

PHOSPHORIC ACID DOPED FUEL CELL MEMBRANES BY RADIATION  
GRAFTING OF 4-VINYLPYRIDINE/COMONOMERS MIXTURES ONTO  
POLY(ETHYLENE-CO-TETRAFLUOROETHYLENE) FILMS

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A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical and Energy Engineering  
Universiti Teknologi Malaysia

MARCH 2018

## **DEDICATION**

To my parents and siblings for their supports and understandings

## ACKNOWLEDGEMENT

I would like to express my sincere thanks to my supervisor, Prof Dr. Mohamed Mahmoud El-Sayed Nasef for the consistent teachings, guidance and ideas to upgrade my work throughout the course. I would like to thank Prof Dr. Arshad, my co-supervisor for the financial support under the LRGS Grant (vote # 4L817).

I wish to express my gratitude to the Membrane Research Unit members for their help, advices and useful discussions throughout the project.

Many thanks to MyBrain under Ministry of Higher Education Malaysia for providing me scholarship for three years.

## ABSTRACT

Proton exchange membrane fuel cell (PEMFC) is one of the most promising green technologies for providing clean and efficient energy and operating above 100 °C is highly desired to enhance the electrodes kinetics and increase tolerance to carbon monoxide impurities from reformed hydrogen. However, the commercially available membranes for fuel cell such as Nafion<sup>®</sup> are expensive and have limited operational temperature ( $\leq 80$  °C). This work aims to develop alternative phosphoric acid (PA) doped membranes using basic radiation grafted precursor films for PEMFC operating at temperatures 120 °C. Particularly, the main objective of this study was to develop three PA doped membranes by radiation induced grafting of mixture of 4-vinylpyridine (4-VP) with glycidyl methacrylate (GMA), 1-vinylimidazole (1-VIm) or triallyl cyanurate (TAC) onto poly(ethylene-co-tetrafluoroethylene) (ETFE) films followed by doping with PA. A membrane obtained by grafting of 4-VP alone onto ETFE film and acid doping was used as a reference. The degree of grafting (DG) was controlled by optimization of the reaction parameters such as absorbed dose, composition of monomer mixture, temperature and reaction time whereas the acid doping level (DL) was manipulated by variation of PA concentration, reaction temperature and time. The properties of the PA doped membranes denoted as ETFE-*g*-P(4-VP)/PA, ETFE-*g*-P(4-VP/GMA)/PA, ETFE-*g*-P(4-VP/1-VIm)/PA, ETFE-*g*-P(4-VP/TAC)/PA together with the corresponding grafted and pristine ETFE films were evaluated in correlation with type and concentration of second monomer added to 4-VP (comonomer) using Fourier transform infrared, field emission scanning electron microscope, thermal gravimetric analysis and x-ray diffraction. The membranes were also subjected to elemental as well as mechanical analysis and their proton conductivity together with fuel cell test were investigated at 120 °C. The DG was found to be strongly dependent upon grafting parameters. The obtained membranes attained high DL which reached 97 %, 115 %, 119 % and 113 % for membranes grafted with 4-VP, 4-VP/GMA, 4-VP/1-VIm and 4-VP/TAC, respectively. All the membranes displayed well-defined structures, good thermal stability, reasonable mechanical strength and high proton conductivity in the range of 33-44 mS/cm (at 120 °C and 0 % RH). The mechanical properties of ETFE-*g*-P(4-VP/TAC)/PA membrane was significantly improved by introducing TAC as a comonomer during grafting, which crosslinked the PA doped grafted chains compared to the other two membranes. ETFE-*g*-P(4-VP/1-VIm)/PA membrane showed the best fuel cell performance (226 mW/cm<sup>2</sup>) at 120 °C and 20 % RH conditions compared to the other two membranes and this is due to the increase of number of protonated pyridine and imidazole rings that could host more PA. The sequence of the membranes' performance in PEMFC represented by power density was ETFE-*g*-P(4-VP/TAC)/PA (84 mW/cm<sup>2</sup>) > ETFE-*g*-P(4-VP/GMA)/PA (76 mW/cm<sup>2</sup>) > ETFE-*g*-P(4-VP/1-VIm)/PA (70 mW/cm<sup>2</sup>) > ETFE-*g*-P(4-VP)/PA (53 mW/cm<sup>2</sup>) under dry conditions. Thus, it can be concluded that grafting of comonomers is an effective method to enhance the conductivity of PA doped membranes in way making them more suitable for fuel cell operation above 100 °C.

