Development of 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 the locally available polystyrene butadiene for fuel cell applications. Chlorosulphonic acid was used as the sulphonating agent and the effect of degree of sulphonation on membrane characteristics was determined. The sulphonated membranes were characterized according to its ion exchange capacity (IEC), degree of sulphonation (DS), proton conductivity, thermal stability and performance in a PEM fuel cell stack. These membranes were found to have proton conductivities in the order of 10⁻³-10⁻²S/cm in their fully hydrated state, which increases with an increase in degree of sulphonation. Other results revealed that the synthesized membranes are thermally stable and its performance in a PEM 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

Puel cells have been identified as one of the most promising and potential clean energy technologies which meet all the requirement 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 perfect combination of the advantages of many existing energy sources [6], [7]. This being the ease of refueling as well as continuous operation potential from internal combustion engines and the highly efficient and quiet operation of batteries. Fuel cells therefore appear as the ideal energy alternative [8]-[11]. Fuel cells generate electricity directly from fuel (i.e. hydrogen) through an efficient electrochemical reaction. They can be used in different ways and have been deployed among electricity consumers as a strategy to their substantial market penetration [12]-[14]. The

interest in research and development in fuel cell technology is increasingly rapidly, such that government, universities and companies are gradually implementing this technology [15]. For instance, fuel cells have been successfully delivering power to several prototypes and specialized application for decades [16]-[18]. The power output of a fuel cell stack can easily be scaled up to provide sufficient voltage/power for laptops, small cars, and city buses etc [19]-[21]. However, fuel cells have not been fully commercialized for many years due 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 the internal combustion engines which are the competitive technologies. In order to achieve the commercialization of the fuel cells especially the proton exchange membrane fuel cell (PEMFC), there is the need to reduce the cost of the membrane, which is the heart of the PEMFC. This can be achieved by utilizing the locally available material i.e. polystyrene butadiene rubber to synthesize proton exchange membrane with good qualities such as low methanol permeability, good proton conductivity, good thermal stability and good performance in a PEM fuel cell which is the focus of this work.

II. EXPERIMENTAL PROCEDURE

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

The ion exchange capacity (IEC) and degree of sulphonation (DS) of the sulphonated polystyrene butadiene rubber (SPSBR) were determined by measuring the sulphur

content in the dry sample of SPSBR using elemental analysis method. The IEC was then calculated using Equation 1 [24]:

$$IEC = \frac{1000S_C}{MW_S} \tag{1}$$

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]:

$$DS = \frac{IEC \times M_{SPBR}}{1 - (IEC \times MW_{SO3H})} \tag{2}$$

Where: IEC is the ion exchange capacity (mol/g), M_{SPBR} is the wolecular weight of the repeating unit of the PSBR (g/mol) and M_{SO3H} is the molecular weight of SO_3H (g/mol)

CASTING AND CHARACTERIZATION OF MEMBRANE

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

MEMBRANE TESTING

The membrane electrode assembly (MEA) was fabricated by sandwiching the synthesized membrane between two 40wt% Pt–CNT 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) diffused through the porous backing layer to the electrolyte/electrode interface where electrocatalytic reactions occurred. The voltage and current were measured using a digital multimeter and the performance of the MEA was evaluated from the polarization curves of voltage versus current density.

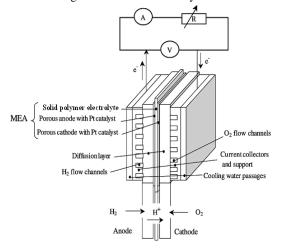


Fig. 1: Schematic of MEA and single cell testing [26]

III RESULTS AND DISCUSSION OF RESULTS Fuel cells are described as a potentially viable alternatives backup power particularly in telecom industry [17], [19]. The traditional backup power technologies use batteries and generator that depend on diesel, gasoline etc. to operate. As at the moment, most of the backup power communication and control system employ a combination of generators and batteries to provide a redundancy and good service distribution. These systems have been proved reliable and well established, but growing concerns about the environmental pollution of batteries and generators are motivating many users to seek for an alternative source of energy that can provide high reliability and durability at a reasonable cost without emission. Compared to batteries, fuel cells offer a continuous and greater durability in harsh outdoor environment. They require lesser maintenance than generators because they have fewer moving parts and they can also be monitored with remote thereby reducing the maintenance time [17]. This paper therefore describes the synthesis of proton exchange membrane for fuel cell application via sulphonation.

Sulphonation is a process used to convert a polymer to be proton conductive. Figs. 2 and 3 represent the Fourier transform infrared (FT-IR) and nuclear magnetic resonance (¹HNMR) 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 3573cm⁻¹ is the O-H vibration from sulphonic acid group upon sulphonation. While the band observed at 1364cm⁻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 1649cm⁻¹ and 1494cm⁻¹ respectively and that of the non-aromatic at 2846 and 2919cm⁻¹.

