

**PREPARATION AND CHARACTERIZATION OF PROTON
EXCHANGE MEMBRANE (PEM) USING POLYSTYRENE
PRECURSORS**

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**FACULTY OF ENGINEERING
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ABSTRACT

In the present dissertation, proton exchange membrane (PEM) was prepared by using virgin polystyrene and polymeric waste precursors. The adopted sulfonation followed an open and reflux conditions in the presence of dichloroethane and chloroform respectively. Thus the obtained sulfonated polystyrene (SPS) were utilized for the membrane casting using suitable solvents. Concentrated sulfuric acid and freshly prepared acetyl sulfate was employed as sulfonating agent for open and reflux methods respectively. The membrane casting was carried out with and without isolating the sulfonated polystyrene. The zeolite was chosen as an inorganic additive. The synthesized membranes were characterized with Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) to identify the $-SO_3H$ functional group attached onto the polymer membrane, thermal stability and surface morphology. The membranes were further examined for their water uptake capacity, swelling behavior and degree of sulfonation. In addition, the crucial performance of the fabricated PEM was scrutinized by experimenting ion exchange capacity (IEC) and proton conductivity analysis. The performed FTIR analysis elucidated the presence of sulfonic and other functional groups in the prepared samples. Further analysis of the degree of sulfonation confirmed the level of sulfonation achieved. The membranes fabricated through an open sulfonation (OS) route exhibited greater swelling characteristics than that of the other samples. The sulfonation via reflux condition using chloroform without zeolite (RCC) and with the inclusion of zeolite (RCC-Z) equivalently displayed good thermal and surface properties. The inclusion of zeolite reduced the water uptake that lead to a less swelling and greater mechanical stability than the one prepared without zeolite. The membranes casted in similar reflux condition

but using waste polystyrene as precursor demonstrated good stability towards hydrated condition. The ion exchange capacity of RCC and RCC-Z was found to be 0.030 meq/g and 0.170 meq/g, where else the one obtained using waste PS with varied acetyl sulfonate volume (1 mL and 5 mL) displayed value of 0.220 and 0.536 meq/g respectively. The proton conductivity of the membrane surged by the inclusion of the zeolite (1.11×10^{-5} S/cm), meanwhile the proton conductivity of membrane fabricated through the waste PS with varied acetyl sulfonate volume (1 mL and 5 mL) exhibited an value of 2.03×10^{-6} S/cm and 6.07×10^{-6} S/cm respectively. The present study disclosed the prospective of waste polymers and its obtained inherent properties endorsed its feasibility towards preparation of PEM that outfits fuel cell applications.

ABSTRAK

Kajian ini adalah mengenai “proton exchange membrane” (PEM) yang disediakan dari bijih polistirena dan polimer terbuang sebagai bahan utama. Proses sulfonikasi dijalankan melalui kaedah sulfonikasi terbuka dan refluks dengan kehadiran bahan pelarut seperti dikloroetana dan klorofom. Proses sulfonikasi menghasilkan polistirena sulfon (SPS) yang akan digunakan untuk menghasilkan membran dengan menggunakan bahan pelarut yang sesuai. Asid sulfurik pekat dan asetil sulfat yang baru disediakan digunakan sebagai agen sulfonikasi untuk kaedah sulfonikasi terbuka dan refluks. Proses pembentukan membran dijalankan dengan mengasingkan dan tanpa mengasingkan terlebih dahulu polistirena sulfonat. Zeolite dipilih sebagai bahan tambahan di dalam salah satu membran yang dihasilkan. Membran yang dihasilkan dianalisis menggunakan “Fourier transform infrared” (FT-IR), “thermogravimetric analysis” (TGA), “field emission scanning electron microscope” (FESEM) dan “atomic force microscopy” (AFM) untuk mengenalpasti kumpulan berfungsi $-SO_3H$ yang dipercayai melekat pada polimer membran, kestabilan termal dan morfologi permukaan. Membran yang dihasilkan kemudian diperiksa dari segi kapasiti pengambilan air, “swelling behavior” dan “degree of sulfonation”. Analisa yang sangat penting bagi PEM ialah kapasiti pertukaran ion (IEC) dan analisis proton kekonduksian. Analisa FT-IR menjelaskan kehadiran ion sulfonik dan kumpulan berfungsi lain yang terdapat di dalam sampel membran yang disediakan. Analisa proton kekonduksian memastikan tahap sulfonikasi yang dicapai. Membran yang dihasilkan melalui kaedah sulfonikasi terbuka (OS) menghasilkan ciri-ciri pengembangan yang lebih berbanding sampel lain. Membran yang dihasilkan melalui kaedah sulfonikasi secara refluks (RCC) tanpa kehadiran zeolite dan dengan kehadiran zeolite (RCC-Z) menunjukkan keadaan termal dan ciri-ciri permukaan yang baik. Penambahan zeolite juga membantu dalam

mengambil air dalam kapasiti tertentu yang menjadikan proses pengembangan terkawal seterusnya tidak menjejaskan kestabilan mekanik dan ciri-ciri membran yang lain berbanding membran yang dihasilkan tanpa penambahan zeolite. Kemudian, membran dihasilkan melalui kaedah refluks tetapi menggunakan polistirena terbuang sebagai bahan utama menunjukkan kestabilan yang baik terhadap keadaan terhidrat. IEC bagi membran RCC dan RCC-Z masing-masing iaitu 0.030 meq/g dan 0.170 meq/g, manakala membran yang dihasilkan melalui polistirena terbuang dengan jumlah asetil sulfat berbeza yang digunakan (1 mL dan 5 mL) menghasilkan IEC masing-masing 0.220 meq/g dan 0.536 meq/g. Kekonduksian proton paling tinggi bagi membran dengan zeolite (1.11×10^{-5} S/cm) manakala membran yang dihasilkan daripada polistirena terbuang masing-masing menunjukkan kekonduksian proton iaitu 6.07×10^{-6} S/cm dan 2.03×10^{-6} S/cm. Kajian ini menunjukkan perkembangan positif bagi tujuan penggunaan polistirena terbuang sebagai bahan utama di dalam penyediaan PEM yang akan digunakan di dalam aplikasi sel bahan api.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols/Abbreviations	Meanings
ac	alternating current
ACNF	activated carbon nanofiber
AFC	alkaline fuel cell
AFM	atomic force microscopy
C=C	alkene groups (carbon double bond)
C=O	amide groups
C-H	carbon - hydrogen
C-N	amine groups
C ₈ H ₈	styrene monomer
C _{NaOH}	concentration of NaOH
dc	direct current
DCE	dichloroethane
DS	degree of sulfonation
DI	distilled
DMFC	direct methanol fuel cell
EIS	electrochemical impedance spectroscopy
EPS	extended polystyrene
FC	fuel cell
FESEM	field emission scanning electron microscope
FTIR	fourier transform infrared
H ⁺	proton
HIPS	high impact polystyrene
HNMR	proton magnetic resonance
IEC	ion exchange capacity
LiClO ₄	lithium perchlorate
MCFC	molten carbonate salt electrolyte fuel cell
MEAs	membrane electrode assemblies
M _n	number-average molecular weight
M _{monomer}	molecular weight of the monomer
M _{sulfonic group}	molecular weight of sulfonic group

M_w	weight-average molecular weight
Na^+	sodium ion
NT/PANI	polyaniline carbon nanotubes composite
OS-A	open sulfonation (non-reflux condition) - acetone
OS-M	open sulfonation (non-reflux condition) – methyl ethyl ketone
O-H	alcohol groups
PBI/ H_3PO_4	phosphoric acid-doped polybenzimidazole
PEEK	poly(ether ether ketone)
PEMFC	proton exchange membrane fuel cell
PFI	perfluorinated ionomer
PGSE	Field gradient spin-echo
polySEPS	poly(styrene-isobutylene-styrene) triblock copolymer
PP	polypropylene
PS	polystyrene
PPy-CNTRs	polypyrrole-coated carbon nanotubes
PTFE	polytetrafluoroethylene
PW	polystyrene waste
PW-U	polystyrene waste – unheated during membrane casting
PW-H	polystyrene waste – heated during membrane casting
R	membrane resistance
RCC	reflux condition using chloroform
RCC-Z	reflux condition using chloroform – addition of zeolite
RCD-1	reflux condition using dichloroethane – add 1 ml of acetyl sulfate
RCD-5	reflux condition using dichloroethane – add 5 ml of acetyl sulfate
R_{cell}	resistance of cell
$R_{membrane}$	resistance of membrane
R_{total}	resistance of system
S	surface area
SAXS	small angle x-ray scattering
SEM	scanning electron microscopy
SiO_2	silicon oxide
SO_3^-	sulfonic acid ion
SO_3H	sulfonic acid molecule

SOFC	solid oxide fuel cell
SPEEK	sulfonated poly(ether ether ketone)
SPS	sulfonated polystyrene
sSBES	sulfonated polystyrene-(ethylene-butylene)-styrene triblock
S-O	sulfur – oxygen
S=C	Sulfonyl chloride groups
S=O	sulfate groups
T	membrane thickness
TGA	thermogravimetric analysis
TiO ₂	titanium dioxide
UV	ultraviolet
V	voltage
V _{NaOH}	volume of NaOH
W _{wet}	weight taken when the membrane in wet condition
W _{dry}	weight taken when the membrane in dry condition
XRD	x-rays diffraction
ZrO ₂	zirconium dioxide
σ	proton conductivity
λ_w	hydration number
Σ	proton conductivity

CHAPTER 1:

INTRODUCTION

1.1 Introduction

Fossil fuel, a well-known non-renewable energy takes millions of years for its formation. Since its discovery, the utilization rate of fossil fuel increases every day and the available reserve depletes rapidly with an alarming rate. Most of the energy related activities across the planet is depend on the availability of fossil fuel. Thus the search of renewable or alternative energy sources has to been initiated well before few decades. These include solar energy, wind power, geothermal, hydro and fuel cell. Though most of these alternative technologies are pollutant-free, fuel cell emerges as a more superior option over the others due to the zero or near-zero emissions, zero moving parts and achieve higher efficiencies at small scale over the rest. Before understanding its limitations, one must know the basics of fuel cell technology.

A fuel cell (FC) is a device that converts the chemical energy from fuel into electrical energy through the reaction of chemical with oxygen or any other oxidizing agent (Khurmi *et al.*, 2013). The example of FC device is presented in Fig. 2.1. The FC technology has high potential to be an emission-free, quiet, high energy efficiency, highly promising alternative energy for future needs and environmental friendly (Aini *et al.*, 2012). Many types of fuel cell are discovered such as alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC), molten carbonate salt electrolyte fuel cell (MCFC), solid oxide fuel cell (SOFC) (Win *et al.*, 2008; Peighambardoust *et al.*, 2010; Ye *et al.*, 2012).

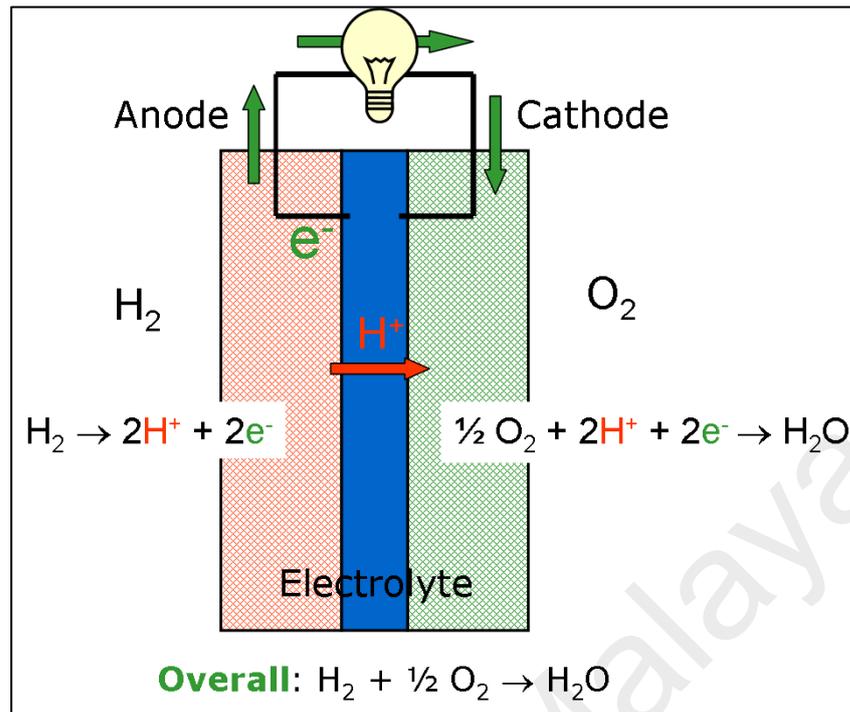


Figure 2.1: Fuel cell device

(<http://addis.caltech.edu/research/FCs%20for%20sustain%20energy.html>)

The type of FC is determined based on the membrane employed in the reactor. Henceforth the membrane becomes one of the major functionality of the FC system. Proton exchange membrane (PEM) is a type of membrane used in PEMFC. PEM usually made by using polymers which have potential as proton conductor. The types of polymers which has potential for PEM synthesis is polystyrene (Bae *et al.*, 2003; Abdulkareem *et al.*, 2010; Mulijani *et al.*, 2014), polybenzimidazole (Glipta *et al.*, 1997) and poly (styrene-isobutylene-styrene) triblock copolymers (Elabd *et al.*, 2004). The polymer base material is sulfonated with sulfur containing compound. The sulfonic acid group is attached onto the polymer during sulfonation process. The presence of sulfonic acid changes the properties of polystyrene from insulator to conductor. The source of sulfonic acid is from sulfuric acid and acetyl sulfate. The successfulness of sulfonation process is confirmed by performing membrane characterization. This will further explained in Chapter 2 and Chapter 3.

The main function of PEM is to transport proton from anode chamber to cathode chamber. The proton transport mechanism is very complex (Lee *et al.*, 2005) and it has been explained in Chapter 2 Section 2.4. Additionally, it separates the anode and cathode to avoid the mixing of fuel and oxidant (Hickner *et al.*, 2004). The focus of this present study is on the transportation of proton through PEM.

This present study contains the development of polystyrene waste from cup lids as PEM base material. This is due to many of the plastics that are available in the market and household usage is made from polystyrene. The concern is to reduce the increasing of polymer waste in the environment. The waste polystyrene is non-degradable and the rising amount of it gives harm to human, animals and environment. The use of polystyrene waste also helps to reduce the cost of PEM production. However, the waste polystyrene that are available in the market do not formulated by hundred per cent polystyrene. The additive varied from one product to another. To reduce the chances of having problems during the synthesis and analysis the waste polystyrene is standardized taken from cup lids. The membrane was first synthesis by using polystyrene beads that are available in the market. This is the fundamental research as to compare with the membrane synthesis by using polystyrene waste.

The fundamental properties of synthesis PEM must be high in proton conductivity, low electronic conductivity, low permeability to fuel and oxidant, low water transport through diffusion and electro-osmosis, oxidative and hydrolytic stability, good mechanical properties, cost and capable to fabricate into membrane (Hickner *et al.*, 2004). The main parameters that have being analysed in PEM synthesis is proton conductivity, water uptake and ion exchange capacity. These three parameters determine the efficiency of PEM in FC applications. The values of these parameters strongly depend on the presence of sulfonic acid in PEM (Hickner *et al.*, 2004). The optimum amount of sulfonic acid attach onto the polymer produces good quality

membrane. The optimum amount of sulfonic acid can be determined based on the result shown by proton conductivity, water uptake and ion exchange capacity. The proton conductivity, water uptake and ion exchange capacity is enhanced by both selective methods and materials during membrane synthesis. The experiment started by deciding which materials and methods need to follow to achieve the objectives highlighted. The methods were then drafted. The work focuses on the amount of starting material, amount of solvent, types of solvent, sulfonation time and the addition of inorganic material. To make the work going smoothly some of the variables are kept constant. The detailed of membrane synthesis and materials is reported in Chapter 3.

The addition of composite material which is zeolite as organic filler helps in increasing the affinity of membrane toward water molecules and enhances the fuel cell performance. The example of zeolite is chabazite and clinoptilolite (Tricoli *et al.*, 2003). The presence of zeolite in PEM is proven increases the proton conductivity based on the result performed in Chapter 4 Section 4.34. Other types of inorganic materials present in PEM are silica, zirconia and titania (Yu *et al.*, 2013).

1.2 Problem statement

Nafion[®] a well predicated commercial PEM employed dominantly for most fuel cell applications. This type of membrane emerged as good candidate owing to its higher proton transfer ability between the electrodes. The higher proton transfer results in enriched efficiency of the electrical output of the system. However, it is expensive and its production contributes many environmental issues. Apart from that, it also has the following disadvantages: leakage from anode to cathode, substrate losses, cation transport, accumulation rather than protons, biofouling of the membrane (Chae *et al.*, 2008) and poor barrier to methanol crossover (Liu *et al.*, 2014). In order to find an

alternative for Nafion[®] many variant of PEM membrane has been developed with varied polymeric sources. However there are still great voids in achieving a membrane with proton conductivity comparable to that of Nafion[®]. Till date virgin polystyrene was considered as the one of the potential styrene based precursor for casting PEM. These polystyrene finds numerous applications in day to day life and resulted in plastic waste generation.

