Determination of Alcohol Permeability on Synthesized Polyisoprene/Polystyrene Blend Electrolyte Membrane for Direct Methanol Fuel Cell

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Abstract

The serious issue of methanol permeation associated with Direct Methanol Fuel Cell (DMFC) has militated against its large scale commercialization. Effort in getting polymer electrolyte membranes of high-methanol-permeation resistivity has been on. This has thus necessitated this study, where methanol permeation was determined on synthesized polymer electrolyte membrane derived from the blend of polyisoprene and polystyrene. The synthesized membrane exhibited ideal ionic conductivity of 10^{-2} S/cm order with moderate water uptake. The concentration change of methanol in aqueous solution at varying degrees of sulphonation (DS) showed that the blended membrane with lower DS manifested higher methanol crossover (1.23 mol/L), while the methanol crossover decreased as DS increased. Hence, the membrane of higher DS (49.37 %) only allowed methanol crossover of 0.79 mol/L, and of course the preceding DS (39.69 %) only allowed 0.92 mol/L. However, methanol crossover was noticed to be highest with the unblended membrane (1.28 mol/L). The overall diffusion coefficient of the synthesized membranes achieved an order of 10^{-7} cm^2/s as against the current state-of-the-art membrane (nafion) (10^{-6} cm^2/s). The study thus showed that the blended membrane manifested a lower methanol permeation by exhibiting high-methanol-permeation resistivity compared to the commercial nafion, suitable for DMFC application.

Keywords: conductivity, crossover, fuel cell, methanol, permeation, polyisoprene, polystyrene.

Introduction

Fuel cells are of different types but they operate on the principle of electrochemical cell in which chemical energy is converted directly into electrical energy (Idibie, 2023). Types of fuel cell include; Direct Methanol Fuel Cell (DMFC), Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Proton Exchange Membrane Fuel Cell (PEMFC), and Solid Oxide Fuel Cell (SOFC). These are all clean, reliable, efficient energy sources that are recognized to serve as alternative energy sources to the world fossil sources of energy that are finite and, now fast depleting due to over dependency (Idibie *et al*., 2009; Idibie, 2017 a). They utilize solid electrolyte membrane for ionic transport, particularly, proton transport between the anode and the cathode (Idibie, 2017 b) in the presence of water molecules (Idibie, 2018). However, the issue of methanol permeation through the electrolyte has remained a serious concern particularly for DMFC (Idibie *et al*., 2009). The polymer electrolyte in concern with this issue is the only commercially available perfluorinated Nafion membrane, and it is also very expensive perhaps due to its monopoly of market. The large methanol permeation causes mixed potential phenomenon which increases over potential of the cathode and thus causing reduction on cell performance as well as fuel efficiency (Idibie *et al*., 2009). Low fuel (methanol) permeable membranes are therefore ideal and recommended as electrolytes especially for DMFC, having been recognized to be very attractive due to its several applications arising from their lower weight and volume in contrast to indirect fuel cells. This backdrop has therefore created the drive in searching for an alternative electrolyte membrane with low methanol permeation and having good ionic conductivity (Yo *et al*., 2004). The synthesis of an electrolyte membrane from a carefully blend of polyisoprene and polystyrene had been carried out in previous study (Idibie *et al*., 2024), having good ionic conductivity comparable to the commercial nafion, and displaying moderate water uptake for ionic mobility with reduced swelling that is appropriate for fuel cell application. Similar result was also achieved with an electrolyte membrane derived from polyisoprene that was impregnated with carbon nanotubes in the same study, but displayed reduced water uptake comparatively with the former, which perhaps could be associated with the carbon nanotube being a hard material. The blend was

important as previous study showed their superior fuel cell properties over the base polymer alone (polyisoprene) (Idibie *et al*., 2024). However, there is the need to investigate the methanol permeability of this electrolyte membrane with superior properties that is derived from the unique blend of polyisoprene and polystyrene for possible DMFC application, and hence, this study.

Materials and Methods

Chemicals used were of analytical grade (> 98 %) and were sourced within and outside the country. These were: 1, 2, dichloroethane, chlorosulphonic acid, ethanol, methanol, sulphuric acid, toluene (Charlec Laboratories, Nigeria), commercial polyisoprene, polystyrene, (Karbochem RSA). Four neck round bottom flask fabricated reactor and a multimeter.

