DEVELOPMENT OF NOVEL NON-AQUEOUS THERMALLY STABLE MEMBRANES FOR THE USE IN POLYMER ELECTROLYTE MEMBRANE FUEL CELL (PEMFC)



Manita Jithunsa

A Dissertation Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy The Petroleum and Petrochemical College, Chulalongkorn University in Academic Partnership with The University of Michigan, The University of Oklahoma, and Case Western Reserve University

2008

511982

Thesis Title:	Development of Novel Non-aqueous Thermally Stable			
	Membranes for the Use in Polymer Electrolyte Membrane Fuel			
	Cell (PEMFC)			
By:	Manita Jithunsa			
Program:	Polymer Science			
Thesis Advisors:	Assoc. Prof. Suwabun Chirachanchai			
	Prof. Kohji Tashiro			

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

.. Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

Nantury Janumet mwabun hirabanciat (Assoc. Prof. Nantaya Yanumet) (Assoc.Prof.Suwabun Chirachanchai) (Prof. Kohji Tashiro) (Asst.Prof. Manut Nithitanakul) Latyphom

(Assoc. Prof. Jatuphorn Wootthikanokkhan)

ABSTRACT

4682010063: Polymer Science Program Manita Jithunsa: Development of Novel Non-aqueous Thermally Stable Membranes for the Use in Polymer Electrolyte Membrane Fuel Cell (PEMFC). Thesis Advisors: Assoc.Prof. Suwabun Chirachanchai, and Prof.Kohji Tashiro 120 pp.
Keywords: Acrylic acid/ 4-Vinylimidazole/ Polymer electrolyte membrane fuel cell/ Anhydrous membrane system/ SPEEK/ Proton conductivity/ Molecular assembly/ Aza-methylene phenol compounds/ Heterocyclic group

The present project stands on a viewpoint of a synthesized polymeric membrane material having a definite functional group, which an effective protontransferring pathway is possible for PEM. Compared with water molecule, the imidazole is expected to function not only for providing better thermal stability but also allowing a similarly effective proton transferring via its specific structure. Here, the work originally proposes a series of imidazole functionalized polymeric material, for example, (i) copolymers of acrylic acid and 4-vinylimidazole including temperature dependency and structural relationships, (ii) SPEEK blended with Poly (AA-co-4VIm). (iii) polyamide functionalized with imidazoles, The goal of the project is to achieve a novel polymeric material for high efficiency proton transferring polymer membrane to be used in PEMFC system.

บทคัดย่อ

มานิตา จิตต์หรรษา : พอลิเมอไรเซชั่น: การพัฒนาเมมเบรนแบบใหม่ที่ส่งผ่าน โปรตอนแบบปราศจากโมเลกุลน้ำและมีความเสถียรต่อความร้อนสำหรับการใช้ในเซลล์เชื้อเพลิง ประเภทพอลิเมอร์อิเลคโทรไลท์ (Development of Novel Non-aqueous Thermally Stable Membranes for the Use in Polymer Electrolyte Membrane Fuel Cell (PEMFC)) อ. ที่ปรึกษา: รศ.ดร. สุวบุญ จิรชาญชัย และศาสตราจารย์โคจิทาชิโระ 120 หน้า