Plastic is well known as non-degradable waste and expected to take over 100 years to decompose. The present available microorganism lacks the metabolism to break the plastic polymer molecules due to complexity of the polymer chain. Alternatively the available simple thermal treatment contribute for the complex unsolvable air pollution issue by releasing harmful gasses like hydrogen cyanide, hydrogen chloride and sulfur dioxide into the atmosphere. Hence it is a serious matter of what will happen if these plastic wastes keep accumulating in the planet. Though dumping into the landfill is practised for years it is an interim solution rather than enduring one. Recycling is the best way of reducing the polymer waste from giveaway the detrimental effects to the environment. Besides, it will also reduce the cost of raw materials and production cost of the commodity. The good effect of using polystyrene waste as material for synthesis is to keep the environment safe by reducing plastic waste. Hence the present study is directed towards the synthesis of PEM using polystyrene waste.

1.3 Objectives

The key objective of the present thesis is to study the feasibility of developing PEM from waste polystyrene materials. This is achieved by adopting the following specific objectives:

- **Preparation:** Synthesizing PEM using polymer beads and waste polystyrene under different sulfonation condition
- **Experimental condition and process parameters:** Exploring the effect of reflux condition, degree of sulfonation, influence of solvents, inclusion of zeolite on the characteristics of membrane.
- **Applicability:** Understanding the proton conductivity of the development membrane that suits FC applications.

1.4 Thesis Overview

Chapter 1 starts with the introduction on the fuel cell and its necessary. This is followed by an introductory note on the role of proton exchange membrane (PEM) in FC applications and the constraints posed by the commercial membrane Nafion[®]. The problems related to the waste plastics were discussed and from there the specific research hypotheses were identified. The chapter ends with the scope and precise objectives with explicit steps.

Chapter 2 furnishes the literature survey relevant to the thesis. In the inception, the chapter elaborates the background of the FC, development of electrodes and membranes. The chapters deliberate on the various types of PEM obtained by the various researchers along with its characteristics. It gives overview of contribution towards the development PEM for FC applications.

Chapter 3 outlines the detailed preparation steps adopted in obtaining the PEM under different process conditions like degree of sulfonation, influence of solvents, effect of zeolite and etc. The experimental procedures adopted for understanding the various materials and physical, electrochemical characteristics of the prepared membrane are elaborated.

Chapter 4 presents the outcome of the thesis findings with comprehensive discussions. The conclusions and recommendations are included in **Chapter 5**.

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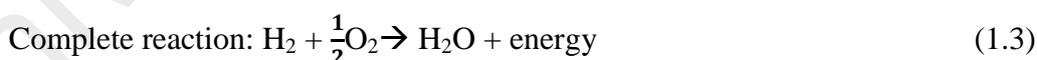
CHAPTER 2:

LITERATURE REVIEW

2.1 Background of fuel cell (FC)

FC is an energy conversion device that converts chemical energy from fuel to electrical energy through the electrochemical redox reaction. The redox reactions occur at FC electrodes which is anode and cathode. Fuel at anode electrode is oxidized to produce electron and proton. The obtained electron passes through external circuit while protons transfer through electrolyte to the cathode electrode. Both electron and proton combined at cathode to form water with presence of oxygen or it will form hydrogen without presence of oxygen. Eq. 1.1 – 1.3 describes the chemical reaction that occurs both in anode and cathode with the presence of oxygen at cathode. Eq. 1.4 – 1.6 present the equation of both anode and cathode with the absence of oxygen at cathode. A schematic of its functioning is portrayed in Fig. 2.1 along with its compartment.

With the presence of oxygen at cathode



With the absence of oxygen at cathode



The material of both electrode at anode and cathode is different due to the different function of those two electrodes. The anode electrode function as electron donor while cathode electrode as electron acceptor. The carbon is chosen as most

suitable electrode material. The carbon can be of any form such as carbon cloth, carbon paper, carbon felt and carbon fibre (Wang *et al.*, 2004; Saha *et al.*, 2010; Zhou *et al.*, 2011).

The rapid growth of nanotechnology introduces new types of electrode made up of nanocomposites materials. These included polypyrrole-coated carbon nanotubes (PPy-CNTRs), polyaniline carbon nanotubes nanocomposite (NT/PANI) and activated carbon nanofiber (ACNF) (Ghasemi *et al.*, 2013).

Based on Fig. 2.1 anode and cathode is separated by electrolyte. There are two types of electrolytes which are of either liquid or solid phase. Electrolyte in solid form is also known as membrane. The type of membrane used in most FC including the microbial fuel cell belongs to PEM. PEM usually used in fuel cell which uses hydrogen and methanol as fuel and it operated at ambient temperature. It needs highly proton conductive polymer membranes to achieve high voltage per current density in the unit cell (Lee *et al.*, 2005). The redox reaction that explained by the Eq. 1.1 – 1.6 could be efficient if the proton conductivity of PEM falls in the range of 10^{-3} and 10^{-2} S/cm (Lee *et al.*, 2005; Abdulkareem *et al.*, 2010; Peighambardoust *et al.*, 2010). Therefore it is important for the researchers to focus on the development of highly proton conductive polymer membrane.

FCs is classified based on the type of electrolyte used in a FC which is alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) (Win *et al.*, 2008; Peighambardoust *et al.*, 2010; Ye *et al.*, 2012).

2.2 Proton exchange membrane (PEM)

PEM plays an important role in most FC system. Its function is not only for electrode separation. It prevents the mixing of the fuel and oxidant and enhances the selectivity by allowing selective ions to pass through it. Redundant ion or other impurities pass through the electrolyte interrupt the chemical reaction in the FC system (Hickner *et al.*, 2004)

PEM classified as high performance membrane based on several factors such as high proton conductivity, low electronic conductivity, low permeability to fuel and oxidant, low water transport through diffusion and electro-osmosis, oxidative and hydrolytic stability, good mechanical properties in both dry and hydrated states, cost and capability for fabrication into membrane electrode assemblies (MEAs) (Hickner *et al.*, 2004; Cánovas *et al.*, 2005). However, from all said factors proton conductivity is considered as most critical one (Lee *et al.*, 2005; Abdulkareem *et al.*, 2010; Peighambardoust *et al.*, 2010).

This crucial parameter is categorized based on the composition of materials employed for membrane synthesis along with preparation methods and is tabulated in the Table 2.2.

Table 2.1: Classification of PEM

Classified based on	Types of membrane	Example
Synthesis material	<ul style="list-style-type: none">• Perfluorinated• Partially fluorinated• Non fluorinated	<ul style="list-style-type: none">• Nafion®• PTFE-g-TFS• SPEEK
Preparation method	<ul style="list-style-type: none">• Acid-base blends• Others	<ul style="list-style-type: none">• SPEEK/PEI• Supported composite membrane

Perfluorinated membrane contains tetrafluoroethylene also known as Teflon as a backbone of the membrane (Gruger *et al.*, 2001; Hickner *et al.*, 2004; Teng, 2012). This backbone combined with sulfonic acid group to form perfluorinated membrane. The most famous perfluorinated membrane is Nafion® which will be discussed consequently.

Non-fluorinated membrane is divided into two; the first requires water to maintain its proton conductivity and the second functions in the absence of water for the proton conductivity mechanism (Hickner *et al.*, 2004; Othman *et al.*, 2010). This type of membrane contains aliphatic or aromatic polymers. It has some advantages compared to perfluorinated membrane because it is less expensive and commercially available (Roziere *et al.*, 2003)

Acid blends membrane is an alternative membrane which can maintain high conductivity at elevated temperature without suffering from dehydration effect. The purpose of having this membrane is considered for FC which involves incorporation of an acid component into an alkaline polymer base for proton conduction. The most successful acid blends membrane under ambient pressure is phosphoric acid-doped polybenzimidazole (PBI/H₃PO₄) (Qingfeng *et al.*, 2001; Li *et al.*, 2004).

2.3 Nafion membrane

Nafion® or persulfonated polytetrafluoroethylene is a variant of PEM. It was synthesized from polyethylene polymer precursor. Other types of perfluorinated membrane that are available in the market are Flemion® and Dow® (Eirkeling *et al.*, 2001; Bae and Kim, 2003; Dunwoody and Leddy, 2005; Othman *et al.*, 2010). It is produced by Dupont and it was developed in the late 1960s (Hickner *et al.*, 2004; Church, 2006; Teng, 2012)

Nafion is prepared via copolymerization method (Hickner *et al.*, 2004). Polyethylene reacted with fluorine to form polytetrafluoroethylene (PTFE). The advantage of fluorine is it will form strong bonding between fluorine atom and carbon molecule. The atom of fluorine is small and has high electronegativity and allow for the strong bond to occur between them. The basic PTFE polymer then needs to react with sulfonic acid for the formation of perfluorinated ionomer (PFI) (Othman *et al.*, 2010; Teng, 2012). To form various types of membrane such as Flemion® and Dow® this PFI need to react with specific group of polymer. The chemical structure of Nafion® membrane is shows in Fig. 2.2.

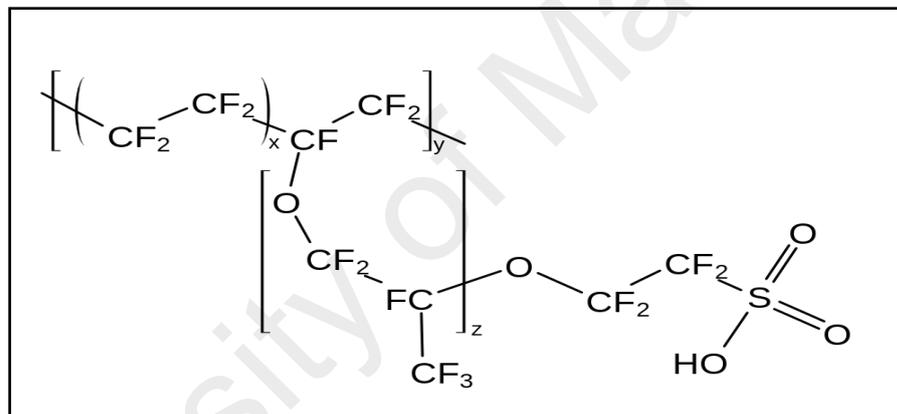


Figure 2.2: Chemical structure of Nafion® (Wikipedia)

Nafion® membrane is commonly used because of its high proton conductivity when fully hydrated and excellent chemical and thermal stability. However, it is high in cost, unstable at high temperature, and a poor barrier to methanol and fuel crossover (Wu *et al.*, 2006; Jang *et al.*, 2013; Liu *et al.*, 2010) which will reduce the fuel efficiency and cathode performance (Bae and Kim, 2003; Aini *et al.*, 2012; Liu *et al.*, 2014; Mondal *et al.*, 2015). It is also due to the safety concerns of tetrafluoroethylene during the synthesis of Nafion® (Hickner *et al.*, 2004; Teng, 2012; Wafiroh *et al.*, 2014).

Researchers are highly motivated for finding a replacement or alternatives with a comparable functionality like Nafion[®]. Some of the reports state that the Nafion[®] has been modified by adding composite into the Nafion[®] structure such as titania/Nafion composite membrane (Satterfield *et al.*, 2006; Ding *et al.*, 2011; Cele *et al.*, 2012), silicon oxide Nafion composite membrane (Adjemian *et al.*, 2002; Pan and Yuan, 2007) and composite Nafion/Sulfated Zirconia membrane (Navarra *et al.*, 2008; D'Epifanio *et al.*, 2009; Siracusano *et al.*, 2012). Few other researchers synthesized different types of PEM for FC applications such as sulfonated polysiloxane (Zhou *et al.*, 1993; Liu *et al.*, 1994; Zhu *et al.*, 2011), sulfonated polybenzimidazole (Glipa *et al.*, 1997; Xu *et al.*, 2007; Bai *et al.*, 2011), sulfonated poly(arylene ether) (Nolte *et al.*, 1993; Wang *et al.*, 2002; Tigelaar *et al.*, 2011) and sulfonated polyimide (Woo *et al.*, 2003; Einsla *et al.*, 2004; Okamoto *et al.*, 2010).

2.4 Significance of proton conductivity

There are many methods to measure the proton conductivity of the membrane. The new attempt for proton conductivity measurement is by measuring the proton mobility through diffusivity of mobile hydrogen ions using pulsed field gradient spin-echo (PGSE) NMR (Roy *et al.*, 2006), the proton transport behaviour by the Grötthaus hopping mechanism and compared the diffusivity determined by estimation of the proton conductivity using the Nernst-Einstein equation (Zawodzinski *et al.*, 1991). However, proton conductivity is generally obtained from the measurement of resistivity of the proton-conductive membrane against the flow of alternating current (ac) or direct current (dc) (Lee *et al.*, 2005).

The mechanism of proton conduction explained in two types of conditions. The proton transport in hydrated polymeric matrices is described based on two principal which is proton hopping or Grotthus mechanism (Gileadi *et al.*, 2006; Peighambardoust *et al.*, 2010). The proton transport in water as vehicle is diffusion mechanism or vehicular mechanism (Peighambardoust *et al.*, 2010; Vilčiauskas *et al.*, 2012; Zuo *et al.*, 2012).

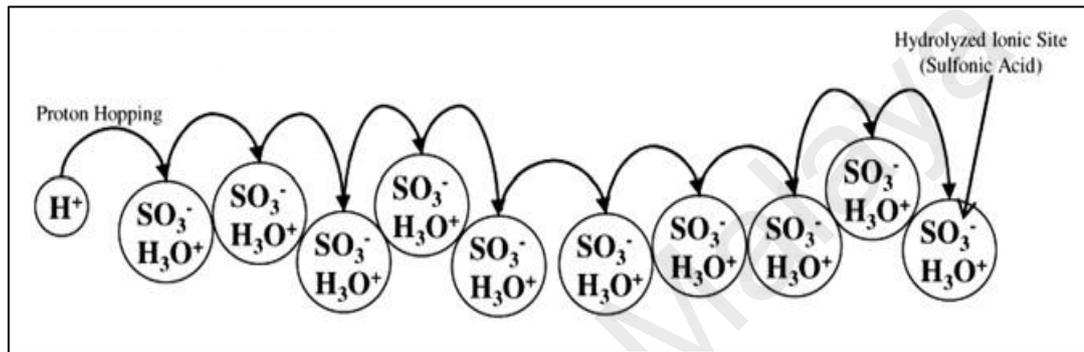


Figure 2.3: Proton hopping mechanism (Peighambardoust *et al.*, 2010)

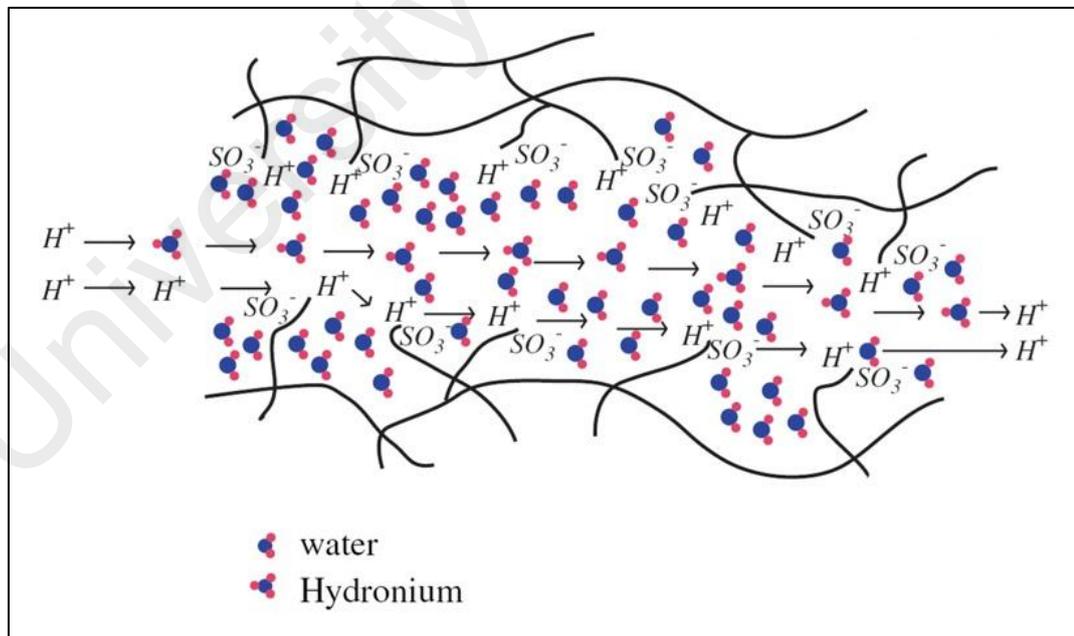


Figure 2.4: Vehicular Mechanism (Peighambardoust *et al.*, 2010)

In the proton hopping mechanism, protons hop from one hydrolyzed ionic site ($\text{SO}_3^- \text{H}_3\text{O}^+$) to another across the membrane. Different proton from same hydronium ion hops on to another water molecule. The hopping mechanism has little contribution to the conductivity of perfluorinated sulfonic acid membrane. The vehicular mechanism the hydrated proton (H_3O^+) diffuse through the aqueous medium based on the electrochemical difference. The existence of free volume within the polymeric chains in PEM allows the transfer of the hydrated proton through the membrane. The water has two transports mechanism during the vehicular mechanism of proton which is electroosmotic drag and concentration driven diffusion (Hickner *et al.*, 2004; Peighambardoust *et al.*, 2010, Zuo *et al.*, 2012).

