STABILITY OF SPEEK NANOCOMPOSITE MEMBRANE UNDER FENTON REAGENT TEST FOR DIRECT METHANOL FUEL CELL APPLICATION

MUHAMMAD TAUFIQ BIN SALLEH

UNIVERSITI TEKNOLOGI MALAYSIA

STABILITY OF SPEEK NANOCOMPOSITE MEMBRANE UNDER FENTON REAGENT TEST FOR DIRECT METHANOL FUEL CELL APPLICATION

MUHAMMAD TAUFIQ BIN SALLEH

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Gas)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

OCTOBER 2016

To Allah

To my beloved father and mother

To my loving family

Thank you.

ACKNOWLEDGEMENT

First of all, I would like to express my deepest gratitude to Allah for giving me strength, courage and fortitude to face my study to graduation. Without His help I might not be able to finish my studies. A million thanks to my father and mother as well as all my family members for their continuous love, moral support and trust. You all are the source of my strength and the drive to my success today.

During my 3 years' study, I have met with many academics and researchers who help a lot in my research process. Heartfelt appreciation goes out to my supervisor, Dr. Juhana binti Jaafar for her advice and guidance over the years. She is like a mother who always cares and gives advice to her students to strive for success. Millions of appreciation also goes to my co-supervisor, Dr. Noorul Anam bin Mohd Norddin for all his opinions, suggestions and thoughts that have been granted to the success of my research.

I also would like to thanks all my fellow friends especially my colleague from AMTEC; Mohamad Azuwa, Muhazri, Mohd Hilmi, Azlan, Arif Akmal, Hanis, Syafikah Huda, Siti Halimah, Noor Shuhaida, Siti Munira, Nur Azureen, Siti Nurfatin Nadhirah, Norfazliana, Nurfadhilatuladha, Hazlina, Nik Nurdhiya, Siti Hidayana, Wan Noor Ezianti, Nuha, Fatin Ermala, and others. Thank you for all of your assistance, support and shared happiness throughout my studies. Last but not least, I would like to express my gratitude to UTM and AMTEC for providing funding and facilities to ensure the success of my research.

ABSTRACT

In this study, the stability of sulfonated poly ether ether ketone (SPEEK) nanocomposite membrane against the radical attack during direct methanol fuel cell (DMFC) operation was elucidated by the Fenton reagent test. The nanocomposite membrane was soaked in the Fenton reagent solution with 0.8, 3, 12, and 50 ppm iron salts concentration for 6, 12, 24, 48, and 96 hours, respectively at room temperature. Pristine SPEEK and Nafion® 117 membranes were used as control samples. The results indicate that the presence of Cloisite® inorganic particles can improve the stability of SPEEK nanocomposite membrane against the radical attack and allowed the nanocomposite membrane to maintain its weight comparable to Nafion® 117 membrane up to 48 hours of testing. The Fourier transform infrared spectroscopy characterization combined with density functional theory study showed that both the C–O–C and $–SO_3H$ bonding with phenylene ring, and hydrogen bonding between the SPEEK, Cloisite®, and 2,4,6-triaminopyrimidine components were the most vulnerable to the radical attack. Loss of these functional groups has caused structural deformation, deterioration of mechanical strength, and changes of hydrophilicity in the SPEEK nanocomposite membrane. Additionally, the changes in its chemical structure have caused its water uptake, proton conductivity, and methanol barrier properties to drop, up to 2 times higher than the Nafion® 117 membrane. However, the selectivity value of the SPEEK nanocomposite membrane (27,037 $S \cdot s/cm^3$) remained higher than the Nafion® 117 membrane (3,292 $S \cdot s/cm^3$) due to the SPEEK nanocomposite membrane's lower methanol permeability value (2.72×10^{-7} cm^2/s) as compared to Nafion® 117 membrane (2.95×10^{-6} cm^2/s). Based on the correlation graph, the SPEEK nanocomposite membrane is predicted to have 9,800 hours' lifespans as polymer electrolyte membrane (PEM) in the DMFC system. As a conclusion, this study has proven that the SPEEK nanocomposite membrane has good stability in DMFC harsh environment and suitable to be employed as PEM for high performance and long lifespan DMFC system.

ABSTRAK

Dalam kajian ini, kestabilan membran komposit nano poli eter eter keton tersulfonat (SPEEK) terhadap serangan radikal ketika operasi bahan api metanol (DMFC) telah diterangkan menggunakan ujian bahan uji Fenton. Membran komposit nano telah direndam di dalam larutan bahan uji Fenton dengan kepekatan garam besi 0.8, 3, 12, dan 50 ppm masing-masing selama 6, 12, 24, 48, dan 96 jam pada suhu bilik. Membran SPEEK asli dan Nafion® 117 telah digunakan sebagai sampel kawalan. Keputusan menunjukkan bahawa kehadiran partikel tak organik Cloisite® boleh meningkatkan kestabilan membran komposit nano SPEEK terhadap serangan radikal dan membolehkan membran ini mengekalkan beratnya setanding dengan membran Nafion® sehingga 48 jam. Gabungan spektroskopi inframerah transformasi Fourier dan kajian ketumpatan teori berfungsi menunjukkan ikatan C-O-C dan -SO_3H dengan gelang fenilena, dan ikatan hidrogen antara SPEEK, Cloisite® dan 2,4,6-triaminopirimidina adalah yang paling lemah terhadap serangan radikal. Kehilangan kumpulan berfungsi ini menyebabkan berlakunya perubahan struktur, kemerosotan kekuatan mekanikal dan perubahan kehidrofilikan kepada membran komposit nano SPEEK. Tambahan pula, perubahan struktur kimia membran komposit nano SPEEK menyebabkan sifat penyerapan air, kekonduksian proton dan halangan metanol menyusut sehingga 2 kali lebih tinggi dari membran Nafion®. Namun begitu, kememilihan membran komposit nano SPEEK kekal lebih tinggi (27,037 S.s/cm^3) daripada membran Nafion® (3,292 S.s/cm^3) kerana nilai kebolehtelapan metanol membran komposit nano SPEEK yang rendah (2.72×10^{-7} cm^2/s) berbanding membran Nafion® 117 (2.95×10^{-6} cm^2/s). Berdasarkan graf korelasi, membran komposit nano SPEEK dijangka mempunyai jangka hayat selama 9,800 jam sebagai membran elektrolit polimer (PEM) di dalam sistem DMFC. Sebagai kesimpulan, kajian ini membuktikan bahawa membran komposit nano SPEEK mempunyai kestabilan yang baik terhadap persekitaran DMFC yang buruk dan sesuai digunakan sebagai PEM untuk sistem DMFC yang berprestasi tinggi dan mempunyai jangka hayat yang panjang.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	**ii**
	DEDICATION	**iii**
	ACKNOWLEDGEMENT	**iv**
	ABSTRACT	**v**
	ABSTRAK	**vi**
	TABLE OF CONTENTS	**vii**
	LIST OF TABLES	**x**
	LIST OF FIGURES	**xi**
	LIST OF ABBREVIATIONS	**xiii**
	LIST OF SYMBOLS	**xiv**
	LIST OF APPENDICES	**xv**
1	**INTRODUCTION**	1
	1.1 Research Background	1
	1.2 Problem Statements	6
	1.3 Research Objectives	7
	1.4 Research Scopes	7
2	**LITERATURE REVIEW**	9
	2.1 Direct Methanol Fuel Cell	9
	2.1.1 Membrane Electrode Assembly	12
	2.1.1.1 Perfluorosulfonic Acid Membrane	13
	2.1.1.2 Non-Fluorinated Membrane	15
	2.1.1.3 Nanocomposite Organic-Inorganic Membrane	18
	2.2 Problems with Direct Methanol Fuel Cell	22

