

**DEVELOPMENT OF MIXED MATRIX SULFONATED POLYSULFONE AND  
POLYETHERSULFONE FOR PROTON EXCHANGE MEMBRANE FUEL  
CELL APPLICATION**

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requirement for the award of the degree of  
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EXCHANGE MEMBRANE FUEL CELL APPLICATION**

**SESI PENGAJIAN : 2005/2009**

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*To my beloved father and mother, Mr Rosman Darus and Madam Noraini Ghazali*

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## ABSTRACT

The objective of this study was to prepare a mixed matrix of sulfonated polysulfone (SPSU) and polyethersulfone (PES) and investigate its potential for proton exchange membrane fuel cell (PEMFC) application. Four samples were prepared in this study, a sample of PSU/PES as a reference and 3 other samples SPSU/PES with the amount of sulfonating agent (trimethylsilyl chlorosulfonate, TMSCS) varied for each sample (10mL, 15mL and 20mL). The sulfonated membrane samples (SPSU/PES 1, SPSU/PES 2 and SPSU/PES 3) were prepared in 20 hours stirring time, 10 minutes of TMSCS dropwise time and 15 minutes of sodium methoxide dropwise time. FTIR test confirmed that the sulfonation process was successful for all three sulfonated samples where wavelength of  $1029.27\text{ cm}^{-1}$  detected for sample SPSU/PES 1,  $1035.75\text{ cm}^{-1}$  for sample SPSU/PES 2 and  $1031.52\text{ cm}^{-1}$  for sample SPSU/PES 3. Referring to water/methanol mixture uptake test, sample SPSU/PES 3 had the highest swelling degree with the amount of 62.93% followed by SPSU/PES 2 (58.95%), SPSU/PES 1 (46.9%) and PSU/PES (33.43%). Elemental analysis was done in order to obtain data for degree of sulfonation calculation. From the calculation, it was found that sample SPSU/PES 3 has the highest degree of sulfonation (72.53%) followed by SPSU/PES 2 (55.49%) and SPSU/PES 1 (38.46%).

## ABSTRAK

Objektif tesis ini ialah untuk menyediakan matriks bercampur sulfonated polysulfone (SPSU) dan polyethersulfone (PES) dan mengkaji potensinya untuk aplikasi sel bahan api penukaran proton. Empat sampel telah disediakan dalam proses tesis ini dengan satu sampel PSU/PES sebagai rujukan dan 3 sampel SPSU/PES yang mengandungi kandungan ejen sulfonan trimethylsilyl chlorosulfonate, TMSCS) yang berlainan (10mL, 15mL and 20mL). Sampel membran tersulfon (SPSU/PES 1, SPSU/PES 2 and SPSU/PES 3) telah disediakan dalam 20 jam masa kacauan, 10 minit masa titisan TMSCS dan 15 minit masa titisan natrium metoksisida. Ujian FTIR mengesahkan bahawa proses sulfonasi bagi ketiga-tiga sampel SPSU/PES telah berjaya di mana panjang gelombang  $1029.27\text{ cm}^{-1}$  dikesan pada sampel SPSU/PES 1,  $1035.75\text{ cm}^{-1}$  untuk sampel SPSU/PES 2 dan  $1031.52\text{ cm}^{-1}$  for sampel SPSU/PES 3. Merujuk kepada ujian pengambilan campuran air/methanol, sampel SPSU/PES 3 mempunyai darjah pembengkakan yan tertinggi dengan jumlah 62.93% diikuti oleh SPSU/PES 2 (58.95%), SPSU/PES 1 (46.9%) dan PSU/PES (33.43%). Analisis elemen telah dijalankan untuk mendapatkan data bagi pengiraan darjah pengulfonan. Daripada pengiraan, didapati bahawa sampel SPSU/PES 3 mempunyai darjah pengulfonan yang tertinggi (72.53%) diikuti oleh SPSU/PES 2 (55.49%) dan SPSU/PES 1 (38.46%).



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## CHAPTER I

### INTRODUCTION

#### 1.1 Background of Study

Power generation with fewer hazards to environment has been a major world concern nowadays. The environmental concern has been a serious issue due to the reducing thickness of the ozone layers and increasing number of global warming and green house effects cases. Scientists, engineers and researchers have been starting to search for alternative fuels that can replace the world's dependency on fossil fuels such as petroleum and natural gas. Most of vehicles in the world nowadays use gasoline and diesel as their fuel. The usage of these types of hydrocarbon will contribute massive amount of pollutants from the effluents of the fuel conversion process.

Although several new inventions had been created in order to reduce the pollution made by gasoline and diesel powered engines such as replacing two strokes engine with four strokes engine for motorcycles and integrating the hybrid electric and fuel system into car engines, the demand for a cleaner, more energy efficient fuel will not stop there as the amount of fossil fuel is decreasing day by day and the price is going sky high per year. This particular matter has encouraged the research in various aspects for fuel cell. Fossil fuel savings, higher energy conversion efficiency, low pollution and noise level and affordable maintenance costs has made fuel cells are the most competitive type among other energy conversion devices (Smitha *et al*, 2005).

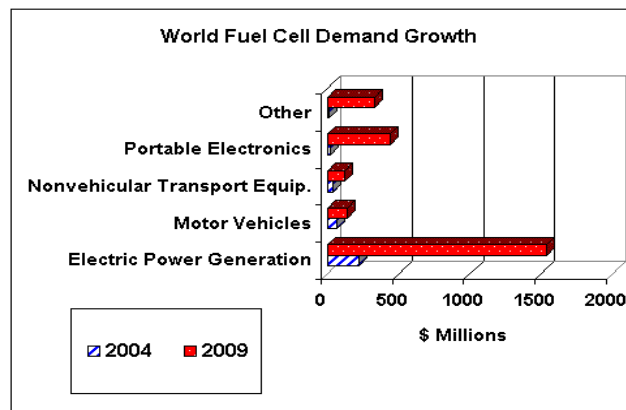
Major countries such as United States, Canada, United Kingdom and Japan are currently competing for the fuel cell application in various fields especially transportation and stationary power generation. The Japanese advance in technologies has made them the leading force for fuel cell implementation among other emerging Asian countries.

Malaysia is set to undertake the fuel cell technology application when ETI Tech (M) Sdn Bhd, a local leading energy solutions provider announced its smart partnership with P21 GmbH, a world class Munich-based international developer and manufacturer of efficient fuel cell powered Uninterrupted Power Supply (UPS) power system in 2006. This partnership is expected to revolutionize the applications of existing conventional high power backup systems. Due to this pioneering step, Malaysia can be considered ready to adapt with the fuel cell implementation in industrial and local applications in the near future.

Due to the environmental concern and decreasing amount of fossil fuels, fuel cell has been introduced to the commercial application. Transportation field has been the medium for fuel cell technology implementation. Smart cars were being developed by major vehicles companies such as General Motors, Toyota, Honda and Nissan to possibly replace conventional fossil fuel powered engine vehicles in the future. Smart cars use PEMFC to convert the fuel (mostly hydrogen) into electrical energy which is used as the car's power source.

Worldwide fuel cell-related sales increased by 41% between 2002 and 2003, according to the first worldwide fuel cell industry survey conducted by Pricewaterhouse Coopers for the US Fuel Cell Council, the national trade association for the fuel cell industry. The world fuel cell demand is expected to reach US\$ 2.6 billion in 2009. Total commercial fuel cell demand in 2004 totaled \$375 million and is anticipated to grow to \$2,580 million by 2009. This anticipated figure includes revenues associated with

prototyping and test marketing activities. By 2014, the forecasted growth should reach \$13.6 billion. World fuel cell spending (including research and development funding and investment in fuel cell enterprises, in addition to commercial sales) will more than double to \$10.8 billion in 2009 (Shirley and Donald Georgi, 2005). Figure 1.1 shows the world's fuel cell demand growth from 2004 to 2009.



**Figure 1.1:** World's Fuel Cell Demand Growth from 2004-2009  
(Shirley and Donald Georgi, 2005)

The characterization of fuel cells is basically differs from each other depending on the electrolyte types and the power they can generate. Due to rapid fuel cell research development internationally, there are many types of fuel cells that were developed and produced. However, there are five types of fuel cells that can be considered as the most commonly used and have high energy efficiency. The five types are:

- (i) Alkaline fuel cell
- (ii) Proton Exchange Membrane fuel cell
- (iii) Phosphoric Acid fuel cell
- (iv) Molten Carbonate fuel cell
- (v) Solid Oxide fuel cell



The proton exchange membrane fuel cell received high demands especially from the transportation field due to its compact size and low operating temperature.

Sulfonation of polymers was used in creating membranes for the proton exchange membrane fuel cells as an alternative method to find possible replacements for the Nafion membrane. The identification of an economical and productive method to create a possible replacement that can overcome the drawbacks of Nafion membrane is crucial since the proton exchange membrane fuel cell needs to have a good and stable membrane to achieve high performance and energy efficiency.

## **1.2 Problem Statement**

Nowadays, many proton exchange membrane fuel cell uses Nafion membrane which is considered as the standard membrane. However, Nafion is manufactured by DuPont only. This matter will make Nafion considered as quite hard to find. Nafion also have certain limitations. One of the major drawbacks of Nafion is it cannot operate at high temperature. It is also too dependant on the water quantity of the membrane. This research was conducted in order to get alternative polymer material for the membrane. The polymer must be low cost and can retain water at very high temperature. Finally, the newly modified polymer must be able to overcome the standard membrane (Nafion) drawbacks. Polysulfones and polyethersulfones have been recognized as the cheapest material among other engineering polymers and also available commercially.

### **1.3 Objective**

The objective of this research was to prepare and produce mixed matrix of sulfonated polysulfone and polyethersulfone for proton exchange membrane fuel cell application.

