

Development of sulfonated polysulfone membranes as a material for Proton Exchange Membrane (PEM)

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Abstract

This paper reports the development of sulfonated polysulfone (SPSU) membrane as potential candidates for proton exchange membrane through sulfonation process. Sulfonated polysulfone membranes have been prepared by conducting sulfonation reaction at room temperature with a mild sulfonating agent, trimethylsilyl chlorosulfonate (TMSCS). The membranes were sulfonated with different molar ratio of sulfonating agent to the polymer repeat unit. The degree of sulfonation was determined by elemental analysis and Fourier Transform Infrared (FTIR) was performed to verify the sulfonation reaction on the polysulfone polymer. The sulfonated polysulfone membranes have been characterized by ion exchange capacity (IEC), water uptake and proton conductivity as a function of molar ratio and degree of sulfonation. It was shown that increases in the molar ratio of the sulfonating agent to polysulfone repeat unit lead to an increasing degree of sulfonation. The water uptake of the sulfonated polysulfone membrane was increased with an increase in degree of sulfonation from 4.1 wt.% up to 26 wt.% with the value of IEC about 0.62 mmol/g and 1.78 mmol/g respectively. Area resistance of the sulfonated membranes were decreases as a function of temperature and degree of sulfonation. The conductivity values in the range of 10^{-4} – 10^{-3} S/cm were obtained for SPSU membranes. The conductivity of the membranes show similar increasing trend as a function of operating temperature.

Keywords: Polysulfone, polymer electrolyte membrane, sulfonated polysulfone, ion exchange capacity, proton conductivity.

1. Introduction

For many years, several polymers have been investigated intensively for their potential as membrane materials in proton exchange membrane fuel cell. Research groups have sought to improve the existing material and to find alternative polymer

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that possess similar performance as the standard Nafion membrane. For low cost, however, a more radical approach is needed and the search has been on for alternative polymer, including 'disposable' hydrocarbon. In order to make the hydrocarbon polymer possible for proton conduction to occur, polymer structure with pendant sulfonic acid group must be obtained. One possibility is to introduce the sulfonate group into the polymer structure by electrophilic substitution via sulfonation.

Direct sulfonation of the polymer backbone has been investigated intensively since the pioneering work of Noshay and Robeson¹, who developed a mild sulfonation procedure for the commercially available bisphenol-A-based poly (ether sulfone). This approach found considerably interest in the area of water desalination through reverse osmosis and related water purification application. Many hydrocarbon polymers such as polysulfones, polyethersulfones, polyetherketones, polyether etherketones, polyimides, polybenzimidazole, polyoxadiazole, polyphosphazenes have been claimed to be a possible substitute for perfluorinated ionomers provided that a charge group (sulfonic) is introduced into the structural unit^{2,3,4,5}. Among the aforementioned polymers, polysulfone was considered to be the most interesting polymer due to its low cost, commercial availability and ease of processing.

Quentin et al.⁶ disclosed the first sulfonation techniques in the US Patent 3,709,841 and since then, many studies have been continued on the process to further improve the techniques and the quality of the outcome polymer. Sulfonating agents employed for the process were also being studied, as some of them could cause polymer chain degradation during the reaction due to their high reactivity and toxicity level. Several pros and cons of the sulfonation reaction have been pointed out by several researchers and have been used as a baseline for upcoming process. Current trend in membrane research shows that sulfonation process has been identified as preferred method for incorporating the sulfonic group into the hydrocarbon polymer structure particularly for polymer electrolyte membrane fuel cell application.

Current increasing research trend in sulfonated polymers has shown comparable results to the state of the art Nafion membrane and some of them has superseded their standard performance. Table 1 depicted some of the sulfonated polymers that have been studied and currently undergoing worldwide to facilitate superior membrane properties for fuel cell applications.

Thereby, the objective of this study is to synthesize and fabricate SPSU membranes with different sulfonation levels by varying the molar ratio of the sulfonating agent to base polymer. Effects of sulfonation process on the produced membrane were studied through water uptake, ion exchange capacity (IEC) and proton conductivity measurement. Details explanation will be given in correlation with degree of sulfonation via molar ratio of the sulfonating agent to polymer unit.

2. Experimental

2.1. Materials

Polysulfone Udel polymers, which were used for the synthesis, were purchased from BP Amoco and dried at 100 °C under vacuum before use. Trimethylsilyl chlorosulfonate (TMSCS) and sodium methoxide was purchased from Fluka and used as received. Chloroform, N, N-dimethylformamide (DMF) and methanol were purchased from commercial source and used in the synthesis.

Table 1
Some of significant sulfonated polymer being studied by various researchers

Researchers	Materials	Sulfonation agent	Characterization test
Quentin ⁶	Sulfonated polysulfone	Chlorosulfonic acid	-
Noshay and Robeson ¹	Sulfonated polysulfone	Sulfur trioxide with triethylphosphate	Structure, thermal behavior and mechanical properties
Mottet et al ⁷	Sulfonated polysulfone	Sulfur trioxide	-
Sivashinsky and Tanny ⁸	Sulfonated polysulfone	Chlorosulfonic acid	TMA, SAXS, TEM
Johnson et al. ⁹	Sulfonated polysulfone	Sulfur trioxide with triethylphosphate	HNMR, FTIR, DSC, TMA, swelling and solubility studies
Chao and Kelsey ¹⁰	Sulfonated polysulfone	TMSCS	Degree of sulfonation
O'gara et al. ¹¹	Sulfonated polysulfone	Sulfur trioxide with triethylphosphate	DSC, TGA, DMTA, SAXS
Arnold and Assink ¹²	Sulfonated polysulfone	Sulfur trioxide with triethylphosphate	FTIR, IEC, DSC, resistance measurement, battery performance
Nolte et al. ¹³	Sulfonated poly (arylene ether sulfone)	Trimethyl chlorosilane	FTIR, IEC, NMR, DSC
Baradie et al. ¹⁴	Sulfonated polysulfone	TMSCS	H and C NMR, FTIR, TGA, XRD
Orifice et al. ¹⁵	Sulfonated polysulfone	Chlorosulfonic acid	AFM, NMR, XPS, SEM
Carretta et al. ¹⁶	Sulfonated polystyrene	Acetyl sulfate	Conductivity, permeability, FTIR
Lufrano et al. ³	Sulfonated polysulfone	TMSCS	Elemental analysis, IEC, Viscosity measurement, THA, DSC, Swelling test, Conductivity test

