

Development of a proton exchange membrane (PEM) for telecom fuel cell applications

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Abstract— The high cost of fuel cells compared to other energy sources creates uncertainty about the projected full-scale commercialization of this device. This paper describes the synthesis of a proton exchange membrane from locally available polystyrene butadiene rubber for fuel cell applications. Chlorosulphonic acid was used as the sulphonating agent and the effect of the degree of sulphonation on the membrane characteristics were determined. Membranes were characterized according to their ion exchange capacity (IEC), degree of sulphonation (DS), proton conductivity, thermal stability and performance in a fuel cell stack. The synthesized membranes were found to have proton conductivities in the order of 10^{-3} - 10^{-2} S/cm in their fully hydrated state, which increased with an increase in the degree of sulphonation. Results obtained revealed that the synthesized membranes are thermally stable and its performance in a fuel cell stack is influenced by the degree of sulphonation.

Index: Current density, Degree of sulphonation, fuel cell, Proton Exchange Membrane, Polystyrene butadiene rubber, Power density.

I. INTRODUCTION

Fuel cells have been identified as one of the most promising and potential clean energy technologies which meet all the requirements for energy security, economic growth and environmental sustainability and have attracted considerable attention as a possible replacement for power generation system [1], [5]. They have been described as a perfect combination of the advantages of existing energy sources [6], [7]. This being the ease of refueling as well as continuous operation potential of internal combustion engines and the highly efficient and quiet operation of batteries. Fuel cells therefore appear as the

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ideal energy alternative [8], [11]. Fuel cells generate electricity directly from fuel (i.e. hydrogen) by way of an efficient electrochemical reaction. They can be used in myriad of different ways and have been deployed amongst electricity consumers as a strategy to increase their market penetration [12]-[14]. The interest in research and development of fuel cell technology is increasing rapidly, such that government, universities and companies are gradually implementing fuel cell technology [15]. For instance, fuel cells have successfully been delivering power to several prototypes and specialized applications for decades [16]-[18]. The power output of a fuel cell stack is easily scalable to provide the correct voltage/power for a laptop, a small car or a city bus [19]-[21]. However, fuel cells have not been fully commercialized for several decades due mainly to the high cost of the development of applications for practical purposes [22], [23]. This has led to fuel cells being far behind when compared to heat engines such as steam and internal combustion engines, which are competitive technologies. In order to achieve the commercialization of fuel cells, especially the proton exchange membrane fuel cell (PEMFC), there is a need to reduce the cost of the membrane, which is the heart of the PEMFC. This can be achieved by utilizing locally available material such as polystyrene butadiene rubber to synthesize a proton exchange membrane, which is the focus of this work.

II. EXPERIMENTAL PROCEDURE

A known weight (10 g) of polystyrene butadiene rubber (Karbochem, South Africa) was dissolved in 250 ml of 1,2 dichloroethane in a stirred 4-neck round bottom flask 1.6 M of chilled chlorosulphonic acid was then added to the solution of rubber in drop wise over a period of time. Adding ethanol terminated the reaction and the precipitated sulphonated polymer was recovered and washed with de-ionized water until a pH of 6-7 was attained. The sulphonated rubber was then dried in an oven at 80°C for 2-3 hours. The sulphonated polymer was then characterized using elemental analysis (to determine the sulphur content), thermo gravimetric analysis (TGA), differential scanning analysis (to determine the thermal stability), FTIR and HNMR (to confirm sulphonation).

The ion exchange capacity (IEC) and degree of sulphonation (DS) of sulphonated polystyrene butadiene rubber (SPSBR) were determined by measuring the sulphur content in the dry sample of SPSBR using an elemental analysis method. The IEC was then calculated using Equation 1 [24]:

$$IEC = \frac{1000S_c}{MW_s} \quad (1)$$

Where: S_c is the sulphur content (percentage weight rate), MW_s is the Molecular weight of sulphur and 1000 is the multiplying factor to obtain IEC value in mmol/g.