### **1.4 Scope of Study**

In order to achieve the objective, the following scope of study has been set:

- (i) Preparation of sulfonated polysulfone by sulfonation process
- (ii) Physicochemical study of the mixed matrix of sulfonated polysulfone and polyethersulfone membrane

## **CHAPTER II**

### **LITERATURE REVIEW**

#### **2.1 Membrane Review**

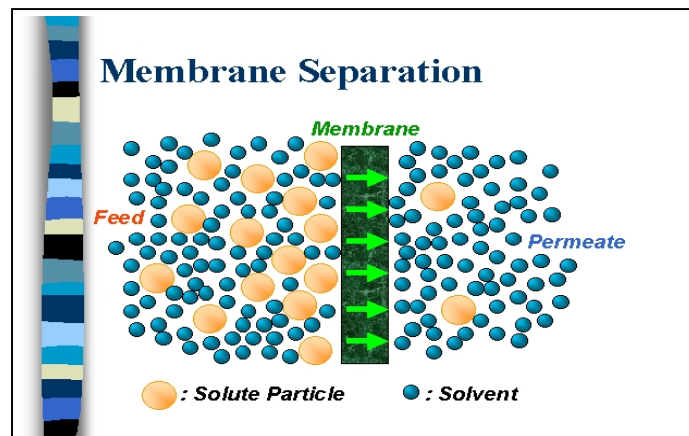
Membrane has been used in various fields in human technologies such as power generation, waste treatment, medical purposes and many more. The selective permeability nature of membrane made it very useful especially in filtration and separation process. The development of proton exchange membrane fuel cell (PEMFC) has made membrane usage in power generation became more important and crucial.

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

The word membrane is derived from a Latin word, *membrana* which means skin. There are various definitions about membrane. In general, membrane can be defined as a selective barrier between two phases, a thin barrier that permits selective mass transport or a phase that acts as a barrier to prevent mass movement but allows restricted and/or regulated passage of one or more species. Barrier or border is the word that can best describe membrane in short (Nunes and Peinemann, 2001).

### 2.1.2 Membrane Separation Process

Membrane uses separation process as its mode of operation. The basic membrane separation process is shown in Figure 2.1.



**Figure 2.1:** Basic Membrane Separation Process (Stookey, 2001)

Membrane separation processes can be separated into several categories and applications. The application of membrane separation process in industrial and commercial field has been expanding since the early discovery of membranes. The Germans are one of the earliest people who used membrane technology in their industries in 1920 followed by the Dutch and the Americans in 1950 and 1955 (Stookey, 2001).

### 2.1.3 Membrane Materials

Material selection in constructing a membrane is crucial as it determines the membrane performance. Several criteria that need to be considered in choosing membrane materials are:

- (i) Material availability
- (ii) Chemical stability
- (iii) Easy formation
- (iv) Approval of food and water contact

Table 2.1 showed the membrane materials and its descriptions.

**Table 2.1: Membrane Materials**

<b>Membrane Materials</b>	<b>Descriptions</b>
Polymer	Polysulfone, polyethersulfone, cellulose acetate and polyamide thin film
Ceramic	Available in microfiltration and ultrafiltration format, great tolerance to acids and alkalis, long life and perceived robustness
Glass	Hollow fiber form, pore size: 10-90 nm and used in biotech industries
Steel	Made from sintered stainless steel, available in tubes, robust, suitable for aggressive environments but not suitable for microfiltration due to large pore size

Polymers have been considered as the most suitable material for the proton exchange membrane fuel cell due to its ability to separate ions and act as a solid electrolyte for the fuel cell. Although interest in synthesizing polymers for different applications has been observed for about a century, major developments in this field were made only in the recent past.

#### **2.1.4 Types of Membranes**

Membranes are classified into several types according to its functions. Mainly, membranes are divided into 2 categories which are biological and non biological

membranes. Biological membranes are the membrane that naturally constructed and usually situated in the body of a living things like humans and animals. Some examples of biological membranes are:

- (i) Cell membrane- a selectively permeable lipid bilayer found in all cells. It contains primarily proteins and lipids.
- (ii) Mucous membrane- situated at several places continuous with skin such as nostrils, genital areas, lips, ears and the anus.
- (iii) Organelle membranes- divided into two; outer and inner. The outer membrane refers to the outside membrane of the Gram-negative bacteria, the mitochondria or the chloroplast. The inner membrane is the biological membrane of an organelle or a Gram-negative bacteria that is within an outer membrane (Baker, 2001).

The non biological membranes are the membranes that constructed artificially or mechanically. It can also refer to some materials that have the characteristics to become a membrane. Examples of non biological membranes are:

- (i) Artificial membrane- prepared for separation tasks in laboratory or industry. Typical usages in industries are water purification and desalination, dehydrogenation of natural gas and as a component in fuel cell. An example for this is ion exchange membrane which is made from ion exchange resins.
- (ii) Semipermeable membrane- allows selective molecules or ions to pass it by diffusion. An example of this is the thin film on the inside of an egg.

### 2.1.5 Ion Exchange Membrane

The core of the ion exchange membrane manufacturing is the preparation of the ion exchange resin. An ion exchange resin is an insoluble matrix (or support structure) normally in the form of small (1-2 mm diameter) beads, usually white or yellowish, fabricated from an organic polymer substrate. The material has highly developed structure of pores on the surface of which are sites with easily trapped and released ions. The trapping of ions takes place only with simultaneous releasing of other ions; thus the process is called ion exchange. There are multiple different types of ion exchange resin which are fabricated to selectively prefer one or several different types of ions. Besides being made as bead-shaped materials, ion exchange resins are produced as membranes. The membranes made of highly cross-linked ion exchange resins that allow passage of ions but not of water are used for electrodialysis. The ion exchange resins are divided into four major groups according to their functional groups:

- (i) strongly acidic (typically, sulfonic acid groups such as sodium polystyrene sulfonate or polyAMPS)
- (ii) strongly basic, (quaternary amino groups, for example, trimethylammonium groups like polyAPTAC)
- (iii) weakly acidic (mostly, carboxylic acid groups)
- (iv) weakly basic (primary, secondary, and/or ternary amino groups, such as polyethylene amine)

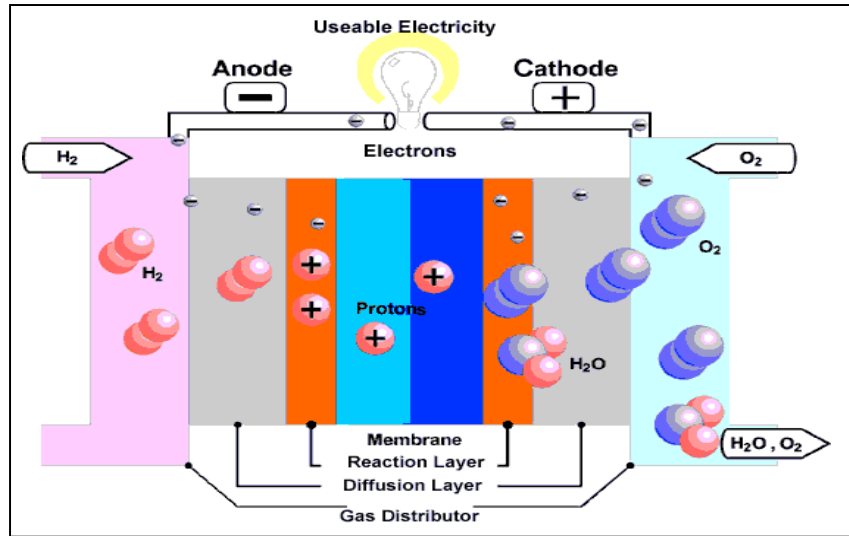
Ion exchange membrane is the major component in a proton exchange membrane fuel cell where it acts as the separator of the fuel molecule (mostly hydrogen). The membrane will let only the protons from the hydrogen molecules to permeate pass it and the electrons will forced to travel through an external circuit, creating a current flow around the fuel cell. The standard membrane used in proton exchange membrane fuel cell nowadays is Nafion, manufactured by DuPont. However, Nafion has several

limitations in its operation such as inability to function in high temperatures (above 80-100°C) and high dependency on water level. One of the characteristics of Nafion is selectively and highly permeable to water. Greater degree of hydration of the Nafion membrane will lower the ion permittivity. Since water is a byproduct of the fuel cell process, this limits the utility for Nafion for proton exchange membrane fuel cells.

## **2.2 Fuel Cell Review**

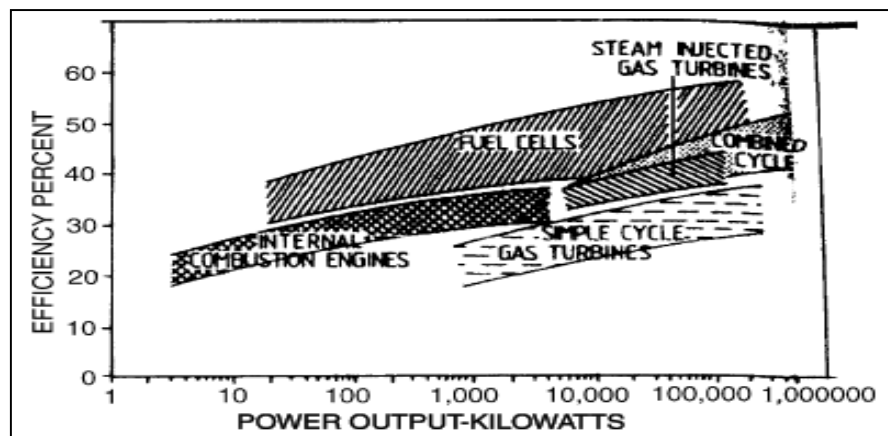
Fuel cell is best defined as an electrochemical conversion device that produces power from the reaction between fuel and oxidant in the presence of electrolyte. The fuel cell also contains electrode, anode (negative) and cathode (positive) where the reaction takes place. The electrolyte functions as a carrier for electrically charged particles from one electrode to another and catalyst to speed up the reaction at the electrodes. Fuel cell is quite similar with dry cell because neither has any moving parts and thus minimal maintenance required. The difference between fuel cell and dry cell is that fuel cell can continuously operate as long as the fuel is supplied with the oxidant whilst dry cell must be replaced or recharged when used up. Figure 2.1 shows the basic operating diagram for a proton exchange membrane fuel cell.





