J. Myanmar Acad. Arts Sci. 2020 **Vol. XVIII.No.1**C

PREPARATION OF PROTON EXCHANGE MEMBRANE (PSS) USED AS AN ELECTROLYTE IN FABRICATED DIRECT METHANOL FUEL CELL (DMFC)

Khin Ei Ei Thein[1], Tin Tin Aye[2], Kyaw Myo Naing[3]

Abstract

Membrane is one of the key performances for Direct Methanol Fuel cell(DMFC). A new polymer electrolyte membrane based on polystyrene sulphonated has been developed. In this research, the polystyrene sulphonated membrane was a casted product that obtained by the sulphonation of polystyrene with concentrated sulphuric acid. The polystyrene sulphonated membranes have been characterized by properties of ion exchange capacity, and water uptake as a function of molar ratio of polystyrene to concentrated H_2SO_4, FTIR, SEM and EDXRF. The S content of the prepared membrane was determined using titration method. Fourier Transform Infrared (FTIR) was performed to verify the sulphonation reaction on the polystyrene polymer. Morphology of the prepared membranes were characterized by Scanning Electron Microscopy (SEM). The chemical constituents of polystyrene sulphonated membranes were detected by using Energy Dispersive X-ray Fluorescence (EDXRF). At the optimal temperature of $40 \pm 2^\circ$C for the time of 2 h, the optimal composition ratio of polystyrene to concentrated H_2SO_4 (w/v) was found to achieve as 1:2. The polystyrene sulphonated membrane has an ion exchange capacity of 0.79 meq/g and S content of 2.53 %. Therefore, the prepared polystyrene sulphonated membranes were suitable for the low temperature fuel cell, especially Direct Methanol Fuel Cell (DMFC) due to the range of ion exchange capacity 0.45-0.79 meq/g.

Keywords: Direct methanol fuel cell, polystyrene sulphonated membrane, ionhange capacity, water uptake

Introduction

Polystyrene Sulphonated Membrane

A variety of membrane materials have been used for fuel cell applications. Nafion (Du Pont), a perfluorosulphonic acid polymer, is the most widely used proton conductor in polymer electrolyte membrane fuel cells (PEMFCs). The membranes are made by copolymerization of tetrafluoroethylene and a substituted perfluorinated alkene (Motokawa, 2005). The stability and toughness of this type of membrane have led to its being the most commonly used in fuel cell as the electrolyte. However, the synthesis of the substituted monomer requires several steps and the ultimate cost of membrane fabrication is high (Larmine, 2002). This perfluorinated ionomer material is confronted with some challenges for PEMFC and DMFC applications. Therefore, many researchers are concerned to develop solid polymer electrolyte with low methanol permeation. Initially, polystyrene sulphonic acid and sulphonated-phenol formaldehyde membranes were used (Halacy, 1966). Membranes for the DMFC have been prepared from the film casting of solutions of homogeneously polymerized sulphonated polystyrene. The thin thermoplastic film, forming from polystyrene, may be used of several types, both as regard their chemical structures and other physical properties (Hogarth, 1996). The plastic film should be capable of being cast into a thin homogeneous film from an organic solvent casting solution. This plastic film is chemically stable, resistant to acids and alkalis and

---

[1] Dr, Lecturer, Department of Chemistry, Banmaw University
[2] Dr, Professor (Retired), Department of Chemistry, Kyaing Tong University
[3] Dr, Associate Professor (Retired), Department of chemistry, Yangon

water insoluble (Geiger, 2002). The aim of this research work is to prepare the cheap proton exchange membrane to be used as an electrolyte instead of Nafion (Du Pont) in fabricated direct methanol fuel cell. To get polystyrene sulphonated membrane, sulphonation process are carried out by using the commercial polystyrene beads and 98 % concentrated sulphuric acid. In polystyrene sulphonated membrane, sulphonic acid (-SO_3H) are present as cation exchange radicals. These -SO_3H radicals attached to the membrane matrix, with sufficient water being held in the membrane matrix by Vander Waals force so that the H^+ ion is extremely mobile in the membrane. Without external supply of water, these membranes will tend to dehydrate and shrink during operation (Carretta *et al*., 2000).

Materials and Methods

Materials

The main source of material for the preparation of the proton exchange membrane is polystyrene (commercial) that was purchased from Academy Chemical Group, 28th street, Pabedan Township, Yangon, Myanmar. The chemicals used in the experimental work were from the British Drug House Chemical Co.Ltd., Kanto Chemical Co.Ltd., Sigma Aldrich Co.Ltd., Walco Chemical Co.Ltd., All chemicals used were of analytical reagent grade. In all investigations, the recommended standard methods and techniques involving both conventional and modern methods were provided.

Preparation of Polystyrene Sulphonated Membrane

Five grams of polystyrene beads were weighed and put into a glass bottle. Then, 100 mL of solvent toluene was poured and the bottle was well stoppered and allowed to stand for overnight. The clear polystyrene solution was obtained and which is used for sulphonation process. The sulphonation process was carried out with different amount of concentrated sulphuric acid (5 mL,10 mL,15 mL, 20 mL), various sulphonation time (1h, 2h, 3h, 4h, 5h) and various sulphonation temperature (40 ± 2, 50 ± 2, 60 ± 2, 70 ± 2, 80 ± 2) °C. The temperature within the reaction bottle was checked by immersing a thermometer. During sulphonation, stirring was continuously carried out by means of magnetic bar and the sulphonating agent was added drop by drop. The obtained brown color polymer solution was then cast into deionized water at room temperature. The resulted films were polystyrene sulphonated (PSS) membranes and named according to the added amount of concentrated sulphuric acid such as PSS5, PSS10, PSS15 and PSS20, respectively. The prepared membranes were used as electrolyte in fabricated direct methanol fuel cell.