2.2.1 Direct Methanol Fuel Cell Lifetime and Accelerated Stress Test 24

3 RESEARCH METHODOLOGY 36

3.1 Research Design 36

3.2 Chemicals and Materials 38

3.3 Fabrication of Pristine SPEEK and SPEEK Nanocomposite Membrane 38

3.4 Fenton Reagent Test 40

3.5 Physicochemical Changes of Pristine SPEEK and SPEEK Nanocomposite Membranes after Fenton Reagent Test 43

3.5.1 Field Emission Scanning Electron Microscopy 43

3.5.2 Tensile Strength Test 43

3.5.3 Contact Angle Measurement 44

3.5.4 Fourier Transform Infrared Spectroscopy 45

3.6 Changes of SPEEK Nanocomposite and Nafion® 117 Membranes' Properties after Fenton Reagent Test 45

3.6.1 Water Uptake Test 45

3.6.2 Proton Conductivity Test 46

3.6.3 Methanol Permeability Test 47

3.6.4 Membrane Selectivity 48

3.7 Lifetime Estimation of SPEEK Nanocomposite Membrane in Direct Methanol Fuel Cell Application 48

4 RESULTS AND DISCUSSION 51

4.1 Stability of Pristine SPEEK, SPEEK Nanocomposite and Nafion 117 Membranes under Fenton Reagent Test 51

4.2 Physicochemical Changes of Pristine SPEEK and SPEEK Nanocomposite Membrane after Fenton Reagent Test 53

4.2.1 Morphological Analysis of Pristine SPEEK and SPEEK Nanocomposite Membranes after Fenton Reagent Test 54

4.2.2 Tensile Strength Analysis of Pristine SPEEK and SPEEK Nanocomposite Membranes after Fenton Reagent Test 58

4.2.3 Contact Angle Analysis 60

4.2.4 FT-IR Spectra Analysis of Pristine SPEEK and SPEEK Nanocomposite Membranes after Fenton Reagent Test 61

4.2.5 Chemical Degradation Mechanisms of SPEEK Nanocomposite Membrane via Free Radical Attack 67

4.3 Changes of SPEEK Nanocomposite and Nafion 117 Membranes' Properties after Fenton Reagent Test 68

4.3.1 Water Uptake of SPEEK Nanocomposite and Nafion® 117 Membranes after Fenton Reagent Test 69

4.3.2 Proton Conductivity of SPEEK Nanocomposite and Nafion® 117 Membranes after Fenton Reagent Test 71

4.3.3 Methanol Permeability of SPEEK Nanocomposite and Nafion® 117 Membranes after Fenton Reagent Test 73

4.3.4 Membrane Selectivity of SPEEK Nanocomposite and Nafion® Membrane after Fenton Reagent Test 77

4.3.5 Lifetime Estimation of SPEEK Nanocomposite Membrane in Direct Methanol Fuel Cell Application 79

5 CONCLUSIONS AND RECOMMENDATIONS 81

5.1 Conclusions 81

5.2 Recommendations for Future Work 82

REFERENCES 84

APPENDIX A 98

LIST OF TABLES

TABLE NO.	TITLE	PAGE
1.1	Types of Fuel Cell.	4
2.1	Development of DMFC prototypes by various organizations [10].	11
2.2	SPEEK nanocomposite membrane performances as compared to Nafion® 112 membrane [19].	22
2.3	Experimental studies on the DMFC durability.	25
2.4	AST test for DMFC lifetime analysis [24].	30
2.5	Previous experimental studies using Fenton reagent test.	33
3.1	Fenton reagent test procedure.	42
3.2	Concentration of OH• radical exposed to membranes under Fenton reagent test.	49
4.1	IR spectrum band for pristine SPEEK membrane's functional group.	62
4.2	Intensity of pristine SPEEK membrane's peaks.	63
4.3	IR spectrum band for SPEEK nanocomposite membrane's functional group.	64
4.4	Intensity of SPEEK nanocomposite membrane's peaks.	66
4.5	Water uptake reduction of SPEEK nanocomposite and Nafion 117 membranes after 96 hours Fenton reagent test.	71
4.6	Proton conductivity reduction of SPEEK nanocomposite and Nafion 117 membranes after 96 hours Fenton reagent test.	73
4.7	Methanol permeability increment of SPEEK nanocomposite and Nafion 117 membranes after 96 hours Fenton reagent test.	76
4.8	Selectivity of SPEEK nanocomposite and Nafion 117 membranes after 96 hours Fenton reagent test.	78

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	A basic fuel cell diagram.	3
2.1	Electrochemical reactions of DMFC [32].	10
2.2	Chemical structures of PFSA membrane [43].	14
2.3	Chemical structures of SPEEK polymer [48], [51].	15
2.4	Water channel formations of Nafion and SPAEK based membranes [52].	17
2.5	Water uptake of SPEEK membrane [32].	18
2.6	Chemical structure of MMT particles.	19
2.7	Chemical structures of dimethyl, dihydrogenated tallow, quaternary ammonium salt surfactant.	20
2.8	Chemical structures of 2,4,6-triaminopyrimidine (TAP).	21
2.9	Impact of well dispersed Cloisite particles in SPEEK/Cloisite/TAP nanocomposite membrane structure to membrane's proton conductivity and methanol permeability properties.	22
3.1	Research design flow chart.	37
3.2	Sulfonation process of PEEK polymer.	38
3.3	Fabrication process of pristine SPEEK membrane.	39
3.4	Fabrication process of SPEEK nanocomposite membrane.	40
3.5	Fenton reagent solution preparation.	41
3.6	Fenton reagent test procedure.	42
3.7	Contact angle measurement.	44
3.8	Schematic diagram of proton conductivity testing cell.	46
3.9	Diffusion cell for methanol permeability test.	48
4.1	Residual weight of pristine SPEEK, SPEEK nanocomposite and Nafion 117 membranes after 96 hours Fenton reagent test.	52
4.2	FESEM images of pristine SPEEK membrane's surface before (a) and after 6 h (b), 12 h (c) and 24 h (d) of Fenton reagent test.	55

4.3	FESEM images of SPEEK nanocomposite membrane's surface before (a) and after 6 h (b), 12 h (c), 24 h (d), 48 h (e), and 96 h (f) of Fenton reagent test.	56
4.4	EDX analysis on particles agglomeration on SPEEK nanocomposite membrane's surface. Image (a) is the SEM image of SPEEK nanocomposite membrane, image (b) and (c) are the dispersion of silicon and aluminium elements on the membrane's surface, and image (d) is the EDX spectra and molecular structure of montmorillonite clay.	57
4.5	Tensile strength changes of pristine SPEEK and SPEEK nanocomposite membranes after Fenton reagent test.	59
4.6	Contact angle of pristine SPEEK and SPEEK nanocomposite membranes after Fenton reagent test.	61
4.7	FTIR spectrum of pristine SPEEK membrane.	62
4.8	FTIR spectrum of SPEEK nanocomposite membrane between (a) 2800-3800 cm^{-1} and (b) 1000-1700 cm^{-1} after 96 h Fenton reagent test.	65
4.9	Suggested chemical degradation mechanisms for SPEEK nanocomposite membrane.	68
4.10	Water uptake of SPEEK nanocomposite and Nafion 117 membranes throughout 96 hours of Fenton reagent test.	70
4.11	Proton conductivity of SPEEK nanocomposite and Nafion 117 membranes after going through Fenton reagent test for 96 h.	72
4.12	Methanol permeability changes of SPEEK nanocomposite and Nafion 117 membranes after undergo 96 h Fenton reagent test.	75
4.13	Calibration curve of Fenton reagent test and DMFC lifetime test.	80