**Figure 2.2:** Basic operating diagram for a proton exchange membrane fuel cell

Savings in fossil fuels, due to high efficiency of energy conversion, low pollution level, low noise and low maintenance costs render fuel cells preferable over other energy conversion devices (Smitha *et al*, 2005). Figure 2.2 shows the comparison of fuel cell over other energy conversion devices.



**Figure 2.3:** Comparison of fuel cell over other energy conversion devices (Smitha *et al*, 2005)

Today, potential applications for fuel cells range from battery replacement in consumer goods and portable computers, through residential scale combined heat and power (CHP) to distributed energy generation.

### **2.2.1 Fuel Cell Applications**

There are many areas in which fuel cells could potentially be used including conventional power equipment, transport and battery replacement.

#### **2.2.1.1 Transport**

Transport applications tend to demand rapid startup and instant dynamic response from fuel cell systems, so a high temperature fuel cell is unlikely to be competitive as the main engine in applications such as cars and buses. The prime candidate for these vehicle propulsion systems is the Proton Exchange Membrane Fuel Cell (PEMFC), which exhibits both of the above characteristics while also having very high power density.

Alkaline Fuel Cell (AFC) systems have been traditionally been used in space applications by NASA in the Gemini, Apollo and space shuttle programs. It is also being investigated for certain transport applications, mainly in vehicles with limited duty cycles such as delivery vehicles and forklifts.

#### **2.2.1.2 Battery Replacement**

An area in which it is possible that fuel cells may break through to commercialization in the very near future is in the replacement of conventional batteries.

Battery power for laptop computers, mobile phones and many other devices is expensive and often inconvenient if recharging is required every few hours. A small fuel cell with an equally small fuel source could potentially operate for longer than a battery, but with refueling only taking a few minutes instead of many hours. Batteries cost much more for the amount of power they can supply than almost any other application. This gives the fuel cell a good chance of entering the market, although it is still expensive.

The ideal fuel cell for this application is the PEMFC, which not only has the high power density required for miniaturization but also has the least challenging electrolyte management issue of the low temperature fuel cell.

### **2.2.2 Fuel Cell Vehicles**

Depending on the fuel they carry, fuel cell vehicles entail various requirements for fuel supply (including production and distribution), fuel storage on the vehicle and on-vehicle fuel processing that might be needed. A fuel cell vehicle operated on gasoline may require minimal changes in existing fuel supply infrastructure but faces special processing requirement onboard the vehicle. Table 2.2 listed the fuel options for fuel cell vehicles.

**Table 2.2:** Fuel Options for Fuel Cell Vehicles (Smitha *et al*, 2005)

	<b>Hydrogen</b>	<b>Methanol</b>	<b>Gasoline</b>
Fuel economy gain	High	Modest	Small
CO2 reduction	Modest	Low	Small
Emissions control need	Zero	Low	Low
Fuel supply	Needs major development	Very limited	Already exists
On-board storage	Needs major development	Readily feasible	Already exists
Fuel processing	Not needed	Under development	Under development
Added car cost/weight	Modest	High	High

### 2.2.3 Types of Fuel Cell

The basic design of a fuel cell consists of two electrodes, anode and cathode separated by a solid or liquid electrolyte. The electrolyte functions as the charged ions or particles carrier between the two electrodes. Catalyst such as platinum is often installed in order to boost up the reaction.

Basically, fuel cells can be divided into two main categories; low and high temperatures fuel cells. The low temperature fuel cells can be distinguished by the following characteristics:

- (i) They require a relatively pure supply of hydrogen as a fuel.
- (ii) Precious metal catalysts incorporated to improve performance.
- (iii) Fast startup time.
- (iv) Commercially available or approaching commercialization.

In contrast, high temperature fuel cells can be classed as having the following general features:

- (i) Fuel flexible, can be operated with a range of hydrocarbon fuels at high efficiency.
- (ii) Reduced need for expensive electrocatalysts.
- (iii) Able to generate useful “waste” heat and are therefore can be integrated into cogeneration systems.
- (iv) Slow startup time.
- (v) High cost due to the expensive material to withstand the operating temperature.
- (vi) Not being commercialized.

Rapid growth in research has resulted in production or invention of many types of fuel cells recently. Several types of preferred fuel cells with their electrolyte, power generated, electrical efficiency and usage costs were listed in Table 2.3.

**Table 2.3:** Fuel Cell Types and Descriptions

<b>Fuel Cell</b>	<b>Electrolyte</b>	<b>Power Generated</b>	<b>Working Temperature (°C)</b>	<b>Electrical Efficiency</b>
Alkaline fuel cell	Aqueous alkaline solution	10kW to 100kW	< 80	Cell: 60-70% System: 62%
Proton exchange membrane fuel cell	Polymer membrane	100W to 500kW	Nafion:50-120 PBI: 125-220	Cell: 50-70% System: 30-50%
Phosphoric acid fuel cell	Molten phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	Up to 10MW	150-200	Cell: 50% System: 40% Cogen: 90%
Molten carbonate fuel cell	Molten alkaline carbonate	100MW	600-650	Cell: 55% System: 47%
Direct methanol fuel cell	Polymer membrane (ionomer)	100kW to 1MW	90-120	Cell: 20-30% System: 10-20%

Among all these types, proton exchange membrane fuel cell has been considered as the most preferable type of fuel cell especially in the automotive field. Low working temperature with high power generation and electrical efficiency has made proton exchange membrane fuel cell become the utmost choice for automakers in their smart cars projects. The compact size of the cell has made the automakers even assumed that proton exchange membrane fuel cell is the only suitable fuel cell for smart vehicles.

### **2.3.1 Proton Exchange Membrane Fuel Cell**

The proton exchange membrane fuel cell, also known as polymer electrolyte membrane fuel cell is currently the type of fuel cell being developed for transportation purpose. Proton exchange membrane fuel cells are believed to be the best type of fuel cell as the vehicular power source to eventually replace the gasoline and diesel internal

combustion engines. The proton exchange membrane fuel cell was invented in the early 1960s by General Electric for the NASA Gemini project but has been replaced by alkaline fuel cells for the Apollo program. The feature of the cell that distinguishes it from other cells is that the low operating temperature range between 50-100°C. It is also differs from other cells due to the presence of the polymer electrolyte membrane.

The conversion of chemical energy into electrical energy is performed during the electrochemical reaction of the hydrogen (fuel) and oxygen (oxidant) as the opposing concept of direct combustion between hydrogen and oxygen that produces thermal energy. The hydrogen stream is delivered to the anode side of the membrane electrode assembly and catalytically split into protons and electrons. This oxidation half-cell reaction is represented by:



The polymer electrolyte membrane lets the newly-formed protons to permeate pass it to the cathode while the electrons travel to the cathode via an external load circuit, creating the current output of the fuel cell. On the other side, a stream of oxygen is delivered to the cathode and reacted with the electrons and protons to produce oxygen gas and water molecules. The reduction half-cell reaction is represented by:



In order to function perfectly, the polymer electrode membrane must let only the protons to permeate pass it. Any permeation of electrons will result in short-circuit of the fuel cell, whereas if gas can permeate pass the membrane, a problem called gas crossover will occur. The catalyst used in the hydrogen-splitting process is currently platinum, since it is the best option. However, platinum is not the appropriate material

for the oxygen-splitting reaction at the cathode. The resistance to the proton flow also must be minimized by making the membrane as thin as possible.

Water management is crucial in polymer electrode membrane, as it will affect the overall fuel cell performance. Too much water will flood the membrane and too little amount of water will make it dry, both will reduce the power output of the fuel cell. The current standard membrane used in proton exchange membrane fuel cell is Nafion, manufactured by DuPont. Nafion functions basically on liquid water humidification to carry the protons so it is not possible to use it on temperature above 80-90°C since it will dry the water content of the membrane (Zadowinski *et al*, 1995).

## **2.4 Polymer Membrane for Proton Exchange Membrane Fuel Cell**

### **2.4.1 Essential Polymer Properties**

The electrolyte of a proton exchange membrane fuel cell which is the proton exchange membrane is basically made from polymers which have negatively charged group attached to the polymer backbone. To achieve high efficiency, the membrane must possess the following desirable properties:

- (i) high proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity
- (ii) adequate mechanical strength and stability
- (iii) chemical and electrochemical stability under operating conditions
- (iv) moisture control in stack
- (v) extremely low fuel or oxygen by-pass to maximize coulombic efficiency
- (vi) production costs compatible with intended application



## **2.4.2 Factors Affecting Membrane Performance**

### **2.4.2.1 Hydration**

As the performance of a membrane mainly relies on proton conductivity, the level of hydration of the membrane is crucial in determining the membrane efficiency. Higher conductivity is supported by higher level of hydration (Smitha *et al*, 2005). However, for operations with wet membranes, there is a possibility of the cathode being flooded which slows down the oxidation reaction. This is in particular a problem with Nafion, because of a phenomenon known as electro-osmotic drag. The electro-osmotic drag coefficient (EODC), which is a quantitative measure of hydration, is defined as the number of water molecules transported per proton (Zadowinski *et al*, 1995).