Table 1 (continue)

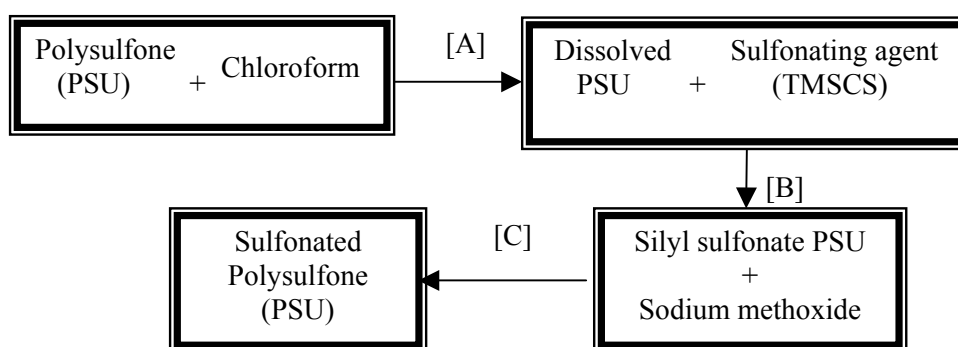
Some of significant sulfonated polymer being studied by various researchers

Researchers	Materials	Sulfonation agent	Characterization test
Genova-Dimitrova et al. ¹⁷	Sulfonated polysulfone with phosphoantimonic acid	TMSCS	¹ H NMR measurement, Viscosimetry measurement, mechanical measurement, Conductivity measurement
Blanco et al. ¹⁸	Sulfonated polyethersulfone	Sulfuric acid	IEC, FTIR, UV-VIS, DSC, Swelling ratio
Staiti et al. ¹⁹	Sulfonated polybenzimidazole	Sulphuric acid	CHNS analysis, IEC, Conductivity measurement, TG and DTA, FTIR, XRD analysis, fuel cell test
Lufrano et al. ⁴	Sulfonated polysulfone	TMSCS	Elemental analysis, IEC, TGA, Proton conductivity measurement, Single cell test
Hasiotis et al. ²⁰	Blend of sulfonated polysulfone with polybenzimidazole	Chlorosulfonic acid	Conductivity, Acid doping level measurement
Genies et al. ²¹	Sulfonated naphthalenic polyimides	Triethylamine with m-cresol	IEC, water swelling, proton conductivity, TGA, FTIR, NMR, SANS (<i>Small-angle neutron scattering</i>)
Mokrini and Costa ²²	Sulfonated Hydrogenated Poly-Butadiene-Styrene copolymer (HPBSL-SH)	Acetyl sulfate	FTIR, DSC, DMA, Impedance spectroscopy analysis
Blanco et al. ²³	Sulfonated Polysulfone	Chlorosulfonic acid, sulfuric acid	IEC, FTIR, UV Spectrophotometry, DSC, Swelling, SEM, Size exclusion chromatography
Pintauro et al. ²⁴	Sulfonated polyphosphazene	Sulfur trioxide, triethyl phosphate, chlorosulfonic acid	IEC, water and methanol uptake, water and methanol diffusivity, proton conductivity, TMA, FTIR, methanol crossover
Wilhelm et al. ²⁵	Blend sulfonated polyether etherketone and polyetherketone	Sulphuric acid	IEC, water uptake, Electric resistance, Selectivity
Wang et al. ²⁶	Sulfonated Poly(arylene ethersulfone)	-	FTIR, DSC, TGA, Solubility and intrinsic viscosities, Water uptake, AFM, Conductivity measurement

Yang et al. ²⁷	Polystyrene sulfonate block	Triethyl phosphate	FTIR and NMR
Kim et al. ²⁸	Sulfonated polystyrene block	Acetyl sulfate	Conductivity, water and methanol uptake, SAXS, SANS, FTIR

2.2. Sulfonation of polymers

Sulfonation reactions were carried out according to procedure described by Chao and Kelsey¹⁰. Typically 40 ~ 80 g of polysulfone was dissolved in 450 ~ 800ml chloroform at room temperature. An inert atmosphere (nitrogen) was provided over the reaction solution to remove HCl effluents formed during the substitution reaction and to reduce the excessive water vapor as they can interfere the sulfonation reaction. The dissolved polysulfone was reacted with a drop wise of 50 ml trimethylsilyl chlorosulfonate (TMSCS) to form an intermediate medium, silyl sulfonate polysulfone. Cleavages of the silyl group was obtained by adding a base medium (sodium methoxide 15% in methanol solution), yielding the desired sulfonated polymer products. To stop the sulfonation reaction, the solutions was decanted into a nonsolvent bath of methanol to obtain a precipitate white fluffy porous product. The sulfonated particles were washed several times with water and methanol, and then dried in a vacuum oven for 24 hours at 80 °C for complete removal of the solvent. Film of sulfonated membrane was prepared by casting on a glass plate by a pneumatically casting machine with 22 ~30 wt.% of SPSU dissolved in dimethylformamide (DMF). After being dried and complete removal of residual solvent at 60 °C for 4 hour, the SPSU membrane was detached from the glass plate by immersing into deionized water. The membrane was converted into acid form by immersion in 1 M HCl overnight. Degree of sulfonation of the membrane sample was determined by elemental analysis based on sulfur to carbon ratio using CHNOS Elemental Analyzer (Vario EL II). Figure 1 shows the sulfonation process sequence.



