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DEVELOPMENT AND CHARACTERIZATION OF SULFONATED POLYETHERSULFONE MEMBRANE AS A POTENTIAL MATERIAL FOR DIRECT METHANOL FUEL CELL

ROSMAINIZA BINTI IBRAHIMI HUSAIMI

A thesis submitted in fulfillment of the
requirement for the award of the Bachelor of
Degree.

Faculty of Chemical Engineering & Natural Resources

University Malaysia Pahang

MAY 2008

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To my beloved mother and father

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ABSTRACT

Sulfonated polyethersulfone membrane is one of the potential candidates to be use as an electrolyte for fuel cell application due to its high thermal resistance. With a high heat deflection temperature of 400°F (204°C), it can withstand continuous exposure to heat and still absorb tremendous impact without cracking or breaking. Sulfonated polyethersulfone membrane has been prepared by conducting sulfonation process with sulfuric acid as a sulfonating agent and then the polymer precipitated had been dissolved in N-Methyl-2-pyrrolidone. The functional groups of sulfonic acids have been successfully incorporated in the PES backbone and detected using FTIR at 1033cm^{-1} wavelength. Membranes with 35.7% degree of sulfonation possess water uptake at the room temperature of 13.1 wt% and the value of IEC is about 11.43 mmol/g. The water uptake of the sulfonated polyethersulfone membrane increased with temperature from 13.1 wt% up to 46 wt%. Meanwhile, the methanol uptake was increased with an increased in concentration from 14.9 wt% to 26.2 wt%. Membranes prepared from SPES showed lower decomposition temperature and have good properties to be applied as a membrane for DMFC.

ABSTRAK

Polyethersulfone membran yang telah ditambah kumpulan asid sulfonic merupakan salah satu calon yang berpotensi untuk digunakan sebagai elektrolit untuk aplikasi bateri kerana mempunyai daya tahan yang tinggi terhadap haba. Dengan suhu pembiasan haba yang tinggi mencecah 400°F (204°C), ia dapat menahan pendedahan berterusan terhadap haba dan terus menyerap pelanggaran yang hebat tanpa retak atau pecah. Polyethersulfone membran disediakan dengan menjalankan proses penambahan kumpulan asid sulfonic dengan menggunakan asid sulfuric sebagai agen penambahan kumpulan asid sulfonic dan hasil turasan polimer dilarutkan menggunakan N-Methyl-2-pyrrolidone. Kumpulan fungsi untuk asid sulfonic yang telah disatukan ke dalam tunjang PES, di kesan menggunakan FTIR pada 1033cm^{-1}. Membran dengan 35.7% kadar penambahan kumpulan asid sulfonic mempunyai kebolehan meyerap air sebanyak 13.1% pada suhu bilik dan nilai kadar perubahan ion adalah sebanyak 11.43mmol/g. Kebolehan polyethersulfone membran yang telah ditambah kumpulan asid sulfonic meyerap air meningkat apabila suhu bertambah dari 13.1% sehingga 46%. Pada masa yang sama, kebolehan polyethersulfone membran yang telah ditambah kumpulan asid sulfonic menyerap metanol meningkat apabila kepekatan methanol yang digunakan meningkat iaitu dari 14.9% sehingga 26.2%. Membran yang dihasilkan dari SPES mempunyai suhu pereputan yang rendah dan mempunyai ciri-ciri yang bagus untuk digunakan sebagai membrane untuk DMFC.

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LIST OF SYMBOLS

W_{wet}	-	weight of the wet membranes
W_{dry}	-	weight of the dry membranes
str	-	strong
wk	-	weak
brd	-	broad
shp	-	sharp
M_{NaOH}	-	concentration of standard NaOH
W	-	mass of sample
V_{NaOH}	-	volume of NaOH solution used to neutralize

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Throughout the world, demand for power generation with environmental friendly is increased. This has encouraged research in various aspect of fuel cell. This is due to the reason that fuel cell is more clean compared to other power source. It can also helps reduce the usage of fossil fuel cell due to the high efficiency of energy conversion, low pollution level, low noise and low maintenance cost (Smitha *et al*., 2005).

Proton exchange membrane fuel cells (PEMFC) work with a polymer electrolyte membrane in the form of a thin, permeable sheet. This membrane is small and light, and it works at low temperatures (about 80°C, or about 175°F). Other types of fuel cells uses electrolytes which require temperatures as high as 1,000°C. The performance of PEM fuel cells which influenced by many parameters such as operating temperature, pressure and relative humidity of the gas stream.

Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells where specially optimized PEFCs can be fed with methanol (or fuels with similar chemical structure), creating a so-called direct methanol fuel cell (DMFC). Conceptually, this could lead to a very simple system with a fuel that has a relatively high energy density and a liquid under ambient conditions (Appleby and Foulkes, 2004). However, the efficiency of direct-methanol fuel cells is low due to the high

permeation of methanol through the membrane, which is known as methanol crossover.

At the current level of technology development, DMFCs are limited in the power that they can produce, but still can store much energy in a small space. This means DMFCs can produce a small amount of power over a long period of time. This makes them ill-suited for powering vehicles, but ideal for consumer goods such as mobile phones, digital cameras or laptops.

The recent categories of membrane that have been center of attention are perfluorinated ionomer (PFI) or perfluorosulfonated compounds (PFSA), non-fluorinated hydrocarbons, sulfonated poly(arylenes) and acid based complexes. Right now, the best choice polymer to be used as fuel cell membrane is Nafion which is perfluorinated membranes. Nafion is a strong, stable in oxidation and reduction and also good in proton conductivities. The problem is, Nafion has a temperature limitation. The crossover problem and loss of hydration occur at 100 °C (Sakari *et al*., 1985). It also expensive due to the operation catalys is noble-metal catalyst (typically platinum) to separate the hydrogen's electrons and protons (Smitha *et al*., 2005).

Therefore, a low cost polymer membrane that can outlast at high temperature is sought off. Among the alternatives candidates are polysulfone, polyphenylsulfone, polyethersulfone, polyether and polyetheryetherketone.

1.2 Problem statement

Demand for power generation with environmental friendly is increased which leading to the growing in research and using of fuel cell as a one of clean source of power generation. Currently, Nafion was the state of the art membrane for fuel cell. However, Nafion have a temperature limitation and high cost in production. Therefore, low cost polymer membrane that can outlast at high temperature is needed in order to overcome this problem.

1.3 Objective of Study

The objective of this study is to develop and characterize the sulfonated polyethersulfone membrane as a potential ion exchange membrane for DMFC fuel cell application.

1.4 Scopes of Study

There are some scopes which need to be a focused in order to meet the objective:

(a) Develop and characterize sulfonated polyethersulfone polymer as a membrane for direct methanol fuel cell (DMFC)
(b) Study the physicochemical of sulfonated polyethersulfone membrane for fuel cell application

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Types and Application

In medicine, microbiology, cellular physiology and biochemistry a membrane is a thin layer that separates various cellular structures or organs. It usually includes lipid bilayer reinforced by proteins and other macromolecules, and can refer to:

a) Basement membrane, the combination of the basal lamina and lamina reticularis or of two basal laminae
b) Biological membrane
c) Mucous membrane
d) Skin, part of the integumentary system

Membrane may also refer to artificial, semipermeable membranes which are used to separate species in a fluid on the basis of size, charge or other characteristics. Membrane have a multipurpose usage such as membrane for separation, filtration and also for fuel cell electrolyte. In separation, membrane acts as a barrier for two certain particles. The bigger particle will be block and the small particle will pass through the membrane. Figure 2.1 show the separation using membrane.

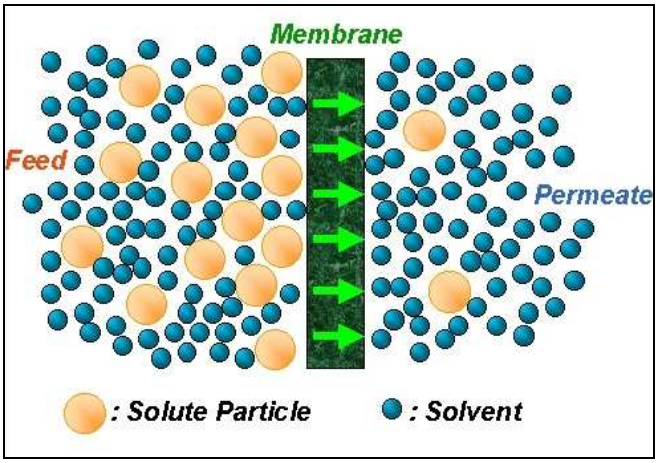


Figure 2.1 : Separation process using membrane

In separation, the membrane acts as a semipermeable barrier and separation occurs by membranes controlling the movements of various two molecules between two liquid phase, gases phase or liquid and gases phase (Geankoplis, 2003). Most separation processes are aiming at one of two results which are to collect the liquid (the filtrate) or to collect the retained sludge (the retentate).

Such membranes are employed in a range of applications from water and wastewater treatment like reverse osmosis, diffuser (sewage), landfill liners, nanofiltration, ultrafiltration and microfiltration to hydrogen fuel cells (proton exchange membrane).

2.2 Background of Fuel Cell

The fuel cell can trace its roots back to the 1800's. A Welsh born, Oxford educated barrister, who practiced patent law and also studied chemistry named Sir William Robert Grove realized that if electrolysis, using electricity, could split water into hydrogen and oxygen then the opposite would also be true. Combining hydrogen and oxygen, with the correct method, would produce electricity. To test his theory Sir William Robert Grove built a device that would combine hydrogen and oxygen to

produce electricity, the world's first gas battery as shown in Figure 2.2, and then later renamed as fuel cell.

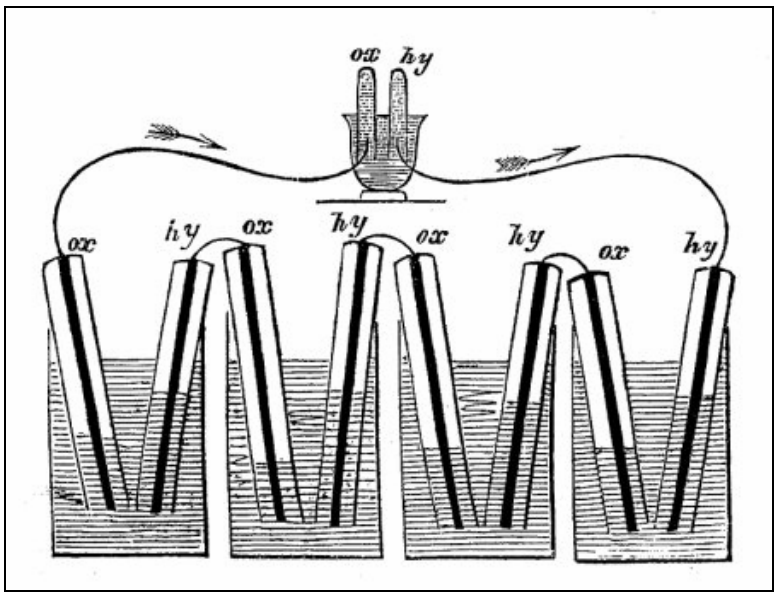


Figure 2.2 : William Grove's 'gas battery', the first fuel cell

Fast-forwarding to the 1960's, a new government agency was about to undertake the first step in maturing fuel cell technology. The National Aeronautics and Space Administration (NASA) were developing the mission critical systems for the first prolonged manned flight into space. Once in space, the orbiter needed a source of electricity. Batteries were ruled out due to the size, weight and toxicity necessary to support a mission of eight days in space. Photovoltaic were not practical, at the time, due to the size and weight of the solar panels necessary. Then fuel cell became the technological solution to NASA's dilemma of how to provide power for extended missions to space.