วิทยานิพนธ์ฉบับนี้เสนอ 3 วิธีการสังเคราะห์วัสดุพอลิเมอร์เมมเบรนที่มีหมู่ฟังก์ชัน เฉพาะที่เอื้อต่อการส่งผ่านโปรตอนสำหรับเมมเบรนแลกเปลี่ยนโปรตอน หมู่ดังกล่าว คือ อิมิดา โชล ซึ่งนอกงากจะให้ก่าคงทนต่อความร้อนที่สูงกว่าโมเลกุลน้ำแล้ว ยังให้คุณสมบัติการส่งผ่าน โปรตอนที่มีประสิทธิภาพดีเทียบเท่ากับโมเลกุลน้ำอีกด้วย งานวิจัยฉบับนี้ขอเสนอแนวคิดริเริ่มที่ เกี่ยวกับวัสดุพอลิเมอร์เมมเบรนที่มีหมู่อิมิดาโชลสำหรับเซลล์เชื้อเพลิง ตัวอย่างเช่น (1) โคพอลิ เมอร์ระหว่างกรดอะคริลิค และ 4-ไวนิลอิมิดาโชล พร้อมทั้งศึกษาการเปลี่ยนแปลงทางอุณหภูมิที่ สัมพันธ์กับโครงสร้างเมมเบรน, (2) พอลิเมอร์ผสมระหว่างซัลโฟเนตเตตพอลิอีเทอร์อีเทอร์คีโตน และพอลิ (กรดอะคริลิค-โค-4-ไวนิลอิมิดาโซล), (3) พอลิเอไมด์ที่มีหมู่อิมิดาโชล จุดมุ่งหมายของ งานวิจัยฉบับนี้มุ่งเน้นที่จะสังเคราะห์ให้ได้วัสดุพอลิเมอร์คุณสมบัติการส่งผ่านโปรตอนที่มี ประสิทธิภาพดีเพื่อใช้ในพอลิเมอร์ประเภทเมมเบรนแลกเปลี่ยนโปรตอน

ACKNOWLEDGEMENTS

Though the following dissertation is an individual work, she could not have been reached the accomplishment without the author's Thai supervisor, Associate Professor Suwabun Chirachanchai, who not only created this work, but also kindly suggested and reviewed the original manuscripts, clarified her thinking, provided material and spiritual support at critical opportune times, vital assistance throughout this research especially the helps to get opportunities for conduct some part of research in Japan and in Germany. Thank you for being her role model and mentor. This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

The authors would like to express her thanks to her co-advisors, Professor Kohji Tashiro (Department of Future Industry-oriented Basic Science and Materials, Toyota Technological Institute, Japan), for the fruitful idea on temperature dependence FTIR, X-ray, and Raman analyses, revising her manuscripts with enlightening her throughout her research, strong supports, good taking care and warm hospitality during her stay in Japan.

Professor Suzana Peireira Nunes (Institute of Polymer Research, GKSS Research Centre, Germany) for the valuable discussions, great support, recommendations, and miscellaneous things during her stay in Germany. The gratitude is also to Assoc. Prof. Bancha Pulpolka for Proton nuclear magnetic resonance (¹H-NMR) measurements. She thanks to Dr. Piyarat Nimmanpipug for good time and fruitful discussion about molecular dynamics simulation. Deep gratitude is also given to Ms. Piyathip Ussavarungsri for the support of poly (ether ether ketone) powder.

The author is grateful for the scholarship and funding of this thesis work provided not only by the National Research Council of Thailand; and the Japan Society for the Promotion of Science, Japan, but also by the National Metal and Materials Center-Chiang Mai University (MTEC-CMU). She wishes to thank Research Task Force Project on Fuel Cell, Chulalongkorn University, for the support for fuel cell test station and conductivity instruments and machines. The author would like to express her appreciation to the dissertation committee for their suggestions and comments. The appreciation would not be able to accomplish if it does not extend to all Professors who have tendered invaluable knowledge to her at the Petroleum and Petrochemical College, Chulalongkorn University.

It is always impossible to personally thank everyone who has facilitated successful completion of the project. To those of you who she did not specifically name, she also gives her thanks for moving her towards her goal. She also would like to thank her boyfriend, Mr. Yasuaki Ota, who patiently and cheerfully supported and encouraged the writing of this thesis book.

Last and surely not least, she very special thanks to the one person whom she owes everything she is today, her parents. She would also like to thank her brothers for their love and support. Her thanks also go out to her late grandfather who showed her the true worth of hard work. She would like to acknowledge her wonderful friends, colleagues, and all her teachers for the support they have lent her during her stay in the college.