[A] = reaction at ambient temperature

[B] = continuous stirring for 24 h

[C] = stir for 1 hour, then added drop wise into methanol bath

(TMSCS) = Trimethylsilyl chlorosulfonate

Note: The solution were continuously stirred under N_2 atmosphere during the process

Figure 1 : Sulfonation process sequence

2.3. Fourier Transform Infrared (FTIR)

FTIR was performed in order to study the chemical structure of organic molecules and potential structural changes that occur as a result of the membrane chemical treatment or degradation. FTIR spectra of thin films were recorded using a Nicolet-Magna 560 IR Spectrometer.

2.4. Ion exchange capacity (IEC) determination

The milliequivalents of reactive $-\text{SO}_3\text{H}$ sites per gram of polymer (mmol/g) was determined theoretically by elemental analysis and experimentally via titration. Sulfonated polysulfone samples were initially immersed in 1 M hydrochloric acid (HCl) at 50°C for 24 hours to assure that the membrane was in the protonic form. Excess amount of hydrochloric acid was eliminated by rinsing the membrane in the deionized water. Subsequently the sample was immersed in 2 M NaCl at 60°C and titrated with 1 M NaOH solution using phenolphthalein as pH indicator.

2.5. Water uptake/ Swelling Test

The swelling characteristics were determined by water uptake measurements. The membrane samples were first immersed in deionized water at 80°C for 24 hours. The wet membrane then blotted dry to remove surface droplets and quickly weighted. The wet membranes were vacuum dried at 80°C – 100°C and weighted again. The water uptake of the membranes was calculated by weight gain of absorbed water with reference to the dry membrane and reported as weight percent water absorption. The water uptake can be calculated as follows,

$$\text{Water uptake} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}}$$

where, m_{wet} is the weight of wet membrane and m_{dry} is the weight of dry membrane.

2.6. Proton Conductivity Measurement

For proton conductivity measurement, a polished and clean copper plate was pressed on both surfaces of the membranes to ensure good electrical contact. An impedance spectrum was recorded from 20 Hz to 1 MHz using Precision LCR Meter, Agilent HP4284A. The area resistance of the film was taken at the high frequency end, which produced the minimum imaginary response. All impedance measurements were performed at 40°C – 80°C under full hydration conditions. The proton conductivity was calculated from the following equation,

$$\sigma \text{ (S/cm)} = (t / R_m)$$

where, t is the thickness of the membrane sample and R_m is the area resistance of the membrane ($\Omega \text{ cm}^2$).

3. Results and discussion

3.1. Sulfonation process

Sulfonation process has been conducted several times by varying the molar ratio of the polymer to sulfonating agent. In this study, the sulfonation was conducted at room temperature (25 –28°C). Though attempts have been made for sulfonation at higher temperatures (up to 50°C), the output was not satisfactory as the solvents tend to evaporate easily with temperature and temperature constant was scarcely obtained. Some difficulties arise on handling the polymer solution at higher temperature as they tend to solvate easily in the precipitation medium after sulfonation process. Several observations have been made through out the process and some preventative measures must be taken for future sulfonation process. Firstly, a sufficient amount of nitrogen supply must be provided, as excess nitrogen will cause the solution to deplete rapidly with time. The nitrogen sources after addition of sodium methoxide must be controlled to avoid rapid accumulation of the solution particle due to the temperature drop below room temperature. The time interval of sodium methoxide dropwise must also be controlled, as the bulk drop wise of the base solution would cause rapid particles precipitation. Despite all the consequences occurred during the reaction, the sulfonation reactions were successfully conducted by varying the molar ratio of sulfonating agent to polysulfone polymer under room temperature condition. Four respective sulfonated polysulfone membranes (SPSU1, SPSU2, SPSU3 and SPSU4) were then characterized and studied as shown in Table 2.

Table 2
Sulfonation process operating condition

Membranes	Molar ratio ^a	Reaction temperature	% Weight	Degree of sulfonation
SPSU1	1.8	25-28 °C	25.0	27.55
SPSU2	2.1	25-28 °C	30.0	41.84
SPSU3	2.5	25-28 °C	24.5	60.20
SPSU4	3.0	25-28 °C	24.3	78.57

^amol sulfonating agent for mol of polysulfone

3.2. Effects of sulfonation process on the characteristics of sulfonated membranes functional group

Sulfonation process of the polysulfone polymer was confirmed qualitatively by FTIR. The results indicated clearly the presence of sulfonic groups in the polymer backbone after sulfonation reaction occurred. This can be observed at 1027 cm⁻¹ in Figure 2 that is the evidence of the SO₃ stretching of the sulfonic groups and in close agreement with 1028 cm⁻¹ obtained by Orifice et al.¹⁵ and Johnson et al.⁹. The infrared assignments of polysulfone and its sulfonated derivatives were illustrated in Table 3.

As can be seen in the spectrum, the intensity of the peak seems to broaden as the degree of sulfonation is increased. This effect can be correlated to the increasing molar ratio of the sulfonating agent to polymer repeat unit employed in the

sulfonation reaction. As the degree of sulfonation is increased, the intensity of the peak becomes more prominent except for SPSU4. This might be due to prolonged supply of nitrogen during the sulfonation process which has stiffen the polymer chain and causes less vibration in the polymer structure. Less of opaqueness of the SPSU4 film compared to other sulfonated samples with high transparency type of film may also contribute to these effects. However, the presence of sulfonic acid group peak can be seen clearly at the forecasted region. The SO₂ symmetric stretching was nakedly observed at 1150 cm⁻¹ and para in-plane aromatic C-H bend could be detected at 1107 cm⁻¹.