The earlier problems of cost and fuel supplies that plagued fuel cells became irrelevant as the spacecraft was already carrying liquid hydrogen and oxygen. An additional benefit of fuel cells over other technology was that the astronauts could consume the fuel cell's water by-product. Since their adoption by the space program, fuel cell technology has achieved widespread recognition by industry and government.

Though fuel cells in principle, could process a wide variety of fuels and oxidants, but the most interest today are those fuel cells that use common fuels or hydrogen as a reductant, and ambient air as the oxidant. Most fuel cell power systems comprise a number of components:

a) Unit cells, in which the electrochemical reactions take place
b) Stacks, in which individual cells are modularly combined by electrically connecting the cells to form units with the desired output capacity
c) Balance of plant which comprises components that provides feed stream conditioning (including a fuel processor if needed), thermal management, and electric power conditioning among other ancillary and interface functions

Operating principle of the fuel cell is the fuel electrode (anode) and the oxygen electrode (cathode) which is interconnected by an ion-conducting electrolyte. The electrodes are electrically coupled to an electricity consumer by external metallic lines outside the cell. In this section of the electric circuit, the electric current is transmitted by the electrons whereas in the electrolyte the current transfer is affected by means of ions. Figure 2.3 shows the principle of a fuel cell. The anode is supplied with hydrogen as the fuel gas which is electrochemically split into protons and electrons at the electrode/electrolyte interface. The electrons which perform electrical work in the outer electric circuit are passed into the cathode where they reduce the oxygen into water at the electrode/electrolyte interface.

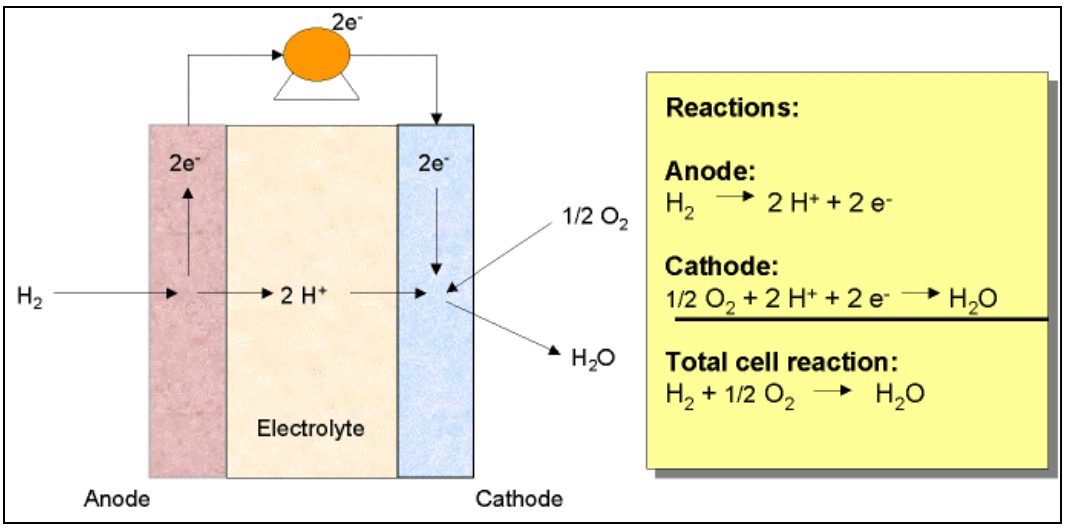


Figure 2.3 : Operating principles of fuel cell

The required protons come from the anode through the electrolyte. As can be seen from the schematic, the electrodes must also be permeable to gas, i.e. porous. A fuel cell reaction normally requires all three phases to be present which is the solid phase (electron conductor), the liquid phase (ion conductor) and the gas phase (electrode pores).

2.3 Types of Fuel Cell

A variety of fuel cells are in different stages of development. The most common classification of fuel cells is by the type of electrolyte used in the cells such as polymer electrolyte fuel cell (PEFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). Broadly, the choice of electrolyte dictates the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell dictates the physicochemical and thermo mechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.). Aqueous electrolytes are limited to temperatures of about 200 °C or lower because of their high vapor pressure and rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the degree of fuel processing required. In low-temperature fuel cells, all the fuel must be converted to hydrogen prior to entering the fuel cell. In addition, the anode catalyst in low temperature fuel cells (mainly platinum) is strongly poisoned by CO. In high-temperature fuel cells, CO and even CH_4 can be internally converted to hydrogen or even directly oxidized electrochemically. Table 2.1 provides an overview of the key characteristics of the main fuel cell types (Appleby and Foulkes, 2004).

Table 2.1 : Summary for different type of fuel cell (Appleby and Foulkes, 2004)

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in $LiAlO_2$	Perovskites (Ceramics)
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite /metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic, or steel
Operating Temperature	40 – 80 °C	65°C – 220°C	205 °C	650 °C	600-1000 °C
Charge Carrier	H+	OH-	H+	CO_3=	O=
External Reformer for Hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels
External Shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO2	No	Yes	Yes
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless based	Ceramic
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Liquid cooling medium or steam generation	Internal Reforming + Process Gas	Internal Reforming + Process Gas

2.3.1 Proton Exchange Membrane Fuel Cell

The PEM fuel cell gained prominence after General Electric (GE) invented a small fuel cell for a program with the U.S. Navy's Bureau of Ships (Electronics Division) and the U.S. Army Signal Corps in 1960s. Based on its simplicity design, weight advantages and combined with optimum compability, PEM fuel cell can be use in many applications. Figure 2.4 shows the schematic overview of PEM fuel cell.

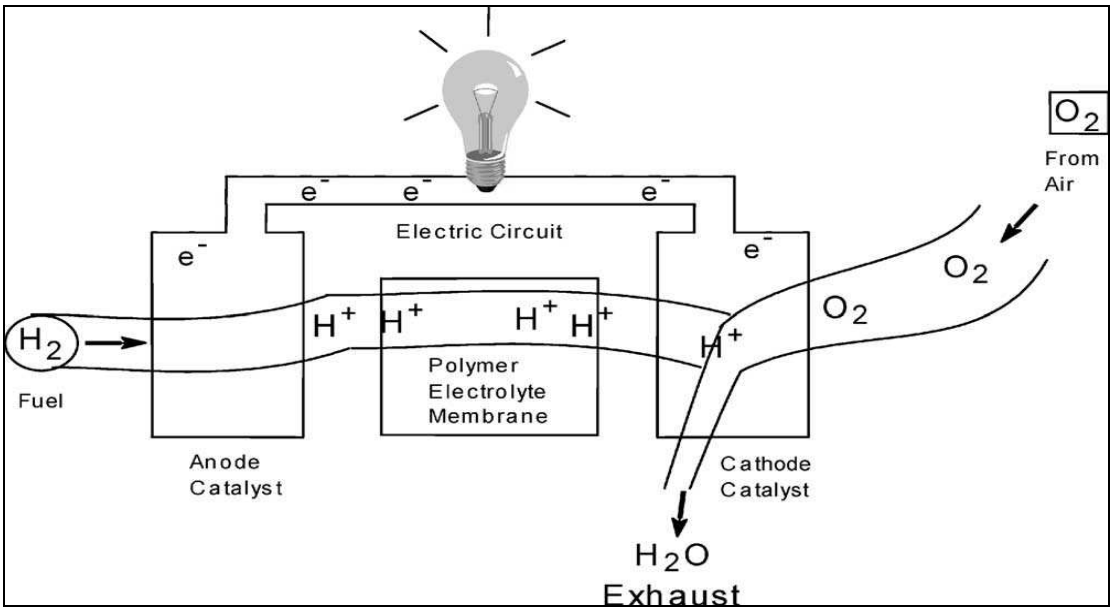


Figure 2.4 : Schematic view of proton exchange membrane fuel cell

PEM fuel cell technology differentiates itself from other fuel cell technologies in that a solid phase polymer membrane is used as the cell separator/electrolyte. Because the cell separator is a polymer film and the cell operates at relatively low temperatures, issues such as sealing, assembly, and handling are less complex than most other fuel cells. The need to handle corrosive acids or bases is eliminated in this system. PEFCs typically operate at low temperatures (60°C to 80°C), allowing for potentially faster startup than higher temperature fuel cells. The PEM fuel cell is seen as the main fuel cell candidate technology for light-duty transportation applications. While PEM fuel cell are particularly suitable for operation on pure hydrogen, fuel processors have been developed that will allow the use of conventional fuels such as natural gas or gasoline.

2.3.2 Direct Methanol Fuel Cell

DMFC is similar to the PEMFC in that the electrolyte is a polymer and the charge carrier is the hydrogen ion (proton). However, the liquid methanol (CH_3OH) is oxidized in the presence of water at the anode generating CO_2, hydrogen ions and the electrons that travel through the external circuit as the electric output of the fuel cell. The hydrogen ions travel through the electrolyte and react with oxygen from the air and the electrons from the external circuit to form water at the anode completing the circuit.

Initially developed in the early 1990s, DMFCs were not embraced because of their low efficiency and power density, as well as other problems. Improvements in catalysts and other recent developments have increased power density 20-fold and the efficiency may eventually reach 40%. These cells have been tested in a temperature range from about 50ºC-120ºC (Williams, 2000). This low operating temperature and no requirement for a fuel reformer make the DMFC an excellent candidate for very small to mid-sized applications, such as cellular phones and other consumer products, up to automobile power plants.

One of the drawbacks of the DMFC is that the low-temperature oxidation of methanol to hydrogen ions and carbon dioxide requires a more active catalyst, which typically means a larger quantity of expensive platinum catalyst is required than in conventional PEMFCs. This increased cost is, however, expected to be more than outweighed by the convenience of using a liquid fuel and the ability to function without a reforming unit.

