined from the difference in the wet and dry weight of membranes divided by the dry weight of the membranes [1]. The membranes were first immersed in de-ionized water at room temperature for 5 days to ensure sufficient water uptake. Upon removal from water, the wet membranes were blotted-dried using a soft tissue to remove surface droplets and the membranes were quickly weighed. The wet membranes were dried at atmospheric conditions for 24 h, and the dried mem-

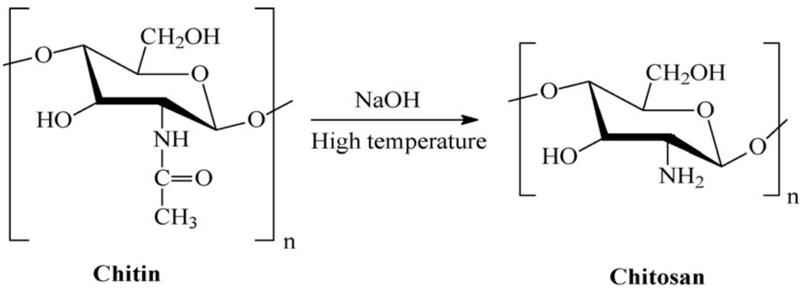

Fig. 2. Chitosan preparation from chitin.

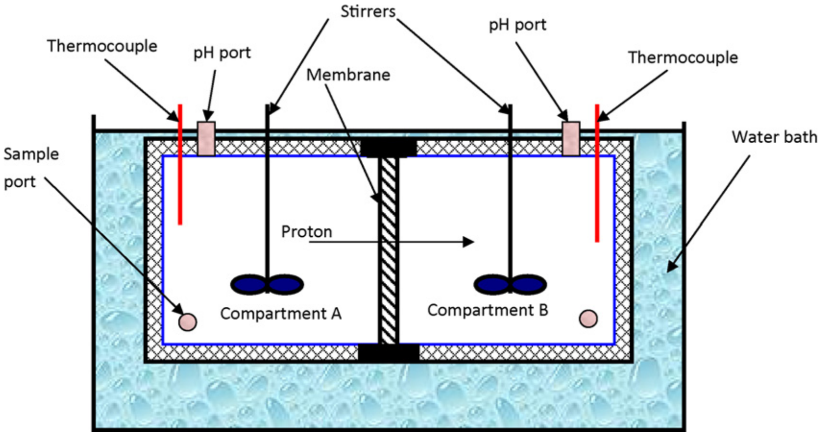

Fig. 4. Experimental setup of proton diffusion and methanol permeation.

branes were further dried in the oven for 1 h at 60 °C. The effect of water uptake on re-hydration was studied at different temperature. This was done by placing dry membrane in distilled water at 30, 60 and 100 °C for 1 h, respectively.

2.4. Thermal stability

Two methods, thermogravimetry (TG) and differential scanning calorimetry (DSC), were used to determine the thermal conditions of membranes with temperature. This is done to sufficiently obtain information about the heat effects on the membranes.

2.4.1. Thermogravimetry (TG)

Membranes were cut to about 9 mm^2, and 10–20 mg was weighed into a platinum pan. Prior to the analysis, the platinum pan was heated under Bunsen burner flame followed by cooling in a dessicator. The pan containing a sample was loaded in a TG (2050) furnace. TG measurements were conducted at a heating rate of 10 °C min^{-1} under nitrogen from room temperature to 600 °C. As the temperature increased, a graph of weight loss (%) versus temperature was plotted. The derivative thermogravimetry (DTG) gives the rate of change in mass as a function of temperature. This analysis gives a series of peaks and the areas under the peaks give the total mass-change of the membrane sample. The DTG is more precise because it allows the reaction temperature with mass loss to be determined accurately.

2.4.2. Differential scanning calorimetry (DSC)

Chs and Nafion 117 membranes were cut to a grain size and 10–20 mg was weighed into aluminium pans. The total mass of the sample, pan and lid was recorded. The pan was tightly closed by applying a pressure of 200–300 kPa. This provided a cold-welded seal necessary for volatile materials. The sample was then placed inside a DSC (2010). Scans were conducted under nitrogen at a heating rate of 10 °C min^{-1} from room temperature to 600 °C. As the temperature increased, a graph of temperature against heat flow was plotted to determine the glass transition temperature. This was done because polymers have a higher heat capacity above glass transition temperature.

