MODIFIED POLYETHER SULFONE INCORPORATED WITH ZEOLITIC IMIDAZOLATE FRAMEWORK-8 POROUS ELECTROLYTE MEMBRANE FOR DIRECT METHANOL FUEL CELL

HAZLINA BINTI JUNOH

UNIVERSITI TEKNOLOGI MALAYSIA

MODIFIED POLYETHER SULFONE INCORPORATED WITH ZEOLITIC IMIDAZOLATE FRAMEWORK-8 POROUS ELECTROLYTE MEMBRANE FOR DIRECT METHANOL FUEL CELL

HAZLINA BINTI JUNOH

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy

School of Chemical and Energy Engineering Faculty of Engineering Universiti Teknologi Malaysia

SEPTEMBER 2021

ACKNOWLEDGEMENT

In preparing this thesis, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my main thesis supervisor, Associate Professor Ts. Dr. Juhana binti Jaafar, for encouragement, guidance, critics and friendship. I am also very thankful to my co-supervisor Dr. Nik Abdul Hadi bin Sapiaa@ Md Nordin for his guidance, advice and motivation. Without their continued support and interest, this thesis would not have been the same as presented here.

I am also indebted to Universiti Teknologi Malaysia (UTM) for funding my Ph.D study as well as to the Advance Membrane Technology Research Centre (AMTEC) for supporting my research activities. Special thanks also go to Mr. Sohaimi, Mr. Ng Be Cheer, Mr. Arif, Mr. Hilmi, Mr. Fahrul and Mr. Nizam for their support in laboratorial activities.

My fellow postgraduate student should also be recognised for their support. My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful for being part in this study.

ABSTRACT

The evolution of research and development of the electrolyte membrane for direct methanol fuel cell (DMFC) has increased since the past few years, particularly on the fabrication of different membrane configurations. This happens due to the promising characteristics of DMFC, especially for portable applications in delivering a high-power supply and easy to handle system. However, the limitation of these types of membranes is their dense structure which may limit the transportation of protons. Nevertheless, the open porous structure is yet to be studied as a new electrolyte membrane due to its well-known drawback of the pores on methanol barrier properties. The main aim of this study was to investigate the potential application of a novel modified porous polyether sulfone (PES) incorporated with zeolitic imidazolate framework-8 (ZIF-8) in direct methanol fuel cell (DMFC). The porous PES membranes prepared by dissolving in different types of solvents (DMAc and NMP) were obtained via non-solvent induced phase separation (NIPS) technique at different solvent evaporation time (SET) from 0 to 5 minutes. The prepared membranes were characterized based on the effect of morphological studies on their physicochemical properties. Later, PES dope solutions containing different loading of cSMMs (0 to 5 wt. %) were cast on a glass plate at optimum SET and solvent type in order to prepare the modified porous PES (PES-cSMMs) membranes. ZIF-8 crystals with the 2methylimidazole (HmIm)/ Zn^{2+} ratio of 6 were grown inside the PES-cSMMs pores by in-situ growth technique via different methods, which are immersion, dead-end filtration and contra-diffusion in order to get fine growth of ZIF-8 crystals inside the pores of the PES-cSMMs flat sheet membranes. The prepared porous PEScSMMs/ZIF-8 composite membranes were evaluated with respect to their proton conductivity, methanol permeability, morphology, mechanical and thermal properties, and DMFC performance in a single DMFC stack. From the scanning electron microscopy, the morphologies of porous PES membrane for both surface and crosssectional images showed changes with respect to the SET. Besides, the pore size of PES membranes increased dramatically as the SET increased. The porous PEScSMMs membranes were fabricated at SET of 3 minutes as a result of the optimum selectivity of PES-DMAc3MIN membranes. The PES-3 wt. % cSMMs exhibited higher selectivity as compared to Nafion® 117 owing to proton conductivity and methanol permeability values of 14.14×10^{-3} Scm⁻¹ and 0.54×10^{-7} cm²s⁻¹, respectively. However, higher loading of cSMMs deteriorated the proton transportations. The incorporation of ZIF-8 via in-situ growth inside the pores of porous PES-cSMMs with a complete rhombic dodecahedron was successfully obtained via immersion technique and was found to significantly improve the proton conductivity $(19.5 \times 10^{-3} \text{ Scm}^{-1})$ and methanol barrier properties $(0.04 \times 10^{-7} \text{ cm}^2 \text{s}^{-1})$ as well as the exhibited power density of 25.2 mWcm⁻². Hence, the promising results obtained in this study have demonstrated the potential of the porous electrolyte membrane, like the porous PEScSMMs/ZIF-8 membrane, which gives a warrant for further investigation in fuel cell applications, specifically DMFC.

ABSTRAK

Evolusi penyelidikan dan pembangunan membran elektrolit untuk sel bahan api metanol langsung (DMFC) telah meningkat sejak beberapa tahun kebelakangan ini terutama pada penghasilan konfigurasi membran yang berbeza jenis. Ini berlaku kerana ciri-ciri DMFC yang menjanjikan suatu sistem mudah alih yang dapat menyediakan bekalan kuasa tinggi dan mudah dikendalikan. Walau bagaimanapun, had membran jenis ini adalah struktur padatnya yang mungkin membatasi pengangkutan proton. Walaupun begitu, struktur berliang terbuka masih belum dapat dikaji sebagai membran elektrolit baharu kerana kelemahannya yang mempunyai liang pada penghalang metanolnya. Tujuan utama kajian ini adalah untuk menyiasat potensi aplikasi baharu polietersulfona (PES) berpori yang diubahsuai yang digabungkan dengan kerangka imidazolat zeolitik-8 (ZIF-8) dalam sel bahan api metanol langsung (DMFC). Membran PES berliang yang disediakan dengan melarutkan dalam pelbagai jenis pelarut (DMAc dan NMP) diperoleh melalui teknik pemisahan fasa bukan pelarut pada masa penyejatan pelarut (SET) yang berbeza dari 0 hingga 5 minit. Membran yang disediakan dicirikan berdasarkan pengaruh kajian morfologi terhadap sifat fizikokimia. Kemudian, larutan dop PES yang mengandungi pemuatan cSMMs yang berbeza (0 hingga 5 wt.%) dituangkan pada piring kaca pada SET dan pelarut optimum untuk menyiapkan membran PES berliang yang diubah suai (PES-cSMMs). Kristal ZIF-8 dengan nisbah 2-metilimidazol (HmIm)/Zn²⁺ dari 6 ditumbuhkan di dalam liang PES-cSMMs dengan teknik pertumbuhan in-situ melalui kaedah yang berbeza iaitu rendaman, penurasan hujung mati dan resapan kontra untuk mendapatkan pertumbuhan halus kristal ZIF-8 di dalam liang membran lembaran rata PES-cSMMs. Membran komposit PES-cSMMs/ZIF-8 yang berliang telah dinilai melalui kekonduksian proton, kebolehtelapan metanol, morfologi, sifat mekanik dan haba, dan prestasi DMFC dalam satu susunan DMFC. Dari mikroskop elektron imbasan, morfologi membran PES berliang untuk kedua-dua imej permukaan dan keratan rentas menunjukkan perubahan berkenaan dengan SET. Selain itu, saiz pori membran PES meningkat secara mendadak ketika SET meningkat. Membran PES-cSMMs berliang yang dibuat pada SET 3 minit terhasil daripada kememilihan optimum membran PES-DMAc_{3MIN}. PES-3 wt.% cSMMs menunjukkan kememilihan yang lebih tinggi berbanding Nafion® 117 kerana kekonduksian proton dan nilai kebolehtelapan metanol masing-masing pada 14.14×10^{-3} Scm⁻¹ dan 0.54×10^{-7} cm²s⁻¹. Walau bagaimanapun, pemuatan cSMMs yang lebih tinggi mengurangkan pengangkutan proton. Penggabungan ZIF-8 melalui pertumbuhan in-situ di dalam liang PES-cSMMs berliang dengan dodekahedron rombus yang lengkap berjaya diperoleh melalui teknik rendaman dan didapati dapat meningkatkan kekonduksian proton (19.5×10⁻³ Scm⁻¹) dan sifat penghalang metanol $(0.04 \times 10^{-7} \text{ cm}^2 \text{s}^{-1})$ dengan ketara serta menunjukkan ketumpatan daya 25.2 mWcm⁻². Oleh itu, hasil yang menjanjikan yang diperoleh dalam kajian ini telah menunjukkan potensi membran elektrolit berpori, seperti membran PES-cSMMs/ZIF-8 berpori yang menjamin penyelidikan lebih lanjut dalam aplikasi sel bahan api, khususnya DMFC.

TABLE OF CONTENTS

TITLE

DI	ECLARATION	iii
DI	EDICATION	iv
A	CKNOWLEDGEMENT	v
AI	SSTRACT	vi
AI	SSTRAK	vii
TA	ABLE OF CONTENTS	viii
LI	ST OF TABLES	xiii
LI	ST OF FIGURES	xvi
LI	ST OF ABBREVIATIONS	XX
LI	ST OF SYMBOLS	xxi
LI	ST OF APPENDICES	xxii
CHAPTER 1	INTRODUCTION	1
1.1	Background of Study	1
1.2	2 Problem Statement	4
1.3	B Objective of the Study	7
1.4	Scope and Limitation of Study	8
1.5	5 Significant of the Study	10

CHAPTER 2	LITERATURE REVIEW	11
2.1	Fuel Cells	11
2.2	Direct Methanol Fuel Cell (DMFC)	15
	2.2.1 System Operation of DMFC	15
	2.2.2 Basic Structure and Working Principle of DMFCs	16
2.3	Limitations in DMFC System	18
	2.3.1 Methanol Crossover and Proton Conductivity	20
2.4	Electrolyte Membrane Technology	24