TABLE OF CONTENTS

Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vii
List of Schemes	xi

List of Schemes	AI
List of Tables	xii
List of Figures	xiii

CHAPTER

PIE	K	
I	INTRODUCTION	1
II	LITERATURE REVIEW	5
	2.1 About Fuel Cell	5
	2.2 Attractive Features of Fuel Cell	6
	2.3 Classification of Fuel Cell	7
	2.4 Solid Electrolyte: Proton Exchange Membrane	
	Fuel Cell (PEMFC)	8
	2.5 Applications and Expectations	10
	2.6 Electrolyte Membranes	11
	2.7 Characteristics of the Traditional PEM and the	
	Requirements for Development	11
	2.8 Development of PEMFCs	12
	2.9 Nafion [®] : A Commercialized PEMFC	13
	2.10 Proton Transport Phenomena	16

PAGE

CHAPTER

30

2.11 Alternative Membranes for PEMFC	18
2.12 Evaluations of PEM	21
2.13 Motivation of the Present Work	26

III PREPARATION OF 4(5)-VINYLIMIDAZOLE -co-ACRYLIC ACID COPOLYMER AND THERMAL PERFORMANCES RELATED TO APPLICABILITY AS PEM FUELCELLS

3.1 Abstract	30
3.2 Introduction	30
3.3 Experimental Section	32
3.4 Results and Discussion	35
3.5 Conclusion	45
3.6 Acknowledgements	45
3.7 References and Notes	46

IV **INVESTIGATION OF STRUCTURAL CHANGES RELATED TO TEMPERATURE: AN UNDERSTANDING OF H-BOND BASED PROTON TRANSFER IN 4-VINYLIMIDAZOLE AND ACRYLIC ACID COPOLYMER MEMBRANE** 48 4.1 Abstract 48 4.2 Introduction 48 4.3 Experimental Section 50 4.4 Results and Discussion 52 4.5 Conclusions 65 4.6 Acknowledgements 66 4.7 References 66

V

POLY (ACRYLIC ACID-CO-	
4VINYLIMIDAZOLE)/SULFONATED	
POLYETHERETHERKETONE (POLY (AA-CO-4VIM)/SPH	EEK)
BLEND MEMBRANES FOR PEM FUEL	
CELL APPLICATIONS (PEMFC)	69
5.1 Abstract	69
5.2 Introduction	69
5.3 Experimental	70
5.4 Results and Discussion	77
5.5 Conclusions	86
5.6 Acknowledgements	86
5.7 References	87

J. / References		

VI	A PROTON CHANNEL OF NOVEL POLYAMIDECONTAINING ADENINE COUPLED WITH N, N'-BIS(2-HYDROXYL-5-ETHYL)CYCLOHEXYLAMINE			
	6.1 Abstract	90		
	6.2 Introduction	90		
	6.3 Experimental	93		
	6.4 Results and Discussion	97		
	6.5 Conclusions	106		
	6.6 Acknowledgements	107		
	6.7 References	107		
VII	CONCLUSIONS AND RECOMMENDATIONS	109		

REFERENCES 111

PAGE

117

LIST OF SCHEMES

SCHEME

PAGE

CHAPTER II

2.1	Chemical structure of Nafion [®]					
2.2	An example of hydrocarbon polymer membranes: (a) Bozkurt					
	et al., 2001, and (b) Bozkurt et al., 2003.	19				
2.3	An example of sulphonated aromatic polymer membranes					
	(Smitha et al., 2005).	20				
2.4	An example of acid-base polymer complex membranes.					
2.5	Instrument and equipment for proton conductivity					
	measurement under anhydrous system	26				

CHAPTER III

3.1	Preparation	of	acrylic	acid	and	4(5)-vinylimidazole	
	copolymer						32

CHAPTER IV

4.1	(a) Proton transfer of M1 and M4 by hydrogen-bonding	
	network and (b) Non-cyclic anhydride formation of M4 at	
	temperatures above 150 °C	53