Determination of substrate ion exchange capacity and degree of sulphonation

These were obtained through elemental analysis of sulphur via sulphonation process of predetermined (70:30 %) 20 g blend of polyisoprene/polystyrene according to prescribed procedure (Idibie, 2018, Idibie, 2017 a). Here, the polymer blend was initially dissolved in 1, 2, dichloroethane in a four neck round bottom flask reactor and was followed by a gradual addition of chlorosulphonic acid of 0.0023 mol/L that had been chilled in an iced bath. The reaction was vigorously stirred in the reactor and under argon atmosphere at room temperature. The reaction proceeded at varying time of 1, 3, 6, 9, 12, 15 and 18 hours, respectively. Thereafter the reaction was halted with the addition of ethanol, where the precipitated, sulphonated PI/PS (SPI/PS) was obtained and washed with deionised water until the wash achieved 6 -7 pH. This was followed by drying of the sulphonated SPI/PS in an oven at 80^{o}C for 2 hours. Thus the ion exchange capacity (IEC) and Degree of sulphonation (DS) were obtained using equations 1 (Bebin, 2005) and 2 below:

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

where: S_c depicts the sulphur content under percentage weight rate, MWs depicts the molecular weight of sulphur, and where 1000 is the multiplication factor to obtain IEC values in mmol/g.

$$DS = \frac{MW_{SPI/PS} \times IEC}{MW_{PI/PS} \times MW_{SO_3H}} \times 100 \quad (2)$$

where: $MW_{SPI/PI}$ = molecular weight of sulphonated polyisoprene and polystyrene, and MW_{SO_3H}= molecular weight of sulphonic acid.

Fabrication of thin film membranes

The sulphonated PI/PS and unblended PI were differently cast into thin membranes of different degrees of sulphonation (DS) by first dissolving 10 g in 250 ml mixture of toluene/dichloroethane (50:50) at elevated temperature to form a casting solution, and thereafter cast onto a polymer paper support using a laboratory doctor blade casting machine that was adjusted to size according to the method described by Idibie (2018). The casting was accomplished by pulling the casting head of the blade along the length of the substrate, and then cured for 4 days. This was followed by drying in the oven (< 80ºC) for 2 hrs and later vacuum dried for additional 2 hrs to completely remove residual solvent.

Water and solvent uptake of fabricated membranes

The water uptake of the synthesized membranes was studied by dipping a known membrane thickness (120, μm) in a beaker, containing distilled water for a few days before attaining saturation. Upon removal from water, the water uptake was determined using a digital weighing balance. The weight difference between the wet and dry membrane was thus calculated using Equation (3):

$$\text{Water uptake } (\%) = \frac{W_{wet} - W_{dry}}{dry} \times 100 \quad (3)$$

where: W_{wet} and W_{dry} represent weights (g) of the wet membranes and dry membranes, respectively.

The solvent uptake of the synthesized membranes was gravimetrically achieved according to prescribed method (Idibie *et al*., 2009). Here, membranes of different DS were dried overnight at 80ºC in order to remove residual solvent and weighed for their dry weights (W_{dry}). Thereafter they were immersed in methanol of various concentrations in mol/L until they attained equilibrium.

Following this, the saturated membranes were blotted against surface solvent and reweighed (W_{wet}), where the overall uptake of solvent molecules per sulphonic acid group in the membrane (λ_{total}) was calculated thus (Idibie *et al*., 2009):

$$\lambda_{total} = \frac{W_{wet} - W_{dry}}{W_{dry}} \cdot \frac{EW}{18x_{water} + 32.04(1 - x_{water})} \quad (4)$$

where: W_{wet} = weight of the wet membrane (g), W_{dry} = weight of dried membrane (g) x_{water} = molar fraction of water in the solution, EW (mol/g) = equivalent weight of the membranes.

According to Shen *et al* (2005), EW = $\frac{1}{IEC}$ (5)

Equation (6) was used to obtain the uptake of methanol molecules per sulphonic acid group ($\lambda_{methanol}$):

$$\lambda_{methanol} = \lambda_{total}\ (1 - x_{water}) \quad (6)$$

Proton conductivity measurement

The measurement of the proton conductivities of the synthesized membranes were ascertained as a function of DS using alternating current impedance with 1M H_2SO_4 as an electrolyte in a known frequency range (1-106Hz) (Idibie, 2018). The intersection value of the high frequency impedance curve was simply taken as the membrane resistance, and the conductivity was calculated using Equation 7:

$$\sigma = \frac{T}{RS} \quad (7)$$

where: σ = proton conductivity (S/cm), T (cm) = membrane thickness, S (cm^2) = surface area of the membrane and R = resistance from the impedance plane.

