

**DEVELOPMENT AND CHARACTERIZATION OF SULFONATED  
POLYSULFONE FOR MEMBRANE FUEL CELL**

**WAN MUHD NADZMI WAN YAAKUB**

**A thesis submitted in fulfillment for the award of the Degree of Bachelor in  
Chemical Engineering (Gas Technology)**

**Faculty of Chemical and Natural Resources Engineering  
Universiti Malaysia Pahang**

**APRIL 2009**

I declare that this thesis entitled “Development and characterization of sulfonated polysulfone for membrane fuel cell” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....  
Name : Wan Muhd Nadzmi Wan Yaakub  
Date : 30 APRIL 2009

*Dedicated, in thankful appreciation for support,  
encouragement and understanding  
to my beloved family and friends.*

## ACNOWLEDGEMENT

In the name of Allah S.W.T. the most gracious and most merciful, Lord of the universe, with His permission Alhamdulillah the study has been completed. Praise to Prophet Muhammad S.A.W., His companions and to those on the path as what He preached upon, might Allah Almighty keep us His blessing and tenders.

First of all, I would like to express my gratitude to my research supervisor, Pn Rosmawati Binti Naim for her valuable guidance, advices, efforts, supervision and enthusiasm given throughout for the progress of this research. Although she always busy with hers work, she still can spend the time in completing this research.

I owe tremendous appreciation to my parents, Wan Yaakub Wan Abd Rahman and Rohani Abd Latiff for their support and motivation during the tough time throughout the duration of this study I also want to thanks to Mohd Norazam Bin Mad Aris and Mohd Shamim Waliyuddin for their kindness to help in accomplished this project

Thank you so much for all. May Allah S.W.T. the Almighty be with us all the time.

## ABSTARCT

Sulfonation process was used to produce ion exchange polymer from a commercial polysulfone .Membranes obtained from the sulfonated polysulfone (SPSU) are potential substitutes for perflourosulfonic acid membrane (Nafion<sup>TM</sup>) used now in polymer electrolyte fuel cell due to its high cost to produce, needs of high pressure and high hydration level to operate effectively. Sulfonations were achieved by varying the degree of sulfonation (DS) in reaction time. Characterizations of different degree of sufonated polysulfone membranes were conducted through elemental analysistal, Fourier Transform Infared (FTIR) and swelling test. Fourier Transform Infared (FTIR) were used to confirm the presence of sulfonic group in the polymer after sulfonation process and it was clearly confirmed by the SO<sub>3</sub> stretching bond at frequency 1020 cm<sup>-1</sup> to 1035cm<sup>-1</sup>. The hydration levels of membrane were measured via swelling test. Result showed the percentages of water and methanol uptake broadening as the degree of sulfonation increased.

## ABSTRAK

Proses pensulfonan telah dikaji untuk menghasilkan polimer kapasiti penukaran ion dari polimer polisulfona . Membran yang terhasil daripada pensulfonan polisulfona (SPSU) adalah berpotensi untuk menggantikan membran berasid (Nafion™) yang buat masa sekarang di guna pakai di dalam sel kering berpolimer elektrolit adalah kerana harganya yang mahal untuk dihasilkan, memerlukan tekanan yang tinggi dan memerlukan kandungan cecair yang tinggi untuk beroperasi secara efektif. Proses pensulfonan dijalankan dengan mempelbagaikan darjah pensulfonan dalam masa reaksi yang berbeza. Karakteristik yang berbeza oleh darjah pensulfonan membran yang diperolehi melalui analisis elemen Spektrokopi Infra-Merah Penukaran Fourier (FTIR). Infra-Merah Penukaran Fourier digunakan untuk mengesan kumpulan berfungsi sulfonik ke dalam struktur polimer setelah proses pensulfonan dan keputusan menunjukkan dengan jelas kehadiran kumpulan berfungsi asid sulfonik ( $\text{SO}_3$ ) pada frekuensi  $1020\text{cm}^{-1}$  hingga  $1035\text{cm}^{-1}$ . Keberaliran membran dikaji dengan menggunakan kaedah keberaliran. Kajian mendapati semakin tinggi darjah pensulfonan semakin tinggi peratusan keupayaan membran untuk meresap air dan methanol.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>DECLARATION</b>	<b>ii</b>
	<b>DEDICATION</b>	<b>iii</b>
	<b>ACKNOWLEDGEMENT</b>	<b>iv</b>
	<b>ABSTRACT</b>	<b>v</b>
	<b>ABSTRAK</b>	<b>vi</b>
	<b>TABLE OF CONTENT</b>	<b>vii</b>
	<b>LIST OF TABLES</b>	<b>xii</b>
	<b>LIST OF FIGURES</b>	<b>xiv</b>
	<b>LIST OF APPENDICES</b>	<b>xvi</b>
<b>1</b>	<b>INTRODUCTION</b>	
	1.1 Research Background	1
	1.2 Problem Statement	3
	1.3 Objectives of Research	3
	1.4 Scope of Research	3
<b>2</b>	<b>LITERATURE REVIEW</b>	
	2.1 Membrane Review	4
	2.1.1 Definition of Membrane	4
	2.1.2 Type of Membrane	5
	2.1.2.1 Microporous Membrane	5
	2.1.2.2 Homogenous Membrane	5
	2.1.2.3 Asymetric Membrane	5
	2.1.2.4 Electrically Charge Membrane	6