The degree of sulphonation of the SPSBR was determined using the value of IEC calculated from Equation 1 in Equation 2 [25]:

$$DS = \frac{IEC \times M_{SPBR}}{1 - (MW_{SO_3H})} \quad (2)$$

Where: IEC is the ion exchange capacity (mol/g), M_{SPBR} is the molecular weight of the repeating unit of the PSBR (g/mol) and M_{SO_3H} is the molecular weight of SO_3H (g/mol).

CASTING AND CHARACTERIZATION OF MEMBRANE

Sulphonated polystyrene butadiene rubber (10 g) was dissolved in 200 ml of 1,2 dichloroethane at elevated temperature to form a casting solution. The solution of sulphonated polystyrene butadiene rubber was then casted using a laboratory scale casting tape to form a thin sheet of membrane. The casted membrane was cured for 4 days by exposing it to the air and then peeled off from the support. The membrane was further dried in an oven at 75°C for 4-5 hours and finally vacuum dried for 4 hours to remove the residual solvent. The membrane was then analyzed to determine the proton conductivity and methanol crossover.

MEMBRANE TESTING

The membrane electrode assembly (MEA) was fabricated by sandwiching the synthesized membrane between two electrodes and then hot pressing at 100°C for 3 minutes at a pressure of 173.53 psi. The MEA fabricated was then tested in a single fuel cell stack shown in Fig.1. The fuel gases (hydrogen and oxygen) diffuse through the porous backing layer and diffused to the electrolyte/electrode interface where electro catalytic reaction takes place. The electrons generated from the anode were connected to a digital multimeter, with an external variable resistance to measure the current and voltage produced by the cell.

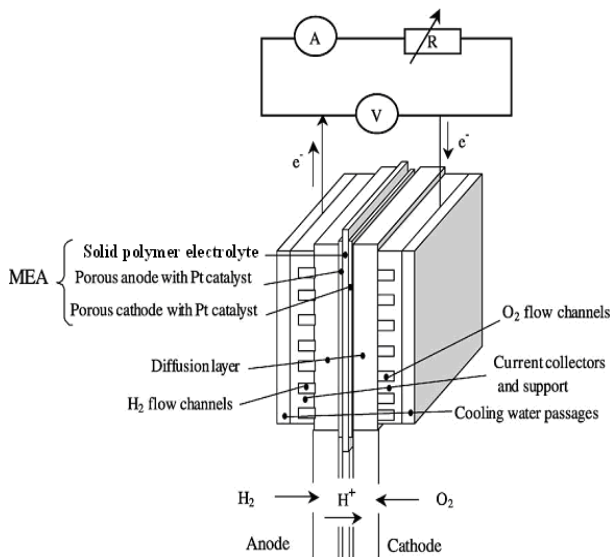


Fig. 1: Schematic of MEA and single cell testing [26]

III. RESULTS AND DISCUSSION OF RESULTS

Sulphonation is described as a process used to convert a polymer to be proton conductive. Figs. 2 and 3 represent the FT-IR and ^1H NMR spectra of the unsulphonated and sulphonated polystyrene butadiene rubber. Fig.2 is the FT-IR spectra of the unsulphonated and sulphonated polymer at different degrees of sulphonation. The weak broad band observed at 3573 cm^{-1} is the O-H vibration from the sulphonic acid group upon sulphonation. While the band observed at 1364 cm^{-1} is as a result of symmetric and asymmetric stretching of S=O which simultaneously increase the intensity of the aromatic C=C and C-C at 1649 cm^{-1} and 1494 cm^{-1} and that of the non-aromatic at 2846 cm^{-1} and 2919 cm^{-1} .