	2.5	Morphology of PEMs	27
	2.6	Porous Membrane Fabrications: PES	30
		2.6.1 Poly (Ether Sulfone) (PES)	36
	2.7	Surface Modifying Macromolecules (SMMs)	38
	2.8	Composite Polymer Electrolyte Membranes	43
	2.9	Metal-Organic Frameworks (MOFs) as Proton Conductor	45
	2.10	Proton Conducting Medium in MOFs: ZIF-8 and Methanol Barrier	51
	2.11	Synthesis Methods for ZIF-8 Crystals	56
	2.12	In-situ Techniques for ZIF-8 Growth within the Pores	60
		2.12.1 Counter-Diffusion/Contra-Diffusion Techniques	60
		2.12.2 Immersion Techniques	65
		2.12.3 Dead-End Filtration Techniques	67
	2.13	Potential to Fabricate Porous Polymer/MOF Electrolyte Membrane	68
	2 14	Summory	70
	2.14	Summary	70
СНАРТН	2.14 ER 3	RESEARCH METHODOLOGY	70
СНАРТН	2.14 E R 3 3.1	RESEARCH METHODOLOGY Introduction	70 71 71
СНАРТЕ	2.14 ER 3 3.1 3.2	RESEARCH METHODOLOGY Introduction Materials and Properties	70 71 71 74
СНАРТЕ	2.14 ER 3 3.1 3.2	RESEARCH METHODOLOGY Introduction Materials and Properties 3.2.1 Poly Ether Sulfone (PES)	70 71 71 74 74
CHAPTE	2.14 ER 3 3.1 3.2	RESEARCH METHODOLOGY Introduction Materials and Properties 3.2.1 Poly Ether Sulfone (PES) 3.2.2 Charged Surface Modifying Macromolecules (cSMMs)	70 71 71 74 74 74
CHAPTE	2.14 ER 3 3.1 3.2	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1 Poly Ether Sulfone (PES)3.2.2 Charged Surface Modifying Macromolecules (cSMMs)3.2.3 N-methyl-2-pyrrolidone (NMP)	70 71 74 74 74 74 75
CHAPTE	2.14 ER 3 3.1 3.2	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1 Poly Ether Sulfone (PES)3.2.2 Charged Surface Modifying Macromolecules (cSMMs)3.2.3 N-methyl-2-pyrrolidone (NMP)3.2.4 N, N-Dimethylacetamide (DMAc)	70 71 74 74 74 74 75 76
CHAPTE	2.14 ER 3 3.1 3.2	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1 Poly Ether Sulfone (PES)3.2.2 Charged Surface Modifying Macromolecules (cSMMs)3.2.3 N-methyl-2-pyrrolidone (NMP)3.2.4 N, N-Dimethylacetamide (DMAc)3.2.5 Zinc Nitrate Hexahydrate Zn (NO ₃) ₂ .6H ₂ O	70 71 74 74 74 74 75 76 77
CHAPTE	2.14 ER 3 3.1 3.2	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1Poly Ether Sulfone (PES)3.2.2Charged Surface Modifying Macromolecules (cSMMs)3.2.3N-methyl-2-pyrrolidone (NMP)3.2.4N, N-Dimethylacetamide (DMAc)3.2.5Zinc Nitrate Hexahydrate Zn (NO ₃) ₂ .6H ₂ O3.2.62-Methylimidazole (HmIm, 99% purity)	70 71 74 74 74 74 75 76 77 77
CHAPTE	2.14 ER 3 3.1 3.2	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1Poly Ether Sulfone (PES)3.2.2Charged Surface Modifying Macromolecules (cSMMs)3.2.3N-methyl-2-pyrrolidone (NMP)3.2.4N, N-Dimethylacetamide (DMAc)3.2.5Zinc Nitrate Hexahydrate Zn (NO ₃) ₂ .6H ₂ O3.2.62-Methylimidazole (HmIm, 99% purity)3.2.7Triethylamine (TEA)	70 71 74 74 74 74 75 76 77 77 78
CHAPTE	2.14 ER 3 3.1 3.2 3.3	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1 Poly Ether Sulfone (PES)3.2.2 Charged Surface Modifying Macromolecules (cSMMs)3.2.3 N-methyl-2-pyrrolidone (NMP)3.2.4 N, N-Dimethylacetamide (DMAc)3.2.5 Zinc Nitrate Hexahydrate Zn (NO ₃) ₂ .6H ₂ O3.2.6 2-Methylimidazole (HmIm, 99% purity)3.2.7 Triethylamine (TEA)Membrane Preparation	70 71 74 74 74 74 75 76 77 77 77 78 79
CHAPTE	2.14 ER 3 3.1 3.2 3.3	SummaryRESEARCH METHODOLOGYIntroductionMaterials and Properties3.2.1 Poly Ether Sulfone (PES)3.2.2 Charged Surface Modifying Macromolecules (cSMMs)3.2.3 N-methyl-2-pyrrolidone (NMP)3.2.4 N, N-Dimethylacetamide (DMAc)3.2.5 Zinc Nitrate Hexahydrate Zn (NO ₃) ₂ .6H ₂ O3.2.6 2-Methylimidazole (HmIm, 99% purity)3.2.7 Triethylamine (TEA)Membrane Preparation3.3.1 Preparation of PES Dope Solution	70 71 74 74 74 75 76 77 77 78 79 79
CHAPTE	2.14 ER 3 3.1 3.2 3.3	Summary RESEARCH METHODOLOGY Introduction Materials and Properties 3.2.1 Poly Ether Sulfone (PES) 3.2.2 Charged Surface Modifying Macromolecules (cSMMs) 3.2.3 N-methyl-2-pyrrolidone (NMP) 3.2.4 N, N-Dimethylacetamide (DMAc) 3.2.5 Zinc Nitrate Hexahydrate Zn (NO ₃) ₂ .6H ₂ O 3.2.6 2-Methylimidazole (HmIm, 99% purity) 3.2.7 Triethylamine (TEA) Membrane Preparation 3.3.1 Preparation of PES Dope Solution 3.3.1.1 Porous PES Membrane Fabrication	70 71 74 74 74 74 75 76 77 77 78 79 79 80

	3.3.2.1	Blended Porous PES-cSMMs Membrane Preparation	82
	3.3.3 Fabricati cSMMs/ZIF-8 M	on of Composite Porous PES- Membrane	82
	3.3.3.1	Immersion Precipitation Method for ZIF-8 Inclusion	83
	3.3.3.2	Dead-end Filtration Method for ZIF- 8 Inclusion	84
	3.3.3.3	Contra-diffusion Method for ZIF-8 Inclusion	85
3.4	Characterization	n and Performance Measurement	86
	3.4.1 Morphol	ogical Study on the Prepared Samples	86
	3.4.2 Pore Size	e and Porosity Measurement	87
	3.4.3 Intrinsic Framework 8 (Z	Phase of Zeolitic Imidazolate IIF-8)	87
	3.4.4 Confirmation 3.4.4 Confirmation Confir	ation of Structural Changes of PES- S-cSMMs/ZIF-8 Membranes	87
	3.4.5 Water U	ptake and Swelling Measurement	88
	3.4.6 Hydroph	ilicity Measurement	89
	3.4.7 Proton C	onductivity Measurement	89
	3.4.8 Methano	l Permeability Measurement	90
	3.4.9 Overall N	Membrane Characteristic	91
	3.4.10 Thermal	Stability Analysis	92
	3.4.11 Mechani	cal Stability Measurement	92
3.5	Single PEM Dir	rect Methanol Fuel Cell Test	93
	3.5.1 Fabricati Assembly (MEA	on of Membrane Electrolyte A)	93
	3.5.2 Single D	MFC Performance System	93
CHAPTER 4	RESULTS AN	D DISCUSSION	95
4.1	Introduction		95
4.2	Effect of Solver Time on Porous	nt's Type and Solvent Evaporation PES Membranes	96
	4.2.1 Morphol	ogy of Porous PES Membranes	96
	4.2.1.1	Effect of Solvent on PES' Morphologies	98

		4.2.1.2	Effect of Solvent Evaporation Time (SET) on PES' Morphologies	101
	4.2.2 PES r	Water Up nembranes	otake and Contact Angle of Porous	104
	4.2.3 Memb	Proton Coranes	onductivity of Porous PES	106
	4.2.4 memb	Methanol oranes	Permeability of Porous PES	108
	4.2.5	Summary	7	112
4.3	Effect cSMN	t of cSMM As Membra	s's Loading on Blended Porous PES- ane	113
	4.3.1 Blend	Morpholo ed Porous	ogies and Structural Analysis of PES-cSMMs Membrane	113
	4.3.2 Analy	Effect of sis on Ble	Morphologies on Physico-Chemical nded Porous PES-cSMMs Membranes	118
	4.3.3 PES-c	Thermal SMMs Me	Stability Study of Blended Porous embranes	122
	4.3.4 cSMN	Mechanio As Membra	cal Properties of Blended Porous PES- anes	125
	4.3.5	Summary	I	126
4.4	Effect Forma Memb	t of Inclusi ation on Co orane	on Techniques on ZIF-8 Crystals omposite Porous PES-cSMMs/ZIF-8	127
	4.4.1 cSMN	Morpholo /Is/ZIF-8 N	ogy of Composite Porous PES- Iembranes	127
	4.4.2 Imida	Confirma zolate Frai	ntion of the Presence of Zeolitic mework-8 (ZIF-8)	132
	4.4.3 Physic cSMN	Effect of co-Chemic //s/ZIF-8 N	Structural Morphologies toward al Studies on Composite Porous PES- Membranes	134
		4.4.3.1	Effect of the Inclusion of ZIF-8 towards Proton Conductivity of Composite PES-cSMMs/ZIF-8 Membranes Based on the Morphological Aspect	137
		4.4.3.2	Effect of the Inclusion of ZIF-8 towards Methanol Permeability and Selectivity of Composite PES- cSMMs/ZIF-8 Membranes Based on the Morphological Aspect	138

	4.4.4 Mechanical Stability of Prepared Membranes	139
	4.4.5 Crystallinity of Porous Composite PES- cSMMs/ZIF-8 Membrane	140
	4.4.6 Thermal Stability Analysis for PES- cSMMs/ZIF-8 Composite Membrane	142
	4.4.7 The comparison study of DMFC performance of PES-cSMMs/ZIF-8immersion and Nafion 117 membranes	144
	4.4.8 Summary	146
CHAPTER 5	CONCLUSION AND RECOMMENDATIONS	147
5.1	Influence of Solvent's Type and Solvent Evaporation Time on Membrane's Morphology and Its Contribution toward Proton and Methanol Permeation	147
5.2	Loading Effect of charged Surface Modifying Macromolecules on Membrane's Morphology and Its Contribution toward Proton and Methanol Permeation	148
5.3	Effect of <i>In-Situ</i> Growth Techniques on the Formation of ZIF-8 Crystals as well as The Performance of PES-cSMMs/ZIF-8 Membranes	149
5.4	Recommendation for Future Works	150
REFERENCES		151
APPENDIX		169
LIST OF PUBLI	ICATIONS	171

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Factor that may influence the performance of DMFC (Spiegel, 2018)	19
Table 2.2	Polymer electrolyte membranes (PEMs) for direct methanol fuel cell (DMFC) applications	22
Table 2.3	Factors that are affecting the fabrication of porous membrane by non-solvent induced phase separation (NIPS)	34
Table 2.4	cSMMs-based electrolyte membrane fabrication in fuel cell applications	41
Table 2.5	MOF-polymer composite membrane for fuel cell application	44
Table 2.6	Type of organic linkers for MOFs	46
Table 2.7	Summarization of MOF-based electrolyte for fuel cell	50
Table 2.8	ZIF-8/polymer composite membrane for DMFC application	54
Table 2.9(a)	Effect of diffusion time on the morphology of ZIF-8 on porous Nylon substrate at room temperature and molar ratio HmIm/ Zn^{2+} was 8 (Yao <i>et al.</i> , 2011)	61
Table 2.9(b)	Effect of concentration $\text{HmIm}/\text{Zn}^{2+}$ on the morphology of ZIF-8 on porous Nylon substrate at room temperature for 24hours (Yao <i>et al.</i> , 2011)	62
Table 2.9(c)	Effect of repeating growth on the morphology of ZIF-8 on porous Nylon substrate at room temperature for 24hours and molar ratio HmIm/Zn ²⁺ was 8 (Yao <i>et al.</i> , 2011)	63
Table 3.1	Properties of PES (source credit to Solvay Veradel [®] (Safety Data Sheet))	74
Table 3.2	Properties of NMP (source credit to RCL Labscan Limited (Safety Data Sheet))	75
Table 3.3	Physical and chemical properties of DMAc (source credit to Sigma-Aldrich (Safety Data Sheet))	76
Table 3.4	Properties of Zn (NO ₃) ₂ .6H ₂ O (98% purity) (source credit to Sigma Aldrich (Safety Data Sheet))	76
Table 3.5	Properties of HmIm (99% purity) (source credit to Sigma Aldrich (Safety Data Sheet))	77

Table 3.6	Properties of TEA (99% purity) (source credit to Sigma Aldrich (Safety Data Sheet))	78
Table 3.7	List of chemicals used in this study	78
Table 3.8	Formulation of designed porous PES electrolyte membranes	79
Table 3.9	Designed flat sheet porous PES electrolyte membranes	80
Table 3.10	Proposed dope solutions	81
Table 3.11	Sample designation for the prepared PES-cSMMs/ZIF-8 composite membranes	85
Table 4.1	SEM images of surface (2000x) and cross-section (1000x) morphologies of 18 wt.% PES in DMAc and NMP at different SET with the relative scale of $30\mu m$, respectively	97
Table 4.2	Solvent-water (H ₂ O) affinity (Thuyavan et al., 2016)	99
Table 4.3	Porosity of prepared porous PES membranes with different solvents	102
Table 4.4	Physical characteristics of prepared PEMs	105
Table 4.5	Performance of prepared samples with respect to proton conductivity and methanol permeability	109
Table 4.6	SEM images of surface (2000x) and cross-section (1000x)	
	morphology of blended PES-(0-5wt.%) cSMMs, respectively	114
Table 4.7	EDX spectrum elemental data for porous PES-(0-5wt.%) cSMMs membranes	116
Table 4.8	Transmission bands of cSMMs powder and porous PES- (0-5wt.%) cSMMs membranes	117
Table 4.9	Physico-chemical characterizations of the blended porous PES-(0-5wt.%) cSMMs membranes	119
Table 4.10	Percentage weight loss of cSMMs and blended porous PES-	
	cSMMs membranes at different degradation temperatures (T_d)	124
Table 4.11	Young's modulus, tensile strength, and elongation at break of PES-(0-5wt.%) cSMMs membranes	125
Table 4.12	Cross-sectional images of composite PES-cSMMs/ZIF-8 membranes from different inclusion methods	129
Table 4.13	EXD data for PES-cSMMs/ZIF-8 membranes, respectively	130