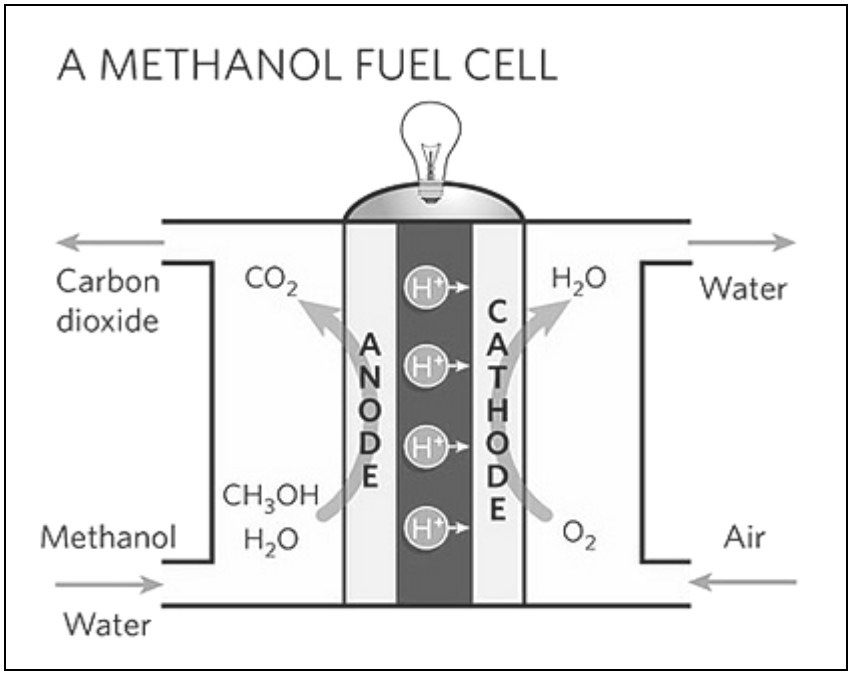


Figure 2.5 : Schematic view of direct methanol fuel cell

2.3.3 Alkaline Fuel Cell

The AFC was one of the first modern fuel cells to be developed, beginning in 1960. The application at that time was to provide on-board electric power for the Apollo space vehicle. The fuel cells on board these spacecraft provide electrical power for on-board systems, as well as drinking water. AFCs are among the most efficient in generating electricity at nearly 70%. Desirable attributes of the AFC include its excellent performance on hydrogen (H_2) and oxygen (O_2) compared to other candidate fuel cells due to its active O_2 electrode kinetics and its flexibility to use a wide range of electro-catalysts, an attribute that provides development flexibility. The schematic view of AFC is shown in Figure 2.6. Developers recognized that pure hydrogen would be required in the fuel stream, because CO_2 in any reformed fuel reacts with the KOH electrolyte to form a carbonate, reducing the electrolyte's ion mobility. However, a significant pressure differential is required across the membrane and the membrane is prohibitive in cost (Williams, 2000).

The sensitivity of the electrolyte to CO_2 requires the use of highly pure H_2 as a fuel is a major disadvantage of this fuel cell (Appleby and Foulkes, 2004). As a

consequence, the use of a reformer would require a highly effective CO and CO_2 removal system. In addition, if ambient air is used as the oxidant, the CO_2 in the air must be removed. While this is technically not challenging, it has a significant impact on the size and cost of the system.

AFCs are not being considered for automobile applications. Their sensitivity to poisoning, which requires use of pure or cleansed hydrogen and oxygen, is an insurmountable obstacle at the present time. Conversely, AFCs operate at relatively low temperatures and are among the most efficient fuel cells, characteristics that would enable a quick starting power source and high fuel efficiency, respectively.

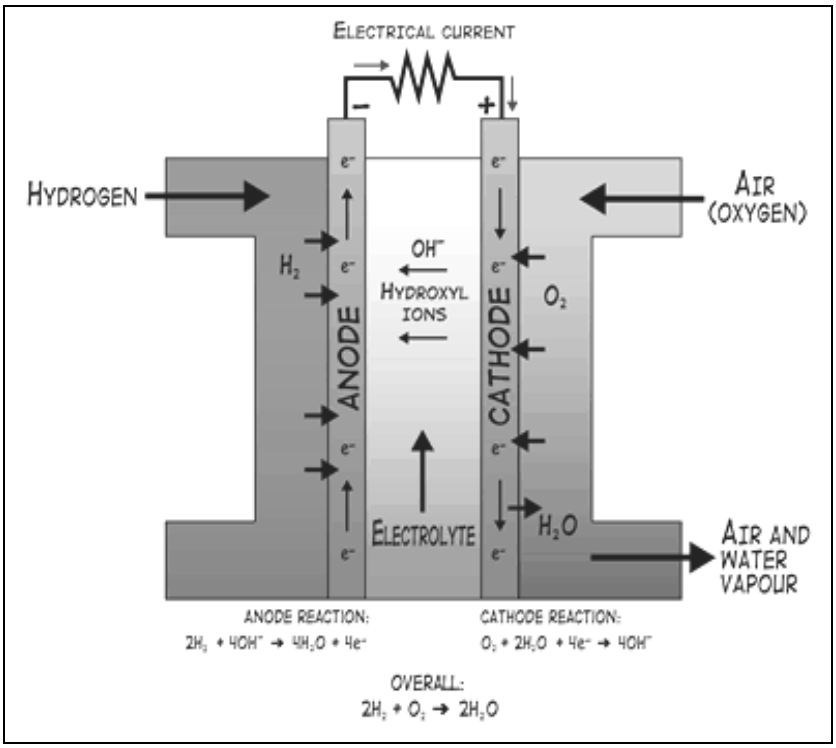


Figure 2.6 : Schematic View of alkaline fuel cell

2.3.4 Phosphoric Acid Fuel Cell

Phosphoric acid, which concentrated to 100 %, is used as the electrolyte in PAFC, which typically operates at 150 to 220 °C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electro-catalyst in the

anode becomes severe. The relative stability of concentrated phosphoric acid is high compared to other common acids, so the PAFC is capable of operating at the high end of the acid temperature range (100 to 220 °C). In addition, the use of concentrated acid (100 percent) minimizes the water vapor pressure so water management in the cell is not difficult (Williams, 2000). Figure 2.7 shows the schematic view of PAFC.

PAFCs are mostly developed for stationary applications. PAFCs are much less sensitive to CO than PEFCs and AFCs. The operating temperature of this fuel cell provides considerable design flexibility for thermal management. PAFCs have demonstrated system efficiencies of 37 to 42 %, which is higher than most PEFC systems could achieve (but lower than many of the SOFC and MCFC systems). In addition, the waste heat from PAFC can be readily used in most commercial and industrial cogeneration applications, and would technically allow the use of a bottoming cycle. Although less complex than for PEFC, PAFCs still require extensive fuel processing, including typically a water gas shift reactor to achieve good performance. Finally, the highly corrosive nature of phosphoric acid requires the use of expensive materials in the stack (especially the graphite separator plates).

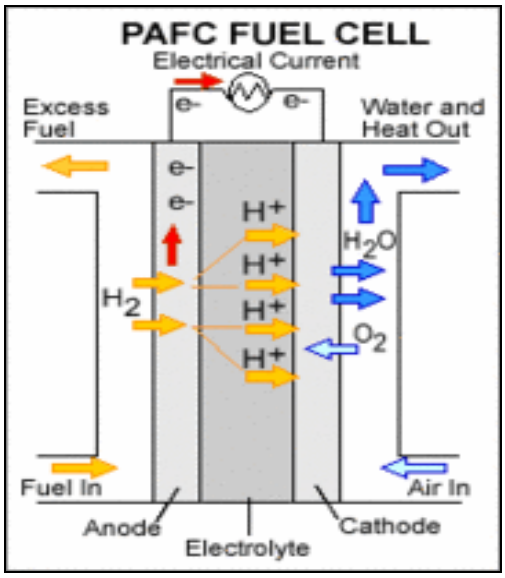


Figure 2.7 : Schematic view of phosphoric acid fuel cell

2.3.5 Molten Carbonate Fuel Cell

MCFC have high operating temperature which is approximately 650°C. This temperature level result in several benefits such as the cell can be made of commonly available sheet metals that can be stamped for less costly fabrication and the cell reactions occur with nickel catalysts rather than with expensive precious metal catalysts. The rejected heat from this fuel cell is sufficiently very high temperature which can use to drive a gas turbine or to produce a high pressure steam for use in a steam turbine or for cogeneration. The focus of MCFC development is for used of larger stationary and marine applications, where the relatively large size and weight of MCFC and slow start-up time are not an issue. Another advantage of the MCFC is that it operates efficiently with CO_2-containing fuels such as bio-fuel derived gases. This fuel cell also has some disadvantages. The electrolyte is very corrosive and mobile, and a source of CO_2 is required at the cathode (usually recycled from anode exhaust) to form the carbonate ion. Figure 2.8 shows the schematic view of MCFC. The operation of MCFC is requires of stainless steel as the cell hardware material. The higher temperatures promote material problems, particularly mechanical stability that can impact life.

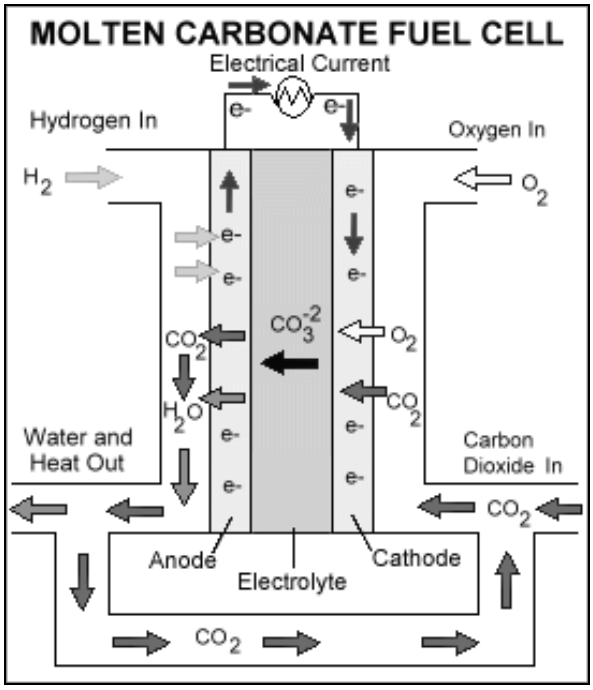


Figure 2.8 : Schematic view of molten carbonate fuel cell

2.3.6 Solid Oxide Fuel Cell

The electrolyte in this fuel cell is a solid, nonporous metal oxide, usually Y_2O_3-stabilized ZrO_2. The cell operates at 600-1000 °C where ionic conduction by oxygen ions takes place. Typically, the anode is Co-ZrO_2 or Ni-ZrO_2 cermet, and the cathode is Sr-doped $LaMnO_3$. Early on, the limited conductivity of solid electrolytes required cell operation at around 1000 °C, but more recently thin-electrolyte cells with improved cathodes have allowed a reduction in operating temperature to 650 – 850 °C. Some developers are attempting to push SOFC operating temperatures even lower. As a consequence of the performance improvements, SOFCs are now considered for a wide range of applications, including stationary power generation, mobile power, auxiliary power for vehicles, and specialty applications (Williams, 2000).

As the SOFC having an electrolyte in a solid form, the cell can be cast into various shapes, such as tubular, planar, or monolithic. Figure 2.9 shows the schematic view of SOFC. The solid ceramic construction of the unit cell alleviates any corrosion problems in the cell. The solid electrolyte also allows precise engineering of the three-phase boundary and avoids electrolyte movement or flooding in the electrodes. The high temperature of the SOFC has its drawbacks and become as a disadvantage for SOFC. There are thermal expansion mismatches among materials, and sealing between cells is difficult in the flat plate configurations. The high operating temperature places severe constraints on materials selection and results in difficult fabrication processes.