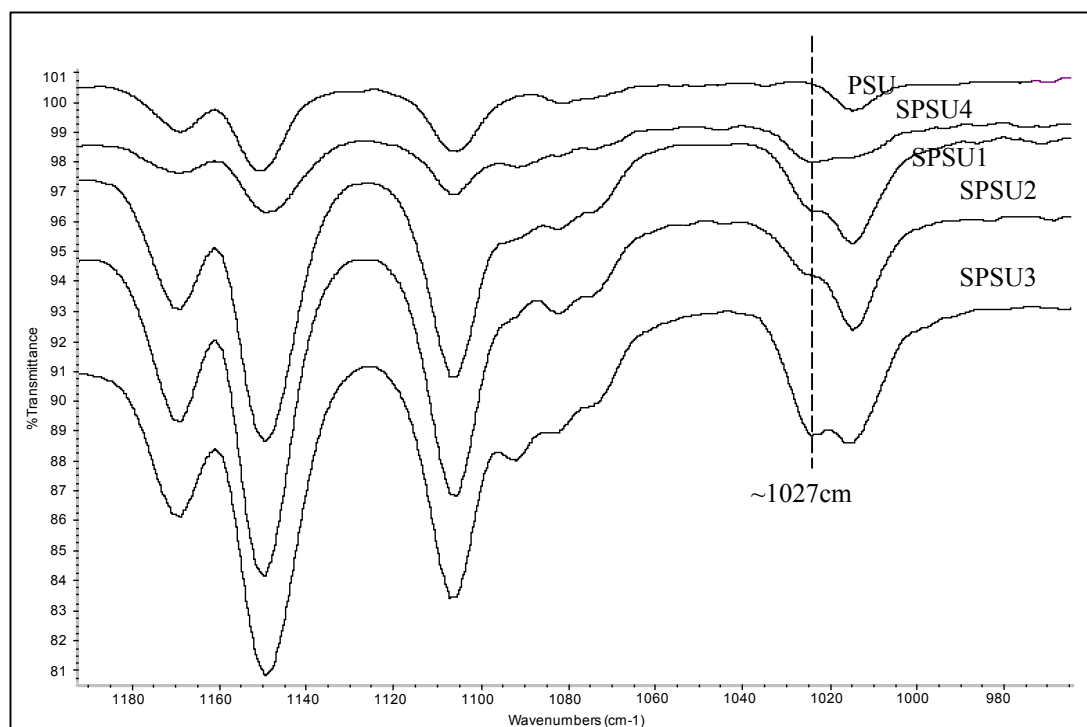


Figure 2 : FTIR spectra of SPSU membranes

Table 3

Infrared assignments of polysulfone and its sulfonated derivative

Frequency (cm ⁻¹)	Assignments
3600 3200	O-H stretching vibrations
2980 2880	Asymmetric and symmetric C-H stretching vibrations involving entire methyl group
1590 1485	Aromatic C=C stretching
1412	Asymmetric C-H bending deformation of methyl group
1365	Symmetric C-H bending deformation of methyl group
1325 1298	Doublet resulting from asymmetric O=S=O stretching of sulfone group
1244	Asymmetric C-O-C stretching of aryl ether group
1170	Asymmetric O=S=O stretching of sulfonate group

1150	Symmetric O=S=O stretching of sulfone group
1107	Aromatic ring vibrations
1092	
1027	Symmetric O=S=O stretching of sulfonate group

In contrary, different trends of spectrum were observed when the sulfonated membranes were hydrated. Water absorption effect of the membrane samples could be seen clearly in Figure 3 where O-H stretching band of SPSU samples was detected at frequency $\sim 3220 \text{ cm}^{-1} - 3560 \text{ cm}^{-1}$. SPSU4 membrane created broad stretching band indicating greater amount of water associated in the membrane samples. This effect was presumed to associate with higher content of molar ratio employed and increasing hydrophilic behavior due to the introduction of the sulfonate group in the polymer structure. Some other peaks provide different intensity due to variations in sample layer thickness, low concentration in polymer and perhaps due to low IR-absorption coefficients. The results of FTIR analysis clearly demonstrated the occurrence of sulfonation process by the presence of sulfonate groups after the reaction in the polymers backbone.