Table 4.14	Transmission bands of ZIF-8 powder and PES-cSMMs/ZIF-8 membranes	133
Table 4.15	Physico-chemical characteristics of prepared porous composite PES-cSMMs/ZIF-8 and Nafion [®] 117 membranes, respectively	135
	respectively	155

LIST OF FIGURES

FIGURE NO	. TITLE	PAGE
Figure 2.1	Roadmap of fuel cells development	11
Figure 2.2	Basic structure of the fuel cell system	12
Figure 2.3	Type of fuel cells and their characteristics, respectively	14
Figure 2.4	Active operation mode of the DMFC	16
Figure 2.5	Schematic diagram of the membrane electrode assembly (MEA)	17
Figure 2.6	Polarization curve for fuel cell	20
Figure 2.7	Proposed microstructure for Nafion and SPEEK membranes, respectively (Othman <i>et al.</i> , 2007)	23
Figure 2.8	Progress on electrolyte development in DMFC application	26
Figure 2.9	Proton conduction modelling: (a) Grotthuss mechanism and (b) vehicle mechanism	27
Figure 2.10	Types of transport mechanism inside the cluster model of Nafion (Tung and Hwang, 2005)	28
Figure 2.11	Phase inversion techniques procedure	30
Figure 2.12	Ternary phase diagram for phase inversion techniques	31
Figure 2.13	Different route for porous membrane preparation via non- solvent induced phase separation (NIPS)	33
Figure 2.14	Chemical structure of PES (Razi et al., 2012)	36
Figure 2.15	Illustration of the migration of SMMs inside the membrane matrix	39
Figure 2.16	Some of the chemical structures that commonly involved in cSMMs fabrication	42
Figure 2.17	Desymmetrized linkers	48
Figure 2.18	(a) nanosheets of Cu-TCPP, (b) crystal structure with dangling carboxyl groups on CU-TCPP nanosheet surface and (c) schematic of the proton-conducting medium on the surface of Cu-TCPP (Xu <i>et al.</i> , 2013)	51

Figure 2.19	Comparative of the kinetic diameter of ZIF-8 hydroxide ion and methanol molecules. The yellow sphere indicates the internal diameter (11.6Å) (Hsu <i>et al.</i> ,2018)	54
Figure 2.20	Mechanism of proton and methanol transports through the Nafion/ZIF-8@GO composite membrane (Yang <i>et al.</i> , 2015)	55
Figure 2.21	Methods involved in preparing ZIF-8 crystals	56
Figure 2.22	Crystallization phase of ZIF-8 over a time interval (Venna <i>et al.</i> , 2010)	57
Figure 2.23	(a) The reaction between Zn^{2+} ion and HmIm precursors, (b) Zn (HmIm) ₄ tetrahedral in 2D, (c) Zn (HmIm) ₄ tetrahedral in 3D and (d) sodalite framework topology at {111} direction of ZIF-8 crystal with aperture size 3.4Å (Yellow= Z atom, blue = N atom, red = C atom and green = H atom) (Yan, 2012)	58
Figure 2.24	Synthesis routes for ZIF-8 membrane formation	59
Figure 2.25	Contra-diffusion setup procedures	60
Figure 2.26	(a) thickness of ZIF-8 crystal at HmIm side; (b) thickness of ZIF-8 crystal at zinc nitrate side; (c) ZIF-8 crystal growth inside Nylon pores; (d) porous Nylon (He <i>et al.</i> , 2013; Yao <i>et al.</i> , 2011)	64
Figure 2.27	Methods in preparing PVDF/ZrP composite membranes	65
Figure 2.28	SEM images of the surface of (a) porous PVDF films, (b) PVDF/ZrP composite films after 12h, (c) PVDF/ZrP composite films after 48h and (d) cross-sectional images of PVDF/ZrP composite films after 48h (Pandey <i>et al.</i> , 2015)	66
Figure 2.29	SEM images of the surface of (a) pristine PES, (b) PES-PDA (reverse), (c) PES-PDA (forward) and cross-sectional image of (d) pristine PES, (e) PES-PDA (reverse) and (f) PES-PDA (forward) membranes, respectively (Fang <i>et al.</i> , 2017)	67
Figure 2.30	(a) Schematic diagram of proton and methanol conduction across porous polymer/MOF and (b) pore-filling type composite membrane of Nafion/inorganic fillers	69
Figure 3.1	Process design flow	73
Figure 3.2	Synthesis reaction of cSMMs from MDI-DEG-HBS (Norddin et al., 2008)	75
Figure 3.3	Single-step dry/wet phase inversion techniques	80
Figure 3.4	Inclusion of ZIF-8 crystal via immersion techniques of <i>in-situ</i> growth	83
Figure 3.5	<i>In-situ</i> growth of ZIF-8 crystals in pores of porous PES- cSMMs via filtration techniques	84

Figure 3.6	Contra-diffusion cell for in-situ growth of ZIF-8 crystals inside the pores of porous PES-cSMMs membranes	85
Figure 3.7	Arrangement for methanol permeability procedure	91
Figure 3.8	Schematic diagram of the DMFC performance test system	94
Figure 4.1	Illustration of the physical interaction process of solute (PES) and solvents (DMAc, NMP)	99
Figure 4.2	(a) physical interaction of PES-H ₂ O-DMAc and (b) physical interaction of PES- H ₂ O- NMP, respectively	100
Figure 4.3	Moisture uptake from the humid atmosphere at a relative humidity (RH) of 66% for porous PES-DMAc and PES-NMP membranes, respectively	103
Figure 4.4	Proton conductivity of 18 wt. % PES in DMAc and NMP, respectively	106
Figure 4.5	Arrangement of the membrane during methanol permeation	
	testing	108
Figure 4.6	Possible pore-blocking for methanol in PES matrix which is (a) cross-linking pores and (b) throat pores blocking	110
Figure 4.7	Possible physical interaction of methanol on PES backbone	111
Figure 4.8	Selectivity of porous PES and Nafion 117 membranes	111
Figure 4.9	FTIR spectra for cSMMs powder and PES-(0-5wt.%) cSMMs membranes	117
Figure 4.10	Selectivity of blended porous PES-cSMMs and Nafion [®] 117	
	membranes, respectively	121
Figure 4.11	TGA and DTG profiles for cSMMs powder and blended	
	porous PES-cSMMs membranes, respectively	123
Figure 4.12	Stress-strain curve for porous PES-(0-5wt.%) cSMMs	
	membranes	125
Figure 4.13	Surface morphology of (a) PES-3wt.% cSMMs and (b) PES-cSMMs/ZIF-8 $_{\rm immersion}$	128
Figure 4.14	Mechanism for ZIF-8 formation via immersion technique	
	(Venna et al., 2010 and Ma and Liu, 2018)	131
Figure 4.15	Mechanism for ZIF-8 formation via filtration techniques	131
Figure 4.16	Mechanism for ZIF-8 formation via contra-diffusion	
	techniques	132

Figure 4.17	FTIR spectra for ZIF-8 powder and PES-cSMMs/ZIF-8 membranes	133
Figure 4.18	Mechanism of methanol transportation across ZIF-8 crystals	138
Figure 4.19	Stress-strain curves for PES-cSMMs membrane and composite PES-cSMMs/ZIF-8 membranes	140
Figure 4.20	XRD patterns for (a) synthesized ZIF-8, (b) cSMMs powder and (c) PES and composite PES-cSMMs/ZIF-8 _{immersion} membranes, respectively	141
Figure 4.21	TGA profiles for synthesized ZIF-8 crystals and PES- cSMMs/ZIF-8 composite membrane, respectively	143
Figure 4.22	Polarization curve of PES-cSMMs/ZIF-8 _{immersion} and Nafion [®] 117, respectively	144

LIST OF ABBREVIATIONS

DMAc	-	Dimethyl Acetamide
EDX	-	Energy Dispersive X-ray
FESEM	-	Field Emission Scanning Electron Microscopy
R&D	-	Research and Development
TGA	-	Thermogravimetric Analyzer
XRD	-	X-ray Diffraction
NMP	-	N-methyl Pyrrolidine
PEM	-	Polymer Electrolyte Membrane
ZIF-8	-	Zeolitic Imidazolate Framework-8
MOFs	-	Metal-Organic Framework
cSMMs	-	Charged Surface Modifying Macromolecules
NIPS	-	Non Induced Phase Separation
SET	-	Solvent Evaporation Time
RH	-	Relative Humidity
MEA	-	Membrane Electrode Assembly
SEM	-	Scanning Electron Microscopy
CA	-	Contact Angle
PEEK	-	Poly Ether Ether Ketone
PI	-	Polyamide

LIST OF SYMBOLS

°C	-	Degree Celsius
σ	-	Proton Conductivity
Р	-	Methanol Permeability
g	-	Gram
cm^3	-	Centimetre Cubic
d	-	Thickness of Membrane
wt.%	-	Percentage of Weight
S	-	Siemen
d_{wet}	-	Thickness of Wet Membrane
d_{dry}	-	Thickness of Dry Membrane
Lwet	-	Length of Wet Membrane
<i>L</i> _{dry}	-	Length of Dry Membrane
W _{wet}	-	Weight of Wet Membrane
W_{dry}	-	Weight of Dry Membrane
μm	-	Micrometre
W	-	Watt

LIST OF APPENDICES

APPENDIX

TITLE

PAGE

Appendix A	Example of Water Uptake, Swelling and Dimensional Change		
	Calculation	169	

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the past decades, fossil fuel was the primary source of generating power, either for remote or inaccessible areas. However, the rapid depletion of fossil fuel has contributed to fuel price increment (Höök and Tang, 2013). This issue is non-stop and may take a long time to recover. The worsening scenario is the burning of fossil fuels, which has caused environmental problems that led to several effects such as climate change, human health, global warming, water and air pollution, and many more. These problems developed the motivation for researchers worldwide to find a sustainable yet environmentally friendlier solution for a healthier life. After a long-term run of numbers research and development (R&D), renewable energy was then introduced since it had shown the potential to replace the current dependency on fossil fuel.

Besides, this renewable energy has offered several advantages which make it feasible than fossil fuel, such as not directly competing the fossil fuel in the mainstream of the world with a stand-alone wholesale price (Khan *et al.*, 2017). "Renewable energy" refers to self-renewing energy derived from various resources such as sunlight, wind, flowing water, biomass, geothermal heat and etcetera (Bull, 2001). Apart from higher investment and weather depending, fuel cell-based energy sources have captivated an enormous potential in the research field since they possess a lightweight and compact design for easy handling (Das *et al.*, 2017). Direct methanol fuel cell (DMFC) is one of the distinguished fuel cells that has been studied for the past few years due to its ability to provide energy for portable applications (Lee *et al.*, 2017).

The performance of DMFC was mainly governed by the membrane electrode assembly (MEA), which consists of electrodes (anode and cathode), catalysts and electrolyte membrane. The electrolyte membrane is a vital part of the DMFC system since it can affect the proton and methanol transport processes. Since the electrolyte was generally prepared from the polymeric-based membrane as a proton conductor, either proton exchange membrane or polymer electrolyte membrane (PEM) terminology can be used (Jaafar *et al.*, 2011; Wang *et al.*, 2011). As concerned, commercial perfluorinated membrane such as Nafion® membrane had been dictated as a competitive PEM for other non-fluorinated membranes due to higher proton conductivity.

For instance, Li *et al.* (2003) had found that at different operating temperature conditions, Nafion[®] 115 membrane could provide high proton conductivity such as 10 Scm⁻¹ at 80°C (100% relative humidity (RH)) and 5-20 Scm⁻¹ at 150°C (0% relative humidity (RH)), respectively compared to sulfonated poly (ether ether ketone) (SPEEK) membrane. Despite the high value of proton conductivity, Nafion suffered from high fuel permeability, mainly when operating in the DMFC system. Thus, several approaches have been introduced to refine the fuel cell performance, such as (1) modifying perfluorinated ionomer membrane/ acid-base blends, (2) modifying ionomer membrane, and (3) preparing new electrolyte composite membrane based on proton conducting materials. The latter approach has marked up the R&Ds for newly designed electrolytes in the past few decades.

