# Organic-Inorganic Hybrid Composites and Nanocomposites: An Approach to Develop Polymer Electrolyte Membranes for Proton Exchange Membrane Fuel Cells (PEMFCs)



ſ∕¶.

Rapee Gosalawit

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

# 512026

Thesis Title:	Organic-Inorganic Hybrid Composites and Nanocomposites:
	An Approach to Develop Polymer Electrolyte Membranes
	For Proton Exchange Membrane Fuel Cells (PEMFCs)
By:	Rapee Gosalwit
Program:	Polymer Science
Thesis Advisor:	Assoc. Prof. Suwabun Chirachanchai

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

Nantayo Yammet College Director

(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:** 

(Asst. Prof. Hathaikarn Manuspiya)

Nantaya Yamimit - Duwabun Chicachemcher

(Assoc. Prof. Nantaya Yanumet) (Assoc. Prof. Suwabun Chirachanchai)

Hathailian Manuspiya Thougalek Chie

(Dr. Thanyalak Chaisuwan)

Jatuphom

(Assoc. Prof. Jatuphorn Wootthikanokkhan)

#### ABSTRACT

4682007063: Polymer Science Program
Rapee Gosalawit: Organic-Inorganic Hybrid Composites and
Nanocomposites: An Approach to Develop Polymer Electrolyte
Membranes for Proton Exchange Membrane Fuel Cells (PEMFCs)
Thesis Advisor: Assoc. Prof. Suwabun Chirachanchai 122 pp.

Keywords: Nafion/ Silica/ Composite/ Nanocomposite/ Proton exchange membrane fuel cell/ Krytox/ Proton conductivity/ High operating temperature/ Montmorillonite/ Sulfonated SPEEK-WC/ PEEK/ SPEEK/ Direct methanol fuel cell/ methanol crossover

Two approaches of organic-inorganic hybrid composite membranes, i.e., (i) inorganic fillers functionalized with Krytox/Nafion<sup>®</sup> composite membranes; and (ii) clay silicate layers functionalized with sulfonic acid groups/ SPEEK (sulfonated polyether ether ketone) composite membranes are proposed for polymer electrolyte membrane fuel cell (PEMFC) applications. For the Nafion®-based composite membranes, a Nafion<sup>®</sup>-like-polymer chains, i.e., Krytox 157 FSL (carboxylic acid terminated perfluoropolyether), immobilized onto the surface of inorganic fillers, i.e., silica particles and montmorillonite, via silane coupling agent are designed for modifying filler surface to be miscible with Nafion<sup>®</sup>. The composite membranes prepared by solution casting process showing the proton conductivity maintained in the wide range of temperature up to 130 °C and the homogeneous membrane as observed by SEM proves us successful "like dissolves like" between Nafion® polymer chains and Krytox-modified fillers. In the case of the SPEEK-based composite membrane, montmorillonite treated with aminosilane coupling agent followed by reacting with 4-sulfophthalic acid is proposed as an approach to improve methanol crossover reduction and proton conductivity to be a potential material for direct methanol fuel cells (DMFCs).

# บทคัดย่อ

ระพี โกศัลวิตร : สารผสมอินทรีย์-อนินทรีย์แบบคอมโพสิท และนาโนคอมโพสิท: แนวทางหนึ่งสำหรับการพัฒนาแมมเบรนพอลิเมอร์อิเล็กโทรไลท์ สำหรับเซลล์เชื้อเพลิงชนิดแมม เบรนแลกเปลี่ยนไอออน (Organic-Inorganic Hybrid Composites and Nanocomposites: An Approach to Develop Polymer Electrolyte Membrane for Proton Exchange Fuel Cells (PEMFCs)) อ.ที่ปรึกษา : รองศาสตราจารย์ คร. สุวบุญ จิรชาญชัย 122 หน้า

