



UNIVERSITI PUTRA MALAYSIA

**CHARACTERIZATION OF SULFONATED, RADIATION-INDUCED
POLYSTYRENE-GRAFTED FLUORINATED BASE POLYMER
PROTON EXCHANGE MEMBRANES**

MUHAMMAD YOUSUF HUSSAIN

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By

MUHAMMAD YOUSUF HUSSAIN

**Thesis submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Fulfilment of the Requirements for the
Degree of Doctor of Philosophy**

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TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABATRAK	vii
ACKNOWLEDGEMENTS	xi
APPROVAL	xiv
SUPERVISORY COMMITTEE	xv
DECLARATION	xvi
LIST OF TABLES	xxi
LIST OF FIGURES	xxiii
LIST OF ABBREVIATIONS	xxix

CHAPTER

I	INTRODUCTION	
1.1	Background of the study	1
1.2	Proton Exchange Membrane (PEM) Electrolytes	3
1.3	Scope of the Present Study	5
1.4	Problem Statement	6
1.5	Objectives of the Present Study	7
1.6	Significance of the Study	8
1.7	Thesis Outline	9
II	LITERATURE REVIEW	
2.0	Introduction	11
2.1	The Present Era Fuel Cells	14
2.1.1	Hydrogen Fuel Cell (HFC) and direct methanol fuel cell (DMFC)	18
2.1.2	Advantages of DMFC	18
2.1.3	Functioning of HFC and DMFC	19
2.1.4	The Vital Components of the HFC and DMFC	22
2.2	Proton Exchange Membranes (PEMs)	22
2.2.1	Various types of PEMs for the fuel cells	23
2.2.2	Present PEMs for the Fuel Cells	24
2.2.3	Potential Candidates of PEMs for DMFC and their modification	25
2.3	Methods of modifications to prepare PEMs	26



2.4	Characterization of modified radiation-induced polystyrene-g-sulfonic acid PEMs	37
III THEORETICAL		
3.0	Interaction of Gamma rays with Matter	51
3.0.1	Types of High Energy Ionizing Radiations	51
3.0.2	Photoelectric Absorption	53
3.0.3	Compton Scattering	55
3.0.4	Pair Production	56
3.1	Radiation Chemistry	58
3.2	Radiation-induced Graft Copolymerization	60
3.3	Different Methods of Radiation-induced Graft Copolymerization	63
3.3.1	Simultaneous Irradiation Method	64
3.3.2	Pre-irradiation Method	66
3.4	Proton exchange membranes (PEMs)	68
3.5	Radiation-induced Graft Copolymerization for the PEM	70
3.6	Distribution of the Grafting and Degree of Grafting (DOG)	71
3.7	Factors Affecting the Degree of grafting	74
3.7.1	Radiation dose and dose rate	75
3.7.2	Nature of the Base Polymer	76
3.7.3	Type of monomer and monomer concentration	77
3.7.4	Type of Solvent	78
IV EXPERIMENTAL		
4.0	Materials	80
4.1	Equipments	81
4.2	Membrane Preparation	82
4.2.1	Sulfonation	83
4.3	Characterization of the Polystyrene-g-Copolymer Films	85
4.3.1	Raman spectroscopy	85
4.4	Characterization of the Sulfonated Membranes	86
4.4.1	Degree of Sulfonation	86
4.4.2	Ion Exchange Capacity	87
4.4.3	Swelling Behaviour	88
4.4.4	Ionic (proton) Conductivity	88
4.4.5	Thermal Properties	89
4.4.6	Chemical Stability	90
4.4.7	Scanning electron microscopy (SEM)	90