Generally, the membrane morphology can be divided into two groups: dense and porous. Regardless of the composition within PEMs, several types of fabricated membranes for DMFC applications mostly in dense structure morphology which can be defined by their configurations-whether layered, sandwiched, or pore-filled membranes. Compared to the corresponding pure polymer membranes and commercial Nafion[®] membranes, many new electrolyte membranes based on proton conducting materials with different configurations show much lower fuel permeability and similar or improved proton conductivity. The combination of the advantages from the base materials and membranes morphology contribute to the aforementioned properties. Adding the proton conducting materials may affect the membrane cell in two ways: 1) a good distribution could provide a winding diffusion pathway for methanol to crossover, and 2) complete morphological structure could allow more proton to diffuse (Wang and Dong, 2007).

Being said, porous PEM with nanoscales pores can increase the cell performance and physicochemical properties of the membrane compared to the dense electrolyte membrane. For instance, Jiang *et al.* (2017) have found that the porous SPEEK does help in collecting more water and induced proton transportation (58 × 10^{-3} Scm⁻¹) in conjunction with a more straightforward pathway given by the pores. Moreover, the inclusion of inorganic fillers via *in-situ* growth techniques within the pores of the base membrane is favourable in developing crystals with smaller diameter sizes which could provide a barrier for methanol yet allowing protons to pass through. Thus, the combination of higher porosity, narrower pores size, and denser distribution of ionic clusters in the polymer electrolyte membrane brings the focus to the study on composite polymer electrolyte membrane within the laboratory and industrial aspect.

1.2 Problem Statement

Nafion[®], a notable membrane that has dominantly been used as a proton exchange membrane in a fuel cell application system (Gagliardi et al., 2020), has significantly shown some drawbacks when operating at high operating temperatures. Nafion[®] membrane suffered from a swelling problem that may affect the membrane's barrier properties, especially in DMFC application. Thus, a new route was discovered by introducing non-fluorinated polymers. Among all, despite high hydrophobicity, polyether sulfone (PES) possessed high chemical and thermal stability ($T_g=220^{\circ}C$), good mechanical strength, and excellent hydrolytic stability, makes it interesting to be studied as an electrolyte in the DMFC system (Unnikrishnan et al., 2010). The substitution of electrophilic and nucleophilic on PES structure seemly feasible due to aromatic rings. This character makes the PES polymer easy to modify to fulfil the electrolyte membrane requirement for fuel cell application. Moreover, the properties possessed by PES make it easy to be altered during the fabrication process either as dense or porous membrane. Previously, a dense PES electrolyte membrane has been fabricated and studied by Elakkiya et al. (2018). However, unfortunately, the proton conductivity value of dense PES is relatively low $(0.22 \times 10^{-4} \text{ Scm}^{-1})$. In order to solve the low proton conductivity of the dense PES membrane, the introduction of nanoscale's pores was believed can enhance the proton conductivity of the pristine PES.

This nanoscale's pores on porous PES can lead to more water collection due to the more straightforward pathway given by those pores, which eventually increase the cell performance of DMFC (Jiang *et al.*, 2017). Previously, many porous PES membranes had been fabricated using different organic solvents such as N-methyl pyrrolidine (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc). Despite the high prices, these organic solvents offer good management toward the environment. As these organic solvents were released into the water, air, and soil, they would eventually be adapted to the environment by chemically converting into another compound that eventually became less toxic (Comyn, 1997). Madaeni and Rahimpour (2005) had studied the effect of solvents such as DMAc, NMP, and DMF toward the porosity of PES membrane. From their study, they concluded that DMAc and NMP could provide a porous PES membrane with higher porosity (>80%) as compared to DMF (=80%). The findings are worth noting that the solvents' types play an important role in determining the membrane's morphology. Apart from that, the solubility of the solvent and polymer is also crucial while preparing adequate thermodynamic stability of the dope solution (Nasir *et al.*, 2014) for electrolyte membrane fabrication. Nonetheless, for porous membrane fabrication, the morphology can be formed either; (1) structure that consists of thin dense skin layer, finger-like and macrovoids layer or (2) consist of macrovoids and sponge-like structure or (3) sponge-like structure.

In the formation of those morphologies, solvent evaporation time (SET) plays a significant role in delivering a good morphology for intended applications. A study by Salim *et al.* (2019) reported that after 5 min SET, the thermodynamic process of solvent exchange was not stable for porous membrane formation and was not suitable for any applications. This unstable thermodynamic process will lead to the formation of holes on the membrane's surface. Nonetheless, in the SET procedure, higher volatile solvents such as DMF and DMSO will lead to the formation of grainy and irregular structure of PES membranes due to rapid evaporation of solvents (Thuyavan *et al.*, 2016).

Thus, upon different raw materials, the distinction in electrolyte microstructure can be relayed on different preparation techniques, leading to a different range of proton conductivity (Zheng and Shen, 2018). This phenomenon occurred due to the tortuosity pathways formed by the microstructure of the electrolyte. However, it was believed that the amendment on dense PES membrane by porous structure only does not impact proton conductivity value due to its hydrophobic backbone, which restricts proton's attachment via the Grotthuss mechanism. To further improve the proton conductivity, both mechanisms of Grotthuss and vehicle should work simultaneously. Thus, in order to improve the hydrophilicity of porous PES membrane, the posttreatment, such as surface modification, by governing a charged surface modifying macromolecules (cSMMs). Countless pioneering work has been done previously, which showed that the addition of cSMMs within the limit (0-5 wt. %) could decrease the dense membrane's contact angle and simultaneously increase the proton conductivity (Norddin *et al.*, 2008). Moreover, the contribution of higher porosity, narrower pores size, and denser distribution of ionic clusters to the addition of cSMMs in the polymer matrix makes it excellent for proton conductivity (Rana *et al.*, 2005) yet could suppress the methanol crossover (Norddin *et al.*, 2008). Despite all the improvement in proton conductivity of the pristine membrane, when dealing with an open porous structure, it cannot be neglected the probability for methanol to crossover due to the kinetic separation that occurred when the pore size is slightly larger than the kinetic diameter of methanol molecules.

The small aperture size of zeolitic imidazolate framework 8 (ZIF-8), which is \sim 3.4Å, can give a tortuous pathway for methanol (kinetic diameter \sim 3.8Å) yet increasing the proton conduction (kinetic diameter of water 2.6 \sim 3.2Å) (Hsu *et al.*, 2018; Yang *et al.* 2015). Also, ZIF-8 is easier to compatible with the polymer matrix due to its imidazolate linkers containing nitrogen-donors. Nevertheless, the hydrophobic properties of ZIF-8 were believed can enhance the stability of electrolyte membranes at higher operating temperatures. Despite the speciality possessed by ZIF-8 crystals, the appropriated inclusion techniques need to be determined since they will influence the degree of ZIF-8 crystal formation within the pores of the porous PES-cSMMs membranes.

A good formation of ZIF-8 crystal is required to produce excellent methanol barrier properties and proton conductivity. To the best of our knowledge, this is the first reported research that employs a fully open porous structure membrane as an electrolyte for DMFC applications. This research postulated that both combination properties of porous PES-cSMMs and ZIF-8 were believed could induce high proton conductivity and methanol barrier properties for the DMFC system. Therefore, in this study, a composite membrane consisting of modified porous PES-cSMMs and ZIF-8 crystals is studied in determining the performance of DMFC single cells.

1.3 Objective of the Study

The main objective of this study is to develop a composite porous PEScSMMs/ZIF-8 membrane with high proton conductivity, high methanol barrier properties, and high performance under DMFC operations compared to commercially available Nafion[®] 117 membrane, respectively. The main concern in the fabrication of composite porous PES-cSMMs/ZIF-8 membrane is the influence of morphology on the membrane's properties. Hence, the objectives of the study are as follows:

- (a) To evaluate the influences of solvent's types and solvent evaporation time (SET) on the physico-chemical properties of the prepared porous PES membrane
- (b) To determine the best cSMMs loading based on the physico-chemical properties of the prepared blended porous PES-cSMMs membrane
- (c) To examine the effect of inclusion techniques toward composite porous PEScSMMs/ZIF-8 membrane based on the influences of the morphological aspect on the physico-chemical properties.
- (d) To evaluate and compare the performance of membrane electrolyte assembly (MEA) fabricated from porous composite PES-cSMMs/ZIF-8 and Nafion 117[®] membranes in a DMFC single cell.

1.4 Scope and Limitation of Study

In order to achieve the objective stated above, the following scopes of study are being drawn:

- (a) Preparing of porous PES membranes
 - i. 18 wt. % of PES dope solutions were synthesized using different types of solvents (DMAc and NMP),
 - ii. Preparing porous PES electrolyte membranes via dry/wet phase inversion techniques
 - iii. Varying the solvent evaporation time, SET (0, 1, 2, 3, 4 and 5 minutes) to produce a porous structure of PES-DMAc and PES-NMP membranes
 - iv. Characterization in terms of morphological aspect toward physicochemical properties such as morphology, hydrophilicity, proton conductivity, methanol permeability and water uptake by using scanning electron microscopy (SEM), contact angle (CA), AC impedance analyzer and permeation cell, respectively.
- (b) Preparing of blended porous PES-cSMMs membranes
 - i. Synthesizing 18wt.% of PES-cSMMs dope solutions with different loading of cSMMs (0, 1, 2, 3, 4 and 5wt.%) via direct blending method,
 - Preparing of blended porous PES-cSMMs membranes via dry/wet phase inversion techniques by controlling the optimum solvent evaporation time (SET)
 - Characterizing the blended porous PES-cSMMs membranes in terms of physicochemical properties such as morphology, hydrophilicity, proton conductivity, methanol permeability, chemical structure, and mechanical stability by using scanning electron microscopy (SEM), contact angle (CA), AC impedance analyzer, permeation cell, Fourier transform infrared spectroscopy (FTIR) and tensile test, respectively

- (c) Preparing of composite porous PES-cSMMs/ZIF-8 membranes
 - i. Fabrication of composite porous PES-cSMMs/ZIF-8 electrolyte membrane by manipulating the inclusion techniques (immersion, contra-diffusion, and filtration) with a constant ratio of ZIF-8 precursor (1:6:500)
 - Characterizing the composite porous PES-cSMMs/ZIF-8 electrolyte membranes in terms of physicochemical properties such as morphology, water uptake, hydrophilicity, proton conductivity and methanol permeability, thermal properties, chemical structure, crystallinity and mechanical stability by using field emission scanning electron microscopy (FESEM), contact angle (CA), AC impedance analyzer, permeation cell, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD) and tensile test, respectively

(d) Evaluating the performance of developed PEM in DMFC system

- The PEM electrode assemblies (MEAs) were prepared by composing membrane with Pt/Ru and Pt/C electrodes at 3 tonnes, 115° C and 1 minute. The PEM electrode assemblies were tested under a single DMFC operation system.
- ii. The operating temperature and relative humidity were controlled at ambient conditions.
- iii. The power density was calculated via the recorder I-V polarization curve and compared to the performance of Nafion[®] 117 membranes.

1.5 Significant of the Study

The fuel cell is one of the promising renewable energy sources that can provide a clean, safe and cost-effective to the community, nation as well as society. The polymer electrolyte membrane (PEM) based on inorganic filler has earned many research and development (R&D) works from other researchers around the world in the past two decades due to its outstanding ability in providing higher performance, especially in direct methanol fuel cell (DMFC) application as compared to native PEM. Despite that, dense morphology possessed by a common composite membrane has limited the transportation of protons within its structure. Thus, a composite electrolyte membrane entirely made up of a porous structure was used as a new electrolyte in the DMFC system. To select the promising materials for PEM in enhancing the methanol barrier properties, this research alternatively fabricated PES polymer as the main backbone for PEM. The replacement of the Nafion[®] with hydrocarbon membrane improved the compatibility of membrane properties and benefited the working operation of the DMFC and cut its operating cost. Despite that, the introduction of hydrophilic additives such as cSMMs and inorganic filler, ZIF-8 improved the proton conductivity, mechanical and thermal properties of the composite membrane. The swelling degree was also enhanced. Furthermore, by studying the inclusion techniques for ZIF-8 embedded into the pores of porous PES-cSMMs, the optimum ZIF-8 crystal formation has remarkably improved the value of proton conductivity and methanol permeability. Moreover, the fabricated composite membrane also has the potential to be used in wastewater treatment and gas separation process due to its asymmetric structure, which can be selective to the intended molecules/species.