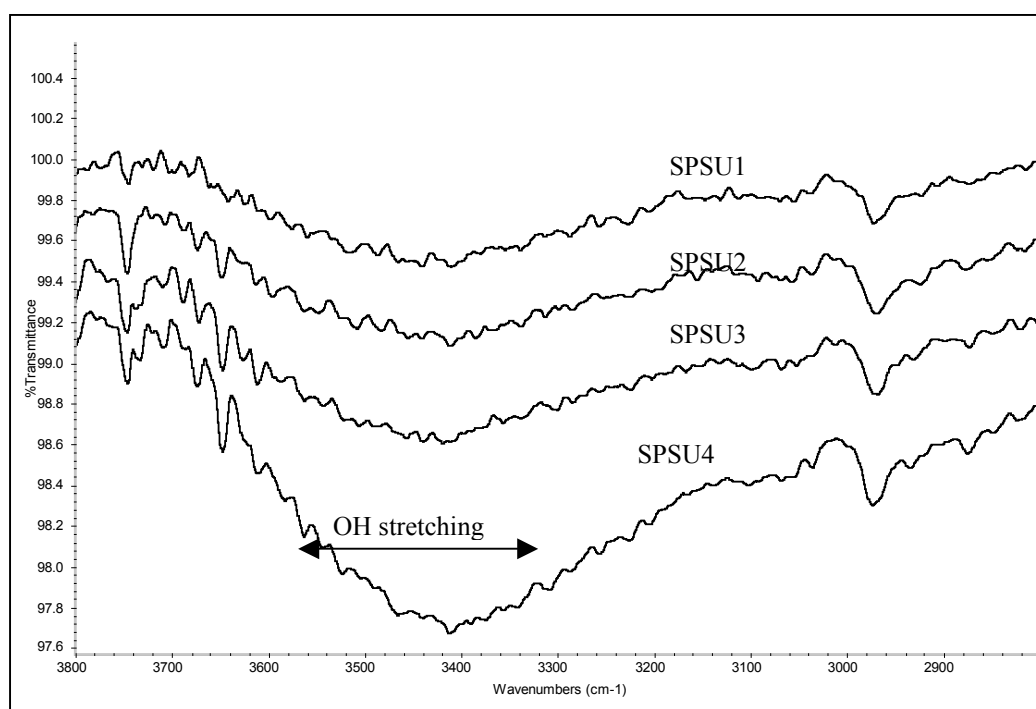


Figure 3. O-H stretching band of SPSU membrane sample

3.3. Effects of sulfonation process on swelling and ion exchange capacity (IEC)

The increased in water uptake of membranes is essential to improve proton conductivity. The result of swelling shows that water sorption is increased with the increase of the sulfonic acid group content, which is contributed by the strong hydrophilicity of the sulfonate group in the polymer backbone. The results are tabulated in Table 4. A clear dependence of the water uptake on the sulfonation degree was observed. Besides the increase in water sorption as a function of the

degree of sulfonation, the dependence on the membrane thickness was also observed. Table 4 illustrated the water uptake as a function of the degree of sulfonation.

From the data, some increasing trend in swelling can be observed as the degree of the sulfonation is increases. With a maximum water sorption of ca. 26 % for SPSU10, sulfonated polysulfone (SPSU) appears as hydrophilic materials compared with unmodified polysulfone that shows values of only 0.3 % water sorption²⁹ in 24 hours time at ambient temperature. Titrations were conducted to quantitatively determine the experimental IECs while elemental analysis were used to determine the calculated IEC value of the SPSU membranes. From Table 5, the experimental results of IEC values were in close agreement with the calculated IEC, assuming that all of the sulfonated polymers were sulfonated. It was observed that increase in the sulfonation levels has enhanced the concentration of SO₃H group, simultaneously improved the water uptake of the sulfonated membrane. These effects can be correlated to the increased hydrophilicity behaviour of the polysulfone polymer as more sulfonic acid group facilitates more hydrogen proton conduction through the membrane matrix. Strong relation between water content and SO₃H group concentration is illustrated in Figure 4.

Table 4
Influence of the degree of sulfonation on the water uptake

Membrane	Sulfonation Degree (%)	Membrane thickness (mm)	% Swelling
SPSU5	27.55	0.03 ± 0.009	3.70
		0.04 ± 0.009	3.96
		0.05 ± 0.009	4.10
SPSU6	41.84	0.05 ± 0.009	7.34
		0.10 ± 0.009	7.52
		0.12 ± 0.009	8.00
SPSU9	60.20	0.04-0.05	11.18
		0.06-0.07	12.36
SPSU10	78.57	0.07 ± 0.009	22.66
		0.08 ± 0.009	24.28
		0.09 ± 0.009	25.91

Table 5
Water uptake of sulfonated polysulfone membrane and ion exchange capacity (IEC) values

Membrane (Molar ratio)	Water uptake (wt.%) ^a	IEC (mmol/g)	
		Calculated	Experimental
SPSU5 (1.8)	4.10	0.62	0.57
SPSU6 (2.1)	8.00	0.95	0.88
SPSU9 (2.5)	12.36	1.36	1.25
SPSU10 (3.0)	25.91	1.78	1.70

^aConducted at ambient temperature.

3.4. Effects of sulfonation process on proton conductivity measurement

Proton conductivity of the SPSU membranes was calculated from resistance measurements in the temperature range from 25°C to 80°C. Results obtained from the proton conductivity measurement were tabulated in Table 6 and Table 7. It was observed from the study and shown in Figure 5 that the membrane conductivity is increased significantly with the increase in the degree of sulfonation. It is probably due to greater content of sulfonic acid groups in the polymer chain, which enhanced the facilitation of the proton transport within the membrane matrix. Nevertheless, the conductivity values of SPSU membranes, which in the range of 10^{-4} – 10^{-3} S/cm are still moderately lower than that of standard Nafion 117 membrane (10^{-1} S/cm). It was observed that some remarkable distinct of conductivity values obtained for Nafion 117 membranes in this study compared with other conductivity values reported by several researchers. This can be explained with the fact that the diverse methods and apparatus applied during the conductivity measurements and conceivably poor contact between electrolyte (membrane) and the electrode could also contribute to lower value of ionic conductivity for the membrane samples. Hwang et al.³⁰ reported that the membrane area resistance is increased with an increase of membrane thickness. However, these were not the case for the SPSU samples as the samples shows lower area resistance with increase temperature as well as degree of sulfonation and independent of the membrane thickness. It was found that the effect of degree of sulfonation on membrane area resistance was more prominent than the membrane thickness.