วิทยานิพนส์ฉบับนี้เสนอ 2 วิธีการในการเตรียมเมมเบรนคอม โพสิทผสมระหว่าง สารอินทรีย์ และสารอนินทรีย์สำหรับเซลล์เชื้อเพลิงชนิดแลกเปลี่ยนไอออน ซึ่งประกอบด้วย (1) เมมเบรนคอม โพสิทระหว่างสารอนินทรีย์ที่ถูกปรับปรุงโครงสร้างด้วยใครทอกซ์ และนาฟีออน และ (2) เมมเบรนคอมโพสิทระหว่างแร่ดินขาวที่ปรับปรุงโครงสร้างด้วยหมู่ซัลโฟนิก และซัลโฟ เนตพอลิอีเทอร์ อีเทอร์ คีโตน ในกรณีที่ 1 ใครทอกซ์ 157 เอฟเอสแอล (สารประกอบกรุคคาร์บอก ซิลิกที่ปลายสายโซ่ของเพอร์ฟลูโอโรพอลิอีเทอร์) ซึ่งเป็นสารที่มีโครงสร้างคล้ายนาฟิออน ถูกติด ้ลงบนพื้นผิวของสารอนินทรีย์ได้แก่ ซิลิกา และ มอนท์มอริลโรไนท์ โดยใช้สารผนวกไซเลนใน การพัฒนาพื้นผิวของสารอนินทรีย์ เพื่อความเข้ากันได้กับนาฟีออน แผ่นฟิล์มคอมโพสิทเตรียมได้ จากการขึ้นรูปของสารละลาย แสคงค่าการนำโปรตอนที่คงที่จนกระทั่งอุณหภูมิสูงถึง 130 °C ความเป็นเนื้อเดียวกันซึ่งแสดงให้เห็นความเข้ากันได้ระหว่างนาฟิออน และสารอนินทรีย์ที่ถูก ปรับปรุงโครงสร้างด้วยไครทอกซ์ ของแผ่นฟิล์มถูกยืนยันด้วยภาพถ่ายจากกล้องจุลทรรศน์ อิเล็กตรอนแบบส่องกราด ในกรณีของเมมเบรนคอมโพสิทของ และซัลโฟเนตพอลิอีเทอร์ อีเทอร์ ้คีโตน และมอนท์มอริลโรไนท์ที่ถูกปรับปรุงโครงสร้างโดยใช้สารผนวกอะมิโนไซเลน ตามด้วย การทำปฏิกิริยากับกรด 4-ซัลโฟพทาลิกนั้น ค่าการซึมผ่านของเมทานอลลดลง และค่าการนำ ้โปรตอนเพิ่มขึ้นซึ่ง แสคงให้เห็นถึงความเป็นไปได้ที่จะใช้เมมเบรนนี้ในเซลล์เชื้อเพลิงชนิดเมทา นอล

#### ACKNOWLEDGEMENTS

The present dissertation would not have been accomplished without the author's Thai supervisor, Associate Professor Suwabun Chirachanchai, who not only originated this work, but also provided her with intensive suggestions, invaluable guidance, constructive criticisms, constant encouragement, inspiration, vital assistance throughout this research especially the helps to get opportunities for conduct some part of research in Italy and in Germany. She also would like to acknowledge the Institute for the Promotion of Teaching Science and Technology (IPST) for the financial support from her undergraduate level to Ph.D. level.

The author would like to express her thanks to her co-advisors, Professor Enrico Traversa (Department of Chemical Science and Technology, University of Roma "Tor Vergata", Rome, Italy), Dr. Angelo Basile (The institute for Membrane Technology, ITM-CNR, University of Calabria, Italy) and Professor Sunzana P. Nunes (Institute of Polymer Research, GKSS Research Center, Germany) for the recommendations, strong supports, and concerns during her stay in Italy and Germany. Deep gratitude is also given to Dr. A. Figoli and Dr. J. C. Jansen for their fruitful discussion, with advice for methanol and gas permeability of the membrane (ITM-CNR, Italy), respectively. The gratitude is also to Dr. I. Buder, Dr. M. L. Ponce and Dr. J. Roeder (GKSS Research Center, Germany) for Proton conductivity measurements and single cell performance tests. She thanks to all members in ITM-CNR and GKSS Research Center for their helps, the good time, and the good memories throughout her stay in Italy and Germany.