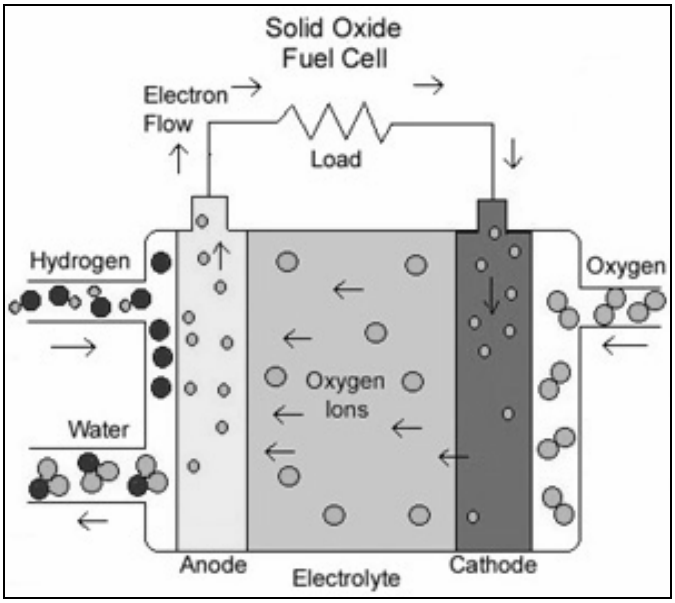


Figure 2.9 : Schematic view of solid oxide fuel cell

2.4 Membrane for Fuel Cell

For the fuel cell, membrane is a core component where the process of ion exchange was occurred. Organic-based cation exchange membranes in fuel cells were originally conceived by William T. Grubb in 1959. That initial effort eventually led to development of the perfluorosulfonic acid polymer used in today's systems. The function of the ion exchange membrane is to provide a conductive path, while at the same time separating the reactant gases. The material is an electrical insulator. As a result, ion conduction takes place via ionic groups within the polymer structure. Ion transport at such sites is highly dependent on the bound and free water associated with those sites. An accelerated interest in polymer electrolyte fuel cells has led to improvements in both cost and performance. To achieve high efficiency, the membrane must have following characteristic:

a) high proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity;
b) adequate mechanical strength and stability;
c) chemical and electrochemical stability under operating conditions;
d) moisture control in stack;

e) extremely low fuel or oxygen by-pass to maximize coulombic efficiency;
f) production costs compatible with intended application.

2.5 Factors Affecting Performance of Membranes for Fuel Cell

2.5.1 Hydration

The performance of membrane depends on proton conductivity, which is also depends on existing levels of hydration. Higher level of hydration will give a higher conductivity (Smitha *et al*., 2005) but to a certain extend, the membrane tend to swelled. However, at higher temperature, dehydration tends to occur and these will reduce the membrane performance via low proton conductivity.

2.5.2 Thickness

One ways to avoid water cross over is reduce the thickness of membranes. Other advantages when the thickness is reduced are rapid hydration, lower membrane resistance and lower cost. However there is a limit in reduce the membrane thickness in order to have a good performances. Susai *et al*. (2001) concluded that, from their studies of PEMFC optimization, a thinner membrane might promote back diffusion and produce a greater concentration gradient of water, on account of enhanced rate of dehydration on higher temperature.

2.5.3 Degree of Sulfonation

Higher sulfonation level of sulfonation will produce higher proton conductivity but other membranes properties may suffer. As the degree of sulfonation is increases, swelling properties also increased. A membrane that is too much hydrophilic would swell greatly and may be weak and do not sufficiently serve as a barrier for the fuel and oxidizer. An optimum degree of sulfonation need to be establishes to produce the polymer electrolyte membrane with the best performance (Naim et al., 2004).

2.6 Type of Membrane for Fuel Cell

There are many type of membranes which is depend to their basis material like perfluorinated ionomer (PFI) or perfluorosulfonated compounds (PFSA), non-fluorinated hydrocarbons, sulfonated poly(arylenes) and acid based complexes. Figure 2.10 shows the classification of the membrane materials used for fuel cell.

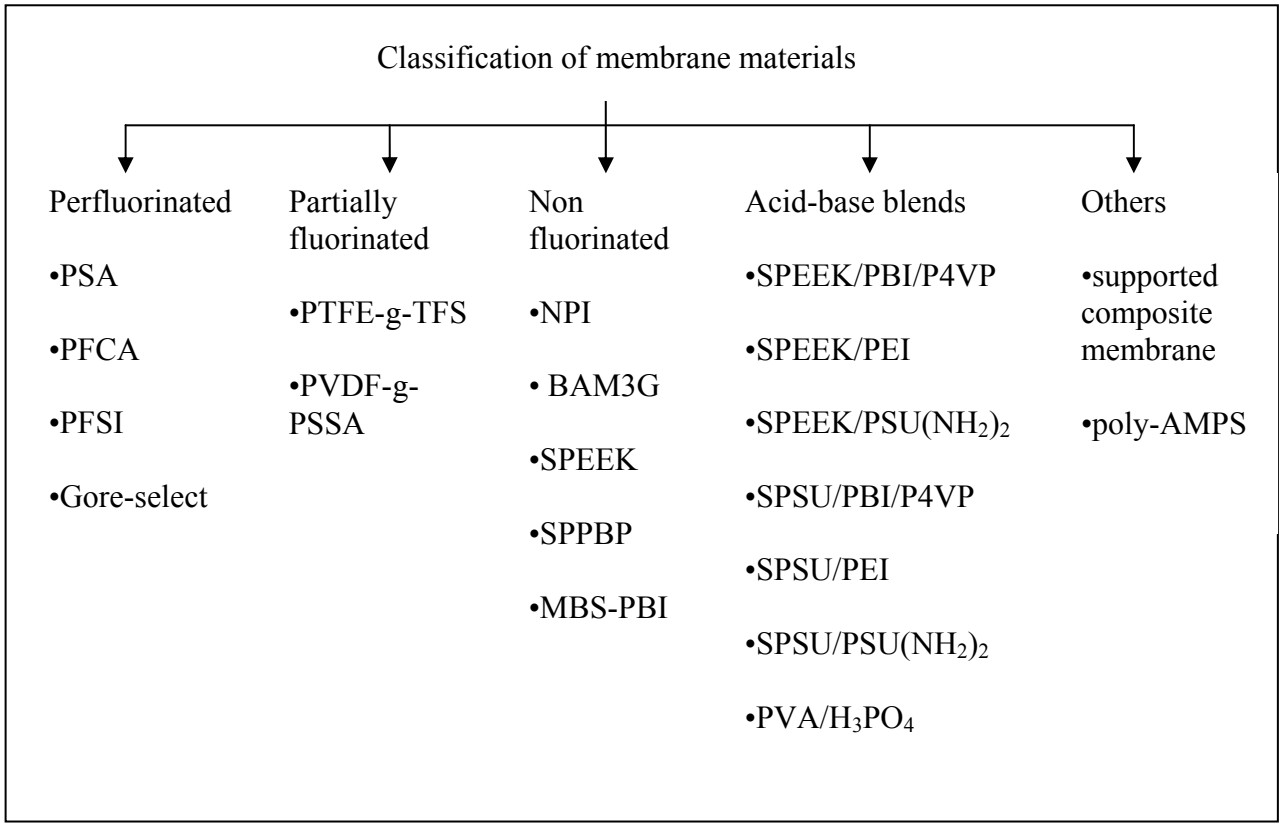
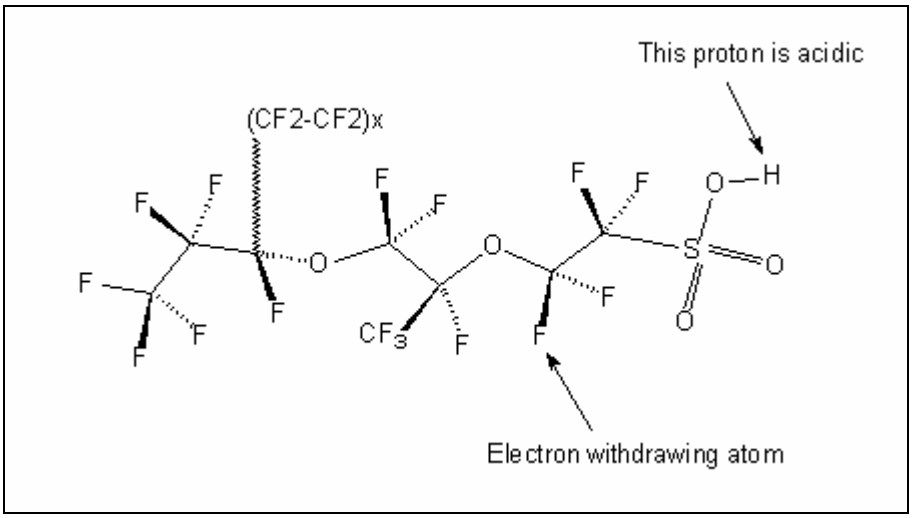


Figure 2.10 : Classification of the membrane materials (Smitha et al, 2005)

2.6.1 Perfluorinated Membranes

Perfluorinated membranes have been subject of research and the perfluorinated polymer that currently used in portable fuel cell application is perfluorinated structure with attachment of sulfonic acid group. The most extensively is Nafion® which discovered in the late 1960s by Walther Grot of DuPont de Nemours. It is the first of a class of synthetic polymers with ionic properties which are called ionomers. Nafion's unique ionic properties are a result of incorporating

perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone. Nafion has received a considerable amount of attention as a proton conductor for proton exchange membrane (PEM) fuel cells because of its excellent thermal and mechanical stability. Figured 2.11 shows chemical structured of Nafion®.



Figured 2.11 : Chemical structured of Nafion®.

Four main applications of Nafion today is to used to fabricate ion-exchange membranes used to produce chlorine gas and lye (sodium hydroxide) by the electrolysis of salt water. Nafion is used to selectively dry or to humidify gases. The largest segment of this application involves drying or humidifying breath for anesthesia, respiratory care, or plethysmography, but many applications exist in the laboratory and in industrial use. Nafion is used as the proton exchange membranes in polymer electrode fuel cells. Nafion is used as a super-acid catalyst in the production of fine chemicals.

Nafion exhibits exceptionally high chemical and thermal stability, and is stable against chemical attack in strong bases, strong oxidizing and reducing acids, Cl_2, H_2, and O_2 at temperatures up to 125°C. Nafion also is good proton conduction.

Despite the generally acknowledged advantages which PEM fuel cells containing Nafion as electrolyte membrane have, there are also some disadvantages. The major disadvantage is their temperature sensitivity, which limits them to low

operating temperatures. Furthermore the polymer membrane always has to be moistened. This requires a sophisticated water management in the fuel cell. Furthermore, the other disadvantage of nafion is expensive due to the operation catalyst is noble-metal catalyst to separate the hydrogen's electron and protons.

2.6.2 Hydrocarbon Membranes

Hydrocarbon membranes provides some definite advantages over perfluorinated sulfonic acid membranes as they are less expensive, commercially available and their structure permits the introduction of polar sites as pendant group in order to increase the water uptake.