### **2.4.2.2 Thickness**

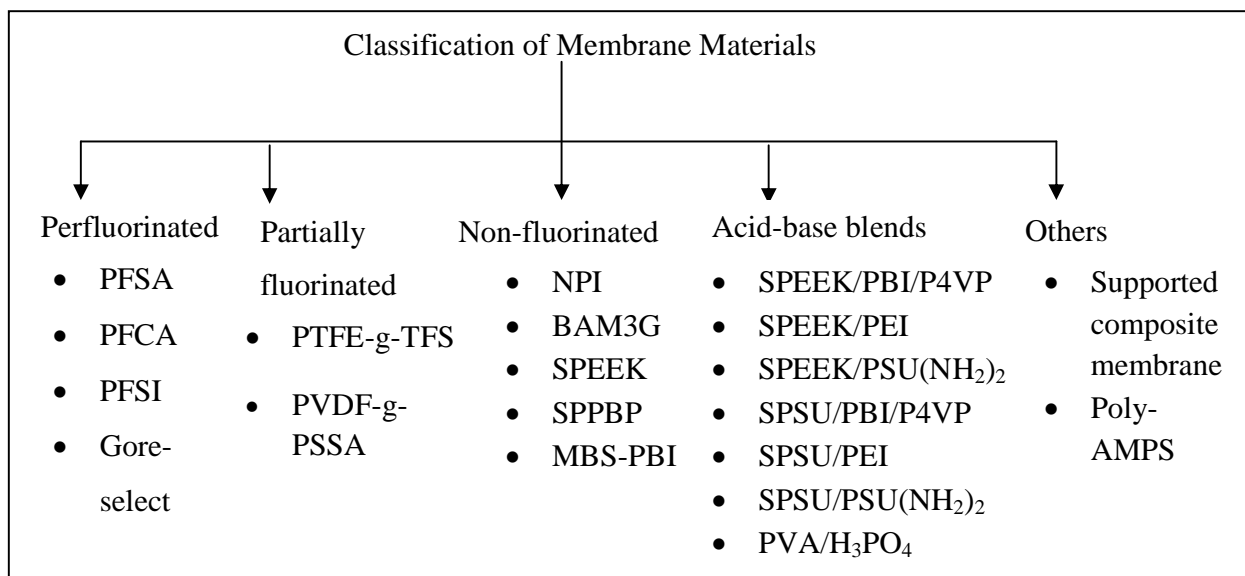
Lowering the membrane thickness is one of the methods to improve the membrane performance. Reduced membrane thickness also results in lower membrane resistance, higher membrane conductivity, lower production cost and rapid hydration. However, there is a limit to the extent to which membrane thickness can be reduced because of difficulties with durability and fuel by-pass. An ideal way to balance this would be to spatially control the acidic regions or increase the charge density in the chemical microstructure of the proton exchange membrane to obtain highly conductive materials. Charge density can be enhanced by synthesizing the membranes in a symmetric or thin film composite form (Smitha *et al*, 2005). For example, asymmetric films of partially sulfonated polystyreneorpoly (phenyleneoxide) can be cast using chloroform as solvent and methanol as non-solvent (Meier-Haack *et al*, 2000).

### 2.4.3 Polymer Types for Fuel Cell Membrane

Polymer materials used for developing membrane in proton exchange membrane fuel cell generally divided into different membrane systems, which can be classified as:

- (i) perfluorinated ionomers
- (ii) partially fluorinated polymers
- (iii) non-fluorinated membranes with aromatic backbone
- (iv) non-fluorinated hydrocarbons
- i) acid–base blends

Figure 2.4 shows the classification of membrane materials.



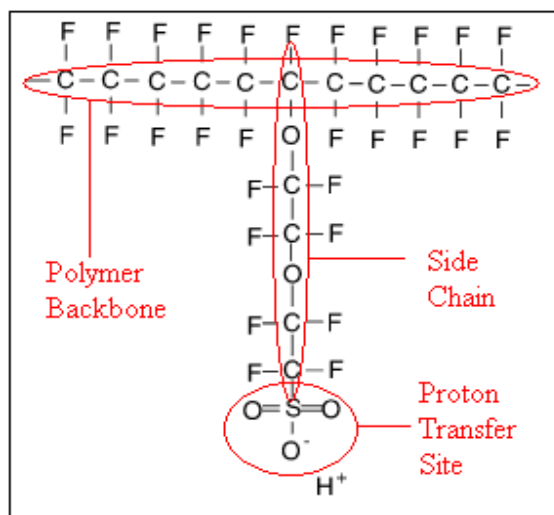
**Figure 2.4:** Classification of Membrane Material (Smitha *et al*, 2005)

The perfluorinated sulfonic acid membranes have been the subject of intense research. The key polymers used are in the solvated form. Hydrocarbon membranes provide some definite advantages over PFSA membranes. They are less expensive,

commercially available and their structure permits the introduction of polar sites as pendant groups in order to increase the water uptake (Smitha *et al*, 2005).

## 2.5 Standard Membrane for Proton Exchange Membrane Fuel Cell

Nowadays, an electrolyte consists of perfluorinated sulfonic acid known as Nafion has been considered as the standard membrane for proton exchange membrane fuel cell. Nafion was introduced by DuPont in the early 1970s. Similar polymers are Flemion produced by Asahi Glass and Aciplex-S produced by AsahiChemical. Among the three major types, the DuPont product is considered to be superior because of its high proton conductivity, good chemical stability and mechanical strength. Figure 2.5 shows the structure of Nafion.



**Figure 2.5:** The Structure of Nafion (Smitha *et al*, 2005)

### 2.5.1 Nafion Properties

Nafion derivatives are first synthesized by the copolymerization of tetrafluoroethylene (TFE) (the monomer in Teflon) and a derivative of a perfluoro (alkyl vinyl ether) with sulfonyl acid fluoride. The latter reagent can be prepared by the pyrolysis of its respective oxide or carboxylic acid to give the olefinated structure (Connolly *et al*, 1996).

The resulting product is a  $\text{SO}_2\text{F}$  containing thermoplastic that is extruded into films. Hot aqueous NaOH converts these sulfonyl fluoride ( $\text{SO}_2\text{F}$ ) groups into sulfonate groups ( $\text{SO}_3\text{-Na}^+$ ). This form of Nafion, referred to as the neutral or salt form, is finally converted to the acid form containing the sulfonic acid ( $\text{SO}_3\text{H}$ ) groups. Nafion can be cast into thin films by heating in aqueous alcohol at 250 °C in an autoclave. By this process, Nafion can be used to generate composite films, coat electrodes, or repair damaged membranes (Heitner-Winguin, 1996).

The combination of the stable Teflon backbone with the acidic sulfonic groups gives Nafion its characteristics;

- (i) It is highly conductive to cations, making it suitable for many membrane applications
- (ii) It resists chemical attack. According to DuPont, only alkali metals (particularly sodium) can degrade Nafion under normal temperatures and pressures
- (iii) The Teflon backbone interlaced with the ionic sulfonate groups gives Nafion a high operating temperature, e.g. up to 190 °C

Table 2.4 shows the typical thickness and basic weight properties while Table 2.5 shows the physical and other properties of Nafion.

**Table 2.4:** Typical Thickness and Basic Weight Properties of Nafion

Membrane Type	Typical Thickness (microns)	Basis Weight (g/m <sup>2</sup> )
N-115	127	250
N-117	183	360
N-1110	254	500

**Table 2.5:** Physical and Other Properties of Nafion

Properties	Typical Value
Tensile Modulus, MPa (kpsi)	
50% RH <sup>c</sup> , 23°C	249 (36)
water soaked, 23°C	114 (16)
water soaked, 100°C	64 (9.4)
Tensile Strength, maximum, MPa(kpsi)	
50% RH <sup>c</sup> , 23°C	43 (6.2) in MD <sup>a</sup> , 32 (4.6) in TD <sup>b</sup>
water soaked, 23°C	34 (4.9) in MD <sup>a</sup> , 26 (3.8) in TD <sup>b</sup>
water soaked, 100°C	25 (3.6) in MD <sup>a</sup> , 24 (3.5) in TD <sup>b</sup>
Elongation at Break, %	
50% RH <sup>c</sup> , 23°C	225 in MD <sup>a</sup> , 310 in TD <sup>b</sup>
water soaked, 23°C	200 in MD <sup>a</sup> , 275 in TD <sup>b</sup>
water soaked, 100°C	180 in MD <sup>a</sup> , 240 in TD <sup>b</sup>
Tear Resistance-Initial, g/mm	
50% RH <sup>c</sup> , 23°C	6000 in MD <sup>a</sup> , TD <sup>b</sup>
water soaked, 23°C	3500 in MD <sup>a</sup> , TD <sup>b</sup>
water soaked, 100°C	3000 in MD <sup>a</sup> , TD <sup>b</sup>
Tear Resistance <sup>3</sup> -Propagating, g/mm	
50% RH <sup>c</sup> , 23°C	>100 in MD <sup>a</sup> , >150 in TD <sup>b</sup>
water soaked, 23°C	92 in MD <sup>a</sup> , 104 in TD <sup>b</sup>
water soaked, 100°C	74 in MD <sup>a</sup> , 85 in TD <sup>b</sup>
Specific Gravity	1.98
Conductivity, S/cm	0.1 min
Available acid capacity, meq/g	0.9 min
Total acid capacity, meq/g	0.95 – 1.01

<sup>a</sup>: MD- Machine direction

<sup>b</sup>: TD- Transverse Direction

<sup>c</sup>: RH- Relative Humidity

### 2.5.2 Nafion modifications

As mentioned in the Nafion properties, high dependency on water level and not able to operate at temperature above 100°C has encouraged researchers to do various modifications to improve the performance of Nafion. Nafion also has quite high price, reaching up to US\$ 700 per square meter. Moreover, it also required supporting equipments and is lacking of safety during manufacturing and usage.

The influence of addition of silica to Nafion was to improve the retention of water in the membrane and to enable the operation of the fuel cell above 130°C. Such a membrane could be used in a direct methanol fuel cell at 145°C with power density of 240mW/cm (Antonucci *et al*, 1999).

A similar method for retaining water in Nafion at higher temperatures is by incorporating silica as well as titanium dioxide into a Nafion composite to enable its use in direct methanol fuel cell. This membrane exhibited a significant improvement in proton conductivity but did not retard methanol crossover (Baradie *et al*, 1998).

