

SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION OF SULFONATED
POLYETHER ETHER KETONE COMPOSITE MEMBRANE FOR DIRECT
METHANOL FUEL CELL

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METHANOL FUEL CELL

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DEDICATION

*To my beloved parents;
Othman Abd. Hamid & Siti Rohana Hj Ahmad
My siblings; Mohd Irman & Nur Safina,
for their unconditional love and affection
that I have been receiving...*

*My husband; Muhamad Nazif Wahab,
for his devotion and love through
all the hard times during my study...*

*My lovely daughter; Aleesya Arissa,
who serve as an inspiration for me to
move on against all odds on my way...*

I dedicated this fruit of my effort...

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ABSTRACT

The high costs of perfluorinated membranes have prompted research for alternative membranes based on hydrocarbon polymer and composite membrane. New composite membranes were prepared using sulfonated polyether ether ketone (SPEEK) polymer and inorganic proton conducting fillers developed from tungstosilicic acids (SiWA) loaded on silica-aluminium oxide ($\text{SiO}_2\text{-Al}_2\text{O}_3$) composite. The SiWA was fixed on stable structure (composite oxide) so that it became insoluble in water. The SPEEK polymers were characterized using hydrogen nuclear magnetic resonance ($^1\text{H NMR}$) and fourier transformed infrared (FTIR). An X-ray diffraction (XRD) analysis was performed on the inorganic proton conducting fillers to reveal the existence of the interaction between SiWA and composite oxide. The membranes morphological structural were characterized using scanning electron microscope (SEM) and their performance were examined in terms of proton conductivity, water uptake and methanol permeability. The result showed that the presence of inorganic proton conducting fillers led to both high water uptake and proton conductivity (maximum value $6.1 \times 10^{-2} \text{ Scm}^{-1}$). Low methanol permeability values were recorded for the membranes which appeared as a very promising material to be used in direct methanol fuel cell (DMFC). In order to obtain the optimum membrane formulations that have optimum response, which are minimum water uptake, maximum proton conductivity and minimum methanol permeability; a central composite experimental design (CCD) combined with response surface methodology (RSM) was carried out. The factors considered were SiWA content (*A*) and SiO_2 content in $\text{SiO}_2\text{-Al}_2\text{O}_3$ (*B*) composite. The data collected were analyzed using Design Expert Version 6.0.8 (StatEase, USA). Two optimum membrane formulation generated were DS66/68.27SIWA/25SO/75AO and DS66/30SIWA/53.86SO/46.14AO. By performing the validation experiments, the models which were developed using CCD-RSM method appeared to be practically accurate and can be used for prediction within the range of the factors studied.

ABSTRAK

Kos membran perfluorosulfonan yang tinggi telah mengalakkan penyelidikan bagi membran alternatif berasaskan polimer hidrokarbon dan membran komposit yang murah. Membran komposit baru telah disediakan dengan menggunakan polimer sulfonan poli eter eter keton (SPEEK) dan pengisi pengalir proton tak organik yang dihasilkan dari asid tungstosilik (SiWA) yang dimuatkan ke atas komposit silika-alumina oksida ($\text{SiO}_2\text{-Al}_2\text{O}_3$). SiWA ditetapkan pada struktur yang stabil (komposit oksida) supaya ia tidak larut dalam air. Pencirian polimer SPEEK dijalankan menggunakan resonans magnetik nuklear hidrogen (^1H NMR) dan inframerah penjelmaan fourier (FTIR). Analisis pembelauan sinaran x-ray (XRD) dijalankan terhadap pengisi pengalir proton tak organik untuk menunjukkan kewujudan interaksi antara SiWA dan komposit oksida. Pencirian struktur membran dan morfologi permukaan dijalankan menggunakan mikroskop imbasan elektron (SEM) dan prestasinya diuji dalam bentuk keberaliran proton, penyerapan air dan kebolehtelapan metanol. Didapati bahawa kehadiran pengisi pengalir proton tak organik membawa kepada penyerapan air dan keberaliran proton yang tinggi (nilai maksimum $6.1 \times 10^{-2} \text{ Scm}^{-1}$). Membran yang disediakan telah merekodkan nilai kebolehtelapan metanol yang rendah menyebabkan ia berpotensi sebagai bahan yang sangat baik untuk diguna pakai dalam bahan api metanol terus (DMFC). Bagi tujuan mendapatkan formulasi membran optimum yang mempunyai respons optimum iaitu penyerapan air yang minimum, keberaliran proton yang maksimum dan kebolehtelapan metanol yang minimum; kaedah eksperimen corak komposit pertengahan (CCD) digabungkan dengan metodologi permukaan respons (RSM) telah dijalankan. Faktor yang dipertimbangkan ialah kandungan SiWA dan kandungan SiO_2 dalam komposit $\text{SiO}_2\text{-Al}_2\text{O}_3$. Data yang dikumpul dianalisa menggunakan Design Expert Versi 6.0.8 (StatEase, USA). Dua formulasi membran optimum adalah DS66/68.27SIWA/25SO/75AO dan DS66/30SIWA/53.86SO/46.14AO. Dengan menjalankan eksperimen pengesahan, model yang dibangun menggunakan kaedah CCD-RSM didapati tepat secara praktikal dan boleh diguna untuk peramalan dalam julat faktor yang dikaji.