CHAPTER V

5.1	Chemical structure of (a) Poly (AA-co-4VIm) and (b)	
	SPEEK.	71

CHAPTER VI

6.1	Preparation steps of bis(hydroxybenzyl)amine based proton	
	transfer polyamide	92

xi

LIST OF TABLES

TABLE

PAGE

8

CHAPTER II

2.1	Fuel cells in currently practical applications and development
	CHAPTER III
3 1	Activity acid (AA) (x) and $4(5)$ -vinvlimidazole (4-VIm) (y)

3.1	Acrylic acid (AA) (x) and $4(5)$ -vinylimidazole (4- v im) (y)	
	monomers with the 4(5)-vinylimidazole content of the	
	copolymers	37

CHAPTER V

5.1	Literature survey on using SPEEK blends for fuel cell	
	applications	72
5.2	Summary of physical modification of the membranes based	
	on polymer blending	73
5.3	Elemental analysis of SPEEK	78
5.4	Transition temperature, water uptake, swelling ratio, and IEC	
	of Nafion [®] 117 and SPEEK blended with Poly (AA-co-	
	4VIm)	79
5.5	Mechanical properties of Nafion [®] 117, SPEEK, and	
	SPEEK/Poly(AA-co-4Vim) blend membranes	83

LIST OF FIGURES

FIGURE

 $1 \leq n \leq 1$

CHAPTER I

1.1	Nafion [®] with three different functional polymers, a)	
	hydrophobic PTFE backbone, b) hydrophilic ionic zone, and	
	c) intermediate region.	2
1.2	Imidazole molecule.	2
1.3	Pyrazole molecule.	3
	CHAPTER II	
2.1	Flows and reactions in a simple fuel cell.	5
2.2	Flows and reactions in Proton Exchange Membrane Fuel	
	Cell.	9
2.3	Single fuel cell and fuel cell stack.	10
2.4	Proton conduction in water. The protonic defect follows the	
	center of symmetry of the hydrogen-bond pattern, which	
	diffuses by hydrogen-bond breaking and forming processes;	
	therefore, the mechanism is frequently termed "Grothuss" or	
	structural mechanism.	17
2.5	Proton transfer in bulk water by defect protons.	18
2.6	Nyquist (impedance) plot $(Z_{im}-Z_{re})$ of a hypothetical PEM	
	fuel cell stack and four losses in the system (Zhang et al.,	
	2007).	23
2.7	Complex impedance plots $(Z_{im}-Z_{re})$ of Nafion [®] 120 at	
	different relative humidities, 25% and 45% (Wintersgill et al.,	
	1998).	24
2.8	Proton conductivity at 100% relative humidity as a function	
	of temperature of SPEEK, SPEKK, and Nafion [®] 117 (Vetter	
	et al., 2005).	25

FIGURE

PAGE

CHAPTER III

3.1	FT-IR spectra of the compound obtained from the reaction of	
	acrylic acid and 4(5)-vinylimidazole: (a) M1, (b) M2, (c) M3, and (d) M4.	36
3.2	¹ H-NMR spectra of copolymers of acrylic acid and 4(5)- vinylimidazole: (a) M1, (b) M2, (c) M3, and (d) M4.	38
3.3	DSC thermograms of copolymer powders of acrylic acid and 4(5)-vinylimidazole: (a) M1, (b) M2, (c) M3, and (d) M4, arrow up for Tg and arrow down for Tm.	39
3.4	DSC thermograms of copolymer films of acrylic acid and 4(5)-vinylimidazole: (a) M1, (b) M2, (c) M3, and (d) M4, arrow up for Tg.	40
3.5	TGA thermograms of copolymer films of acrylic acid and 4(5)-vinylimidazole: (a) M1, (b) M2, (c) M3, and (d) M4.	41
3.6	WAXD patterns of the copolymers: (a) M1, (b) M2, (c) M3, and (d) M4.	42
3.7	WAXD with high temperature dependency and DSC first heating cycle of the copolymers: (a) M1, (b) M2, (c) M3, (d) M4.	43
3.8	Proton conductivities in anhydrous system of copolymers: (•) M1, (\Box) M2, (•) M3, (•) M4, and (▲) Nafion [®] 115.	44