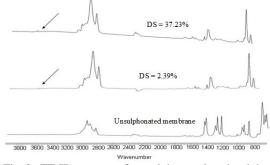


Fig 2: FT-IR spectra of unsulphonated and sulphonated PSBR

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

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

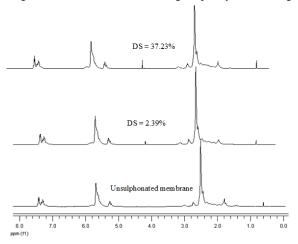


Fig. 3: 1HNMR spectra of unsulphonated and sulphonated polymer.

The degree of sulphonation which represent the average number of sulphonic groups present in the sulphonated polymer was investigated and the results obtained are shown in Table 1. It is seen from this Table that the sulphonation time influence the degree of sulphonation of the sulphonated polymer. For instance, sulphonation time of 0.5hrs produced a degree of sulphonation of 2.39% while the sulphonation time of 24hrs resulted in membrane with degree of sulphonation of 37.23%. The effect of sulphonated time on the methanol permeability of the synthesized membranes was also investigated. Methanol crossover is the capacity of the membrane to block the fuel passing through the membrane, and it is considered as the quality of the membrane that determines its performance in fuel cell application [27].

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

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Time	SC (%)	DS (%)	σ (S/cm)	P	ф
(Hrs)				(mol/cm ² s)	
0.5	0.48	2.39	0.00198	7.31X10 ⁻⁷	2.71
1.0	1.62	8.25	0.0027	6.48×10^{-7}	4.19
2.0	1.91	9.80	0.0034	$6.30 \text{X} 10^{-7}$	5.40
20.0	5.04	28.17	0.0072	$4.81X10^{-7}$	14.9
24.00	6.40	37.23	0.0129	$4.62X10^{-7}$	27.9

SC = sulphur content, DS = degree of sulphonation, σ = proton conductivity, P = methanol permeability, φ = characteristic factor.

The fuel crossover through the membrane results in decrease in the cathode potential and energy efficiency [28]. Hence, it is important to use a synthesized membrane with low methanol permeability. The results obtained on the effect of sulphonation time on the methanol permeability (Table 1) show that as the sulphonation time increases and the permeability to membrane decreases. Increase in sulphonation time increased the degree of sulphonation which also resulted to reduction in equivalent weight that produces more sites for the distribution of methanol in the

membrane matrix. The results obtained on the methanol permeability reveal that the methanol permeability of the synthesized membrane is lower than that of the Nafion[®] (3.15X10⁻⁶mol/cm²s), the commercially available membrane.

The proton conductivity of the synthesized membranes was measured by alternating current impedance over a frequency range of $1\text{-}10^6$ Hz using 1M H_2SO_4 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:

$$\sigma = \frac{T}{RS} \tag{3}$$

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

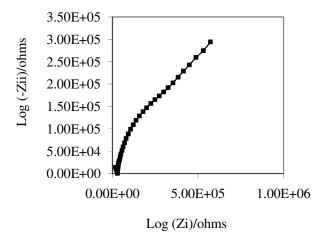


Fig. 4: Impedance curve

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

$$\Phi = \frac{\sigma}{p} \tag{4}$$

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 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) methods. The DSC analysis of the sulphonated and unsulphonated polystyrene butadiene rubber was carried out using 822E DSC analyzer. Measurement was obtained over the range of 30-400°C at the heating rate of 5°C/minute under nitrogen atmosphere flushed at 75ml/min, the results obtained are presented in Fig. 5. The DSC curve shown in Fig 5 reveals that polystyrene butadiene rubber is highly stable thermally with a glass transition temperature T_g of 198°C (This is the point of inflexion on the slope of change of DSC curve). This curve also shows that the T_g of the sulphonated membrane is in the range of 200-220°C which is influenced by the degree of sulphonation. The final peak on the curve represent the final scission of the main chain of the membrane which is in the range of 360-364°C.

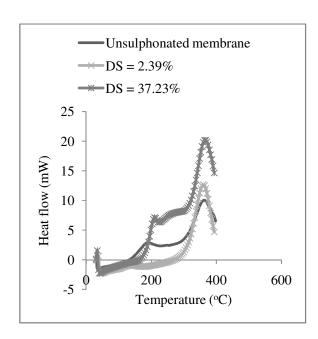


Fig. 5: DSC curve of the unsulphonated and sulphonated membrane

The TGA analysis which determines the change in weight relative to temperature was also used to investigate the thermal stability of unsulphonated and sulphonated membrane samples. The TGA analysis was conducted with Perker Elmer Pyris TGA/DTA analyzer where the samples were heated to 800°C at 10°C/minute in nitrogen gas flushed at 150ml/min. The results obtained on the TGA analysis of the unsulphonated and sulphonated membrane (Fig 6) reveal that the synthesized membrane is thermally stable with three transition of loss in weight. The first transition temperature (about 22°C) can be attributed to the loss of moisture and some other chemicals such as dichloro ethane in the samples. The second drop in mass (between 312-316°C) represents the splitting off of the sulphonic group in the membrane. The final drop in weight (between 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 at high temperature fuel cell applications.