Characterization of the Prepared PSS Membranes

The prepared PSS membranes were characterized by modern techniques such as EDXRF, FT IR, and SEM. Moreover, the properties such as tensile strength, thickness, solubility, and the other parameters of the prepared PSS membranes were carried out by means of materials testing and titration methods.

Results and Discussion

Optimal Conditions of Sulphonation Process

In this investigation, the polystyrene used was pure polystyrene and was dissolved in toluene. Table 1 shows the weight of polystyrene in toluene with respect to the volume of concentrated sulphuric acid used for sulphonation. Based on sulphonation time of 2 h (Williams,1966), sulphonation process was done. Qualitatively polystyrene sulphonated membranes were with respect to 1:1, 2:1, 3:1, 4:1. Concentrated sulphuric acid volume to polystyrene weight shows the nature of the membrane sheets that were casted in deionized water. On the basis of the texture and nature of the casted membrane, it was found that 2:1 (v/w) indicates a very smooth uniform in texture and nature compared to those in all other membranes. Higher ratios of 3:1 and 4:1 showed very brittle and easily torn up type of membrane on this aspect.

Table 1 indicates those membranes possessing satisfactory results of sulphonation. The membrane designated as PSS10 that is membrane casted by using the ratio of 2:1(v/w) (concentrated sulphuric acid : polystyrene) in the sulphonation process, probably indicates the most soluble membrane to be used as an electrolyte. However, it is very possible that lower sulphonation temperature may produce more suitable types of membrane.

On this aspect, Table 2 and Figure 2 show the change in IEC (meq/g) as well as the S content in percentage achieved with respect to variation in temperature from 40 to 80℃. Sulphonation was done based on selected polystyrene mixture 2:1 (v/w). It can be seen from Figure 2 that the optimal sulphonation temperature was about 40℃. At this optimal temperature the IEC value as well as the S content of the prepared PSS membranes indicate the highest value compared to the values of the other prepared PSS membranes which were prepared at higher temperature.

Table 3 and Figure 3 show the various sulphonation times used in the sulphonation of PSS10 at the sulphonation temperature 40 ±2 ℃. It can be seen from Table 3 and Figure 3. The optimal sulphonation time was 2 h. The IEC and S content in percentage were the highest value corresponding to the polystyrene sulphonated membrane prepared at 40 ±2℃.

It can be inferred that the operational optimal conditions of the casted PSS membranes, the weight ratio of sulfuric acid to polystyrene should be 2:1 (v/w), temperature should be 40 ±2℃ and the time of sulphonation should be 2 h.The membrane obtained at these optimal conditions showed the highest IEC value of 0.79 meq/g with a S content (%) of 2.53. Regarding PSS10 membrane, it was also found to possess smooth surface texture and the more uniform cavitated pores. The prepared PSS10 membrane is shown in Figure1.

Figure 1 The prepared proton exchange membrane

Table 1 Sulphonation of Polystyrene with Different Amounts of Concentrated Sulphuric Acid

Membranes	Vol. of con. H_2SO_4(mL)	Sulphur content (%)	Remark
PSS 5	5	1.60	Satisfactory
PSS 10	10	1.66	very uniform smooth
PSS 15	15	1.32	torn-up
PSS 20	20	1.54	very brittle

Note: Amount of polystyrene = 5g, Sulphonation time = 2 h, Sulphonation temp. = 80 ± 2 °C

Table 2 Sulphonation of Polystyrene at Various Sulphonation Temperatures

Membranes	Sulphonation temp. (°C)	IEC (meq/g)	S-content (%)
PSS10	40±2	0.79	2.53
PSS10	50±2	0.70	2.24
PSS10	60±2	0.67	2.14
PSS10	70±2	0.71	2.27
PSS10	80±2	0.52	1.66

Note: Sulphonation time = 2 h

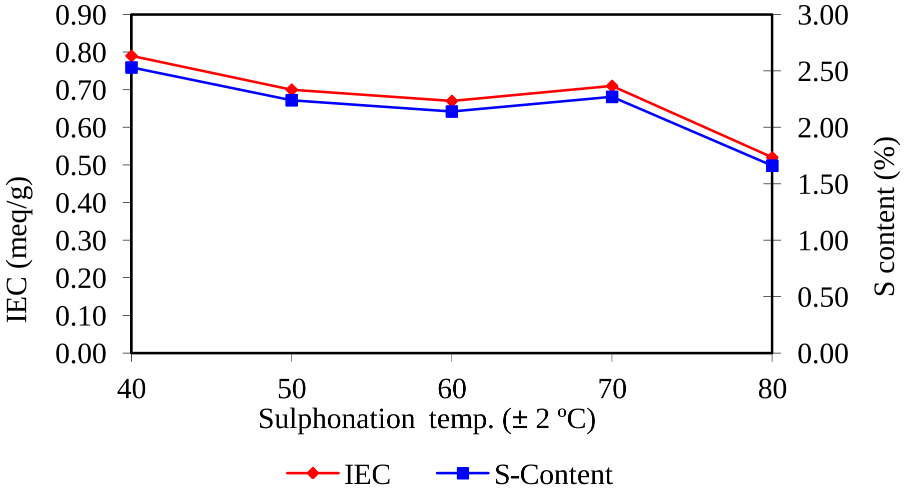


Figure 2 Variation of IEC and sulphur content as a function of sulphonation temperature