2.5. Membrane resistance

Proton diffusion tests were conducted on chitosan and Nafion 117 membranes to determine the membrane resistance to proton flow. Tests were carried out in a two-compartment diffusion cell constructed of polyurethane materials manufactured at the Technology Station of Vaal University of Technology, Vanderbijlpark. A DC power supply (HY3005D-3) was used to supply voltage to a motor. A DAWE® stroboscope (1214 B) was used to measure the motor speed. Fig. 4 shows the schematic setup of proton diffusion cell. The diffusion cell was immersed in a water bath for temperature control. Initially compartment A was filled with 300 ml of HCl (pH = 3.01) and compartment B was filled with an equal volume of distilled water. The solutions were kept under constant stirring conditions to avoid any concentration build-up. Three trials were completed at a stirring speed of 150, 300 and 410 rpm, respectively. The pH in both compartments was recorded with time using a Eutech cyberscan pH meter (PC 5000).

2.5.1. Determination of membrane resistance

The membrane resistance was determined with Fick's Law of diffusion model. In using Fick's Law of diffusion, the following assumptions were made: (1) proton flux is established across the membrane due to concentration difference; (2) the flux across the membrane reaches a pseudo-steady state over a very short time; (3) there is no concentration gradient within the compartment because the solution is well stirred [9]. Fig. 4 was considered as a system in which there is proton transfer from compartment A to compartment B.

The total mass flux across the membrane is given as:

$$N = J + C_1V_1 \tag{1}$$

where N is total mass flux, J is the diffusive flux and C_1V_1 is the convective flux. For a dilute solution, Eq. (1) yields:

$$N = J \tag{2}$$

From Fick's Law of diffusion:

$$J = -D\frac{dC}{d\ell} \tag{3}$$

where D is the diffusion coefficient and $dC/d\ell$ is the concentration gradient across the diffusion path.

For a well stirred solution, the concentration of solution in the bulk will be the same on the solution–film interface. Rearranging Eq. (3) and integrating over a film thickness ℓ on the feed side, gives:

$$J_1 = \frac{D}{\ell}(C_1 - C_{1\ell}) \tag{4}$$

where C_1 is the concentration of solute in the bulk solution on the feed side of the membrane as shown in Fig. 5, $C_{1\ell}$ is the concentration of the solute on the film side adjacent to the membrane. Eq. (4) can be written in the form of mass transfer coefficient as:

$$J_1 = k_1(C_1 - C_{1\ell}) \tag{5}$$

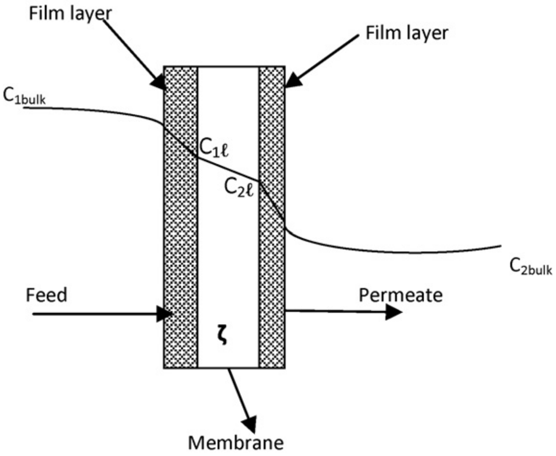

Fig. 5. Concentration profile across a film layers and membrane.

where $D/\ell = k_1$, the film mass transfer coefficient on the feed side. The reciprocal of k_1 is the film mass transfer resistance. On the permeate side of the membrane, the mass flux across the membrane is characterized by the boundary layer to give:

$$J_2 = k_2(C_{2\ell} - C_2) \tag{6}$$

where k_2 is the mass transfer coefficient on the permeate side of the membrane, $C_{2\ell}$ is the concentration of solute of the film side adjacent to the membrane and C_2 is the bulk solute concentration on the permeate side of the membrane. If the membrane resistance is ζ, for a steady state system, the flux is a constant therefore, $J_1 = J_2 = J$. The overall mass transfer coefficient, K, is the sum of the individual resistances, thus:

$$\frac{1}{K} = \frac{1}{k_1} + \zeta + \frac{1}{k_2} \tag{7}$$

If the stirring rates are equal $k_1 = k_2 = k$

$$\frac{1}{K} = \frac{2}{k} + \zeta \tag{8}$$

For the purpose of this experiment, Fig. 5, C_1 bulk = C_A for compartment A and C_2 bulk = C_B for compartment B. Therefore from Eqs. (3) through (8), the total molar flux can be represented as:

$$J = K(C_A - C_B) \tag{9}$$

Rewrite Eq. (9) to determine the mass transfer coefficient for compartments A and B.