LIST OF ABBREVIATIONS

AST	-	Accelerated stress test
DMFC	-	Direct methanol fuel cell
PEMFC	-	Polymer electrolyte membrane fuel cell
PEEK	-	Poly (ether ether) ketone
PFSA	-	Perfluorosulfonic acid membrane
SPEEK	-	Sulfonated poly (ether ether) ketone
N117	-	Nafion® 117
CL	-	Cloisite® 15A
TAP	-	2,4,6-triaminopyrimidine
SP/CL/TAP	-	Sulfonated poly (ether ether) ketone/Cloisite® 15A/2,4,6-triaminopyrimidine nanocomposite membrane
PEM	-	Polymer electrolyte membrane
EERE	-	Office of Energy Efficiency and Renewable Energy, United States of America
PAEK	-	Poly aryl ether ketone

LIST OF SYMBOLS

O_2	-	Oxygen gas
H_2	-	Hydrogen gas
Pt	-	Platinum
H_2SO_4	-	sulfuric acid
H_2O_2	-	hydrogen peroxide
SO_3H	-	sulfonate acid group

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
Appendix A	List of Publications	79

CHAPTER 1

INTRODUCTION

1.1 Research Background

The energy sector is one of the important sectors in modern civilizations. Industries, transportations, accommodations, appliances activities and practices have contributed to the expansion of the energy production industry. Based on the British Petroleum Statistical Review of World Energy 2015 [1], the world's energy consumption in 2014 was 12,928 million tonnes of equivalent oils, which have increased by 0.9 % from 2013. It is expected that energy demands will continue to increase in the future due to population expansion and increasing demands. The statistics also mentioned that 86.3 % of world energy consumption is coming from carbon-based fuels (oil, natural gas, and coal). The use of carbon-based fuels has produced carbon dioxide (CO_2) and several greenhouse gases, which give the huge negative impact on the environment and climate [2]. According to International Energy Agency [3], the CO_2 emission comes from the energy production sector has increased more than 50 % in two and half decades period (1990-2015). This phenomenon had caused the Earth's temperature to rise up to 4 °C higher than the Earth's temperature during the early Industrial Age period [4]. Ice polar cap melting, sea water level rising, flood, famine, and formation of extreme weather are several impacts that result from the heated Earth's atmosphere due to the greenhouse effect from the excessive release of greenhouse gases to the atmosphere. The high CO_2 content in our atmosphere also causes an increase in the acidity of the oceans and fresh water. This situation has affected the Earth's biosphere and ecosystem since water is essential for all living things to survive on earth. Thus, development and investment in renewable and environmentally friendly energy production technologies are crucial in order to preserve and sustain our nature for future generations.

Fuel cell is one of renewable energy technologies that have been proposed as a potential technology to replace conventional energy production. A fuel cell is an electrochemical device that converts free energy from redox reaction directly into electrical energy with heat energy as the by-product [5]. Figure 2.1 shows the schematic diagram of the typical fuel cell operation. There are several advantages that attract researchers to develop fuel cell as the next generation of energy production technology. Since fuel cell generates electricity directly from the chemical reaction using electrochemical principle, the energy loss due to heat production is lower than the conventional energy production technology, which can increase the fuel cell energy conversion efficiency. O'Hayre *et al.* [6] stated in their book (*Fuel Cell Fundamental*s) that the fuel cell efficiency is around 60 %, which is higher than any conventional energy production, which has efficiency around 40 % only. Higher energy conversion efficiency means that the fuel cell needs less fuel to produce similar energy output as generated by the existing energy production technology. Therefore, the fuel cell will produce less greenhouse gas by-products as compared to the established energy production technology. This can reduce the carbon footprint issue [6]. Other than that, fuel cell system is simple since the fuel cell only needs anode and cathode electrode layer, and an electrolyte to produce electricity. Therefore, the fuel cell can be scaled up or scaled down according to the energy requirement, whereby the fuel cell does not experience energy losses issue when scaling down to smaller size as compared to gas turbines or reciprocating engines [7]. Based on these benefits of the fuel cell such as low emission, high efficiency, simple system, and smaller footprint, it is expected that the fuel cell holds a good potential to be commercialized as the next generation energy production technology in the future [8].

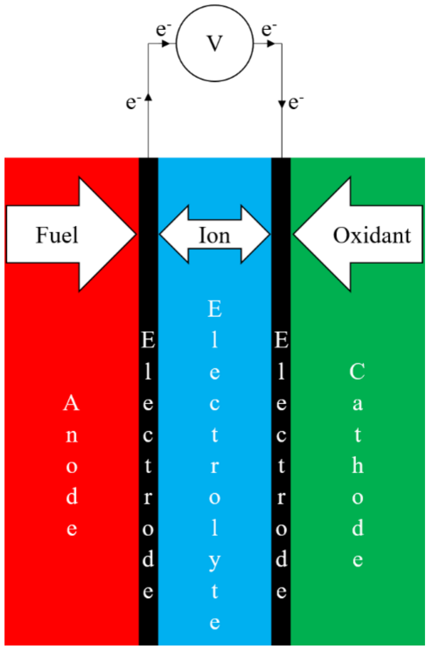

Figure 1.1 A basic fuel cell diagram.

Several types of fuel cells have been developed since its first invention by Sir William Groove in 1839 [9]. The current fuel cell technology can be classified based on three criteria: operating temperature, electrolyte used and fuel consumed. Table 1.1 tabulates all fuel cell types with their corresponding operating temperature, its electrolyte, fuel used, and their efficiency. Direct methanol fuel cell (DMFC) is one types of fuel cell that utilize methanol as its fuel. DMFC operates at low operating temperature, use liquid fuel, which simplifies fuel refuelling and handling, emit minimal CO_2 gas by-product, and theoretically has high energy density, and high efficiency [10]. Due to its simple system design and easy to scale down, researchers are working on DMFC actively. It is believed that DMFC can become the future replacement of the energy source for portable devices.

Table 1.1 Types of Fuel Cell.

Fuel Cell Type	Fuel	Electrolyte	Operating Temperature	Efficiency
PEMFC	H_2	Polymeric membrane	<150 °C	40-50%
DMFC	CH_3OH	Polymeric membrane	<100 °C	30-40%
DEFC	C_2H_5OH	Polymeric membrane	<100 °C	30-40%
MFC	$C_6H_{12}O_6$	Polymeric membrane	<40 °C	40-50%
AFC	H_2	KOH alkaline solution	80-200 °C	45-60%
PAFC	H_2	Concentrated H_3PO_4 acid	200-250 °C	40-45%
MCFC	CH_4, CO, H_2	Molten Li-K carbonate	600-700 °C	45-55%
SOFC	CH_4, CO, H_2	Ion conducting ceramic	700-1000 °C	50-65%
DCFC	Coal	Ion conducting ceramic	600 °C - 1000 °C	40-60%

Since the invention of the world first mobile phone by Joel Engel on 3 April 1973, portable and wearable devices have become part of human society [11]. Each iteration of new mobile gadget introduced more powerful processor than their predecessor and become more "intelligent" to help mankind to cope with their daily activities. Despite that, the use of lithium-ion battery to power the mobile appliances still limiting the portability of the devices because of its limited power capacity. Moreover, an external charger is needed to recharge the battery after the power stored in the battery is drained [12]. Due to these limitations, the DMFC has advantages over lithium battery because it can supply continuous power to the mobile devices as long as the fuel is available. In addition, since the methanol fuel is in liquid form, it is easy to carry around and refill when it is needed. However, in real-life applications, the DMFC suffers from low energy density and low efficiency. This is due to the occurrence of methanol crossover problem in commercial Nafion® polymer electrolyte membrane (PEM) that creates an internal shorting and reduce the DMFC power output [13]. Thus, the new membrane with better methanol barrier properties is needed in order to overcome this problem and improves the DMFC performance and efficiency.