The author is grateful for the scholarship and funding of this thesis work provided by the Petroleum and Petrochemical College; and the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand. 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. She never forgets the friendship from college staff members, and all her friends at the Petroleum and Petrochemical College. Last but not least, she wishes to express her gratitude to her family for their love, understanding, encouragement, limitless sacrifice, and for being a constant source of her inspiration throughout her study.

# **TABLE OF CONTENTS**

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

#### CHAPTER

Ι	INTRODUCTION	1
II	LITERATURE REVIEW	5
	2.1 Polymer electrolyte membrane fuel cell (PEMFC)	
	and its compartments	5
	2.2 Polymer electrolyte membrane (PEM)	6
× •	2.3 Evaluation of PEM	9
	2.4 Commercialized pefluorosulfonic acid (PFSA) membranes	18
	2.5 Alternative membranes for PEMFC systems	22
	2.6 Motivation of the Present Research	26
III	<b>KRYTOX-SILICA-NAFION<sup>®</sup> COMPOSITE MEMBRANE:</b>	

A HYBRID SYSTEM FOR MAINTAINING PROTO	N
CONDUCTIVITY IN A WIDE RANGE OF OPERA	TING
TEMPERATURE	29
3.1 Abstract	29
3.2 Introduction	29
3.3 Experimental	32

СНАР	TER	PAGE
	3.4 Results and discussion	35
	3.5 Conclusion	42
	3.6 Acknowledgements	43
	3.7 References	43
IV	THERMO AND ELECTROCHEMICAL	
	CHARACTERIZATION OF SULFONATED PEEK-WC	
	<b>MEMBRANES AND KRYTOX-SI-NAFION<sup>®</sup></b>	
	COMPOSITE MEMBRANES	45
	4.1 Abstract	45
	4.2 Introduction	45
	4.3 Experimental	48
	4.4 Results and discussion	52
	4.5 Conclusion	61
	4.6 Acknowledgements	62
	4.7 References	62
V	<b>KRYTOX-MONTMORILLONITE-NAFION<sup>®</sup></b>	
	NANOCOMPOSITE MEMBRANE FOR EFFECTIVE	
	<b>METHANOL CROSSOVER REDUCTION IN DMFCs</b>	65
	5.1 Abstract	65
	5.2 Introduction	65
	5.3 Experimental	67
	5.4 Results and discussion	73
	5.5 Conclusion	83
	5.6 Acknowledgements	84
	5.7 References	84

VI	SULFONATED MONTMORILLONITE/SULFONATED		
	POLY(ETHER ETEHR KETONE) (SMMT/SPEEK)		
	NANOCOMPOSITE MEMBRANE FOR DIRECT		
	<b>METHANOL FUEL CELLS (DMFCs)</b>	87	
	6.1 Abstract	87	
	6.2 Introduction	87	
	6.3 Experimental	89	
	6.4 Results and discussion	96	
	6.5 Conclusion	108	
	6.6 Acknowledgements	109	
	6.7 References	109	
VII	CONCLUSIONS AND RECOMMENDATIONS	112	
	REFERENCES	114	
	CURRICULUM VITAE	120	

#### LIST OF SCHEMES

#### SCHEME

# PAGE

# **CHAPTER II**

2.1	Fuel cell and stack	6
2.2	Structure of Nafion <sup>®</sup>	7
2.3	Schematic draw for gas permeability measurement	10
2.4	Duffusion system	11
2.5	Pervaporation system	12
2.6	Instruments and equipments for proton conductivity	
	measurement with anhydrous (a) and humidity control systems (b)	14
2.7	Membrane electrode assembly (MEA) preparation, single	
	cell and instruments for fuel cell performance evaluation	16
2.8	Schematic view in PFSA membranes based on (a) cluster	
	network model; (b) random network model	19
2.9	Structures of some polyarylene used for PEM: (a) sulfonated	
	polysulfone and (b) sulfonated polyether ether ketone	24
2.10	Structure of Krytox 157 FSL	27
2.11	Tortuous pathway of inorganic fillers in the polymer matrix	27