V RESULTS AND DISCUSSIONS

5.0	Introduction	91
5.1	Graft copolymerization of styrene onto PTFE, ETFE, and PVDF base polymer films	92
5.1.1	Mechanism of radiation-induced grafting of polystyrene onto the base films	94
5.1.2	Effect of the type of solvent on the grafting of polystyrene onto the base polymer films	99
5.1.3	Effect of monomer concentration on grafted polystyrene onto base films	109
5.1.4	Effect of absorbed dose on the grafted polystyrene onto the base films	114
5.1.5	Dose dependent grafting kinetics	118
5.2	Sulfonation of the polystyrene grafted onto PTFE, ETFE, and PVDF base polymer films	123
5.2.1	Sulfonated PTFE-g-polystyrene membrane	124
5.2.2	Sulfonated ETFE-g-polystyrene membrane	128
5.2.3	Sulfonated PVDF-g-polystyrene membrane	133
5.3	Ion Exchange Capacity of the Sulfonated Membranes	135
5.3.1	PTFE-g-polystyrene Sulfonic Acid Membranes	135
5.3.2	ETFE-g-polystyrene Sulfonic Acid Membranes	139
5.3.3	PVDF-g-polystyrene Sulfonic Acid Membranes	141
5.4	Analysis Based on the Constituent Contents of Ion Exchange Membranes	144
5.4.1	PTFE Sulfonated Membranes	147
5.4.2	ETFE Sulfonated Membranes	151
5.4.3	PVDF Sulfonated Membranes	155
5.4.4	SC of Sulfonated Polystyrene	158
5.5	Swelling Behaviour of the Sulfonated Membranes	160
5.5.1	PTFE-g-polystyrene Sulfonic Acid Membranes	160
5.5.2	ETFE-g-polystyrene Sulfonic Acid Membranes	163
5.5.3	PVDF-g-polystyrene Sulfonic Acid Membranes	165
5.6	DC proton conductivity and activation energy of the sulfonated membranes	169
5.6.1	PTFE-g-polystyrene Sulfonated Membranes	170
5.6.2	ETFE-g-polystyrene Sulfonated Membranes	178
5.6.3	PVDF-g-polystyrene Sulfonated Membranes	186
5.7	Thermal Properties of the Raw, Grafted Films and Sulfonated membranes	194
5.7.1	PTFE-g-polystyrene Sulfonated Membranes	195
5.7.2	ETFE-g-polystyrene Sulfonated Membranes	203
5.7.3	PVDF-g-polystyrene Sulfonated Membranes	208



5.8	Chemical Stability of the Raw, Grafted Films and Sulfonated membranes	214
5.8.1	PTFE-g-polystyrene Sulfonated Membranes	214
5.8.2	ETFE-g-polystyrene Sulfonated Membranes	219
5.8.3	PVDF-g-polystyrene Sulfonated Membranes	223
5.9	Surface Morphology of the Sulfonated Membranes	228
5.9.1	SEM Micrograph of PTFE	228
5.9.2	SEM Micrograph of ETFE	233
5.9.3	SEM Micrograph of PVDF	236
VI	CONCLUSIONS AND FUTURE WORKS	
6.1	Conclusions	239
6.2	Future Work	243
	REFERENCES	245
	BIODATA OF THE AUTHOR	254
	LIST OF PUBLICATIONS	255



DEDICATION

*To the beloved Prophet MUHAMMAD (PBUH) who always emphasized to earn
knowledge and whose saying is
“To seek knowledge even go to China”*

To:

**My father; My wife Dr. Saeeda Yousuf;
My children: Hasnain Yousuf, Saqlain
Yousuf, Zulqarnain Yousuf Zain, Noor-ul-
Ain Saman, Hussain Yousuf Sunain and
My Niece Farheen Naz**



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
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By

MUHAMMAD YOUSUF HUSSAIN

July 2007

Chairman: Professor Elias bin Saion, PhD

Faculty: Science

The world's future is critically energy dependent and the concerns of the global warming caused by the present-day depleting non-renewable fossil fuels push the development of new technologies for clean, efficient, reliable, and portable power sources based on electrochemical devices such as fuel cells. The hydrophilic proton exchange membranes (PEMs) seem to be a vital component of fuel cells. Currently, the commercial perfluoro-sulfonated PEMs are inheritably very expensive and an alternative PEM must be sought after, which possess properties suitable for fuel cell applications. Rationalizing this circumstance, sulfonated membranes have been developed by graft copolymerization of styrene onto PTFE, ETFE and PVDF base polymer films using a simultaneous gamma irradiation method and their physico-chemical properties were investigated.



Factors affecting the grafting yield, namely the radiation dose, styrene concentration and type of solvent have been identified. Dichloromethane solvent was found to enhance the grafting yield considerably without the formation of homopolymer, unlike methanol and toluene tested, and therefore, dichloromethane was used in the subsequent grafting of styrene (20-100% v/v) onto the base films. The PTFE-g-polystyrene, ETFE-g-polystyrene, and PVDF-g-polystyrene films of different grafting yields were sulfonated using chlorosulfonic acid (30% v/v) diluted in dichloroethane (70% v/v) at the reactor temperature of 90 °C for 4 h in order to permit sulfonic acid functional group, SO₃H attachment to the phenyl group of grafted polystyrene and consequently alternative PEMs were materialized.