Sulfonated poly ether ether ketone or also known as SPEEK is one of the non-fluorinated polymers that has potential to be develop as high performance PEM for DMFC operation due to its high chemical stability and thermal stability [14], decent proton conductivity, and low methanol permeability properties [15], [16]. However, high water uptake properties of SPEEK membrane due to the high concentration of sulfonated acid groups in its structure have reduced the mechanical stability of the membrane. Therefore, modification of SPEEK membrane by adding inorganic particles has been done by various researchers to overcome its high water uptake problem and improves the membrane's performance.

Montmorillinite (MMT) is one of the inorganic particles that have been integrated with SPEEK polymer membrane due to its high cation exchange capacity, surface area, surface reactivity, and adsorptive properties. The MMT also has the high length to width aspect ratio, which creates longer diffusion path for methanol to permeate [17]. Incorporation of Cloisite® 15A particles (a modified commercial MMT) into SPEEK matrix can improve the proton conductivity and methanol permeability of SPEEK/Cloisite composite membrane as compared to pristine SPEEK membrane [18].

However, the Cloisite® particles fail to disperse homogenously in SPEEK matrices due to poor interaction between SPEEK polymer and Cloisite® particles. This leads to severe agglomeration of Cloisite® particles on the SPEEK/Cloisite® membrane's surface. Thus, in order to solve the Cloisite® dispersion problem, Jaafar *et al.* [19] added 2,4,6-triaminopyrimidine (TAP) as a compatibilizer to improve the interaction between SPEEK polymer and Cloisite® particles. The NH_2 functional groups in TAP chemical structure have properties to form strong bonding with both organic polymer and inorganic particles [20], which provides an additional interaction site for SPEEK and Cloisite® to form bonding, thus improves the dispersion of Cloisite® particles in SPEEK matrices [18]. The new developed SPEEK nanocomposite membrane with 2.5% Cloiste® particles loading and 5.0% loading of TAP compatibilizer was able to outperform the commercial Nafion® 112 membrane in term of proton conductivity, methanol permeability, and produce the higher power output in DMFC performance test. Thus, this type of nanocomposite membrane has good potential to be developed as the new high performance PEM membrane for DFMC applications.

Even though DMFC has high theoretical energy density and efficiency, the DMFC performance in real-life application was lower than expected. Methanol crossover, cathode flooding, mechanical fatigue, and chemical degradation are several problems that caused DMFC performance to deteriorate as time goes by, thus shorten its lifespan. DMFC lifetime test was used to study DMFC lifespan in order to achieve 5,000 hours operational lifespan as outlined in the United States Hydrogen Energy Program report [21], [22]. However, conducting DMFC lifetime test is not practical because it requires lengthy testing time and consumes large resources [23], [24]. Moreover, the test can only assess the overall durability of the system, not the individual components. Thus, accelerated stress test (AST) is introduced as an alternative test to study fuel cell lifetime and degradation mechanisms that occurred during its operation.

AST is a term used for a group of tests which expose the fuel cell to similar real-life DMFC working condition. However, the test is conducted at a higher degree of severity to shorten the testing time [25]. Fenton reagent test is one of AST tests that used to study the effect of radical attack towards PEM's durability as the production of free radical in Fenton reagent solution is similar to the production of free radical during DMFC operation [26]. Furthermore, the Fenton reagent test is done externally, which is outside the DMFC operation. Therefore, the Fenton reagent test can be used to study the durability of the membrane solely without taking into consideration of the durability of other DMFC components [27].

1.2 Problem Statements

Even though the SPEEK nanocomposite membrane shows a better performance than commercial Nafion® membrane in term of proton conductivity, methanol permeability, and power output, so far, there is no research reported on the durability of this membrane in the DMFC application. Durability and stability test for

PEM membrane using Fenton reagent test is more feasible than the DMFC lifetime test due to shorter testing time, and its ability to study the durability of PEM membrane solely without taking into consideration of the durability of other DMFC components. At the same time, the Fenton reagent test can replicate similar radical formation that occur during the DMFC operation. Many studies have been done to study the durability of PEM membrane against radical attack using the Fenton reagent test [23], [25], [28]. However, most of the research only reported on the stability of the testing membrane against radical attack, and only a few follow-up study was conducted to determine the impact of radical attack towards PEM membrane's physicochemical characteristics. Thus, this study was designed to study the impact of radical attack towards SPEEK nanocomposite membrane's physicochemical characteristics and properties related to DMFC operation.

1.3 Research Objectives

Based on the problem statements stated in section 1.2, several objectives were proposed in order to address these problems:

1) To study the physicochemical changes of SPEEK nanocomposite membrane and determine the weak bonds in SPEEK nanocomposite structure.
2) To study the changes of SPEEK nanocomposite membrane's properties related to DMFC operation after Fenton reagent test and correlate the lifetime of SPEEK nanocomposite membrane in DMFC operation.

1.4 Research Scopes

Based on research objectives as outlined above, several scopes were outlined in order to achieve these objectives:

1) Preparing SPEEK nanocomposite solution using solution intercalation method and casting the SPEEK nanocomposite membrane using modified phase inversion technique. The Cloisite® and TAP loadings were 2.5 wt% and 5.0 wt% respectively.
2) Conducting the Fenton reagent degradation test for SPEEK nanocomposite membrane at room temperature using 5 wt% hydrogen peroxide solution and four different ferum ion (Fe^{2+}) concentrations (0.8, 3.0, 12.0, and 50.0 ppm) from 6 to 96 hours.
3) Characterizing the physicochemical of degraded SPEEK nanocomposite membrane using field emission scanning electron microscopy (FESEM), tensile strength, contact angle and Fourier transform infrared spectroscopy (FTIR). Pristine SPEEK membrane is used as a control sample and comparison.
4) Correlating the physicochemical characterization of SPEEK nanocomposite membrane with density functional theory (DFT) by Zhao *et al.* [29] to predict the weak bonds in SPEEK nanocomposite membrane structure that vulnerable to free radical attack.
5) Evaluating the membrane properties of SPEEK nanocomposite membrane in terms of water uptake, proton conductivity, methanol permeability and selectivity. Nafion® 117 membrane is used as a control sample and comparison.
6) Correlating the selectivity of SPEEK nanocomposite membrane in Fenton reagent test with DMFC lifetime test to predict the lifetime of SPEEK nanocomposite membrane in DMFC operation.

REFERENCES

[1] British Petroleum, “BP Statistical Review of World Energy,” London, UK, 2015.

[2] J. Hansen, M. Sato, P. Kharecha, D. Beerling, R. Berner, V. Masson-Delmotte, M. Pagani, M. Raymo, D. L. Royer, and J. C. Zachos, “Target Atmospheric CO2: Where Should Humanity Aim?,” *Open Atmos. Sci. J.*, vol. 2, no. 1, pp. 217–231, 2008.

[3] International Energy Agency, “Energy and Climate Change: World Energy Outlook Special Report,” Paris, France, 2015.

[4] United Nations Environment Programme, “Global Environment Outlook 5 (GEO-5),” Valletta, Malta, 2012.

[5] L. Carrette, A. Friedrich, and U. Stimming, “Fuel Cells - Fundamentals and Applications,” *Fuel Cells - Fundam. Appl. Wiley online Libr.*, vol. 1, no. 1, pp. 5–39, May 2001.

[6] R. O’Hayre, S.-W. Cha, W. G. Colella, and F. B. Prinz, *Fuel Cell Fundamentals*, 2nd ed. New Jersey, US: Wiley, 2009.

[7] S. Giddey, S. P. S. Badwal, A. Kulkarni, and C. Munnings, “A comprehensive review of direct carbon fuel cell technology,” *Prog. Energy Combust. Sci.*, vol. 38, no. 3, pp. 360–399, 2012.

[8] S. Srinivasan, *Fuel Cells*, 1st ed. New York, NY: Springer New York, 2013.

[9] L. J. M. J. Blomen and M. N. Mugerwa, *Fuel Cell Systems*, 1st ed. Boston, MA: Springer US, 2013.