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NOMENCLATURES

A	-	Membrane cross-sectional area for methanol permeability
C_A	-	Concentration of methanol in the feed compartment
C_B	-	Concentration of methanol in the permeate compartment
E	-	Voltage
I	-	Current
L	-	Thickness of the membrane samples
P	-	Methanol permeability
S	-	Area of the membrane samples
t	-	Time
V_A	-	Volume of methanol
V_B	-	Volume of water
W_d	-	Weight of initial dried membranes
W_w	-	Weight of the wet membranes
Z'	-	Real impedance
Z''	-	Imaginary impedance
σ	-	Proton conductivity
α	-	Slope of the graph C_B versus t
Φ	-	Overall membrane characteristic

ABBREVIATIONS

FC	-	Fuel cell
DMFC	-	Direct methanol fuel cell
PEMFC	-	Polymer electrolyte membrane fuel cell/ Polymer exchange membrane fuel cell
PEEK	-	Polyether ether ketone
SPEEK	-	Sulfonated polyether ether ketone
SiO ₂	-	Silica oxide
Al ₂ O ₃	-	Aluminium oxide
HPA	-	Heteropolyacid
SiWA	-	Tungstosilicic acid
SSR	-	Sum of square due to regression
SSE	-	Sum of square for error
SST	-	Total sum of square of deviation
FTIR	-	Fourier transform infrared
XRD	-	X-ray diffraction
SEM	-	Scanning electron microscope

CHAPTER I

INTRODUCTION

1.1 Research Background

Fuel cells are the energy converting devices with a high efficiency and low or zero emission. They have been attracting more and more attention in recent decades due to high-energy demands, fossil fuel depletions, and environmental pollution throughout (Lui *et al.*, 2006). Countries like the United States, United Kingdom, Japan and Canada are currently in the race for the reality makeover of fuel cell technology in multiple fields especially in transportation, stationary power and micro electronic devices (Lee *et al.*, 2002).

Malaysia also has embarked into fuel cell technology since 1998 under Intensify Research in Priority Area (IRPA) grant and currently there are also several organizations that actively conducting R&D of fuel cells which are Universiti Teknologi Malaysia, Universiti Kebangsaan Malaysia and etc. Pusat Tenaga Malaysia (PTM) was developed in 1998 as a not-for-profit company where the rationale behind PTM's establishment is to fulfill the need for a national energy research centre that will co-ordinate various activities, specifically energy planning and research, energy efficiency, and technological research, development and

demonstration (R,D&D) undertaken in the energy sector due to the long lead time for energy projects to come on stream. In fact, PTM will eventually become a one-stop focal point for linkages among the universities, research institutions, industries and other various national and international organizations on energy matters. From this effort, Malaysia has emerged to be one of the possible contributors to this viable technology.