Proton conductivity is very important parameter in PEM. The purpose of FC which is to convert the chemical energy into the electrical energy cannot be achieved if the proton conductivity does not meet the requirement. Good proton conductivity must be in the order of magnitude 10^{-3} up to 10^{-2} (Abdulkareem *et al.*, 2010; Xu *et al.*, 2010; Jang *et al.*, 2013). However, in achieving that range of proton conductivity many other parameters also need to be considered as the mechanism of PEM properties are related to each other.

For example, high proton conductivity PEM cannot be achieved if the water uptake in the membrane is not enough. PEM need optimum amount of water for the transportation of proton from anode electrode to the cathode electrode. The function of water in the membrane is as proton carrier. The important of achieving optimum amount of water for the proton transportation is proven by the changes of mechanical properties of the membrane if the water uptake is too much. For example, too much of water leads swelling and reduce the membrane performance. If the water content is too low it will lower the amount of proton transfer to the cathode and result in low proton conductivity. Hence, it is very important to maintain a suitable water content level to guarantee the

high proton conductivity (Hickner *et al.*, 2004; Peighambardoust *et al.*, 2010; Jang *et al.*, 2013; Liu *et al.*, 2014).

Both proton conductivity and water uptake can be balanced by determining the ion exchange capacity (IEC) of the membrane. The most common indicator for IEC in PEM is sulfonic acid group. Maximum proton conductivity will be achieved by increase the value of IEC. However, excessive value of sulfonic acid group in membrane lead to the swelling to occur as the sulfonic acid group absorbs water. Therefore, the swelling ratio was not tested for the rest of samples since the conclusion can be made through the value of proton conductivity and water uptake.

Therefore, these three parameters which are proton conductivity, water uptake and IEC are the most important related parameters calculated and determined for PEM. However, other standard important polymer science and engineering parameters such as molecular weight, morphology, topography and mechanical behaviour cannot be neglected (Bae and Kim, 2003; Martins *et al.*, 2003; Hickner *et al.*, 2004; Liu *et al.*, 2014).

2.5 Synthesis of PEM

There are four different methods of preparation of PEM. First is grafting polymerization method with using the γ -ray irradiation. Second is grafting polymerization method using plasma (Bae and Kim, 2003). Third is the crosslinking method and forth is direct polymerization of monomers (Othman *et al.*, 2010). The method that is used for PEM preparation in this report is by direct polymerization of monomers. This method is a new and traditional method of preparing PEM (Othman *et al.*, 2010). There are several types of membrane that has been synthesized using

polystyrene polymer. Polystyrene was chosen as an inexpensive and facile model polymer to be sulfonated by a mild method (Ju *et al.*, 2010).

The example of PEM made by polystyrene polymer as base is polystyrene-butadiene rubber. They concerned on the effect of degree of sulfonation (DS) in producing good quality of membrane. The DS is very dependent on the IEC of the membrane. The membrane analysis involves FTIR and HNMR to verify the sulfonic acid group attached to the polymer and to identify the site available for proton conduction. The thermal stability of the sulfonated polymer was determined by using thermo gravimetric and differential scanning analysis. In order to determine the DS and IEC, the amount of sulfur was analysed. The elemental analysis of sulfur was used electrochemical impedance spectroscopy (EIS). It is to determine the proton conductivity of the membrane. The result shows that an increasing weight of polymer will reduce the degree of sulfonation while an increase in sulfonation time will increase the degree of sulfonation. The proton conductivity recorded at 10^{-3} S/cm. Proton conductivity increase with an increase in temperature and degree of sulfonation (Abdulkareem *et al.*, 2010). The correlation of the parameters mention above is shown in Fig. 2.5.

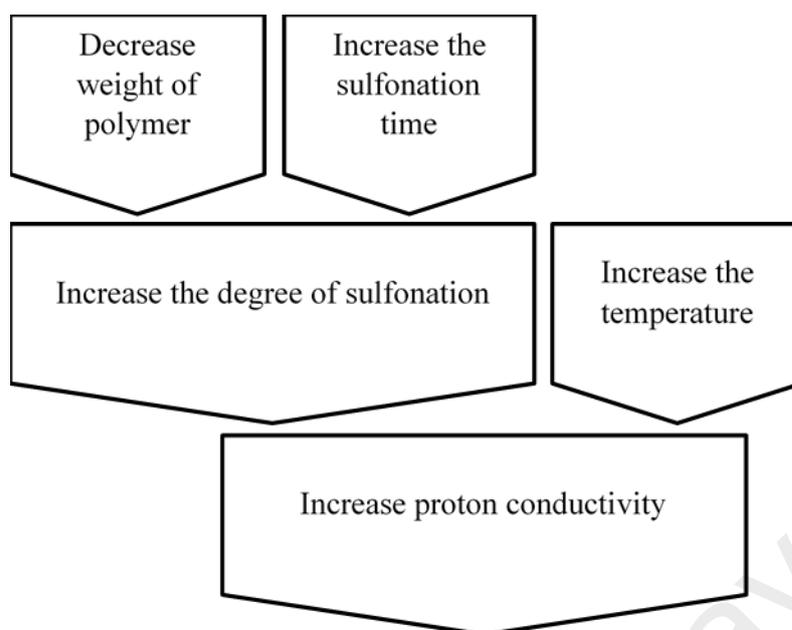


Figure 2.5: Correlation between parameters during synthesis and proton conductivity

Sulfonated polystyrene-(ethylene-butylene)-styrene triblock proton exchange membrane (sSBES) is synthesized to reduce the methanol crossover. The different ratio of swollen are studied by small angle X-ray scattering (SAXS), ATR-FTIR and AFM. In order to prevent the methanol crossover, a selective thin layer is mounted on top of membrane by simple plasma treatment in the presence of maleic anhydride. Hydrophobic anhydride properties act as a barrier to the methanol to prevent the decreasing of proton conductivity, the hydrolysis of anhydride groups to carboxylic acid has been done. This process facilitated transport site for proton conductivity. After hydrolysis, the proton conductivity was recovered and the recovery rate of proton conductivity by hydrolysis was higher than of methanol permeability (Won *et al.*, 2003). Other sulfonated polystyrene membrane are sulfonated polystyrene (SPS), grafted polypropylene (PP), composite electrolyte membranes (Bae and Kim, 2003) and sulfonated polystyrene (SPS/polytetrafluoroethylene (PTFE) composite membranes) (Shin *et al.*, 2005).

Sulfonation is a versatile route to polymer modification (Zaidi, 2003). The basic sulfonation process occurs when the polymer is attached to the sulfonic acid group through the chemical reaction between polymer sulfonic acid groups. Sulfonic acid groups also known as sulfonating agent. The types of sulfonic acid group are sulfuric acid (Aini *et al.*, 2012), chlorosulfonic acid (Shin *et al.*, 2005), acetyl sulfate (Bae and Kim, 2003) and complex sulfur tioxide (Zaidi, 2003). During the synthesis the duration and concentration of the sulfonic acid group sources were varied to control the DS. DS is the amount of sulfonic acid group molecule which attached to the polymer. Different DS results in different properties of polymer. Sulfonation is an electrophilic reaction that will depend on the substituents present on the ring. Electron-donating substituents will favour reaction and whereas electron-withdrawing groups will not (Zaidi, 2003). The attachment of sulfonic acid group to the PEEK polymer is shown in the Fig. 2.6. The properties of the polymer will be changed after the sulfonation has been done due to the changes of chemical structure.

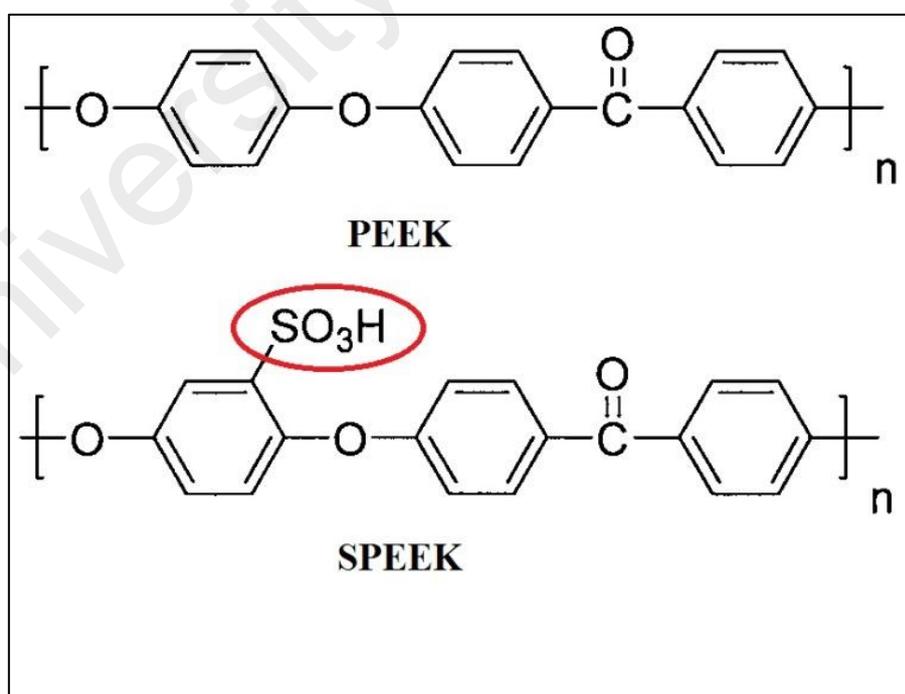


Figure 2.6: Sulfonic acid group ($\sim\text{SO}_3\text{H}$) attached to the PEEK polymer molecule after the sulfonation process (<http://www.google.com/patents/WO2008009102A1?cl=en>)

A good quality membrane that achieved high proton conductivity was reported by Shin *et al.*, (2005). The proton conductivity for the sulfonated polystyrene/PTFE composite membrane prepared is 0.082 S/cm compared to Nafion which has the ion conductivity of 0.080 S/cm. This membrane is composite type membrane because polymer electrolyte is impregnated in porous polytetrafluoroethylene (PTFE). The porous composite helps in increasing the mechanical and chemical stability, reduce the preparation cost and enhance the crosslinking of the PEM. For proton conductivity purpose, the PTFE was then sulfonated with the chlorosulfonic acid as sulfonating agent (Shin *et al.*, 2005).

The objective of using grafting method (Bae and Kim, 2003) is also to improve the ion conductivity of the prepared membrane. Bae and Kim (2003) prepared the sulfonated polystyrene membranes for direct methanol fuel cell. The base of membrane is microporous polypropylene (PP). The plasma treatment is introduced to produce radical site on the surface of PP substrate. The PP polymer was then grafted with styrene monomer in a vacuum chamber. Then it was sulfonated using acetic sulfate solution as sulfonating agent. The IEC of grafted PS is slightly increased from 1.5 to 2.9 meq/g with the increase of sulfonation and grafting reaction time. The highest proton conductivity shown during the experiment is 0.019 S/cm (Bae and Kim, 2003).

However, some articles also focus on other properties. The purpose of surface modification of sulfonated polystyrene-(ethylene-butylene)-styrene triblock is to reduce the methanol crossover (Won *et al.*, 2003)

2.6 Addition of zeolite in PEM

The addition of hydrophilic ceramic/organic filler such as SiO₂, TiO₂, ZrO₂, sepiolite and zeolite helps to retain water in composite membrane. This filler will absorb water and facilitate in proton conductivity of membrane. It is also helps to retain water at high temperature and low relative humidity value (Jalani *et al.*, 2005; Sahu *et al.*, 2009; Peighambardoust *et al.*, 2010; Beauger *et al.*, 2013).

Zeolite is also used as an additive to improve the properties of PEM chitosan since the usage of chitosan as membrane base lacks many properties such as proton conductivity, swelling and poor thermal stability. The addition of zeolite improves the PEM chitosan properties. The methanol permeability and proton conductivity is 1.26 kg/m²h and 2.2×10^{-4} S/cm respectively (Wafiroh *et al.*, 2014).

Chabazite and clinoptilolite are the types of zeolite which are added into the present Nafion membrane for the purpose of membrane modification. These zeolites are low cost, chemically stable in aqueous solutions, good ion exchange conductivity, having small pore sizes compared to other types of zeolite and the pores network is three dimensional. Small pore size will lead to good ion exchange conductivity and low methanol permeability. Hence, three dimension pores size produce superior transport properties compared with two-dimensional or mono-dimensional pores. The zeolite fillers are produce superior transport properties compared with two dimensional or mono-dimensional pores. It happened when the zeolite fillers are randomly oriented in the membrane matrix. The research involves the characterization of the sample by using SEM and X-rays diffraction (XRD), conductivity measurement and permeability determinations (Tricoli *et al.*, 2003; Chen *et al.*, 2006; Peighambardoust *et al.*, 2010).

2.7 Synthesis of PEM from waste polymers

Owing to environmental concern, for past two years a few researchers start to focus on the synthesis of PEM using waste polymeric materials. Sulfonated polystyrene copolymer has been synthesized and characterized for direct methanol fuel cell application (DMFC) using polystyrene waste (Mulijani *et al.*, 2014). The PEM membrane was synthesized from Styrofoam waste for the usage of lithium battery (Arcana *et al.*, 2013).

Sulfonated polystyrene copolymer was synthesized for two purposes. The first one is to produce the sulfonated polystyrene and the next is to manipulate abundance of waste into valuable materials. The base polymer for the synthesis is the Styrofoam waste. It is undergone normal sulfonation process by varying the amount of sulfonating agent based on trial and error process. Then it went through the cross-linked process to enhance the mechanical properties and to control the water uptake in order to reduce the methanol crossover. The highest proton conductivity is reported as 3.8 $\mu\text{S}/\text{cm}$ at the temperature range of 25 - 75°C (Mulijani *et al.*, 2014).

The PEM for lithium-ion battery applications also produced using Styrofoam waste. This type of membrane was synthesized with focus to produce low cost lithium battery and to create the lithium battery with environmental friendly PEM. The waste polystyrene is sulfonated using acetyl sulfate as sulfonating agent with addition of lithium perchlorate (LiClO_4). The synthesis of PEM is successful with the increasing of proton conductivity as the content of LiClO_4 increase. However, the problems transpire when the mechanical strength of the membrane decrease and surface morphology of the membrane become less uniform (Arcana *et al.*, 2013). The waste polystyrene generated in the society due to various activities and dumped in the landfill or recycled for else polymeric products. In the present study the feasibility of the waste polystyrene was experimented for PEM preparation aiming for FC application.

CHAPTER 3:

MATERIALS AND METHODS / METHODOLOGY

3.1 Introduction

The research activity carried out in the present dissertation follows different steps in sequence for attaining the PEM. In the first phase of the typical preparation of PEM virgin polystyrene (PS) precursor was subjected to the open and reflux sulfonation with varied solvents. After successful sulfonation membrane were casted with and without using solvent. Zeolite, an inorganic material was used as enhancer. The zeolite was added for the PEM prepared using the virgin PS only. Thus prepared membrane was dissected for its various materials and membrane characteristics. Based on the dissection reports, the testing was continued for the samples with better quality while analysis was discontinued for inferior samples.

Similarly the PEM was prepared by replacing the virgin PS beads with waste PS. This study signifies the feasibility of the polystyrene waste as a potential precursor. This experiment successfully synthesized two types of membranes. Thus obtained characteristics of the PEM from different precursors were compared. In whole study PEM achieved from virgin PS was compared with the latter. A schematic of the adopted preparation was simplified and presented in the Fig. 3.1.