Table 3 Sulphonation of Polystyrene at Various Sulphonation Times

Membranes	Sulphonation Time(h)	IEC (meq/g)	S-content (%)
PSS10	1	0.45	1.44
PSS10	2	0.79	2.53
PSS10	3	0.78	2.49
PSS10	4	0.73	2.34
PSS10	5	o.74	2.37

Note: Sulphonation temp. = 40 ± 2 °C

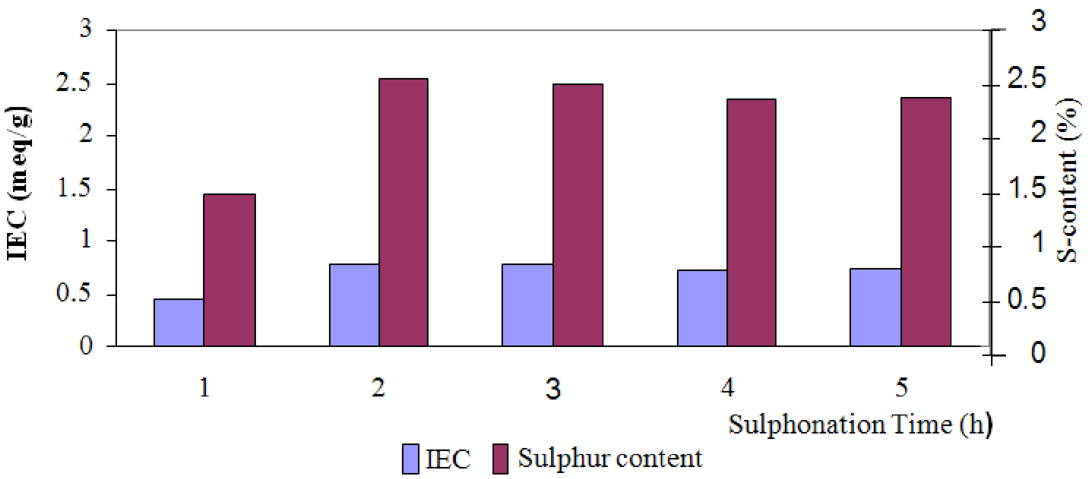


Figure 3 Variation of S content and IEC with various sulphonation time

Identification of Polystyrene Sulphonated Membranes (PSS10)

FT IR analysis of PSS10 membrane

Figure 4 shows the FT IR spectrum of PSS10 membrane. The corresponding FT IR spectrum assignment is presented in Table 4. The FT IR spectrum of PSS10 membrane observes the C-H stretching of CH_3, CH_2 and CH at 302 5, 2923, 2851 cm^{-1}. The band at 1068-1028 cm^{-1} indicates the S=O stretching of sulphonic acid group and the band at 756-699 cm^{-1} shows the C-S stretching. Therefore, the FT IR spectrum of polystyrene sulphonated membrane indicates the presence of sulphonic acid group.

Table 4 FT IR Spectral Assignment for PSS10 Membrane

Observed Frequency (cm^{-1})	Frequency Range (cm^{-1})	Assignment	Group and Class
3442	3400-3200	O-H stretch	$-SO_3H$ group
3025	3100-3000	aromatic C-H stretching vibration	
2923	3000-2800	Aliphatic C-H stretching vibration	$-CH_2-$ group
2851	2870-2840	CH_2 sym stretch	CH_2- group
1600-1492	1600-1450	Aromatic C=C stretching vibration	C=C group
1451	1470-1431	C-H deformation vibration	$-CH_3-$
1181-1155	1190-1120	SO_2 sym stretching vibration	$-SO_2$ group
1068-1028	1060-1020	S=O stretch	S=O group
756 - 699	720 - 660	C-H bending monosubstituted benzene	C-S group

(Silverstein, 1991)

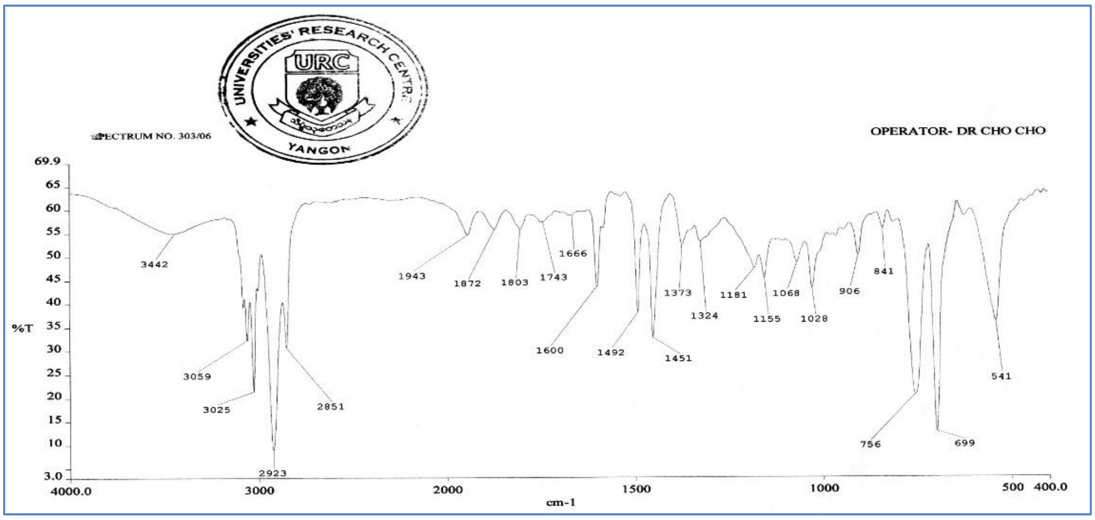
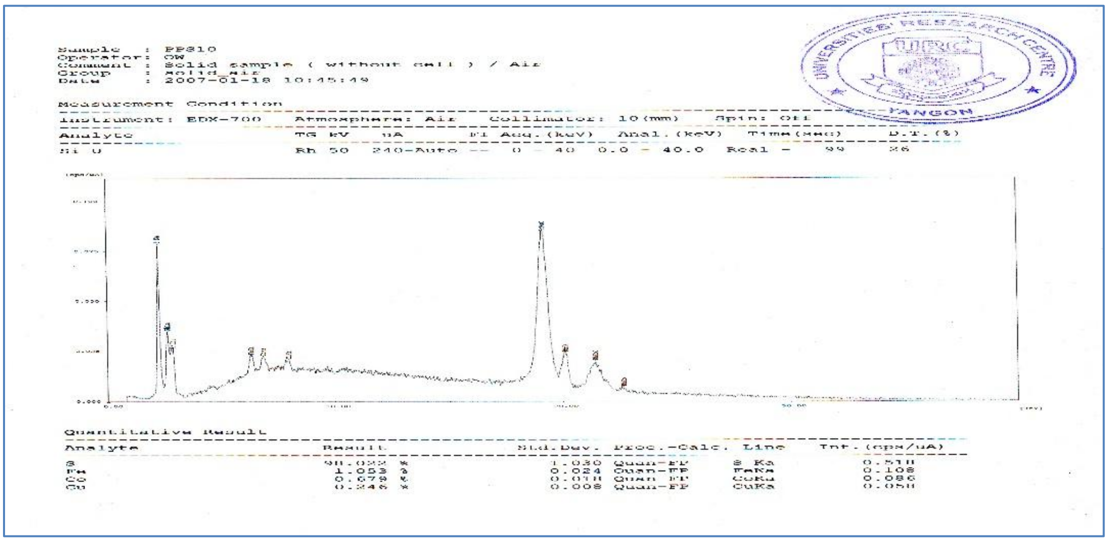