## ABSTRAK

Sel bahan api membran penukaran proton (PEMFC) adalah salah satu teknologi hijau yang paling berpotensi untuk menyediakan tenaga yang bersih dan cekap dan operasi lebih daripada 100 °C sangat dikehendaki untuk meningkatkan kinetik elektrod dan meningkatkan toleransi terhadap bendasing karbon monoksida yang terhasil daripada hidrogen diperbaharui. Bagaimanapun, membran komersial untuk sel bahan api seperti Nafion® adalah mahal dan mempunyai suhu operasi terhad ( $\leq 80$  °C). Kerja ini bertujuan untuk menghasilkan membran alternatif terdop asid fosforik (PA) dengan menggunakan filem prapenanda cantuman radiasi asas untuk PEMFC beroperasi pada suhu 120 °C. Khususnya, objektif utama kajian ini adalah untuk menghasilkan tiga membran terdop PA melalui cantuman teraruh radiasi yang mengandungi campuran 4-vinylpiridin (4-VP) dengan glycidyl metakrilat (GMA), 1-vinylimidazol (1-VIm) atau *triallyl cyanurate* (TAC) terhadap filem poli(etilena-kotetrafluoroetilena) (ETFE) diikuti pengdopan PA. Membran terhasil melalui cantuman 4-VP sahaja terhadap filem ETFE dan pengdopan asid dijadikan sebagai rujukan. Tahap cantuman (DG) dikawal dengan pengoptimuman parameter tindak balas seperti dos terserap, campuran komposisi monomer, suhu dan masa tindak balas manakala tahap pengdopan asid (DL) telah dimanipulasi oleh perubahan kepekatan PA, suhu tindak balas dan masa. Sifat-sifat membran terdop PA dilabelkan sebagai ETFE-*g*-P(4-VP)/PA, ETFE-*g*-P(4-VP-*co*-GMA)/PA, ETFE-*g*-P(4-VP-*co*-1-VIm)/PA dan ETFE-*g*-P(4-VP-*co*-TAC)/PA dinilai bersama dengan filem-filem tercantum dan ETFE asal berdasarkan jenis dan kepekatan monomer kedua yang ditambah kepada 4-VP (komonomer) menggunakan spektroskopi infra-merah transformasi Fourier, medan pemancaran mikroskopi pengimbas elektron, analisis gravimetrik haba dan pembelauan sinar-X. Analisis berunsur serta mekanikal dan kekonduksian proton membran berserta ujian sel bahan api telah diuji pada 120 °C. DG didapati sangat bergantung kepada parameter cantuman. Membran dengan DL yang tinggi masing-masing diperolehi sampai 97 %, 115 %, 119 % dan 113 % untuk membran 4-VP, 4-VP/GMA, 4-VP/1-VIm dan 4-VP/TAC. Semua membran menunjukkan struktur yang baik, kestabilan terma baik, kekuatan mekanikal yang munasabah dan kekonduksian proton tinggi dalam lingkungan 33-44 mS/cm (pada 120 °C dan 0 % RH). Sifat mekanikal membran ETFE-*g*-P(4-VP/TAC)/PA telah bertambah baik dengan memperkenalkan TAC sebagai komonomer ketika cantuman menyebabkan rantai cantuman yang terdop PA tersilang berbanding dengan dua membran lain. Membran ETFE-*g*-P(4-VP/1-VIm)/PA telah menunjukkan prestasi sel bahan api terbaik (226 mW/cm<sup>2</sup>) pada 120 °C dan 20 % RH berbanding dengan dua membran lain yang disebabkan oleh peningkatan bilangan piridin proton dan gelang imidazol yang boleh menampung lebih PA. Prestasi membran dalam PEMFC disenaraikan mengikut urutan ketumpatan kuasa adalah ETFE-*g*-P(4-VP/TAC)/PA (84 mW/cm<sup>2</sup>) > ETFE-*g*-P(4-VP/GMA)/PA (76 mW/cm<sup>2</sup>) > ETFE-*g*-P(4-VP/1-VIm)/PA (70 mW/cm<sup>2</sup>) > ETFE-*g*-P(4-VP)/PA (53 mW/cm<sup>2</sup>) dalam keadaan kering. Kesimpulannya, cantuman komonomer adalah satu kaedah berkesan untuk meningkatkan kekonduksian membran yang terdop dengan PA untuk lebih sesuai beroperasi dalam sel bahan api pada suhu lebih daripada 100 °C.