$$V_A \frac{dC_A}{dt} = -KA(C_A - C_B) \tag{10}$$

$$V_B \frac{dC_B}{dt} = KA(C_A - C_B) \tag{11}$$

If the density of the solution does not change significantly:

$$V_A \cdot C_A + V_B \cdot C_B = \text{constant} \tag{12}$$

At $t = 0$, all the solutes present must remain in its respective compartment. Thus differentiating Eq. (12) and integrating combining with Eqs. (10) and (11) yields:

$$\text{In}\left[\frac{C_A(t) - C_B(t)}{C_A(0) - C_B(0)}\right] = -K \cdot A\left[\frac{1}{V_A} + \frac{1}{V_B}\right] t \tag{13}$$

Having known V_A, V_B, and A from experimental measurements, K can be determined from the slope of the plot of Eq. (13). The membrane resistance ζ is determined according to the method used by Welty et al. [10]. The value of K is obtained at different rotational speed (ω), and the inverse of K is plotted against $1/\omega^n$. The value of n, which in most cases ranges between 0 and 1 is use to get the best straight line. The intercept of the straight line is equal to ζ.

2.6. Methanol permeability

Methanol permeability through Chs and Nafion 117 membranes was measured using the experimental set-up of Fig. 4. Initially one compartment of the cell was filled with 200 ml of 8 M MeOH. The other compartment was filled with an equal volume of water. Both compartments were stirred continuously at a constant speed of 150 rpm. At a regular time interval, 4 ml of the solution in both compartments was collected and methanol concentration was analyzed with a Varian Gas Chromatograph (Cp-3380). The effect of concentration on methanol permeability was studied by increasing MeOH concentration to 12.5 and 18 M. The effect of temperature on methanol permeability was investigated at 20 and 60 °C, respectively.

2.7. Fabrication of MEA

2.7.1. Preparation catalytic inks

Catalytic carbons of 20 wt% Pt/XC-72 for the cathode and 40 wt% PtRu/XC-72 for the anode were purchased from ETEK. The anode and cathode inks were prepared by mixing the catalytic carbons with distilled water and isopropanol (20 parts distilled water to 80 parts isopropanol) to form a thick paste. The mixture was sonicated and the catalyst particles were dispersed in ionomer solution (5 wt% in lower aliphatic alcohols, Ion-Power Inc.). The electrode catalytic inks were sprayed on 3.3 cm^2 carbon paper (TGPH-09, Toray) and they were dried in the air.

The cathode hydrophobic diffusion layer ink was prepared as follows: 15 wt% carbon black (Vulcan XC 72, Chemiphos) was dried and grounded using a mortar and pestle. A 50 ml of isopropanol was added to 1 g of carbon black and mixed on a magnetic stirrer followed by ultrasonication until smooth slurry was formed. After 5 min of stirring, a perfluoropolyalkylether (PTFE) suspension (Werk Gendorf 84504 Burgkirchen, Dyneon) was added to the slurry. The slurry was then sprayed onto a carbon cloth and dried in air. The coated carbon cloth was later sintered at 335 °C for 2 h.

2.7.2. Membrane electrode assemblies

Chs and Nafion membranes (4.4 cm^2) were removed from water and the surface water was removed with a soft tissue. The electrolyte membrane was immediately sandwiched between the coated carbon paper electrodes (3.3 cm^2). The membrane with the coated carbon paper was then hot pressed by applying a weight of about 1800 kg with a Pasadena Hydraulics press (Q-240C) at optimum temperature of 60 °C (Chs membrane) and 110 °C (Nafion 117

Table 1
Catalyst deposition onto Chs and Nafion 117 membranes.

Sample	Membrane	Catalyst	Initial mass (g)	Final mass (g)	Catalyst deposited (g)
1	Chs	Pt/C	0.1181 ($\pm 5 \times 10^{-3}$)	0.1468 ($\pm 5 \times 10^{-3}$)	0.0287 ($\pm 3 \times 10^{-3}$)
2	Nafion 117	Pt/C	0.1166 ($\pm 5 \times 10^{-3}$)	0.1375 ($\pm 5 \times 10^{-3}$)	0.0209 ($\pm 2 \times 10^{-3}$)
3	Chs	Pt Ru/C	0.1125 ($\pm 5 \times 10^{-3}$)	0.1279 ($\pm 5 \times 10^{-3}$)	0.0282 ($\pm 2 \times 10^{-3}$)
4	Nafion 117	Pt Ru/C	0.1192 ($\pm 5 \times 10^{-3}$)	0.1447 ($\pm 5 \times 10^{-3}$)	0.255 ($\pm 2 \times 10^{-3}$)