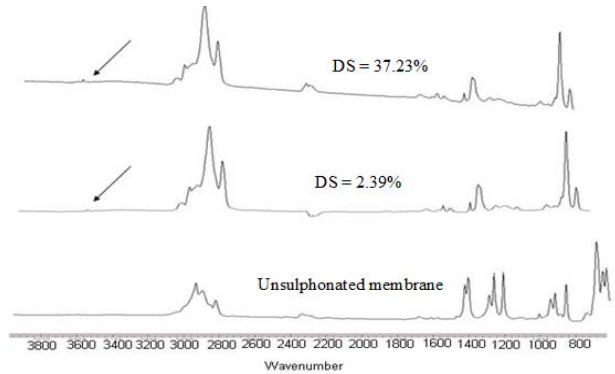


Fig 2: FT-IR spectra of unsulphonated and sulphonated PSBR

The ^1H NMR spectra of the unsulphonated and sulphonated polystyrene butadiene presented in Fig.3 is also used to confirm the presence of the sulphonic group in the sulphonated rubber. The hump appearing between 4 and 5 ppm indicated the presence of sulphonic acid linkage on the aromatic benzene ring, which confirms the substitution to be limited to the para- position of the phenyl group [27]. It can be observed from the ^1H NMR spectra (Fig.3) that there is no significant change in the signals at 7.3 and 7.6 ppm for both unsulphonated and sulphonated rubber.

Results obtained on the various analyses conducted on the synthesized membrane at different sulphonation time are presented in Table 1. Results obtained reveal that both ion exchange capacity and degree of sulphonation increases with increase in sulphonation time. Ion exchange capacity described the number of mil equivalent of ions in 1 g of the dry polymer is used to confirm the extent at which the polymer is converted from non-conductive to proton conductive material. Results show that a sulphonation time of 24 Hrs gives the maximum ion exchange capacity of 2 mmol/g.

The degree of sulphonation, which represent the average number of sulphonic groups present in the sulphonated polymer, was investigated and the results obtained are presented in Table 1. Results obtained shows that sulphonation time influence the degree of sulphonation of the sulphonated polymer. For instance sulphonation time of 0.5 hours gives degree of sulphonation of 2.39% while the sulphonation time of 24 hours resulted in membrane with

degree of sulphonation of 37.23%.

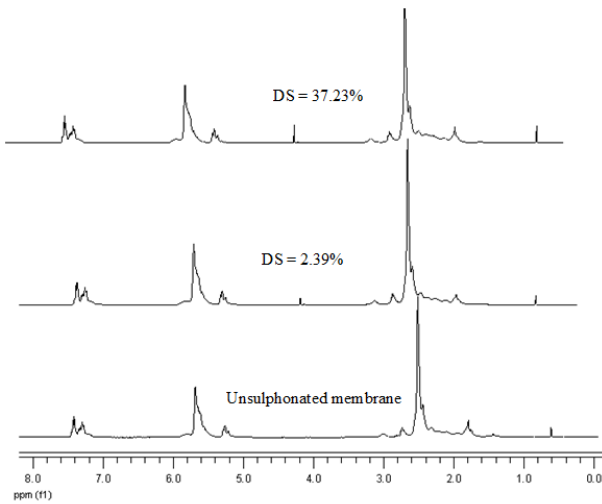


Fig. 3: ¹H NMR spectra of unsulphonated and sulphonated polymer.

Table 1: Effects of sulphonation time on the qualities of the synthesized membrane

Sulpho nation time (Hrs)	Sulphur content (%)	Degree of sulphona tion (%)	Proton conduct ivity (S/cm)	Methanol permeabil ity (mol/cm ² s)	Chara cterist ic factor
0.5	0.48	2.39	0.00198	7.31X10 ⁻⁷	2.71
1.0	1.62	8.25	0.0027	6.48X10 ⁻⁷	4.19
2.0	1.91	9.80	0.0034	6.30X10 ⁻⁷	5.40
20.0	5.04	28.17	0.0072	4.81X10 ⁻⁷	14.85
24.00	6.40	37.23	0.0129	4.62X10 ⁻⁷	27.89