REFERENCES

- Akbari, E., Nikoukar, A., Kheirandish, A., Khaledian, M. and Afroozeh, A. (2016)
 'Sensor application in Direct Methanol Fuel Cells (DMFCs)', *Renewable and Sustainable Energy Reviews*, 60, pp. 1125-1139.
- Alaei Shahmirzadi, M. A., Hosseini, S. S., Ruan, G. and Tan, N. R. (2015). 'Tailoring PES nanofiltration membranes through systematic investigations of prominent design, fabrication and operational parameters', *RSC Advances*, 5, pp. 49080-49097.
- Alberti, G. and Casciola, M. (2003) 'Composite membrane for medium-temperature PEM fuel cells', *Annual Review of Materials Research*, 33, pp. 129-154.
- Alwin, S., Bhat, S. D., Sahu, A. K., Jalajakshi, A., Sridhar, P., Pitchumani, S. and Shukla, A. K. (2011) 'Modified-pore-filled-PVDF-membrane electrolytes for direct methanol fuel cells', *Journal of The Electrochemical Society*, 158.
- Aranda, M. A. G., Leon-reina, L., Rius, J., Demadis, K. D., Moreau, B., Villemin, D., Palomino, M., Rey, F. and Cabeza, A. (2012) 'High proton conductivity in a flexible, cross-linked, ultramicroporous magnesium tetraphosphonate hybrid Framework', *Inorganic Chemistry*, 51, pp. 7689-98.
- Aricò, A. S., Baglio, V. and Antonucci, V. (2009) Direct methanol fuel cells: history, status and perspectives, in Liu, H. and Zhang, J. (Eds.) Electrocatalysis of direct methanol fuel cells: from fundamentals to applications. John Wiley & Sons, pp, 1-78.
- Awang, N., Jaafar, J., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Yusof, N., Aziz, F., Salleh, W. N. W., Suradi, S. S., Ilbeygi, H., Wan Mohd Noral Azman, W. N. E. and Arthanareeswaran, G. (2017) 'Development of dense void-free electrospun SPEEK-Cloisite15A membrane for direct methanol fuel cell application : Optimization using response surface methodology', *International Journal of Hydrogen Energy*, 42, pp. 26496–26510.
- Azimi, M., Peighambardoust, S. J. and Hosseini, M. G. (2012) Modification of Nafion membranes with different clays for direct methanol fuel cell applications, in *Proceeding of the 6th Iranian Fuel Cell Seminar*, Tehran, Iran, March 2012.

- Bakangura, E., Ge, L., Muhammad, M., Pan, J., Wu, L. and Xu, T. (2015) 'Sandwich structure SPPO/BPPO proton exchange membranes for fuel cells: Morphology-electrochemical properties relationship', *Journal of Membrane Research*, 475, pp, 30-38.
- Baker, R. W. (2012) Membrane Technology and Applications. John Wiley & Sons.
- Balsara, N. P. and Beers, K. M. (2011) 'Proton conduction in materials comprising conducting domains with widths less than 6 nm', *European Polymer Journal*, 47, pp. 647-650.
- Bao, Q., Lou, Y., Xing, T. and Chen, J. (2013) 'Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) in aqueous solution via microwave irradiation', *Inorganic Chemistry Communications*, 37, pp. 170-173.
- Barbosa, P., Rosero-Navarro, N. C., Shi, F. N. and Figueiredo, F. M. L. (2015) 'Protonic conductivity of nanocrystalline zeolitic imidazolate framework 8', *Electrochimica Acta*, 153, pp. 19-27.
- Bazzarelli, F., Giorno, L. and Piacentini, E. (2015) *Porous membrane*, in Drioli, E and Giorno, L. (Eds.) *Encyclopaedia of membranes*. Germany: Springer, pp. 1-3.
- Bruggen, B. Van Der. (2009) 'Chemical modification of polyethersulfone nanofiltration membranes: A review', *Journal of Applied POlymer Science*, 114, pp. 630-642.
- Bull, S. R. (2001) Renewable energy today and tomorrow, in *Proceedings of the IEEE*, 89, pp. 1216–1226.
- Bux, H., Liang, F., Li, Y., Cravillon, J., Wiebcke, M. and Caro, J. (2009) 'Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis', *Journal of The American Chemical Society*, 131, pp. 16000-16001.
- Cai, Y. Y., Yang, Q., Zhu, Z. Y., Sun, Q. H., Zhu, A. M., Zhang, Q. G. and Liu, Q. L. (2019) 'Achieving efficient proton conduction in a MOF-based proton exchange membrane through an encapsulation strategy', *Journal of Membrane Science*, 590, p. 117277.
- Cao, X., Qiu, M., Qin, A., He, C. and Wang, H. (2014) 'Effect of additive on the performance of pvdf membrane via non-solvent induced phase separation', *Materials Science Forum*, 789, pp. 240-248.

- Cavaliere, S., Subianto, S., Savych, I., Jones, D. J. and Rozi, J. (2011) 'Electrospinning: designed architectures for energy conversion and storage devices', *Energy and Environmental Science*, 4, pp. 4761-4785.
- Čejka, J., Corma, A. and Zones, S. (2010) Zeolites and Catalysis: Synthesis, Reactions and Applications. Wiley-VCH.
- Chen, B., Yang, Z., Zhu, Y. and Xia, Y. (2014) 'Zeolitic imidazolate framework materials : recent progress in synthesis and applications', *Journal of Material Chemistry A*, 2, pp. 16811-16831.
- Cheng, T., Feng, M., Huang, Y. and Liu, X. (2017) 'SGO/SPEN-based highly selective polymer electrolyte membranes for direct methanol fuel cells', *Ionics*, 23, pp. 2143-2152.
- Chu, F., Zheng, Y., Wen, B., Zhou, L., Yan, J. and Chen, Y. (2018) 'Adsorption of toluene with water on zeolitic imidazolate framework-8/graphene oxide hybrid nanocomposites in a humid atmosphere', *RSC Advances*, 8, pp. 2426–2432.
- Comyn, J. (1997) 'Handbook of organic solvent properties: Ian M. Smallwood Arnold £65.00. ISBN 0340645784. 306 pages + xxi', *International Journal of Adhesion and Adhesives*, 17, p. 177.
- Das, V., Padmanaban, S., Venkitusamy, K., Selvamuthukumaran, R., Blaabjerg, F. and Siano, P. (2017) 'Recent advances and challenges of fuel cell based power system architectures and control-A review', *Renewable and Sustainable Energy Reviews*, 73, pp. 10–18.
- Daud, W. R. W., Rosli, R. E., Majlan, E. H., Hamid, S. A. A., Mohamed, R. and Husaini, T. (2017) 'PEM fuel cell system control: A review', *Renewable Energy*, 113, pp. 620–638.
- Devi, A. U., Divya, K., Rana, D., Abirami, M. S. and Nagendran, A. (2018) 'Highly selective and methanol resistant polypyrrole laminated SPVdF-co-HFP/PWA proton exchange membranes for DMFC applications', *Materials Chemistry* and Physics, 212, pp. 533–542.
- Di Palma, L., Bavasso, I., Sarasini, F., Tirillò, J., Puglia, D., Dominici, F. and Torre, L. (2018) 'Synthesis, characterization and performance evaluation of Fe₃O₄/PES nano composite membranes for microbial fuel cell', *European Polymer Journal*, 99, pp. 222-229.

- Díaz, M., Ortiz, A., Vilas, M., Tojo, E. and Ortiz, I. (2014) 'Performance of PEMFC with new polyvinyl-ionic liquids based membranes as electrolytes', *International Journal of Hydrogen Energy*, 39, pp. 3970-3977.
- Divya, K., Rana, D., Alwarappan, S., Saraswathi, M. S. S. A. and Nagendran, A. (2019) 'Investigating the usefulness of chitosan based proton exchange membranes tailored with exfoliated molybdenum disul fi de nanosheets for clean energy applications', *Carbohydrate Polymer*, 208, pp. 504-512.
- Doğan, H., Inan, T. Y., Koral, M. and Kaya, M. (2011) 'Organo-montmorillonites and sulfonated PEEK nanocomposite membranes for fuel cell applications', *Applied Clay Science*, 52(3), pp. 285-294.
- Elabd, Y. A., Walker, C. W. and Beyer, F. L. (2004) 'Triblock copolymer ionomer membranes: Part II. Structure characterization and its effects on transport properties and direct methanol fuel cell performance', *Journal of Membrane Science*, 231(1-2), pp. 181-188.
- Elakkiya, S., Arthanareeswaran, G., Venkatesh, K. and Kweon, J. (2018). 'Enhancement of fuel cell properties in polyethersulfone and sulfonated poly (ether ether ketone) membranes using metal oxide nanoparticles for proton exchange membrane fuel cell', *International Journal of Hydrogen Energy*, 43(47), pp. 21750–21759.
- Ercelik, M., Ozden, A., Devrim, Y. and Colpan, C. O. (2017) 'Investigation of Nafion based composite membranes on the performance of DMFCs', *International Journal of Hydrogen Energy*, 42(4), pp. 2658–2668.
- Erkartal, M., Usta, H., Citir, M. and Sen, U. (2016) 'Proton conducting poly (vinyl alcohol) (PVA)/poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS)/zeolitic imidazolate framework (ZIF) ternary composite membrane', *Journal of Membrane Science*, 499, pp. 156–163.
- Fahrina, A., Maimun, T., Humaira, S., Rosnelly, C. M., Lubis, M. R. and Bahrina, I.
 (2018) 'The morphology and filtration performances of poly (ether sulfone) membrane fabricated from different polymer solution', in *MATEC Web of Conference*, p. 197.
- Fang, X., Li, J., Li, X., Pan, S., Zhang, X., Sun, X., Shen, J., Han, W. and Wang, L. (2017) 'Internal pore decoration with polydopamine nanoparticle on polymeric ultrafiltration membrane for enhanced heavy metal removal', *Chemical Engineering Journal*, 314,pp. 38–49.

- Furukawa, H., Cordova, K. E., Keeffe, M. O. and Yaghi, O. M. (2013) 'The chemistry and applications of metal-organic frameworks', *Science*, 341, p. 1230444.
- Gagliardi, G. G., Ibrahim, A., Borello, D. and El-Kharouf, A. (2020) 'Composite polymers development and application for polymer electrolyte membrane technologies-A review', *Molecules*, 25(7).
- Gates, B., Yin, Y. and Xia, Y. (1999) 'Fabrication and characterization of porous membranes with highly ordered three-dimensional periodic structures', *Chemistry of Materials*, 11(10), pp. 2827-2836.
- Guillen, G. R., Pan, Y., Li, M. and Hoek, E. M. V. (2011) 'Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review', *Industrial and Engineering Chemistry Research*, 50(7), pp. 3798-3817.
- Guo, Y., Jiang, Z., Ying, W., Chen, L., Liu, Y., Wang, X., Jiang, Z., Chen, B and Peng, X. (2018) 'A DNA-threaded ZIF-8 membrane with high proton conductivity and low methanol permeability', *Advanced Materials*, 30, p. 1705155.
- Hacquard, A. (2005). Improving and understanding direct methanol fuel cell (DMFC) performance, *PhD Thesis*, Worcester (May), 107.
- Haile, S. M. (2003) 'Fuel cell materials and components', *Acta Materialia*, 51, p. 5981-6000.
- He, M., Yao, J., Li, L., Zhong, Z., Chen, F. and Wang, H. (2013) 'Aqueous solution synthesis of ZIF-8 films on a porouos nylon substrate by contra-diffusion method', *Microporous and Mesoporous Materials*, 179, pp. 10-16.
- Heinzel, A. and Barragán, V. M. (1999) 'A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells', *Journal of Power Sources*, 84(1), pp. 70-74.
- Hess, S. C., Grass, R. N. and Stark, W. J. (2016) 'MOF channels within porous polymer film: Flexible, self-supporting ZIF-8 poly(ether sulfone) composite membrane', *Chemistry of Materials*, 28(21), pp. 7638-7644.
- Hołda, A. K., Aernouts, B., Saeys, W. and Vankelecom, I. F. J. (2013) 'Study of polymer concentration and evaporation time as phase inversion parameters for polysulfone-based SRNF membranes', *Journal of Membrane Science*, 442, pp. 196-205.
- Höök, M. and Tang, X. (2013) 'Depletion of fossil fuels and anthropogenic climate change-A review', *Energy Policy*, 52, pp. 797-809.