A significant improvement in the conductivity of Nafion at elevated temperatures is by incorporating perfluorinated ionomers in Nafion matrix and by doping it with heteropolyacids such as phosphotungstic acid, phosphomolybdic acid or phosphotriacid in Nafion (Bahar *et al*, 1996).

Beside of modifying the standard Nafion membrane, researchers also ventured into finding alternative membrane material that can overcome the drawbacks of Nafion. One of the methods that has been discovered in the recent past was by using sulfonated polymers to replace perfluorinated sulfonic acid material of Nafion.

## 2.6 Sulfonation Process

Sulfonation of complex molecules is a widely used technique in chemical processing. The process is used widely in industrial field to make various kinds of products including dyes, drugs, pesticides and organic intermediates.

Polymers are sulfonated in order to convert them into ionomers and to grant their proton conducting ability. Recent increasing researches in sulfonated polymers have produced equivalent results to the standard Nafion membrane and some of them have successfully surpassed the Nafion performance in proton conducting ability.

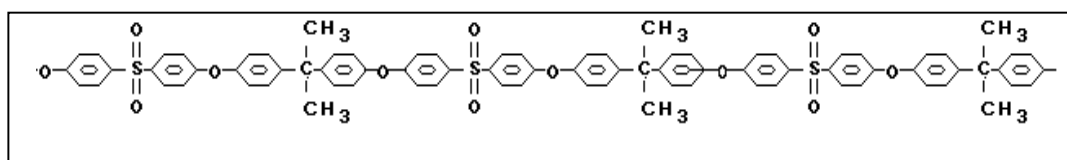
The key components in sulfonation process are the polymer itself, solvent and the sulfonating agent. The sulfonating agent itself plays the main role in sulfonation process where different usage of sulfonating agent resulted in different sulfonation effect. Most frequently used sulfonating agents are chlorosulfonic acid, trimethylsilyl chlorosulfonate and sulphuric acid. Among these agents, trimethylsilyl chlorosulfonate (TMSCS) was the preferred agent because it preserves the chain length of the starting base polymer.

## 2.7 Sulfonated Membrane in Fuel Cell

Much effort has gone into the development of PEMFC via polymer modification. One method is to prepare advanced molecules for fuel cells by modifying the polymers without sacrificing their excellent physical and other properties.

### 2.7.1 Sulfonated Polysulfone

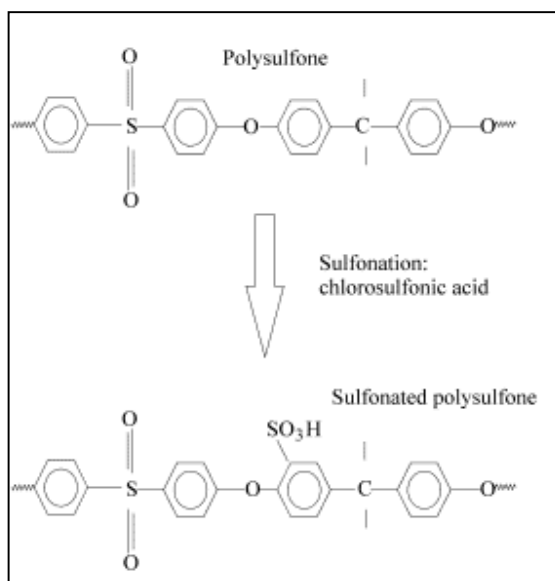
There are various methods to sulfonate polysulfone according to sulfonating agent and reaction condition. Polysulfone describes a family of thermoplastic polymers. These polymers are known for their toughness and stability at high temperatures. They contain the subunit aryl-SO<sub>2</sub>-aryl, the defining feature of which is the sulfone group. Polysulfones were introduced in 1965 by Union Carbide. Due to the high cost of raw materials and processing, polysulfones are used in specialty applications and often are a superior replacement for polycarbonates. Figure 2.6 showed the structure of polysulfone;



**Figure 2.6:** Polysulfone Structure (Chao and Kelsey, 1986)

Normally, sulfonation of sulfonated polysulfone yield is determined by the degree of sulfonation (the number of moles of -SO<sub>3</sub>H groups) per monomer unit. Figure 2.7 showed the sulfonation process of polysulfone.





**Figure 2.7:** Sulfonation Process of Polysulfone (Chao and Kelsey, 1986)

The addition of polyethersulfone to the sulfonated polysulfone in this study was to recognize the effect of polyethersulfone addition to the degree of sulfonation of the mixed matrix.

## **CHAPTER III**

### **RESEARCH METHODOLOGY**

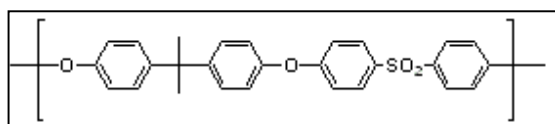
This chapter described all the experimental methods in this study. The developed membranes then were tested with several experiments including swelling test, elemental analysis, degree of sulfonation and FTIR. Finally, the obtainable result was evaluated.

#### **3.1 Material**

Polysulfone was selected in this study due to its mechanical strength, low cost and commercial availability. Dimethylformamide was used as the dissolving agent for the polymers. Sulfonation process was done on polysulfone to transform it into ionomer and granting it the proton conducting ability. Trimethylsilyl chlorosulfonate (TMSCS) was selected as the sulfonating agent due to its ability to preserve the chain length of the starting base polymer. Sodium methoxide was used as the base solution to cleave the silyl group. Nitrogen functioned as an inert gas to prevent hydrochloric acid formation and water vapor interference during the sulfonation process. In addition, polyethersulfone was added to the sulfonated polymer to study the addition effect.

### 3.1.1 Polysulfone

Udel polysulfone (PSU) is a rigid, high-strength, semi-tough thermoplastic that has a heat deflection temperature of 345°F (174°C), and maintains its properties over a wide temperature range. Udel excels in many fluid-handling applications and has over 10 years of success replacing brass in pressurized hot water plumbing applications. Figure 3.1 showed the chemical structure of polysulfone while Table 3.1 summarized the physical and chemical properties of polysulfone.



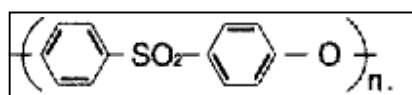
**Figure 3.1:** Chemical Structure of Polysulfone (Chao and Kelsey, 1986)

**Table 3.1:** Physical and Chemical Properties of Polysulfone

Physical/Chemical Properties	Values
Appearance	Rigid, high strength, transparent
Operating Temperature	-100°C - 150°C
Glass Transition Temperature	185°C
Resistivity	Highly resistant to mineral acids, alkali and electrolytes with pH ranging from 2-13. Resistant to oxidizing agents, washable with bleach.
Solubility	Stable in aqueous acids and bases and many non-polar solvents. Soluble in organic solvents such as dichloromethane, dimethylformamide and methylpyrrolidone.

### 3.1.2 Polyethersulfone

Polyethersulfone (PES) is a heat-resistant, transparent, amber, non-crystalline engineering plastic. PES is a tough and rigid resin similar to conventional engineering plastics, such as polycarbonate, at room temperature. The greatest characteristic of PES is that it has by far better high-temperature properties than conventional engineering plastics. Specifically, PES remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200°C. Figure 3.2 showed the molecular structure of polyethersulfone while Table 3.2 summarized the physical and chemical properties.



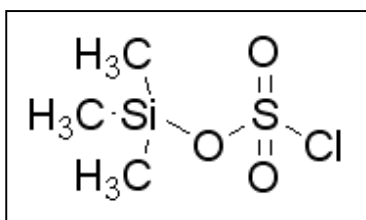
**Figure 3.2:** Molecular Structure of Polyethersulfone (Manea and Mulder, 2001)

**Table 3.2:** Physical and Chemical Properties of Polyethersulfone

Physical/Chemical Properties	Values
Appearance	Amber, non-crystalline, transparent
Operating Temperature	-105°C - 158°C
Glass Transition Temperature	Up to 200°C
Resistivity	Highly resistant to mineral acids, alkali and electrolytes with pH ranging from 2-13 Resistant to oxidizing agents, washable with bleach
Solubility	Stable in aqueous acids and bases and many non-polar solvents Soluble in organic solvents such as dichloromethane and dimethylformamide

### 3.1.3 Trimethylsilyl Chlorosulfonate (TMSCS)

Trimethylsilyl chlorosulfonate [ $\text{ClSO}_3\text{Si}(\text{CH}_3)_3$ ] is a mild sulfonating agent that has been utilized widely in sulfonation process. The ability to preserve the chain length of the starting polymer has made TMSCS the most preferred choice of sulfonating agent. Figure 3.3 showed the molecular structure of TMSCS and Table 3.3 summarized the physical properties.



**Figure 3.3:** Molecular Structure of Trimethylsilyl Chlorosulfonate

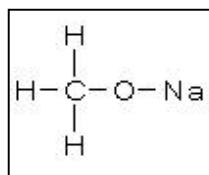
**Table 3.3:** Physical Properties of Trimethylsilyl Chlorosulfonate

Properties	Values
Assay	99%
Refractive index	$n_{20/D}$ 1.424
Boiling Point	168-169 °C 62-64 °C/10 mmHg
Melting Point	-26 °C
Density	1.225 g/mL at 25 °C

### 3.1.4 Sodium Methoxide

To yield the desired sulfonated product, a solution of base is essential to cleave the trimethylsilyl group into the polymer backbone. In this study, sodium methoxide ( $\text{NaOCH}_3$ ) was used. Sodium methoxide is a colourless solid, which is formed by the deprotonation of methanol. It is a widely used reagent in industry and the laboratory. It

is also a dangerously caustic base. Figure 3.4 showed the molecular structure of sodium methoxide and the physical properties are summarized in Table 3.4.