2.2	Membrane Separation Process	6
2.2.1	Separation Process	6
2.2.2	Type of Membrane Separation Process	7
2.2.2.1	Ultrafiltration	7
2.2.2.2	Microfiltration	7
2.2.2.3	Reverse Osmosis or Hyperfiltration	8
2.2.2.4	Electrodialysis	8
2.2.3	Ion Exchange Membrane Separation	10
2.2.3.1	Definition of ion exchange	10
2.2.3.2	Basic concept of Ion Exchange	10
2.3	Fuel Cell Technology Review	11
2.3.1	PEM Fuel Cell	11
2.3.2	Basic Concept of Fuel Cell	11
2.3.3	History of Fuel Cell	12
2.3.4	Type of Fuel Cell	14
2.3.4.1	Proton Exchange Membrane Fuel Cell	14
2.3.4.2	Phosphoric Acid Fuel Cell (PAFC)	15
2.3.4.3	Molten Carbonate fuel cell (MCFC)	15
2.3.4.4	Solid Oxide Fuel Cell (SOFC)	16
2.3.4.5	Alkaline Fuel Cell (AFC)	16
2.3.4.6	Direct Methanol Fuel Cell (DMFC)	16
2.3.4.7	Regeneration Fuel Cell	17
2.3.4.8	Zink Air Fuel Cell (ZAFC)	17
2.3.4.9	Proton Ceramic Fuel Cell (PCFC)	18
2.3.4.10	Microbial Fuel Cell (MFC)	18
2.3.5	Advantages of Fuel Cell	19
2.3.6	Disadvantages of Fuel Cell	20
2.4	Membrane PEMFC	20
2.4.1	Factor Affecting Membrane	21
2.4.1.1	Hydration	21
2.4.1.2	Thickness	21
2.4.2	Water Management Membrane	22



2.4.3	Type of Membrane of PEMFC	22
2.4.4	Standard Membrane for PEMFC	23
2.5	Sulfonation Process	24
2.6	Sulfonated Polysulfone	25
<b>3</b>	<b>RESEARCH METHODOLOGY</b>	<b>26</b>
3.1	Material Solution	26
3.1.1	Polysulfone	26
3.1.2	Sulfuric Acid	27
3.1.3	Sodium Methoxide	28
3.1.4	Solvent	28
3.2	Research Design	29
3.3	Experiment Stages	29
3.3.1	Sulfonation Process	30
3.3.2	Polymeric Sulfonation Making	31
3.3.3	Membrane Fabrication	31
3.3.4	Acid Membrane PreTreatment	32
3.3.5	Membrane Characterization	32
3.3.5.1	Swelling Test	32
3.3.5.2	Fourier Transform Infrared (FTIR)	32
<b>4</b>	<b>RESULT &amp; DISCUSSION</b>	<b>33</b>
4.1	Sulfonation Process	33
4.2	CHNS Elemental Analysis	34
4.3	Calculation of Degree of Sulfonation	35
4.4	Confirmation by FTIR	37
4.5	Swelling Test	39
<b>5</b>	<b>CONCLUSION</b>	<b>41</b>
5.1	Conclusion	41
5.2	Recommendation	42
	<b>REFERENCES</b>	<b>43</b>

**GANTT CHART**

46

Appendices 1-8

47-51

**LIST OF TABLE**

<b>TABLE NO.</b>	<b>TILTLE</b>	<b>PAGE</b>
2.1	The Characteristics of Membranes	9
3.1	Polysulfone Properties	27
3.2	Properties of Sulfuric Acid	28
3.3	Properties of Sodium Methoxide	29
3.3	Properties of Dimethylforamide	29
4.1	Sulfonation Process Condition	33
4.2	Atomic Composition of CHNS	34
4.3	Sulfur and Carbon Percentages in Samples	35
4.4	Degree of Sulfonation	36
4.5	Wavelentgh of Membrane Samples	38
4.6	Water.Uptake Percentages	39
4.7	Methanol Uptake Percentages	40

