PHOSPHORIC ACID MEMBRANE BY RADIATION INDUCED GRAFTING OF 4-VINYLPYRIDINE ONTO POLY (ETHYLENE-*CO*-TETRAFLUORO ETHYLENE) FILM FOLLOWED BY PHOSPHORYLATION

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To my parents for years, their endless supports

and encouragements

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IN THE NAME OF ALLAH, MOST GRACIOUS, MOST COMPASSIONATE

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ABSTRACT

Proton conducting membrane prepared by phosphoric acid doping of poly 4-vinylpyridine **(**4-VP**)** grafted onto poly **(**ethylene-co-tetrafluoroethylene**)** ETFE film was studied**.** The effect of grafting conditions of 4-VP onto ETFE film, such as i) irradiation dose ii) monomer concentration iii) reaction time iv) reaction temperature and v) solvent type on degree of grafting (G%) was studied. The G% was found to be increased as the irradiation dose increased. Moreover, the increase in the i) monomer concentration ii) reaction time iii) reaction temperature was found to lead to an increase in the G% until a maximum value was reached at a concentration of 60 vol.% beyond which, it dropped. Among all employed solvents, ethanol for 4-VP was found to be the best diluents**.** Optimization using response surface method (RSM) by The Box-Behnken module available in the design expert software was used to optimize the grafting parameters; i) absorbed dose ii) monomer concentration, iii) grafting time v) grafting temperature varied in four levels in correlation with the degree of grafting G%. A maximum degree of grafting of 57% was experimentally achieved at optimum parameters; i) monomer concentration of 48 vol.% ii) absorbed dose of 64 kGy iii) reaction time of 4h iv) reaction medium temperature of 69°C. The value of G% was found to be 4% lower than that predicted by model i.e. 61%, which is very acceptable. The grafted film then functionalized with phosphoric acid doping in various G% .The membranes achieved proton conductivity as a function of level of acid doping and G%. Fourier transform infrared (FTIR), thermo gravimetric analysis (TGA) and x-ray diffraction (XRD) were used to investigate the properties of the obtained membranes and provide evidence for grafting and phosphorylation.

ABSTRAK

Membran Proton menjalankan yang disediakan oleh asid fosforik doping poli 4-vinylpyridine (4-VP) ditambah kepada poli (etilena-co-tetrafluoroethylene) ETFE filem. Kesan cantuman syarat-syarat 4-VP ke filem ETFE, khususnya reaksi i) dos penyinaran ii) kepekatan monomer iii) masa iv) tindak balas suhu v) jenis pelarut pada tahap cantuman (G%) telah dikaji. % G didapati meningkat kerana kenaikan dos penyinaran. Tambahan pula, peningkatan dalam i) kepekatan monomer ii) masa iii) reaksi tindak balas suhu didapati membawa kepada peningkatan dalam% G sehingga nilai maksimum dicapai pada kepekatan 60 vol% di luar yang turun. Daripada semua pelarut etanol untuk 4-VP telah didapati merupakan yang terbaik untuk pelarutan. Pengoptimuman menggunakan kaedah respons permukaan (RSM) dengan modul-Behnken Keselamatan terdapat dalam perisian pakar reka bentuk telah digunakan untuk mengoptimumkan parameter cantuman i) dos penyerapan ii) kepekatan monomer, iii) cantuman masa v) cantuman suhu yang berbeza-beza dalam empat peringkat dalam korelasi dengan ijazah cantuman% G. Tahap maksimum cantuman sebanyak 57% adalah uji kaji dicapai pada parameter yang optimum; i) kepekatan monomer 48 vol% ii) dos yang diserap daripada 64 kGy iii) tindak balas masa 4H iv) suhu medium tindak balas suhu 69 ° C. Nilai G% didapati 4% lebih rendah daripada yang diramalkan oleh model iaitu 61%, yang sangat diterima. Filem yang dicantumkan berfungsi dengan asid fosforik dadah dalam pelbagai % G membran mencapai kekonduksian proton sebagai fungsi tahap doping asid dan % G. Fourier transforms infrared (FTIR), thermo gravimetric analysis (TGA) and x-ray diffraction (XRD) telah digunakan untuk menyiasat ciri-ciri membran yang diperoleh dan dijadikan bukti untuk cantuman dan pemfosforilan.

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LIST OF ABBREVIATIONS

4-VP	4-Vinylpyridine
ETFE	Poly **(**ethylene-*co*-tetrafluoroethylene**)**
G%	Degree of grafting
Volume %	Vol. %
RSM	Response surface method
FTIR	Fourier transforms infrared
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
PEM	Polymer electrolyte membrane
RIG	Radiation induced grafting
PVDF	Poly(vinylidene fluoride)
PTFE	Poly(tetrafluoroethylen)
FEP	Poly (tetrafluoroethylene-co-hexafluoropropylene)
PFA	Perfluoroalkoxy
UHMWPE	Ultra high molecular weight polyethylene
HDPE	High density polyethylene
DVB	Divinylbenzene
BVPE	Bis(vinyl phenyl)ethane
AN	Acrylonitrile

MAN	Methylacrylonitrile
PEMFC	Polymer electrolyte membrane fuel cell

LIST OF SYMBOLS

Wg - Weight of grafted film (g)

W_o - Weight of original film (g)

T - Thickness of the membrane sample (cm)

A - Membrane sample surface area (cm^2)

L - The distance between probes (cm)

R - Resistance (Ohms)

W - Width (cm)

σ - Conductivity (S/cm)

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Preparation of polymer electrolyte membranes (PEM) by using radiation induced grafting (RIG) method is currently received a growing interest in many research institutes. Due to the versatility and its ability to introduce new functional groups, this method can be performed on polymer films to overcome the difficulty of shaping functional membranes [1]. In addition, the availability of various monomer and polymer films combination can be reacted under controlled parameters to allow designing high quality membranes with desired compositions and identifying some specific applications. Thus, RIG became an attractive method for developing alternative proton exchange membranes (PEMs) for fuel cell application [2]. Preparation of PEM membrane to bear sulfonic acid for fuel cell by doing RIG has been frequently reported in literature. These membranes are obtained from grafting of styrene, styrene derivatives, styrene/crosslinking agents and styrene/co-monomers on fluorinated polymer films to follow the reaction of sulfonation [3-14]. The literature also reported a direct method for obtaining sulfonic acid membrane in a single step to graft of sodium styrene sulfonate onto poly (vinylidene fluoride) (PVDF) [1, 15]. Table1.1 presents examples of latest progress in the radiation grafting by using different grafting systems to obtain precursors for sulfonic acid membranes [16, 17].