The grafting and sulfonation yields have been interpreted in terms of conventional two-compartmental analysis that gives the degrees of grafting (DOG) and sulfonation (DOS) and in terms of new three-compartmental analysis, which assumed the membrane consists of base polymer, polystyrene, and sulfonic acid, to yield the polystyrene content (PC) and the sulfonic acid content (SC). It was found that the DOG increases with radiation dose until the maximum DOG value of 73% for ETFE-g-polystyrene, 33% for PVDF-g-polystyrene, and 30% for PTFE-g-polystyrene at 25 kGy attributed to the initiation and propagation of graft copolymerization. Upon sulfonation, it was found that the DOS increases in



proportionality to the DOG for all the sulfonated membranes. The results also revealed the dependences of the SC on PC and the DOS on DOG. Moreover, the mass ratio of the SC to the sulfonated polystyrene (PC+SC) is found in the range 55-59 % for higher grafting yield of sulfonated ETFE membranes and 51-54% for low grafting yield of sulfonated PTFE and PVDF membranes independent of the PC and SC obtained. Our DOS or SC results seem to differ to some previous results which openly declared the DOS values of 100% that is in contradicting to the physical nature of sulfonation mechanism.

The physico-chemical i.e. ion exchange capacity (IEC) and activation energy behaviours of the sulfonated membranes were studied as functions of DOG (PS) and DOS (SC). The IEC is proportional to the DOS or SC. The IEC values vary between 0.721 and 1.095 mmol/g at DOS between 10.0 and 18.8% (SC between 9.0 and 17.6%) for the sulfonated PTFE- membranes, between 1.361 and 1.997 mmol/g at DOS between 26.8 and 55.3% (SC between 21.1 and 35.5%) for the sulfonated ETFE membranes, and between 0.360 and 0.432 m mol/g at DOS between 12.4 and 17.1% (SC between 11.1 and 14.6%) for the sulfonated PVDF membranes. The activation energies on the other hand vary between 0.327 and 0.275 eV at DOG between 10.4 and 22.0% (PC between 8.6 and 14.9%) for the sulfonated PTFE- membranes, between 0.227 and 0.170 eV at DOG between 25.4 and 60.9% (PC between 16.0 and 24.4%) for the sulfonated ETFE membranes, and



between 0.3297 and 0.289 eV at DOG between 12.6 and 17.0% (PC between 9.9 and 12.4%) for sulfonated PVDF membranes.

The effects of DOG (or PS) and DOG (or SC) on the thermal properties and chemical stability were also investigated. The glass transition temperature of the grafted membranes was found to show at a value of ~ 115 °C. The sulfonated membranes showed a chemical stability up to a temperature of ~ 300 °C above to which they undergo a multi step degradation pattern due to dehydration, desulfonation, decomposition of the polystyrene and sulfonic acid in the polymer matrices. For the purpose of morphological investigations, SEM micrographs of the grafted films and sulfonated membranes were taken while the SEM micrographs of their original and grafted samples were used as references respectively. This study revealed that for the low grafting yield the grafting concentrated at the surface of the graft copolymer and when the yield increases, the styrene monomer penetrated to the bulk and for the highest grafting yield achieved, the micrographs show the grafting presence until in the middle of the base films.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENCIRIAN DARI SULFONASI MEMBRAN, PERTUKARAN PROTON
TERFLURIN BERTAUT-POLISTIRENA YANG DIARUH-SINARAN**

Oleh

MUHAMMAD YOUSUF HUSSAIN

Julai 2007

Pengerusi: Profesor Elias bin Saion, PhD

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Masa hadapan aktiviti dunia bergantung kepada tenaga dan kesannya kepada kepanasan alam sekitar tidak dapat dielakkan dengan penggunaan sumber tenaga sekarang yang semakin berkurangan. Oleh kerana itu pembangunan teknologi baharu tertumpu kepada pengeluaran sumber tenaga yang lebih bersih, cekap, stabil dan mudah alih berasaskan peralatan elektrokimia seperti sel bahanapi. Membran pertukaran proton (PEM) berhidrofilik merupakan komponen penting sel bahanapi. Pada masa kini PEM berflurosulfonik dipasaran secara semulajadinya sangat mahal dan suatu PEM alternatif perlu dicari yang cirinya bersesuaian dengan kegunaan sel bahanapi. Meninjau keadaan ini beberapa membran tersulfonik telah dibinakan dengan menggunakan kaedah induksi tautan sinar gama serentak bagi pengkopolimeran stirena ke atas film polimer asas PTFE, ETFE and PVDF serta ciri-ciri kimia fiziknya diselidiki.