The cell performance is one of the main evaluation parameters of fuel cells. The test results obtained in a single PEM fuel cell stack at different degrees of sulphonation using 40 wt% Pt-CNT catalyst electrodes are presented in Figs. 7 and 8. Fig.7 represents the voltage generated by the membrane at different degree of sulphonation while Fig. 8 shows the power density of the synthesized membranes. These results reveal that increase in degree of sulphonation enhanced the performance of the membrane. This can be explained by the fact that increase in degree of sulphonation increased the sulphonic acid group in the membrane matrix which in turn facilitated proton transfer ability of the membrane. The higher the proton transfer the higher the voltage generated and the more the power density produced. For instance, at the degree of sulphonation is equal to 2.39% the maximum density of 10.38mW/cm², while at higher degree of sulphonation (DS = 37.23%), the maximum power density produced by the membrane is 71.47mW/cm² which translate to 58.85 %

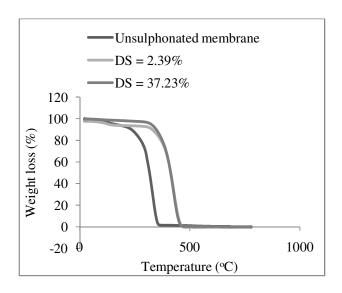


Fig 6: TGA curve of unsulphonated and sulphonated membrane.

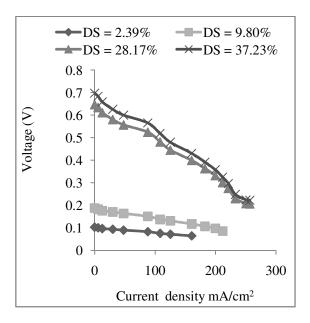


Fig. 7: Effect of degree of sulphonation on the performance of membrane

IV CONCLUSION

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 source of clean energy. Fuel cells have been identified as alternative source of energy for power backup in telecom industry. On a life cycle basis, fuel cells can offer significant cost saving over battery -generator system. High cost of the fuel cell components especially the PEM hinders the availability of fuel cell for commercial purpose. Alternative PEM was synthesized in this work and the results obtained revealed that the membrane produced from the local material is thermally stable with moderate proton conductivity. The synthesized membrane produced power density in the range of 10.38-71.47mW/cm² depending on the sulphonation time. The synthesized membrane can therefore be used for telecom fuel applications

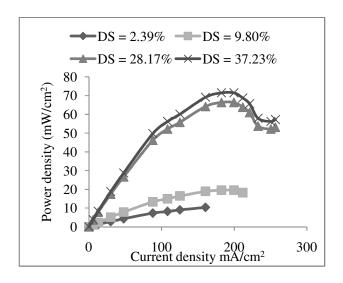


Fig. 8: Effect of degree of sulphonation on the power density.

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REFERENCES

- [1] A.J Appleby, "Fuel Cell Technology and Innovation," Power Sources J., vol 37 pp 223-239, 1992
- [2] S.Wang ,G. Sun, G. Wang , Z. Zhou, X. Zhao , H. Sun, X. Fam , B. Yi and Q. Xin "Improvement of direct methanol fuel cell performance," Electrochemistry Communication J., vol 7 pp 1007-1012, 2005
- [3] T. Klaiber "Fuel Cells for Transport: Can the Promise be fulfilled? Technical Requirements and Demands from Customers,". Power Sources J., vol 61pp 61-69, 1996
- [4] W.S Li, D.S Lu, J.L Luo and K.T Chyang "Chemical and energy co generation from direct hydrocarbon oxygen proton exchange membrane fuel cell" Power Sources J., volume 145 pp 376 382, 2005
- [5] S. Chen, A. B Bocarsly and J. Benzinger "Nafion-layered sulfonated polysulfone fuel cell membranes," Power Sources J., volume 152 pp 129-135, 2005
- [6] X. Shang, S. Tian, L. Kong and Y. Meng "Synthesis and characterization of sulfonated fluorene-containing poly (arylene ether ketone) for proton exchange membrane," Membrane Science J., vol 266 pp 94-101, 2005
- [7] M. Bischoff "Large stationary fuel cell systems: Status and dynamic requirements," Power Sources J., vol 154 pp 461-466, 2006
- [8] J. Ch Schlake, Ch. Preusse, J. Winkelhake and U. Konigorski "State space model of the direct methanol fuel cell," Power Sources J, vol 153 pp 100-107, 2006
- [9] A. Oedagaard and C. Hentschel "Characterisation of a portable DMFC stack and a methanol-feeding concept," Power Sources J., vol 158 pp 177-187, 2006