2.7 Research Done by Other Researcher in Sulfonated Membranes

Current increasing research trend in sulfonated membranes were shown in Table 2.2.

Table 2.2 : Research done by other researcher in sulfonated membranes

Researcher	Membrane Material	Result/ Findings	
Nasef *et al*., 2000	FEP-*g*-polystyrene Nafion 117	Degree of Grafting from 5 to 52%, IEC (meq/g): 0.4-2.3 0.9-1.9	
Bae *et al*., 2002	S-PPBP PBI-BS	Proton conduction still depends on the relative humidity, even at highly sulfonated S-PPBP. High proton conductivity at high temperatures with low humidity conditions	
Zubir *et al*., 2004	polystyrene pore-filled electrolyte PTFE	Grafting yield from 5.45 to 28.85%, water uptake is 7.28 to 32.07 wt% and methanol uptake is 3.15 to 16.75 wt %	
Naim *et al*., 2004	SPSU5 SPSU6 SPSU9 SPSU10	Water Uptake (%) 4.10 8.00 12.36 25.91	IEC (mmol/g) by experimental 0.57 0.88 1.25 1.70
Shin *et al*., 2005	SPS/PTFE Nafion® 117	Water Uptake (wt %) 45 to 68 36.6	IEC (meq./g) 2.3 to 4.0 1.2
Li and Wang, 2006	SPES-C PWA/SPES-C Nafion 115	Water Uptake (%) 15 52 32	Conductivity ($S\ cm^{-1}$) at 110°C 3.4×10^{-2} 6.7×10^{-2} 4.7×10^{-2}
Xing *et al.,* 2007	Ag-SiO2/SPSUBP SPSU-BP	Water uptake (wt %) at 90°C 100 97	

Water absorption is depends on the degree of sulfonation. It can be observe that if the degree of sulfonation is higher, the greater the water uptake (Shen *et al.,* 2004). Membranes prepared from SPESs showed a decrease in tensile strength as DS increased but water uptakes of SPES membranes increased with DS. There was nearly no absorption when degree of sulfonation is low but when the degree of sulfonation is reached some extent, the water up-take increasing significantly (Guan *et al*., 2005).

The ion exchange capacity determination is also a way to show the presence of fixed acid groups in the modified polymers instead of FTIR characterization. For non-sulfonated films, the IEC was found to be zero and the value of IEC for sulfonated films is depends on the degree of sulfonation (Blanco *et al.,* 2001).

The DS and IEC of SPES membranes increased as the increasing amount of sulfonating agent. The proton conductivity of SPES membranes in the longitudinal direction was measured at 25 °C in water and the results show that conductivity increase with increasing of degree of sulfonation (Dai *et al*., 2007).

At constant time, the degree of sulfonation increased with increasing acid ratio. The sulfonated polymer with higher acid ratio needed shorter time to achieve the same degree sulfonation. For example, 1:3 of acid ratios, only 3hours were spent to obtain DS of 37%, whereas 10 h were needed to obtain relatively the similar DS when using 1:7 of acid ratios. It can also be seen that, 24hours of reaction time was required to get DS of 35% by using sulfuric acid (H_2SO_4) alone as the sulfonating agent (Jaafar, 2007).

CHAPTER 3

RESEARCH AND METHODOLOGY

3.1 Materials

3.1.1 Polyethersulfone (PES)

Polyethersulfone or Radel® A PES is a high temperature amorphous thermoplastic offering a superior combination of better chemical resistance and higher dry heat capability than polysulfone (Udel®) or polyetherimide (Ultem®). Polyethersulfone may also be referred to as polyarylsulfone. Polyethersulfone provides a greater margin of performance in such areas as toughness in comparison with other plastics. Polyethersulfone is available in transparent, opaque as well as filled grades. It is used for lighting fixtures, electrical and electronic components, surgical and medical devices, chemical process equipment, automotive and food service components. It is available in amber transparent and opaque colors. Figure 3.1 shows polyethersulfone chemical structure.

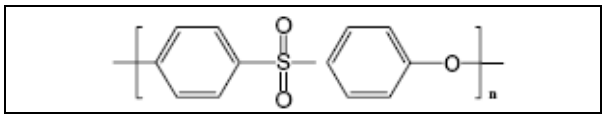


Figure 3.1: Polyethersulfone (PES) structure

Other advantages of PES are it has a high heat deflection temperature of 400°F (204°C), good hydrolytic stability, and chemical resistance to many commonly used acids and bases. Because of its advantage, PES have been applied

and used in water treatment, gas separation, medical purification, food and beverages concentration, dairy filtration, ion exchange and many more. Table 3.1 shows the properties of PES.

Table 3.1: Polyethersulfone properties

Physical Properties	**Unit**
Specific Gravity	1.37
Density	$1.37 gcm^{-3}$
Water absorption - over 24 hours	0.54%
Shear strength	57 MPa
Thermal Properties	**Unit**
Heat-deflection temperature - 1.8MPa	200°C
Thermal conductivity	$0.24\ W\ m^{-1}\ K^{-1}$
Self-ignition temperature	502°C
Oxygen Index	39%

3.1.2 Methanol

Methanol is a clear, colorless liquid with a faint odor like alcohol. The smell is not very strong and is considered a poor indicator of vapor concentration. Methanol, also known as methyl alcohol or carbinol is a chemical compound with chemical formula CH_3OH as shown in Figure 3.2. It is the simplest alcohol, and is a light, volatile, flammable and poisonous liquid with a distinctive odor. At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethyl alcohol.

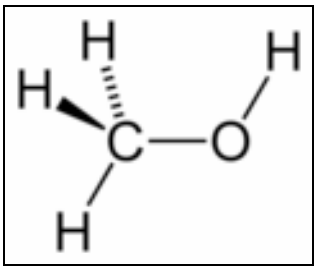


Figure 3.2: Methanol structure

Methanol is used as a solvent for lacquers, paints, varnishes, cements, inks, dyes, plastics and various industrial coatings. It is also used in the production of pharmaceuticals, formaldehyde and other chemical products. Methanol appears as an

ingredient in many products, from industrial solvents to windshield-washer fluid and nail-polish remover. It is also used as a fuel. Table 3.2 shows the properties of methanol.

Table 3.2: Pysical properties of methanol

Physical properties	Unit
Physical state	Liquid
Boiling point:	64.7 °C
Melting point:	-98 °C
Specific gravity/density:	7910 g/cm3
Solubility in water:	miscible
Vapour pressure, at 20°C:	128 mm Hg
Molecular Weight:	32.04 g/mol
Flash point:	11 °C
Auto-ignition temperature:	464 °C
Explosive limits, vol% in air: Lower Upper	6.0 36.00

3.1.3 N-Methyl-2-pyrrolidone (NMP)

N-Methyl-2-pyrrolidone (NMP) is a chemical compound with a clear to slightly yellow liquid miscible with water (molecule) and solvents like ethyl acetate, chloroform, benzene and lower alcohols or ketones. It also belongs to the class of dipolar aprotic solvents which includes also dimethylformamide, dimethylacetamide and dimethyl sulfoxide. Other names for this compound are: 1-methyl-2-pyrrolidone, *N*-methyl-2-pyrrolidinone and m-pyrrole. Figure 3.3 show the structure of NMP.

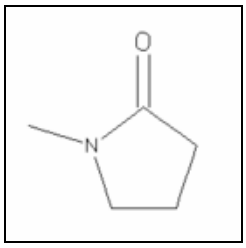


Figure 3.3: N-Methyl-2-pyrrolidone (NMP) structures

Due to its good solvency properties, it is used to dissolve a wide range of chemicals, especially in the polymers field. It also used as a solvent for surface treatment of textiles, resins and metal coated plastics or as a paint stripper. Table 3.3 shows the physical properties for NMP.

Table 3.3: N-Methyl-2-pyrrolidone physical properties

Physical Properties	Unit
Molecular weight	99.1
Density-Liquid (20°C) (40°C) (60°C)	1,030kg/m3 1,020kg/m3 990kg/m3
Boiling point (760 mm Hg)	477K
Freezing point (760 mm Hg)	249.6K
Viscosity (20°C) (50°C) (80°C)	1.7mPa-s 1.0mPa-s 0.9mPa-s
Heat of Vaporization (100°C)	510kJ/kg
Specific Heat-Liquid (0°C) (50°C) (100°C)	1.68kJ/kg-K 1.89kJ/kg-K 2.10kJ/kg-K
Specific Heat-Vapor (25°C)	1.26kJ/kg-K
Vapor Pressure (40°C) (60°C) (80°C)	133Pa 465Pa 1270Pa
Refractive Index	1.4700
Heat of Combustion	30,500kJ/kg
Flash Point (ASTM-D 93-72)	364K
Ignition Temperature (DIN 51794)	518K
Flammable limits in air: Upper Lower	9.5 vol% 1.3 vol%
Thermal conductivity (25°C)	0.163 W/m-K

3.1.4 Sulfonating Agent

3.1.4.1 Sulfuric acid

Sulfuric acid is also known as sulfuric acid (H_2SO_4), is a strong mineral acid. It was once known as oil of vitriol, and sulfuric acid has many applications, and is one of the top products of the chemical industry. It is soluble in water at all concentrations. Principal uses include ore processing, fertilizer manufacturing, oil

refining, wastewater processing, and chemical synthesis. Figure 3.4 shows the structure of sulfuric acid.

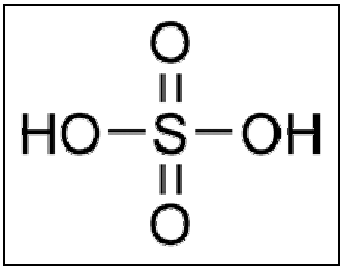


Figure 3.4: Sulfuric acid structure

Sulfuric acid also called hydrogen sulfate, is a dense, colorless, oily and corrosive liquid. Sulfuric acid is a very strong acid; in aqueous solutions it ionizes completely to form hydronium ions and hydrogen sulfate ions. In one of its most familiar applications, sulfuric acid serves as the electrolyte in lead-acid storage batteries. The properties of sulfuric acid are shown in Table 3.4.

Table 3.4: Properties of sulfuric acid

Properties	Unit
Molecular Weight	98.08 g/mole
Solubility	Easily soluble in cold water, soluble in water with liberation of much heat and soluble in ethyl alcohol.
Melting point	-35°C
Boiling point	270 - 340 °C
Vapor pressure (20 °C)	ca. 10 mbar
pH	Acidic.
Specific gravity	1.84

3.2 Research Design

The flowchart of the membranes preparation and characterization test is as shown in Figure 3.5.