Generally, fuel cells are also known as “battery replacements” and one type of renewable energy. They are like batteries and not subjected to the thermodynamic Carnot cycle energy conversion efficiency of heat engines because the generation of electricity in a fuel cell occurs directly through electrochemical reactions without combustion. They can operate at high efficiency with emission levels far below most government standards (Kordesch and Simader 1996).

Driven by a market that calls for reliable, inexpensive, and environmentally sound sources of energy, researchers are working to boost fuel cell efficiency and performance, while simultaneously reducing size, weight and cost. Whereas fuel cells were once confined to expensive niche applications like the space program, fuel cells are now expected to broadly impact energy production (Brett *et al.*, 2003).

The types of fuel cells are distinguished by the electrolyte material. This determines the kind of chemical reactions that take place in the cell, the type of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications as shown in the table below:-

Table 1.1: Types of fuel cell

Type	Electrolyte	Fuel/ Oxidant	Operating Temperature (°C)	Application
Molten Carbonate (MCFC)	Carbonate (Lithium Potassium Mixture)	Salt & Carbonate	H ₂ /O ₂ ~ 650	Stationary
Phosphoric Acid (PAFC)	Pottasium hydroxide solution	H ₂ /O ₂	~ 220	Stationary
Solid Oxide (SAFC)	Solid Ceramic	H ₂ /O ₂	~ 1000	Vehicle Stationary
Alkaline (AFC)	Potassium Hydroxide Solution	H ₂ /O ₂	60-120	Vehicle Spatial
Polymer Electrolyte (PEMFC)	Solid Ion Exchange Membrane	H ₂ /O ₂	50-100	Vehicle Stationary Portable Power
Direct Methanol (DMFC)	Solid Ion Exchange Membrane	CH ₃ OH/ O ₂	50-120	Vehicle Portable Power

Among various types of fuel cells, proton exchange membrane (PEM) fuel cells (also called polymer electrolyte membrane fuel cells) have attracted significant amount of research interest in the past decade, especially in stationary and mobile power generators and electric vehicles. Such cells, that use a solid polymer membrane as the electrolyte, offer several advantages. The immobilized electrolyte and absence of corrosive liquid simplifies sealing and minimizes corrosion. The low operating temperature allow for fast start ups and immediate responses to changes in power demand. Most importantly, such compact cells can deliver high power densities which reduced the weight, cost, and volume, along with improved performance (Bret *et al.*, 2003).

There are primarily two types of PEM fuel cells, namely the hydrogen PEM fuel cell and the direct methanol fuel cell (DMFC), both of which are efficient and clean replacements for conventional electricity generators (Shaoduan and Luke, 2005). Hydrogen gas fed fuel cells is mostly used in automotive and residential applications while the DMFC are for portable electronic and vehicular, due to its important attributes; quick refuelling, low temperature and pressure operation, low cost of methanol, no liquid electrolyte, compact cell design and etc. (Ge and Liu, 2005).

For hydrogen gas fed fuel cells at their current technological state, hydrogen production, storage, and transportation are the major challenges in addition to cost, reliability and durability issues. DMFC using liquid and renewable methanol fuel have been considered to be favourable in terms of fuel usage and feed strategies. Compared to hydrogen fed fuel cells, which have a reforming unit, or low capacity in thy hydrogen storage tank, DMFC uses liquid methanol fuel, which is easily stored and transported and simplifies the fuel cell system (Lui *et al.*, 2006).

DMFC uses methanol directly as the reducing agent to produce electrical energy. This is an extremely exciting technology because it eliminates the need for an onboard methanol reformer, which will reduce the overall weight and cost of the fuel cell engine. However, the major technical challenges of a DMFC are slow methanol oxidation kinetics and high methanol crossover through the polymer electrolyte membrane. This results in wasted fuel as well as deterioration in fuel cell performance. Thus, the development of alternative electrolyte membranes that provide significantly reduced methanol crossover with high fuel cell power would facilitate the commercialization of the direct methanol fuel cell.