CHAPTER IV

4.1	(a) FTIR and (b) Raman spectra of copolymer membranes,	
	M1-M4, at room temperature.	54
4.2	(a) FTIR spectra of M1 and M2 at various temperatures, and	
	(b) Variation of the normalized absorbance at ν_{3413} of	
	copolymers: M1, M2, M3, and M4.	55
4.3	(a) FTIR spectra of M4 at various temperatures (A_L = lower	
	absorbance and A_H = higher absorbance), and (b) Variation	
	of the normalized absorbance at ν_{1805} and ν_{1060} of	57
	copolymers: M3 and M4.	
4.4	Differential radial distribution function (DRDF), $4\pi r^2$ ($\rho(r)$ -	
	ρ_0), of the type of copolymers at various temperatures,	
	<u> </u>	
	123 °C , 147 °C corresponding intensity	
	functions: (a) M1, (b) M2, (c) M3, and (d) M4.	60
4.5	Atomic distances (blank) and peak height (solid) of	
	copolymers under various temperatures: (a) M1, (b) M2, (c)	
	M3 , and (d) M4 .	61
4.6	Overlay plots of the normalized absorbance at (OH)N and	
	COO bands, DSC thermograms at first heating cycle, the	
	representative RDF values, and the proton conductivities of	63
	copolymers: (a) M1, (b) M2, (c) M3, and (d) M4.	

CHAPTER V

5.1	FTIR spectra of SPEEK blended with copolymers of acrylic	
	acid and 4-vinylimidazole: (a) SPEEK, (b) SPEEK/M1, (c)	
	SPEEK/M2, (d) SPEEK/M3, and (e) SPEEK/M4.	78
5.2	TGA thermograms of SPEEK blended with copolymers of	
	acrylic acid and 4-vinylimidazole under nitrogen: (a) SPEEK,	
	(b) SPEEK/M1, (c) SPEEK/M2, (d) SPEEK/M3, and (e)	
	SPEEK/M4	81
5.3	SEM photographs of cross-sectional SPEEK/Poly (AA-co-	
	4VIm) membranes with different blend compositions: (a)	
	Nafion [®] 117, (b) SPEEK, (c) SPEEK/M1, (d) SPEEK/M2,	
	(e) SPEEK/M3, and (f) SPEEK/M4.	82
5.4	Proton conductivity of blended membranes between SPEEK	
	and copolymer of acrylic acid and 4-vinylimidazole.	84
5.5	Arrhenius plot of conductivity vs temperature of ()	
	SPEEK/M1, (▲) SPEEK/M2, (●) SPEEK/M3, and	
	(85

CHAPTER VI

FTIR spectra of: (a) 4-hydroxybenzoic acid, and (b) 1.	98
¹ H-NMR spectrum of 1.	98
FTIR spectra of: (a) 1, (b) 2, and (c) 3.	99
¹ H-NMR spectrum of 2 .	100
¹ H-NMR spectrum of 3 .	101
FTIR spectra of: (a) 3, (b) 4, and (c) 5.	102
¹ H-NMR spectrum of 4 .	103
¹ H-NMR spectrum of 5.	104
FTIR spectra of 6.	105
¹ H-NMR spectrum of 6 .	106
	FTIR spectra of: (a) 4-hydroxybenzoic acid, and (b) 1. ¹ H-NMR spectrum of 1. FTIR spectra of: (a) 1, (b) 2, and (c) 3. ¹ H-NMR spectrum of 2. ¹ H-NMR spectrum of 3. FTIR spectra of: (a) 3, (b) 4, and (c) 5. ¹ H-NMR spectrum of 4. ¹ H-NMR spectrum of 5. FTIR spectra of 6. ¹ H-NMR spectrum of 6.