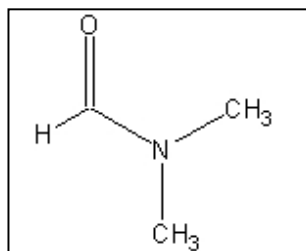
**Figure 3.4:** Molecular Structure of Sodium Methoxide

**Table 3.4:** Physical Properties of Sodium Methoxide

<b>Properties</b>	<b>Values</b>
Molecular Formula	CH <sub>3</sub> NaO
Molar Mass	54.03
Appearance	White solid
Melting Point	>300 °C

### 3.1.5 Dimethylformamide

The solvent in the sulfonation reaction must be able to dissolve the polymer base and inert to the sulfonating agent. In this study, dimethylformamide (DMF) was used as the solvent. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. The molecular structure was shown in Figure 3.5 while Table 3.5 summarized the physical and chemical properties.



**Figure 3.5:** Molecular Structure of Dimethylformamide

**Table 3.5:** Physical and Chemical Properties of Dimethylformamide

Physical Properties	Values
Molecular formula,	$C_3H_7NO$
Molar mass	73.09 g/mol
Appearance	Clear liquid
Density	0.944 g/cm <sup>3</sup> liquid
Melting point	-61 °C (212 K)
Boiling point	153 °C (426 K)
Solubility in water	Miscible
Refractive index ( $n_D$ )	1.4305 (20 °C), $\epsilon_r = 36.71$ (25°C)
Viscosity	0.92 cP at 20 °C

### 3.1.6 Nitrogen

Inert gas functions to remove hydrochloric acid formed during the sulfonation process and to prevent water vapors from interfering the process. In this study, nitrogen was used as the inert gas.

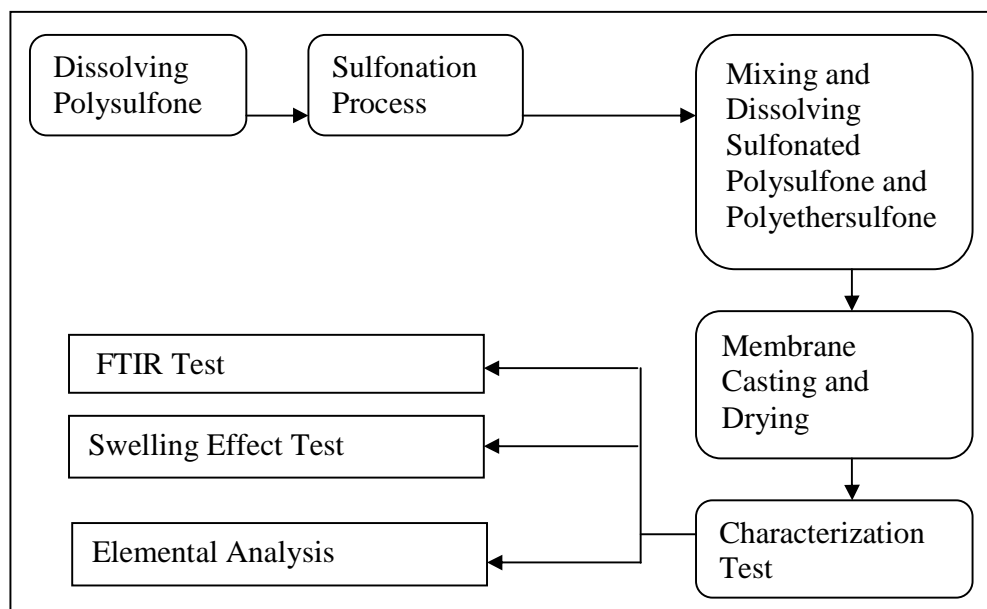
## 3.2 Research Design

Sulfonation process has been identified to be influenced by several factors such as sulfonating agent, reaction condition and base solution used. In this study, the

parameter that had been varied is the amount of sulfonating agent added to each sample. 4 samples were prepared, the first sample is a pure PES/PSU mixture dissolved in DMF without undergoing any sulfonation process while the other 3 sample were prepared by preparing sulfonated polysulfone with 10mL, 15mL and 20mL addition of TMSCS, the sulfonating agent. Other parameters such as reaction time, temperature, molar ratio of sulfonated polysulfone to polyethersulfone and type of solvent used were fixed for every sample.

### 3.3 Experimental Stages

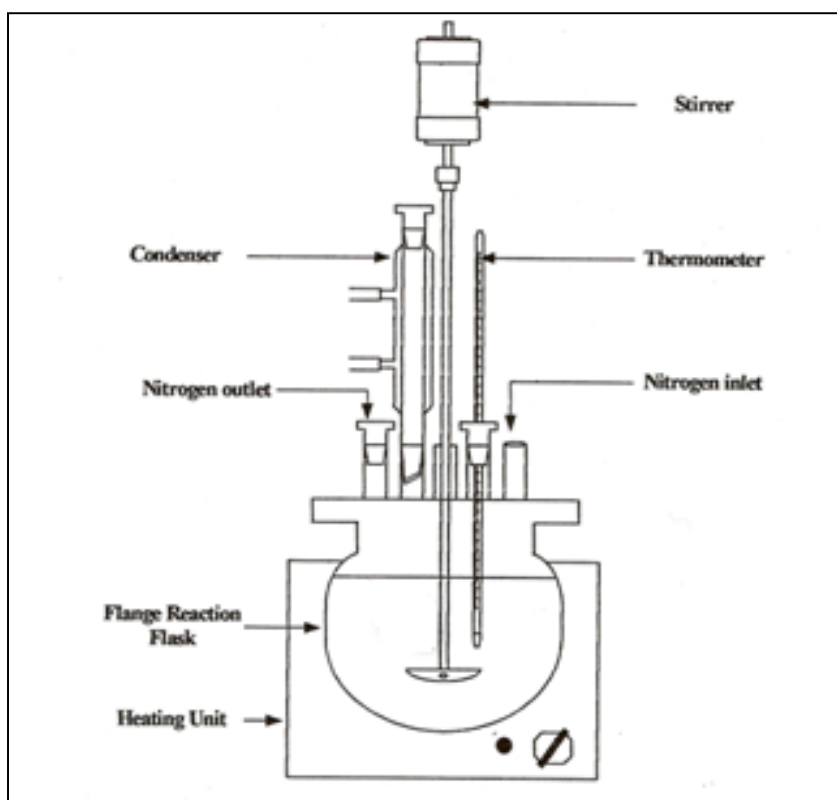
The experimental methods in this study involve several stages. Figure 3.3 showed the experimental stages in this study.



**Figure 3.6:** Experimental stages of this study

Figure 3.7 showed the experimental apparatus for the sulfonation process.





**Figure 3.7:** Experimental Apparatus for Sulfonation Process

### 3.3.1 Polymer Dissolving

The initial step of this study was dissolving the polymer that was needed to be sulfonated. 50g of polysulfone pellets were dried in oven with temperature 60-70 °C overnight before dissolved in 200mL DMF for around 4-5 hours in room temperature (25-28 °C) with constant stirring speed (300-350 rpm).

### **3.3.2 Sulfonation Process**

The sulfonation process was carried out according to Chao and Kelsey, (1986). The dissolved polysulfone solution was added with 10mL of TMSCS dropwise for 10 minutes. Stirring was continued for about 20 hours and nitrogen circulation is provided during the process to prevent hydrochloric acid formation and water vapor interference during the process. After 20 hours of stirring in constant speed and room temperature, 10g of 25% w/w sodium methoxide in methanol solution is added to cleave the silyl group. After a few hours more of stirring, white fluffy precipitate was formed at the bottom of the flask. The solution was poured into a water bath and the precipitates were quickly torn into small pieces. Then the product was soaked several times with water to remove the acid trace and the solvent. After that, the precipitates were left on filter papers to remove excess water. Then, the precipitates were dried in the oven with temperature 60-70 °C overnight to completely remove the solvent. Finally, Waring blender was used to crush the precipitates into smaller pieces to make it dissolve easier.

### **3.3.3 Polymer Mixing**

50g of sulfonated polysulfone were then combined with 50g of polyethersulfone and dissolved in 400mL of DMF. The dissolving process was done under the same condition as with dissolving polysulfone process. The previous 3 processes were repeated for each sample, except that the amount of TMSCS added during sulfonation process was varied.

### **3.3.4 Membrane Casting and Drying**

The polymeric solution was finally casted on a flat glass plate using a manual casting knife. After casting, the plate was immersed in water bath slowly for around 5 minutes. The membrane was then wiped smoothly with lab tissue before dried in oven at 40°C for 30 minutes.

### **3.3.5 Characterization Test**

Several characterization tests were carried out to identify the potential of sulfonated polysulfone and polyethersulfone mixed matrix in fuel cell application. The tests were:

- (i) Fourier Transform Infrared Spectroscopy (FTIR)
- (ii) Swelling Test
- (iii) CHNOS Elemental Analysis
- (iv) Degree of Sulfonation Calculation

#### **3.3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FTIR), Fourier transform (FT) nuclear magnetic resonance, mass spectrometry and electron spin resonance spectroscopy. There are several methods for measuring the temporal coherence of the light, including the continuous wave Michelson

or Fourier transform spectrometer and the pulsed Fourier transform spectrograph (which is more sensitive and has a much shorter sampling time than conventional spectroscopic techniques, but is only applicable in a laboratory environment).

In this study, FTIR test was conducted to determine whether the sulfonation process of the polymer succeeded or not by detecting certain wavelength that has been identified as the wavelength of SO<sub>3</sub>H functional group.

### 3.3.5.2 Swelling Test

The swelling test or sorption test was conducted in order to determine solvent uptake ability of the membranes. In this study, the sorption ability of the membranes were tested in water, methanol and water/methanol mixture. The samples were cut into a small piece for each samples and then weighed. After that, each sample was stored in petri dishes containing water, methanol and water/methanol mixture and left for 24 hours under room temperature. Finally, the samples were weighed again to determine the wet mass. The solvent uptake then calculated using this equation:

$$SD = \frac{M_w - M_d}{M_w} \quad (3.1)$$

where  $M_w$  is the wet weight of the membrane and  $M_d$  is the dried weight of the membrane (Manea and Mulder, 2001). The result can be considered as number of water molecules associated with each SO<sub>3</sub>H group.