Methanol permeability

Permeation of methanol through the synthesized membranes at different degrees of sulphonation was carried out according to prescribed method (Idibie *et al*., 2009) using two identical chamber containers. Each membrane (with approximate surface area of 6.90 cm^2) was placed between identical chambers of volume 70cm^3 where one of the chambers contained concentrated methanol, while the second chamber contained water. However, the liquids in the two chambers were stirred

using a magnetic stirrer to achieve a homogenous solution. Following this, a small amount of liquids was drawn from the second chambers at different time interval to determine the amount of crossover methanol, and with the use of a UV-VIS VIS model spectrometer the methanol concentration in water was measured.

Results and Discussion

Substrate ion exchange capacity and degree of sulphonation

The ion exchange capacity (IEC) was used to derive the degree of sulphonation of SPI/PS, and result as presented in Figure 1 shows that the IEC has a linear relationship to DS with the varying time of sulphonation. Using 0.023 mol/L of acid, the IEC values obtained were 9.37, 13.12, 17.5, 21.87, 25, 28.12, and 30.31 mmol/g with corresponding DS of 17.02, 23.82, 31.76, 39.69, 45.37, 51.08, and 55.01 %, respectively. This shows that the attachment of the sulphonic group to the substrate increases with interaction time of the sulphonation process and thereby enhancing the IEC and DS. Therefore the acid concentration in the substrate is related to the amount of ionic groups present and, thus ascribed as the degree of sulphonation (Idibie et al., 2018b), whereas the IEC is a pointer of the proton conduction sites (Sagetha, 2005).

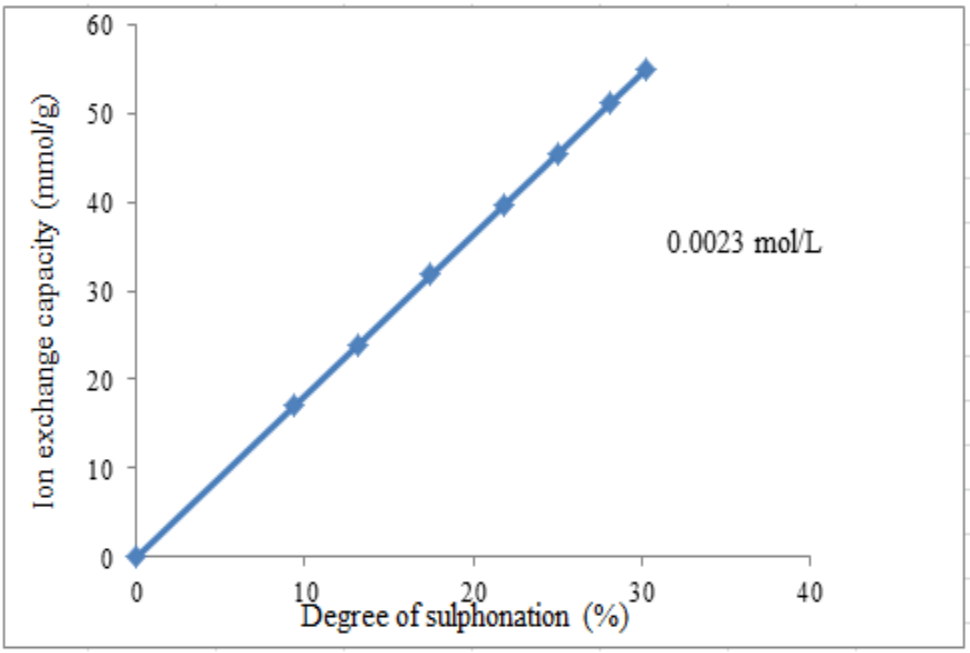

Figure 1: Degree of sulphonation as a function of IEC.