membrane) for 3 min. Layers of Pt/C catalyst on the cathode and Pt/RuC on the anode were transferred from the carbon paper to the membrane. The amount of Pt/C and PtRu/C deposited onto the membranes was determined by measuring the mass of paper before and after deposition as shown in Table 1. The membranes were also directly sprayed with the catalysts in order to compare hot pressing to electrospraying. However, catalytic deposition through electrospraying was not successful for chitosan and Nafion 117 membranes. Chitosan membranes are highly crystalline in their dried form and as a result the sprayed Pt/C and PtRu/C catalytic layers would detach from the membrane surface when immersed in a mixture of water and methanol. The pressure effects on fabrication with hot pressed ensured the membrane and catalysts remained intact.

2.7.3. *Single cell testing*

Different MEA's (commercial Nafion 117 membrane, hot pressed Nafion 117 membrane, and Chs membrane) were tested in a free-breathing commercial single cell DMFC (5.5 cm^2). DMFC performance tests were conducted under atmospheric conditions with 1 M methanol concentration. The current voltage (*I*–*V*) experimental data were obtained from a Mobile Dyesol testing station connected to a testing cell fitted with an internal electronic load. The initial open circuit voltage (OCV) was recorded after stabilization using a digital multimeter. A graph of the cell voltage versus the current density was plotted in order to determine the cell performance. The current density is calculated as follows:

$$I_\rho = \frac{I}{A_m} \tag{14}$$

And also the plot of the power density versus the current density was plotted. The power density is calculated as follows:

$$P_\rho = V \cdot I_\rho \tag{15}$$

where I_ρ is the current density (A cm^{-2}), I is the current (A) and A_m is the membrane active area (cm^2) and P_ρ is the power density (W cm^{-2}).

3. Results and discussion

3.1. *Membrane water uptake*

The membranes water uptake determined at various temperatures is presented in Table 2. Chs membranes were found to have higher water content than Nafion 117 membrane. Chs is highly hydrophilic with a hydroxyl (OH$^-$) and the amino (NH$_2$) groups on its backbone. The hydrophilic groups cause the swelling on Chs membrane [11].

Table 2
The dependence of membrane water uptake on drying temperature.

Membrane	% water content				
	Drying condition		Re-hydration condition		
	20 °C	60 °C	30 °C	60 °C	100 °C
Chs	60.1	65.1	58.3	58.4	58.8
Nafion 117	24.2	30.1	28.1	30.1	27.8

There was a significant weight loss when the membranes were further dried in an oven at 60 °C for 1 h. An increase in water content of up to 65% for Chs membranes was found. In the case of Nafion 117, the water uptake was 30.1%, which was less than that of the Chs membranes. Nafion membrane has hydrophobic groups on their backbones and hydrophilic groups on their sulfonate heads [12]. Their hydrophobicity was extremely high due to the presence of the sulfonic acid group on hydrophilic side chain which reduces the water uptake.

The results of hydration temperature on water uptake are presented in Table 2. There are no significant changes in the water content of the membranes with re-hydration temperature. What is interesting is that, the Chs membranes were able to withstand mechanical degradation at boiling temperatures, and this is perhaps due to the ionic interaction between the amine group and the sulfate ions during cross-linking.

3.2. *Thermal stability*

3.2.1. *Thermogravimetry*

The weight loss and the derivative weight loss thermograms for Chs and Nafion 117 membranes are shown in Figs. 6 and 7, respectively. The thermograms show several decomposition steps. The first decomposition stages for Chs membrane are between 220 and 230 °C while those of Nafion 117 are at 330 °C. TG curves show a gradual weight loss of 16% at 240 °C for Chs membrane. This decomposition step is attributed to water leaving the membrane [13]. At higher heating temperature, a second decomposition step was observed around 290 °C with a 42% weight loss, and a third decomposition step was observed between 280 and 450 °C with a 60% weight loss for Chs membrane. At temperatures above 450 °C, Chs membrane continued to decompose until about 70% weight loss was observed at 580 °C. Chs membrane did not completely lose their weight at this temperature range. The DTG curve of Chs membranes shows the maximum decomposition rate of 2% per °C at 280 °C with a weight loss of 30%.