**LIST OF FIGURE**

<b>FIGURE NO</b>	<b>TILTLE</b>	<b>PAGE</b>
2.1	Basic Concept of PEM Fuel cell	12
2.2	Fuel Cell	13
2.3	Classification of Membrane Material	23
2.4	The Structure of Nafion™	23
2.5	Sulfonation Process of Polysulfone	25
3.1	Polysulfone Structure	26
3.2	Electrophilic Substitution by Sulfuric Acid	27
3.3	Factor Influencing the Characteristic Sulfonated Membrane	29
3.4	Experimental Stages	30
3.5	Sulfonation Process and Polymer Making Apparatus	31
3.6	Casting Knife	31
4.1	Result FTIR for PSU	37
4.2	Result FTIR for SPSU6	37
4.3	Result FTIR for SPSU16	38
4.4	Result FTIR for SPSU26	38

**LIST OF APPENDICES**

<b>APPENDIX NO</b>	<b>TILTLE</b>	<b>PAGE</b>
1	Polymer Dissolved Process	47
2	Sulfonation Process	48
3	Sulfonated Polysulfone Particle	49
4	Sulfonated Polysulfone Dissolved Process	49
5	Degasses Process	50
6	Sulfonated Polysulfone Solution After Degasses Process Structure	50
7	Casting Apparatus	51
8	Membrane Produced	51

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Now days the world is actively pushing for cleaner energy technologies. This is because of the public concern about the environments condition. Ozone layer has rapidly become thinner day by day because of the dangerous toxic release during the energy conversion. This has prompted research for clean and efficient alternatives for power generation and one of the most attractive alternatives is electrochemical fuel cell technology. Fuel cells have several advantages that make them attractive power sources for high thermal efficiency, extremely low or zero emissions, and low noise and vibration in comparison to conventional power trains.

Fuel cell used hydrogen and oxygen to produce electricity, water and heat as by-product. As long as fuel is supplied the fuel cell will continue to generate power. . In principle, a fuel cell operates like a battery. Unlike a battery, a fuel cell does not run down or require recharging.

The awareness about environment and fossil fuel limited resource in this century had led many countries especially United State of America, United Kingdom Japan and Canada to give more attention in development and implementation of this fuel cell to multiple field mainly transportation, stationary power, and micro electronic devices. These also enhanced big company in transportation business such as Daimler Chrysler, Ford, Ballard, Honda and Toyota to give more work in this type of energy conversion device. Several experiments

have been conducted in order to verify the performance and upgrade the current fuel cell system. Meanwhile for high capacity power generation, Solid Oxide Fuel Cell.

(SOFC) has made their remarked as a higher performance and efficiency for high capacity power supply and distributed generation compared to other type of fuel cell.

The common membranes used in fuel cell application are Proton Exchange Membrane (PEM) Fuel Cell has gain more attention due to its ability in high power density and high flexibility. Scientists and engineers are carrying out specific research into the structural design, thermodynamics, and heat transfer processes of one class of this PEM fuel cell. Commercially, Nafion<sup>TM</sup> membrane manufactured by DuPont de Nemours has been used as the polymer electrolyte membrane material for fuel cell. This was due to its outstanding chemical and mechanical stability which composed of perflourinated carbon chains and sulfuric acid group at the end of side chains. However this type of membrane sensitive to contaminants and methanol cannot operate above 80°C its more expensive cost due the complicated production process (Zydney *et al*, 1996).

In oder to get the most efficient system of PEMFC, the membrane develop need to have a good and stable membrane operating at desired temperature and pressure. The need of developing membrane that satisfies this condition with the minimum cost of production and maintenance are recommended.

## **1.2 Problem Statement**

Currently, common membrane for Proton Exchange Membrane Fuel Cell (PEMFC) is perfluorosulfonic acid called Nafion<sup>TM</sup>. Until now Nafion remains as standard for industry but it was very expensive to produce and require heat, high pressure and high level hydration in order to perform effectively. Thus the main research in membrane fuel cell is to develop cost-effective material and membrane that can operate at low pressure and at high temperature.

## **1.3 Objective of Research**

The objective of this research is to develop and characterize the sulfonated polysulfone membrane for Proton Exchange Membrane Fuel Cell (PEMFC) application.