[10] A. S. Aricò, V. Baglio, and V. Antonucci, “Direct Methanol Fuel Cells: History, Status and Perspectives,” in *Electrocatalysis of Direct Methanol Fuel Cells: From Fundamentals to Applications*, 1st ed., H. Liu and J. Zhang, Eds. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2009, pp. 1–78.

[11] T. Murphy, "40 Years After the First Cell Phone Call: Who Is Inventing Tomorrow's Future?," *IEEE Consum. Electron. Mag.*, vol. 2, no. 4, pp. 44–46, Oct. 2013.

[12] A. Kundu, J. H. Jang, J. H. Gil, C. R. Jung, H. R. Lee, S. H. Kim, B. Ku, and Y. S. Oh, "Micro-fuel cells-Current development and applications," *J. Power Sources*, vol. 170, no. 1, pp. 67–78, 2007.

[13] S. P. Nunes, B. Ruffmann, E. Rikowski, S. Vetter, and K. Richau, "Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells," *J. Memb. Sci.*, vol. 203, no. 1–2, pp. 215–225, Jun. 2002.

[14] D. J. L. Brett, M. Manage, E. Agante, N. P. Brandon, E. Brightmann, R. J. C. Brown, I. Staffell, D. J. Jones, C. Hartnig, L. Jorissen, J. Scholta, W. Lehnert, J. S. Cooper, S. Grot, S. Knights, K. J. J. Mayrhofer, M. Arenz, P. Trogadas, T. F. Fuller, P. P. Mukherjee, V. P. Schulz, J. Becker, E. Glatt, A. Wiegmann, J. Hinebaugh, A. Bazylak, A. A. Franco, F. Lapicque, S. Didierjean, C. Bonnet, D. Conteau, and O. Lottin, *Polymer Electrolyte Membrane and Direct Methanol Fuel Cell Technology Volume 1: Fundamentals and Performance of Low Temperature Fuel Cells*, 1st ed. Cambridge: Elsevier, 2012.

[15] M. H. D. Othman, a F. Ismail, and a Mustafa, "Physico-Chemical Study of Sulfonated Poly (Ether Ether Ketone) Membranes for Direct Methanol Fuel Cell Application," *Malaysian Polym. J.*, vol. 2, no. 1, pp. 10–28, 2007.

[16] J. Jaafar, A. F. Ismail, and A. Mustafa, "Physicochemical study of poly(ether ether ketone) electrolyte membranes sulfonated with mixtures of fuming sulfuric acid and sulfuric acid for direct methanol fuel cell application," *Mater. Sci. Eng. A*, vol. 460–461, pp. 475–484, Jul. 2007.

[17] J.-M. Thomassin, C. Pagnoulle, G. Caldarella, A. Germain, and R. Jérôme, "Contribution of nanoclays to the barrier properties of a model proton exchange membrane for fuel cell application," *J. Memb. Sci.*, vol. 270, no. 1–2, pp. 50–56, Feb. 2006.

[18] J. Jaafar, A. F. Ismail, and T. Matsuura, "Effect of dispersion state of Cloisite15A® on the performance of SPEEK/Cloisite15A nanocomposite membrane for DMFC application," *J. Appl. Polym. Sci.*, vol. 124, no. 2, pp. 969–977, Apr. 2012.

[19] J. Jaafar, A. F. Ismail, T. Matsuura, and K. Nagai, "Performance of SPEEK based polymer-nanoclay inorganic membrane for DMFC," *J. Memb. Sci.*, vol. 382, no. 1–2, pp. 202–211, 2011.

[20] H. H. Yong, H. C. Park, Y. S. Kang, J. Won, and W. N. Kim, "Zeolite-filled polyimide membrane containing 2,4,6-triaminopyrimidine," *J. Memb. Sci.*, vol. 188, no. 2, pp. 151–163, Jul. 2001.

[21] E. A. Wargo, C. R. Dennison, E. C. Kumbur, S. C. Gittleman, F. D. Coms, Y.-H. Lai, S. S. Kocha, A. El-kharouf, B. G. Pollet, H. Tawfik, Y. Hung, D. Mahajan, A.-K. Srouji, M. M. Mench, M. L. Perry, R. Balliet, R. M. Darling, F.-Y. Zhang, S. G. Advani, A. K. Prasad, Y. Morimoto, and S. Yamakawa, *Polymer Electrolyte Fuel Cell Degradation*, 1st ed. Oxford, US: Elsevier, 2012.

[22] Y. Wang, K. S. Chen, J. Mishler, S. C. Cho, and X. C. Adroher, "A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research," *Applied Energy*, vol. 88, no. 4. Elsevier Ltd, pp. 981–1007, 2011.

[23] S. Zhang, X. Yuan, H. Wang, W. Mérida, H. Zhu, J. Shen, S. Wu, and J. Zhang, "A review of accelerated stress tests of MEA durability in PEM fuel cells," *Int. J. Hydrogen Energy*, vol. 34, pp. 388–404, 2009.

[24] J. Zhang, H. Zhang, J. Wu, and J. Zhang, "Fuel Cell Degradation and Failure Analysis," in *PEM Fuel Cell Testing and Diagnosis*, 1st ed., no. 1, Oxford, UK: Elsevier, 2013, pp. 283–335.

[25] X. Z. Yuan, H. Li, S. Zhang, J. Martin, and H. Wang, "A review of polymer electrolyte membrane fuel cell durability test protocols," *J. Power Sources*, vol. 196, no. 22, pp. 9107–9116, 2011.

[26] C. Walling, "Fenton's reagent revisited," *Acc. Chem. Res.*, vol. 8, no. 4, pp. 125–131, 1975.

[27] I. Bloom, L. K. Walker, J. K. Basco, T. Malkow, A. Saturnio, G. De Marco, and G. Tsotridis, “A comparison of Fuel Cell Testing protocols – A case study: Protocols used by the U.S. Department of Energy, European Union, International Electrotechnical Commission/Fuel Cell Testing and Standardization Network, and Fuel Cell Technical Team,” *J. Power Sources*, vol. 243, pp. 451–457, Dec. 2013.

[28] M. P. Rodgers, L. J. Bonville, H. R. Kunz, D. K. Slattery, and J. M. Fenton, “Fuel cell perfluorinated sulfonic acid membrane degradation correlating accelerated stress testing and lifetime,” *Chem. Rev.*, vol. 112, no. 11, pp. 6075–6103, Nov. 2012.

[29] Y. Zhao, E. Tsuchida, Y.-K. Choe, J. Wang, T. Ikeshoji, and A. Ohira, “Theoretical studies on the degradation of hydrocarbon copolymer ionomers used in fuel cells,” *J. Memb. Sci.*, vol. 487, pp. 229–239, Aug. 2015.

[30] R. Dillon, S. Srinivasan, A. S. Aricò, and V. Antonucci, “International activities in DMFC R&D: Status of technologies and potential applications,” in *Journal of Power Sources*, 2004, vol. 127, no. 1–2, pp. 112–126.

[31] B. Gurau and E. S. Smotkin, “Methanol crossover in direct methanol fuel cells: A link between power and energy density,” *J. Power Sources*, vol. 112, no. 2, pp. 339–352, 2002.

[32] J. Jaafar, “Development of Sulfonated Poly (ether ether ketone) Triaminopyrimidine Nanocomposite Membrane for Direct Methanol Fuel Cell,” Universiti Teknologi Malaysia, 2011.

[33] B. . McNicol, D. a. . Rand, and K. . Williams, “Direct methanol–air fuel cells for road transportation,” *Journal of Power Sources*, vol. 83, no. 1–2. pp. 15–31, 1999.

[34] R. G. Hockaday, “Surface replica fuel cell for micro fuel cell electrical power pack,” US 5759712, 1998.