Figure 4 FT IR spectrum of PSS10 membrane

EDXRF analysis of PSS10 membrane

Figure 5 shows the EDXRF spectrum of PSS membrane. According to EDXRF spectrum, PSS membrane contains sulphur which was the main component, iron and copper were the trace constituents. The content of sulphur is relevant to any influencing factors on fuel cell performance.

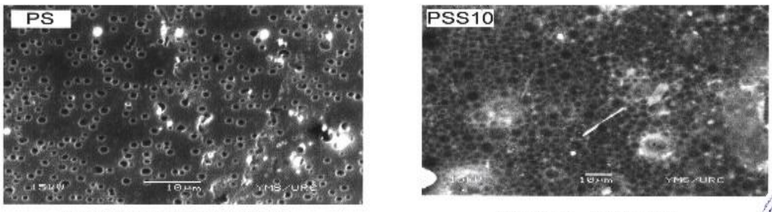


```
Sample   : PPS10
Operator : OW
Comment  : Solid sample ( without cell ) / Air
Group    : Solid_Air
Date     : 2007-01-18 10:45:49

Measurement Condition
------------------------------------------------------------------------------
Instrument: EDX-700   Atmosphere: Air   Collimator: 10(mm)   Spin: Off
------------------------------------------------------------------------------
Analyte          TG kV   uA         Fi Acq.(keV)  Anal.(keV)  Time(sec)   D.T.(%)
------------------------------------------------------------------------------
Si U             Rh 50   240-Auto --   0 - 40    0.0 - 40.0  Real -  99   26

Quantitative Result
------------------------------------------------------------------------------
Analyte            Result         Std.Dev.  Proc.-Calc.  Line     Int.(cps/uA)
------------------------------------------------------------------------------
S                  [illegible] %  1.030     Quan-FP      S Ka     [illegible]
Fe                 1.053 %        0.024     Quan-FP      FeKa     0.108
Co                 0.679 %        [illegible] Quan-FP    CoKa     0.086
Cu                 0.246 %        0.008     Quan-FP      CuKa     [illegible]
```

Figure 5 EDXRF spectrum of PSS10 membrane

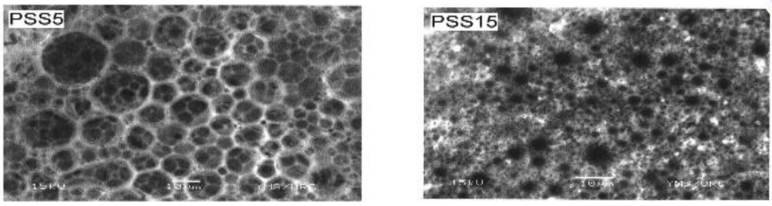
Scanning electron microscopy of the prepared PSS membranes

SEM micrographs Figures 6(b), (c), and (d) show the surface morphology of PSS membranes and Figure 6(a) is the SEM micrograph of PS membrane which is not sulphonated. From the SEM results, it is clear that the surface texture of PSS membranes were different with different amount of concentrated sulphuric acid. Among them, PSS10 membrane shows uniform pores size. Surface morphology of these membranes were also relevant to the sulphonation time. According to SEM micrographs Figures 7(d), and (e) are typical, they are brittle and their pores size are not uniformed. In addition, the surface texture of Figure 7(b) is characterized by the presence of imperfections, probably due to the presence of aggregates of sulphonic groups at the film surface. Hence, in accordance to the spectra and resulting data of FT IR, EDXRF and the results presented by SEM,can be inferred that sulphonation of polystyrene was successfully achieved.