# **CHAPTER III**

3.1	Krytox-Silica-Nafion <sup>®</sup> hybrid structure	31
3.2	Krytox-Silica-Nafion <sup>®</sup> hybrid material preparation	33

#### **CHAPTER V**

5.1	Krytox-Montmorillonite-Nafion <sup>®</sup> hybrid material preparation	68
5.2	Methanol permeability measurement equipment	72

#### **CHAPTER VI**

6.1	SMMT/SPEEK nanocomposite preparation	91
-----	--------------------------------------	----

#### **LIST OF TABLES**

TABLE		PAGE	
	CHAPTER I		
1.1	Types of fuel cell	2	
	CHAPTER III		
3.1	Water uptake at 60°C, degradation temperature (T <sub>d</sub> ),		
	and enthalpy of water evaporation ( $\Delta H_{water}$ )	38	
3.2	Proton conductivity of 4b	41	
	CHAPTER IV		
4.1	Water uptake and ion exchange capacity (IEC) of		
	the membranes	54	
4.2	Gas permeability of all membranes	57	
	CHAPTER V		
5.1	Water uptake and degradation temperatures $(T_d)$		
	of the membranes	77	
5.2	Activation energy ( $E_a$ ) and selectivity ( $\beta$ ) of the membranes	83	
	CHAPTER VI		
6.1	Degree of sulfonation (DS) and solubility behavior in		
	1.5 M methanol aqueous solution at 50 °C of SPEEK	97	
6.2	Swelling ratio at room temperature (25 °C), degradation		
	$(T_{d})$ and glass transition $(T_{g})$ temperatures and strength		
	at break $(\sigma_{\gamma})$ of the SPEEK membrane containing the		
	different SMMT loading contents	103	
6.3	Linear expansion rate in 1.5 M methanol aqueous		
	solution at 65 °C of the acid-treated membranes	106	

#### **LIST OF FIGURES**

#### **FIGURE**

## **CHAPTER I**

1.1	Schematic view of PEM fuel cell	3

## **CHAPTER II**

2.1	Effect of different proton conducting membranes on	
	PEMFC performance: H <sub>2</sub> /O <sub>2</sub> reactants (E-TEK electrodes,	
	20 % Pt/C, 0.4 mg Pt cm <sup>2</sup> ); 95 °C; P=5 atm	8
2.2	Impedance plot $(Z_{im}-Z_{re})$ of hypothetical PEM fuel cell	
	stack and four losses in the system	13
2.3	Proton conductivity versus temperature of poly(diphenylether-	
	1,3,4-oxadiazole) with different IEC	15
2.4	Polarization curve of hydrogen based fuel cell system	17

#### **CHAPTER III**

3.1	FTIR spectra of 1 (a), 2 (b), 3 (c), and 4 (d)	36
3.2	SEM micrographs of: membrane surface (a), silica	
	mapping mode (b), and cross-section (c) of 4c	39
3.3	Complex impedance of $4b$ at $40^{\circ}C$ ( $\bullet$ ), $60^{\circ}C$ ( $\circ$ ),	
	80°C (△), 100°C (▲), and 130°C (■)	40
3.4	Proton conductivity of 5 ( $\bullet$ ), 4a (O), 4b ( $\blacktriangle$ ), and	
	<b>4c</b> ( $\Delta$ ) at 20-140°C with no moisture conditioning	42

#### **CHAPTER IV**

4.1	(a) PEEK-WC and (b) Kritox-Silica Nafion <sup>®</sup>	47
4.2	Pervaporation plant	52