Water absorption of spi/ps fabricated membrane

The hydrodynamic behavior of the synthesized membrane as regards its water absorption at different DS with membrane of 120 µm thickness is shown in Figure 2. Membranes of three different DS were studied; 31.76, 39.69 and 45.37 % and their lowest and highest water absorption were; 19.35 and 42.91, 39.14 and 65.49, 43.67 and 70.12 weight %, respectively. The result shows that membrane of the lowest DS (31.76 weight %) absorbed the lowest and which will not encourage good and efficient ionic transport, while membrane of 39.69 weight % exhibited moderate water absorption ideal for ionic transport without the fear of swelling and disintegration, whereas the membrane with the highest DS (45.37 weight %) absorbed very highly and which would lead to membrane swelling, disintegration and failure under fuel cell operation (Idibie *et al*. 2024).

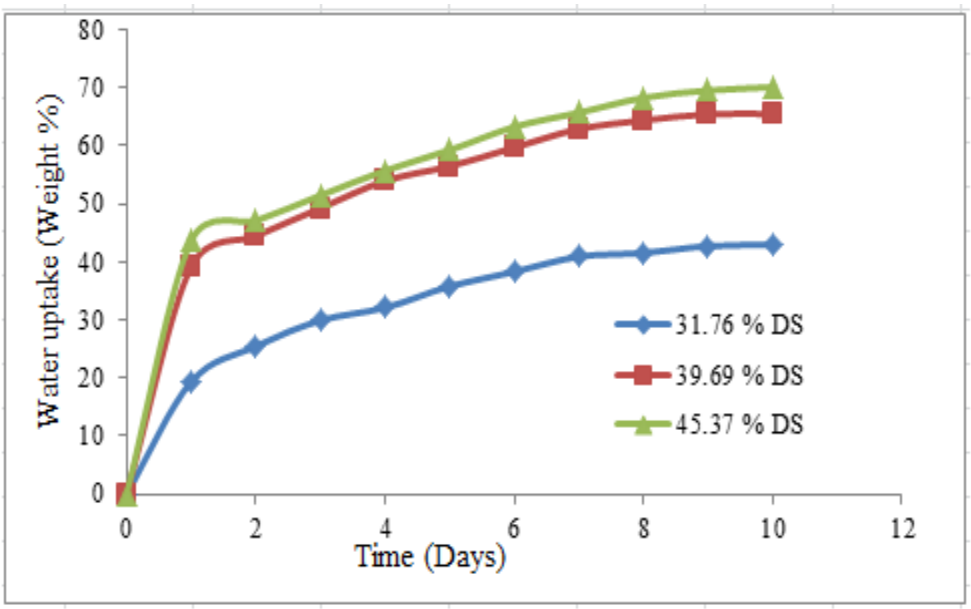

Figure 2: Water uptake ability of the synthesized membrane over time.

Ionic conductivity of fabricated membrane

The proton conductivity of the synthesized membrane of 120 µm thickness of different DS as investigated is shown in Figure 3. The result reveals that conductivity of the membrane increases with increasing DS as membrane of 23.82, 31.76, 39.69, 45.37, 51.08 and 55.01 % achieved conductivities of 9.8 x 10^{-3}, 4.4 x 10^{-2}, 8.7 x 10^{-2}, 8.9 x 10^{-2}, 9.3 x 10^{-2} and 9.7 x 10^{-2} S/cm, respectively. Suffice to emphasize that the membrane that exhibited the ideal water uptake for ionic transport (39.69 % DS) without possible fear of swelling and disintegration but didn't achieve the highest conductivity was able to achieve a promising conductivity that is competitive with the present state-of-the-art membrane (nafion) in the order of 10^{-2} S/cm. However, membranes having DS >39.69 (i.e. 45.37, 51.08 and 55.01 %), though exhibited higher conductivities but carry the fear and risk of swelling, disintegration and failure under use.