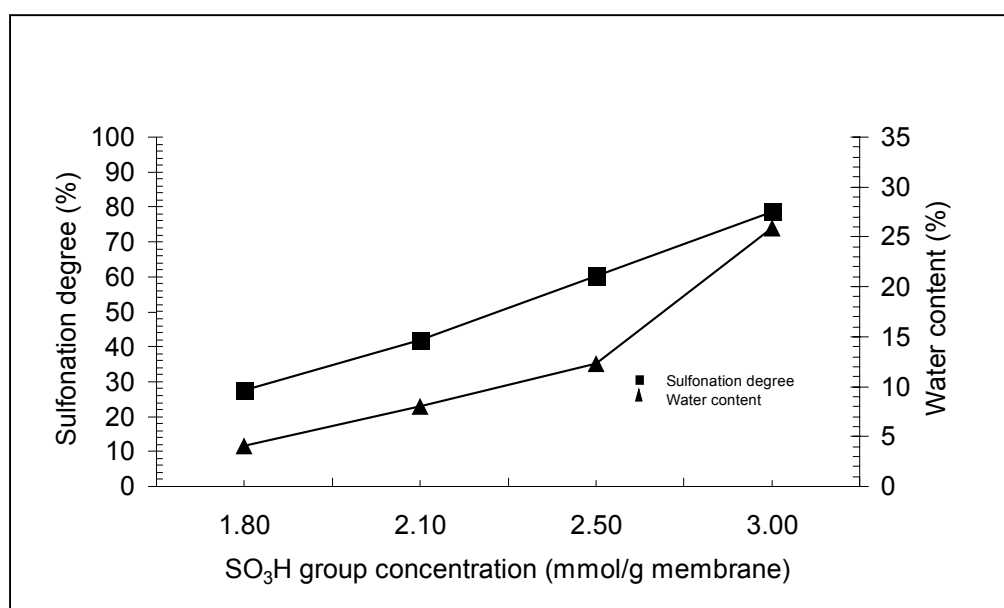


Figure 4 : SO₃H concentration of SPSU sample as a function of sulfonation degree and water content

Table 6.
Area resistivity (R_{area}) of sulfonated membranes and Nafion 117 membrane

Membranes /Thickness	Area resistivity ($\Omega \text{ cm}^2$)				
	SPSU1 (0.065 mm)	SPSU2 (0.105 mm)	SPSU3 (0.085 mm)	SPSU4 (0.077 mm)	Nafion 117 (0.190 mm)
Temperature					
25 °C	44.781	44.903	23.765	31.704	2.284
50 °C	44.140	39.480	20.125	18.636	2.170
60 °C	43.697	35.090	19.654	15.411	2.100
70 °C	40.667	28.122	17.133	7.954	2.087
80 °C	35.698	18.016	13.945	7.233	1.998

Table 7
Ionic conductivity of sulfonated polymer and Nafion 117 membranes

		Proton conductivity (S/cm)				
Temperatures (°C)		25	50	60	70	80
Membrane	% SO_3H					
SPSU1	27.55	1.451×10^{-4}	1.473×10^{-4}	1.488×10^{-4}	1.598×10^{-4}	1.821×10^{-4}
SPSU2	41.84	2.338×10^{-4}	2.660×10^{-4}	2.992×10^{-4}	3.734×10^{-4}	5.828×10^{-4}
SPSU3	60.20	3.577×10^{-4}	4.221×10^{-4}	4.325×10^{-4}	4.961×10^{-4}	6.095×10^{-4}
SPSU4	78.57	2.429×10^{-4}	2.738×10^{-4}	4.996×10^{-4}	9.680×10^{-4}	1.064×10^{-3}
Nafion 117	-	7.719×10^{-3}	8.754×10^{-3}	9.052×10^{-3}	9.105×10^{-3}	9.510×10^{-3}

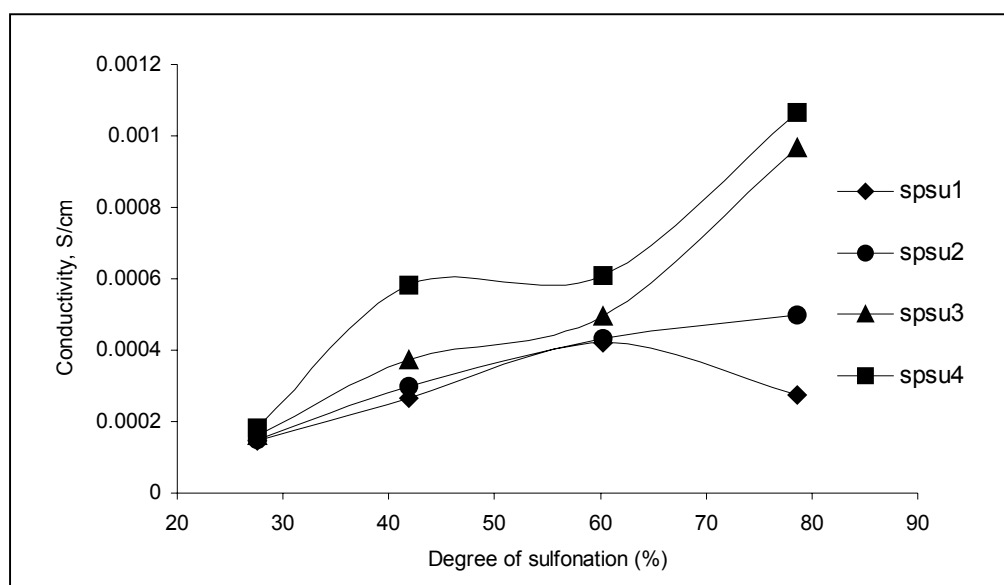


Figure 5: Proton conductivity of sulfonated PSU membranes as a function of degree of sulfonation at different operating temperatures

The type of casting solvent employed in the experiments also believed to play a significant role, affecting the membrane proton conductivity and mechanical strength. This was found true by Kaliguine et al.³¹ as they claimed that dimethylformamide (DMF) was found to strongly decrease the membrane conductivity of sulfonated polyether etherketone (SPEEK) membrane in comparison with other solvents studied. The HNMR result yields no evidence of hydrogen-bonded data when DMAc solvent was used and found that dimethylformamide molecule is particularly prone to hydrogen bonding with $-\text{SO}_3\text{H}$ groups. This phenomenon explained the reason of the large discordances of more than an order of magnitude between the conductivity values of sulfonated polysulfone in these study than other reported results for similar materials. It was also found that residual of hydrochloric acid, which is very difficult to eliminate from highly sulfonated polysulfone, also affects its conductivity; under high temperature treatment, enters into reaction with DMF causing their degradation. As discussed in the present contribution, the conductivity measurement technique may also be a reason for discrepancy in the reported conductivity characteristics of sulfonated polysulfone membranes.