(a) which is not sulfonated
IEC (-)
S-content (-)

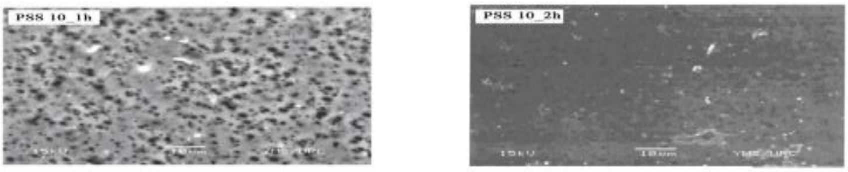
(c) PS:S 1:2 (w/v)
IEC (0.52 meq/g)
S-content (1.66 %)



(b) PS:S – 1:1 (w/v)
IEC (0.50 meq/g)
S-content (1.60 %)

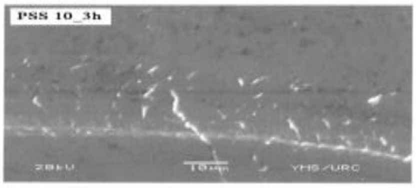
(d) PS:S – 1:3 (w/v)
IEC (0.56 meq/g)
S-content (1.79 %)

Figure 6 SEM micrographs of PSS membranes with various amounts of con.H_2SO_4

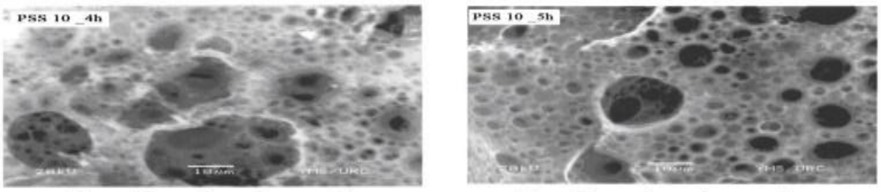


(a) sulfonation time - 1hr
IEC (0.45 meq/g)
S-content (1.44 %)

(b) sulfonation time - 2hr
IEC (0.79 meq/g)
S-content (2.53 %)



(c) sulfonation time - 3hr
IEC (0.78 meq/g)
S-content (2.49 %)



(d) sulfonation time - 4hr
IEC (0.73 meq/g)
S-content (2.34 %)

(e) sulfonation time - 5hr
IEC (0.74 meq/g)
S-content (2.37 %)

Figure 7 SEM micrographs of PSS10 membrane with various sulphonation times

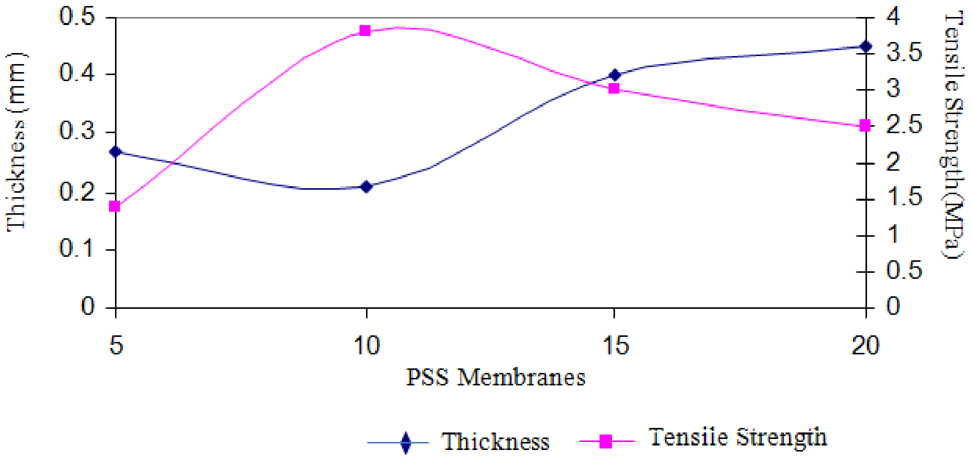
Evaluation of Physicochemical and Physicomechanical Properties of the Prepared Membranes

Tables 5, 6, 7 describe the data obtained from the determination of ion exchange capacity of PSS membranes. From the experimental point of view, amount of sulphonating agent, sulphonation temperature and duration of sulphonation are the most important factors, which play the role of preparation of ion exchange membranes. It has been found that the PSS membrane which has been prepared by sulphonation of polystyrene with increasing amounts of concentrated sulphuric acid. At the high amount of sulphuric acid, water uptake decreases with increasing IEC value. The samples also have become more fragile.These results are shown in Table 5 and Figures 8 and 9. From the results, PSS20 showed a high IEC value (0.59 meq/g), but its water uptake had decreased (i.e. 50.26%).The sample has become more brittle,so tensile strength was lowered (2.5 MPa).The IEC value of PSS10 (0.52 meq/g) was much lower than that of PSS20, but it has a high water uptake property.

Table 5 Physical Properties of PSS Membranes with Different Amounts of Con.H_2SO_4