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**LIST OF SYMBOLS**

E (%)	-	Elongation at break (%)
L	-	Distance between probes (cm)
r	-	Reactivity ratio (-)
R	-	Membrane resistance ( $\Omega$ )
	-	Universal Gas constant (8.314 J/mol K)
T	-	Thickness of the membrane (cm)
W	-	Width of the membrane (cm)
$W_g$	-	Weight of the film after grafting (g)
$W_0$	-	Weight of the film before grafting (g)
$W_d$	-	Weight of the film after doping with phosphoric acid (g)
$\sigma$	-	Proton conductivity (mS/cm)

**LIST OF ABBREVIATIONS**

4-VP	-	4-vinylpyridine
1-VIm		1-vinylimidazole
EB	-	Electron Beam
ETFE	-	Poly (ethylene- <i>alt</i> -tetrafluoroethylene)
DG	-	Degree of grafting
DL	-	Doping level
FTIR	-	Fourier Transform Infrared Spectroscopy
FEP	-	Poly (tetrafluoroethylene-co-hexafluoropropylene)
FE-SEM	-	Field Emission Scanning Electron Microscope
GDE	-	Gas diffusion electrode
GMA	-	Glycidyl methacrylate
HTPEM	-	High temperature proton exchange membrane
MEA	-	Membrane electrode assembly
PA	-	Phosphoric acid
PBI	-	Polybenzimidazole
PD	-	Power density
PE	-	Polyethylene
PEM	-	Proton exchange membrane

PFA	-	Poly (tetrafluoroethylene- <i>co</i> -perfluorovinyl ether)
PVDF	-	Poly (vinylidene fluoride)
PTFE	-	Poly (tetrafluoroethylene)
RH	-	Relative humidity
TAC	-	Triallyl cyanurate
TGA	-	Thermal Gravimetric Analysis
TS	-	Tensile strength
XRD	-	X-Ray diffraction