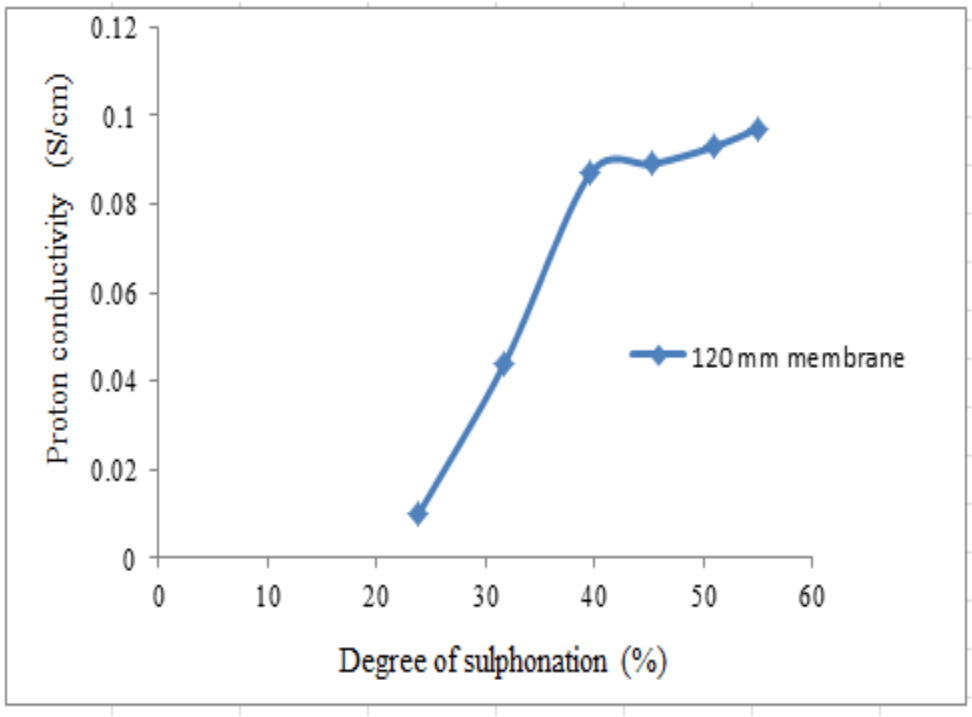

Figure 3: Proton conductivity at different DS with membrane of 120 µm.

Study of methanol uptake, crossover and permeability

The characteristic of membrane in methanol crossover is a major quality which determines its performance in fuel cell applications, and that is why Direct Methanol Fuel Cell (DMFC) has been recognized to have suffered serious drawback in commercialization due to its associated problem of methanol crossover because this problem results in decrease in the cathode potential as well as energy efficiency (Jiang *et al*., 2006; Hikita *et al*., 2001). Result shown in Figure 4 is the uptake of methanol solution at different DS. The result revealed that uptake of methanol per sulphonic group increases with increase in concentration of methanol, and which can be associated with the availability of the methanol at higher concentration than at lower concentration (Idibie *et al*., 2009). More so, the result showed that methanol uptake per sulphonic group decreases with increase in DS. This is in accordance with result in previous study (Idibie *et al*., 2009) and which was attributed to the decrease in equivalent weight as the DS increases (Idibie *et al*., 2009). However, membrane synthesized from the base material alone (PI) exhibited the highest methanol

uptake per sulphonic group despite having the lowest DS amongst its counterpart. This shows that blending of the base material with polystyrene (PS) improved the membrane property