Also investigated is the effect of sulphonation time on the methanol permeability of the synthesized membranes. Methanol crossover is the capacity of the membrane to block the fuel going through the membrane, and it is considered as the quality of the membrane that determines its performance in fuel cell application [27]. Fuel crossover through the membrane results in decrement in the cathode potential and energy efficiency [28]. Hence, it is important to synthesized membrane with low methanol permeability. Results obtained on the effect of sulphonation time on the methanol permeability are presented in Table 1. Results obtained show that as the sulphonation time increases, the permeability to membrane decreases. Increase in sulphonation time resulted in increment in degree of sulphonation, which also resulted in reduction in equivalent weight, that produces more sites for the distribution of methanol in the membrane matrix. Results obtained on the methanol permeability reveals that the methanol permeability of the synthesized membrane is lower that of the Nafion[®] (3.15 X10⁻⁶ cm²/s), the commercially available membrane.

The proton conductivity of the synthesized membranes was measured by alternating current impedance over a frequency range of 1-10⁶ Hz using 1M H₂SO₄ as electrolyte. The value of the intersection of the high frequency

impedance curve (Fig.4) with the real axis was taken as the membrane resistance and the proton conductivity was calculated from Equation 3:

$$\sigma = \frac{T}{RS} \quad (3)$$

Where: σ is the proton conductivity (S/cm), T is the membrane thickness (cm) and S is the surface area of the membrane (cm²) and R the resistance in Ohm. Before the proton conductivity of the synthesized membrane was measured, the membrane sample was soaked in distilled water until full hydration of the membrane was attained. Hydration is essential for membrane that relies on sulphonic acid to conduct protons before it can attain a desirable level of proton conductivity. Results obtained on the effects of sulphonation time on proton conductivity of the synthesized membranes. The results obtained revealed that proton conductivity of the synthesized membrane is in the order of 10⁻³-10⁻² S/cm.

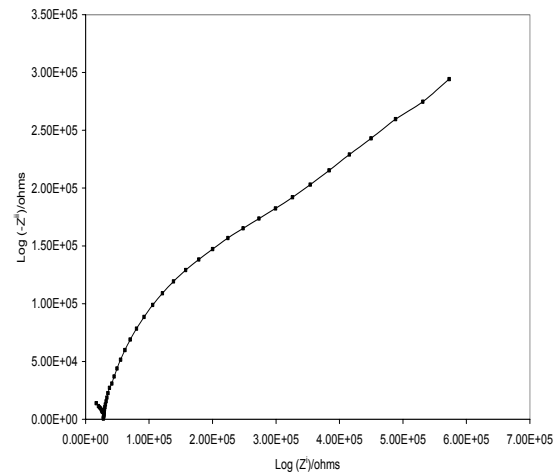


Figure 4: Impedance curve

Characteristic factor (ϕ) which is the ratio of proton conductivity to the methanol permeability of the membrane as shown in Equation 4 is a factor used to verify the performance of the proton exchange membrane in fuel cell application. Compared the characteristic values of the synthesized membrane with that of Nafion[®] which is 8 shows that the synthesized membrane with higher degree of sulphonation (i.e. DS = 28.17% and DS = 37.23%) exhibited characteristic factor of 14.85 and 27.89 respectively as shown in Table 1.

$$\phi = \frac{\sigma}{P} \quad (4)$$

Where: σ is the proton conductivity (S/cm) and P is the methanol permeability (mmol/cm²s)

Thermal stability is a major factor affecting the use of Nafion[®] in fuel cell applications operating at high temperature in the range of 100-150°C. The thermal stability of the synthesized membrane was investigated using differential scanning (DSC) and thermo gravimetric analysis (TGA) method. The DSC analysis of sulphonated and unsulphonated polystyrene butadiene rubber was carried out using 822E DSC analyzer. Measurement was performed over the range of 30-400°C at the heating rate of 5°C/minute under nitrogen atmosphere flushed at 75ml/minutes; the

results obtained are presented in Fig.5. The DSC curve shown in Fig 5 reveals that polystyrene butadiene rubber is thermally highly stable with a glass transition temperature T_g of 198°C (This point is the point of inflexion on the slope of change of DSC curve). The DSC curve also shows that the T_g of the sulphonated membrane is in the range of 200-220°C, which is influenced by degree of sulphonation. The final peak on the curve represents the final scission of the main chain of the membrane, which is in the range of 360-364°C.