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## CHAPTER 1

### INTRODUCTION

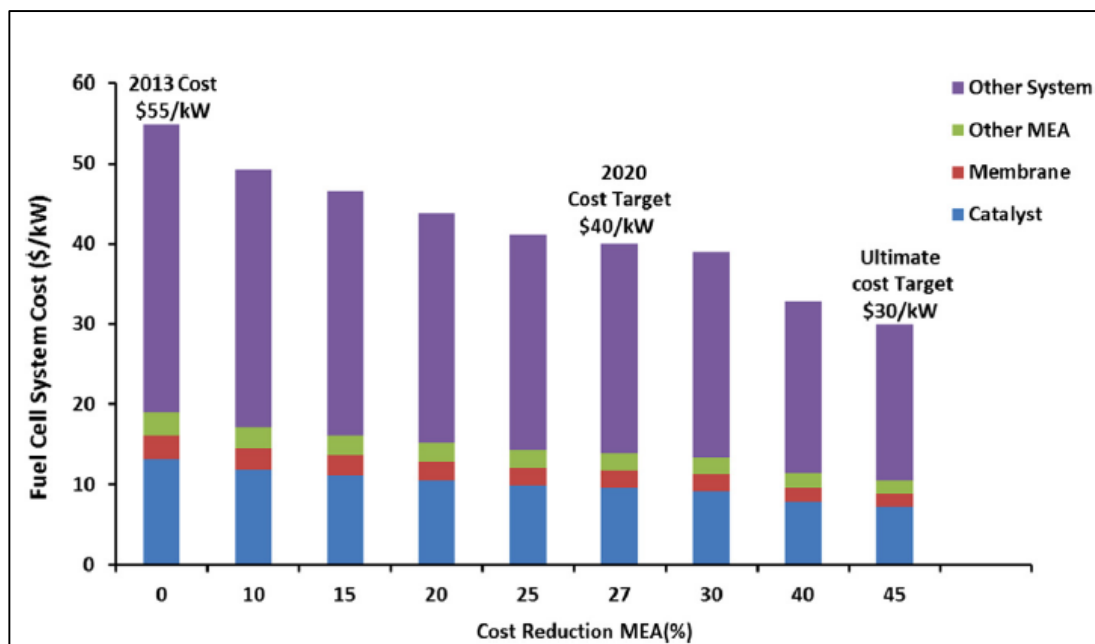
#### 1.1 Background

Energy has become the currency of political and economic power, the determinant of the hierarchy of nations, a new marker, even, for success and material advancement. Rising demand for energy and the global economy's dependence for the continuous availability and affordability of energy necessitates research into alternate renewable sources. Currently, the most abundant energy sources are fossil fuels: coal, natural gas and crude oil. Although these fossil fuels are rather cheap and are of high energy density, reserves are limited and supply can be interrupted as result of conflicts in production areas. Moreover, the combustion of fossil fuels emits carbon dioxide (CO<sub>2</sub>), which acts like a planet-sized greenhouse that traps the sun's heat and increases global temperatures (Dincer, 1998). The CO<sub>2</sub> emissions contribute to climate change and profoundly affects every life on Earth. One solution to mitigate the problems and to satisfy growing energy demands is by employing renewable energy technologies on a large scale. Alternative energy sources such as wind power, geothermal, solar biomass are fast growing. However, they have low efficiency and it is difficult to find suitable means for energy storage due to the intermittent nature of these primary energies (Ibrahim *et al.*, 2008).

One of the emerging sources which have received an increasing attention in the last two decades is fuel cell technology. Fuel cells are known as an electrochemical energy conversion device that can replace fossil fuel extraction and



processing activities and its use which emits harmful greenhouse gases. The chemical energy stored in hydrogen can be converted to electrical energy by fuel cells to generate pollution-free power. The production of hydrogen as a source of energy can reduce fossil fuel dependency because a wide range of feedstocks can be used to produce hydrogen. The relative ease and inexpensive of producing hydrogen could improve access to energy around the world. Moreover, if fuel cell technology is implemented, the widespread use of this clean green energy technology since its by-product of vaporised water does not harm the environment. In summary, fuel cells have a number of advantages compared to internal combustion engine such as higher efficiency and power density, low emission, silent operation in addition of absence of dependency on conventional fuels such as oil or gas and can therefore reduce economic reliance on fossil fuel and creating greater energy security for the user nation. This suggests that fuel cells are a sustainable energy supply and can help to avert energy shortage crisis. The global fuel cell market is expanding vastly, and several automobile makers have already started to market green cars at affordable prices which are aimed at the middle-income population. Figure 1.1 shows the progress of the fuel cell cost and the costs have significantly reduced and are approaching the U.S. Department of Energy (DOE)'s goal for 2020 which is targeted at \$40/kW (Guerrero Moreno *et al.*, 2015). Based on Figure 1.1, while reducing the membrane electrode assembly (MEA) cost up to 27%, the target cost can be achieved, corresponding to a total reduction on catalyst cost of about \$10/kW and \$2.5/kW on membrane cost. The MEA cost refers to the sum of catalyst, membrane, and other MEA cost such as gas diffusion layer and gaskets. Meanwhile, the cost for other systems includes bipolar plates, humidifier, gas supply, fuel cell stack and so on.