As the state of the art in fuel cell technology moves toward higher temperature operation to increase the efficiency and reduce the dependence on water which is essential for proton conduction in low temperature fuel cell, alternative membranes bearing other functional groups that can stand temperature above 100 ^{o}C are sought. Acid/base complexes membranes achieved by radiation induced grafting of polar heterocyclic monomer such as 4-vinypyridine (4-VP) on irradiated fluorinated polymer films, i.e. poly (ethylene-co-tetraflouroethene) (ETFE) film followed by doping with phosphoric acid were attempted as a polymer electrolyte membrane for proton conduction in high temperature Polymer Electrolyte Membrane Fuel Cells (PEMFC) [18]. The 4-VP was selected to provide a basic canter ($–N^{+}-$) that conducts protons at temperatures above 100 ^{o}C when doped with phosphoric acid. More studies focusing on grafting 4-VP onto irradiated ETFE [19] and poly-(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) [20] with respect to the role of solvent together with other reaction parameters such as monomer concentration and dose were recently reported. The former study was carried out using the pre-irradiation method with γ-rays whereas in the latter one, grafting was performed by simultaneous irradiation with γ-rays. Earlier, the effect of solvents with respect to type of alcohols and composition of binary alcohol/water mixtures of FEP-G-4vp with method of preirradiation was also evaluated [21]. However, an optimization study on grafting of 4-VP onto ETFE has not been reported.

Ion exchange membranes can be prepared by chemical, photochemical, mechanical and radiochemical techniques [22]. Using as a solid polymer electrolyte in various electrochemical applications, including, water electrolysis, chlor-alkali industry and fuel cells have offered for membranes such as cation exchange membrane [23-25]. Amongst a variety of electrochemical cells, attention to proton exchange membrane (PEM) fuel cells increased through their high efficiency that excited their improvement for different purposes.

Table 1.1: Examples of various grafting systems used for obtaining precursors for sulfonic acid membrane.

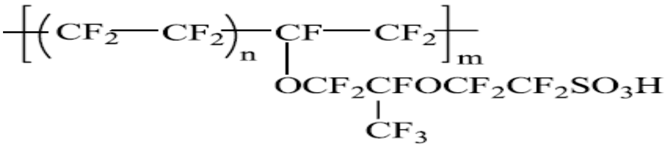
Monomer system	**Base polymer**	**Radiation source**	**Refs.**
Styrene	PTFE[a], FEP[b] and PFA[c]	Gamma rays	3
	ETFE	Electron beam	4
	UHMWPE[d]	Gamma rays	5
	Crosslinked PTFE	Gamma rays	6
α, β,trifluorostyrene	ETFE	Gamma rays	7
Vinyltoluene	ETFE	Gamma rays	8
m,*p*-methylstyrene or *p-tert*-butylstyrene/DVB or BVPE			
Styrene/DVB[f]	PFA	Gamma rays	9
Styrene/BVPE[g]	Crosslinked PTFE	Gamma rays	10
Styrene +α-methylstyrene/DVB	Crosslinked PTFE	Electron beam	11
Styrene +M AN[h]	FEP	Electron beam	12
Methylstyrene/MAN[i]	FEP	Electron beam	13
Sodium styrene sulfonate + acrylic acid	HDPE[e]	Electron beam	14
Sodium styrene sulfonate	PVDF	Electron beam	1,15

[a]PTFE = poly(tetrafluoroethylene); [b]poly(tetrafluoroethylene-co-hexafluoropropylene); [c]poly(tetrafluoroethylene-co-perfluorvinylether); [d]UHMWPE = ultrahigh molecular weightpolyethylene; [e]HDPE = high density polyethylene; [f]DVB = divinylbenzene; [g]BVPE =bis(vinyl phenyl)ethane; [h]AN = acrylonitrile; [i]MAN = methylacrylonitrile

At present, Nafion (duPont de Nemours) membrane is the standard commercial material for such application. This is due to their high conductivity, excellent chemical stability and low resistivity [26-28].

Radiochemical grafting (radiation-induced graft copolymerization) is a rather versatile method to produce tailored ion exchange membranes .The attractiveness of this method arises from its ability to introduce desirable properties to pre-exist polymer substrate that already have the membrane physical shape with no altering of its bulk properties [29, 30]. Furthermore, it offers the capability to intimately control the composition of the graft copolymer, and its properties through the proper grafting selection conditions [30]. In general, grafting of hydrophilic vinyl monomers onto hydrophobic polymer layers prepared by radiation induced grafted of ion exchange membranes [31, 32]. Irradiation of such grafting system causes a formation of free radicals on the polymer substrate, which can initiate copolymerization in the existence of monomer molecules [28, 33]. The polymer substrate could be either hydrocarbon or fluorocarbon polymer depending on the membrane stability required for a certain application [34]. Characterization of cation exchange membranes by evaluating their physico-chemical properties is an essential step of particular importance, as the capability of the membrane for a certain use will be determined based on its properties. The property of the membranes is depending mainly on grafting content (G%) that is a grafting conditions function [35, 36].

Nafion as Perfluoronated ionomer is shown in figure 1.1, fulfill the main fundamental due to having of their high proton conductivity as well as their significant chemical and mechanical properties. As a state of the art material for low temperature fuel cells, Nafion is expensive and also have limitation for the operation temperature which motivated the investigation for the improvement of alternative made to attach acid groups, like sulfonic groups on the main chain of aromatic polymeric backbones. Introducing of the sulfonic groups onto polymeric materials can produce membranes with high water uptake and ionic conductivities.



$$-\!\left[\left(CF_2-CF_2\right)_n-\underset{\underset{\underset{CF_3}{|}}{OCF_2CFOCF_2CF_2SO_3H}}{\overset{}{CF}}-CF_2\right]_m\!-$$

Figure 1.1: Chemical structure of Nafion® [38]

During FC operation, in some cases, sulfonated aromatic polymers have a limitation on the operating temperature due to the required thermal and oxidative stability. The dependence on the existence of water for the ionic conductivity of all the above-mentioned polymers, limits their operation temperature below 100 ^{o} C [38].

Operating at higher temperatures in compare to the lower, suggests many advantages such as, simplified heat management temperatures, higher-energy efficiency, and better CO acceptance of the Platinum (Pt) electrodes. As a result, many researchers have focused on improvement of new polymer electrolytes that have high conductivity values in low humidity or anhydrous conditions. Phosphoric acid doping of Polybenzimidazole (PBI) and its combinations with numerous modifications of its chemical structure show high proton conductivity and thermal stability [39-45].