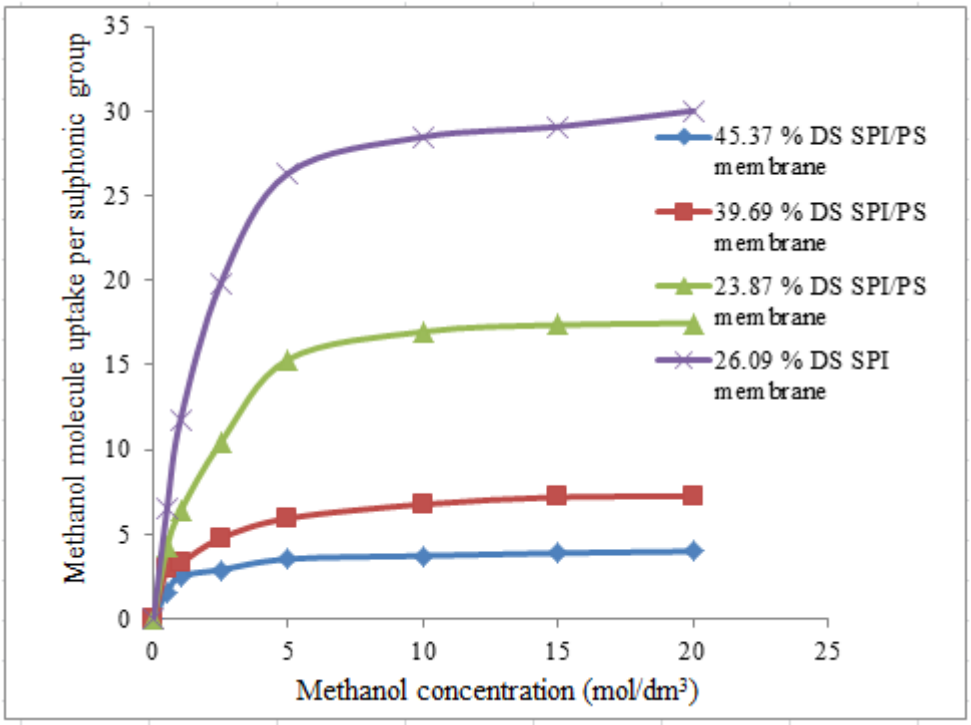

Figure 4: Methanol molecule uptake per sulphonic group at different conc. of methanol and DS with membrane of 120 µm.

against high methanol uptake. Following this, Figure 5 presents concentration change of methanol in aqueous solution at varying DS. The result shows that blended membrane with lower DS manifested higher methanol crossover (1.23 mol/L), and decreases as the DS increases, as the membrane of higher DS (49.37 %) only allowed methanol crossover of 0.79 mol/L. However, methanol crossover was noticed to be highest with the unblended membrane (1.28 mol/L), and of course the preceding DS (39.69 %) only allowed 0.92 mol/L. This result pattern was attributed to decrease in equivalent weight as DS increases, and with the reduction in equivalent weight, more sites resulted for the distribution of methanol within the matrix of the membrane (Idibie *et al*.,

2009). The excess methanol at saturation point of the membrane thus crosses to the other side of the membrane.

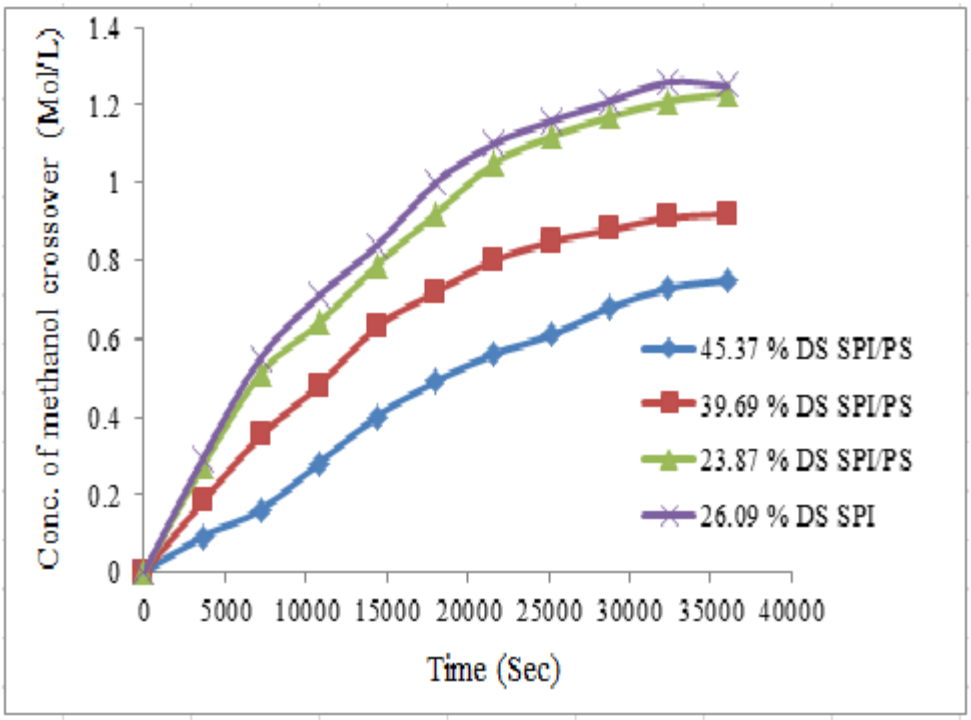

Figure 5: Methanol crossover concentration at different DS with membrane of 120 µm.

However, the results achieved from the methanol crossover were used in determining the overall diffusion coefficient and methanol permeability according to prescribed relation (Gao *et al.*, 2003), and following the below stated assumptions:

i. Methanol solution diffuses through the membrane and obeys Fick's law.
ii. Methanol solutions at either side of the membrane are at equilibrium due to stirring.
iii. There is Proportional relationship between methanol concentration of bulk solution and membrane wall in contact with the solution.