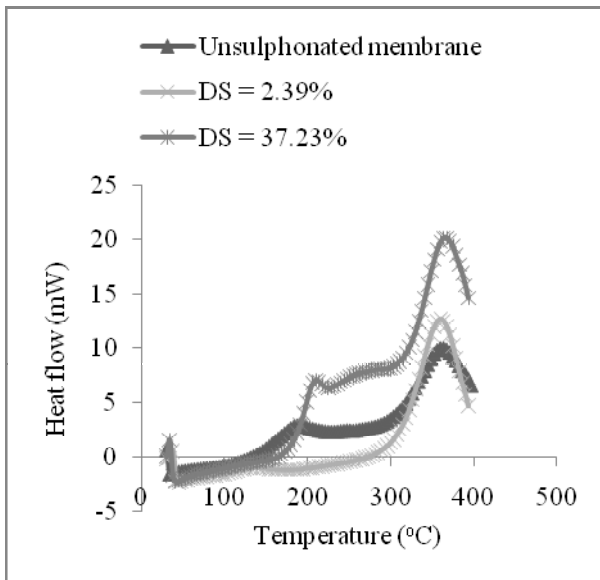


Fig. 5: DSC curve of the unsulphonated and sulphonated membrane

Thermo gravimetric analysis, which determines the change in weight relative to temperature, was also used to investigate the thermal stability of the unsulphonated and sulphonated membrane. The TGA analysis was conducted with a Perker Elmer Pyris TGA/DTA analyzer. The sample was heated to 800°C at 10°C/minute in nitrogen gas flushed at 150ml/minutes. Results obtained on the TGA analysis of the unsulphonated and sulphonated membrane are presented in Fig 6. The results obtained reveal that the synthesized membrane is thermally stable with three transition in weight in three range of temperature. The first transition temperature around 22°C can be attributed to the loss of moisture and some other chemicals in the samples. The second drop in mass around 312-316°C represent the splitting off of the sulphonic group in the membrane. The final drop in weight around 354-365°C represents the decomposition temperature of the membrane. It can be inferred from the thermal stability analyses that the synthesized membrane is thermally stable and can be employed in high temperature fuel cell applications.

The cell performance is one of the main evaluation parameters for fuel cells. The test results in a single fuel cell stack at different degrees of sulphonation and 40 wt% catalyst electrodes are presented in Figs. 7 and 8. Fig.7 represents the voltage generated by the membrane at different degrees of sulphonation while Fig. 8 shows the power density of the synthesized membranes.

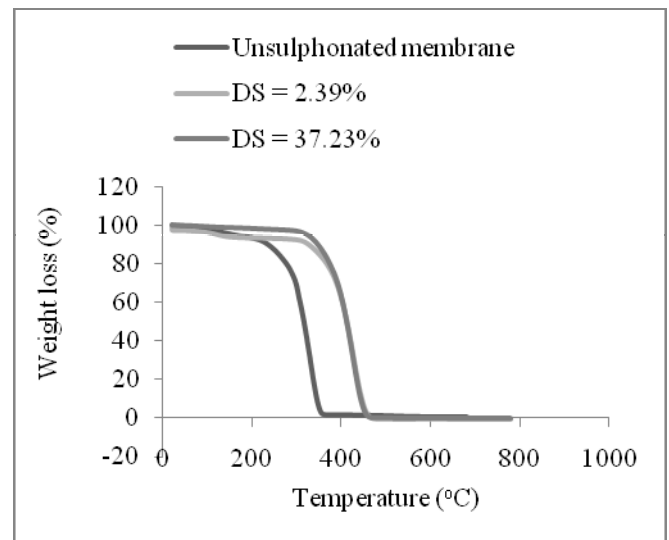


Fig 6: TGA curve of unsulphonated and sulphonated membrane.