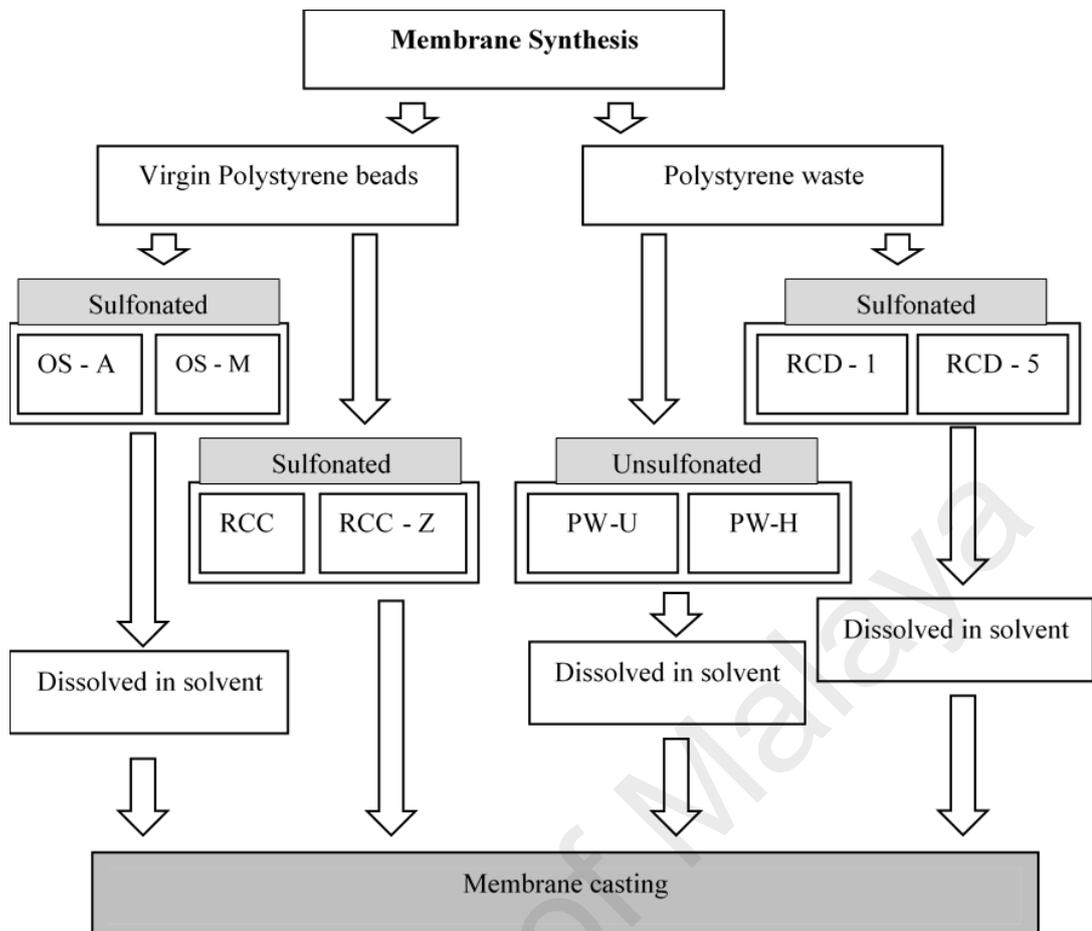


Figure 3.1: Simplified process flows of the experiments

Below is the acronyms description of adopted sulfonation conditions

- ✓ OS-A → Open Sulfonation (Non reflux condition) – Acetone
- ✓ OS-M → Open Sulfonation (Non reflux condition) – Methyl ethyl ketone
- ✓ RCC → Reflux Condition using Chloroform (Solvent)
- ✓ RCC-Z → Reflux Condition using Chloroform (Solvent) – addition of zeolite
- ✓ PW-U → Polystyrene waste – unheated during membrane casting
- ✓ PW-H → Polystyrene waste – heated during membrane casting
- ✓ RCD-1 → Reflux Condition using Dichloroethane (Solvent) – used 1 ml of acetyl sulfate
- ✓ RCD-5 → Reflux Condition using Dichloroethane (Solvent) – used 5 ml of acetyl sulfate

3.2 Materials

Polystyrene (PS) beads ($M_w = 350,000$ g/mol, $M_w/M_n = 2.06$) purchased from Sigma-Aldrich is used as polymeric precursor, polystyrene waste (cup lid) as polymeric precursor, methyl ethyl ketone (R&M), acetone (R&M), sulfuric acid (95%), acetic anhydride (MERCK), dichloroethane (R&M), chloroform, dimethylacetamide (R&M), benzene (R&M) and zeolite powder (<45 μ m) purchased from Sigma-Aldrich were used without further modifications. The properties of polystyrene beads are tabulated in Table 3.1.

Table 3.1: Properties of polystyrene beads

Polystyrene Properties	Value
Mn	140,000 g/mol
Mw	230,000 g/mol
Mn/Mw	1.64

The polystyrene waste used in this experiment is portrayed in Fig. 3.2, and the type of polystyrene is the High Impact Polystyrene (HIPS). The PS waste was collected from the cafeteria of 12th residential college in University of Malaya, Kuala Lumpur, Malaysia. The properties of polystyrene waste are unknown. It was utilized without any further modifications.



Figure 3.2: Polystyrene cup lids employed as PS waste precursor

3.3 Membrane synthesis

As explained in the inception, the membrane synthesis involves two stages which are sulfonation process and membrane casting. The general process of membrane preparation is shown by Fig. 3.3. Since varied operation conditions like temperature, solvent nature were adopted those data's were not presented in the flow chart.

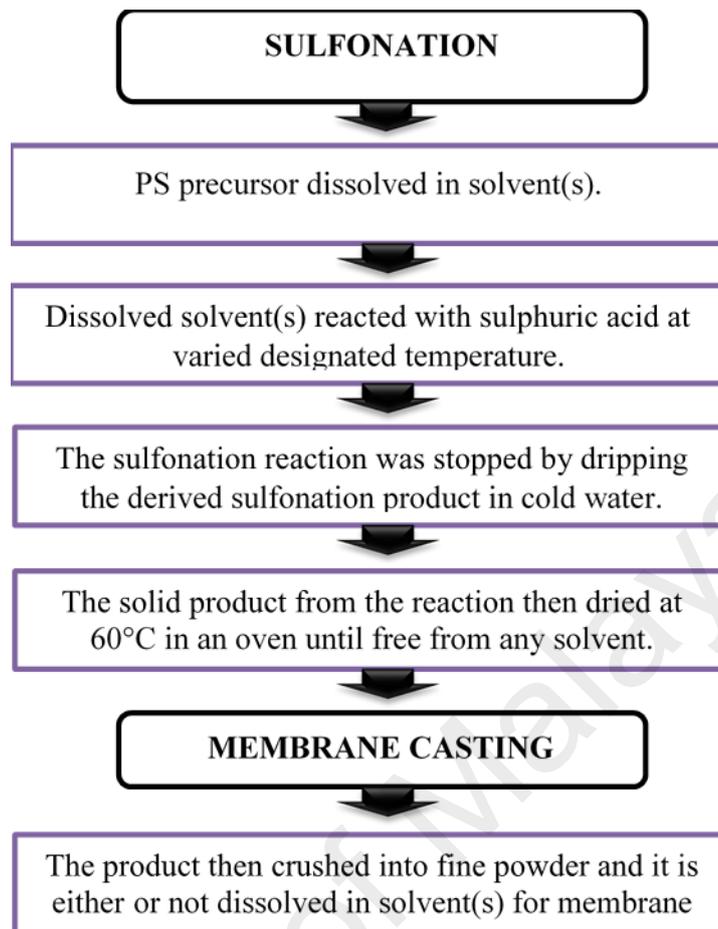


Figure 3.3: General flow chart of membrane synthesis

3.4 Sulfonation Methods

The sulfonation process of polystyrene precursor were conducted using different sulfonation methods. The details of each are explained as follows:

3.4.1 Open Sulfonation (OS) method

Synthesis of membrane through OS used polystyrene beads as starting material. The beads were dissolved in two types of solvent for sulfonation phase. These solvents are methyl ethyl ketone (MEK) and acetone. Both solutions were heated at 60 °C in sulfuric acid (95%) accordingly. The solid products appeared at the end of the process is sulfonated polystyrene (SPS). The obtained SPS was washed with deionized water until

the pH is 7 and dried at room temperature to evaporate the solvent. The step follows the membrane casting, in the typical casting the 2 g of obtained SPS was dissolved in 20 mL of benzene. The membrane sulfonation using MEK was labeled as OS-M while the one with acetone as OS-A.

After the characterization has been done the result shown the membrane prepared by using this method is lacking in properties and criteria as FC membrane. This is due to the non-reflux conditions that lead to material losses during the membrane synthesis. An alternative approach has been implemented and the method proceeds with the RCC method.

3.4.2 Reflux Condition (Chloroform) Sulfonation Method

In the reflux condition sulfonation method, 10.4 g of polystyrene beads were dissolved in 50 mL chloroform under reflux condition in 250 mL bottom flask reactor equipped with mechanical agitation, vertical condenser and thermometer. The flask containing the solution was heated at 50 °C for 30 minutes. Acetyl sulfate was employed as sulfonating agent and was freshly prepared each time. The acetyl sulfate was prepared by adding 6 mL of acetyl anhydride to 50 mL of dichloroethane (DCE) and the solution mixture was cooled to 10 °C. Followed by 3 mL of 95% H₂SO₄ was carefully added to the mixture. A 1 mL of freshly prepared acetyl sulfate was added to the flask for promoting the sulfonation reaction. The reaction mixture was heated to about 50 °C and stirrer for 6 h. The solution mixture was directly poured into the petri dish for the membrane casting. The poured solution was air dried for 24 h. The solution mixture with addition of zeolite was poured into the separate petri dish and was air dried in similar way.

The result for the membrane prepared following this method has wide pores. The wide pores will affect the FC performance. Membrane should only allow proton to transfer through it. Wide pore membrane will allow other cation and molecules to transfer. The membrane produced must be dense membrane. It needs to increase in membrane density to make membrane denser. The RCD method has been implemented by retaining the reflux condition and replacing chloroform with dichloroethane.

3.4.3 Reflux Condition (Dichloroethane) Sulfonation Method

This experiment used polystyrene (PS) waste as a precursor with varied (1 mL and 5 mL) acetyl sulfate solution volume for sulfonation agent. 10.4 g of PS waste is dissolved in 50 mL of DCE in a 250 mL three-neck round-bottomed flask and was stirred for half an hour. 1 mL of freshly prepared acetyl solution was dropped in a dissolved PS solution. The reaction was carried out for 2 h at 50 °C. The sulfonation was terminated decanting the sulfonated polymeric solution into cold water. A dark brown jelly like substances was obtained after the sulfonation and the sample was dried in incubator at 60 °C for 24 h. The sample obtained through this pathway is designated as RCD-1. The RCD-5 was prepared in the similar way by altering the acetyl sulfate volume to 5 mL. The prepared samples were dissolved in dimethylacetamide solvent for membrane casting. The solution formed after dissolving sulfonated PS was poured into petri dish and air dried for 24 h. Thus prepared membranes were tagged as RCD-1 and RCD-5 respectively.

3.4.4 Unsulfonated Polystyrene Waste

The unsulfonated membrane from polystyrene waste was casted by dissolving waste polystyrene in diacetamide solvent. The liquefying waste PS was carried out in room and raised temperature conditions. The membrane prepared at room temperature is designated as PW, while the one prepared in raised temperature condition (60 °C) is designated PW-H. The purpose is to compare the membrane performance of unsulfonated and sulfonated one and also to investigate the influence of temperature in liquefying the PS.

3.4.5 Comparison of RCC and RCD method

RCC and RCD methods have been compared and presented in the Table 3.1. Based on the Table 3.1, the difference between the synthesis method of RCC and RCD membrane is based on the solvent used. Better solvent produced better membrane and have good physical properties and membrane performance. Solvent has ability to determine the properties of final product in terms of water uptake and dense membrane. It also improves the value of proton conductivity and ion exchange capacity. The right solvent is important in membrane production and is strongly dependent on the types of polymer as a starting material.

Table 3.2: Comparison of RCC and RCD methods

Purpose	RCC method	RCD method
Starting material	Polystyrene (PS) beads	Polystyrene (PS) waste
PS solvent	Chloroform	Dichloroethane
Sulfonation process	Acetic Anhydride; Dichloroethane; Sulfuric Acid	Acetic Anhydride; Dichloroethane; Sulfuric Acid
SPS Solvent	Benzene	Diacetamide

3.5 Membrane Materials characterization

Fourier Transform Infrared (FT-IR) spectroscopy analysis was performed using Nicolet iS10 FTIR spectrometer with diamond ATR crystal (ThermoScientific, USA) under the wavenumber ranging between 800 cm^{-1} and 3500 cm^{-1} . Thermogravimetric analysis (TGA) was performed between 28°C and 500°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere in STA 449 F3Jupiter, Netzsch (Germany). The surface morphology of the prepared membranes was investigated using Field Emission Scanning Electron Microscope (FESEM) (LIBRa 200 FE, Carl Zeiss, Germany). Surface roughness of the membranes was captured using atomic force microscopy (AFM) (Ambios Technology, USA).

3.6 Membrane Performance

3.6.1 Water uptake

The water uptake and the number of water molecules per sulfonic group are calculated using the mass of dry and wet membrane. The membranes were cut into 5 cm × 5 cm using doctor's blade and dried at 60 °C for 2 h. The membranes were then kept in a desiccator to cool to the room temperature and the dry mass of the membrane was measured. The membranes were then immersed in DI water for 24 h at room temperature. The membranes are taken out and the surface water was removed by careful and quick blotting with Kimwipes[®]. The mass of the wet membranes were measured. The water uptake capacity of the membranes was calculated using Eq. 3.1.

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (3.1)$$

where W_{wet} (g) and W_{dry} (g) is the mass of wet and dry membranes respectively. The reported water uptake is the average of three membranes, respectively.

The number of water molecules absorbed per sulfonic group (ionic site) was calculated using Eq. 3.2

$$\lambda_w = \frac{\text{Water uptake}}{M_w \times IEC} \quad (3.2)$$

where, λ_w is the number of water molecules adsorbed, IEC is the ion exchange capacity (value obtained from ion exchange experiment) and M_w is the molecular weight of the immersed liquid (i.e. water, $M_w = 18$ g/mol).

3.6.2 Swelling ratio

After measuring the mass of membranes during water uptake experiments, the change in dimensions (length and width) of the membranes are measured. The extent of swelling is measured in terms of swelling ratio using Eq. 3.3.

$$\text{Swelling ratio} = \frac{D_{wet} - D_{dry}}{D_{dry}} \times 100 \quad (3.3)$$

where D_{wet} and D_{dry} are the average dimensions of wet and dry membranes. The average dimension refers to the geometric mean of wet [$(D_{wet} = (L_{wet1} \times B_{wet2})^{1/2})$] and dry [$(D_{dry} = (L_{dry1} \times B_{dry2})^{1/2})$], respectively where L and B denotes length and breadth of the membrane. Square (5 cm × 5 cm) samples are used in this work, L_{dry1} and B_{dry2} are same.

3.6.3 Ion Exchange Capacity (IEC)

The IEC of the membranes were determined by the back-titration method. A known mass of the membrane sample (≈ 0.3 g) was soaked in 1 M NaCl aqueous solution for 24 h to convert the acid form (H^+) of the membrane to sodium form (Na^+). Then, the exchanged H^+ ion in the solution was titrated with 0.01 M NaOH solution using methyl orange as an indicator. IEC is a measure of number of exchangeable protons per unit mass of dry polymer and the value is obtained by Eq. 3.4.

$$\text{IEC (in milliequivalents)} = \frac{C_{NaOH} \times V_{NaOH}}{W_{dry}} \times 1000 \quad (3.4)$$

where, C_{NaOH} is the concentration of NaOH (mol/L) and V_{NaOH} is the volume of NaOH used in the titration (ml) and W_{dry} is the mass of the dry membrane before immersed in NaCl (g).

3.6.4 Degree of sulfonation (DS)

The DS is the average number of sulfonic groups (SO₃H) per repeating unit in a polymer and estimated by rearranging the theoretical relationship between IEC and DS as shown in Eq. 3.5.

$$IEC = \frac{DS}{M_{monomer} + M_{sulfonic\ group} \times DS} \quad (3.5)$$

where $M_{monomer}$ is the molecular weight of the monomer (g/mol) and $M_{sulfonic\ group}$ is the molecular weight of the sulfonic group. Molecular weight of styrene monomer (C₈H₈) is 104 and the molecular weight of sulfonic group (SO₃H) is 81. Applying these values and rearranging Eq. 3.5 will obtain the equation for DS as shown in Eq. 3.6.

$$DS = \frac{104(IEC)}{1 - 81(IEC)} \quad (3.6)$$

3.6.5 Proton conductivity

Proton conductivity (σ) of full hydrated membranes was measured at room temperature by the two-probe alternating current impedance method (Autolab PGSTAT128N, Netherlands). A 5 cm × 5 cm hydrated membrane was clamped between two chambers (each chamber has 125 mL capacity) containing DI water as electrolyte. Two carbon cloth electrodes were used as electrodes to measure the proton conductivity at room temperature (30±2 °C) with relative humidity of 55±5%. Resistance of the membrane was measured by recording the voltage (V) for a known applied current (A). The actual resistance offered by the membrane was obtained by subtracting cell resistance from total resistance (i.e. $R_{total} = R_{membrane} + R_{cell}$). Cell resistance, R_{cell} was

measured without the membrane under the same operating condition. The proton conductivity (σ in S/cm) of membrane is determined from Eq. 3.7.

$$\sigma = \frac{T}{RS} \quad (3.7)$$

where, T is the membrane thickness of the membrane (cm), S is the surface area of membrane (cm²) and R is membrane resistance (Ω). The thicknesses of the membranes are measured using a dial gauge (precision of ± 0.01 mm) and the thickness used in the calculation is the average of 12 measurements.

University of Malaya

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Membrane Characterization

Membrane characterization is presented in two sections. The first section will focus on the materials characterization while the latter on the membrane performance that suits the fuel cell application.

4.2 Material characterization

4.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

PS is a thermoplastic and hydrophobic polymer with aromatic backbone. To obtain ionic conductivity of PS membranes, sulfonic acid groups (SO_3H) are introduced to PS backbone through an electrophilic substitution reaction. Fig. 4.1 - 4.3 depicts the FT-IR spectra of membranes obtained through OS, RCC and RCD membranes respectively. FT-IR spectra were used to identify the substitution of sulfonic group (SO_3H) with the hydrogen and aromatic groups. Sulfonic group vibration bands are detected between 1000 and 1080 cm^{-1} for all the prepared membranes (Martins *et al.*, 2003; Xu *et al.*, 2010; Aini *et al.*, 2012). Though there was a good indication for the sulfonation, the intensity of the peak signifies the lower degree of sulfonation. The absorption band at 1027 cm^{-1} corresponds to the symmetric stretching vibration of SO_3H group and S-O vibration band at 1180 cm^{-1} . Aromatic C-H deformation bands appeared at wavenumbers ranging between 750 and 850 cm^{-1} . The band at 1154 cm^{-1} corresponds to sulfonate anion attached to aromatic rings. All membranes recorded almost analogous spectrum for wavenumber below 3000 cm^{-1} .