Another capable approach of aromatic polyether is mechanical and thermal properties with their low cost. The introduction of polar groups offers the interaction sites with phosphoric acid to the required ionic conductivity [46-49].

A Polymer Electrolyte Fuel Cell (PEFC) includes a solid polymer membrane and two electrodes which perform as an electrolyte. The polymer electrolyte membrane is sandwiched between two platinum porous electrodes such as carbon paper and mesh. There are a number of single cell assemblies which are able to mechanically compress across electrically conductive separators to fabricate electrochemical stacks. Generally, PEFCs require humidified gases, hydrogen and oxygen (or air) as a fuel for their operation [50].

A proton exchange membrane is coated with a thin platinum catalyses layer and a gas-permeable electrode made of graphite Paper. A solid polymer as electrolyte is applied to describe the PEMFC as a group of fuel cell types. The maximum operating temperature is around 100 °C. Hydrogen (or reformate) or methanol is consumed as anode fuel [50].

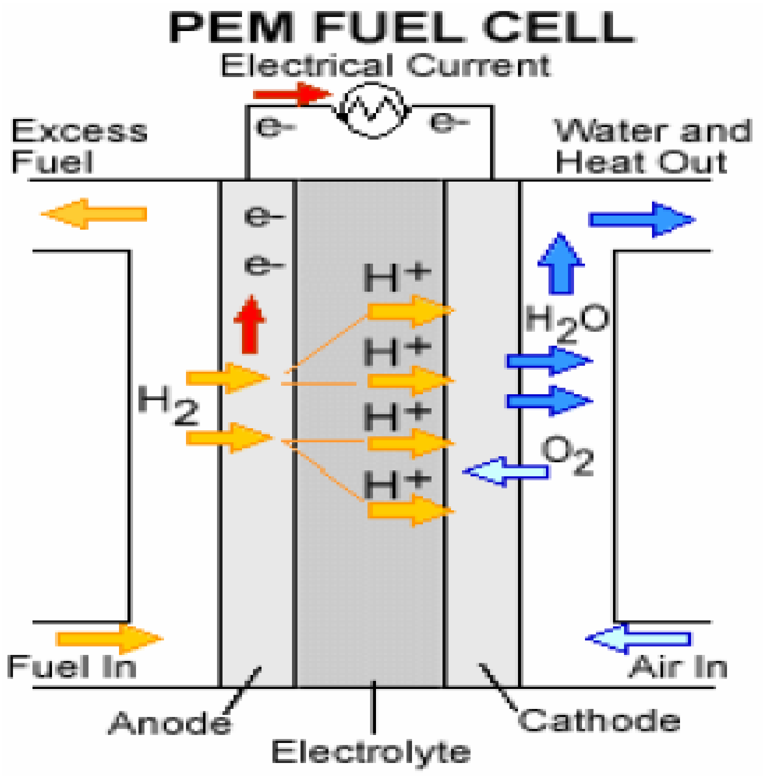


Fig. 1.2 Polymer Electrolyte Membrane Fuel Cell [51].

The fuel (typically hydrogen) which is illustrated in figure 1.2, electrochemically oxidized (oxidant: usually air or pure oxygen) to water. The overall redox reaction is separated into two half-cell reactions which are occurred at the two electrodes, anode and cathode. An ion-conducting electrolyte (often a solid electrolyte) separates the two electrodes. A fuel cell takes direct voltage into the electron transfer only through the external circuit [52].

$$\text{Anode:} \quad H_2 \rightarrow 2H^+ + 2e^- \qquad (1.1)$$

$$\text{Cathode:} \quad 2H^+ + 2e^- + 1/2\ O_2 \rightarrow H_2O \qquad (1.2)$$

Unlike a battery, there is no internal fuel storage for fuel cells but rather works exclusively as an energy converter. Therefore, no time-consuming charging circuits are required.

It is well known that pollutant emissions of fuel cells are very low or even zero which depend on the applied fuels. Lastly, the essential element related to the building of power plants is possibility of relative uncomplicated serial connection of several cells and the main components of a single cell represented by cathode, anode, and electrolyte [2, 53].

Polymer electrolyte membrane (PEM) is used as an electrolyte in fuel cell technology as a solid polymer membrane. The rule of membrane is a barrier to avoid the mixing of reaction gases and also to transport the proton from the anode to cathode. Because the cell separator is a flexible polymer film, it has some features such as ease assembly, handling, and sealing. It is often less complex than the other fuel cell systems. Moreover, the corrosive acids and bases in this system are reduced. The applications of PEM in Polymer electrolyte membranes fuel cell (PEMFC) supposed to show: good electrochemical, high proton conductivity, adequate mechanical properties, chemical, thermal stability, low permeability to reactants; and also low swelling in water. They must easily process into membrane electrode assemblies (MEAs) to reproduce for fabrication and preparation [37].The fuel cell types and their major differences illustrated in table 1.2.

Table 1.2: Summary of major differences of the fuel cell types [54]

	PEFC	PAFC	MCFC	SOFC
Electrolyte	Ion Exchange Membrane	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic
Operating Temperature	80˚C	205˚C	650˚C	800-1000℃ Now,600-1000˚C In 10 to 15 years
Change Carrier	H^+	H^+	CO_3^{2-}	O^{2-}
External Reformer for CH_4(below)	Yes	Yes	No	No
Prime Cell Components	Carbon-Based	Graphite- based	Stainless Steel	Ceramic
Catalyst	Platinum	Platinum	Nickel	Perovskites
Product Water Management	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas+Independent Cooling Medium	Process Gas+Independent Cooling Medium	Internal Reforming + Process Gass	Internal Reforming + Process Gas

1.2 Problem Statement

Since, Nafion, perfluorinated polymer is one of the few materials that deliver set of chemical and mechanical properties, it requires to perform as a good electrolyte in proton exchange membrane fuel cells (PEMFCs). However, Nafion presents disadvantages such as limiting the operational temperature of the fuel system (80 ˚C) and suffers chemical crossover [55]. The limitation of operation temperature is because of its inability to retain water at higher temperatures. It is worth to mention that ethylene-tetra fluoro ethylene copolymer (ETFE) has a special position amongst fluoropolymers. It includes alternating structural units of polyethylene and poly (tetra fluoroethylene) $[–(CF_2–CF_2–CH_2–CH_2)\ n–]$ which confers its unique combination of properties imparted from both hydrocarbon and fluorocarbon polymers [56]. Moreover, it offers an excellent superior resistance and thermal stability to common solvents (as does PTFE) besides showing a high resistance to radiation and fatigue [57]. Therefore, ETFE can be a good candidate for preparation of membranes, ion exchange resins, polymer electrolytes and advanced composite materials [58].