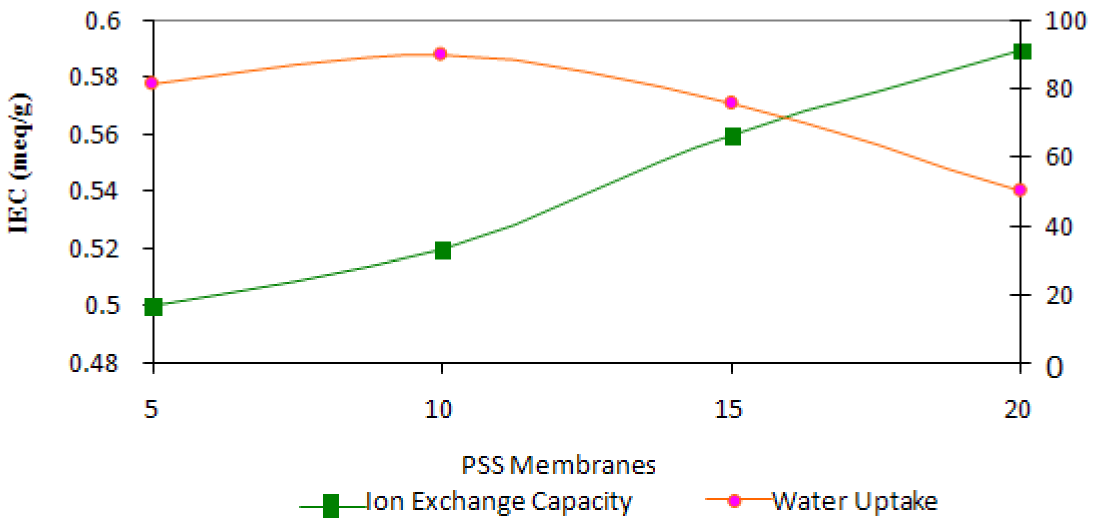
Type	Thickness (mm)	Tensile Strength (MPa)	Ion Exchange Capacity (meq/g)	Water Uptake Wt (%)
PSS 5	0.27	1.40	0.50	81.22
PSS 10	0.21	3.80	0.52	90.32
PSS 15	0.40	3.00	0.56	75.68
PSS 20	0.45	2.50	0.59	50.26

Note: Sulphonation temperature was controlled at (80±2)°C for 2 h.



5 = PSS5 membrane prepared with 5 % conc: H_2SO_4
10 = PSS10 membrane prepared with 10 % conc: H_2SO_4
15 = PSS15 membrane prepared with 15 % conc: H_2SO_4
20 = PSS20 membrane prepared with 20 % conc: H_2SO_4

Figure 8 Thickness and tensile strength vs. prepared membranes



5 = PSS5 membrane prepared with 5 % conc: H_2SO_4
10 = PSS10 membrane prepared with 10 % conc: H_2SO_4
15 = PSS15 membrane prepared with 15 % conc: H_2SO_4
20 = PSS20 membrane prepared with 20 % conc: H_2SO_4

Figure 9 IEC and water uptake vs. prepared membranes

The variation of ion exchange capacity as a function of sulphonation temperature under controlled temperatures; (40±2) ˚C, (50±2) ˚C, (60±2) ˚C, (70±2) ˚C, (80±2) ˚C are presented in Table 6 and Figures 10 and 11. It can be seen that the ion exchange capacity of polystyrene sulphonated membrane at low temperatures showed maximum IEC values and then decreases with increasing sulphonation temperature.

Table 6 Physical Properties of PSS10 Membranes with Various Sulfonation Temperature

Membranes	**Sulfonation Temp. (˚C)**	**Thickness (mm)**	**Tensile Strength (MPa)**	**IEC (meq/g)**	**Water Uptake (Wt.%)**
PSS10	40 ± 2	0.25	3.5	0.79	95.50
PSS10	50 ± 2	0.23	3.3	0.70	92.44
PSS10	60 ± 2	0.28	3.5	0.67	98.44
PSS10	70 ± 2	0.26	3.9	0.71	96.50
PSS10	80 ± 2	0.21	3.8	0.52	90.32

Note: Sulfonation time was controlled at 2 h.