An increasing trend of conductivity with temperature can be observed in all of membrane samples as shown in Figure 6. An increasing trend of conductivity with temperature can be correlated to the increased in the activation energy in the system, which enhanced the water mobility within the membranes hence increase the amount of proton transferred. The fundamental of the ionic conductivities were clearly obeyed here as the ion (which is proton) diffusion charge carriers were created thermally³², in this case ascribe by the increased in the conductivity value with operating temperature. Though the idea of higher conductivity with increasing temperature seems acceptable, a great deal of intricacy was encountered as some membrane materials loss their water content at higher temperature and the temperature dependent membrane appeared to be ambiguous.

While higher sulfonation levels of sulfonation will provide higher proton conductivity, other membrane properties may suffer. A membrane that is too hydrophilic would swell greatly yielding a hydrogel and may be weak and do not sufficiently serve as a barrier for the fuel and oxidizer. As a result, an optimum degree of sulfonation needs to be established to produce the polymer electrolyte membrane with the best performance.

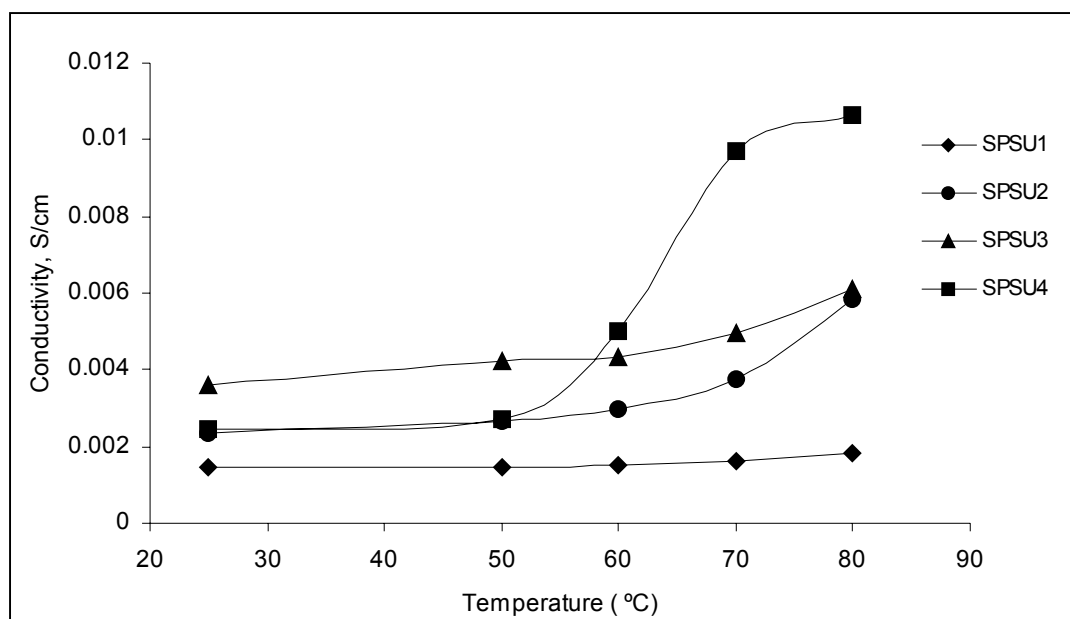


Figure 6: Conductivity of SPSU membrane and Nafion 117 membrane as a function of operating temperature (25°C – 80°C).

4. Conclusions

Sulfonated polysulfone with moderate water uptake, ion exchange capacity and proton conductivity values have been prepared by the sulfonation reaction with varying molar ratio of sulfonating agent to polysulfone polymer. Elemental analysis has confirmed the sulfonation reactions of the polymer and degree of sulfonation from 22.3% to 73% were successfully achieved. From swelling effect and IEC determination, it is clearly observed that sulfonation process have significantly improving the water uptake of the sulfonated membrane compared to the origin polymer by the introduction of hydrophilic sulfonic acid group in the polymer skeleton. The water uptake and IEC value of the sulfonated membrane increases as the sulfonation is increased. This was in agreement with FTIR measurement, which revealed broader O-H stretching band of water absorption for higher degree of sulfonation. However, optimum degree of sulfonation need to be established, as the higher degree of sulfonation would enhancing the conductivity values but at the same time other membranes properties will suffer e.g. too much swelling would ruptured the membrane matrix. The ionic conductivity measurement of the sulfonated polysulfone membrane was found to increase with temperature and degree of sulfonation. Remarkable distinct of conductivity values for Nafion 117 membranes in this study may be explained with the fact that the diverse methods and apparatus applied during the conductivity measurements and conceivably poor contact between electrolyte (membrane) and the electrode that also contribute to lower value of ionic conductivity of the membrane samples.