1.3 Objectives

The objective of this work is to prepare proton exchange membrane by radiation induced grafting of 4-vinylpyridine onto poly (ethylene-co-tetraflouroethene) followed by doping with phosphoric acid under controlled conditions. The objective can be divided into:

i) To graft 4-VP onto ETFE film under control parameters.

ii) To optimize parameters of grafting; monomer concentration, absorbed dose, grafting temperature and time by using response surface method (RSM) available in the design expert software.

iii) To functionalize the grafted ETFE films by doping with phosphoric acid .

iv) To characterize the obtained grafted membranes using chemical and materials research aspects.

1.4 Scope of Study

The scopes of this work are presented in flow chart shown in figure 1.3.This includes the following:

i) Irradiation of ETFE with electron beam accelerator under nitrogen atmosphere.

ii) Graft copolymerization of 4-vinylpyridine onto irradiated ETFE film under different controlled parameter

iii) Optimization of reaction parameters using response surface method.

iv) Phosphoric acid doping of the grafted film.

v) Investigation and characterization of properties of the obtained membrane for possible use in high temperature PEM fuel

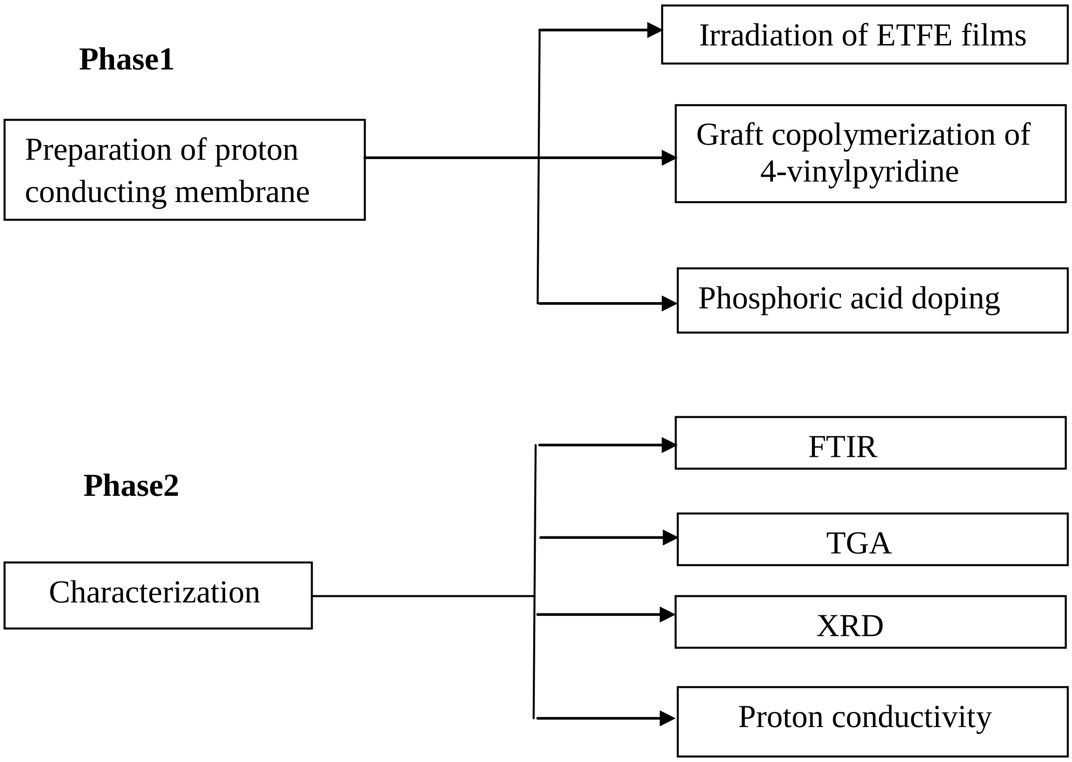


Figure 1.3: A flow chart of work scope

1.5 Thesis Outline

This research investigates the possibility of the development of proton exchange membranes applicable for electrochemical applications, particularly, high temperature proton exchange membrane fuel cell (HTPEMC).

Chapter 1 includes an introduction to preparation of polymer electrolyte membranes by radiation induced grafting (RIG), ion exchange membranes, and the importance of increasing operating temperature of fuel cell by 4-vinypyridine (4-VP) grafting onto irradiated fluorinated polymer films such as poly (ethylene-*co*-tetraflouroethene) (ETFE) film followed by doping with phosphoric acid. A concise conception of fuel cell basic unit and its operation are also highlighted. In chapter 2, a review of the basic fundamentals of radiation-induced graft copolymerization process and its application in the preparation of proton exchange membrane and also general methods to characterize the membrane are mentioned. Chapter 3 states the equipments, materials and methods used to prepare and characterize the proton exchange membranes. Moreover, optimization of reaction parameters using response surface method is also described. In Chapter 4 the results concerning grafting conditions affect on the grafting degree and properties of the produced membranes are revealed and analyzed. Conclusions are declared in chapter 5.

REFERENCES

1. Nasef, M. M., Saidi, H. & Mohd Dahlan, K. Z. ,Kinetic investigations of graft copolymerization of sodium styrene sulfonate onto electron beam irradiated poly(vinylidene fluoride) films. *Radiation Physics and Chemistry*, 2011. 80(1)**:** 66-75.

2. Nasef, M. M. & Hegazy, E.-S. A. , Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films. *Progress in Polymer Science,*2004.29(6): 499-561.

3. Lappan, U., Geißler, U. & Uhlmann, S. , Pre-Irradiation Grafting of Styrene into Modified Fluoropolymers. *Macromolecular Symposia*,2007.254(1)**:** 254-259.

4. Rohani, R., Nasef, M. M., Saidi, H. & Dahlan, K. Z. M.,Effect of reaction conditions on electron induced graft copolymerization of styrene onto poly (ethylene-co-tetrafluoroethylene) films: Kinetics study.*Chemical Engineering Journal*,2007.132(1-3)**:** 27-35.

5. Sherazi, T. A., Ahmad, S., Kashmiri, M. A. & Guiver, M. D. ,Radiation-induced grafting of styrene onto ultra-high molecular weight polyethylene powder and subsequent film fabrication for application as polymer electrolyte membranes: I. Influence of grafting conditions. *Journal of Membrane Science*,2008.325(2)**,** 964-972.

