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

V RESULTS AND DISCUSSIONS

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 fulfilment of the requirement for the degree of Doctor of Philosophy

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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 ^{o}C for 4 h in order to permit sulfonic acid functional group, SO_3H 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 ^{o}C. The sulfonated membranes showed a chemical stability up to a temperature of ~300 ^{o}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**

Fakulti: **Sains**

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 bahabapi. 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 ^{o}C dalam masa 4 jam untuk membenarkan fungsi kumpulan asid sulfonik, SO_3H dilekatkan pada kumpulan phenyl polistirena dan menghasilkan PEM alternatif.

Penghasilan tautan dan pengsulfonik 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 polistrena (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. Keputusantentang 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 pengsulfonik 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 ^{o}C. Membran tersulfonik menunjukkan kesetabilan kimia sehingga ~300 ^{o}C dan jika melebihi paras ini membran mengalami kemusnahan kerana penghidratan, pengnyah sulfonik dan penguraian polistirena dan diikuti oleh polimer asas. Dalam kajian morpologi 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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share of fatherly love. I am also thankful to my niece Ms Faraheen Naz for her love and prayers. My thanks are also to my sisters Dr Amina and Dr Rubina for their love and affection for me. Without all of your love and cooperation, this work would have not been possible.

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:

Elias bin Saion, PhD
Professor
Faculty of Science
University Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD
Professor
Faculty of Science
University Putra Malaysia
(Member)

Zainal Abidin Talib, PhD
Associate Professor
Faculty of Science
University Putra Malaysia
(Member)

Zaki Abd Rahman, PhD
Associate Professor
Faculty of Science
University Putra Malaysia
(Member)

Khairul Zaman Hj Mohd Dahlan, PhD
Director
Radiation Processing Technology Division, MNA
(Member)

AINI IDERIS, PhD
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 9 AUGUST 2007

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:

Azmi Zakaria, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zaidan Abd. Wahab, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Zainal Abidin Sulaiman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Abdul Kariem Mohd. Arof, PhD
Professor
Faculty of Science
Universiti Malaya
(External Examiner)

HASANAH MOHD. GHAZALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 3 AUGUST 2007

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.

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MUHAMMAD YOUSUF HUSSAIN

Date: 1 AUGUST 2007

LIST OF TABLES

LIST OF FIGURES