## **1.4 Scope of the Research**

In order to accomplish the set objectives, the following scope of works has been drawn

- i. Development and fabrication the sulfonated polysulfone as a membrane for fuel cell.
- ii. Study the effect of reaction time, for various degree of sulfonation.
- iii. Study the physical and chemical characteristic of sulfonated polysulfone membrane using FTIR, Elemental Analysis, and water swelling



## **CHAPTER II**

### **LITERATURE REVIEW**

#### **2.1 Membrane Review**

A membrane is a layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, molecules, or substances when exposed to the action of a driving force. Some components are allowed passage by the membrane into a permeate stream, whereas others are retained by it and accumulate in the retentate stream (Larminie *et al*, 2000).

##### **2.1.1 Definition of Membrane**

Membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 100  $\mu$ m to several mm (Nunes *et al*, 2003).

## **2.1.2 Type of Membrane**

There are several types of membrane but most of them still have the same basic principle and structure.

### **2.1.2.1 Microporous Membranes**

Membrane behaves almost like a fiber filter and separates by a sieving mechanism determined by the pore diameter and particle size. Materials such as ceramics, graphite, metal oxide and polymers are used in making such membranes (Scott *et al*, 1998).

### **2.1.2.2 Homogeneous Membranes**

This type of membrane is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be depends on their concentration (Scott *et al*, 1998).

### **2.1.2.3 Asymmetric Membranes**

An asymmetric membrane comprises a very thin (0.1-1.0 micron) skin layer on a highly porous (100-200 microns) thick substructure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of membrane material or pore size, and the mass transport rate is determined mainly by the skin thickness. Porous sub-layer acts as a support for the thin, fragile skin and has little effect on the separation characteristics (Scott *et al*, 1998)

#### **2.1.2.4 Electrically Charged Membranes**

These are necessarily ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges. These are mainly used in the electro-dialysis (Nunes *et al*, 2003).

## **2.2 Membrane Separation Process**

### **2.2.1 Separation Process**

In chemistry and chemical engineering, a separation process is used to transform a mixture of substances into two or more distinct products. The separated products could differ in chemical properties or some physical property, such as size, or crystal modification or other. Barring a few exceptions, almost every element or compound is found naturally in an impure state such as a mixture of two or more substances. Many times the need to separate it into its individual components arises (Baker *et al*, 2000).

A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane. Whereas the concentrate stream contains the constituents that have been rejected by the membrane. The proper choice of a membrane should be determined by the specific application objective: particulate or dissolved solids removal, hardness reduction or ultra pure water production, removal of specific gases/chemicals etc. The end-use may also dictate selection of membranes for industries such as potable water, effluent treatment, desalination or water supply for electronics or pharmaceutical manufacturing (Baker *et al*, 2000).

## **2.2.2 Type of Membrane Separation Process**

There are several different type of membrane process and all based on the same principle which allowed the selected particle or ion pass through their body. But the way how it's operated will exactly differ with each other.

### **2.2.2.1 Ultrafiltration**

Ultrafiltration (UF) designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. In UF, the membrane pore size is larger allowing some components to pass through the pores with the water. It is a separation/ fractionation process using a 10,000 MW cutoff, 40 psig, and temperatures of 50-60°C with polysulfone membranes (Meier *et al*, 2000).

### **2.2.2.2 Microfiltration**

Microfiltration designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. Membrane pore size allowing particles in the range of 0.2 to 2 micrometers to pass through. The pressure used is generally lower than that of UF process (Meier *et al*, 2000).

### **2.2.2.3 Reverse Osmosis or Hyperfiltration**

Reverse osmosis (RO) designates a membrane separation process, driven by a pressure gradient, in which the membrane separates the solvent (generally water) from other components of a solution. The membrane configuration is usually cross-flow. With reverse osmosis, the membrane pore size is very small allowing only small amounts of very low molecular weight solutes to pass through the membranes. It is a concentration process using a 100 MW cutoff, 700 psig, temperatures less than 40°C with cellulose acetate membranes and 70-80°C with composite membranes (Meier *et al*, 2000).

### **2.2.2.4 Electrodialysis**

Electrodialysis is used for demineralization of milk products and whey for infant formula and special dietary products. Also used for desalination of water. Under the influence of an electric field, ions move in an aqueous solution. The ionic mobility is directly proportioned to specific conductivity and inversely proportioned to number of molecules in solution.  $3-6 \times 10^2$  mm/sec charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations (Nunes *et al*, 2003).