6. Yamaki, T., Kobayashi, K., Asano, M., Kubota, H. & Yoshida, M., Preparation of proton exchange membranes based on crosslinked polytetrafluoroethylene for fuel cell applications. *J.Polymer,* 2004.45(19)**:** 6569-6573.

7. Momose, T., Yoshioka, H., Ishigaki, I. & Okamoto, J. ,Radiation grafting of α, β, β-trifluorostyrene onto poly(ethylene-tetrafluoroethylene) film by preirradiation method. I. Effects of preirradiation dose, monomer concentration, reaction temperature, and film thickness. *Journal of Applied Polymer Science,*1989. 37(10): 2817-2826.

8. Chen, J., Asano, M., Yamaki, T. & Yoshida, M. ,Preparation and characterization of chemically stable polymer electrolyte membranes by radiation-induced graft copolymerization of four monomers into ETFE films. *Journal of Membrane Science*,2006.269(1-2): 194-204.

9. Nasef, M. M. & Saidi, H. ,Preparation of crosslinked cation exchange membranes by radiation grafting of styrene/divinylbenzene mixtures onto PFA films. *Journal of Membrane Science*,2003.216(1-2): 27-38.

10. Yamaki, T., Tsukada, J., Asano, M., Katakai, R. & Yoshida, M. , Preparation of Highly Stable Ion Exchange Membranes by Radiation-Induced Graft Copolymerization of Styrene and Bis(vinyl phenyl)ethane Into Crosslinked Polytetrafluoroethylene Films. *Journal of Fuel Cell Science and Technology,* 2007.4(1): 56-64.

11. Li, J., Muto, F., Miura, T., Oshima, A., Washio, M., Ikeda, S., Iida, M., Tabata, Y., Matsuura, C. & Katsumura, Y. , Improving the properties of the proton exchange membranes by introducing α-methylstyrene in the pre-irradiation induced graft polymerization. *European Polymer Journal,* 2006.42(6):.1222-1228.

12. Ben Youcef, H., Gubler, L., Gürsel, S. A., Henkensmeier, D., Wokaun, A. & Scherer, G. G. , Novel ETFE based radiation grafted poly(styrene sulfonic acid-co-methacrylonitrile) proton conducting membranes with increased stability. *Electrochemistry Communications,* 2009**.**11(5): 941-944.

13. Gubler, L., Slaski, M., Wallasch, F., Wokaun, A. & Scherer, G. G. , Radiation grafted fuel cell membranes based on co-grafting of α-methylstyrene and methacrylonitrile into a fluoropolymer base film. *Journal of Membrane Science,*2009.339(1-2)**:** 68-77.

14. Zu, J., Zhang, J., Sun, G., Zhou, R. & Liu, Z. , Preparation of cation-exchange membrane containing bi-functional groups by radiation induced grafting of acrylic acid and sodium styrene sulfonate onto HDPE: Influence of the synthesis conditions.*Journal of Radioanalytical and Nuclear Chemistry,*2009.279(1)**:** 185-192.

15. Nasef, M. M., Saidi, H. & Dahlan, K. M. , Comparative investigations of radiation-grafted proton-exchange membranes prepared using single-step and conventional two-step radiation-induced grafting methods. *Polymer International,*2011.60(2): 186-193

16. Nasef, M.M., Fuel Cell Membranes by Radiation-Induced Graft Copolymerization: Current Status, Challenges, and Future Directions. *Polymer Membranes for Fuel Cells*, S.M.J. Zaidi and T. Matsuura, Editors. 2009: 87-114.

17. Gubler, L. & Scherer, G. G.,Trends for fuel cell membrane development. *Desalination,*2010. 250(3): 1034-1037.

18. Schmidt, C. & Schmidt-Naake, G. , Proton Conducting Membranes Obtained by Doping Radiation-Grafted Basic Membrane Matrices with Phosphoric Acid. *Macromolecular Materials and Engineering,*2007.292(10-11)**:** 1164-1175.

19. Işıkel Şanlı, L. & Alkan Gürsel, S. , Synthesis and characterization of novel graft copolymers by radiation-induced grafting. *Journal of Applied Polymer Science,*2011.120(4)**:** 2313-2323.

20. Rath, S. K., Palai, A., Rao, S., Chandrasekhar, L. & Patri, M. , Effect of solvents in radiation-induced grafting of 4-vinyl pyridine onto fluorinated ethylene propylene copolymer. *Journal of Applied Polymer Science*,2008. 108(6)**:** 4065-4071.

21. Kaur, I., Misra, B. N. & Kohli, A. , Synthesis of Teflon-FEP grafted membranes for use in water desalination. *Desalination,*2001.139(1-3): 357-365.

22. Nasef, M. M. , *Preparation and Characterization of Cation Exchange Resins Based on Locally Fabricated Polythylene Pallets*. VOT 77503 Project Report, Universiti Teknologi Malaysia;2009.

23. Kinoshita, K. , In Proceedings of Symposium on Diaphragm, Sperators, and Ion Exchange Membranes*;*Van Zee, J. W.; White, R. E.; Kinoshita, K.; Burney, H. S., Eds. *The Electrochemical Society Inc***.**,1986: 133.

24. Risen, W. M. , *In Ionomers: Characterization, Theory and Applications* ;Schlick, S., Ed. *CRC* Press Inc.: New Jersy,1996:p. 284.

25. Gray, F. M.,*Polymer Electrolytes.* The Royal Society of Chemistry: London,1998: 158.

26. Kinoshita, K.*In Encyclopedia of Chemical Technology*. New York: John Wiley & Sons,1994. Vol. 2: 1098.

27. Appleby, A. J.; Foulks, F. R. *Fuel Cell Handbook*; Van Nostrand-Reinhold: New York, 1994: 284.

28. Ellinghorst, G., Niemöller, A. & Vierkotten, D. , Radiation initiated grafting of polymer films an alternative technique to prepare membranes for various separation problems. *Radiation Physics and Chemistry* (1977), 1983.22(3-5): 635-642.

29. Okamoto, J. , Radiation synthesis of functional polymer. *Radiation Physics and Chemistry,*1987. 29: 469-475.

30. Chapiro, A., *Radiation Chemistry of Polymeric Systems. Interscience*, New York. New York: John Wiley and sons, 1962.481.

31. Gen, Y.-P. , Preparation of charged micro-mosaic membrane via radiation-induced grafting of styrene and methyl methacrylate onto Teflon FEP films. *Desalination,*1987. 62**:** 265-273.