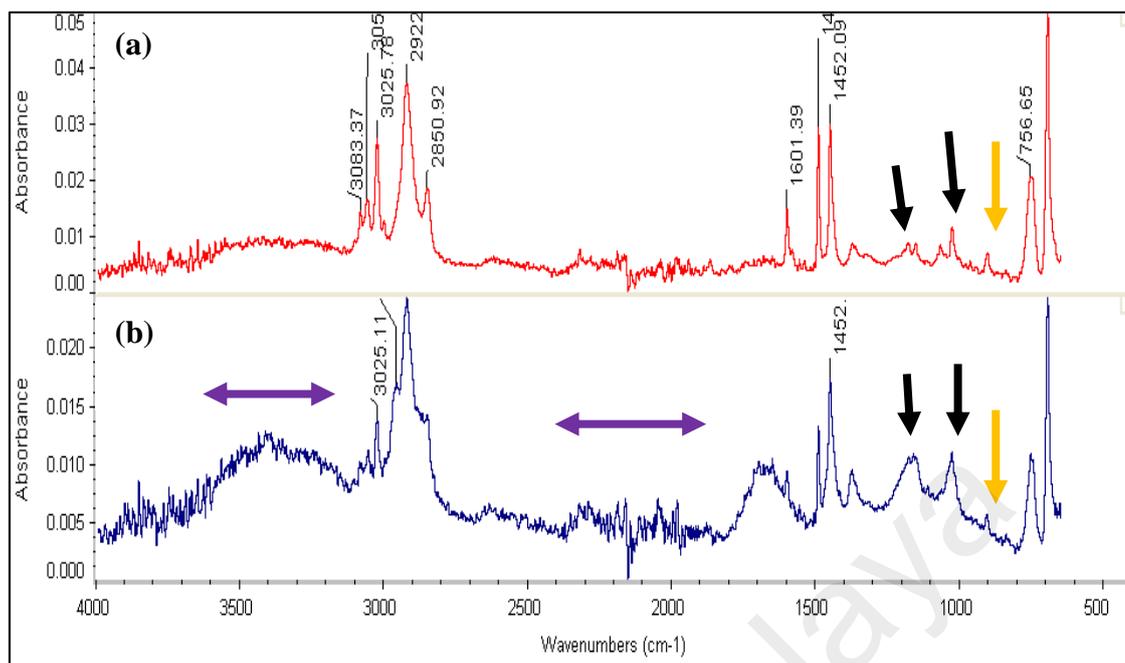


Figure 4.1: FT-IR spectra of (a) OS-A and (b) OS-M membrane

The obtained spectrum clearly confirms the efficacious sulfonation. In the case of zeolite incorporation into the membrane (RCC-Z), no significant changes were seen in the FT-IR spectrum, it also had similar results as seen in the rest of the samples without zeolite. However, the broad spectrum between 3100 and 3700 cm⁻¹ seen in RCC-Z membrane is attributed to the hydroxyl groups (>3500 cm⁻¹) associated with the zeolite metal ion and C-H stretching bonds of the zeolite as shown in Fig. 4.2. The RCC method also resulted in similar intensity of sulfonation as seen in OS method. This was due the lower sulfonation reaction time adopted in the step.

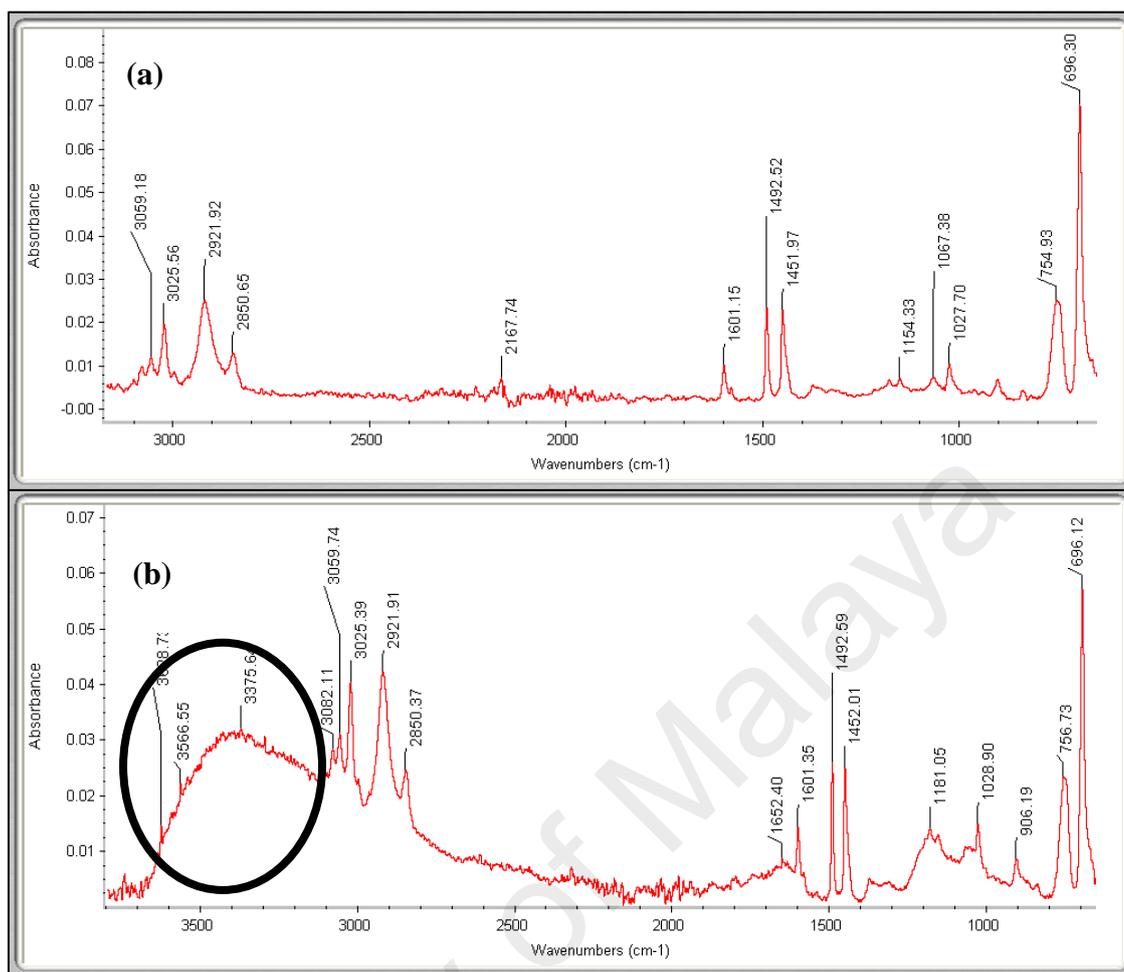


Figure 4.2: FT-IR spectra of (a) RCC and (b) RCC-Z membrane

Fig. 4.3 presents the obtained spectrum for the RCD membrane, the peak at 3413.36 cm^{-1} indicates the presence of alcohol (O-H) groups and amines (N-H) groups, and the peak at 1653 cm^{-1} attributes to the presence of alkenes (C=C) and amide groups (C=O). The presence of above said functional groups after sulfonation was attributed to the solvent used in dissolving PS. The RCD also exhibited a characteristic peak at 2360 cm^{-1} , indicating the presence of phosphine groups (P-H). Both the RCD-1 and RCD-5 membrane contains sulfonic groups too, at 1373 cm^{-1} , indicates presence of sulfate groups (S=O). Peaks at 1180 cm^{-1} and 1028 cm^{-1} for RCD-5 signifies the presence of sulfonyl chloride (S=C) and amine group (C-N) respectively. These obtained peaks are ascribed to the asymmetric and symmetric stretching vibration of the sulfonic acid

group (-SO₃) (So *et. al.*, 2011; Park *et. al.*, 2011). The absorption band at 600 cm⁻¹ is assigned to S-O stretch of the sulfonic groups. All these obtained peaks well correlate the successful and robust attachment of the sulfonic groups to the RCD membrane.

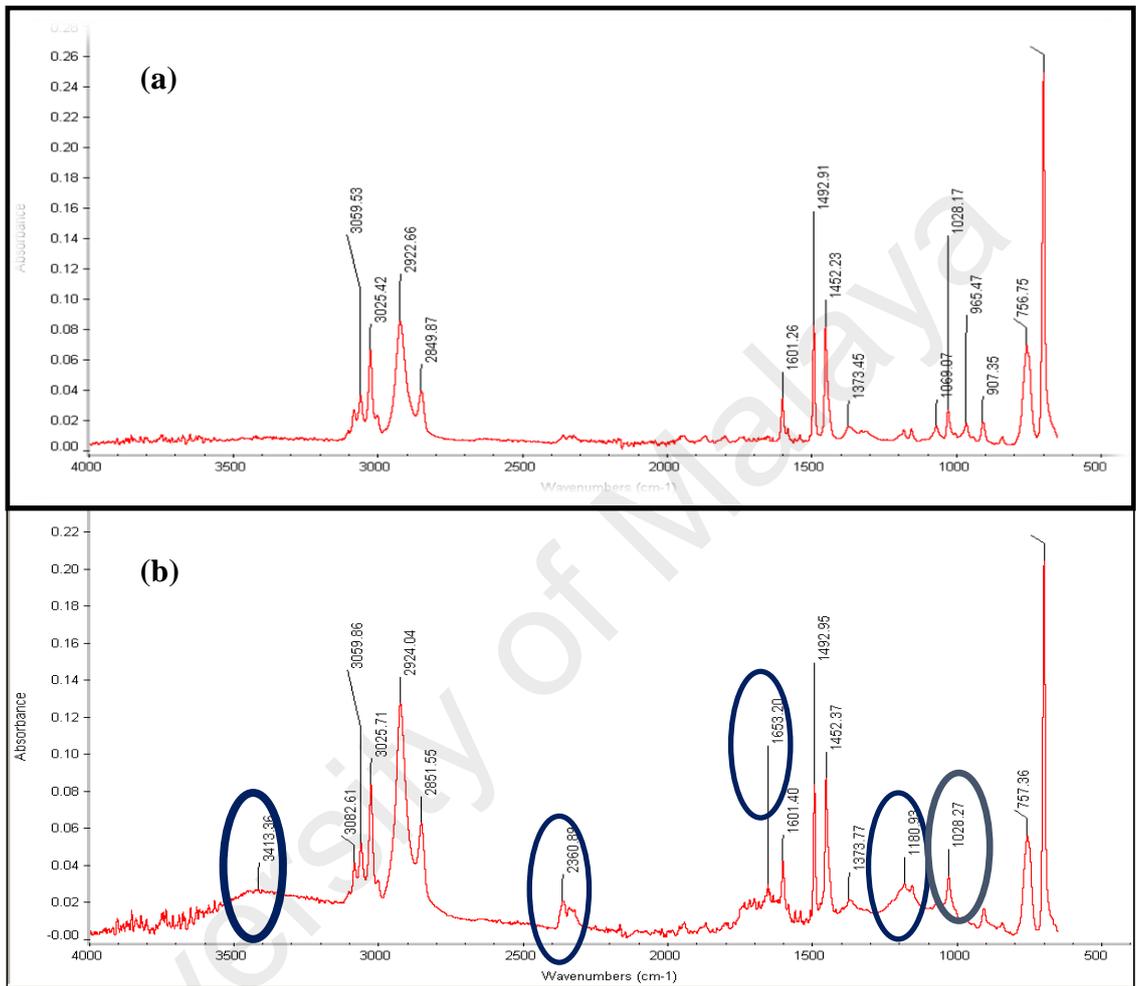


Figure 4:3 FT-IR spectra of (a) RCD-1 and (b) RCD-5 membrane

Thus executed functional group analysis well revealed the presence of the various sulfonic groups of the prepared membrane. FT-IR was not done for PW-U and PW-H because the samples were not involve with sulfonation process.

4.2.2 Thermogravimetric analysis (TGA)

The obtained TGA curve for RCC and RCD samples were shown in Fig. 4.4 - 4.5. The virgin PS degradation temperature is at 400 °C (Martins *et al.*, 20013) while PW degrade at half of that temperature. Hence, both are able to be in FC application.

The addition of zeolite on RCC-Z might cause structural modification and will affect the membranes' degradation behaviour (Ashraf *et al.*, 2013). The onset of weight loss process for RCC and RCC-Z membranes is found to be at 380 and 400 °C, respectively. A minor difference in the overall weight loss of RCC and RCC-Z membranes is attributed to the physisorbed moisture present in the zeolite powder. In addition, the zeolite incorporation would improve the surface properties but has detrimental effect in the proton exchange capacity.

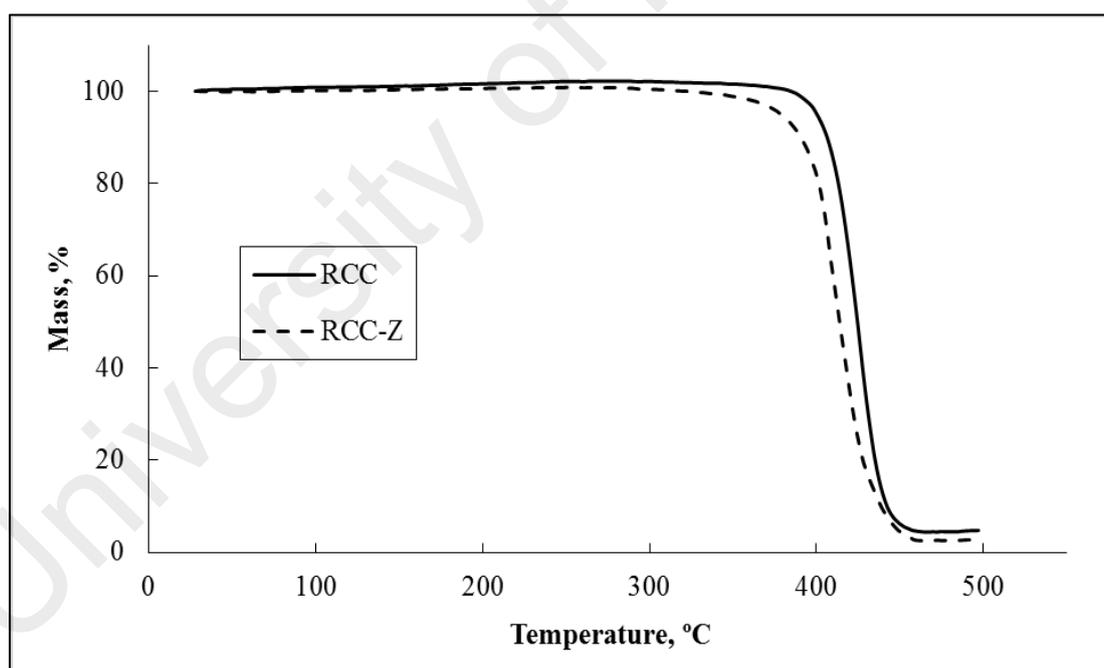


Figure 4.4: TGA analysis of RCC and RCC-Z

The RCD membranes were analyzed from 25 °C to 500 °C. There are two mass degradation steps for RCD-1 and RCD-5 membrane consequently which found to be at 400 °C and 430 °C, respectively. A minor difference in the overall weight loss of RCD-1 and RCD-5 membranes is attributed to the different amount of acetyl sulfate added

during the sulfonation process. From 100 °C to about 400 °C, the first mass degradation of the RCD-5 membrane occurred due to the loss of absorbed water and decomposition of sulfonic acid groups (-SO₃H) in both membranes (Jang and Han, 2013).

The high value of degradation temperature (>380 °C) indicates the structural rigidity of RCC and RCD membranes. A significant decrease in the thermal stability of RCC and RCD membranes do not affect its use in FC applications, since the operation is carried out at lower temperatures than the degradation temperature of both membranes. Furthermore almost a similar observation is expected for the other samples hence the analysis was limited only to these samples rather than rest.

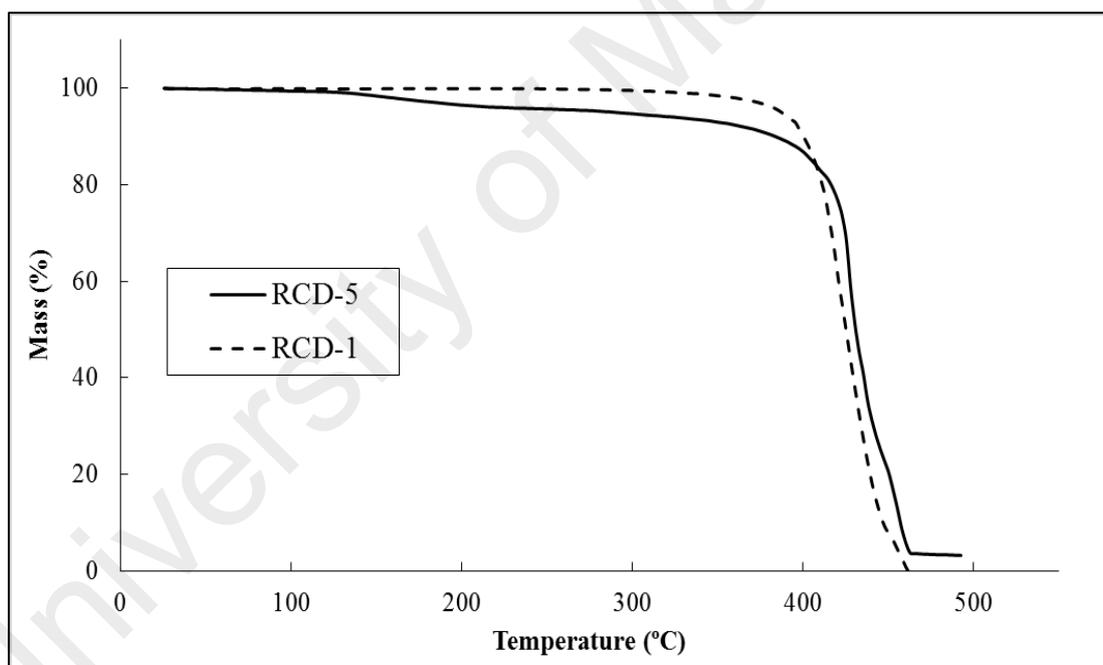


Figure 4.5: TGA analysis of RCD-1 and RCD-5

4.2.3 Surface morphology characterization

The surface roughness analyzed through AFM shown in Fig. 4.6 and 4.7 explained the roughness of the membrane surface. The roughness of membrane is one of the factors that can cause fouling. Higher roughness contributes for relatively high adhesive force that leads to a greater fouling on the surface. From the obtained images a

higher value of roughness was attained for the membrane casted through the MEK solvent where else the one casted with the acetone has lower roughness. The reason for such a greater variation in the roughness was attributed to the hydrophobic nature of the employed solvents.