**Figure 1.1** Fuel cell system cost with cost reduction in MEA for 500,000 units/year (Guerrero Moreno *et al.*, 2015).

Fuel cells are available in different types, which can be classified based on the type of electrolyte used or operating temperature requirements of different manufacturers and systems. Fuel cells that are currently under investigation include polymer electrolyte or proton exchange membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), solid oxide cells (SOFCs), phosphoric acid fuel cells (PAFCs) and molten carbonate fuel cells (MCFCs) (Steele and Heinzel, 2001). Of all, PEMFC have a number of advantages such as compact construction, large current density, solid electrolyte, low working temperature and fast start-up that made them more suitable not only for stationary applications, but also for mobile (transportation) and portable applications (Sharaf and Orhan, 2014).

PEM fuel cells have been tested widely with Nafion<sup>®</sup> membranes (DuPont) as PEM that is operated under full hydration to low temperature up to 80 °C (to maintain high relative humidity, RH). However, at this temperature, the accompanied heat and water required appropriate management systems making the fuel cell complex. Moreover, the platinum (Pt) catalyst on the electrodes can be easily contaminated by CO and SO<sub>2</sub> originated from hydrogen obtained from reformat hydrocarbon. However, these limitations can be overcome by increasing

the operating temperature above 100 °C (Li *et al.*, 2014; Liu *et al.*, 2016b). Although Nafion<sup>®</sup> membranes possess superior chemical and mechanical stabilities along with long term durability, it has number of limitations such as dehydration at temperatures above 80 °C and increase of gas crossover in addition to high cost (Li *et al.*, 2003; Mahreni *et al.*, 2009; Markova *et al.*, 2009).

To tackle the high cost of fuel cells, which is mainly caused by the high cost of PEM (e.g. Nafion<sup>®</sup> membrane) and expensive electrode materials (platinum), various research efforts have been made to speed the commercialization of PEMFC especially for transportation applications (Gubler, 2014; Nasef *et al.*, 2016b). This led to a progress towards significant reduction in fuel cells in a way approaching the U.S. Department of Energy (DOE)'s goal for 2020 which is targeted at \$40/kW (Bakangura *et al.*, 2016). In the search for PEM with reduced cost, radiation induced grafting (RIG) has been found to be a cost effective method for preparation of PEMs for fuel cell applications and can be tailor made to exhibit wide range of properties to prepare membranes (Gubler *et al.*, 2005; Gubler *et al.*, 2006; Nasef *et al.*, 2016b; Nasef and Güven, 2012).

## 1.2 Problem Statement

PEMFC is widely tested with perfluorosulfonic acid (PFSA) membranes such as Nafion<sup>®</sup> which showed good chemical stability and high conductivity about 100 mS/cm under fully hydrated conditions at 80 °C. However, Nafion<sup>®</sup> membranes have some limitations that need to be overcome to boost the commercialization of PEMFC. This includes the low proton conductivity at temperatures above 80 °C and relative humidity (RH) below 50% as a result of instant water evaporation (Mishra *et al.*, 2012; Nasef, 2014; Yin *et al.*, 2016). In an attempt to substitute Nafion<sup>®</sup>, researchers also tried to develop a combination of acid base polymers such as phosphoric acid doped polybenzimidazole (PBI). These membranes were found to have excellent properties operating at elevated temperature of up to 200 °C under anhydrous conditions due to the low volatility of phosphoric acid that acts as the

proton carrier. However, PBI membranes have some drawbacks, such as insufficient proton conductivity, acid leaching problem, and the decrease in mechanical property under HT-PEMFC operation conditions, which limited the performance of such membranes in HT-PEMFC (Araya *et al.*, 2016). More details on PA membranes based on PBI can be found in the reviews by Li *et al.* (2009), Subianto (2014), Zeis (2015), Zhang and Shen (2012a) and Zhang and Shen (2012b).