- Hou, C., Xu, Q., Peng, J., Ji, Z. and Hu, X. (2013) '(101)-oriented ZIF-8 thin films on ITO with controllable thickness', *ChemPhysChem*, 14(1), pp. 140-144.
- Hsu, P., Hu, T., Kumar, S. R., Chang, C., Wu, K. C., Tung, K. and Lue, S. J. (2018) 'Highly zeolite-loaded polyvinyl alcohol composite membranes for alkaline fuel-cell electrolytes', *Polymers*, 10(1), pp. 102.
- Huang, Q., Luo, Q., Chen, Z., Yao, L., Fu, P. and Lin, Z. (2018) 'The effect of electrolyte concentration on electrochemical impedance for evaluating polysulfone membranes', *Environmental Science: Water Research and Technology*, 4(8), pp. 1145-1151.
- Hurd, J. a, Vaidhyanathan, R., Thangadurai, V., Ratcliffe, C. I., Moudrakovski, I. L. and Shimizu, G. K. H. (2009) 'Anhydrous proton conduction at 150°C in a crystalline metal-organic framework', *Nature Chemistry*, 1(9), pp. 705-710.
- Hwang, H. Y., Kim, S. J., Oh, D. Y., Hong, Y. T. and Nam, S. Y. (2011) 'Proton conduction and methanol transport through sulfonated poly(styrene-bethylene/butylene-b-styrene)/clay nanocomposite', *Macromolecular Research*, 19(1), pp. 84-89.
- Idris, A., Man, Z., Maulud, A. S. and Khan, M. S. (2017) 'Effect of phase separation behavior on morphology and performance of polycarbonate membranes', *Membranes*, 21, pp. 1-18.
- Ilbeygi, H., Ismail, A. F., Mayahi, A., Nasef, M. M., Jaafar, J. and Jalalvandi, E. (2013) 'Transport properties and direct methanol fuel cell performance of sulfonated poly (ether ether ketone)/Cloisite/triaminopyrimidine nanocomposite polymer electrolyte membrane at moderate temperature', *Separation and Purification Technology*, 118, pp. 567-575.
- Jaafar, J., Ismail, A. F., Matsuura, T. and Nagai, K. (2011) 'Performance of SPEEK based polymer-nanoclay inorganic membrane for DMFC', *Journal of Membrane Science*, 382(1-2), pp. 202-211.
- Jiang, Y., Hao, J., Hou, M., Hong, S., Song, W., Yi, B. and Shao, Z. (2017) 'A novel porous sulfonated poly (ether ether ketone)-based multi-layer composite membrane for proton exchange membrane fuel cell application', *Sustainable Energy anf Fuels*, 1(6), pp. 1405-1413.
- Josephine, M., Ordo, C., Jr, K. J. B., Ferraris, J. P. and Musselman, I. H. (2010) 'Molecular sieving realized with ZIF-8/Matrimid[®] mixed-matrix membranes', *Journal of Membrane Science*, 361(1-2), pp. 28-37.

- Khabibullin, A., Minteer, S. D. and Zharov, I. (2014) 'The effect of sulfonic acid group content in pore-filled silica colloidal membranes on their proton conductivity and direct methanol fuel cell performance', *Journal of Materials Chemistry A*, 2(32), pp. 12761-12769.
- Khan, M. I., Yasmeen, T., Shakoor, A., Khan, N. B. and Muhammad, R. (2017) '2014 oil plunge: Causes and impacts on renewable energy', *Renewable and Sustainable Energy Reviews*, 68(1), pp. 609-622.
- Kharisov, B. I., Elizondo Martínez, P., Jiménez-Pérez, V. M., Kharissova, O. V., Nájera Martínez, B. and Pérez, N. (2010) 'recent advances on ditopic ligands', *Journal of Coordination Chemistry*, 63(1), pp. 1-25.
- Kim, S., Dawson, K. W., Gelfand, B. S., Taylor, J. M. and Shimizu, G. K. H. (2013) 'Enhancing proton conduction in a metal-organic framework by isomorpous ligand replacement', *Journal of The American Chemical Society*, 135, pp. 963-966.
- Klaysom, C., Ladewig, B. P., Lu, G. Q. M. and Wang, L. (2011) 'Preparation and characterization of sulfonated polyethersulfone for cation-exchange membranes', *Journal of Membrane Science*, 368(1-2), pp. 48-53.
- Kumar, G. G. and Nahm, K. S. (2011) Polymer nanocomposites-fuel cell applications, in Advances in Nanocomposites-synthesis, characterization and industrial applications, InTech.
- Kumar, M., Khan, M. A., Al-Othman, Z. A. and Choong, T. S. Y. (2013) 'Recent developments in ion-exchange membranes and their applications in electrochemical processes for *in situ* ion substitutions, separation and water splitting', *Separation and Purification Reviews*, 42(3), pp. 187-261.
- Kuo, C.-Y., Lin, H.-N., Tsai, H.-A., Wang, D.-M. and Lai, J.-Y. (2008) 'Fabrication of a high hydrophobic PVDF membrane via nonsolvent induced phase separation', *Desalination*, 233(1-3), pp. 40-47.
- Kusworo, T. D., Budiyono, Ikhsan, D., Rokhati, N., Prasetyaningrum, A., Mutiara, F.
 R. and Sofiana, N. R. (2017) 'Effect of combination dope composition and evaporation time on the separation performance of cellulose acetate membrane for demak brackish water treatment', in *MATEC Web of Conferences*, 101.

- Kwon, H. T. and Jeong, H.-K. (2013) 'Highly propylene-selective supported zeoliteimidazolate framework (ZIF-8) membranes synthesized by rapid microwaveassisted seeding and secondary growth', *Chemical Communications*, 49, pp. 3854-3856.
- Ladewig, B. and Al-Shaeli, M. N. Z. (2017) Fundamentals of membrane processes, in Fundamentals of membrane Bioreactors. Springer transactions in civil and environmental engineering, Singapore: Springer, pp. 13-37.
- Lai, L. S., Yeong, Y. F., Ani, N. C., Lau, K. K. and Shariff, A. M. (2014) 'Effect of synthesis parameters on the formation of zeolitic imidazolate framework 8 (ZIF-8) nanoparticles for CO₂ adsorption', *Particulate Science and Technology*, 32(5), pp. 520-528.
- Lalia, B. S., Kochkodan, V., Hashaikeh, R. and Hilal, N. (2013) 'A review on membrane fabrication : Structure , properties and performance relationship', *Desalination*, 326, pp. 77-95.
- Lee, J., Lee, S., Han, D., Gwak, G. and Ju, H. (2017) 'Numerical modeling and simulations of active direct methanol fuel cell (DMFC) systems under various ambient temperatures and operating conditions', *International Journal of Hydrogen Energy*, 42(3), pp. 1736-1750.
- Lee, Y. R., Jang, M. S., Cho, H. Y., Kwon, H. J., Kim, S. and Ahn, W. S. (2015) 'ZIF-8: A comparison of synthesis methods', *Chemical Engineering Journal*, 271, pp. 276-280.
- Li, A.-L., Gao, Q., Xu, J. and Bu, X.-H. (2017) 'Proton-conductive metal-organic frameworks: Recent advances and perspectives', *Coordination Chemistry Reviews*, 344, pp. 54-82.
- Li, Chenxu, Huang, N., Jiang, Z., Tian, X., Zhao, X., Xu, Z., Yang, H. and Jiang, Z. (2017) 'Sulfonated holey graphene oxide paper with SPEEK membranes on its both sides: a sandwiched membrane with high performance for semi-passive direct methanol fuel cells', *Electrochimica Acta*, 250, pp. 68-76.
- Li, J.-R. and Zhou, H. (2009) 'Metal-organic hendecahedra assembled form dinuclear paddlewheel nodes and mixtures of ditopic linkers with 120 and 90° bend angles', *Angewandte Chemie*, 121(45), pp. 8617-8620.
- Li, L., Zhang, J. and Wang, Y. (2003) 'Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell', *Journal of Membrane Science*, 226, pp. 159-167.

- Li, M., Li, D., O'Keeffe, M. and Yaghi, O. M. (2014) 'Topology analysis of metalorganic frameworks with polytopic linkers and/or multiple building units and the minimal transitivity principle', *Chemical Reviews*, 114(2), pp. 1343-1370.
- Li, S.-L. and Xu, Q. (2013) 'Metal-organic frameworks as platforms for clean enery', *Energy and Environmental Science*, 6(6), pp. 1656-1683.
- Liu, S., Yue, Z. and Liu, Y. (2015) 'Incorporation of inidazole within the metal-organic framework UiO-67 for enhanced anhydrous proton conductivity', *Dalton Transactions*, 44(29), pp. 12976-12980.
- Liu, W. and Yin, X.-B. (2016) 'Metal-organic frameworks for electrochemical applications', *TrAC Trends in Analytical Chemistry*, 75, pp. 86-96.
- Lu, W. Wei, Z., Gu, Z.-Y., Liu, T.-F., Park, J., Park, J., Tian, J., Zhang, M., Zhang, Q., Gentle III, T., Bosch, M., and Zhou, H.-C. (2014) 'Tuning the structure and function of metal-organic frameworks *via* linker design', *Chemical Society Reviews*, 43(16), pp. 5561-5593.
- Lucia, U. (2014) 'Overview on fuel cells', *Renewable and Sustainable Energy Reviews*, 30, pp. 164-169.
- Lufrano, F. and Baglio, V. (2015) 'Selectivity of direct methanol fuel cell membranes', *Membranes*, 5(4), pp. 793-809.
- Ma, X. and Liu, D. (2018). 'Zeolitic imidazolate framework membranes for light olefin/paraffin separation', *Crystals*, 9, pp. 1-26.
- Madaeni, S. S. and Rahimpour, A. (2005) 'Effect of type of solvent and non-solvents on morphology and performance of polysulfone and polyethersulfone untrafiltration membranes for milk concentration', *Polymers for Advanced Technologies*, 16(10), pp. 717-724.
- Mekhilef, S., Saidur, R. and Safari, A. (2012) 'Comparative study of different fuel cell technologies', *Renewable and Sustainable Energy Reviews*, 16, pp. 981-989.
- Meng, X., Wang, H.-N., Song, S.-Y. and Zhang, H.-J. (2017) 'Proton-conducting crystalline porous materials', *Chemical Society Reviews*, 46(2), pp. 464-480.
- Miyake, T. and Rolandi, M. (2016) 'Grotthuss mechanisms: from proton transport in wires to bioprotonic devices', *Journal of Physics: Condensed Matter*, 28(2), pp. 23001.
- Mohanapriya, S., Rambabu, G., Bhat, S. D. and Raj, V. (2018) 'Pectin based nanocomposite membranes as green electrolytes for direct methanol fuel cells', *Arabian Journal of Chemistry*, 13(1), pp. 2024-2040.

- Mondal, S., Soam, S. and Kundu, P. P. (2014) 'Reduction of methanol crossover and improved electrical efficiency in Direct Methanol Fuel Cell by the formation of a thin layer on Nafion 117 membrane : Effect of dip-coating of a blend of sulphonated PVdF-co-HFP and PBI', *Journal of Membrane Science*, 474, pp. 140-147.
- Mosqueda-Jimenez, D. B., Narbaitz, R. M. and Matsuura, T. (2004) 'manufacturing conditions of surface-modified membranes: effects on ultrafiltration performance', *Separation and Purification Technology*, 37(1), pp. 51-67.
- Muthumeenal, A., Abirami, M. S., Rana, D. and Nagendran, A. (2017) 'Fabrication and electrochemical properties of highly selective SPES/GO composite membranes for direct methanol fuel cells', *Journal of Environmental Chemical Engineering*, 5(4), pp. 3828-2822.
- Muthumeenal, A., Neelakandan, S., Rana, D., Matsuura, T., Kanagaraj, P. and Nagendran, A. (2014) 'Sulfonated polyethersulfone (SPES)-charged surface modifying macromolecules (cSMMss) blends as a cation selective membrane for fuel cells', *Fuel Cells*, 14(6), pp. 853-861.
- Nagarkar, S. S., Unni, S. M., Sharma, A., Kurungot, S. and Ghosh, S. K. (2014) 'Twoin-one: Inherent anhydrous and water-assisted high proton conduction in a 3D metal-organic framework', *Angewandte Chemie-International Edition*, 53(10), pp. 2638–2642.
- Nasir, R., Mukhtar, H. and Man, Z. (2014) 'Miscibility studies of polyethersulfone (PES), N-Methyl-2-Pyrrolidone (NMP) and alkanolamines on the basis of Hansen solubility parameters', *International Journal of Scientific Engineering* and Technology, 3(5), pp. 450-453.
- Nawi, N. I. M., Chean, H. M., Shamsuddin, N., Bilad, M. R., Narkkun, T., Faungnawakij, K. and Khan, A. L. (2020) 'Development of hydrophilic PVDF membrane using vapour induced pahse separation method for produced water treatment', *Membranes*, 10(6), pp. 1–17.
- Neelakandan, S., Kanagaraj, P., Sabarathinam, R. M. and Nagendran, A. (2015) 'Polypyrrole layered SPEES/TPA proton exchange membrane for direct methanol fuel cells', *Applied Surface Science*, 359, pp. 272–279.