The TG thermogram of Nafion 117 membrane also shows several decomposition steps. There was a gradual weight loss of 10–15% at temperature between 30 and 330 °C, which is attributable to water

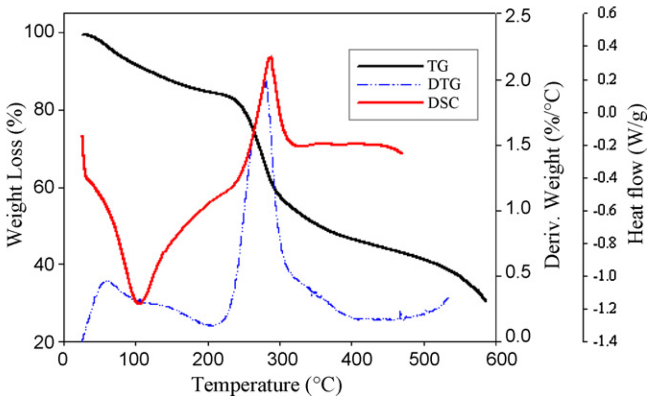

Fig. 6. TG, DTG and DSC thermograms for Chs membrane under nitrogen.

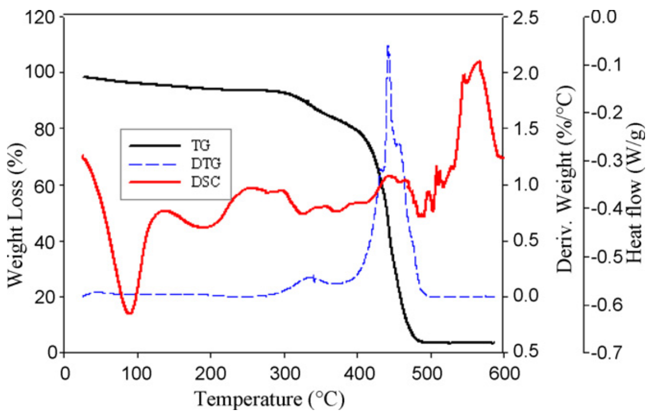

Fig. 7. TG, DTG and DSC thermograms for Nafion 117 membranes under nitrogen.

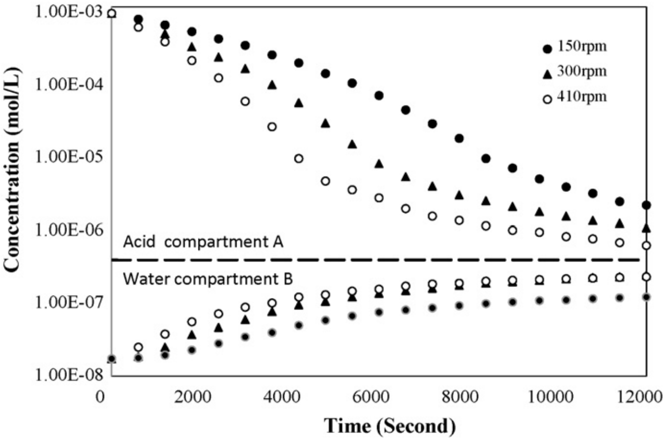

Fig. 8. The change in hydronium ion concentration in compartment A and compartment B with time through Chs membranes.

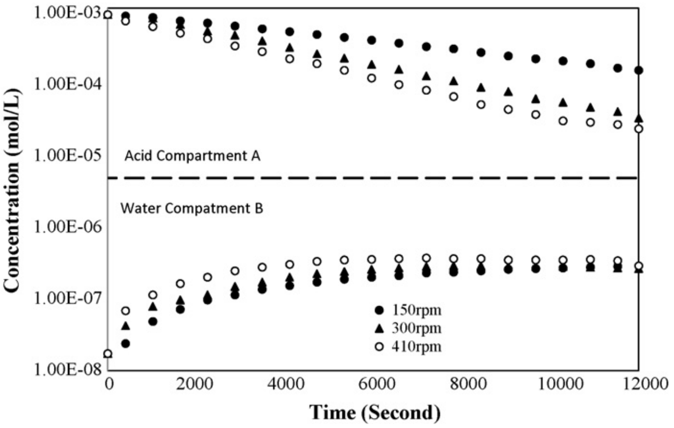

Fig. 9. The change in hydronium ion concentration in compartment A and compartment B with time through Nafion 117 membranes.