[35] C. K. Witham, “Performance of Direct Methanol Fuel Cells with Sputter-Deposited Anode Catalyst Layers,” *Electrochem. Solid-State Lett.*, vol. 3, no. 11, p. 497, 1999.

[36] H. Chang, J. R. Kim, J. H. Cho, H. K. Kim, and K. H. Choi, “Materials and processes for small fuel cells,” *Solid State Ionics*, vol. 148, no. 3–4, pp. 601–606, 2002.

[37] J. J. Martin, W. Qian, H. Wang, V. Neburchilov, J. Zhang, D. P. Wilkinson, and Z. Chang, “Design and testing of a passive planar three-cell DMFC,” *J. Power Sources*, vol. 164, no. 1, pp. 287–292, 2007.

[38] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, and T. Osaka, “MEMS-based design and fabrication of a new concept micro direct methanol fuel cell (μ-DMFC),” *Electrochem. commun.*, vol. 6, no. 6, pp. 562–565, Jun. 2004.

[39] S. W. Lim, S. W. Kim, H. J. Kim, J. E. Ahn, H. S. Han, and Y. G. Shul, “Effect of operation parameters on performance of micro direct methanol fuel cell fabricated on printed circuit board,” *J. Power Sources*, vol. 161, no. 1, pp. 27–33, Oct. 2006.

[40] V. Baglio, A. Stassi, F. V. Matera, A. Di Blasi, V. Antonucci, and A. S. Aricò, “Optimization of properties and operating parameters of a passive DMFC mini-stack at ambient temperature,” *J. Power Sources*, vol. 180, no. 2, pp. 797–802, Jun. 2008.

[41] D. T. Hallinan and N. P. Balsara, “Polymer Electrolytes,” *Annu. Rev. Mater. Res*, vol. 43, no. 1, pp. 503–25, Jul. 2013.

[42] G. S. Rani, M. K. Beera, and G. Pugazhenthi, “Development of Sulfonated Poly (ether ether ketone)/Zirconium Titanium Phosphate Composite Membranes for Direct Methanol Fuel Cell,” Universiti Teknologi Malaysia, 2011.

[43] M. Rikukawa and K. Sanui, “Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers,” *Prog. Polym. Sci.*, vol. 25, no. 10, pp. 1463–1502, 2000.

[44] N. H. Behling, *Fuel Cells: Current Technology, Challenges and Future Research Needs*, 1st ed. Oxford, UK: Elsevier, 2013.

[45] B. Smitha, S. Sridhar, and A. A. Khan, “Synthesis and characterization of proton conducting polymer membranes for fuel cells,” *J. Memb. Sci.*, vol. 225, no. 1–2, pp. 63–76, 2003.

[46] V. Neburchilov, J. Martin, H. Wang, and J. Zhang, "A review of polymer electrolyte membranes for direct methanol fuel cells," *J. Power Sources*, vol. 169, no. 2, pp. 221–238, 2007.

[47] T. Higashihara, K. Matsumoto, and M. Ueda, "Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells," *Polymer (Guildf).*, vol. 50, no. 23, pp. 5341–5357, 2009.

[48] S. M. . Zaidi, S. . Mikhailenko, G. . Robertson, M. . Guiver, and S. Kaliaguine, "Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications," *J. Memb. Sci.*, vol. 173, no. 1, pp. 17–34, Jul. 2000.

[49] P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang, and S. Kaliaguine, "Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes," *J. Memb. Sci.*, vol. 229, no. 1–2, pp. 95–106, 2004.

[50] A. Iulianelli and A. Basile, "Sulfonated PEEK-based polymers in PEMFC and DMFC applications: A review," *Int. J. Hydrogen Energy*, vol. 37, no. 20, pp. 15241–15255, 2012.

[51] D. J. Kim, M. J. Jo, and S. Y. Nam, "A review of polymer-nanocomposite electrolyte membranes for fuel cell application," *J. Ind. Eng. Chem.*, vol. 21, pp. 36–52, Jan. 2015.

[52] K. D. Kreuer, "On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells," *J. Memb. Sci.*, vol. 185, no. 1, pp. 29–39, Apr. 2001.

[53] M. L. Di Vona, A. D'Epifanio, D. Marani, M. Trombetta, E. Traversa, and S. Licoccia, "SPEEK/PPSU-based organic-inorganic membranes: proton conducting electrolytes in anhydrous and wet environments," *J. Memb. Sci.*, vol. 279, no. 1–2, pp. 186–191, Aug. 2006.

[54] S. Zhong, X. Cui, T. Fu, and H. Na, "Modification of sulfonated poly(ether ether ketone) proton exchange membrane for reducing methanol crossover," *J. Power Sources*, vol. 180, pp. 23–28, 2008.

[55] V. Delhorbe, X. Thiry, C. Cailleteau, E. Mourier, M. Bathfield, L. Chikh, O. Fichet, B. Ameduri, R. Mercier, S. Vidal, L. Augier, E. Espuche, F. Gouanv??, G. Gebel, and A. Morin, "Fluorohexane network and sulfonated PEEK based semi-IPNs for fuel cell membranes," *J. Memb. Sci.*, vol. 389, pp. 57–66, 2012.

[56] R. K. Nagarale, W. Shin, and P. K. Singh, "Progress in ionic organic-inorganic composite membranes for fuel cell applications," *Polym. Chem.*, vol. 1, no. 4, pp. 388–408, 2010.

[57] B. P. Tripathi and V. K. Shahi, "Organic-inorganic nanocomposite polymer electrolyte membranes for fuel cell applications," *Prog. Polym. Sci.*, vol. 36, no. 7, pp. 945–979, 2011.

[58] A. Kraytsberg and Y. Ein-Eli, "Review of Advanced Materials for Proton Exchange Membrane Fuel Cells," *Energy & Fuels*, vol. 28, no. 12, pp. 7303–7330, Dec. 2014.

[59] X. Liu, M. Hu, and Y. Hu, "Chemical composition and surface charge properties of montmorillonite," *J. Cent. South Univ. Technol.*, vol. 15, no. 2, pp. 193–197, Apr. 2008.

[60] S. M. L. Silva, C. R. C. Braga, M. V. L. Fook, C. M. O. Raposo, L. H. Carvalho, and E. L. Canedo, "Application of Infrared Spectroscopy to Analysis of Chitosan/Clay Nanocomposites," in *Infrared Spectroscopy - Materials Science, Engineering and Technology*, 1st ed., T. Theophanides, Ed. Rijeka, Croatia: InTech, 2012, pp. 43–62.

[61] M. Tsapatsis, H.-K. Jeong, and S. Nair, "Layered silicate material and applications of layered materials with porous layers," US 6863983 B2, 2005.

[62] Z. Gaowen and Z. Zhentao, "Organic/inorganic composite membranes for application in DMFC," *J. Memb. Sci.*, vol. 261, no. 1–2, pp. 107–113, Sep. 2005.

[63] M. Wang and S. Dong, "Enhanced electrochemical properties of nanocomposite polymer electrolyte based on copolymer with exfoliated clays," *J. Power Sources*, vol. 170, no. 2, pp. 425–432, Jul. 2007.

[64] S. Sedaghat, "Synthesis of clay-CNTs nanocomposite," *J. Nanostructure Chem.*, vol. 3, no. 1, p. 24, 2013.

[65] K. A. Carrado, “Synthetic organo- and polymer–clays: preparation, characterization, and materials applications,” *Appl. Clay Sci.*, vol. 17, no. 1–2, pp. 1–23, Jul. 2000.

[66] E. Amendola, “Epoxy Nanocomposites Based on Silylated Montmorillonite: Effect of the Coupling Agents Structure on the Mechanical Properties,” *Open Macromol. J.*, vol. 6, no. 1, pp. 33–36, May 2012.

[67] M. Huskić, I. Brnardić, M. Žigon, and M. Ivanković, “Modification of montmorillonite by quaternary polyesters,” *J. Non. Cryst. Solids*, vol. 354, no. 28, pp. 3326–3331, Jun. 2008.