1.2 Problem Statement

A number of different polymer electrolyte membranes are being investigated for use in DMFC. The main requirements of a desired membrane are low methanol crossover, high proton conductivity and good mechanical and chemical stabilities during DMFC operation. Nafion consists of a polytetrafluoroethylene (PTFE) backbone which gives it high chemical resistance. The side chains consist of perfluorinated vinyl polyethers which are attached to the PTFE backbone through ether oxygen. The side chains terminate in sulfonic acid groups, $-\text{SO}_3\text{H}$, that give Nafion its proton exchange capability.

The Nafion had been considered as an industry standard and the choice for hydrogen/air fuel cells but there are some of the drawbacks that limited their usage in DMFC. The first problem is the methanol crossover that causing loss of fuel. The presence of methanol in the cathode side reduced the cathode voltage and efficiency of fuel cell. The high production cost of the Nafion membrane limits the large scale commercialization and a reduction in proton conductivity at operating temperature above 100°C because of dehydration (Kaliaguine *et al.*, 2003). Various efforts have been made to modify the perfluorinated membranes in order to achieve better performance. These include reducing thickness of membranes, impregnating hygroscopic oxide nanoparticles and/or solid inorganic proton conductors.

The high costs of perfluorinated membranes have also prompted research for alternative membranes based on hydrocarbon polymer that are cheap and available commercially. Some of the non-fluorinated membranes include polyether sulfone (PES), polyether ether ketone (PEEK), polyether ether ketone ketone (PEEKK), polybenzimidazoles (PBI), polyimide, etc., that have excellent chemical resistance, high thermo-oxidative stability and good mechanical properties.

Most of the polymers have been functionalized by electrophilic sulfonation to improve their membrane properties in term of better wettability, higher water flux, good mechanical properties, high proton conductivity and optimized membrane properties which makes it promising as an alternative material for DMFC application. Yang and Manthiram (2003) studied sulfonated polyether ether ketone membranes for use in a DMFC. It was reported that a membrane with 50% degree of sulfonation exhibited comparable DMFC performance to Nafion 115, while the methanol crossover was 2 times lower than the Nafion membrane. Sulfonated hydrocarbon polymers have also been used as host matrix for preparation of inorganic/organic composites, aiming at high operational temperature.

A new candidate of proton conducting electrolyte membranes that have been attracting attention currently is based on composite materials. They are promising materials because they possess both inorganic and organic functionally. The inorganic component allows the thermal stability to be increased and combines it with the mechanical and proton conductivity of the organic polymer. Similarly, the inorganic phase can improve chemical stability with the increase of water retention up to higher temperature (Aparicio *et al.*, 2003). Some examples of inorganic materials that are widely used in fuel cell are zirconium phosphate, zirconium oxide, titanium oxide, silica oxide and heteropoly acids.

Generally, the membrane conductivity in DMFC is dependent on the number of available acid groups and their dissociation capability in water, accompanied by the generation of protons. Since water molecules dissociate acid functionality and facilitate proton transport, the water uptake becomes an important parameter in studying electrolyte membranes for fuel cell application. However, if the water uptake is too high, it will affect the mechanical strength of the membrane. Therefore, it is crucial to fully understand the relationship between the water uptake and proton conductivity. The additions of high proton conducting inorganic materials to the organic polymer matrix were hoped to reduce the dependency of membrane conductivity on water molecule.

Gomes *et al.* (2005) reported that composite membrane comprises of heteropolyacid, sulfonated poly (arylene ether sulfone), benzimidazole derivatives had outstanding proton conductivity at 110°C. Zaidi *et al.* (2000) also had prepared series of membranes embedded with powdered heteropolycompounds and found out that the proton conductivity of the membranes exceeded 10^{-2} S/cm at room temperature. Despite a lot of research on composite material especially involving heteropolyacids, there have been few studies involving incorporation of silica oxide-aluminium oxide ($\text{SiO}_2\text{-Al}_2\text{O}_3$) with heteropolyacids (HPAs).