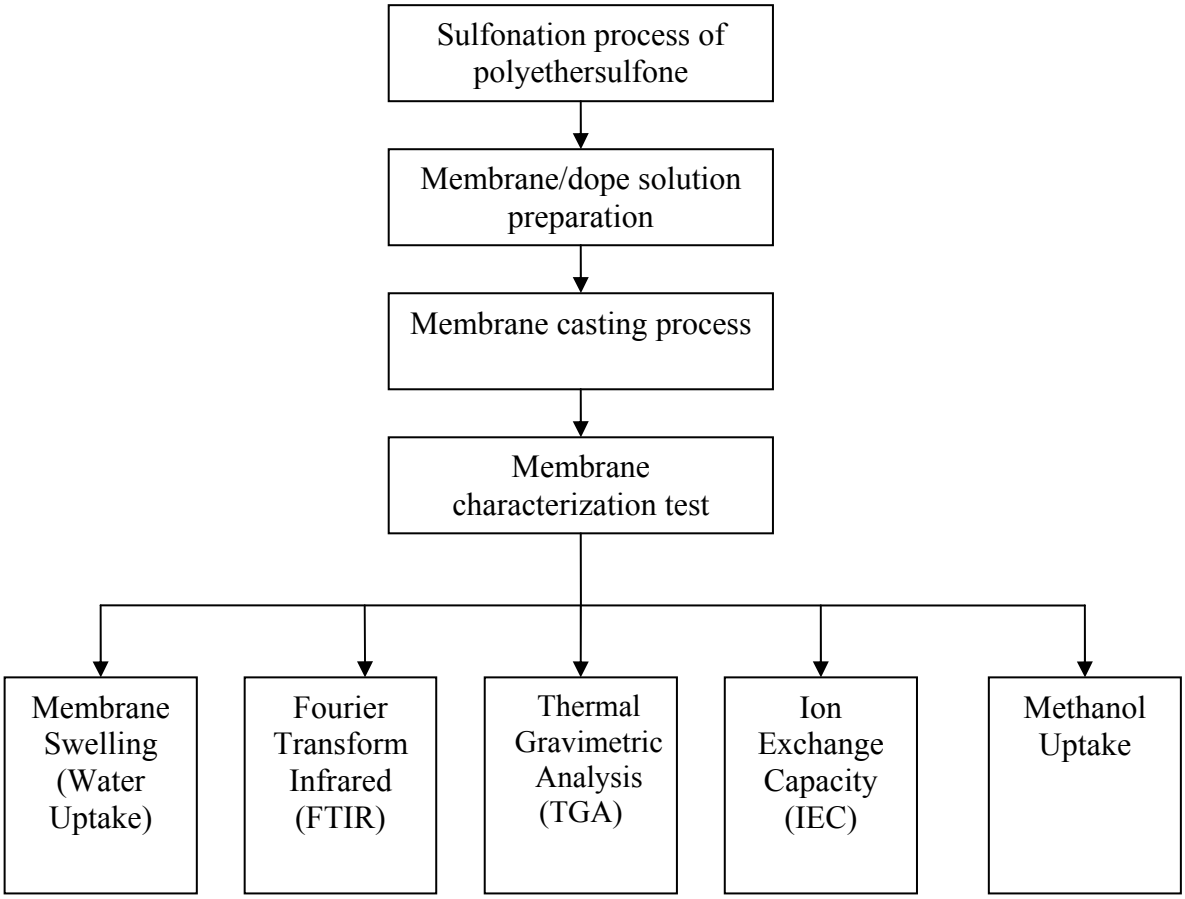


Figure 3.5: Flowchart of membranes preparation and characterization test

3.3 Sulfonated Membrane Preparation

3.3.1 Sulfonation of Polyethersulfone

The sulfonation process of polyethersulfone starts by dissolving certain amount of polyethersulfone in concentrated sulfuric acid (98%) at room temperature. The apparatus set up is shown in Figure 3.6. The solution was keep stirring for 24 hours until the polymer was completely dissolved under nitrogen condition. The solution is then cooled to room temperature, and gradually precipitated into ice-cold deionized water. The precipitated polymer recovers by filtration and washed with deionized water until the pH~6-7.

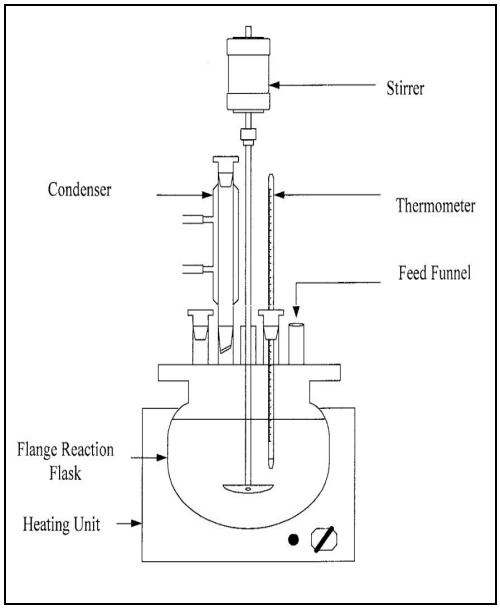


Figure 3.6: Apparatus set up for sulfonation process

3.3.2 Casting Process

Certain amount of sulfonated PES polymer was dissolved in NMP solution for several hours. The solution then poured into a glass bottle and degassed in ultrasonic bath for an hour to eliminate the bubbles. The sulfonated dope solution was poured onto a clean glass plate at room temperature and it was manually caste on a glass plate using casting knife with a gap thickness of 200 μm as shown in Figure 3.7. The glass plate with the caste film was immediately immersed in the distilled water at room temperature after casting. After a few minutes of initiating the phase inversion, a thin polymeric membrane film was separated out from the glass. The cast membranes are keep dried at 60°C for 6 hour to remove the solvents. The membrane was kept in distilled water until further membrane evaluation.

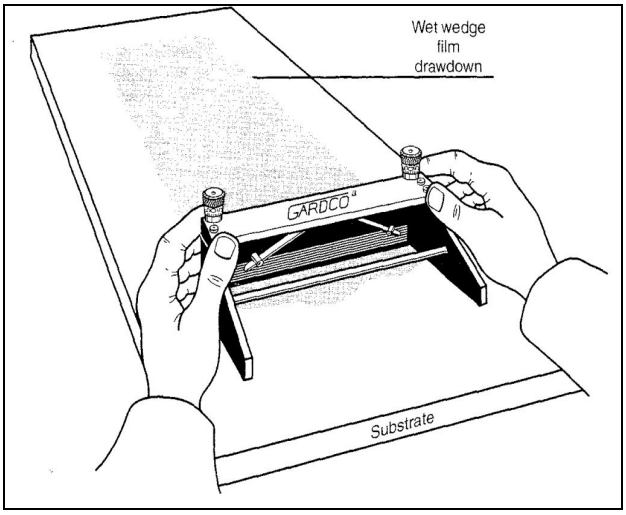


Figure 3.7: Casting process using casting knife

3.4 Membrane Characterization

3.4.1 Water and Methanol Uptake

Water uptake is conduct to check the ability of membrane to absorb water. The ability of membrane was estimate by immersion of pieces of about 0.1g of polymer films in water at 50°C during hours and weighting in analytical balance. After that, carefully dried the surface of membrane and weighted again in analytical balance (E.Parceto *et al.,* 2006).

The other way that water uptake test can be done is, the membranes were dried in an oven at 60°C for 48 h, weighed, soaked in deionized water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture, and reweighed (Li and Wang, 2006).

For methanol uptake, test can be done in methanol solution and designated as methanol uptake content. Methanol or water uptake was calculated from:

$$\text{Water / methanol uptake} = \frac{Wwet - Wdry}{Wdry}$$

Where, W_{wet} is the weight of the wet membranes and W_{dry} the weight of the dry membranes (Park and Yamazaki, 2005).

3.4.2 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

3.4.3 Fourier Transform Infrared (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra in order to trace the functional group of sulfonic acids that has been incorporated in the PES backbone. In order to trace functional group, each group has their own frequency and wavelength as shown in Table 3.5.

Table 3.5: Typical infrared absorption frequencies and wavelength

Functional Group	Characteristic Absorptions	
	Frequency (cm^{-1})	**Wavelength (μ)**
Sulfur Functions		
S-H thiols	2550-2600 (wk & shp)	3.92 - 3.84
S-OR esters	700-900 (str)	14.28 - 11.11
S-S disulfide	500-540 (wk)	20 - 18.51
C=S thiocarbonyl	1050-1200 (str)	9.52 - 8.33
S=O sulfoxide sulfone sulfonic acid sulfonyl chloride sulfate	1030-1060 (str) 1325 & 1140 (both str) 1345 (str) 1365 & 1180 (both str) 1350-1450 (str)	9.7 - 9.43 7.54 & 8.77 7.43 7.32 & 8.47 7.4 - 6.89
Silicon Functions		
Si-H silane	2100-2360 (str)	4.76 - 4.23
Si-OR	1000-11000 (str & brd)	10 - 0.9
Si-CH_3	1250 (str & shp)	8

3.4.4 Ion Exchange Capacity (IEC)

The miliequivalents of reactive $-SO_3H$ sites per gram of polymer (mmol/g) was determined theoretically by acid-base titration technique (Naim et al., 2004). One method to check the ion exchange capacity is by dissolved known amount of dry polymer (about 0.5 g) in 10 ml N,N-dimethylformamide (DMF), the released amount of H^+ was then determined by titration with a standard NaOH solution using phenolphthalein as indicator. The following equations were used to calculate the DS:

$$DS = \frac{0.232 M_{NaOH} \times V_{NaOH}}{[W - 0.08 M_{NaOH} \times V_{NaOH}]} \times 100\,\%$$

After getting the value for DS, the IEC can be calculating by using following equation:

$$IEC = \frac{1000 DS}{(232 + 81 \times DS)}$$

Where M_{NaOH} was the concentration of standard NaOH solution (mol/L), V_{NaOH} the NaOH solution volume used to neutralize (ml), W the sample mass (g), 232 the molecular weight of PES repeat unit and 81 the molecular weight of the $-SO_3H$ (Guan *et al*., 2005).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Water and Methanol Uptake

It has been known that water absorption depends on the degree of sulfonation which is the higher the degree of sulfonation, the greater the water uptake. It can be shown by Table 4.1 that the water uptake for SPES is higher compared to PES due to the corporation of hydrophobic backbone and hydrophilic sulfonic group. For the same degree of sulfonation, the values of the water uptake varies depend on the temperature.

Table 4.1: Water uptake for PES and SPES

Polymer	Degree of sulfonation (%)	Water uptake (%)
SPES	35.7	13.1
PES	-	0.3

The higher the operating temperature, the value of water uptake also increases but at certain temperature, the value starts to decreased. As shown in Table 4.2 below, the highest water uptake is at 60 ºC.

The overall reduced swelling of the composite membrane can be explained assuming that the filler induces morphological modification of the membrane and that the oxide hydration water molecules generate a connection between the polymer sulfonic acid moieties, creating different hydrophilic paths that favor proton transfer. The effect becomes negligible at higher temperature when a decrease in the

interactions between polymer chains is known to favor a greater hydration of the polymer (Mecheri et al, 2008).