#### FIGURE

4.3	FTIR spectra (A) of PWC (), SPWC24 ()	
	and SPWC48 (); (B) of hydrolyzed (3-aminopropyl)	
	triethoxysilane (a), SiAS (b), Krytox 157 FSL (c)	
	and KSi (d)	53
4.4	Proton conductivity of the recast Nafion ( ),	
	KSiN1.5 (▲), KSiN2.5 (●), KSiN (♠), SPWC24 (□)	
	and SPWC48 ( $\Delta$ )	55
4.5	DSC diagram (A) of SPWC48 at first (a) and second	
	heating run (b); (B) of SPWC24; (C) of Nafion <sup></sup>	
	KSiN1.5 (b), KSiN2.5 (c) and KSiN5 (d)	59
4.6	Methanol flux at 25 °C of SPWC48 (×), SPWC24 (□),	
	Nafion <sup>®</sup> 117 ( <b>■</b> ), KSiN2.5 (●) and KSiN5 (0); at 80 °C	
	of KSiN2.5 ( $\blacktriangle$ ) and KSiN5 ( $\triangle$ )	60
4.7	SEM micrographs of KSiN5 composite membrane,	
	surface (a) and cross section (b)	61

#### **CHAPTER V**

	CHAI IER V	
5.1	FTIR spectra of 1 (a), 2 (b), Krytox 157 FSL (c) and 3 (d)	73
5.2	X-ray diffraction patterns of MMT (a), 2 (b), the recast	
	Nafion <sup>®</sup> (c), $4a$ (d) and $4b$ (e)	75
5.3	Cross-section of 4a observed by SEM	75
5.4	AFM topographic images of the surface of $4a$ (a) and $4b$ (b)	76
5.5	Methanol permeability of Nafion membrane: (a)	
	methanol concentration in compartment B, (C <sub>B</sub> )	
	vs. permeation time at 60 °C of the recast	
	Nafion <sup>®</sup> ( $\bullet$ ), <b>4a</b> ( $\blacktriangle$ ) and <b>4b</b> ( $\blacksquare$ ); (b) methanol	
	permeability at 25 °C ( $\diamond$ ) and at 60 °C ( $\blacklozenge$ )	79
5.6	Proton conductivity of the reast Nafion <sup>®</sup> ( $\bullet$ ), 4a ( $\blacktriangle$ )	
	and $4b (\blacksquare)$	81

PAGE

. .

PAGE

108

5.7	Arrhenius plot of the recast Nafion <sup>®</sup> ( $\bullet$ ), 4a ( $\blacktriangle$ )	
	and <b>4b</b> (■)	82
	CHAPTER VI	
6.1	FT-IR spectra of PEEK (a) and SPEEK (b)	96
6.2	FT-IR spectra of MMT (a), SiMMT (b), 4-sulfophthalic	
	acid (c) and SMMT (d)	98
6.3	X-ray diffraction patterns of MMT (a), SiMMT	
	(b) and SMMT (c)	99
6.4	SEM cross-sectional images of SPEEK (a) and	
	its composite membranes containing 1 wt. % (b),	
	3 wt. % (c) and 5 wt. % (d) of SMMT	100
6.5	AFM images (phase contrast mode) of the	
	SPEEK composite membranes containing 1 wt. % (a),	
	3 wt. % (b) and 5 wt. % (c) of SMMT	101
6.6	Methanol flux of the SPEEK membranes	
	containing the different SMMT loading content	104
6.7	Proton conductivity of Nafion <sup>®</sup> 117 (), SPEEK (+),	
	and the SPEEK composite membranes containing	
	SMMT (filled symbol) and MMT (blank symbol)	
	for 1 wt. % ( ●), 3 wt. % ( ▲) and 5 wt. % ( ■)	105
6.8	Current density-voltage (filled symbol) and power	
	density curves (blank symbol) of the DMFC single	
	test cell at 60 °C of Nafion <sup>®</sup> 117 (48 h) (), SPEEK	
	(12 h) ( $\blacksquare$ ) and the composite membranes of 1 wt.%	
	(24 h) (♦ ), 3 wt. % (36 h) (▲) and 5 wt. % (48 h) (●)	107
6.9	Membrane selectivity (the ratio of the proton	
	conductivity (60 $^{\circ}$ C) to the methanol permeability)	

# FIGURE

of the membranes