32. Y. Tabata, Y. I., S. Tagawa ,*CRC Handbook of Radiation Chemistry.* Boca Raton: CRC Press .1991.

33. Vivian T, S. ,Radiation grafting state-of-the-art. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry,*1990.35(1-3)**:** 82-87.

34. Nasef , M. M.. *Proton Exchange Membrane by Radiation-InducedGraft Copolymerization of Styrene onto Fluorinated Polymers.* Ph.D.Thesis. University Teknologi Malaysia; 1999.

35. *Gupta, B. & Scherer, G. G. ,Proton exchange membranes by radiation grafting of styrene onto FEP films. I. Thermal characteristics of copolymer membranes. Journal of Applied Polymer Science,*1993. 50(12): 2129-2134.

36. Gupta, B., Büchi, F. N., Staub, M., Grman, D. & Scherer, G. G. , Cation exchange membranes by pre-irradiation grafting of styrene into FEP films. II. Properties of copolymer membranes. *Journal of Polymer Science, Part A:* Polymer Chemistry,1996. 34(10): 1873-1880.

37. Yang, Y., Siu, A., Peckhamt, T. & Holdcroft,S.,*Structural and Morphological Features of Acid-Bearing Polymers for PEM Fuel Cells. In: Fuel Cells I.*,Scherer, G. (ed.),Springer Berlin / Heidelberg, 2008: 55-126.

38. Papadimitriou, K. D., Andreopoulou, A. K. & Kallitsis, J. K. , Phosphonated fully aromatic polyethers for PEMFCs applications. *Journal of Polymer Science, Part A: Polymer Chemistry,* 2010.48(13)**:** 2817-2827.

39. Wainright, J. S., Wang, J. T., Weng, D., Savinell, R. F. & Litt, M. Acid-doped polybenzimidazoles: A new polymer electrolyte. *Journal of the Electrochemical Society,*1995.142(7)**:** L121-L123

40. Deimede, V., Voyiatzis, G. A., Kallitsis, J. K., Qingfeng, L. & Bjerrum, N. J. , Miscibility behavior of polybenzimidazole/sulfonated polysulfone blends for use in fuel cell applications. *Macromolecules*,2000. 33**:** 7609-7617.

41. Li, Q., He, R., Jensen, J. O. & Bjerrum, N. J. , Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100 °C. *Chemistry of Materials,* 2003.15**:** 4896-4915.

42. Ma, Y. L., Wainright, J. S., Litt, M. H. & Savinell, R. F. , Conductivity of PBI membranes for high-temperature polymer electrolyte fuel cells. *Journal of the Electrochemical Society*,2004. 151**:** A8-A1.

43. Yamada, M. & Honma, I. , A Biopolymer Composite Material as an Anhydrous Proton-Conducting Membrane. *Angewandte Chemie International Edition,*2004. 43(28): 3688-3691.

44. Carollo, A., Quartarone, E., Tomasi, C., Mustarelli, P., Belotti, F., Magistris, A., Maestroni, F., Parachini, M., Garlaschelli, L. & Righetti, P. P. , Developments of new proton conducting membranes based on different polybenzimidazole structures for fuel cells applications. Journal *of Power Sources*, 2006.160(1)**:** 175-180.

45. Li, Q., Jensen, J. O., Savinell, R. F. & Bjerrum, N. J. , High temperature proton exchange membranes based on polybenzimidazoles for fuel cells. *Progress in Polymer Science,*2009. 34(5)**:** 449-477.

46. Smith, C. D., Grubbs, H., Webster, H. F., Gungör, A., Wightman, J. P. & Mcgrath, J. E.,Unique characteristics derived from poly(arylene ether phosphine oxide)s. *High Performance Polymers,*1991.3(4)**:** 211-230.

47. Gourdoupi, N., Andreopoulou, A. K., Deimede, V. & Kallitsis, J. K. , Novel Proton-Conducting Polyelectrolyte Composed of an Aromatic Polyether Containing Main-Chain Pyridine Units for Fuel Cell Applications. *Chemistry of Materials,* 2003.1**.** 5(26): 5044-5050.

48. Pefkianakis, E. K., Deimede, V., Daletou, M. K., Gourdoupi, N. & Kallitsis, J. K. , Novel Polymer Electrolyte Membrane, Based on Pyridine Containing Poly(ether sulfone), for Application in High-Temperature Fuel Cells. *Macromolecular Rapid Communications*, 2005.26**:** 1724-1728.

49. Kallitsis, J. K., Geormezi, M. & Neophytides, S. G. ,Polymer electrolyte membranes for high-temperature fuel cells based on aromatic polyethers bearing pyridine units. *Polymer International,*2009. 58(11)**:** 1226-1233.

50. Rikukawa, M. & Sanui, K. , Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers. *Progress in Polymer Science,* 2000.25: 1463-1502.

51. Schlesinger, M., M.H. Eikerling, and K. Malek, *Electrochemical Materials for PEM Fuel Cells: Insights from Physical Theory and Simulation Modeling and Numerical Simulations*. Springer New York,2009: 169-247.

52. Ledjeff, K., Mahlendorf, F., Peinecke, V. & Heinzel, A. , Development of electrode/membrane units for the reversible solid polymer fuel cell (RSPFC). *Electrochimica acta,* 1995.40(3): 315-319.

53. Ticianelli, E. A., Derouin, C. R., Redondo, A. & Srinivasan, S. , Methods to Advance Technology of Proton Exchange Membrane Fuel Cells. *Journal of the Electrochemical Society,* 1998.135(9)**:** 2209-2214.

54. Hirschenhofer, J.H., Stauffer, D.B., . Engleman R.R. and Klett**,** M.G., *Fuel Cell Handbook*, Fourth Edition, Department of Energy - Fossil Energy Technology Center, November 1998.

55. Jurado R. J. ,Protonic conductors for proton exchange membrane fuel cells: An overview, Instituo, *de Ceramics y Vidrio*, *CSIC*, Madrid, Spain 2002,doi:10.2298/Hemind0206264J.

56. Forsythe, J. S. & Hill, D. J. T. , Radiation chemistry of fluoropolymers. *Progress in Polymer Science* (Oxford),2000. 25(1): 101-136.

57. Carlson, D. P.*;* Schmiegel, *W., In Ullmann's Encyclopedia of Industrial Chemistry;* Gerhartz, W.*, Ed.;* VCH*:* Weinheim, Germany, 1998.Vol. A11*:* 393–429.