Table 4.2: Water uptake for SPES at different temperature

Temperature, ºC	Degree of sulfonation (%)	Water uptake (%)
27	35.7	13.1
60	35.7	29.4
80	35.7	46.5
100	35.7	19.3

For sulfonated polyethersulfone with same degree of sulfonation, the value of methanol uptake vary depend on the concentration of the methanol. From the Table 4.3, value of methanol uptake was increased with the increment of methanol concentration. Methanol uptake increased as a function of temperature and concentration. Indicating high temperature and high concentration gradient can accelerate the mobility of methanol–water molecules by increasing swelling capacity in the membrane (Park and Yamazaki, 2005).

Table 4.3: Methanol uptake for SPES at different concentration

Concentration, M	Methanol uptake, (%)
1	14.9
3	22.3
6	26.2

4.2 Ion Exchange Capacity

The increased in water uptake of SPES membrane showed that the polymer is good in proton conductivity which is the membrane having a good water permeability properties and this allowed a high proton exchange activity too. Titration is conducted to quantitatively determine the experimental value of IEC. From the data in Table 4.4, the ion exchange capacity for SPES with 35.7 % of degree sulfonation is about 11.43 mmol/g.

Table 4.4: Ion exchange capacity for SPES

Sample	Degree of sulfonation, (%)	IEC, (mmol/g)
1	35.1	11.41
2	35.6	11.43
3	36.4	11.45
Average	35.7	11.43

4.3 Thermo Gravimetric Analysis (TGA)

The thermal stabilities of the SPES and PES were determined by thermo gravimetric analysis. Figure 4.1 showed the degradation curves of PES and SPES. The parent of PES is a thermal stable polymer with only one sharp weight loss that was described to the decomposition of polymer main chain at 500 ºC (Guan *et al*, 2005). For the SPES membrane, three transition of weight loss in three separate temperature range can be observed in the TGA curve. The first curve at around 50 ºC is related to the desorption of water bonded to the sulfonic acid group followed by the curve at around 500 ºC which could describe the decomposition of the sulfonic acid group. The third thermal degradation curves illustrated the degradation of the polymer main chain which occurred around 550 ºC. The region between 50 to 600 ºC was observed because at temperature higher than 600 ºC, the decomposition of the sulfonated polymer will occurred.

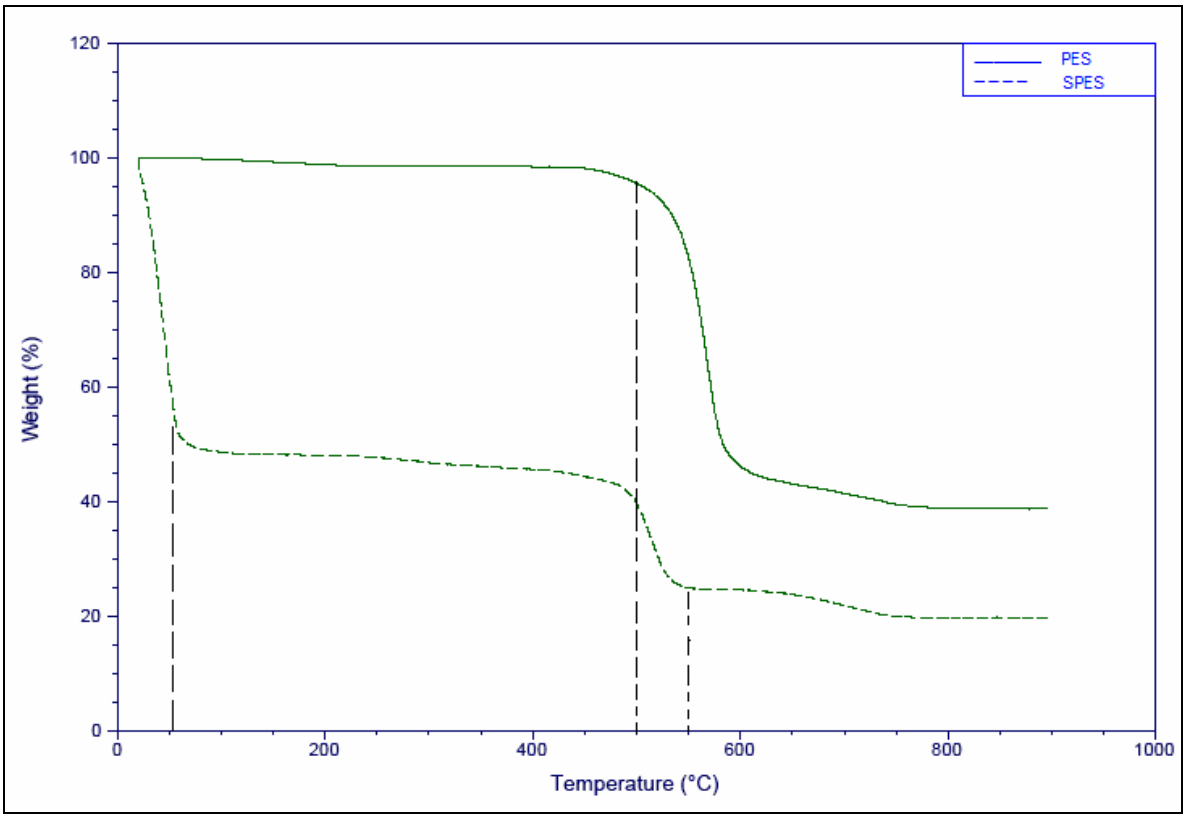


Figure 4.1: TGA curves for PES and SPES

4.4 Fourier Transform Infrared (FTIR)

Infrared spectroscopy was conducted in order to check whether the sulfonation process is successful or not. The sulfonic group can be observed at 1033cm^{-1} as shown in Figured 4.2. The asymmetric stretching vibration band of the sulfonic group can be observed at 1113cm^{-1}. The presence of sulfonic group in the modified polymer is thus ascertained.

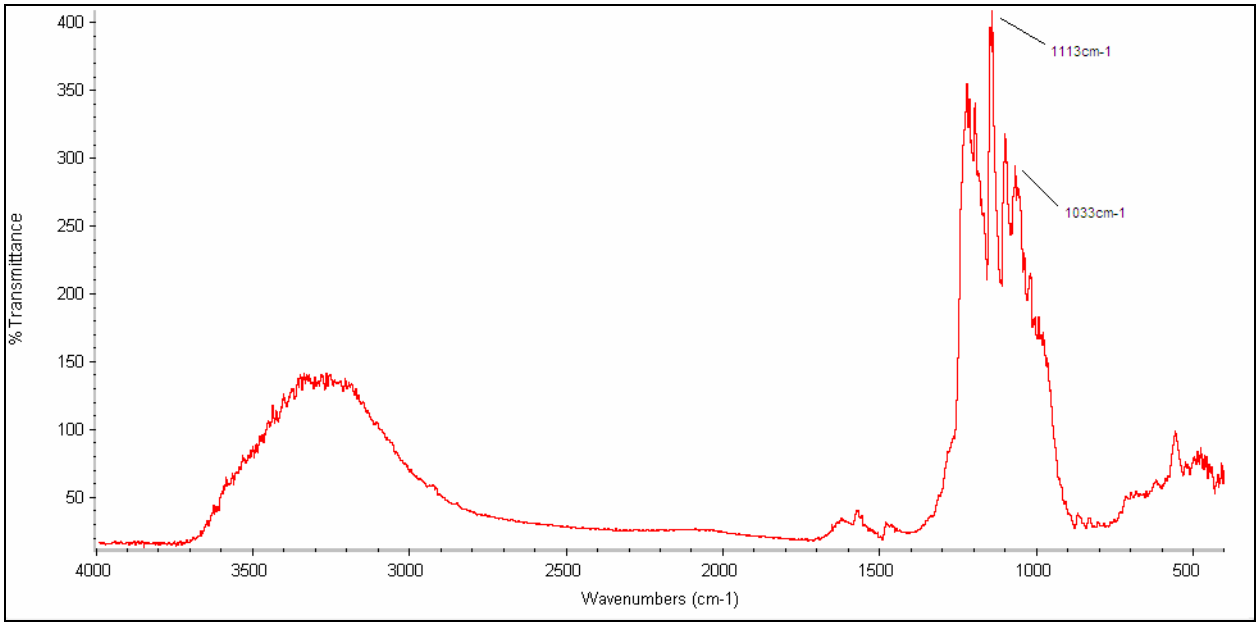


Figure 4.2: FTIR spectra of SPES

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Sulfonation of polyethersulfone (PES) was conducted with sulfuric acid as a sulfonating agent. The sulfonation of SPES was confirmed by FTIR. Membranes prepared from SPES showed lower decomposition of temperature. With the same degree of sulfonation, the water uptake of SPES is higher compared to the sulfonated poly(ether ether ketone), SPEEK that had been study by Jaafar *et al.,* (2007). Methanol uptake gave good result as absorption of methanol is increasing due to the concentration. However, the water uptake of SPES is lower compared to the Nafion 115 which is having 32% of water uptake (Li and Wang, 2006). SPES membrane shows good properties as candidates to be use as an electrolyte for fuel cell application especially for DMFC. Results of this study proved SPES are the potential membrane material for direct methanol fuel cell.

5.2 Recommendation

In order to further improve the performance of SPES in this study, following recommendation was drawn.

1. Another sulfonating agent can be use or using two type of sulfonating agent with different volume to get different degree of sulfonation.

2. The experiment can also be done by varying the reaction time to investigate the performance of membrane with different time reaction.

3. The experiment can also be done by preparing two type of membrane with different polymer and compare their characteristic to determine the best choice of membrane's material for fuel cell.

REFERENCES

Appleby A.J. and Foulkes F.R, (2004). *Fuel Cell Handbook*. 7th ed. EG&G Technical Services, Inc.

Ani Idris and Norashikin Mat Zain, (2006). Jurnal Teknologi © Universiti Teknologi Malaysia, *Effect of Heat Treatment on the Performance and Structural Details of Polyethersulfone Ultrafiltration Membranes.* 44(F): 27–40

Bae J.-M, Honma I, Murata M, Yamamoto T, Rikukawa M, and Ogata N, (2002). Solid State Ionics. *Properties of Selected Sulfonated Polymers as Proton-conducting Electrolytes for Polymer Electrolyte Fuel Cells.* 147: 189–194

Barbara Mecheri, Alessandra D'Epifanio, Enrico Traversa and Silvia Licoccia, (2008). Journal of Power Sources. *Sulfonated Polyether Ether Ketone and Hydrated Tin Oxide Proton Conducting Composites for Direct Methanol Fuel Cell Applications.* 178: 554-560.

BASF Corporation. (1998). *N-Methylpyrrolidone Storage and Handling.* Mount Olive, NJ: NMP Brochure.

Blanco J.F, Nguyen Q.T, Schaetzel P, (2001). Journal of Membrane Science. *Novel Hydrophilic Membrane Materials: Sulfonated Polyethersulfone Cardo.* 186: 267–279

Cristie Geankoplis (2003). *Transport Processes and Separation Process Principle*. 2nd ed. Prentice Hall PTR.