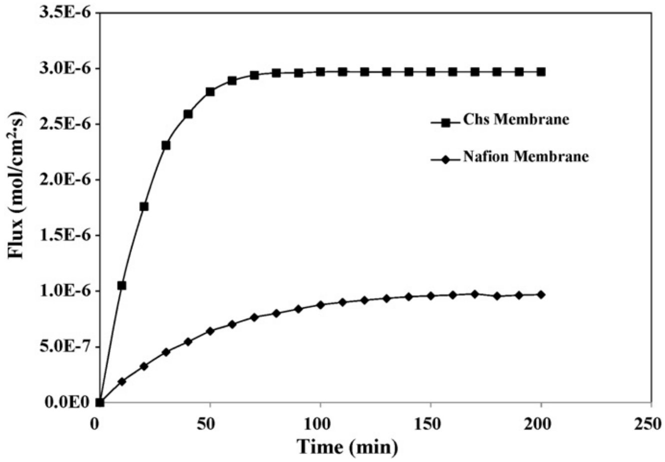

Fig. 10. The change in flux (J) with time through Chs and Nafion 117 membranes at 20 °C.

evaporating from the membrane. The next decomposition stage with a weight loss of 20% was observed at ranges between 300 and 430 °C and associated with the desulfonation process (i.e. the loss of $-SO_3H$ groups) [6,14]. At temperatures above 430 °C, Nafion membranes continue to decompose until about 99.5% was lost at 590 °C. This weight loss is attributed to the decomposition of the perfluoropolyalkylether (PFPAE) side chains and the polytetrafluoroethylene (PTFE) chains on its backbone [1]. The DTG thermogram of Nafion 117 membranes showed a maximum decomposition rate of 2.3% per °C at 430 °C and the weight loss in this step is 44%. TG scan shows that Nafion 117 membranes have better thermal properties than Chs membrane primarily because their main chain decomposes at 430 °C while their initial decomposition occurs at 330 °C, which is higher than that of Chs.

3.2.2. Differential scanning calorimetry

Fig. 6 shows the DSC thermogram for Chs membrane, and it represents the endotherm between 30 and 140 °C. The endotherm is attributed to the water leaving the membrane. An exotherm is observed at 280 °C. According to Ge et al. [15] the exotherm is related to the membrane starting to crystallize whereas Mukoma et al. [2] associated the exotherm to the glass transition temperature. Immediately after the exotherm, an endotherm is indicated at 280 °C. This endothermic transition is associated with the polymer starting to melt before it decomposes above 280 °C. It was evident that the heating temperature significantly affected the structure of Chs membrane.

In the case of Nafion membrane, the DSC curve shows a broad endothermic peak between 30 and 250 °C as shown in Fig. 7. This is validated by the work of Mukoma et al. [2] who also observed an endotherm at 110 °C. The exothermic peak above 500 °C shows the decomposition of the main polymer chains. The DSC thermogram clearly shows that Nafion 117 membrane possesses better thermal properties than Chs membrane since the main polymer chain decomposes above 520 °C.

3.3. Membrane resistance

The overall mass transfer resistance and the membrane resistance were determined for Chs- and Nafion 117 membranes at 20 °C. This was achieved by completing three trials at mixing speeds of 150, 300 and 410 rpm for each membrane. Figs. 8 and 9 show the dependence of the hydronium ion concentration on time for Chs- and Nafion 117 membranes, respectively. The decrease in concentration with time observed in compartment A is associated with the loss of hydronium (H^+) ions as they diffuse through the membrane into compartment B. This in turn increases the H^+ concentration in compartment B.

Table 3 gives the values of K and the total mass flux at different mixing speeds. As the speed increased, the boundary layer was reduced and the film resistance decreased thereby increasing the value of K. The change in flux (J) through Chs- and Nafion membranes at 150 rpm; 20 °C, is given in Fig. 10. It was observed that the flux increases with speed until a pseudo-steady state was reached.

The membrane resistance (ζ) to proton flow was determined from the y-intercept of the plot of the overall mass transfer resistance versus the inverse of the mixing speed to the power n as shown in Fig. 11. The ζ for Chs- and Nafion membranes are given in Table 4. Nafion 117 membrane had a high ζ when compared to chitosan membranes. This is associated with Nafion 117 mem-

Table 3
Comparison of proton diffusion properties of Chs- and Nafion 117 membranes.