- Neelakandan, S., Kanagaraj, P., Nagendran, A., Rana, D., Matsuura, T. and Muthumeenal, A. (2015) 'Enhancing proton conduction of sulfonated poly (phenylene ether ether sulfone) membrane by charged surface modifying macromolecules for H₂/O₂ fuel cells', *Renewable Energy*, 78, pp. 306–313.
- Neelakandan, S., Rana, D., Matsuura, T., Muthumeenal, A., Kanagaraj, P. and Nagendran, A. (2014) 'Fabrication and electrochemical properties of surface modified sulfonated poly (vinylidene fluoride-co-hexafluoropropylene) membranes for DMFC application', *Solid State Ionics*, 268, pp. 35-41.
- Nguyen, T. H. and Wang, X. (2009) 'Fabrication of the porous polyimide film as a matrix of the composite membrane of the direct methanol fuel cell', *Separation and Purification Technology*, 67(2), pp. 208-212.
- Norddin, M. N. A. M., Ismail, A. F., Rana, D., Matsuura, T., Mustafa, A. and Tabemohammadi, A. (2008) 'Characterization and performance of proton exchange membranes for direct methanol fuel cell: Blending of sulfonated poly(ether ether ketone) with charged surface modifying macromolecules', *Journal of Membrane Science*, 323(2), pp. 404-413.
- Norddin, M. N. A. M., Ismail, A. F., Rana, D., Matsuura, T. and Tabe, S. (2009) 'The effect of blending sulfonated poly(ether ether ketone) with various charged surface modifying macromolecules on proton exchange membrane performance', *Journal of Membrane Science*, 328(1-2), pp. 148-155.
- Nordin, N. A. H. M., Ismail, A. F., Mustafa, A., Goh, P. S., Rana, D. and Matsuura, T. (2014) 'Aqueous room temperature synthesis of zeolitic imidazole framework 8 (ZIF-8) with various concentrations of triethylamine', *RSC Advances*, 4(63), pp. 33292-33300.
- Oke, S., Higashi, K., Shinohara, K., Izumi, Y., Takikawa, H., Sakakibara, T., Itoh, S., Yamaura, T., Xu, G., Miura, K., Yoshikawa, K., Sakakibara, T., Sugawara, S., Okawa, T. and Aoyagi, N. (2008) 'Dispersion of Pt/Ru catalyst onto arc-soot and its performance evaluation as DMFC electrode', *Chemical Engineering Journal*, 143(1–3), pp. 225–229.
- Othman, M. H. D., Ismail, A. F. and Mustafa, A. (2007) 'Physico-Chemical Study of Sulfonated Poly (Ether Ether Ketone) Membranes for Direct Methanol Fuel Cell Application', *Malaysian Polymer Journal*, 2(1), pp. 10-28.

- Padmavathi, R., Karthikumar, R. and Sangeetha, D. (2012) 'Multilayered sulphonated polysulfone/silica composite membranes for fuel cell applications', *Electrochimica Acta*, 71, pp. 283–293.
- Pan, Y. and Lai, Z. (2011) 'Sharp separation of C2/C3 hydrocarbon mixtures by zeolitic imidazolate framework-8 (ZIF-8) membranes synthesized in aqueous solutions', *Chemical Communications*, 47(d), pp. 10275–10277.
- Pandey, J., Seepana, M. M. and Shukla, A. (2015) 'Zirconium phosphate based proton conducting membrane for DMFC application', *International Journal of Hydrogen Energy*, 40(30), pp. 9410–9421.
- Papporello, R. L., Miró, E. E. and Zamaro, J. M. (2015) 'Secondary growth of ZIF-8 films onto copper-based foils. Insight into surface interactions', *Microporous* and Mesoporous Materials, 211, pp. 64–72.
- Pardo, E., Train, C., Gontard, G., Boubekeur, K., Fabelo, O., Liu, H., Dkhil, B., Lloret, F., Nakagawa, K., Tokoro, H., Ohkoshi, S. I. and Verdaguer, M. (2011) 'High proton conduction in a chiral ferromagnetic metal-organic quartz-like framework', *Journal of the American Chemical Society*, 133, pp. 15328– 15331.
- Park, K. S., Ni, Z., Côté, A. P., Choi, J. Y., Huang, R., Uribe-Romo, F. J., Chae, H. K., O'Keeffe, M. and Yaghi, O. M. (2006) ' Exceptional chemical and thermal stability of zeolitic imidazolate frameworks', *Proceedings of the National Academy of Sciences of the United States of America*, 103, pp. 10186–10191.
- Parnian, M. J., Gashoul, F. and Rowshanzamir, S. (2017) 'Studies on the SPEEK membrane with low degree of sulfonation as a stable proton exchange membrane for fuel cell applications', *Iranian Journal of Hydrogen and Fuel Cell*, 3(2016), pp. 221–232.
- Parthiban, V., Akula, S. and Sahu, A. K. (2017) 'Surfactant templated nanoporous carbon-Nafion hybrid membranes for direct methanol fuel cells with reduced methanol crossover', *Journal of Membrane Science*, 541, pp. 127–136.
- Perez, E. V, Jr, K. J. B., Ferraris, J. P. and Musselman, I. H. (2009) 'Mixed-matrix membranes containing MOF-5 for gas separations', *Journal of Membrane Science*, 328(1-2), pp. 165-173.

- Pili, S., Argent, S. P., Morris, C. G., Rought, P., García-Sakai, V., Silverwood, I. P., Easun, T. L., Li, M., Warren, M. R., Murray, C. A., Tang, C. C., Yang, S. and Schröder, M. (2016) 'Proton conduction in a phosphonate-based metal-organic framework mediated by intrinsic "free diffusion inside a sphere', *Journal of the American Chemical Society*, 138(20), pp 6352–6355.
- Ponomareva, V. G., Kovalenko, K. A., Chupakhin, A. P., Dybtsev, D. N., Shutova, E. S. and Fedin, V. P. (2012) 'Imparting high proton conductivity to a metal-organic framework material by controlled acid impregnation', *Journal of the American Chemical Society*, 134(38), pp. 15640–15643.

Rajendran, R. G. (2005) 'Polymer electrolyte', MRS Bulletin, 30, pp. 587-590.

- Ramaswamy, P, Wong, N. E. and Shimizu, G. K. (2014) 'MOFs as proton conductors--challenges and opportunities', *Chemical Society Reviews*, 43, pp. 5913–5932.
- Ramaswamy, Padmini, Wong, N. E., Gelfand, B. S. and Shimizu, G. K. H. (2015) 'A Water Stable Magnesium MOF That Conducts Protons over 10⁻² S cm⁻¹', *Journal of the American Chemical Society*, 137(24), pp. 7640–7643.
- Rana, D., Matsuura, T., Narbaitz, R. M. and Feng, C. (2005) 'Development and characterization of novel hydrophilic surface modifying macromolecule for polymeric membranes', *Journal of Membrane Science*, 249(1–2), pp. 103–112.
- Ranjani, M., Jin, D. and Gnana, G. (2018) 'Sulfonated Fe₃O₄@SiO₂ nanorods incorporated sPVdF nanocomposite membranes for DMFC applications', *Journal of Membrane Science*, 555(March), pp. 497–506.
- Rao, A. S., Manjunatha, D. V., Jayarama, A., Achanta, V. G., Duttagupta, S. P. and Pinto, R. (2019) ' Power enhancement of passive micro-direct methanol fuel cells with self-sulfonation of P(VDF-TrFE) copolymer during lamination on Nafion membrane', *International Journal of Hydrogen Energy*, 44(57).
- Razi, F., Sawada, I., Ohmukai, Y., Maruyama, T. and Matsuyama, H. (2012) 'Surface Functionalization by Grafting (2-Dimethylamino) ethyl Methacrylate Methyl Chloride Quaternary Salt (DMAEMAq) onto Hollow Fiber Polyethersulfone (PES) Membranes for Improvement of Antibiofouling Properties', *Solvent Extraction Research and Development, Japan*, 19, pp. 101–115.
- Remanan, S., Sharma, M., Bose, S. and Ch, N. (2018) 'Recent advances in preparation of porous polymeric membranes by unique techniques and mitigation of fouling through surface modification', *Chemistry Select*, 3(2), pp. 609–633.

- Ren, Y., Chia, G. H. and Gao, Z. (2013) 'Metal-organic frameworks in fuel cell technologies', *Nano Today*, 8(6), pp. 577–597.
- Rowsell, J. L. C. and Yaghi, O. M. (2004) 'Metal-organic frameworks: a new class of porous materials', *Microporous and Mesoporous Materials*, 73(1-2), pp. 3-14.
- Sadakiyo, M., Yamada, T. and Kitagawa, H. (2009) 'Rational designs for highly proton-conductive metal-organic frameworks', *Journal of the American Chemical Society*, 131(29), 9906–9907.
- Sahoo, S. C., Kundu, T. and Banerjee, R. (2011) 'Helical water chain mediated proton conductivity in homochiral metal-organic frameworks with unprecedented zeolitic unh -topology', *Journal of the American Chemical Society*, 133(44), pp. 17950–17958.
- Salim, N. E., Nor, N. A. M., Jaafar, J., Ismail, A. F., Qtaishat, M. R., Matsuura, T., Othman, M. H. D., Rahman, M. A., Aziz, F. and Yusof, N. (2019) 'Effects of hydrophilic surface macromolecule modifier loading on PES/O-g-C₃N₄ hybrid photocatalytic membrane for phenol removal', *Applied Surface Science*, 465(May 2018), pp. 180–191.
- Sanabria-chinchilla, J., Kim, Y., Li, D., Baltruschat, H. and Soriaga, M. P. (2010). *Theory and experiment in electrocatalysis*. New York: Springer.
- Sen, S., Nair, N. N., Yamada, T., Kitagawa, H. and Bharadwaj, P. K. (2012) 'High proton conductivity by a metal-organic framework incorporating Zn₈O clusters with aligned inidazolium groups decorating the channels', *Journal of the American Chemical Society*, 134(47), pp. 19432-19437.
- Sen, U., Erkartal, M., Kung, C., Ramani, V. K., Hupp, J. T. and Farha, O. K. (2016) 'Proton conducting self-assembled metal-organic framework/polyelectrolyte hollow hybrid nanostructures', *Applied Materials and Interfaces*, 8(35), pp. 23015-23021.
- Shaari, N., Kamarudin, S. K., Basri, S., Shyuan, L. K., Masdar, M. S. and Nordin, D. (2018) 'Enhanced proton conductivity and methanol permeability reduction via sodium alginate electrolyte-sulfonated graphene oxide bio-membrane', *Nanoscale Research Letters*, 13.
- Shao, Z. and Hsing, I. (2002) 'Nafion membrane coated with sulfonated poly(vinyl alcohol)-nafion film for direct methanol fuel cells', *Electrochemical and Solid-State Letters*, 5(9), A185.