58. Brack, H.-P., Buhrer, G.H., Bonorand, L., Scherer, G.G., Grafting of pre-irradiated poly(ethylene-alt-tetrafluoroethylene) film with styrene: influence of base polymer film properties and processing parameters. *J. Mater. Chem.*, 2000.10,1795; Gal'Pein, Y.L., Tsvankin, D.Y., 1976. Vysolomol.Soedin. Ser. A18: 2691 (*Translated in Polym. Sci*. USSR 1977; 19: 3073).

59. Choi, Y.-J., Kang, M.-S., Kim, S.-H., Cho, J. & Moon, S.-H.,Characterization of LDPE/polystyrene cation exchange membranes prepared by monomer sorption and UV radiation polymerization. *Journal of Membrane Science,* 2003.223(1-2)**:** 201-215.

60. Wavhal, D. S. & Fisher, E. R. , Hydrophilic modification of polyethersulfone membranes by low temperature plasma-induced graft polymerization. *Journal of Membrane Science,* 2002.209(1)**:** 255-269.

61. Xu Z, Wang J, Shen L, Men D, Xu Y.,Microporous polypropylene hollow fiber membrane. I. Surface modification by the graft polymerization of acrylic acid. *Journal of Membrane Science*, 2002.196(2): 221–229.

62. Hegazy EA, Kamal H, Maziad N, Dessouki A. Membranes prepared by radiation grafting of binary monomers for adsorption of heavy metals from industrial wastes. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials, and At*oms, 1999.151(1-4):386–392.

63. Betz N, Begue J, Goncalves M, Gionnet K, Deleris G, Le Moel A. ,Functionalisation of PAA radiation grafted PVDF. *Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms,* 2003.208: 434-441.

64. Abdel-Bary EM, El-Nesr EM. , Methods, characterization, and application of grafting. In: Cheremisinoff NP, editor. *Handbook of engineering polymeric materials.* New York: Marcel Dekker, 1997: 501.

65. Chapiro, A., Radiation induced grafting, *Int. J. Radiation Physics and Chemistry,* 1977. 9(1-3)**:** 55-67.

66. Guilmeau I, Esnouf S, Betz N, Le Moel A., Kinetics and characterization of radiation-induced grafting of styrene on fluoropolymers. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* 1997. 131(1-4): 270-275.

67 Gupta B, Scherer G. , Proton Exchange Membranes by Radiation-Induced Graft Copolymerization of Monomers into Teflon-FEP Films. *CHIMIA International Journal for Chemistry*.1994. 48(5): 127-137.

68 Nasef M, Saidi H, Nor H., Radiation-induced graft copolymerization for preparation of cation exchange membranes: a review. *Nucl. Sci. J. Malaysia*, 1999.17: 27–43.

69. McRae W., Applications of ion exchange membranes, current state of the technology after 45 years. In: Paterson R, editor. Effective membrane processes: new perspectives. London: *Mechanical Engineering Publications Limited*, 1993: 149.

70. Lyons B., The radiation crosslinking of fluoropolymers. In: *Modern fluoropolymers, Scheirs J,* editor. New York: Wiley, 1997: 336.

71. Aydinli B, Tincer T., Radiation grafting of various water soluble monomers on ultra-high molecular weight polyethylene powder. I. Grafting conditions and grafting yield. *Radiat Phys Chem*; 2001.60:p. 237–243.

72. Geissel H, Weick H, Scheidenberger C, Bimbot R, Gardes D. , Experimental studies of heavy-ion slowing down in matter. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 2002. 195(1): 3-54.

73. Nasef, M.M., Application of electron beams for preparation of membranes. *Paper Presented in the Executive Seminar on the Application of Electron Accelerator and FNCA Workshop*, 18–22 August,2003,Kuala Lumpur, Malaysia.

74. Dworjanyn, P.A.; Garnett, J.L. Radiation Grafting on Monomers on Plastic Fibers. In Progress in Polymer Processing. *Radiation Processing of Polymer*, Shing, A.; Silvernaan, J., Eds., Hanser: Munich, 1992.3: 93.
.

75. Kabanov, V.Y., R. Aliev, and L. Sidorova, Effect of solvents on radiation-induced ionic graft polymerization. *Journal of Polymer Science: Polymer Chemistry Edition*, 1980. 18(3): 871-878.

76. Ivanov, V.S., *Radiation Chemistry of Polymers*, VSP, Utrecht, The Netherlands, 1992: 58.

77. Omichi, H. and J. Okamoto, Solvent effects on the synthesis of ion-exchange membranes by radiation-induced graft polymerization of methyl α,β,β-trifluoroacrylate. *Journal of Polymer Science:* Polymer Chemistry Edition, 1982. 20(6): 1559-1568.

78. El-Assy NB. , Effect of mineral and organic acids on radiation grafting of styrene onto polyethylene. *J Appl Polym Sci*, 1991.42: 885–889.

79. Nasef M.M., Effect of solvents on radiation-induced grafting of styrene onto fluorinated polymer films. *Polym Int,* 2001, 50: 338–346.

80. Gupta, B., N. Anjum, and A. Gupta, Influence of solvents on radiation-induced graft copolymerization of acrylamide into polyethylene films. *Journal of Applied Polymer Science,* 2000. 77(6): 1401-1404.

81. Walsby, N., Paronen, M., Juhanoja, J. and Sundholm F., Radiation grafting of styrene onto poly (vinylidene fluoride) films in propanol: The influence of solvent and synthesis conditions. *Journal of Polymer Science Part A: Polymer Chemistry,* 2000. 38(9): 1512-1519.

82. Machi S, Kamel I, Silverman J. Effect of swelling on radiation-induced grafting of styrene to polyethylene. *J. Polym. Sci.,* 1970.8: 3329–3337.

83. El-Nesr, E., Effect of solvents on gamma radiation induced graft copolymerization of methyl methacrylate onto polypropylene. *J Appl Polym Sci*, 1997.63:p.377–82.

84. Gupta B, Scherer G., Proton exchange membranes by radiation-induced graft copolymerization of monomers into Teflon-FEP films. *Chimia,* 1994. 48(5): 127-137.

85. Gupta, B., F.N. Büchi, and G.G. Scherer, Cation exchange membranes by pre-irradiation grafting of styrene into FEP films. I. Influence of synthesis conditions. *Journal of Polymer Science Part A: Polymer Chemistry,* 1994. 32(10): 1931-1938.

86. Dargaville T, George G, Hill D, Whittaker A. ,High energy radiation grafting of fluoropolymers. *Progr Polym Sci.,* 2003.28: 1355–1376.

87. Hegazy EA, Ishigaki I, Okamoto J., Radiation grafting of acrylic acid onto fluorine-containing polymers. I. Kinetic study of pre-irradiation grafting onto poly (tetrafluoroethylene*). J Appl Polym Sci*., 1981.26: 3117–24.