Following the assumptions above, methanol will diffuse from compartment A to B because $C_A > C_B$. As a result, the methanol permeation is obtained with the methanol concentration of the compartment B with relation to time according to Equation (8):

$$\frac{dC_B}{dt} = Am\frac{\mathcal{P}_{ABK^m}}{d_m V_o}\ (C_{AO} - C_B) \qquad (8)$$

where: C_A = concentration of methanol in compartment A, C_B = concentration of methanol in compartment B. $V_0 = V_A + V_B$, and V_A as well as V_B are the volume of methanol in compartment A and B, respectively, A_m = area of the membrane and dm = membrane thickness.

And integrating Equation (8), you have Equation (9) which is the relationship between changes in concentration as a function of time:

$$\frac{\frac{1}{2}lnC_{A0}}{C_{A0}-2C_B} = A_m\frac{\mathcal{P}_{Am\,K^m}}{d_m V_o}t \qquad (9)$$

where: $\mathcal{P}_{Am}$ = diffusion coefficient, K_m = Proportional constant and $P_m K^m$ = overall methanol diffusion coefficient. The slope of the plot of $\frac{\frac{1}{2}lnC_{A0}}{C_{A0}-2C_B}$ vs time as shown in Figure 6 = $A_m\frac{\mathcal{P}_{Am\,K^m}}{d_m V_o}$. From the slop, the overall diffusion coefficient was achieved.

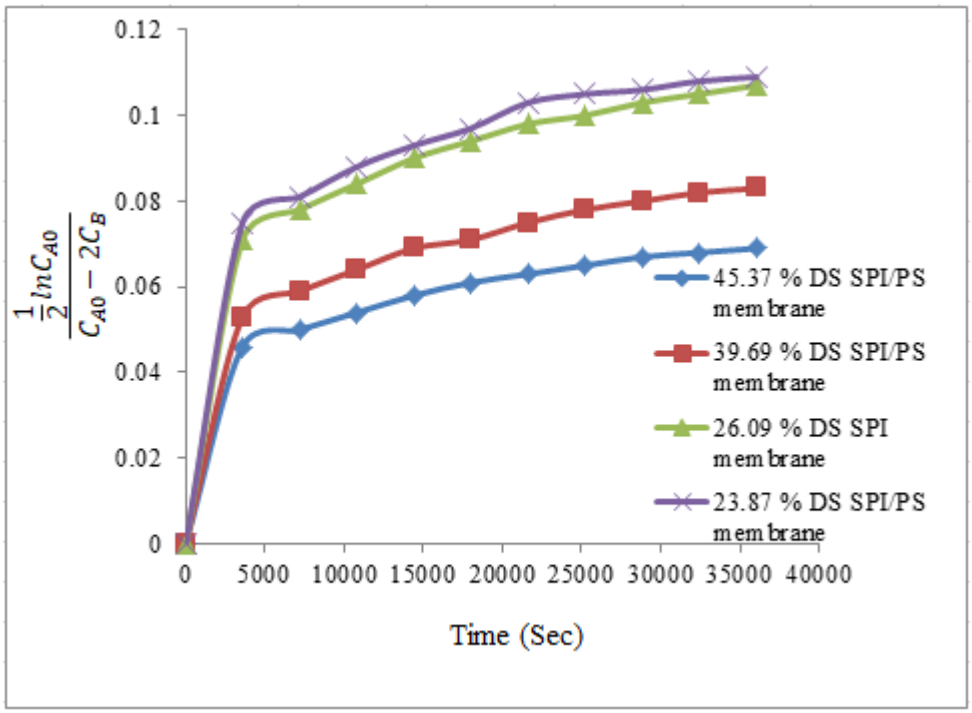

Figure 6: Plot of $\frac{\frac{1}{2}lnC_{A0}}{C_{A0}-2C_B}$ against time at different DS using 120 µm.

Table 1 presents the overall diffusion coefficient of the synthesized membranes, where they obtained an order of 10^{-7} cm^2/s as against the current state-of-the-art membrane (nafion) with an order of 10^{-6} cm^2/s (Idibie et al., 2009). Although the trend shows that the overall diffusion coeffient has an inverse relationship to the DS, but the unblended membrane (from sulphonated PI) had a higher overall diffusion coefficient.

Table 1: Overall diffusion coefficient of synthesized membranes.