In order to increase the proton conductivity, the acid doping level of the PBI membrane needs to be enhanced, but such move is likely to weaken the membrane mechanical properties. Significant efforts have been made to modify PBI membranes for HT-PEMFC application by converting them into composite membrane by incorporating of phosphotungstic acid (Staiti *et al.*, 2000), silica (Ghosh *et al.*, 2011a; Pu *et al.*, 2009), clay (Ghosh *et al.*, 2011b; Plackett *et al.*, 2011) and sulfonated mesoporous organosilicate (Tominaga and Maki, 2014). However, a major improvement to PBI based composite membranes could not be made leaving their fabrication technology far from commercialization. This is obviously due to the poor fuel cell performance caused by the transport limitation of the reactants ( $H_2/O_2$ ) resulting from the leaching of phosphoric acid (Liang *et al.*, 2015). Therefore, one of the most critical challenges in developing new HT-PEMFC membranes is to have membranes capable of enhancing the fuel cell performance at temperature above 100 °C.

Of all attempted alternative fuel cell membranes, radiation grafted membranes showed the potential to substitute conventional counterparts on basis of the ease of preparation and cost effectiveness. These membranes are prepared by radiation induced grafting (RIG) of vinylic monomers like styrene onto fully fluorinated or partially fluorinated films followed by functionalization reactions such as sulfonation (Nasef, 2014). Among fluorinated polymer films, poly(ethylene-co-tetrafluoroethylene) ETFE was reported to have high resistance to high-energy radiation (gamma rays or electron beam) and common solvents. ETFE also has excellent thermal stability, which made its films suitable substrates for preparation of proton exchange membranes.

RIG method is well known to be versatile graft copolymerization method because the grafted membranes compositions can be accurately tuned and the properties can be tailored to suit particular applications. Therefore, this method was found to be suitable for preparation of large number of functional materials and membranes for various energy, environmental and separation applications. More details on various preparation routes for radiation membranes and their potential application can be found in the reviews by Nasef and Hegazy (2004), Nasef and Güven (2012) and Nasef *et al.* (2016b).

Few studies reported the preparation of alternative radiation grafted membrane doped with PA obtained by RIG of nitrogenous monomers such as 4-vinylpyridine (4-VP) onto ETFE films followed by PA doping (Nasef *et al.*, 2013a; Nasef *et al.*, 2013c; Sanli and Gursel, 2011). The 4-VP monomer was selected because the nitrogen present in its pyridine ring has the tendency to establish positive site prompting basic character to the grafted film when it is protonated. In addition, RIG of 4-VP was proven to be advantageous because it has a minimal radiation damage on ETFE structure due to the fast grafting reaction caused by the high reactivity of 4-VP monomer and thus high grafting levels can be easily obtained at lower absorbed dose (Sanli and Gursel, 2011). In the previous studies conducted at Centre of Hydrogen Energy (CHE) by Nasef *et al.* (2013a); (Nasef *et al.*, 2013c), preparation of PEM membranes was carried out by RIG of 4-VP onto ETFE films followed by acid doping and the work was extended by replacing 4-VP with 1-vinylimidazole (1-VIm) as a grafting monomer with different partially fluorinated polymers including poly(vinylidene fluoride) and ETFE films. The obtained membranes showed reasonable proton conductivity with less water dependent behaviour. However, these membranes did not have sufficient stability and proton conductivity to sustain operation in PEMFC at 120 °C. This is due to leaching of PA which could be increased to high levels with higher temperatures.