Faktor kesan terhadap penghasilan tautan iaitu dos sinaran, kepekatan stirena dan jenis peluntur telah dikenal pasti. Didapati bahawa diklorometana menambahkan penghasilan tautan tanpa membentuk homopolimer tidak seperti pelarut metanol dan toluen. Oleh itu dalam proses tautan polimer asas seterusnya diklorometana (20%) telah digunakan dengan stirena (20-100%). Film-film PTFE-g-polistirena, ETFE-g-polistirena, and PVDF-g-polistirena yang berlainan penghasilan tautan telah disulfonik dengan asid klorosulfonik (30% v/v) yang dicairkan dalam dikloroetana (70% v/v) pada suhu reactor 90 °C dalam masa 4 jam untuk membenarkan fungsi kumpulan asid sulfonik, SO₃H dilekatkan pada kumpulan phenyl polistirena dan menghasilkan PEM alternatif.

Penghasilan tautan dan pengulfonik telah diinterpretasikan dengan kaedah biasa analisis dua-bahagian yang memberikan darjah tautan (DOG) dan darjah sulfonan (DOS) serta dengan kaedah baharu analisis tiga-bahagian, yang mana membrane terdiri daripada polimer asas, polistirena dan asid sulfonik lalu menghasilkan kandungan polistirena (PC) dan kandungan asid sulfonik (SC). Daripada kajian ini didapati DOG bertambah dengan dos sinaran sehingga 25 kGy yang memberikan nilai DOG maksimum 73% untuk ETFE-g-polistirena, 33% untuk PVDF-g-polistirena dan 30% untuk PTFE-g-polirena disebabkan oleh proses permulaan dan pengandaan tautan kopolimeran. Setelah disulfonik didapati bahawa DOS bertambah berkadar terus dengan DOG untuk semua membran tersulfonik. Keputusan juga menunjukkan bahawa pergantungan SC kepada PC atau DOS



kepada DOG. Selanjutnya, didapati nisbah jisim SC terhadap jisim polistirena tersulfonik (PC+SC) adalah dalam julat 55-59 % bagi tautan tinggi membran tersulfonik ETFE dan dalam julat 51-54% bagi tautan rendah membran tersulfonik PTFE dan PVDF serta tak bergantung kepada nilai PC atau SC yang diperolehi. Keputusan tentang DOS atau SC ini menunjukkan nilainya berbeza dengan sebahagian keputusan penyelidik lain yang secara terbuka mengatakan bahawa mereka mendapati nilai DOS melebihi 100%, bertentangan dengan mekanisme pengulfonik yang sebenar.

Ciri kimia fizik membran tersulfonik iaitu keupayaan menukar ion (IEC) dan tenaga pengaktifan telah juga dikaji sebagai fungsi kepada (PS) dan DOS (SC). Nilai IEC adalah berkadar terus dengan DOS atau SC. Nilai IEC berubah diantara 0.721 dan 1.095 m mol/g dengan DOS diantara 10.0 dan 18.8% (SC diantara 9.0 dan 17.6%) bagi membran tersulfonik PTFE, diantara 1.361 dan 1.997 m mol/g dengan DOS diantara 26.8 dan 55.3% (SC diantara 21.1 dan 35.5%) bagi membran tersulfonik ETFE, serta diantara 0.360 dan 0.432 m mol/g dengan DOS diantara 12.4 dan 17.1% (SC diantara 11.1 dan 14.6%) bagi membran tersulfonik PVDF. Tenaga pengaktifan pula nilainya berubah diantara 0.327 dan 0.275 eV dengan DOG diantara 10.4 dan 22.0% (PC diantara 8.6 dan 14.9%) bagi membran tersulfonik PTFE, diantara 0.227 dan 0.170 eV dengan DOG diantara 25.4 dan 60.9% (PC diantara 16.0 dan 24.4%) bagi membran tersulfonik ETFE, serta



diantara 0.3297 dan 0.289 eV dengan DOG diantara 12.6 dan 17.0% (PC diantara 9.9 dan 12.4%) bagi membran tersulfonik PVDF.

