# PROTON DONOR AND ACCEPTOR POLYMER CHAINS UNDER LAYERED-BY-LAYERED STRUCTURE OF POLYMER ELECTROLYTE MEMBRANE FUEL CELL (PEMFC)



Nattawut Rattanaapiromyakit

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma,
And Case Western Reserve University

2012

Thesis Title:

Proton Donor And Acceptor Polymer Chains Under Layered-

by-Layered Structure For Polymer Electrolyte Membrane

Fuel Cell (PEMFC)

By:

Nattawut Rattanaapiromyakit

Program:

Polymer Science

Thesis Advisor:

Prof. Suwabun Chirachanchai

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

(Asst. Prof. Pomthong Malakul)

**Thesis Committee:** 

(Prof. Suwabun Chirachanchai)

(Asst. Prof. Hathaikarn Manuspiya)

Hathailam M.

(Dr. Rapee Gosalawit)

Rapee Gosalawit

#### **ABSTRACT**

5372011063: Polymer Science Program

Nattawut Rattanaapiromyakit: Proton Donor And Acceptor Polymer

Chains Under Layered-by-Layered Structure For Polymer

Electrolyte Membrane Fuel Cell (PEMFC).

Thesis Advisor: Prof. Suwabun Chirachanchai 32 pp.

Keywords: Proton donor-acceptor/Layered-by-Layered structure/Polymer

electrolyte membrane

This research focuses on the development of proton conductive performance of polymer membrane for using at high temperature under anhydrous system. Heterocyclic molecules such as imidazole and benzimidazole, etc. as a proton conductive species demonstrate the high hydrogen bond interaction with varied number of heterocyclic units. Moreover, the acid functional group plays an important role in providing protons, which have an effect on proton conductive performance. To combine the concepts of proton donor-acceptor with uniform molecular arrangement of heterocyclic molecules to enhance proton conductive performance under anhydrous system, the layered-by-layered structure membrane is proposed.

## บทคัดย่อ

ณัฐวุฒ รัตนอภิรมยกิจ : ชื่อหัวข้อวิทยานิพนธ์ การพัฒนาประสิทธิภาพในการนำโปร ตอนของพอลิเมอร์อิเล็กโตร ไลท์เมมเบรนภายใต้ โครงสร้างแบบชั้นต่อชั้นสำหรับเซลล์เชื้อเพลิง แบบพอลิเมอร์อิเล็กโตร ไลท์ (Proton Donor And Acceptor Poylmer Chains under Layered-by-Layered Structure For Polymer Electrolyte Membrane) อ. ที่ปรึกษา : ศาสตราจารย์ คร. สุวบุญ จิรชาญชัย 32 หน้า

งานวิจัยฉบับนี้ได้มุ่งเน้นการพัฒนาประสิทธิภาพในการนำโปรตอนของพอลิเมอร์เมม เบรนสำหรับใช้ในที่อุณภูมิสูงภายใต้สภาวะที่ปราสจากการใช้น้ำ โมเลกุลประเภทเฮเทอโรไซคลิก ตัว อย่างเช่น อิมิดาโซล และ เบนซิมิดาโซล ซึ่งเป็นโมเลกุลจำพวกที่สามารถนำโปรตอนได้ โดย โมเลกุลของเฮเทอโรไซคลิกได้แสดงให้ว่าอันตรกิริยาของพันธะไฮโดรเจนมีความสัมพันธ์กับการ เพิ่มจำนวนของหน่วยเฮเทอโรไซคลิก นอกจากนั้นหมู่กรดยังมีหน้าที่สำคัญในการให้โปรตอนซึ่งมี อิทธิพลต่อประสิทธิภาพในการนำโปรตอน เพื่อที่จะรวมแนวความคิดของโมเลกุลที่สามารถให้และ รับโปรตอนได้ ซึ่งมีการจัดเรียงตัวของโมเลกุลของเฮเทอโรไซคลิกอย่างเป็นระเบียบเพื่อเพิ่ม ประสิทธิภาพในการนำโปรตอนภายใต้ระบบที่ไม่ใช้น้ำ ฉะนั้นเมมเบรนที่มีโครงสร้างแบบชั้นต่อ ชั้นจึงได้ถูกนำเสนอในงานนี้

#### **ACKNOWLEDGEMENTS**

This thesis work is funded by the Petroleum and Petrochemical College; and the Center of Excellence on Petrochemicals, and Materials Technology, Thailand.

The author would like to express his thanks to his advisor, Prof. Suwabun Chirachanchai, who not only originated this work, but also provide him with intensive suggestion, invaluable suggestions, constructive criticism, constant encouragement and vital assistance throughout this research. He would also like to acknowledge Asst. Prof. Hathaikarn Manuspiya for her recommendations, strong support and precious comments.

The author is also thankful to the dissertation committee for their suggestion and comments in the reading of the thesis book. He appreciates all Professors who have tender ed invaluable knowledge to him at the Petroleum and Petrochemical College, Chulalongkorn University.