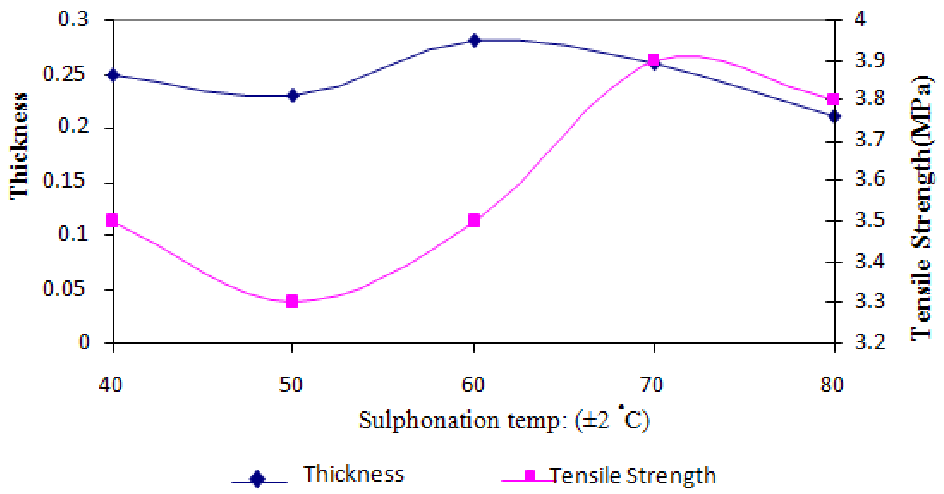


Figure 10 Thickness and tensile strength vs. sulphonation temperature

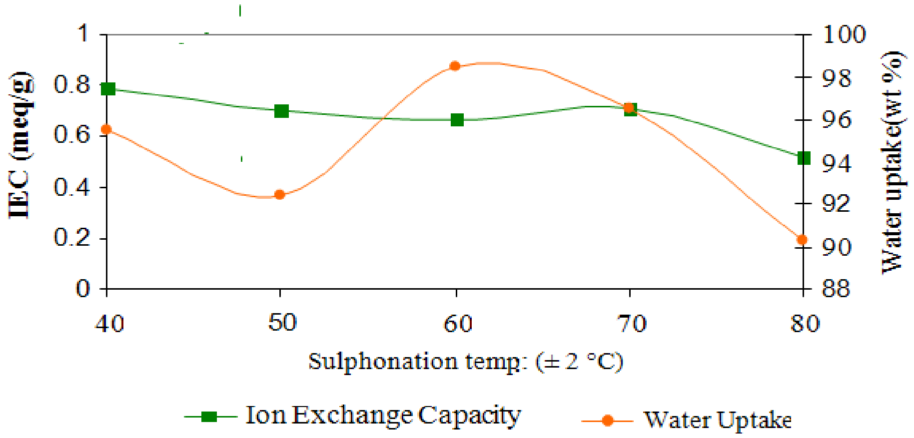


Figure 11 IEC and water uptake vs. sulphonation temperature

In sulphonation of polystyrene, sulphonation temperature that close to the room temperature are suitable, thus it is preferably kept under 50 ˚C or less. IEC value depends on sulphonation time. These results are shown in Table 7 and Figures 12 and 13. From the results, IEC values of PSS10 membranes except PSS10 (1 h) membrane, were slightly different but water uptake were different and lesser because of surface texture was more fragile.

Table 7 Physical Properties of PSS10 Membranes with Various Sulfonation Time

Membranes	Sulphonation Tememperature (h)	Thickness (mm)	Tensile Strength (MPa)	Ion Exchange Capacity (meq/g)	Water Uptake (Wt. %)
PSS10	1	0.24	3.3	0.45	90.55
PSS10	2	0.25	3.5	0.79	95.50
PSS10	3	0.45	3.5	0.78	85.60
PSS10	4	0.45	3.0	0.73	66.67
PSS10	5	0.40	3.2	0.74	65.63

Note: Sulphonation temperature was controlled at (40±2) °C

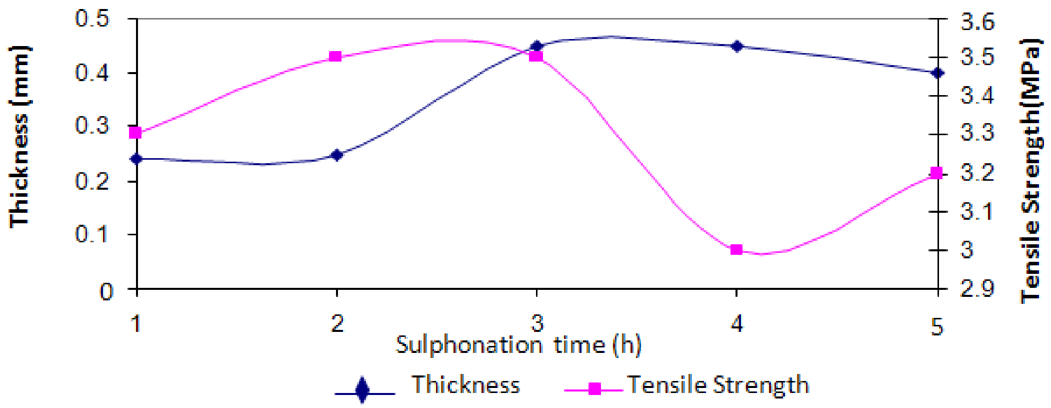


Figure 12 Thickness and tensile strength vs. sulphonation time

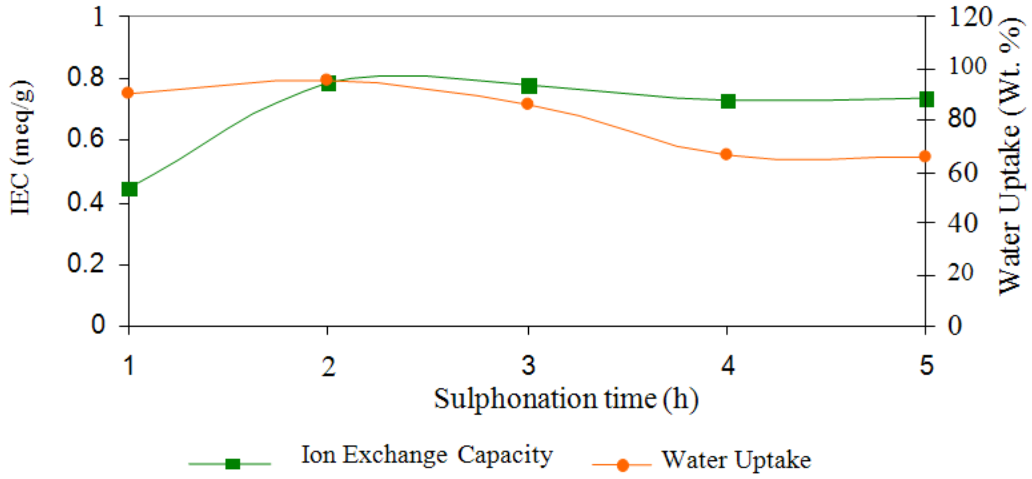


Figure 13 IEC and water uptake vs. sulphonation time

The solubility characteristics of prepared PSS membranes are shown in Table 8. From the experimental point of view, PSS membrane is highly hydrophobic and insoluble in water and in most organic solvents such as ethanol, methanol, petether. They are soluble in butanone, toluene and slightly soluble in acetone. Moreover, these membranes are not soluble in sulfuric acid, hydrochloric acid, nitric acid, potassium hydroxide and sodium hydroxide at room temperature. According to the results, The optimum conditions for preparing sulphonated polystyrene membrane (PSS10) were found to be ; 5 g of polystyrene, 10 mL of 98 % concentrated sulphuric acid,100 mL of toluene as solvent, sulphonation time of 2 h, and sulphonaton temperature of 40 ± 2 ˚C. The photograph of the stack of unit cells in series are shown in Figure 14. The stack of unit cell was able to produce only about 2.6 V. To produce stabilized output voltage.The assembly needs to be modified by using bipolar plates.