Overall diffusion coefficient (cm^2/s) 10^{-7}		
26.09 % DS	2.5	SPI
23.87 % DS	2.4	SPI/PS
39.69 % DS	2.3	SPI/PS
45.37 % DS	1.9	SPI/PS

The overall diffusion coefficient as determined was used to determine the methanol permeation according to Equation (10):

$$J = \mathrm{P}_{Am} \frac{dC_m}{d_m} \qquad (10)$$

The result however shown in Figure 7 reveals that methanol permeability decreases with increasing DS with an order of 10^{-7} cm^2/s which is comparatively lower to the commercial nafion of 10^{-6} cm^2/s order, and that of the unblended membrane from SPI, and thus achieve low methanol permeation or rather high-methanol-permeation resistivity for Direct Methanol Fuel Cell (DMFC). This of course, an improvement on the limitation of methanol permeation that is associated with DMFC, and which will now improve its performance. This result is in consonant with previous work (Idibie *et al*., 2009) on polystyrene-butadiene rubber that shared rubber-plastic domains. Suffice to mention that the unblended membrane experiences higher methanol permeation compared to the blended with PS. Thus the introduction of PS has improved the alcohol resistance of the base material.

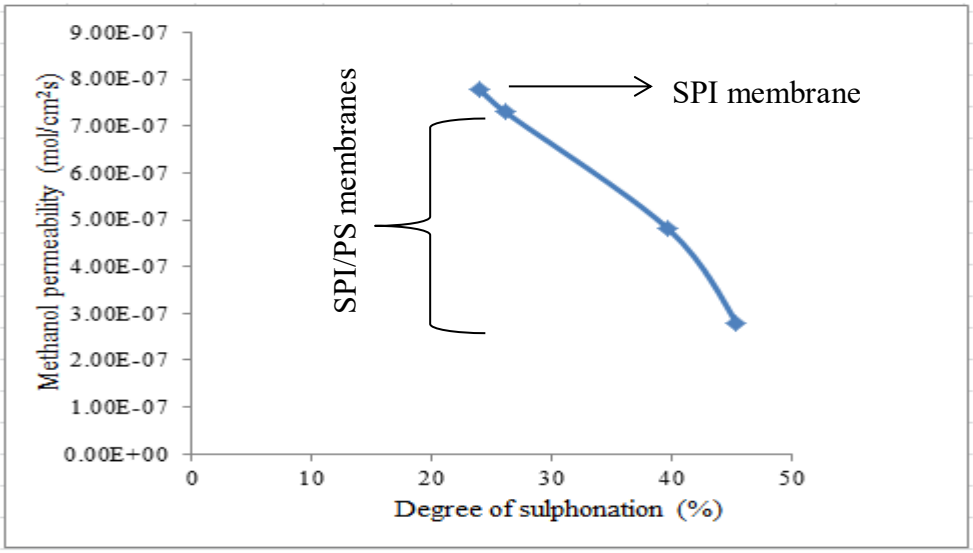

Figure 7: Methanol permeation vs DS with membrane of 120 µm thickness.

Observed discrepancy and scientific explanation

The study of the methanol crossover/permeation showed that the unblended membrane derived from SPI exhibited higher methanol crossover/permeation despite ranking below the membrane with the lowest DS (23.87 %). It has a DS of 26.09 %, and was supposed to exhibit a lower methanol crossover/permeation since methanol crossover/permeation decreases with increasing DS. This can be attributed to morphological differences. Morphology of membranes; porous or dense in structure can affect the permeability of methanol, as membranes of dense morphological structure exhibit better resistance to methanol permeation than membranes of porous morphology and, thereby enhancing polymer electrolyte membrane performance (Junoh *et al*., 2020). The membranes derived from the blend of PI/PS as expected are of denser morphological structure than the unblended membrane from PI, and thus displayed a superior methanol resistance even with the lowest DS (23.87 %).

Conclusion

Synthesis of polymer electrolyte membrane from the blend of Polyisoprene and polystyrene agrees with the general belief that no single polymer material has the excellent properties needed for membranes, and as such, polymer materials require modification to enhance their performance for specific application in fuel cell. This study showed that the blend of SPI/PS membrane is able to achieve low methanol crossover and high-methanol-permeation resistivity for DMFC with an order of 10^{-7} cm^2/s compared to the present state-of-the-art nafion membrane of 10^{-6} cm^2/s.

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