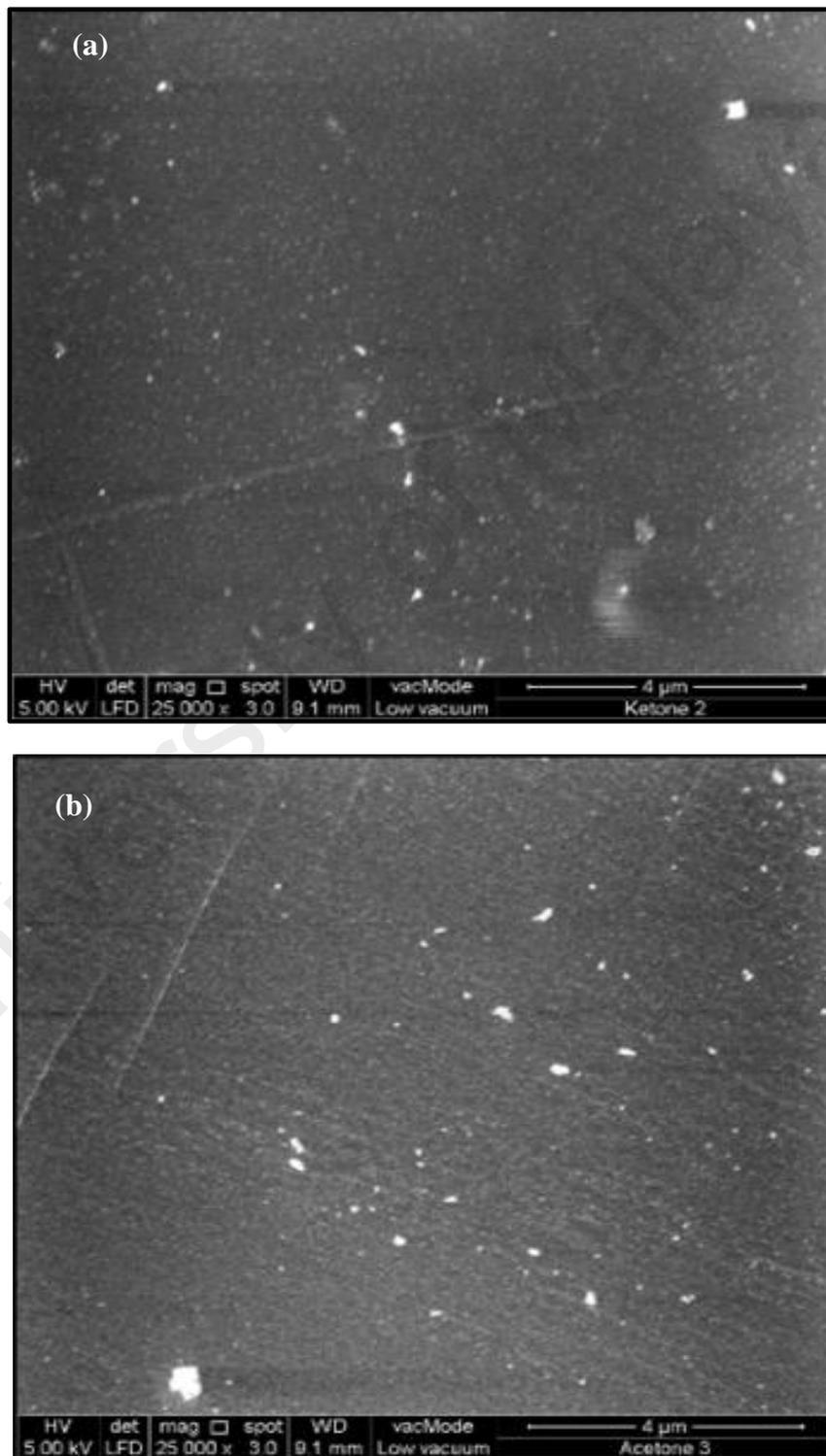


Figure 4.6: FESEM image of (a) OS-A and (b) OS-M

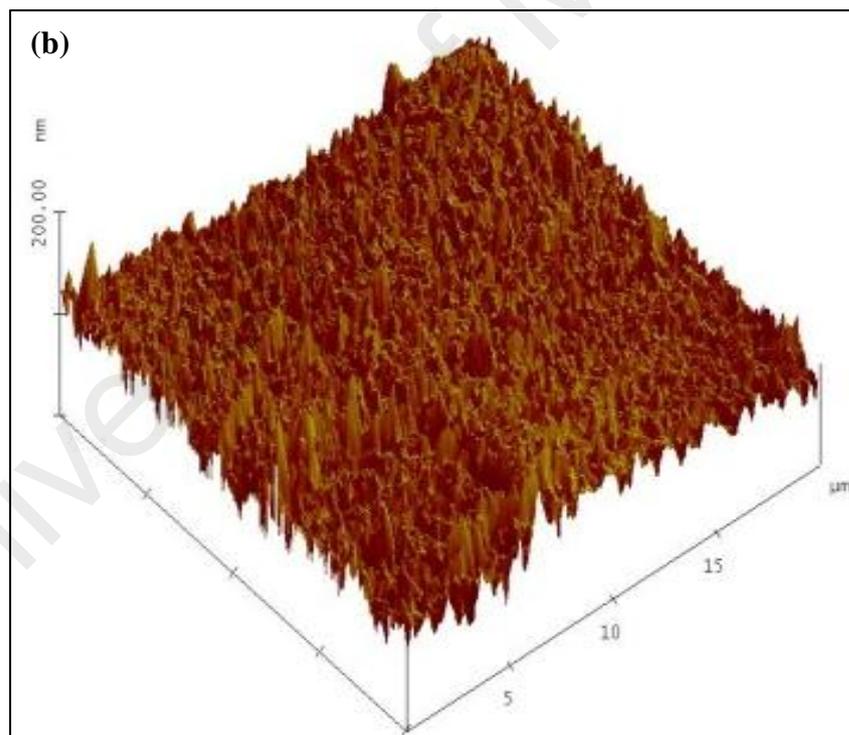
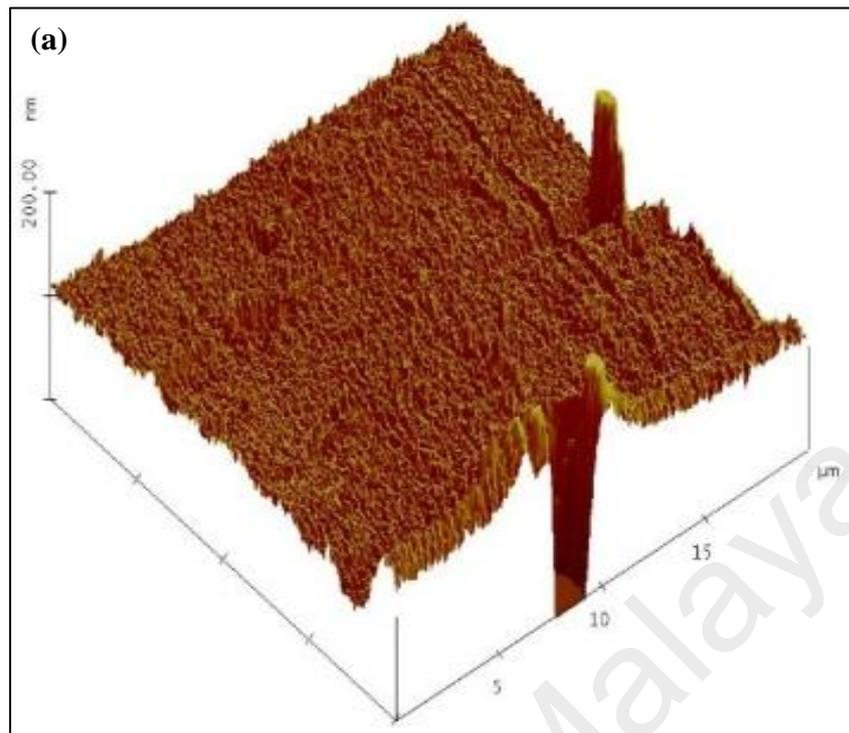


Figure 4.7: AFM image of (a) OS-A and (b) OS-M

The AFM analysis for the RCC and RCC-Z is depicted in Fig. 4.9. The obtained images showed a considerable increase in the roughness of the RCC-Z membranes. However, if the surface is rough, bacteria and impurities may trap onto the surface and reduce the performance of membrane. The physical appearance of this membrane must be improved by following proper membrane preparation process and maintain the cleanliness of the workspace.

AFM also showed the rough surface of RCC membrane compared to RCC-Z membrane. This is because of the simple decanting method and temperature of the liquid during membrane formation. The liquid polymer must be poured gently and spread evenly with the help of glass rod. This condition might also be caused by the high temperature of the polymer during the decantation, causing the membrane to form unevenly. The cooling of polymer to the certain degree is needed before pouring is done. For RCC-Z membrane the zeolite is shown as well attach onto the membrane surface result in more flat surface compared to the result taken by FESEM. The surfaces are rough and small pores shown with the presence of lines on both of the membrane surface. This pore-like surface morphology is attributed by the evaporation of solvent during the synthesis.

Since very few information was obtained from these analysis and membrane performance does not depend greatly on these results, similar analysis was not carried out for the samples prepared from the PS waste.

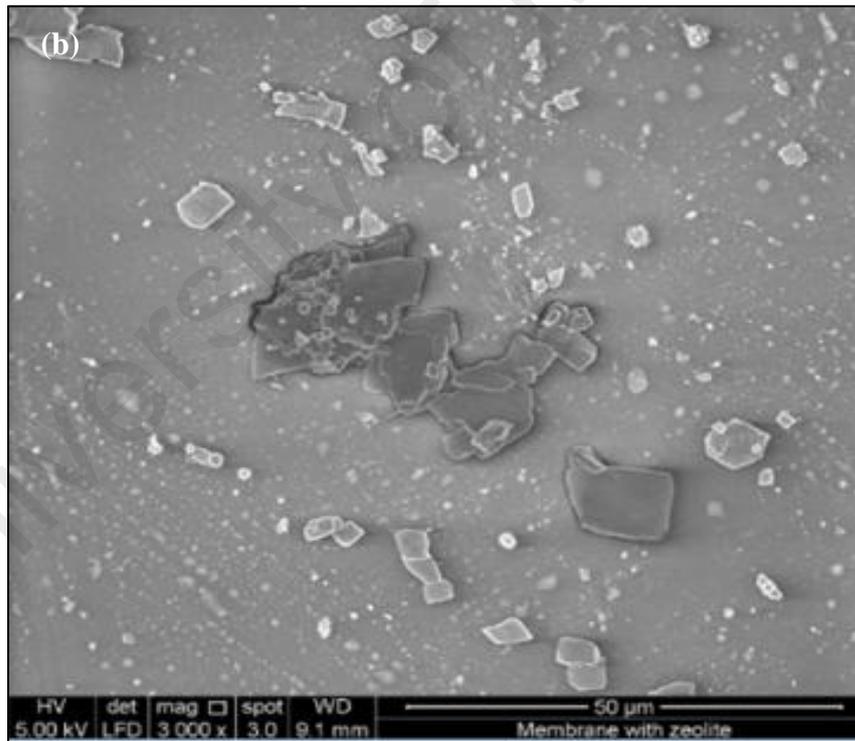
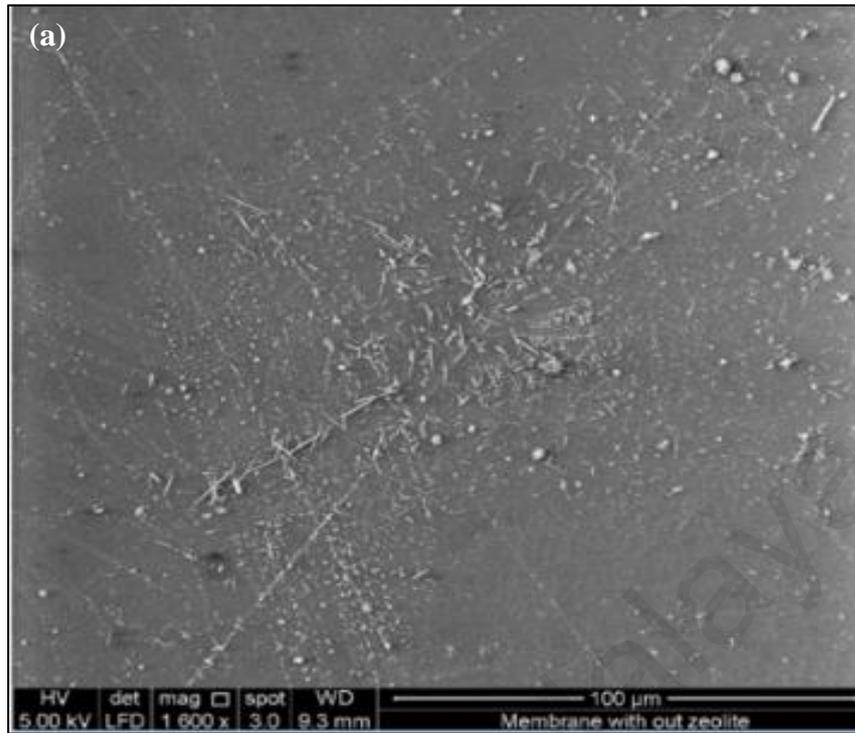


Figure 4.8: FESEM image of (a) RCC and (b) RCC-Z

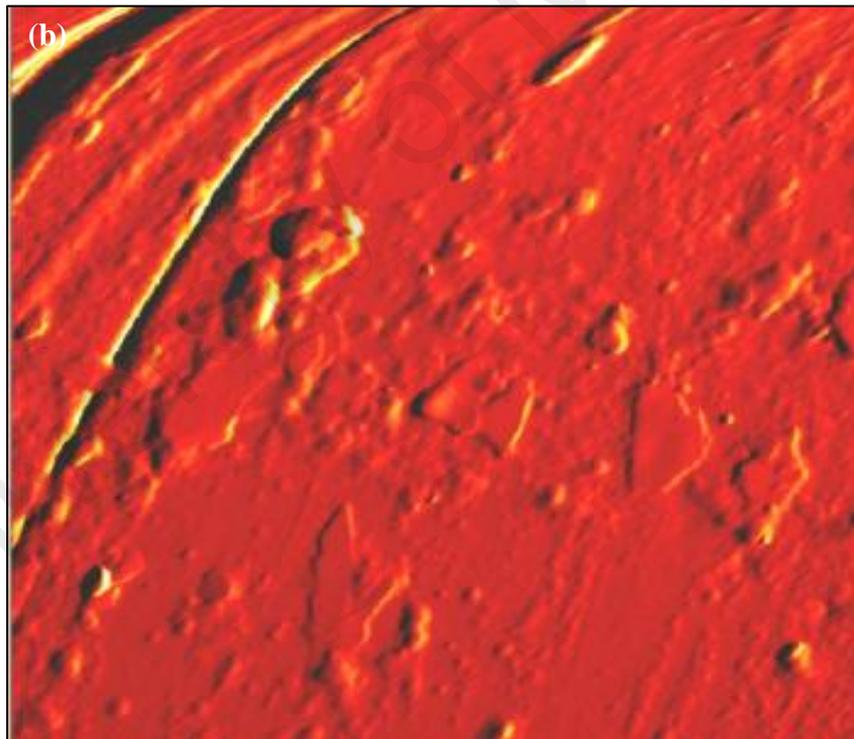
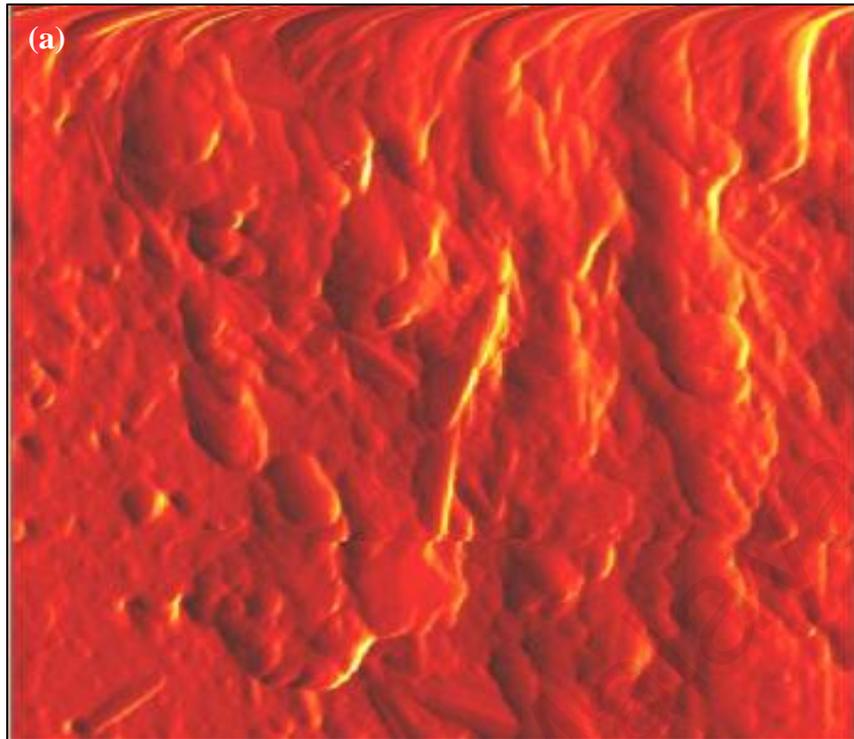


Figure 4.9: AFM image of (a) RCC and (b) RCC-Z

4.3 Membrane performance

4.3.1 Water uptake

In general, a PEM must absorb adequate water to assist the transportation of protons from anode to the cathode. The water uptake is dependent on the types of sulfonation adopted before membrane casting. Different types of sulfonation results in varied water uptake and it is unpredictable in most cases. The action can be taken that lower the water uptake if the membrane has small sulfonic group and vice versa. It is because excessive absorption of water would induce the loss of the dimensional stability and mechanical properties (Jang and Han, 2013). Previous studies stated that the presence of sulfonic ion in the membrane increases water uptake (Lim et al., 2012). Water uptake increases with increasing amount of sulfonic groups attached to the membranes. Hence, a good PEM should possess an optimum water uptake and low swelling ratio. However, there is no fixed value for optimum water uptake as it is dependent on the procedure of membrane synthesis, synthesis material and operating condition of the membrane during analysis (Elabd *et al.*, 2004; Jang *et al.*, 2013; Wu *et al.*, 2006).