Anion and cation exchange membranes are arranged alternately in parallel between an anode and a cathode. The distance between the membranes is 1mm or less. A plate and frame arrangement similar to a plate heat exchanger or a plate filter is used. The solution to be demineralized flows through gaps between the two types of membranes. Each type of membrane is permeable to only one type of ion. Thus, the anions leave the gap in the direction of the anode and cations leave in the direction of the cathode. Both are then taken up by a concentrating stream (Scott *et al*, 1998).

**Table 2.1:** The characteristics membranes used in different membrane separation (Nunes *et al.*, 2003).

Process	Membrane type and pore radius	Membrane material	Process driving force	Application
Microfiltration	Symmetric microporous, 0.1-10 microns	Cellulose nitrate or acetate, Polyvinylidene difluoride (PVDF), Polyamides, Polysulfone, PTFE, Metal Oxides etc.	Hydro-static pressure difference at approx. 10-500 kPa	Sterile filtration, Clarification
Ultrafiltration	Asymmetric microporous, 1-10 nm	Polysulfone, Polypropylene, Nylon 6, PTFE, PVC, Acrylic Copolymer	Hydrostatic pressure difference at approx. 0.1-1.0 Mpa	Separation of macromolecular solutions
Reverse Osmosis	Asymmetric skin-type, 0.5-1.5 nm	Polymers, Cellulosic acetate, Aromatic Polyamide	Hydrostatic pressure difference at approx. 2-10 Mpa	Separation of salts and microsolute from solutions
Electrodialysis	Cation and anion exchange membrane	Sulfonated cross-linked polystyrene	Electrical potential gradient	Desalting of ionic solutions
Gas Separation	Asymmetric homogeneous polymer	Polymers & copolymers	Hydrostatic pressure and concentration gradients	Separation of gas mixtures
Pervaporation	Asymmetric homogenous polymer (A non-porous membrane)	Polyacrylonitrile, Polymers	Vapour pressure gradient	Separation of azeotropic mixtures
Nanofiltration	Thin-film membranes	Cellulosic Acetate and Aromatic Polyamide	9.3-15.9 bar	Removal of hardness and desalting

## 2.2.3 Ion Exchange Membrane Separation

### 2.2.3.1 Definition of Ion Exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers' (Nunes *et al*, 2003).

### 2.2.3.2 Basic Concept of Ion Exchange

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials ( (Nunes *et al*, 2003).

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical examples of ions that can bind to ion exchangers are  $H^+$  (proton) and  $OH^-$  (hydroxide), single charged monoatomic ions like  $Na^+$ ,  $K^+$ , or  $Cl^-$ , Double charged monoatomic ions like  $Ca^{2+}$  or  $Mg^{2+}$  and polyatomic inorganic ions like  $SO_4^{2-}$  or  $PO_4^{3-}$ . Ion exchange is a reversible process and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions (Nunes *et al*, 2003).

## **2.3 Fuel Cell Technology Review**

### **2.3.1 Polymer Exchange Membrane Fuel Cell**

Fuel cells are electrochemical devices that generate electricity by directly converting the chemical energy associated with the oxidation of a fuel into direct current (DC) electricity. The chemical processes by which the electric current is produced are electrochemical, rather than thermochemical, in nature. Since no combustion reactions are involved in these processes fuel cells do not produce any of the undesirable products normally associated with the oxidation of fossil fuels in conventional energy conversion systems. The byproduct produce are heat and H<sub>2</sub>O. As a result, fuel cells do not emit CO<sub>2</sub>, SO<sub>2</sub>, oxides of nitrogen, or particulate matter. Thus, fuel cells are environmentally friendly (Cook *et al*, 2002).

### **2.3.2 Basic Concept of Fuel Cell**

A fuel cell consists of two electrodes sandwiched around an electrolyte. Oxygen passes over one electrode and hydrogen over the other, generating electricity, water and heat. Hydrogen fuel is fed into the "anode" of the fuel cell. Oxygen (or air) enters the fuel cell through the cathode. Encouraged by a catalyst, the hydrogen atom splits into a proton and an electron, which take different paths to the cathode. The proton passes through the electrolyte. The electrons create a separate current that can be utilized before they return to the cathode, to be reunited with the hydrogen and oxygen in a molecule of water. A fuel cell system which includes a "fuel reformer" can utilize the hydrogen from any hydrocarbon fuel - from natural gas to methanol, and even gasoline. Since the fuel cell relies on chemistry and not combustion, emissions from this type of a system would still be much smaller than emissions from the cleanest fuel combustion processes (Ogata *et al*, 1995).