Membrane	Speed (rpm)	K (cm s^{-1})	J ($\times 10^{-6}$ mol cm^{-2} s^{-1})
Chs-	150	0.0022	1.74
	300	0.0025	2.64
	410	0.0027	2.73
Nafion 117	150	0.0006	0.49
	300	0.0011	1.02
	410	0.0012	1.12

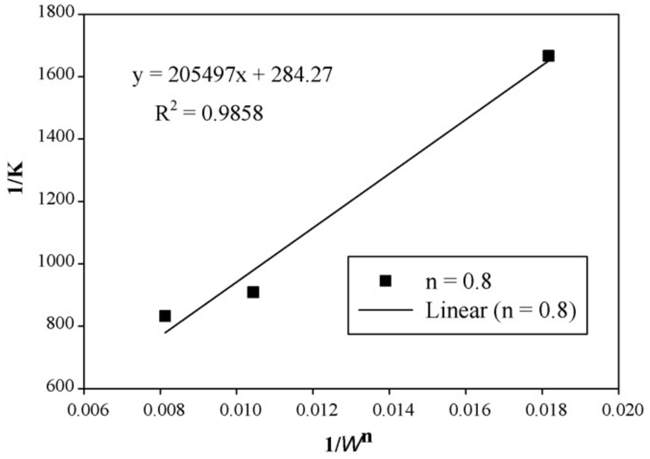

Fig. 11. Determination of the membrane resistance for Nafion 117 membranes.

brane's hydrophobicity which reduces the water uptake in the membranes thereby minimizing the mobility of protons through the membrane.

3.4. Methanol permeability

The influence of methanol feed concentration on permeability is shown in Table 5. It was found that permeability increases with increase in methanol concentration. The permeability values at 8, 12.5 and 18 M MeOH are 3.02×10^{-6}, 3.22×10^{-6} and 3.92×10^{-6} cm^2 s^{-1} respectively for Chs membrane. Similar trends were found for Nafion 117 membranes. These results indicate less methanol permeability through Chs membrane than through Nafion 117 membranes [16].

The permeability at temperatures of 60 °C was determined, and the results are in parenthesis given in Table 5 for Chs membrane. The methanol permeability was found to increase with increase in solution temperature. These results were found to be higher when compared to the permeability found at 20 °C for the same membrane. Kreuer [17] also found an increase in methanol permeability with an increase in temperature with Nafion and sulfonated polyetherketones membranes.

3.5. MEA performance

Prior to cell assembly, Chs MEAs were hydrated to prevent them from breaking; Chs membranes usually shrink after drying due to their hydrophilic nature. Figs. 12 and 13 show the performance of a passive single cell air breathing DMFC under atmospheric conditions and 1 M methanol was tested for Chs MEA, and Nafion 117 MEA. The initial OCV after 1 h of wetting was 338 and 483 mV (Digital Multimeter) for Chs MEA and Nafion 117 MEA, respectively.

Table 4
Determination of the membrane resistance for Nafion 117 and Chs-membranes.

Membrane	*n*	ζ (s cm^{-1})
Chs	0.8	205.7
Nafion 117	0.8	284.3

Table 5
Comparison of methanol permeability properties of Chs and Nafion 117 membranes at 20 °C, and permeability at 60 °C is in parenthesis.

Membrane type	Thickness (cm)	Permeability ($\times 10^{-6}$ cm^2 s^{-1})		
		8 *M*	12.5 M	18 M
Chs	0.020	3.09(3.46)	3.22 (4.36)	3.92 (5.62)
Nafion 117	0.018	3.90	5.03	8.26

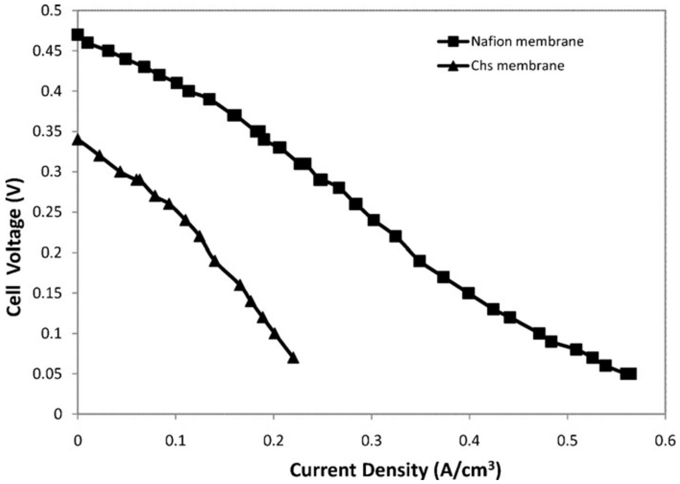

Fig. 12. Plot of cell voltage against current density for a DMFC fed by 1 M methanol under atmospheric temperature with Chs MEA and Nafion 117 MEA.