By referring to Fig. 4.10, the water uptake for both OS-A and OS-M membrane is very high and the reading shows 75% and 40% respectively. For this case, OS-M is better compared to OS-A membrane because the water uptake lower and it can maintain the dimensional stability and mechanical properties of the OS-M membrane. The unsatisfactory performance of these membranes discontinued the further membrane performance analyses.

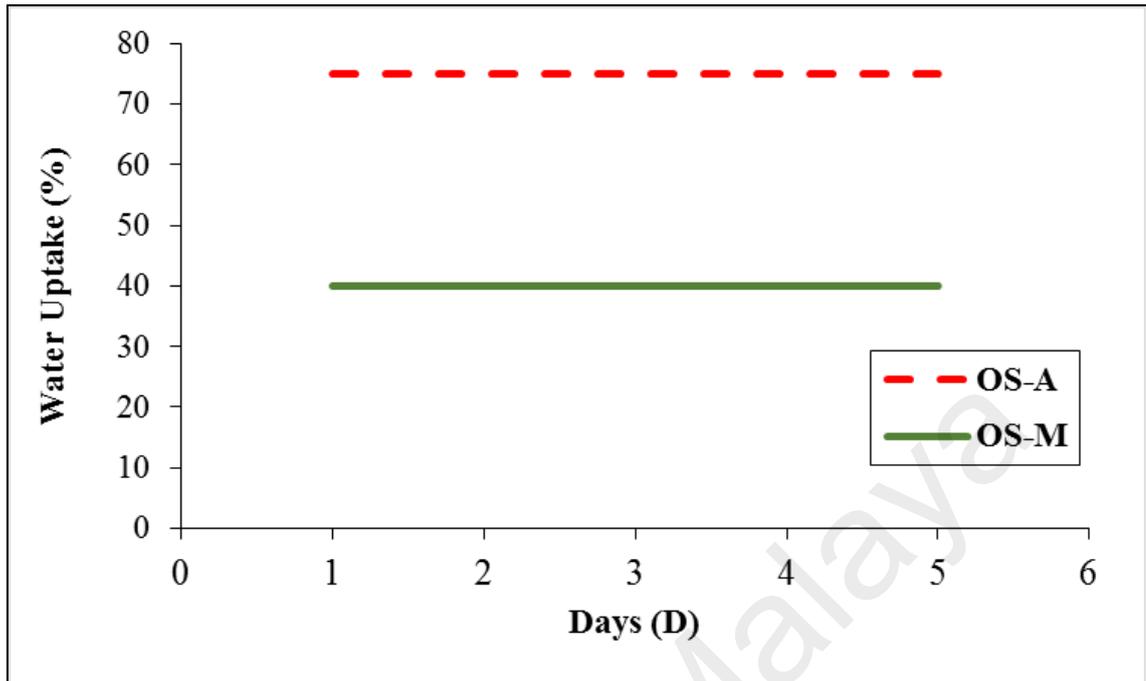


Figure 4.10: Water uptake of OS-A and OS-M membrane

The water uptake of the RCC and RCC-Z membranes for different days of immersion in DI water is depicted in Fig. 4.11. The results confirm that both the membranes are saturated within 24 h of immersion and the water uptake capacity remains constant. The water uptake capacity of RCC membrane is found to be higher (3.5%) than that of RCC-Z (2.5%) membrane. The water uptake is due to the hydration of the sulfonic groups. In general, high value of water uptake leads to higher proton conductivity attributed to the water residing in the hydrophilic domains of the membranes that facilitates the transport of protons. However the high value of water uptake has a negative effect attributed to swelling that reduces the mechanical stability as well as the performance of the membrane. Incorporation of zeolite to RCC reduces the polymer chain mobility and free volume that leads to more rigid and compact structures of the RCC-Z membranes, thus reduces the water uptake capacity. This is confirmed with the hydration number (λ_w) that is the number of absorbed water

molecules per sulfonic group. The λ_w of RCC and RCC-Z membranes are found to be 6.48 and 0.82 respectively. In general, the addition of zeolite increases the hydrophobicity of the membrane that would be helpful in reducing membrane fouling. The 28.5% reduction in water uptake of RCC-Z membrane than the RCC membrane has detrimental effect in proton exchange capacity; however this can be compromised with reduction in fouling. In general, the hydration of the sulfonic acid group during water uptake causes swelling of the ionic clusters. The swelling ratio of RCC and RCC-Z membrane measured at room temperature is found to 10% and 6%, respectively. Lower percentage of swelling obtained for RCC-Z membrane is due to increased hydrophobicity. The low swelling ratio of both RCC and RCC-Z membranes compared to Nafion 117[®] membrane (18%) indicates that the prepared membranes have good mechanical stability.

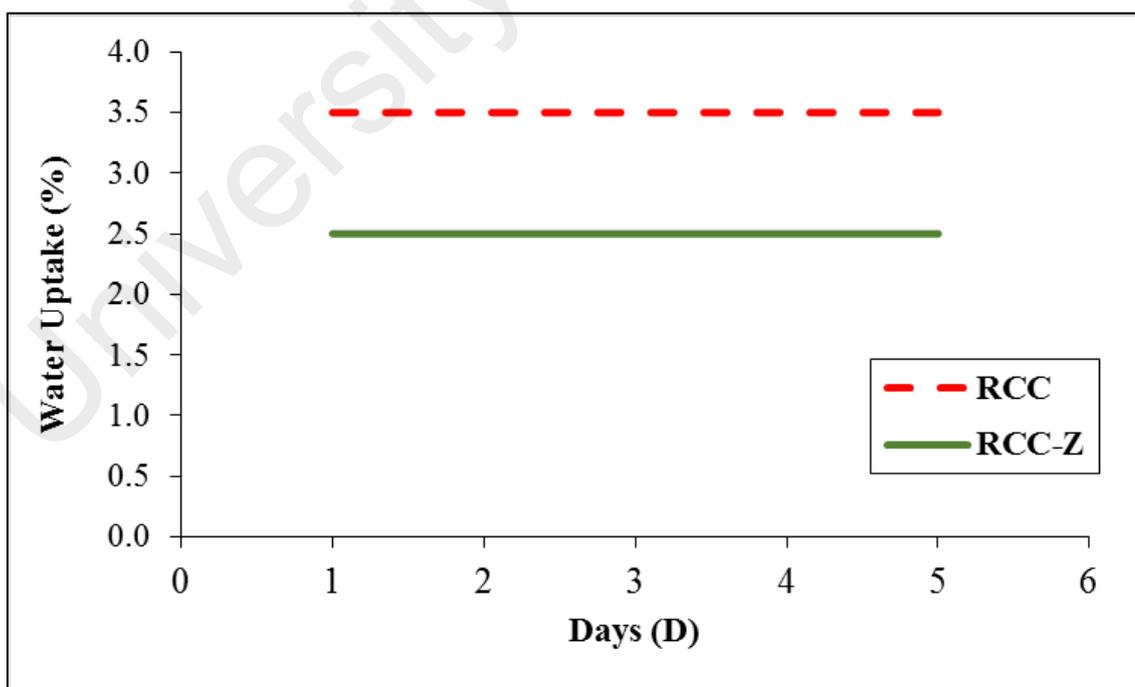


Figure 4.11: Water uptake of RCC and RCC-Z membranes

Fig. 4.12 illustrates inconsistency of water uptake characteristics of both RCD-1 and RCD-5. The water uptake is highest at day 1 and keep decreasing until it is constant started from day 3 till day 5. The trend is quite identical for both the samples with variation in the water uptake quantity. The highest water uptake of 1.43 % was exhibited by RCD-1 where else RCD-5 with 1.11 % at day 1 and it is drop till 1.27 % and 0.51 % respectively at day 2. This situation leads to the ability of the membrane to absorb water when it is in dry condition rather than in wet condition. During day 1 the membrane is fully hydrated and the record show on day 1 the reading is high due to high capability of membrane to absorb water. Then the membranes were weighted at day 2 and the weight different is slightly decrease from day 1. The value decrease continuously until a certain point and it will become constant. That is why the range of 5 days is chosen for the water uptake testing.

By comparing the water uptake of membranes prepared from waste polymer with (RCD membrane) and without sulfonation (PW membrane) the tendency is obviously different (Refer Table 4.1). The value of PW membrane shows approximately zero or no water was absorbed and it shows that skipping sulfonation process devoid the water absorption ability of the PS. This also led to influence the other dependent parameters like DS, IEC and proton conductivity.

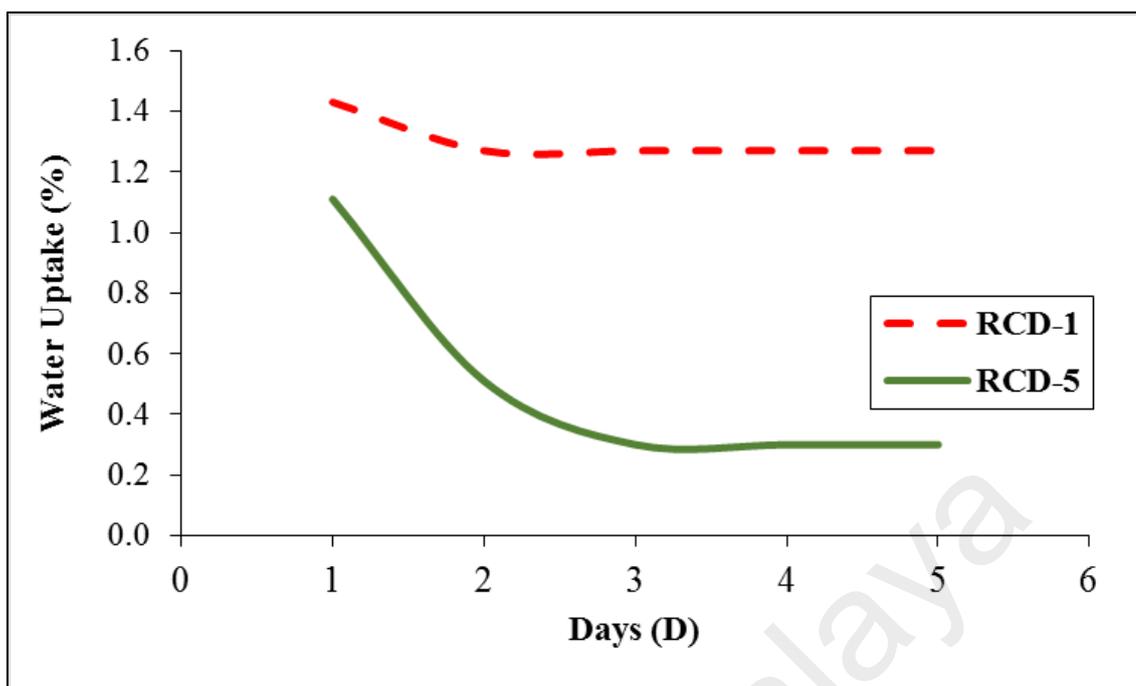


Figure 4.12: Water uptake of RCD-1 and RCD-5 membranes

The water uptake also varied according to the warmth of water employed in the experimenting condition, types of membrane (Lin *et al.*, 2013), the equivalent weights of membrane (Othman *et al.*, 2010) and also the DS (Wu *et al.*, 2006). The consistency of the water uptake reading cannot be simply concluded because different types of membrane give big gap of value for water uptake. As for sulfonated poly(styrene-isobutylene-styrene) triblock copolymer membrane the water uptake increases up to 351 wt% after the sulfonation has been done (Elabd *et al.*, 2004). The value of water uptake for poly(ether sulfone)/sulfonated poly(ether ether ketone) blends membrane is in the range of 6.5 wt% up to 85.0 wt% according to the degree of sulfonation (Wu *et al.*, 2006). Medium range of water uptake taken by sulfonated polystyrene-block-poly(ethyl-ran-propylene)-block-polystyrene (polySEPS) membrane which is from 10 wt% up to 70 wt% based on the temperature and different composition of chlorosulfonic acid (Jang *et al.*, 2013).

The comparison of various PEM studied by researchers is simplified in Table 4.1 along with the present findings.

Table 4.1: Water uptake comparison

Author	Membrane Type	Water uptake (wt%)	Factors
Elabd <i>et al.</i> , 2004	Sulfonated poly(styrene-isobutylene-styrene) triblock copolymer	351.0	-
Wu <i>et al.</i> , 2006	Poly(ether sulfone)/sulfonated poly(ether ether ketone) blends	6.5 – 85.0	Different degree of sulfonation
Jang <i>et al.</i> , 2013	Sulfonated polystyrene-block-poly(ethyl-ran-propylene)-block-polystyrene (polySEPS)	10.0 – 70.0	Different temperature and acid composition
Yu <i>et al.</i> , 2013	Sulfonated poly(arylene ether sulfone)/sulfonated zeolite	45.0 – 80.0	Different loading of sulfonated zeolite
Li <i>et al.</i> , 2005	Sulfonated poly(ether ether ketone ketone)	9.0 – 50.0	Different amount of monomer during polymer synthesis
Present study	RCC	3.7	-
Present study	RCC-Z	2.5	-
Present study	PW-U	0.0	The membrane unable to absorb any water
Present study	PW-H	0.0	The membrane unable to absorb any water
Present study	RCD-1	1.43	-
Present study	RCD-5	1.10 – 0.30	-

4.3.2 Ion exchange capacity (IEC)

The IEC represents the amount of exchangeable ions in unit grams of the dry polymer and depends on the number of sulfonic acid groups present in the membrane (Abdulkareem *et al.*, 2010; Shim *et al.*, 2005) and is determined by titration method (Zhang, 2009).

As mentioned previously the rest of analysis including IEC was not performed for the membranes prepared through open sulfonation method, owing to its abrupt water uptake potential that leads to poor stability and thus diminishing its applicability in fuel cells. The IEC of RCC and RCC-Z membranes is found to be 0.03 and 0.17 meq/g respectively. The results indicate that the addition of zeolite enhanced the IEC. In general, the IEC strongly depends on DS. Since the sulfonation time is fixed for both the membranes, the DS is same for both the membranes. However the addition of zeolite to the RCC polymer solution reduces the reduction in sulfonic acid group in the unit volume of the casting solution. This would actually decrease the IEC of RCC-Z membrane than the RCC membrane. However, the increased IEC of RCC-Z membrane is attributed to the ions released by the zeolites. In general, the movement of the ionic groups from one cluster to another in RCC membrane is responsible for the transportation of ions. The lower value of IEC of SPS membrane might be attributed to the lower level of connectivity of the ionic groups compared to that of RCC-Z membrane under the same fabrication conditions. The higher value of connectivity between the regularly spaced styrene side chains and sulfonic acid groups because of zeolite addition might also be a reason for high IEC of RCC-Z membrane. The IEC values of RCC-Z membrane is comparable or higher than the Nafion 117[®] membrane (IEC = 0.16 meq/g) under the same experimental conditions. This suggests that the RCC-Z membrane have potential for proton exchange and can be used in fuel cell applications.