88. Hegazy EA, Ishigaki I, Dessouki A, Rabie A, Okamoto J., The study on radiation grafting of acrylic acid onto fluorine containing polymers. III. Kinetic study of preirradiation grafting onto poly(tetrafluoroethylene-hexafluoropropylene). *J Appl Polym Sci.,* 1982.27: 535-43.

89. Hegazy EA, El-Dessouky M, El-Sharabasy S., Some investigations on the post radiation grafting of acrylamide onto polyethylene films. *Radiat Phys Chem,* 1986.27: 323–8.

90. Ishigaki I, Sugo T, Senoo K, Takayama T, Machi S, Okamoto J, Okada T.
, Synthesis of ion exchange membrane by radiation grafting of acrylic acid onto polyethylene. *Radiat Phys Chem.,* 1981.18: 899–905.

91. Ishigaki I, Sugo T, Senoo K, Okada T, Okamoto J, Machi S., Graft polymerization of acrylic acid onto polyethylene film by pre-irradiation method. I. Effects of pre-irradiation dose, monomer concentration, reaction temperature, and film thickness. *J Appl. Polym. Sci;* 1982.27: 1033–41.

92. Gupta B, Chapiro A., Preparation of ion-exchange membranes by grafting acrylic acid into pre-irradiated polymer films. 1. Grafting into polyethylene. *Eur Polym J*; 1989.25: 1137–43.

93. Gupta B, Chapiro A., Preparation of ion-exchange membranes by grafting acrylic acid into pre-irradiated polymer films. 2. Grafting into Teflon-FEP. *Eur Polym J;* 1989.25:p.1145–1148.

94 Nasef M.M., Saidi H, Dessouki A, El-Nesr E. , Radiation induced grafting of styrene onto poly(tetrafluoroethylene) (PTFE) films. I. Effect of grafting conditions and properties of the grafted films. *Polym Int;* 2000.49: 399–406.

95. Nasef M.M., Saidi H, Nor H., Proton exchange membranes prepared by simultaneous radiation grafting of styrene onto poly (tetrafluoroethylene-co-hexafluoropropylene) films. I. Effect of grafting conditions. *J Appl Polym Sci*; 2000, 76: 220–7.

96. Nasef M M, Saidi H, Nor H, Dahlan K, Hashim K., Cation exchange membranes by radiation-induced graft copolymerization of styrene onto PFA copolymer films. I. Preparation and characterization of the graft copolymer. *J Appl Polym* Sci; 1999.73: 2095–102.

97. Rao, V., Ashokan, P.V. Shridhar**,** M.H., *Materials Science and Engineering: A*, 2000, Vol.276 (1-2): 266-268.

98. Shi, Z., K.G. Neoh, and E.T. Kang, Surface-Grafted Viologen for Precipitation of Silver Nanoparticles and Their Combined Bactericidal Activities. Langmuir, 2004. 20(16): 6847-6852.

99. Material Safety Data Sheet 4-Vinylpyridine MSDS, www.sciencelab.com 06/08/2011

100. Momose T, Yoshioka H, Ishigaki I, Okamoto J., Radiation grafting of *α, β, β*-trifluorostyrene onto poly(ethylene-tetrafluoroethylene) film by preirradiation method. I. Effects of preirradiation dose, monomer concentration, reaction temperature, and film thickness.*Journal of Applied Polymer Science,* 1989.37: 2817–26.

101. Kreuer, K.-D, Paddison S.J, Spohr E., and Schuster M, Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology. *Chemical Reviews,* 2004. 104(10): 4637-4678.

102. Bouchet, R. and Siebert, E., Proton conduction in acid doped polybenzimidazole. *Solid State Ionics,* 1999. 118(3): 287-299.

103 Li Q., Hjuler, H.A. and Bjerrum, N.J., Phosphoric Acid Doped Polybenzimidazole Membranes: Physiochemical Characterization and Fuel Cell Applications. *Journal of Appl. Electrochem,*, 2001. 31: 773-779.

104. Schmidt, C. and Schmidt-Naake, G Proton Conducting Membranes Obtained by Doping Radiation-Grafted Basic Membrane Matrices with Phosphoric Acid. *Macromolecular Materials and Engineering*, 2007. 292(10-11): 1164-1175.

.

105. El-Nesr E., Effect of solvents on gamma radiation induced graft copolymerization of methyl methacrylate onto polypropylene. *J Appl Polym Sci;* 1997.63:377–82.

106. Brandrup, J.; Immergut, E. H. (eds), Polymer Handbook; Wiley Interscience Publications: 1989, New York.

107. Brandrup, J., Immergut, E.H., Grulke, E.A, Eds., *Polymer Handbook*, 4th Edition, John Wiley, 1999, New York, VII /675-711.

108. Bozzi, A., & Chapiro, A. , Synthesis of perm-selective membranes by grafting acrylic acid into air-irradiated Teflon-FEP films. [doi:10.1016/1359-0197(88)90184-1]. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry,*1988. 32(2): 193-196.

109. Gürsel, S.A., Ben youcef, H., Wokaun, A., Gunther G. Scherer ,Influence of reaction parameters on grafting of styrene into poly(ethylene-alt-tetrafluoroethylene) films. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* 2007. 265(1): 198-203.

110. Li, Q., He, R., Berg, R. W., Hjuler, H. A., & Bjerrum, N. J. , Water uptake and acid doping of polybenzimidazoles as electrolyte membranes for fuel cells. *Solid State Ionics*, 2004.168(1-2): 177-185.

111. He, R., Li, Q., Jensen, J.O. & Bjerrum,N.J, Doping phosphoric acid in polybenzimidazole membranes for high temperature proton exchange membrane fuel cells. *Journal of Polymer Science Part A: Polymer Chemistry,* 2007. 45(14): 2989-2997.

112. He, R., Che, Q. and Sun, B., The acid doping behavior of polybenzimidazole membranes in phosphoric acid for proton exchange membrane fuel cells. *Fibers and Polymers,* 2008. 9(6): 679-684.

113. Nasef, M. M., Saidi, H. & Dahlan, K. M.M., Electron beam irradiation effects on ethylene-tetrafluoroethylene copolymer films. *Radiation Physics and Chemistry,* 2003. 68 (5): 875-883.

114. Glipa, X., Bonnet, B., Mula, B., J. Jones, D. & Roziere, J., Investigation of the conduction properties of phosphoric and sulfuric acid doped polybenzimidazole. *Journal of Materials Chemistry,* 1999. 9(12): 3045-3049.