Danmin Xing, Huamin Zhang, Liang Wang, Yunfeng Zhai, and Baolian Yi, (2007). Journal of Membrane Science. *Investigation of the Ag-SiO2/sulfonated Poly (biphenyl ether sulfone) Composite Membranes for Fuel Cell*. 296: 9–14

Ethel Parceto, Rafael Herrera, Suzana P. Nunes (2006). Journal of Membrane Science. *Phosphonated and Sulfonated Polyphenylsulfone membranes for Fuel Cell Application*. 285: 206-213

Hua Dai, Rong Guan, Cuihua Li, Jianhong Liu, (2007). Solid State Ionics. *Development and Characterization of Sulfonated Poly(ether sulfone) for Proton Exchange Membrane Materials.* 178: 339–345

Jaafar J, Ismail A.F, and Mustafa A. (2007). Materials Science and Engineering. *Physicochemical Study of Poly(ether ether ketone) Electrolyte Membranes Sulfonated with Mixtures of Fuming Sulfuric Acid and Sulfuric Acid for Direct Methanol Fuel Cell Application*. 460–461: 475–484

Jeong-Pil Shin, Bong-Jun Chang, Jeong-Hoon Kim, Soo-Bok Lee, and Dong Hack Suh (2005). Journal of Membrane Science. *Sulfonated Polystyrene/PTFE Composite Membranes.* 251: 247–254

Lei Li and Yuxin Wang (2006). Journal of Power Sources. *Proton Conducting Composite Membranes from Sulfonated Polyethersulfone Cardo and Phosphotungstic Acid for Fuel Cell Application.* 162: 541–546

Mark C. Williams, (2000). *Fuel Cell Handbook*. 2nd ed. Science Applications International Corporation: EG&G Services Parsons, Inc.

Naim R, Ismail A. F, Saidi H and Saion E. (2004). Development of Sulfonated Polysulfone Membranes as a Material for Proton Exchange Membrane (PEM). Regional Symposium on Membrane Science and Technology 2004*, 21-25 April 2004. Universiti Teknologi Malaysia Institutional Repository: Universiti Teknologi Malaysia, 1-17*

Nasef M.M, Saidi H, Mohd Nor H and Ooi M.F, (2000). Journal of Applied Polymer Science. *Proton Exchange Membranes Prepared by Simultaneous Radiation Grafting of Styrene onto Poly(tetrafluoroethylene-co-hexafluoropropylene) Films. II. Properties of Sulfonated Membranes.* 78: 2443– 2453

Richard W. Baker (2004). *Membrane Technology and Applications*. 2nd ed. Menlo Park, California: John Wiley & Sons, Ltd.

Rong Guan, Hua Zou , Deping Lu, Chunli Gong, and Yanfang Liu, (2005). European Polymer Journal. *Polyethersulfone Sulfonated by Chlorosulfonic Acid and Its Membrane Characteristics.* 41: 1554-1560

Sakari T, Takenata H, Wakabayashi N, Kawami Y, and Tori K. (1985). J. Electrochem. Soc. *Gas Permeation Properties of SPE membranes*. 132:1328

Sciencelab.com, Inc. Material Safety Data Sheet, *Dimethylacetamides MSDS* International Programme on Chemical Safety and the European Commission© IPCS 2006

Shen LQ, Xu ZK, Yang Q, Sun HL, Wang SY, Xu YY,(2004). J Appl Polym Sci *Preparation and Characterization of Sulfonated Polyetherimide /polyetherimide Blend Membranes*. 92: 1709.

Smitha B, Sridhar S and Khan A.A (2005). Journal of Membrane Science. *Solid Polymer Electrolyte Membranes for Fuel Cell Application- a review.* 259: 10-26

Susai T, Kaneko M, Nakatoa K, Isono T, Hamada A, and Miyake Y, (2001). Int. J. Hyd. Energy. *Optimization of Proton Exchange Membranes and the Humidifying Conditions to Improve Cell Performance for Polymer Electrolyte Membranes*. 26:631-637

Young-Sun Park, and Yohtaro Yamazaki (2005). Journal of Membrane Science. *Low Water Uptake Content and Low Water/Methanol Transport in CP/Nafion Hybrid Membrane with High Non-hydrogen Bonding.* 261: 58–66

Zubir N.A, Ismail A.F, Nasef M.M and Dahlan K. Z. M. (2004). Physico-chemical Study of Sulfonated Polystyrene Pore-filled Electrolyte Membranes by Electrons Induced Grafting. *Regional Symposium on Membrane Science and Technology 2004*, 21-25 April 2004. Universiti Teknologi Malaysia Institutional Repository: Universiti Teknology Malaysia, 1-11

Zubir N.A, Ismail A.F, Nasef M.M and Dahlan K. Z. M. and Saidi H. (2004). Sulfonated Polystyrene Pore-Filled Electrolytes Membranes By Electrons Induced Grafting Of Styrene Into PTFE Films: Thermal Stability and Structural Investigation. *Regional Symposium on Membrane Science and Technology 2004*, 21-25 April 2004. Universiti Teknologi Malaysia Institutional Repository: Universiti Teknologi Malaysia, 1-11

APPENDIX A

Calculation for water and methanol uptake:

$$\text{Water uptake} = \frac{Wwet - Wdry}{Wdry}$$

For SPES at 27 °C:

Sample	$Wdry$, (g)	$Wwet$, (g)	Water uptake, (%)
1	0.067	0.075	11.94
2	0.117	0.133	13.66
3	0.08	0.091	13.75
Average			13.1

Sample 1: $$\text{Water} = \frac{0.075 - 0.067}{0.067} \times 100\%$$

$$= 11.94\%$$

Sample 2: $$\text{Water} = \frac{0.133 - 0.117}{0.133} \times 100\%$$

$$= 13.66\%$$

Sample 3: $$\text{Water} = \frac{0.091 - 0.080}{0.080} \times 100\%$$

$$= 13.75\%$$

For SPES at 60 °C:

Sample	$Wdry$, (g)	$Wwet$, (g)	Water uptake, (%)
1	0.34	0.44	29.41
2	0.38	0.48	26.32
3	0.40	0.53	32.50
Average			29.41

Sample 1: $$\text{Water} = \frac{0.44 - 0.34}{0.34} \times 100\%$$
$$= 29.41\%$$

Sample 2: $$\text{Water} = \frac{0.48 - 0.0.38}{0.38} \times 100\%$$
$$= 26.32\%$$

Sample 3: $$\text{Water} = \frac{0.53 - 0.40}{0.40} \times 100\%$$
$$= 32.50\%$$

For SPES at 80 °C:

Sample	$Wdry$, (g)	$Wwet$, (g)	Water uptake, (%)
1	0.51	0.75	47.05
2	0.49	0.74	51.02
3	0.46	0.66	41.30
Average			46.46

Sample 1: $$\text{Water} = \frac{0.75 - 0.51}{0.51} \times 100\%$$
$$= 47.05\%$$

Sample 2: $$\text{Water} = \frac{0.74 - 0.49}{0.49} \times 100\%$$
$$= 51.02\%$$

Sample 3: $$\text{Water} = \frac{0.66 - 0.46}{0.46} \times 100\%$$

$$= 41.30\%$$

For SPES at 100 °C:

Sample	*Wdry* , (g)	*Wwet* , (g)	Water uptake, (%)
1	0.27	0.32	18.51
2	0.30	0.36	20.00
3	0.26	0.31	19.23
Average			19.25

Sample 1: $$\text{Water} = \frac{0.32 - 0.27}{0.27} \times 100\%$$

$$= 18.51\%$$

Sample 2: $$\text{Water} = \frac{0.36 - 0.30}{0.30} \times 100\%$$

$$= 20.00\%$$

Sample 3: $$\text{Water} = \frac{0.31 - 0.26}{0.26} \times 100\%$$

$$= 19.23\%$$

$$\text{Methanol uptake} = \frac{Wwet - Wdry}{Wdry}$$

For SPES at 1M methanol:

Sample	$Wdry$, (g)	$Wwet$, (g)	Methanol uptake, (%)
1	0.323	0.357	10.50
2	0.272	0.296	8.80
3	0.228	0.860	25.44
Average			14.91

Sample 1: Methanol $= \frac{0.357 - 0.323}{0.323} \times 100\%$

$= 10.50\%$

Sample 2: Methanol $= \frac{0.296 - 0.272}{0.272} \times 100\%$

$= 8.80\%$

Sample 3: Methanol $= \frac{0.860 - 0.228}{0.228} \times 100\%$

$= 25.44\%$

For SPES at 3M methanol:

Sample	$Wdry$, (g)	$Wwet$, (g)	Methanol uptake, (%)
1	0.216	0.299	28.40
2	0.212	0.244	15.09
3	0.233	0.288	23.61
Average			22.37

Sample 1: Methanol $= \frac{0.299 - 0.216}{0.216} \times 100\%$

$= 28.40\%$

Sample 2: Methanol $= \frac{0.244 - 0.212}{0.212} \times 100\%$

$= 15.80\%$

Sample 3: Methanol $= \frac{0.288 - 0.233}{0.288} \times 100\%$

$= 23.61\%$

For SPES at 6M methanol:

Sample	$Wdry$, (g)	$Wwet$, (g)	Methanol uptake, (%)
1	0.65	0.80	23.07
2	0.68	0.86	26.47
3	0.69	0.89	28.98
Average			26.18

Sample 1: Methanol $= \frac{0.80 - 0.65}{0.65} \times 100\%$

$= 23.07\%$

Sample 2: Methanol $= \frac{0.86 - 0.68}{0.68} \times 100\%$

$= 26.47\%$

Sample 3: Methanol $= \frac{0.89 - 0.69}{0.69} \times 100\%$

$= 28.98\%$

APPENDIX B

Calculation for degree of sulfonation:

$$DS = \frac{0.232M_{NaOH} \times V_{NaOH}}{[W - 0.08M_{NaOH} \times V_{NaOH}]} \times 100\,\%$$

M_{NaOH}= 0.05M

Sample	W, (g)	V_{NaOH}, (%)	Degree of sulfonation, (%)
1	0.500	13.5	35.1
2	0.410	11.2	35.6
3	0.405	11.3	36.4
Average			35.7

$$DS = \frac{0.232(0.05) \times 13.5}{[0.5 - 0.08(0.05) \times 13.5]} \times 100\,\%$$

$$= 35.1\%$$

$$DS = \frac{0.232(0.05) \times 11.2}{[0.41 - 0.08(0.05) \times 11.2]} \times 100\,\%$$

$$= 35.6\%$$

$$DS = \frac{0.232(0.05) \times 11.3}{[0.405 - 0.08(0.05) \times 11.3]} \times 100\,\%$$

$$= 36.4\%$$

APPENDIX C

Calculation for ion exchange capacity:

$$IEC = \frac{1000DS}{(232 + 81 \times DS)}$$

Sample	Degree of sulfonation, (%)	IEC, (mmol/g)
1	35.1	11.41
2	35.6	11.43
3	36.4	11.45
Average	35.7	11.43

$$IEC_1 = \frac{1000(35.1)}{(232 + 81 \times 35.1)}$$

$$= 11.41$$

$$IEC_2 = \frac{1000(35.6)}{(232 + 81 \times 35.6)}$$

$$= 11.43$$

$$IEC_3 = \frac{1000(36.4)}{(232 + 81 \times 36.4)}$$

$$= 11.45$$