The use of comonomers i.e. a second monomer added to the main monomer forming a mixture of two monomers is an appealing approach to improve the properties of these membranes which is capable of boosting the basic characters when grafted onto ETFE films with RIG method. Particularly, grafting of 4-VP as the primary monomer with comonomers such as glycidyl methacrylate (GMA), 1-

vinylimidazole (1-VIm) and triallyl cyanurate (TAC) is likely to improve the properties of the membranes. The addition of GMA to grafting monomer mixture introduces epoxy rings to the grafted chains that can be functionalized in a post grafting mild reaction with various ionic groups such as sulfonic acid (Abdel-Hady *et al.*, 2013; Kim and Saito, 2000), amines (Choi *et al.*, 2004; Yang *et al.*, 2009), phosphoric acid (Choi and Nho, 1999; Tsuneda *et al.*, 1991), and others (Kim *et al.*, 1991a; Kim *et al.*, 1991b). Particularly, phosphonation of epoxy ring is of high interest to enhance proton conductivity of the membranes obtained by grafting mixture of GMA with nitrogenous monomer. On the other hand, the incorporation of 1-VIm, which is a nitrogenous monomer, is capable of imparting more basic moiety to the grafted films when it is combined with 4-VP during grafting reaction (Nasef *et al.*, 2013a; Nasef *et al.*, 2013b; Schmidt and Schmidt-Naake, 2007a, b). The presence of two basic nitrogen atoms originated from the grafted pyridine and imidazole rings per repeating unit resembles PBI and provides more basic centres for PA complexation suitable for proton conduction at temperatures above 100 °C. On the other hand, the incorporation of TAC, which is polyfunctional nitrogenous monomer acting as a crosslinker, is likely to improve the mechanical properties of membranes (Alkan Gürsel *et al.*, 2008; Gubler *et al.*, 2005; Gubler and Scherer, 2010). The advantages of TAC is in the presence of three ether linkages in the allyl side chains that imparts flexibility to the crosslinked grafted chains allowing reasonable molecular chain motions (Chen *et al.*, 2006b; Gupta *et al.*, 1994; Nasef, 2000). However, the content of TAC has to be optimized to avoid formation of highly crosslinked dense structure that reduces the membrane swelling (Gubler *et al.*, 2005).

It is noteworthy stating that, the knowledge about the suggested comonomers and their properties prompt their consideration for the development of new proton exchange membranes for HT-PEMFC with improved properties including acid doping level, proton conductivity, stability and less-water dependency. Specifically, preparation of three membrane precursors with grafting of comonomers mixtures such as 4-VP/GMA, 4-VP/1-VIm or 4-VP/TAC followed by PA doping is appealing for improving the properties of 4-VP grafted membrane obtained in the previous work. Moreover, the approach implemented in this study was not reported in literature before.

### 1.3 Objectives

The aim of this study is to develop new phosphoric acid (PA) containing membranes with improved properties based on three different basic grafted films obtained by radiation induced grafting of 4-vinylpyridine (4-VP) and its mixtures with glycidyl methacrylate (GMA), 1-vinylimidazole (1-VIm) or triallyl cyanurate (TAC) onto poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films followed by PA doping suitable for high temperature PEMFC.

The objectives can be stated as follow:

- i. To establish membranes preparation procedures by optimization of the reaction parameters affecting the degree of grafting and acid doping level for the three grafting systems in addition kinetic behaviour.
- ii. To evaluate the various physical and chemical properties of the newly synthesized membranes.
- iii. To evaluate the performance of the developed membranes in terms of polarization characteristics and power density in proton exchange membrane fuel cell (PEMFC) operating above 100 °C.