[68] A. Esfandiari, H. Nazokdast, A.-S. Rashidi, and M.-E. Yazdanshenas, “Review of Polymer-Organoclay Nanocomposites,” *J. Appl. Sci.*, vol. 8, no. 3, pp. 545–561, Mar. 2008.

[69] S. Kim, E.-J. Hwang, Y. Jung, M. Han, and S.-J. Park, “Ionic conductivity of polymeric nanocomposite electrolytes based on poly(ethylene oxide) and organo-clay materials,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 313–314, pp. 216–219, Feb. 2008.

[70] J. M. Cervantes-Uc, J. V. Cauich-Rodr??guez, H. V??zquez-Torres, L. F. Garfias-Mes??as, and D. R. Paul, “Thermal degradation of commercially available organoclays studied by TGA-FTIR,” *Thermochim. Acta*, vol. 457, no. 1–2, pp. 92–102, Jun. 2007.

[71] H. Ilbeygi, A. F. Ismail, A. Mayahi, M. M. Nasef, J. Jaafar, and E. Jalalvandi, “Transport properties and direct methanol fuel cell performance of sulfonated poly (ether ether ketone)/Cloisite/triaminopyrimidine nanocomposite polymer electrolyte membrane at moderate temperature,” *Sep. Purif. Technol.*, vol. 118, pp. 567–575, Oct. 2013.

[72] J.-Y. Park, J.-H. Lee, J. Sauk, and I. Son, “The operating mode dependence on electrochemical performance degradation of direct methanol fuel cells,” *Int. J. Hydrogen Energy*, vol. 33, no. 18, pp. 4833–4843, 2008.

[73] M. Broussely and G. Archdale, “Li-ion batteries and portable power source prospects for the next 5-10 years,” *J. Power Sources*, vol. 136, no. 2 SPEC. ISS., pp. 386–394, Oct. 2004.

[74] S. K. Kamarudin, F. Achmad, and W. R. W. Daud, “Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices,” *Int. J. Hydrogen Energy*, vol. 34, no. 16, pp. 6902–6916, 2009.

[75] J. Han and H. Liu, “Real time measurements of methanol crossover in a DMFC,” *J. Power Sources*, vol. 164, no. 1, pp. 166–173, 2007.

[76] G. Zhang, T. Fu, K. Shao, X. Li, C. Zhao, H. Na, and H. Zhang, “Novel sulfonated poly(ether ether ketone ketone)s for direct methanol fuel cells usage: Synthesis, water uptake, methanol diffusion coefficient and proton conductivity,” *J. Power Sources*, vol. 189, no. 2, pp. 875–881, 2009.

[77] C. K. Lin, J. F. Kuo, and C. Y. Chen, “Preparation of nitrated sulfonated poly(ether ether ketone) membranes for reducing methanol permeability in direct methanol fuel cell applications,” *J. Power Sources*, vol. 187, no. 2, pp. 341–347, 2009.

[78] J.-H. Wee, “A feasibility study on direct methanol fuel cells for laptop computers based on a cost comparison with lithium-ion batteries,” *J. Power Sources*, vol. 173, pp. 424–436, 2007.

[79] R. Rashidi, I. Dincer, G. F. Naterer, and P. Berg, “Performance evaluation of direct methanol fuel cells for portable applications,” *J. Power Sources*, vol. 187, no. 2, pp. 509–516, 2009.

[80] H. Cha, C. Chen, and J. Shiu, “Investigation on the durability of direct methanol fuel cells,” *J. Power Sources*, vol. 192, no. 2, pp. 451–456, 2009.

[81] Y.-C. Park, D.-H. Peck, S.-K. Kim, S. Lim, D.-H. Jung, J.-H. Jang, and D.-Y. Lee, “Dynamic response and long-term stability of a small direct methanol fuel cell stack,” *J. Power Sources*, vol. 195, no. 13, pp. 4080–4089, Jul. 2010.

[82] P. Hartmann and D. Gerteisen, “Local degradation analysis of a real long-term operated DMFC stack MEA,” *J. Power Sources*, vol. 219, pp. 147–154, Dec. 2012.

[83] L. Zhang and S. Mukerjee, “Investigation of Durability Issues of Selected Nonfluorinated Proton Exchange Membranes for Fuel Cell Application,” *J. Electrochem. Soc.*, vol. 153, p. A1062, 2006.

[84] J. Prabhuram, N. N. Krishnan, B. Choi, T. H. Lim, H. Y. Ha, and S. K. Kim, "Long-term durability test for direct methanol fuel cell made of hydrocarbon membrane," *Int. J. Hydrogen Energy,* vol. 35, no. 13, pp. 6924–6933, 2010.

[85] M. K. Jeon, K. R. Lee, K. S. Oh, D. S. Hong, J. Y. Won, S. Li, and S. I. Woo, "Current density dependence on performance degradation of direct methanol fuel cells," *J. Power Sources*, vol. 158, no. 2 SPEC. ISS., pp. 1344–1347, 2006.

[86] J. Park, M. A. Scibioh, S.-K. Kim, H. Kim, I. Oh, T. G. Lee, and H. Y. Ha, "Investigations of performance degradation and mitigation strategies in direct methanol fuel cells," *Int. J. Hydrogen Energy*, vol. 34, no. 4, pp. 2043–2051, 2009.

[87] N. Wongyao, A. Therdthianwong, and S. Therdthianwong, "The fading behavior of direct methanol fuel cells under a start-run-stop operation," *Fuel*, vol. 89, no. 5, pp. 971–977, 2010.

[88] N. Wongyao, A. Therdthianwong, S. Therdthianwong, S. M. Senthil Kumar, and K. Scott, "A comparison of direct methanol fuel cell degradation under different modes of operation," *International Journal of Hydrogen Energy*, vol. 38, no. 22. Elsevier Ltd, pp. 9464–9473, 2013.

[89] L. Gubler, S. M. Dockheer, and W. H. Koppenol, "Radical (HO●, H● and HOO●) Formation and Ionomer Degradation in Polymer Electrolyte Fuel Cells," *J. Electrochem. Soc.*, vol. 158, no. 7, p. B755, 2011.

[90] F. Wang, H. Tang, M. Pan, and D. Li, "Ex situ investigation of the proton exchange membrane chemical decomposition," *Int. J. Hydrogen Energy*, vol. 33, no. 9, pp. 2283–2288, 2008.

[91] W. Lu, D. Lu, J. Liu, C. Li, and R. Guan, "Preparation and characterization of sulfonated poly(phenylene oxide) proton exchange composite membrane doped with phosphosilicate gels," *Polym. Adv. Technol.*, vol. 18, no. 3, pp. 200–206, Mar. 2007.

[92] H. Tang, M. Pan, F. Wang, P. K. Shen, and S. P. Jiang, "Highly durable proton exchange membranes for low temperature fuel cells," *J. Phys. Chem. B,* vol. 111, no. 30, pp. 8684–8690, Aug. 2007.

[93] L. Wang, B. L. Yi, H. M. Zhang, and D. M. Xing, “Pt/SiO2 as addition to multilayer SPSU/PTFE composite membrane for fuel cells,” *Polym. Adv. Technol.*, vol. 19, no. 12, pp. 1809–1815, Dec. 2008.

[94] J. Qiao, T. Okada, and H. Ono, “High molecular weight PVA-modified PVA/PAMPS proton-conducting membranes with increased stability and their application in DMFCs,” *Solid State Ionics*, vol. 180, no. 23–25, pp. 1318–1323, Oct. 2009.

[95] D. Zhao, B. L. Yi, H. M. Zhang, H. M. Yu, L. Wang, Y. W. Ma, and D. M. Xing, “Cesium substituted 12-tungstophosphoric (CsxH3−xPW12O40) loaded on ceria-degradation mitigation in polymer electrolyte membranes,” *J. Power Sources*, vol. 190, no. 2, pp. 301–306, May 2009.