### **3.3.5.3 Elemental Analysis**

Elemental analysis was conducted prior to determining the theoretical amount of elements for each sample. The data were then used for degree of sulfonation calculation. The analysis gave number of carbon, hydrogen, nitrogen, oxygen and sulfur content in the sample.

### **3.3.5.4 Degree of Sulfonation Calculation**

The data obtained from CHNOS elemental analysis were then used to calculate degree of sulfonation for each sample. Degree of sulfonation for each sample can be calculated by taking the S/C ratio of each sample (Staiti *et al*, 2001).

## **CHAPTER IV**

### **RESULTS AND DISCUSSIONS**

#### **4.1 Sulfonation Process**

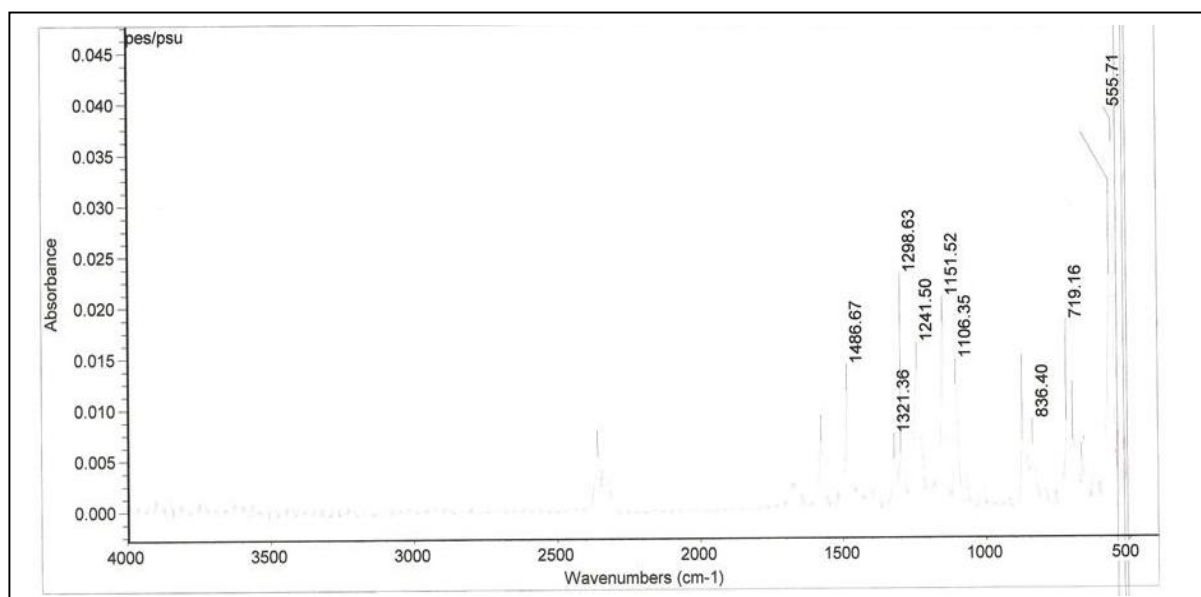
Sulfonation process was conducted 3 times in this study to yield 3 samples of SPSU/PES mixed matrix. The first sample prepared was standard PSU/PES polymer to be the reference point to the other 3 samples. Sulfonation process for each sample was varied on the amount of sulfonating agent (TMSCS) added to each sample. For all the samples, sulfonation process was conducted under room temperature (24-30°C) to avoid solvent vaporization. Sulfonating agent (TMSCS) also must be added dropwise in a fixed time interval (10 minutes) to let it settle down with the solution first since TMSCS is highly volatile. The base solution (sodium methoxide) was also need to be added dropwise in a fixed time interval (15 minutes) to avoid rapid precipitation of the solution. 3 samples of SPSU/PES mixed matrix were successfully prepared despite all the consequences. The samples were differed based on the amount of sulfonation agent added. Table 4.1 summarized the samples prepared in this study.

**Table 4.1:** Sulfonation Process Sample Summary

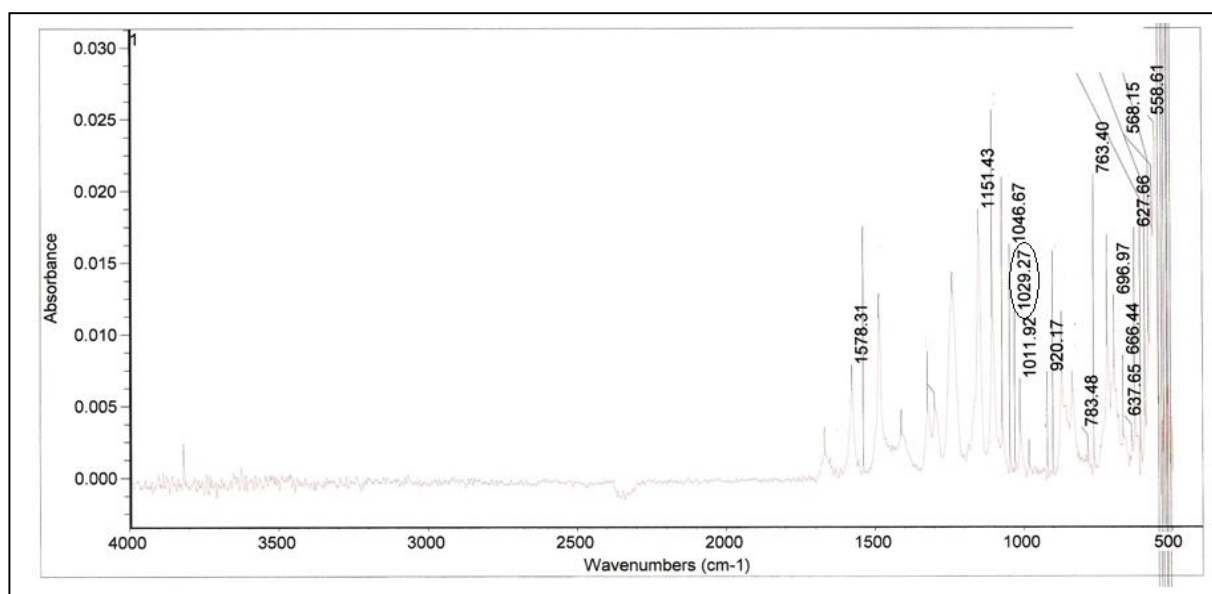
Sample	Reaction time (hour)	Reaction temperature (°C)	TMSCS amount (mL)	TMSCS dropwise time (min)	Sodium Methoxide amount (g)	Sodium Methoxide dropwise time
PSU/PES	5	24-30	-	-	-	-
SPSU/PES 1	20	24-30	10	10	10	15
SPSU/PES 2	20	24-30	15	10	10	15
SPSU/PES 3	20	24-30	20	10	10	15

#### 4.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR test was conducted in order to determine whether the sulfonation process succeeded or not. The PSU/PES membrane spectrum showed no trace for sulfonic ( $\text{SO}_3\text{H}$ ) group. However, for sample SPSU/PES 1, the value  $1029.27\text{ cm}^{-1}$  was obtained which in close agreement with  $1028\text{ cm}^{-1}$  obtained by Johnson *et al* (1984). For sample SPSU/PES 2, the value  $1035.75\text{ cm}^{-1}$  obtained was slightly differed from  $1036\text{ cm}^{-1}$  obtained by Staiti *et al* (2001). The value  $1031.52\text{ cm}^{-1}$  obtained for sample SPSU/PES 3 was in close contrary with  $1030\text{ cm}^{-1}$  obtained by Wang *et al* (2002). So, it can be concluded that the introduction of  $\text{SO}_3\text{H}$  groups in each sulfonated samples were successful. The value of wavelength obtained for each sample differed because the positioning of the samples on FTIR and also due to the different characteristics of the samples. Figure 4.1 to 4.4 showed the FTIR spectra obtained for each sample.