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References

- [1] A. Noshay and L.M. Robeson, Sulfonated Polysulfone, *J. Appl. Polym. Sci.* 20 (1976) 1885.
- [2] R. W. Kopitzke, Investigation of Sulfonated High Temperature Polymers as Proton Exchange Membrane Electrolytes. Florida Institute of Technology: (1999) Ph.D.Thesis.
- [3] F. Lufrano, G. Squadrito, A. Patti and E. Passalacqua, Sulfonated PSU as Promising Membrane for PEFC. *J. Appl. Polym. Sci.* 77 (6) (2000). 1250 – 1256.
- [4] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci and E. Passalacqua Sulfonated polysulfone ionomer membrane for FCs, *Solid State Ionics.* 145 (2001) 47-51.
- [5] M. Hogarth and X. Glipa, High Temperature Membranes for Solid Polymer Fuel Cells. Contract Technical Report. Johnson Matthey Technology Centre. (2001).
- [6] J. P. Quentin, Sulfonated Polyarylethersulfones (1973) U.S. Patent 3,709,841
- [7] C. Mottet, A. Revillion, P. L. Percec, M.F. Llauro and A. Guyot, Analogous Reaction for Maximum Sulfonation of Polysulfones. *Polymer Bulletin.* 8 (1982) 511-517.
- [8] N. Sivashinsky and G.B. Tanny, Ionic heterogeneities in sulfonated polysulfone films. *J. Appl. Polym. Sci.* 28 (1983). 3235-3245.
- [9] B.C. Johnson, I. Yilgor, C. Tran, M. Iqbal, J.P. Wightman, D.R Lloyd and J.E. Mcgarth, "Synthesis and characterization of sulfonated poly(arylene ether sulfones), *J.Polym. Sci.* 22 (1984) 721-737.
- [10] H. S. Chao and D. R. Kelsey, Process for preparing sulfonated poly (aryl ether) resins. (1986) U.S. Patent 4,625,000.
- [11] J.F. O'Gara, D.J. Williams, W.J. MacKnight and F.E. Karasz, Random homogeneous sodium sulfonated polysulfone ionomers: preparation, characterization and blend studies. *J. Polym. Sci. Part B. Polymer Physics.* 25 (1987) 1519-1536.
- [12] C. J. Arnold and R.A. Assink, Development of Sulfonated Polysulfone Membranes for Redox Flow Batteries, *J.Membr. Sci.* 38 (1988) 71-83.
- [13] R. Nolte, K. Ledjeff, M. Bauer and R. Mulhaupt, Partially sulfonated poly (arylene ether sulfone) - A versatile proton conducting membrane material for modern energy conversion technologies. *J. Membr. Sci.* 83 (1993) 211-220.
- [14] B. Baradie, C. Poinsignon, J.Y. Sanchez, Y. Piffard, G. Vitter, N. Bestaoui, D. Foscallo, A. Denoyell, D. Delabouglise, and M. Vaujany, Thermostable ionomeric filled membrane for H₂/O₂ fuel cell. *J. Power Sources.* 74 (1998) 8-16.

- [15] R.L Orifice and A. Brennan, *Materials Research* Vol.1, No.1, (1998) 19-28.
- [16] N. Carretta, V. Tricoli, and F. Picchioni, Ionomeric membranes based on partially sulfonated polystyrene: synthesis proton conduction and methanol permeation, *J.Membr. Sci.* 166 (2000) 189 - 197.
- [17] P. G. Dimitrova, B. Baradie, D. Foscallo, C. Poinignon and J.Y. Sanchez, Ionomeric membranes for proton exchange membrane fuel cell (PEMFC): sulfonated polysulfone associated with phosphoantimonic acid, *J.Membr. Sci.* 185 (2001) 59 - 71.
- [18] J.F. Blanco, Q.T. Nguyen and P. Schaetzel, Novel hydrophilic membrane materials:sulfonated polyethersulfone Cardo, *J.Membr. Sci.* 186 (2001) 267-279.
- [19] P. Staiti, and M. Minutoli, Influence of composition and acid treatment on proton conduction of composite polybenzimidazole membranes. *J. Power Sources.* 94. 1 (2001) 9 - 13.
- [20] C. Hasiotis, V. Deimede and C. Kontoyannis, New polymer electrolytes based on blend of sulfonated polysulfone with polybenzimidazole, *Electrochemical Acta.* 46 (2001) 2401-2401.
- [21] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel and M. Pineri, Soluble sulfonated naphthalenic polyimides as materials for proton exchange membranes, *Polymer.* 42 (2001) 359.
- [22] A. Mokrini and J.L. Acosta, Studies of sulfonated block copolymer and its blends, *Polymer.* 42 (2001) 9-15.
- [23] J.F. Blanco, Q.T. Nguyen, P. Schaetzel, Sulfonation of Polysulfone: Suitability of the Sulfonated Materials for Asymmetric Membrane Preparation. *J.Appl. Polym. Sci.* 84 (2002) 2461-2473.
- [24] P. N. Pintauro and H. Yang, Sulfonated polyphosphazenes for proton exchange membrane fuel cells, (2002) US Patent 6,365,294.
- [25] F.G. Wilhelm, I.G.M. Punt, N.F.A. Van Der Vegt, H. Strathman, M. Wessling, Cation permeable membranes from blends of Sulfonated polyether etherketone (SPEEK) and Sulfonated Polyether sulfone (PES), *J.Membr. Sci.* 199 (2002) 167-176
- [26] F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski and J.E. McGarh, Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton, *J. Membr. Sci.* 197 (2002) 231 – 242.
- [27] J.C. Yang, M.J. Jablonsky, J.W. Mays, NMR and FT-IR studies of sulfonated styrene-based homopolymers and copolymers, *Polymer.* 43 (2002) 5125-5132.
- [28] J. Kim, B. Kim, B. Jung, Proton conductivities and methanol permeabilities of membranes from partially sulfonated polystyrene-block-poly(ethylene-ran-butylene) block-polystyren copolymers, *J. Membr. Sci.* 5316 (2002) 1-9

- [29] H. Elias and F. Vohwinkel, *New Commercial Polymers 2*. Gordon and Breach Science Publishers, New York. Chapter 8 (1986).
- [30] G.J. Hwang, H. Ohya and T. Nagai, Ion exchange membrane based on block copolymers. Part III: preparation of cation exchange membrane, *J. Membr. Sci.* 156 (1999) 61-65.
- [31] S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P. Xing, G. Robertson, and M. Guiver, Properties of SPEEK based PEMFs for fuel cell application, *Catalysis Today*. 82 (2003) 213-222.
- [32] Ph. Colomban, Latest developments in proton conductors, *Annual Chemistry Science Materials*, 24 (1999) 1-18.