### 1.4 Scope of Study

The scope of the present study is outlined as follows:

- i. Preparation of three membrane precursors (basic grafted films) by RIG of monomer mixtures consisting of 4-VP/GMA, 4-VP/1-VIm or 4-VP/TAC onto ETFE films. The effects of grafting parameters on degree of grafting was investigated including absorbed dose (20-100 kGy), monomer concentration (30-70 vol%, 20-100 vol% and 10-60 vol %), reaction temperature (50-70 °C,

40-80 °C, 40-80 °C) and reaction time (0.5-2.5 h, 8-24 h and 0.5-5 h) for 4-VP/GMA, 4-VP/1-VIm and 4-VP/TAC grafting systems respectively.

- ii. Determination of the reactivity ratios of 4-VP/GMA and 4-VP/1-VIm mixtures during the graft copolymerization reaction.
- iii. Functionalization of the membrane precursors by doping with PA and optimization of the reaction parameters affecting the acid doping level such as PA concentration (40 -85 wt%), reaction temperature (30 -80°C) and reaction time, (1-5 days). Functionalization of membrane precursor from 4-VP/GMA grafting systems was conducted with additional step under reaction conditions at PA concentration of 85 wt% under variation of reaction temperatures (30, 80 and 100 °C) and reaction time was varied in the range of (1-6 h).
- iv. Determination of the chemical, morphological, structural, thermal stability and mechanical properties of the obtained membranes in comparison with grafted and pristine counterparts using Fourier transform infrared (FTIR), field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and universal mechanical tester, respectively. Measuring the proton conductivity using the impedance spectroscopy. Evaluation of the membrane chemical stability in terms of acid loss was tested by measuring the weight loss after placing the acid doped membranes in an oven at a desired period of time.
- v. Fabrication of membrane electrode assembly (MEA) by hot pressing of the obtained membrane between the electrodes and the developed membranes.
- vi. Testing the membrane's performance using the prepared MEA at temperatures higher than 100°C by measuring the cell polarization characteristics (voltage and current density) and power density.



## 1.5 Contribution of the Study

The following contributions are made from the present study:

- i. Three new simplified routes to prepare basic membrane precursors using RIG that can be converted to proton conducting membrane by doping with PA. The obtained membranes acquired higher acid doping level and stability previously developed 4-VP based membranes with respect of proton conductivity and fuel cell performance.
- ii. Three grafting systems involving grafting of unprecedented comonomers mixtures of GMA, 1-VIm or TAC with 4-VP onto ETFE films using RIG were kinetically established and reported for the first time.
- iii. A method for increasing the acid doping level of these composite (acid/base) membranes by incorporating mixtures of nitrogen-containing monomers and the versatile GMA in the grafting step was established.
- iv. A method for determination of the reactivity ratios of monomers involved in RIG of 4-VP/GMA or 4-VP/1-VIm mixtures onto ETFE films was established for the first time which is useful in understanding the copolymerization behaviour of the comonomers and its mechanism.
- v. New three types of proton exchange membranes with improved properties and suitable for application in PEMFC at high temperature were established.

## 1.6 Thesis Outline

This thesis is divided into five chapters. In chapter 1, the background of the research is presented with the emphasis on the growing renewable energy demands and current status of PEMFC as renewable energy power source together with problem statement, objectives of the study, scope of work and the contribution of this study. Chapter 2 contains the necessary information needed to support the study included a comprehensive literature review on various aspects of fuel cells, current status of commercial PEM and fundamentals of RIG techniques. The effect of reaction parameters on the degree of grafting and the use of RIG techniques for preparation of PEMs together with the progress took place in preparation of various PEMs were also reviewed. Chapter 3 reports on the methodology adopted in this study including the materials, equipment and experimental procedure used to prepare, characterize and test the developed membranes with respect to fuel cell applications. In chapter 4 the results of the preparation and characterization of three membranes with the reference membranes involving the grafting of monomer mixtures of GMA, 1-VIm or crosslinker TAC with 4-VP are discussed. The conclusions and recommendations to improve the work in future studies are discussed in Chapter 5.

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