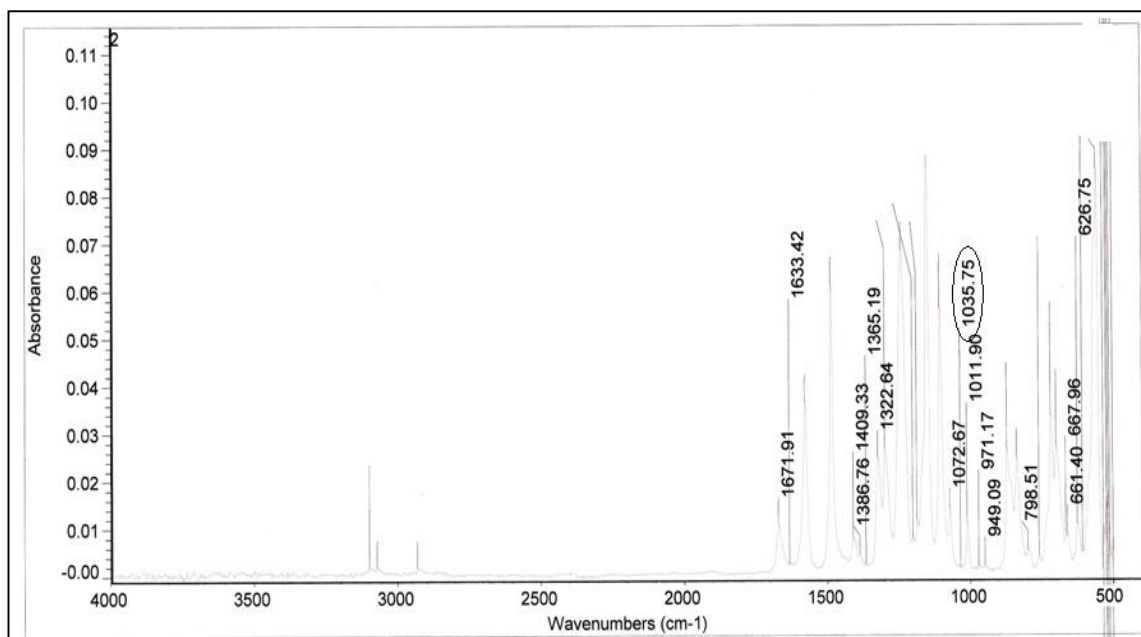


**Figure 4.1:** FTIR Spectrum for PSU/PES Membrane

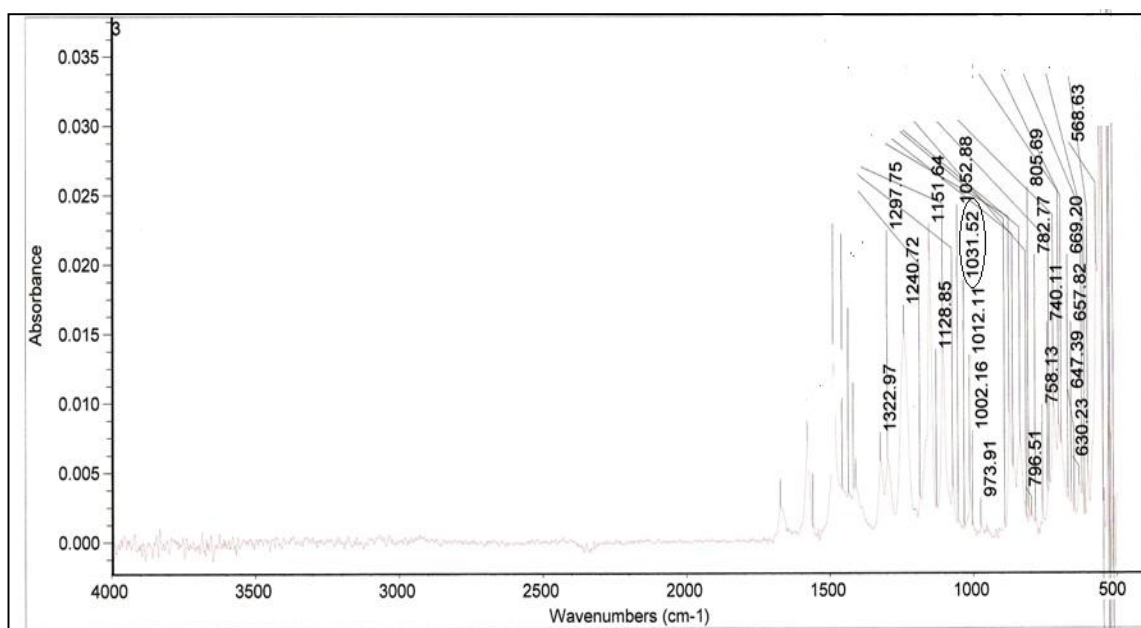


**Figure 4.2:** FTIR Spectrum for SPSU/PES 1 Membrane





**Figure 4.3:** FTIR Spectrum of SPSU/PES 2 Membrane



**Figure 4.4:** FTIR Spectrum of SPSU/PES 3 Membrane

### 4.3 Swelling Test

As explained earlier in the previous chapter, solvent uptake increased with the sulfonation degree. Higher sulfonate group content in the membrane increased the hydrophilicity and thus making the membrane retain solvent better. In this study, the sorption ability of each sample was measured with water, methanol and water/methanol mixture. Table 4.2, Table 4.3 and Table 4.4 summarized the swelling effect tests for the samples.

**Table 4.2:** Summary of Water Uptake Test

Sample	Dry Mass (g)	Wet Mass (g)	Swelling Degree (%)
PES/PSU	0.0231	0.0356	35.11
SPSU/PES 1	0.0258	0.0458	43.67
SPSU/PES 2	0.0161	0.0398	59.55
SPSU/PES 3	0.0441	0.1145	61.48

**Table 4.3:** Summary of Methanol Uptake Test

Sample	Dry Mass (g)	Wet Mass (g)	Swelling Degree (%)
PES/PSU	0.0156	0.0235	33.62
SPSU/PES 1	0.0211	0.0395	46.58
SPSU/PES 2	0.0138	0.0325	57.54
SPSU/PES 3	0.0429	0.1088	60.57

**Table 4.4:** Summary of Water/Methanol Mixture Uptake Test

Sample	Dry Mass (g)	Wet Mass (g)	Swelling Degree (%)
PES/PSU	0.0225	0.0338	33.43
SPSU/PES 1	0.0192	0.0362	46.96
SPSU/PES 2	0.0117	0.0285	58.95
SPSU/PES 3	0.0281	0.0758	62.93

The results showed that for every solvent uptake tests, sample SPSU/PES 3 has the highest swelling degree among all the samples. It also increased the possibility that sample SPSU/PES 3 has the highest degree of sulfonation.

#### 4.4 Elemental Analysis

Elemental analysis was conducted in order to obtain experimental data for degree of sulfonation calculation. The results were tabulated in Table 4.5.

**Table 4.5:** Summary of Elemental Analysis

Sample	Elemental Analysis (%)				
	C	H	N	O	S
PSU/PES	68.731	5.300	0.613	16.133	6.234
SPSU/PES 1	63.225	5.321	0.098	19.553	7.995
SPSU/PES 2	60.148	5.328	0.075	21.336	8.512
SPSU/PES 3	57.992	5.361	0.058	24.057	9.128

The results showed that sample SPSU/PES 3 has the highest sulfur, oxygen and hydrogen content due to the highest amount of TMSCS added to the sample among others. The data of sulfur and carbon content of each sample was used to calculate degree of sulfonation.

#### 4.5 Degree of Sulfonation Calculation

Degree of sulfonation was defined as the percentage of  $\text{SO}_3\text{H}$  group associated with the polymer ( $\%\text{SO}_3\text{H}$ ). The formula to calculate degree of sulfonation was stated as:

$$\left[ \% SO_3H = \frac{(s/c)_{experimental}}{(s/c)_{theoretical}} \times 100\% \right] \quad (4.1)$$

where the value of (S/C) theoretical was the amount of sulfur content over the amount of carbon content in the PES/PSU membrane while the value of (S/C) experimental is the value of sulfur content over the amount of carbon content in the sulfonated samples (SPSU/PES 1, SPSU/PES 2 and SPSU/PES 3) minus the (S/C) theoretical value. Table 4.6 summarized the sulfur and carbon content obtained from CHNOS elemental analysis for each sample.

**Table 4.6:** Sulfur and Carbon Content Summary

Sample	Carbon Content (%)	Sulfur Content (%)
PSU/PES	68.731	6.234
SPSU/PES 1	63.225	7.995
SPSU/PES 2	60.148	8.512
SPSU/PES 3	57.992	9.128

The value of (s/c) theoretical is calculated as follows:

$$(s/c)_{theoretical} = \frac{S_{PSU/PES}}{C_{PSU/PES}} = \frac{6.234}{68.731} = 0.091 \quad (4.2)$$

Then the experimental values for each sample were calculated:

$$(s/c)_{experimental_{SPSU/PES1}} = \frac{S_{SPSU/PES1}}{C_{SPSU/PES1}} = \frac{7.995}{63.225} = 0.126$$

$$(s/c)_{\text{experimental}}_{SPSU/PES2} = \frac{S_{SPSU/PES2}}{C_{SPSU/PES2}} = \frac{8.512}{60.148} = 0.1415$$

$$(s/c)_{\text{experimental}}_{SPSU/PES3} = \frac{S_{SPSU/PES3}}{C_{SPSU/PES3}} = \frac{9.128}{57.992} = 0.157$$

Finally, the degree of sulfonation is calculated based on the relation:

$$\%SO_3H = [(s/c)_{\text{experimental}} - (s/c)_{\text{theoretical}}] / (s/c)_{\text{theoretical}} \times 100\% \quad (4.3)$$

The results were tabulated in Table 4.7 below.

**Table 4.7:** Degree of Sulfonation for each Sample

Sample	Degree of Sulfonation (%)
PSU/PES	-
SPSU/PES 1	38.46
SPSU/PES 2	55.49
SPSU/PES 3	72.53

The result of degree of sulfonation calculation confirmed that sample SPSU/PES 3 has the highest degree of sulfonation and explained why it exhibited the characteristics in swelling test. Sample SPSU/PES 3 has the highest degree of sulfonation because it possessed highest amount of TMSCS added during the sulfonation process.

## **CHAPTER V**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 Conclusion**

In this study, it was found that the degree of sulfonation and swelling effect has great impact on the performance of a proton exchange membrane. The production of mixed matrix of the sulfonated polysulfone with polyethersulfone was purposely to combine both polymer characteristics and expected to improve the overall performance. The characterization tests confirmed that the mixed matrix polymer has the ability to become electrolyte in PEMFC. As a conclusion, the mixed matrix SPSU/PES samples developed in this study were valid alternatives for polymer electrolyte in PEMFC. Sample SPSU/PES 3 was identified to be the best sample since it exhibited good characteristics in water, methanol and water/methanol mixture uptake tests and had the highest degree of sulfonation.

#### **5.2 Recommendations**

In order for future improvisation in sulfonated polymer membrane studies, here are some recommendations considering the results obtained from this study:

- i) Sulfonation process should be conducted at various parameters. Many other parameters that can be varied on sulfonation process such as reaction time, temperature, sulfonating agents and solvent used.
- ii) Several more tests should be included in the physicochemistry study of the membrane including thermogravimetric and differential scanning calorimetry test. Scanning electron microscopy test also should be conducted to study the cross section of the membrane
- iii) Pneumatically controlled casting machine should be used instead of manual casting knife. In this way, the thickness of the membrane can be varied and set as a parameter in the study.

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