Heteropolyacids (HPAs) compounds such as tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid are the crystalline materials with very high proton conduction (Nakamura *et al.*, 1979). They were studied for a long time at the Institute CNR-TAE and it was evidenced that phosphotungstic acid utilize in PEMFC gave power density of about 700mW/cm^2 (Giordano *et al.*, 1996 and Staiti *et al.*, 1997).

However, due to its high solubility, HPAs tend to dissolve when water is present in the membrane (Staiti *et al.*, 2001 and Zaidi *et al.*, 2006). To avoid this problem HPAs need to be loaded onto stable support in such a way that it was not washed away by the water generated in the fuel cell and to retain its conductivity characteristics. In this research, the tungstosilicic acid was preferred to phosphotungstic acid because it can be supported on silica in higher amount as described by Staiti (2001a). It also forms more stable materials when adsorbed on silica at the similar conditions and display higher proton conductivity (Staiti and Minutoli, 2001).

Surface characteristic of the ceramic oxide fillers play important role for the membrane performance (Arico *et al.*, 2003). Since that, the composites membrane containing various compositions of acidic (SiO_2) and basic (Al_2O_3) ceramic oxide was chosen as host material. Studies by Nagai and Chiba (2005) also shows that by combining the above material, high proton conductivity and mechanical strength can

be achieved rather than using SiO_2 or Al_2O_3 individually. Silica is very hygroscopic which meant it can absorb more water. The high absorption of water will increase the water uptake hence facilitate the proton transport. However, higher water uptake is not so undesirable because it will affect the mechanical properties of the membrane. The mechanical strength will be reduced and the membranes become fragile due to the swollen effect. Therefore, by combining SiO_2 and Al_2O_3 , acceptable water uptake can be obtained. The inorganic materials used were in the powder form and thus to form membranes, the introduction of a binding polymer was necessary. The polyether ether ketone (PEEK) polymer was chosen as the binding agent for its good mechanical properties, high thermal stability up to 250°C and low cost. PEEK needs to undergo a sulfonation process to increase the hydrophilicity hence increasing the proton conductivity. To the best of our knowledge, the combination of SPEEK-SiWA- SiO_2 - Al_2O_3 has never been studied before.

1.3 Research Objectives

Based on the background of study and the problem statements discussed, therefore the objectives of this research are:-

- i. To synthesize and fabricate a composite membrane for direct methanol fuel cell application having acceptable water uptake, high proton conductivity and low methanol permeability.
- ii. To investigate the effects of polyether ether ketone (PEEK) sulfonation degree at various reaction temperatures, content of SiWA and content of SiO_2 in SiO_2 - Al_2O_3 composite on membrane performance and morphological structures.
- iii. To obtain an optimum membrane formulation to optimize response of water uptake, proton conductivity and methanol permeability.

1.4 Research Scopes

In order to fulfill the research objectives, the following scopes were outlined:-

- i. Performing the sulfonation reactions of polyether ether ketone (PEEK) at varying reaction temperature ranging from 55°C to 75°C.
- ii. Performing Hydrogen Nuclear Magnetic Resonance (H-NMR) and Fourier Transform Infrared (FTIR) analysis in order to determine the degree of sulfonation (DS) and structural changes during the sulfonation process.
- iii. Synthesizing the inorganic proton conducting materials by varying the composition of tungstosilicic acid (SiWA) and the ratio of silica oxide to the aluminum oxide and characterizing using X-ray Diffraction (XRD) analysis.
- iv. Preparing the dope solution and fabricating the composite membranes using pneumatically-controlled casting machine.
- v. Optimizing the membrane formulation using Response Surface Methodology (RSM) combined with Central Composite Design (CCD) analysis.
- vi. Characterizing the performance of fabricated membrane by measuring the water uptake, proton conductivity and methanol permeability.
- vii. Characterizing the membrane morphological structure using Scanning Electron Microscope (SEM).