Solubility of the Prepared PSS10 Membrane

Table 8 Solubility of the Prepared PSS10Membrane

Solvents	Prepared PSS10 Membranes
Water	-
Sulphuric acid (1M)	-
Hydrochloric acid (1M)	-
Nitric acid (1M)	-
Potassium hydroxide (1M)	-
Sodium hydroxide (1M)	-
Methanol	-
Ethanol	-
Petether	-
Acetone	±
Butatone	+
Toluene	+

Note : + Soluble, - Insoluble, ± Slightly soluble

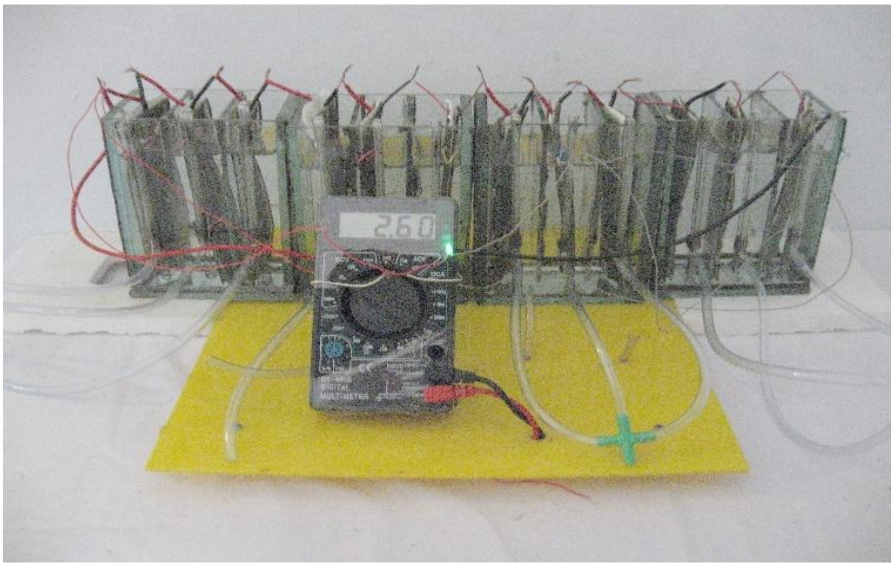


Figure 14 Photograph of constructed DMFC in series

Conclusion

PSS membranes were characterized in terms of its quality, intrinsic properties such as ion exchange capacity (IEC), water uptake and tensile strength. All these parameters can be adjusted to the PSS membrane suitable for its end uses. The determination of IEC is one of the most important characteristic and most widely used in preparation of ion exchange membrane. Several methods are available for the determination of IEC of ion exchange membrane. From the experimental point of view, amount of sulphonating agent, sulphonation temperature and duration of sulphonation are the most important factors, which play the role of preparation of ion exchange membranes.This investigation has shown that it is feasible to prepare sulphonated polystyrene by using 98 % concentrated sulphuric acid as a sulphonating agent. The optimum conditions for preparing sulphonated polystyrene membrane (PSS10) were found to be ; 5 g of polystyrene, 10 mL of 98 % concentrated sulphuric acid, 100 mL of toluene as solvent, sulphonation time of 2 h and sulphonation temperature of 40 ± 2℃.

The desired membranes were prepared by casting in deionized water at ambient temperature and were immersed in 1M H_2SO_4 for about 24 h so that the conductivity of prepared membranes can be promoted. The presence of $-SO_3H$ groups were able to achieve by cation exchange capacity (titration method). IEC and water uptake of prepared PSS membranes were calculated by using the formula. The maximum cation exchange capacity of PSS10 membrane was 0.79 meq/g. Using the sulphonation process a polymer that can perform an ion exchange capacity of from 0.50 to 4.10 (From Literature) can be obtained. From the results, it clearly showed that all the PSS membranes have ion exchange capacity ranging from 0.45-0.79 meq/g. Therefore, the prepared polystyrene sulphonated membranes were suitable for the low temperature fuel cell, especially direct methanol fuel cell.

Acknowledgements

The authors would like to express their profound gratitude to the Myanmar Academy of Arts and Science for giving permission to submit this paper and to professor Dr Myint Myint Sein, Chemistry Department, Banmaw University, for her kind encouragement.

References

Carretta, N. (2000). "Ionomeric Membrane Based on Paritcally Sulphonated Poly (Styrene): Synthesis,Proton Conduction and Methanol Permeation" *J. Mem. Sci*. vol. 166, pp.189 – 197

Geiger, A. (2002). *Characterization and Development of Direct Methanol Fuel Cells*. PhD Thesis, Zurich: Swiss Federal Institute of Technology, pp. 110-113

Halacy, D.S, Jr., (1966). *Fuel Cells: Power for Tomorrow*. Canada: Nelson, Faster & Scott Ltd. pp. 22-31

Hogarth. M.P. and Hards. G. R. (1996). “Direct Methanol Fuel Cells” , vol, 40, pp. 150-159

Larmine, J. (2002). *Fuel Cell Power Systems.* New York: John Wiley and Sons, pp.37-53

Motokawa, S. (2005). *Design and Fabrication of Micro Direct Methano Fuel Cell with New Concept Planar Structure by Means of Micro Electro Mechanical Systems*. PhD (Thesis), Japan: Waseda University, pp. 47-52

Silverstein, R. M. (1991) *Spectrometric Identification of Organic Compounds*. New York: John Wiley and Sons, pp. 99-164

Williams, K. R (1966). *An Introduction to Fuel Cell.* New York: Elsevier Publishing Company, pp. 111