- [10] W. Ying, Y. Sohn, W. Lee, J. Ke and C. Kim "Three-dimensional modeling and experimental investigation for an air-breathing polymer electrolyte membrane fuel cell (PEMFC),"Power Sources J, vol 145 pp 563-571, 2006
- [11] K. Haraldsson and P. Alvfors "Effects of ambient conditions on fuel cell vehicle performance," Power Sources J., vol 145 pp 298-306, 2005
- [12] S. Millet and K. Mahadevan "Commercialization scenarios of polymer electrolyte membrane fuel cell for stationary power generation in United State by the year 2015," Polymer Science J., vol 150 pp 187 191, 2005
- [13] T. Shuo, L. Yuan, X. Wenchuan, L. Jianqiu and Y. Minggao "Advanced ECU Software Development Method for Fuel Cell Systems,". Tsinghua Science and Technology., vol 10 (5) pp 610-617, 2005
- [14] M. Shibasaki, T. Yachi and T. Tatsuo "A new direct methanol fuel cell with a zigzag folded membrane electrode assembly," Power Sources J., vol 145 pp 477-484, 2005
- [15] E. Kjeang, J. Goldak, M. R. Golriz, J. Gub, D. James and K. Kordesch "A parametric study of methanol crossover in a flowing electrolyte-direct methanol fuel cell," Power Sources J., vol 153 pp 89-99, 2006
- [16] S.J Lee, A. Chang-Chien, S.W Cha, Y.I OHayre and F.B Prinz "Design and fabrication of a micro fuel cell array with "flip-flop" interconnection," Power Sources J., vol 112 pp 410-418, 2002
- [17] S. Hikita, K. Yamane and Y Nakajima "Measurement of methanol crossover in direct methanol fuel cell," JSAR Review., vol 22 pp 151-156, 2001
- [18] J.O Schumacher, P. Gemmar, M. Denne, M. Zedda and M. Stueber "Control of miniature proton exchange membrane fuel cells based on fuzzy logic," Power Sources J., vol 129 pp 143-154, 2004
- [19] J. Ge and H. Liu "Experimental studies of a direct methanol fuel cell," Power Sources J., vol 142 pp 56-69, 2005
- [20] C. Nitsche, S. Schredl, W. Weiss and E. Pucher "Rapid (practical) methodology for creation of fuel cell systems models with scalable complexity," Power Sources J., vol 145 pp 383-391, 2005
- [21] J.Lawrence and M. Boltze "Auxiliary power unit based on a solid oxide fuel cell and fuelled with diesel," Power Sources J., vol 154 pp 479-488, 2006
- [22]T. Schultz and K. Sundmacher "Rigorous dynamic model of a direct methanol fuel cell based on Maxwell–Stefan mass transport equations and a Flory–Huggins activity model: Formulation and experimental validation," Power Sources J., vol 145 pp 435-462, 2005
- [23] H.P Dhar "Medium term stability testing of proton exchange membrane fuel cells stacks as independent power units," Power Sources J., vol 143 pp 185 – 190, 2005
- [24] P. Bebin, M. Caravanier and H. Galiano "Nafion/Clay –SO₃H membrane for proton exchange membrane fuel cell application," Membrane Science J., vol 278 pp35-42, 2006
- [25] L. Paturzo, A. Basile, A. Julianelli, J.C Jansen, I. Gatto and E. Passalacqua "High temperature proton exchange membrane fuel cell using a sulfonated membrane obtained via H₂SO₄ treatment of PEEK-WC," Catalysis Today., vol 104 pp 213-218, 2005

- [26] S.E Iyuke, A.B Mohammed, A.H Kadhum, W.R Daud and C. Rachid "Improved membrane and electrode assemblies for proton exchange membrane fuel cells," Power Sources J., vol 114 pp195 2002, 2003
- [27] S. Nobuhiro and S.P Roger "A reconsideration of the kinetics of aromatic sulfonation by sulphuric acid," Macromol J., vol 27 pp 6267-6271, 1994
- [28] W. Han-Lang, M.M Che-Chi, L. Chia-Itsun, L. Tzong-Ming, C. Chin-Lung and W.Chen "Sulfonated poly(ether ether ketone)/poly (amide imide) polymer blends for proton conducting membrane,"Membrane Science J., vol 280 pp 501-508, 2006

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