Kesan DOG (atau PC) dan DOG (atau SC) ke atas ciri terma dan kesetabilan kimia telah juga dikaji. Suhu peralihan kaca membran tertaut didapati bernilai ~ 115 °C. Membran tersulfonik menunjukkan kesetabilan kimia sehingga ~ 300 °C dan jika melebihi paras ini membran mengalami kemusnahan kerana penghidratan, pengnyah sulfonik dan penguraian polistirena dan diikuti oleh polimer asas. Dalam kajian morfologi mikrograf SEM membran tersulfonik PTFE-, ETFE- and PVDF-g-polistirena telah digunakan dan dibandingkan dengan sampel polimer asas asal dan sampel bertaut polistirena. Kajian ini mendapati bahawa dengan penghasilan tautan rendah polistirena tertumpu di permukaan dan apabila penghasilan tautan bertambah monomer stirena boleh memasuki pukal membran. Seterusnya pada penghasilan tautan tinggi mikrograf menunjukkan polistirena boleh memasuki di dalam film polimer asas.



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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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I certify that an Examination Committee has met on 2nd July 2007 to conduct the final examination of Muhammad Yousuf Hussain on his Doctor of Philosophy thesis entitled “Characterization of the Sulfonated, Radiation-Induced Polystyrene-Grafted Fluorinated Base Polymer Proton Exchange Membranes” in accordance with Universti Pertanian Malaysia (Higher Degree) Act 1980 and Universti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MUHAMMAD YOUSUF HUSSAIN

Date: 1 AUGUST 2007



LIST OF TABLES

Table		Page
2.1	Present era various types of fuel cells, their characteristics, applications and limitations	16
2.2.	Commercial perfluorinated ionomer membranes	25
2.3	A summary of some important studies on the preparation of radiation-induced grafted proton exchange membranes	36
2.4	A summary of the Physico-chemical properties of the radiation-induced grafted PFA polystyrene-sulfonic-acid (PSSA) membranes	41
2.5	A summary of the characterization of the radiation-grafted polystyrene sulfonated proton exchange membranes based on PTFE, ETFE, PVDF and LDPE films	43
2.6	A summary of the properties of NEM 20 and NEM 21 sulfonated membranes	44
2.7	A summary of the physico-chemical properties of the SPS/PTFE composite membranes along with Nafion [®] 117 at 25 °C	46
2.8	A summary of some important studies on the characterization of radiation grafted proton exchange membranes	50
3.1	Commercial perfluorinated ionomer membranes	68
5.1	Structure and properties of fluorinated polymer base films used in this study	94
5.2	Effect of various solvents on the DOG of styrene onto PTFE, ETFE and PVDF base films for 60 % styrene concentration at 25 kGy gamma dose	105
5.3	Dose sensitivity parameter $1/D_0$ of grafting yield Y (%) of styrene copolymer onto PTFE, ETFE and PVDF base films at various doses 0-25 kGy for 40, 60, and 80 % styrene concentrations in dichloromethane solvent	122



5.4	Raman shifts of styrene, polystyrene, ETFE (raw) and polystyrene (grafted) ETFE copolymer	132
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LIST OF FIGURES

Figure		Page
2.1	Comparison between direct energy conversion with fuel cells and conventional indirect ICEs technology	14
2.2	A functional schematic of direct methanol fuel cell (DMFC) and the hydrogen fuel cell (HFC)	18
2.3	Schematic of a Hydrogen Fuel Cell (HFC)	20
2.4	Schematic of a Direct Methanol Fuel Cell (DMFC)	21
3.1	Typical photoelectric absorption process: (a) Photon enters atom (b) electron ejected from inner shell: kinetic energy equals energy of photon minus binding energy (c) vacancy in inner shell filled by electron dropping from outer shell (d) virtual X-ray collides with electron in outer shell (e) electron ejected from outer shell (Auger electron): kinetic energy equals energy of virtual X-ray minus second ionization potential of atom	54
3.2.	Illustration of the Compton scattering process	55
3.3	Pair production process	57
3.4	General schematic of a graft copolymer	61
3.5	Graft polymerization of a base polymer	62
5.1	The mechanism of radiation-induced grafting of styrene onto PTFE films to produce PTFE-g-polystyrene copolymer	96
5.2	The mechanism of radiation-induced grafting of styrene onto ETFE films to produce ETFE-g-polystyrene copolymer	97
5.3	The mechanism of radiation-induced grafting of styrene onto PVDF films to produce PVDF-g-polystyrene copolymer	98