The IEC value for membranes prepared from PS waste RCD-1 and RCD-5 was found to be 0.220 meq/g and 0.536 meq/g respectively. This proves that high sulfonic acid group attached to the polymer lead to the increasing in IEC since RCD-5 membrane has high amount of acetyl sulfate added during the sulfonation phase. The unsulfonated samples resulted in 0.105 meq/g and 0.124 meq/g for PW-U and PW-H respectively which is lower as expected. Further it is well clear that the membrane casted from the PS waste excelled with a greater IEC value than that of the one prepared through PS beads. This was due to the better sulfonation than that of the former.

In general IEC determines the amount of H^+ ion in the membrane. These ions known as an ion exchangeable group which is responsible for proton transfer (Aini *et al.*, 2012). The value of IEC for Nafion® 117 reported as 1.13 meq/g. This value can be used as references for the comparison of the IEC value from other types of membrane that also reported. For the polySEPS membrane the IEC shows higher value compared to Nafion® 117 which is 1.36 meq/g by using same ionic content (Jang *et al.*, 2013). For UV Irradiated SPEEK/chitosan membrane the value of IEC is in the range of (0.01 to 0.19) meq/g which is quite low (Aini *et al.*, 2012). The range of IEC value for sulfonated polystyrene butadiene rubber reported by Abdulkareem *et al.*, 2010 is in between 0.13 meq/g to 0.63 meq/g. The finding is summarized in Table 4.2 included various finding by other researchers.

Table 4.2: Ion exchange capacity comparison

Author	Membrane Type	Ion Exchange Capacity (IEC) meq/g
Jang <i>et al.</i> , 2013	Nafion® 117	1.13
Jang <i>et al.</i> , 2013	Sulfonated polystyrene-block-poly(ethyl-ran-propylene)-block-polystyrene (polySEPS)	1.36
Aini <i>et al.</i> , 2012	UV Irradiated SPEEK/Chitosan	0.010 to 0.190
Abdulkareem <i>et al.</i> , 2010	Sulfonated polystyrene butadiene rubber	0.130 to 0.630
Yu <i>et al.</i> , 2013	Sulfonated poly(arylene ether sulfone)/sulfonated zeolite	2.31 – 2.56
Li <i>et al.</i> , 2005	Sulfonated poly(ether ether ketone ketone)	0.72 – 1.93
Xu <i>et al.</i> , 2002	Sulfonated poly(phenylene oxide)	2.0 – 3.21
Present study	RCC	0.030
Present study	RCC-Z	0.170
Present study	PW-U	0.105
Present study	RCC-Z	0.170
Present study	RCD-1	0.220
Present study	RCD-5	0.536

4.3.3 Degree of sulfonation (DS)

The sulfonation process converts the properties of polystyrene polymer from insulator to conductor (Abdulkareem *et al.*, 2010). DS is based on how successful the SO_3^- attached to the polystyrene polymer.

After 6 h of sulfonation reaction, the DS of the formed RCC membrane is found to be 0.31%. The DS of the RCC-Z membrane is assumed to be the same due to the addition of zeolite was done after the sulfonation process. RCC-Z membrane is a RCC zeolite composite membrane and not RCC membrane on zeolite surface. The degree of polymerization can be controlled by the reaction time and temperature. Since the membrane is prepared without isolating the sulfonation reaction, a lower DS is better to reduce the swelling behaviour of the membrane.

The DS for both RCD-1 and RCD-5 is 2.33% and 5.83% respectively and it is higher than that of the samples prepared from the RCC method. The increase in the DS percentage for RCD-5 was due to higher volume of acetyl sulfate added during the sulfonation reaction. However, for RCC and RCC-Z membrane the sulfonation process is the same but the membrane casting is different and it nowhere affected the value of DS.

The DS value of PW membrane which is 1.10% for PW-U and 1.30% for PW-H. This indicated the presence of sulfur compound in the PW membrane casting. However, it cannot be identified either it is sulfonic acid group or vice versa since this membrane does not show any capability to absorb water during water uptake testing because based on the theory the presence of sulfonic acid helps in absorption of water.

4.3.4 Proton conductivity

Proton conductivity of RCC and RCC-Z membranes at 55% relative humidity and at room temperature ($30\pm 2^\circ\text{C}$) are estimated from the measured resistance and the current-voltage characteristic curves of the membranes are presented in Fig. 4.13. The details of the conductivity experiments of RCC and RCC-Z are tabulated in Table 4.3. The addition of zeolite onto RCC membrane increased the proton conductivity by one order of magnitude confirms that the role of zeolite in enhancing proton conductivity of RCC membrane. This is contradictory with the water uptake result, where higher absorption of water usually leads to higher proton conductivity. Although RCC-Z membrane has lower water uptake, it has higher proton conductivity compared to RCC membrane. The RCC-Z membrane showed lower resistance than the RCC membrane attributed to the larger average separation of neighbouring sulfonic acid group and hydrophilic/hydrophobic interface of the zeolite in the RCC-Z membrane, which reduces the resistance for proton transport to pass through the membrane.

In addition, the conductivity of a Nafion 117[®] membrane at the same experimental conditions is measured for reference. The conductivity obtained for Nafion 117[®] agrees well with literature values (Di Vona *et al.*, 2007; Bae and Kim, 2003). Thus, it can be inferred that zeolite enhanced the properties of the membrane through other means instead of increasing the water uptake of the membrane. Bae and Kim (2003) reported that the proton conductivity increased linearly with the sulfonation time to 6 h, beyond which no distinguishable increase of proton conductivity was observed (Bae and Kim, 2003). The proton conductivity of the RCC and RCC-Z membranes is comparable or higher than the Nafion 117[®] membrane under the same experimental conditions indicates that the fabricated membranes have good potential for membrane applications. The ranges of proton conductivity result based on the references are in the range of 10^{-8} to 10^{-2} (S/cm). Higher conductivity values reported in

literatures are usually conducted at 100% relative humidity and at high temperature (>80°C).

Table 4.3: Proton Conductivity of RCC and RCC-Z membranes

Membrane	Resistance (Ω)	Thickness ($\times 10^{-2}$ cm)	Area (cm^2)	Proton Conductivity (S/cm)
RCC	544.61	2.286	25	1.68×10^{-6}
RCC-Z	82.31	2.286	25	1.11×10^{-5}

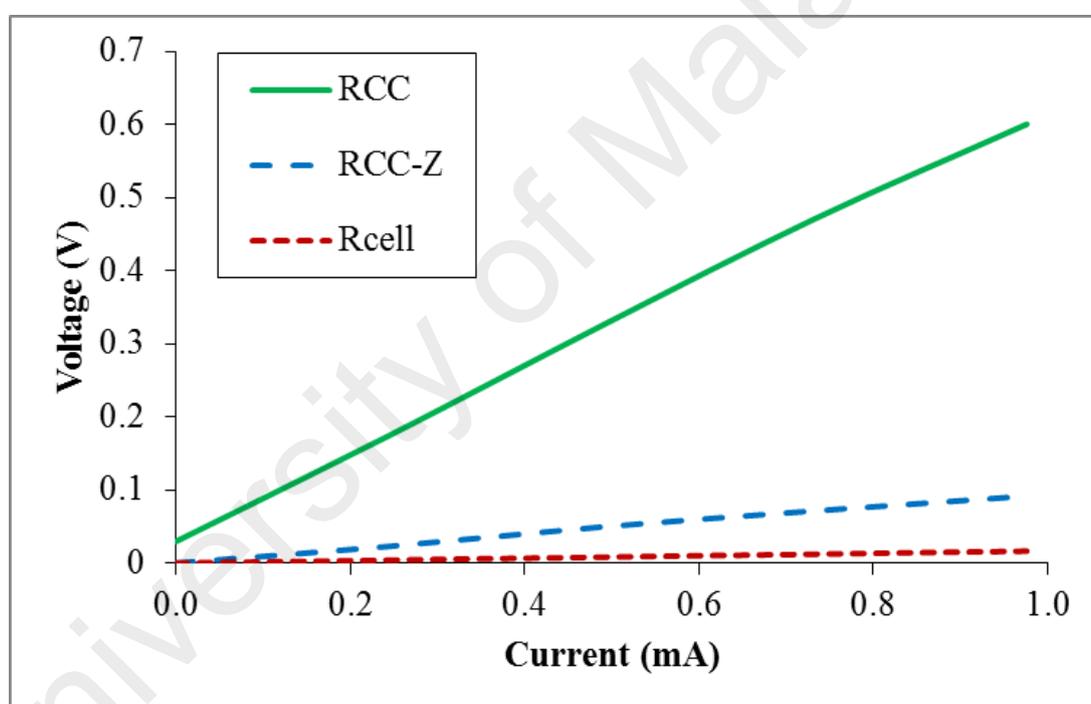


Figure 4.13: Current-voltage characteristic curves of RCC and RCC-Z membranes

From the Table 4.5 the membrane resistance for RCD-5 is higher compared to RCD-1. This is directly influenced by the addition of high amount of acetyl sulfate added during the sulfonation. It is also evident that the addition of sulfonic group well supported for the superior proton conductivity. The formula or Eq. 3.7 is used in

calculating proton conductivity for PEM. The proton conductivity for PW membrane as shown in Table 4.4 is slightly lower compared to the RCD membrane.

Table 4.4: Proton Conductivity of PW-U and PW-H membranes

Membrane	Resistance (Ω)	Thickness ($\times 10^{-2}$ cm)	Area (cm^2)	Proton Conductivity (S/cm)
PW-U	2427.3	2.286	7.07	1.33×10^{-6}
PW-H	1948.0	2.743	7.07	1.99×10^{-6}

Table 4.5: Proton Conductivity of RCD-1 and RCD-5 membranes

Membrane	Resistance (Ω)	Thickness ($\times 10^{-2}$ cm)	Area (cm^2)	Proton Conductivity (S/cm)
RCD-1	2225.3	3.200	7.07	2.03×10^{-6}
RCD-5	1066.1	4.572	7.07	6.07×10^{-6}

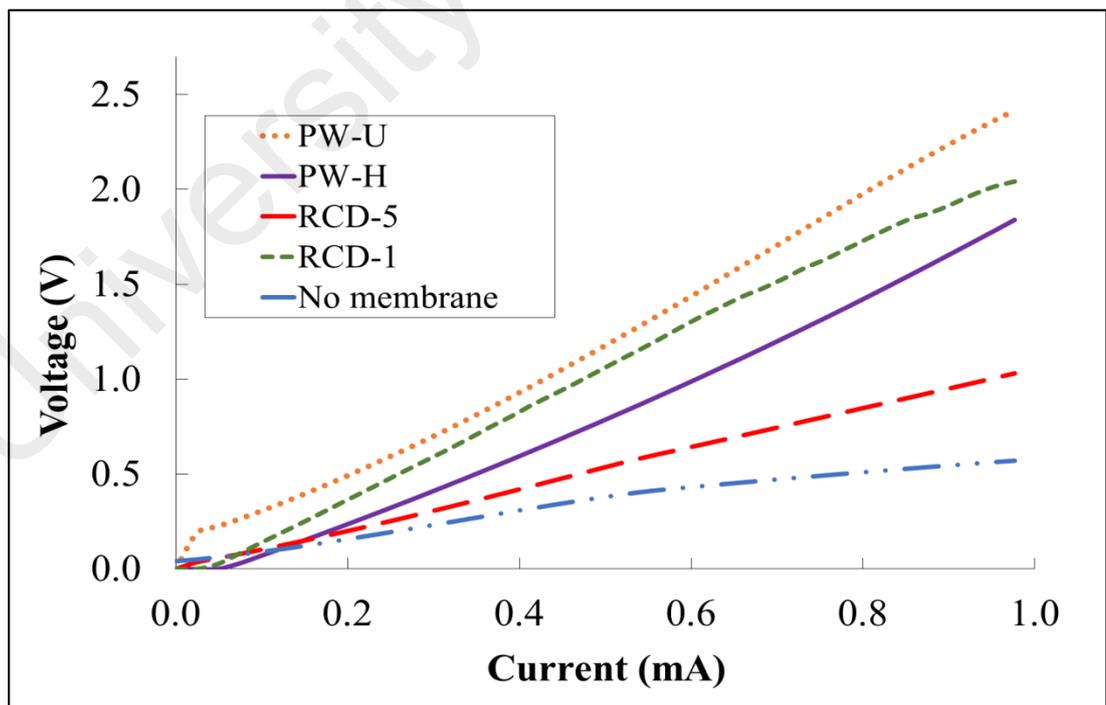


Figure 4.14: Current-voltage characteristic curves of PW and RCD membranes

A major possession of PEM that needs to be focused is proton conductivity. The relative humidity condition and temperature of the experimental area affect the value of proton conductivity of the same membrane (Lee *et al.*, 2005; Othman *et al.*, 2010). Hence, the comparison only can be made with the membrane tested under same condition while the value from reports that are available can be used as references or bench mark. High proton conductivity is greatly needed to obtain high voltage per current density in the unit cell. The proton conductivity has been report as in the range of 0.3×10^{-2} S/cm (Abdulkareem *et al.*, 2010) and 2.85×10^{-7} S/cm (Aini *et al.*, 2012). The value of proton conductivity is also affected by other factors such as the addition of other materials like chitosan which drop the reading of proton conductivity by magnitude of 10^{-4} (Aini *et al.*, 2012). Changes in degree of sulfonation and temperature during membrane synthesis also affected the value of proton conductivity (Abdulkareem *et al.*, 2010).

As presented in this report, the value of proton conductivity proton conductivity for RCC and RCC-Z are 1.68×10^{-6} S/cm and 1.11×10^{-5} S/cm respectively. It has shown the increment by the magnitude of 10^1 and it achieve the objective of sulfonation as the objective is to increase the value of proton conductivity with the addition of zeolite particle into RCC membrane. For the waste polystyrene the proton conductivity value are all in the magnitude of 10^{-6} and the value is increasing after the sulfonation and after the addition of acetyl sulfate. The finding is summarized in Table 4.6 also included other researchers result as comparison.

Table 4.6: Proton conductivity comparison

Author	Membrane Type	Proton Conductivity (S/cm)
Abdulkareem <i>et al.</i> , 2010	Sulfonated polystyrene butadiene rubber	0.30×10^{-2}
Aini <i>et al.</i> , 2012	UV Irradiated SPEEK/Chitosan	2.85×10^{-7}
Mulijani <i>et al.</i> , 2014	Sulfonated polystyrene	3.80×10^{-6}
Yu <i>et al.</i> , 2013	Sulfonated poly(arylene ether sulfone)/sulfonated zeolite composite	$(0.17 - 0.30) \times 10^{-1}$
Li <i>et al.</i> , 2005	Sulfonated poly(ether ether ketone ketone)	$3.6 \times 10^{-4} - 1.0 \times 10^{-1}$
Present study	RCC	1.68×10^{-6}
Present study	RCC-Z	1.11×10^{-5}
Present study	RCD-1	2.03×10^{-6}
Present study	RCD-5	6.07×10^{-6}
Present study	PW-U	1.33×10^{-6}
Present study	PW-H	1.99×10^{-6}

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Different types of PEM were synthesized using polystyrene beads and waste and its calibre was examined through series of analyses. The obtained decision drawn from those analyses were presented below:

- The open sulfonation resulted in a membrane with deprived degree of sulfonation thus lead to a very higher water uptake and poor mechanical stability and limiting its chances as a suitable candidate for fuel cell applications.
- The RCC method overhauled the limitations of the OS method and emerged with better water uptake, IEC and proton conductivity.
- The study showed the influence of inorganic additive on the membrane stability and proton conductivity; whereby appreciable proton conductivity was exhibited by PEM with zeolite. Thus, presentation its critical role in improving proton conductivity.
- The membranes obtained from the polystyrene waste showed a higher degree of sulfonation, water uptake and greater potential IEC than that of the one obtained from virgin PS beads.
- The studies signified the impact of sulfonic acid group attached onto the polymer structure toward various membrane characteristics like water uptake, IEC and proton conductivity.
- The present study successfully prepared a PEM from a waste PS with a membrane characteristic comparable to that prepared from virgin PS. Although there was a negligible difference in the proton conductivity, but

still it has competence almost equivalent to that of the one obtained from virgin PS beads. The inclusion of the zeolite into the RCD membrane will irrefutably contribute for the appreciable proton conductivity characteristics.

- Over all the PEM synthesized using waste PS which is RCD-5 membrane excelled with a potential alternative and replacement for the traditional precursors based on the result shown in membrane performance analysis.

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5.2 Recommendations

The following recommendations are taken into considerations for future research works.

- Zeolite shows positive improvement in increasing proton conductivity. Hence, the optimization of zeolite quantity can be done to improve the performance of the membrane. Furthermore, other hydrophilic ceramic/organic filler such as SiO_2 , TiO_2 , and ZrO_2 can also be used as additive.
- Good result is shown by RCD-5 which was synthesized using waste polystyrene. Extended research can be done using different types of expanded polystyrene (EPS) for PEM such as hot beverage cup, meat trays and vegetables trays.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

Paper Published

1. Anis Nurdhiani Rosdi, Yee Li Kang, Purushothaman Monash, Shaliza Ibrahim, Pichiah Saravanan (2015). Preparation and Characterization of Zeolite Polymer Composite Proton Exchange Membrane. *Desalination and Water Treatment*, 2015, 1 – 9.

Conference Presentation

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