As shown in Fig. 12, the maximum current density for Chs MEA and Nafion 117 MEA was 0.22 and 0.56 A cm^{-2} respectively and the maximum power density was 0.0274 and 0.0747 W cm^{-2} respectively. Under similar experimental conditions, it can be seen that better performance can be achieved with Nafion 117 membranes.

Due to the lower methanol permeability of Chs membranes, it was expected that they would perform better than Nafion 117, but this was not the case because proton conductivity also plays an important role in the performance. The high OCV attained for Chs membrane is mainly associated to the lower methanol permeability, but its lower performance is primarily due to its low ionic conductivity [1]. The maximum power density for commercial Nafion 117 membranes was 0.698 W cm^{-2}, which is higher than that of the Nafion 117 membranes fabricated in the laboratory. This result suggests that either the fabrication technique or the amount of catalyst loading was not sufficient. An exact explanation for this behavior is yet to be found.

A further investigation was performed on Chs MEA over a 68 h period and results were noted after 1, 48 and 68 h in order to study the effect of time on the DMFC performance. As can be seen from Table 6, the performance deteriorated with time. Since tests were conducted on a passive DMFC, it is possible that over time a concentration build-up would occur and some methanol might evaporate causing the performance to deteriorate.

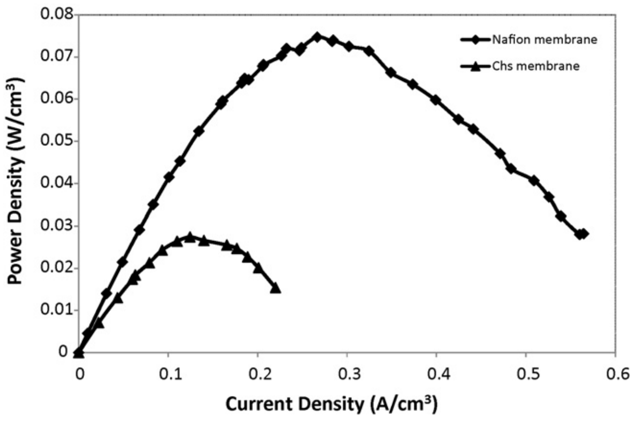

Fig. 13. Comparison of power density against current density for DMFC fed by 1 M methanol at atmospheric conditions with Chs- and Nafion 117 MEAs.

Table 6
Measured values of current density and cell voltage for Chs membrane over time.

Time (h)	OCV (V)	Current density ($A\,cm^{-2}$)	Power density ($W\,cm^{-2}$)
1	338	0.220	0.0274
48	247	0.137	0.0144
68	207	0.130	0.0177

4. Conclusion

Chs and Nafion 117 membranes were characterized in terms of the thermal stability, water uptake, membrane resistance and methanol permeability. The TG and DSC thermograms have shown that Nafion 117 membranes have good thermal properties over Chs membranes since they initially decompose at 330 °C without losing a lot of weight. Chs membranes decomposed at 240 °C hence it lost more weight than Nafion 117. This proves that Nafion membranes exhibit better thermal properties as opposed to Chs membrane.

The water uptake of chitosan membranes was three times higher than that of Nafion 117 membranes hence indicating a better proton transport through the membrane. This finding was supported by the lower membrane resistance to proton transport found for chitosan membranes than that for Nafion 117 membranes. The methanol permeability through Chs membranes was less than that of Nafion 117 membranes. Permeability increases with increase in concentration and temperature for all membranes. The permeability of Nafion 117 membranes was high when compared to Chs membrane. Hot pressing was suitable for depositing catalyst layers of Pt/C and PtRu/C on Chs membrane. Hot pressing however had negative effects on Chs MEA because the membranes lost their retained water very quickly. With comparison to the commercial MEA, hot pressed Nafion 117 membranes exhibited a very low performance hence it can be suggested that the fabrication technique needs further improvement. Although the performance of Chs MEA was however very low when compared to Nafion 117 membranes, it was found to be suitable membranes for fuel cell applications.

To improve performance of chitosan membranes, further work is required in order to study and optimize the quality of chitosan membranes. Therefore it is suggested that:

- The hydrophilicity of chitosan membranes must be reduced. The possibility of blending PTFE and chitosan will render chitosan hydrophobic which will increase their ionic conductivity.
- Chitosan membranes performance is also dependent on ionic conductivity; therefore, adding a composite material such as methane-diphosphonic acid may increase its conductivity [18].
- The method of MEA fabrication can be re-investigated and the effect of catalyst loading on the DMFC performance must be studied.
- The modified MEA can also be tested on a PEMFC and results compared to the DMFC to determine the highest performance that can be achieved.

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