- Shimizu, G. K. H., Taylor, J. M. and Kim, S. (2013) 'Proton conduction with metalorganic frameworks', *Science*, 341(6144), pp. 354-355.
- Shin, D. W., Guiver, M. D. and Lee, Y. M. (2016) 'Hydrocarbon-based polymer electrolyte membranes: importance of morphology on ion transport and membrane stability', *Chemical Reviews*, 117(6), pp. 4759-4805.
- Son, N. H. and Nguyen, N.-T. (2020) 'A study in development and application of a virtual fuel cell test platform', *The Int. J. Eng. Sci.*, 9, pp. 29-37.
- Spiegel, C. (2018, March 27). Direct Methanol Fuel Cell, Improvement in Fuel Cell Basics. *Fuelcell Store*. Retrieved 2021 August 17, from http://www.fuelcellstore.com.
- Stassen, I., Campagnol, N., Fransaer, J., Vereecken, P., De Vos, D. and Ameloot, R. (2013) 'Solvent-free synthesis of supported ZIF-8 films and patterns through transformation of deposited zinc oxide precursors', *Crystal Engineering Communications*, 15, pp. 9308.
- Suk, D. E., Chowdhury, G., Matsuura, T., Narbaitz, R. M., Pleizier, G. and Deslandes, Y. (2002) 'Study on the kinetics of surface migration of surface modifying macromolecules in membrane preparation', *Macromolecules*, 35, pp. 3017-3021.
- Sun, H., Tang, B. and Wu, P. (2017) 'Two-dimensional zeolitic imidazolate framework / carbon nanotube hybrid networks modi fi ed proton exchange membranes for improving transport properties', *Applied Materials and Interfaces*, 9(40), pp. 35075-35085.
- Tao, K., Cao, L., Lin, Y., Kong, C. and Chen, L. (2013) 'A hollow ceramic fiber supported ZIF-8 membrane with enhanced gas separation performance prepared by hot dip-coating seeding', *Journal of Materials Chemistry A*, 1(3), pp. 13046–13049.
- Taylor, J. M., Dawson, K. W. and Shimizu, G. K. H. (2013) 'A water-stable metalorganic framework with highly acidic pores for proton-conducting applications', *Journal of the American Chemical Society*, 135, pp. 1193–1196.
- Thuyavan, Y. L., Anantharaman, N., Arthanareeswaran, G. and Ismail, A. F. (2016) 'Impact of solvents and process conditions on the formation of polyethersulfone membranes and its fouling behavior in lake water filtration', *Journal of Chemical Technology and Biotechnology*, 91(10), pp. 2568–2581.

- Tung, S. P. and Hwang, B. J. (2005) 'Synthesis and characterization of hydrated phosphor-silicate glass membrane prepared by an accelerated sol-gel process with water/rapor management', *Journal of Materials Chemistry*, 15(34), pp. 3532-3538.
- Umeyama, D., Horike, S., Inukai, M., Hijikata, Y. and Kitagawa, S. (2011) 'Confinement of mobile histamine in coordination nanochannels for fast proton transfer', *Angewandte Chemie - International Edition*, 50(49), 11706–11709.
- Unnikrishnan, L., Nayak, S. K., Mohanty, S. and Sarkhel, G. (2010) 'Polyethersulfone membranes: The effect of sulfonation on the properties', *Polymer - Plastics Technology and Engineering*, 49(14), 1419–1427.
- Venna, S. R., Jasinski, J. B. and Carreon, M. A. (2010) 'Structural evolution of zeolitic imidazolate framework-8', *Journal of the American Chemical Society*, 132(51), pp. 18030-18033.
- Verweij, H. (2012) 'Inorganic membranes', Current Opinion in Chemical Engineering, 1(2), pp. 156–162.
- Wang, D. and Lai, J. (2013) 'Recent advances in preparation and morphology control of polymeric membranes formed by nonsolvent induced phase separation', *Current Opinion in Chemical Engineering*, 2(2), 229–237.
- Wang, F. and Tarabara, V. V. (2008) 'Pore blocking mechanisms during early stages of membrane fouling by colloids', *Journal of Colloid and Interface Science*, 328(2), pp. 464–469.
- Wang, J., Zheng, X., Wu, H., Zheng, B., Jiang, Z., Hao, X. and Wang, B. (2008) 'Effect of zeolites on chitosan/zeolite hybrid membranes for direct methanol fuel cell', *Journal of Power Sources*, 178(1), 9–19.
- Wang, L. S., Lai, A. N., Lin, C. X., Zhang, Q. G., Zhu, A. M. and Lin, Q. (2015) 'Orderly sandwich-shaped graphene oxide / Na fi on composite membranes for direct methanol fuel cells', *Journal of Membrane Science*, 492, pp. 58–66.
- Wang, Y., Chen, K. S., Mishler, J., Cho, S. C. and Adroher, X. C. (2011) 'A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research', *Applied Energy*, 88(4), pp. 981–1007.
- Wei, Y. S., Hu, X. P., Han, Z., Dong, X. Y., Zang, S. Q. and Mak, T. C. W. (2017) 'Unique proton dynamics in an efficient mof-based proton conductor', *Journal* of the American Chemical Society, 139(9), pp. 3505–3512.

- Wu, Q. X., Zhao, T. S., Chen, R. and An, L. (2013) 'A sandwich structured membrane for direct methanol fuel cells operating with neat methanol', *Applied Energy*, 106, pp. 301–306.
- Xu, G., Otsubo, K., Yamada, T., Sakaida, S. and Kitagawa, H. (2013) 'Superprotonic conductivity in a highly oriented crystalline metal-organic framework nanofilm', *Journal of the. American Chemica. Society*, 135(20), 7438–7441.
- Xu, W., Lu, T., Liu, C. and Xing, W. (2005) 'Low methanol permeable composite Nafion/silica/PWA membranes for low temperature direct methanol fuel cells', *Electrochimica Acta*, 50(16-17), pp. 3280-3285.
- Yaghi, O. M., Davis, C. E., Li, G. and Li, H. (1997) 'Selective guest binding by tailored channels in a 3-d porous zinc (II) -benzenetricarboxylate network', *Journal of the American Chemical Society*, 119(12), pp. 2861-2868.
- Yamaguchi, B. T., Zhou, H., Nakazawa, S. and Hara, N. (2007) 'An extremely low methanol crossover and highly durable aromatic pore-filling electrolyte membrane for direct methanol fuel cells', *Advanced Materials*, 19, pp; 592-596.
- Yan, M. P. (2012). Crystal growth of the metal-organic framework ZIF-8, *PhD Thesis*, University of Manchester.
- Yan, X. H., Wu, R., Xu, J. B., Luo, Z. and Zhao, T. S. (2016) 'A monolayer graphenee Nafion sandwich membrane for direct methanol fuel cells', *Journal of Power Sources*, 311, pp. 188–194.
- Yang, C., Lee, Y. and Ming, J. (2009) 'Direct methanol fuel cell (DMFC) based on PVA / MMT composite polymer membranes', *Journal of Power Sources*, 188, pp; 30–37.
- Yang, F., Huang, H., Wang, X., Li, F., Gong, Y., Zhong, C. and Li, J. R. (2015) 'Proton conductivities in functionalized UiO-66: tuned properties, thermogravimetry mass, and molecular simulation analyses', *Crystal Growth and Design*, 15(12), pp. 5827–5833.
- Yang, L., Tang, B. and Wu, P. (2015) 'Composites : a facile method to highly improve the proton conductivity of PEMs operated under low humidity', *Journal of Materials Chemistry A: Materials for Energy and Sustainability*, 3(31), pp. 15838–15842.
- Yao, J., Dong, D., Li, D., He, L., Xu, G. and Wang, H. (2011) 'Contra-diffusion synthesis of ZIF-8 films on a polymer substrate', *Chemical Communications*, 47(9), pp. 2559-2561.

- Yee, R. S. L., Zhang, K. and Ladewig, B. P. (2013) 'The effects of sulfonated poly(ether ether ketone) ion exchange preparation conditions on membrane properties', *Membranes*, 3(3), pp. 182-195.
- Yeow, M. L., Liu, Y. T. and Li, K. (2004) 'Morphological study of poly (vinylidene fluoride) asymmetric membranes : effects of the solvent , additive , and dope temperature', *Journal of Applied Polymer Science*, 92(3), pp. 1782-1789.
- Yoon, M., Suh, K., Natarajan, S. and Kim, K. (2013) 'Proton conduction in metalorganic frameworks and related modularly built porous solids', *Angewandte Chemie - International Edition*, 52, 2688–2700.
- Zaidi, S. M. J. (2005) 'Preparation and characterization of composite membranes using blends of SPEEK / PBI with boron phosphate', *Electrochimica Acta*, 50, pp. 4771–4777.
- Zanon, A., Chaemchuen, S., Mousavi, B. and Verpoort, F. (2017) '1 Zn-doped ZIF-67 as catalyst for the CO₂ fixation into cyclic carbonates', *Journal of CO₂ Utilization*, 20(July), pp. 282–291.
- Zhang, B., Cao, Y., Li, Z., Wu, H., Yin, Y. and Cao, L. (2017) 'Proton exchange nanohybrid membranes with high phosphotungstic acid loading within metalorganic frameworks for PEMFC applications', *Electrochimica Acta*, 240, pp. 186–194.
- Zhang, H., Liu, D., Yao, Y., Zhang, B. and Lin, Y. S. (2015) 'Stability of ZIF-8 membranes and crystalline powders in water at room temperature', *Journal of Membrane Science*, 485, pp. 103–111.
- Zhang, L., Chae, S., Hendren, Z., Park, J. and Wiesner, M. R. (2012) 'Recent advances in proton exchange membranes for fuel cell applications', *Chemical Engineering Journal*, 204–206, pp. 87–97.
- Zhao, D., Shui, J.-L., Chen, C., Chen, X., Reprogle, B. M., Wang, D. and Liu, D.-J. (2012) 'Iron imidazolate framework as precursor for electrocatalysts in polymer electrolyte membrane fuel cells', *Chemical Science*, 3, pp. 3200– 3205.
- Zheng, K. and Shen, S. (2018) 'The microstructure effect on ion conduction in composite electrolyte', *International Journal of Energy Research*, 42, pp. 4229-4234.
- Zuo, Z., Fu, Y. and Manthiram, A. (2012) 'Novel blend membranes based on acidbase interactions for fuel cells', *Polymers*, 4, pp. 1627-1644.

LIST OF PUBLICATIONS

Journal with Impact Factor

- Junoh, H., Jaafar, J., Nordin, N. A. H., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Aziz, F., Yusof, N., & Daud, S. N. S. S. (2021). Porous polyether sulfone for direct methanol fuel cell application: Structural analysis. *International Journal of Energy Research*. 45(2), 2277-2291 (Q1, IF: 3.741).
- Junoh, H., Jaafar, J., Nordin, N. A. H., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Aziz, F., & Yusof, N. (2020). Performance of polymer electrolyte membrane for direct methanol fuel cell application: Perspective on morphological structure. *Membranes*. 10(3), 34 (Q2, IF: 3.094).

Indexed Journal

- Junoh, H., Jaafar, J., Nordin, N. A. H., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Aziz, F., Yusof, N., & Salleh, W. N. W. (2019). Porous proton exchange membrane based zeolitic imidazolate framework 8 (ZIF-8). *Journal* of Membrane Science and Research. 5(1), 65-75 (Indexed by Scopus).
- Junoh, H., Jaafar, J., Nordin, N. A. H., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Yusof, N., & Aziz, F. (2021). Inclusion of zeolitic imidazolate framework-8 (ZIF-8) crystals within porous polyether sulfone (PES) via filtration methods as potential electrolytes for DMFC applications. *Materials Today: Proceedings*. (Indexed by Scopus- *in press*).

Indexed and Non-Indexed Conference Proceedings

 Junoh, H., Jaafar, J., Nordin, N. A. H., & Ismail, A. F. (2018). Fabrication of porous poly ether sulfone by non-solvent induced phase separation (NIPS) techniques. 7th International graduate conference on engineering, science and humanities (*IGCESH*), Universiti Teknologi Malaysia, Johor. 13-15 August. (Abstract, Indexed by Scopus)

Book Publications

 Junoh, H., Jaafar, J., Nordin, N. A. H., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Aziz, F., & Yusof, N. (2020). Chapter 15- Synthetic polymerbased membranes for direct methanol fuel cell (DMFC) applications. In Synthetic Polymeric Membranes for Advanced Water Treatment, Gas Separation, and Energy Sustainability. 337-363. Elsevier