[96] P. U. Hongting, L. I. N. Wang, P. A. N. Haiyan, and W. A. N. Decheng, “Synthesis and characterization of fluorine-containing polybenzimidazole for proton conducting membranes in fuel cells,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 48, no. 10, pp. 2115–2122, May 2010.

[97] Z. Wang, H. Tang, H. Zhang, M. Lei, R. Chen, P. Xiao, and M. Pan, “Synthesis of Nafion/CeO2 hybrid for chemically durable proton exchange membrane of fuel cell,” *J. Memb. Sci.*, vol. 421–422, pp. 201–210, Dec. 2012.

[98] W. Qian, Y. Shang, S. Wang, X. Xie, and Z. Mao, “Phosphoric acid doped composite membranes from poly (2,5-benzimidazole) (ABPBI) and CsxH3-xPW12O40/CeO 2 for the high temperature PEMFC,” *Int. J. Hydrogen Energy*, vol. 38, no. 25, pp. 11053–11059, Aug. 2013.

[99] Z. Si, F. Gu, J. Guo, and F. Yan, “Phosphoric acid-doped imidazolium ionomers with enhanced stability for anhydrous proton-exchange membrane applications,” *J. Polym. Sci. Part B Polym. Phys.*, vol. 51, no. 17, pp. 1311–1317, Sep. 2013.

[100] Y. Zhu, S. Pei, J. Tang, H. Li, L. Wang, W. Z. Yuan, and Y. Zhang, “Enhanced chemical durability of perfluorosulfonic acid membranes through incorporation of terephthalic acid as radical scavenger,” *J. Memb. Sci.*, vol. 432, pp. 66–72, Apr. 2013.

[101] C. D'Urso, C. Oldani, V. Baglio, L. Merlo, and A. S. Aric??, "Towards fuel cell membranes with improved lifetime: Aquivion?? Perfluorosulfonic Acid membranes containing immobilized radical scavengers," *J. Power Sources*, vol. 272, pp. 753–758, Dec. 2014.

[102] J. Park and D. Kim, "Effect of cerium/18-crown-6-ether coordination complex OH quencher on the properties of sulfonated poly(ether ether ketone) fuel cell electrolyte membranes," *J. Memb. Sci.*, vol. 469, pp. 238–244, Nov. 2014.

[103] Y. Zhu, J. Mai, H. Li, J. Tang, W. Z. Yuan, and Y. Zhang, "Enhanced stability of PFSA membranes for fuel cells: Combined effect between supercritical carbon dioxide treatment and radical scavenger incorporation," *Polym. Degrad. Stab.*, vol. 107, pp. 106–112, Sep. 2014.

[104] S. Rowshanzamir, S. J. Peighambardoust, M. J. Parnian, G. R. Amirkhanlou, and A. Rahnavard, "Effect of Pt-Cs2.5H0.5PW12O40 catalyst addition on durability of self-humidifying nanocomposite membranes based on sulfonated poly (ether ether ketone) for proton exchange membrane fuel cell applications," *Int. J. Hydrogen Energy*, vol. 40, no. 1, pp. 549–560, Jan. 2015.

[105] L. Sha Wang, A. Nan Lai, C. Xiao Lin, Q. Gen Zhang, A. Mei Zhu, and Q. Lin Liu, "Orderly sandwich-shaped graphene oxide/Nafion composite membranes for direct methanol fuel cells," *J. Memb. Sci.*, vol. 492, pp. 58–66, Oct. 2015.

[106] T. Ishimoto and M. Koyama, "A review of molecular-level mechanism of membrane degradation in the polymer electrolyte fuel cell," *Membranes (Basel).*, vol. 2, no. 3, pp. 395–414, Jul. 2012.

[107] T. Rigg, W. Taylor, and J. Weiss, "The Rate Constant of the Reaction between Hydrogen Peroxide and Ferrous Ions," *J. Chem. Phys.*, vol. 22, no. 4, p. 575, 1954.

[108] J. De Laat and H. Gallard, "Catalytic Decomposition of Hydrogen Peroxide by Fe(III) in Homogeneous Aqueous Solution: Mechanism and Kinetic Modeling," *Environ. Sci. Technol.*, vol. 33, no. 16, pp. 2726–2732, Aug. 1999.

[109] E. Neyens and J. Baeyens, "A review of classic Fenton's peroxidation as an advanced oxidation technique," *J. Hazard. Mater.*, vol. 98, no. 1–3, pp. 33–50, Mar. 2003.

[110] V. Melin, A. Henríquez, C. Radojkovic, B. Schwederski, W. Kaim, J. Freer, and D. Contreras, “Reduction reactivity of catecholamines and their ability to promote a Fenton reaction,” *Inorganica Chim. Acta*, vol. 453, pp. 1–7, Nov. 2016.

[111] N. Ohguri, A. Y. Nosaka, and Y. Nosaka, “Detection of OH Radicals Formed at PEFC Electrodes by Means of a Fluorescence Probe,” *Electrochem. Solid-State Lett.*, vol. 12, no. 6, pp. B94–B96, 2009.

[112] N. Ohguri, A. Y. Nosaka, and Y. Nosaka, “Detection of OH radicals as the effect of Pt particles in the membrane of polymer electrolyte fuel cells,” *J. Power Sources*, vol. 195, no. 15, pp. 4647–4652, Aug. 2010.

[113] A. A. Shah, T. R. Ralph, and F. C. Walsh, “Modeling and Simulation of the Degradation of Perfluorinated Ion-Exchange Membranes in PEM Fuel Cells,” *J. Electrochem. Soc.*, vol. 156, no. 4, pp. B465–B484, 2009.

[114] J. K. Pandey, K. Raghunatha Reddy, A. Pratheep Kumar, and R. P. Singh, “An overview on the degradability of polymer nanocomposites,” *Polym. Degrad. Stab.*, vol. 88, no. 2, pp. 234–250, May 2005.

[115] T. K. Kim, M. Kang, Y. S. Choi, H. K. Kim, W. Lee, H. Chang, and D. Seung, “Preparation of Nafion-sulfonated clay nanocomposite membrane for direct methanol fuel cells via a film coating process,” *J. Power Sources*, vol. 165, no. 1, pp. 1–8, Feb. 2007.

[116] J. P. G. Villaluenga, M. Khayet, M. A. López-Manchado, J. L. Valentin, B. Seoane, and J. I. Mengual, “Gas transport properties of polypropylene/clay composite membranes,” *Eur. Polym. J.*, vol. 43, no. 4, pp. 1132–1143, Apr. 2007.

[117] A. Panchenko, “DFT investigation of the polymer electrolyte membrane degradation caused by OH radicals in fuel cells,” *J. Memb. Sci.*, vol. 278, no. 1–2, pp. 269–278, Jul. 2006.

[118] C. Perrot, L. Gonon, M. Bardet, C. Marestin, A. Pierre-Bayle, and G. Gebel, “Degradation of a sulfonated aryl ether ketone model compound in oxidative media (sPAEK),” *Polymer (Guildf).*, vol. 50, no. 7, pp. 1671–1681, 2009.

[119] T. H. Yu, Y. Sha, W. G. Liu, B. V. Merinov, P. Shirvanian, and W. A. Goddard, “Mechanism for degradation of nafion in PEM fuel cells from quantum mechanics calculations,” *J. Am. Chem. Soc.*, vol. 133, no. 49, pp. 19857–19863, 2011.

[120] H. Sun, M. Yu, Z. Li, and S. Almheiri, “A Molecular Dynamic Simulation of Hydrated Proton Transfer in Perfluorosulfonate Ionomer Membranes (Nafion 117),” *J. Chem.*, vol. 2015, pp. 1–10, 2015.