He would like to thank his seniors, Dr. Rapee Gosalawit, for her help, invaluable guidance and suggestions throughout this research. He would like to thank the college staffs members, and all his friend at the Petroleum and Petrochemical College.

Finally, he wishes to express his thank to his family for their love, understanding encouragement, and for being a constant source of his inspiration throughout his study.

## TABLE OF CONTENTS

			PAGE		
	Title F	Page	i		
	Abstract (in English)				
	Abstract (in Thai)				
	Acknowledgements				
	Table of Contents				
	List of Schemes				
	List of	Figures	X		
CHA	PTER				
	I	INTRODUCTION	1		
	II	THEORETICAL BACKGROUND AND LITERATURE			
		REVIEW	3		
		2.1 Basic Principle of Polymer Electrolyte Membrane (PEM)	3		
		2.2 Proton Conductive Polymer	4		
		2.2.1 Nafion <sup>®</sup> Membrane	4		
		2.2.2 Sulfonated Poly (Ether Ether Ketone), SPEEK	5		
		2.3 Heterocyclic Molecules	5		
		2.4 Proton Transfer Mechanism	6		
		2.5 Layered-by-Layered Assembly Technique	7		
		2.6 Motivation of Research	8		
	III	EXPERIMENTAL	9		
		3.1 Materials	9		
		3.2 Instruments and Equipment	9		
		3.3 Experimental	10		
		3.3.1 Sulfonated of Poly (Ether Ether Ketone) (SPEEK)	10		
		3.3.2 SPEEK Membrane	10		

CHAPTER		PAGE
	3.3.3 Preparation of Multibenzimidazole Branched	
	Polyethyleneimine (MPEI)	10
	3.3.4 Preparation of Acid Polymer Solution	11
	3.3.5 Preparation of Basic Polymer Solution	11
	3.3.6 Layered-by-Layered Membrane Fabrication	11
IV	PROTON DONOR AND ACCEPTOR POLYMER	
	CHAINS UNDER LAYERED-BY-LAYERED	
	STRUCTURE OF POLYMER ELECTROLYTE	
	MEMBRANE	12
	4.1 Abstract	12
	4.2 Introduction	13
	4.3 Materials and Methods	14
	4.3.1 Materials	14
	4.3.2 Polymer Syntheses and Membrane Preparation	14
	4.3.3 Multibenzimidazole Branched Polyethyleneimine	14
	4.3.4 Preparation of SPEEK Membrane	15
	4.3.5 Preparation of Basic Polymer Solution	15
	4.3.6 Preparation of Acid Polymer Solution	15
	4.3.7 Layered-by-Layered Membrane Fabrication	15
	4.4 Characterizations	16
	4.4.1 FTIR	16
	4.4.2 <sup>1</sup> H-NMR	16
	4.4.3 Layered-by-Layered Obsrevation	16
	4.4.3.1 Thickness Gauge and Balance	16

CHAPTER	PAGE
4.4.3.2 Contact Angle	16
4.4.3.3 SEM	16
4.4.4 Conductivity Measurement	17
4.5 Results and Discussion	17
4.6 Conclusions	27
4.7 Acknowledgement	27
4.8 References	28
V CONCLUSIONS AND RECOMMENDATIONS	30
CURRICULUM VITAE	31

### LIST OF SCHEMES

SCHEME		PAGE
	CHAPTER II	
2.1		3
2.2		5
	CHAPTER III	
3.1		10
3.2		11
	CHAPTER IV	
4.1		15

## LIST OF FIGURES

FIGURE		PAGE	
	CHAPTER II		
2.1	Chemical structure of perfluoro sulfonic acid polymers		
	(Nafion <sup>®</sup> ).	4	
2.2	Chemical structure of sulfonated poly (ether ether ketone),		
	SPEEK.	5	
	CHAPTED IV		
4.1	CHAPTER IV	1.0	
4.1	FTIR spectrum of multibenzimidazole branched	18	
4.0	polyethylenimine (MPEI).	1.0	
4.2	<sup>1</sup> H-NMR spectrum of MPEI.	18	
4.3	FTIR spectrum of sulfonated poly (ether ether ketone)		
	(SPEEK).	19	
4.4	<sup>1</sup> H-NMR spectrum of SPEEK.	20	
4.5	Thickness of LBL SPEEK membrane with varied number of		
	layers.	21	
4.6	Weight of LBL SPEEK membrane with varied number of		
	layers.	22	
4.7	Plot of contact angle between MPEI layers and PAA layers.	23	
4.8	Cross-section of a) no layer coating, b) 1 bilayer, c) 2		
	bilayers, <b>d)</b> 3 bilayers and <b>e)</b> 4 bilayers.	24	
4.9	FTIR spectrum of LBL formative steps.	25	
4.10	Proton conductivity of LBL SPEEK membrane measured in		
	the temperature range from 30 °C to 170 °C at (■) 1 bilayer,		
	(•) 2 bilayers, (▲) 3 bilayers, and (▼) 4 bilayers		
	respectively.	26	