The results obtained revealed that an increase in the degree of sulphonation resulted in an increment in the performance of the membrane. Since the increase in the degree of sulphonation resulted in an increment in the sulphonic acid group in the membrane matrix which in turn facilitates the proton transfer ability of the membrane. The higher the proton transfer the higher the voltage generated and the better the power density produced. For instance, when the degree of sulphonation is equal to 2.39% the maximum density is equal to 10.38mW/cm², while at higher degree of sulphonation (DS = 37.23%), the maximum power density produced by the membrane is equal to 71.47mW/cm² which translate to a 58.85 % increment.

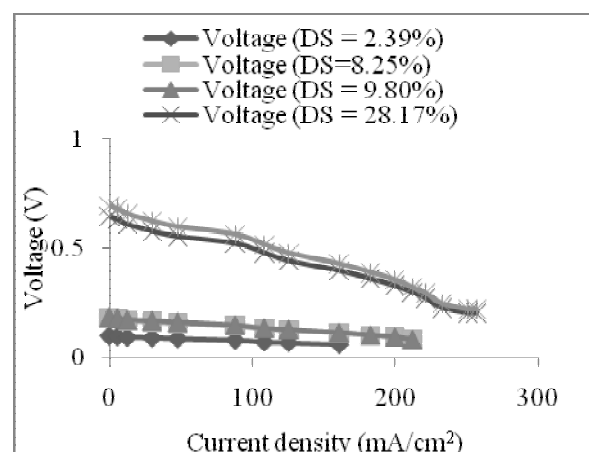


Fig. 7: Effect of degree of sulphonation on the performance of the membrane

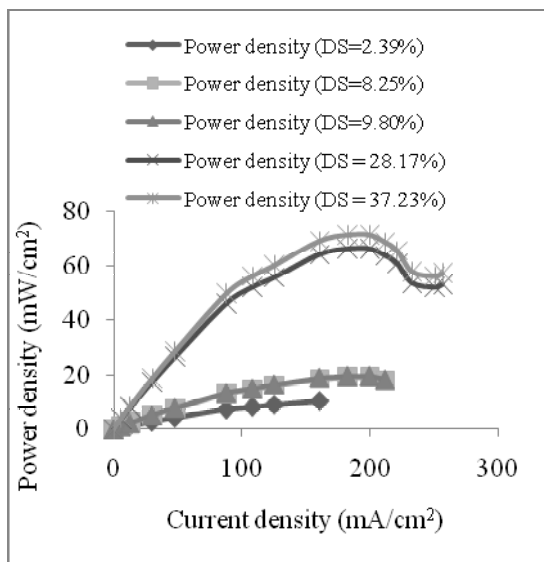


Fig. 8: Effect of degree of sulphonation on the power density.

IV. CONCLUSIONS

The concern for the efficient use of clean energy all over the world has gathered rapid momentum and there is awareness on the advantages of electrochemical power as a source of clean energy. The high cost of fuel cell components hinders the application of fuel cells for commercial purposes. The results obtained revealed that the membrane produced from the local material is thermally stable with moderate proton conductivity. The synthesized membrane produced power densities in the range of 10.38-71.47 mW/cm² depending on the sulphonation time.

V. ACKNOWLEDGMENT

Vaal University of Technology is acknowledged for providing funding for this work. Karbochem (Pty) Ltd, South Africa is acknowledged providing the polymer. Professor Sigalas and Dr Liversage are acknowledged for providing the laboratory scale casting tape.

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