DEVELOPMENT OF SULFONATED POLY (ETHER ETHER KETONE) TRIAMINOPYRIMIDINE NANOCOMPOSITE MEMBRANE FOR DIRECT METHANOL FUEL CELL

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To my beloved mother (Pn. Noorain Baharom), late father (En. Jaafar Adam), husband (Mohd Lukman Musa @ Ab Ghani), daughter (Nur Ardini Safiya) and son (Muhammad Izdihar Amzar)

Thank you for your support and love

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ABSTRACT

Methanol crossover problem, which significantly occurred in direct methanol fuel cell (DMFC) using commercial Nafion® membrane, encouraged number of studies on the development of novel proton exchange membrane (PEM). This research was conducted to synthesize and characterize polymer-inorganic nanocomposite sulfonated poly (ether ether ketone) (SPEEK) membranes filled with Cloisite15A® clay by introducing 2,4,6-triaminopyrimidine (TAP) as a compatibilizer for direct methanol fuel cell (DMFC) application. The influences of different degree of sulfonation (DS) of SPEEK filled with Cloisite15A® and TAP loadings on the membrane properties were investigated. SPEEK with 63% of DS (SP63) was found to be the optimum membrane based on its higher overall membrane characteristics compared to SPEEK with other DS. Therefore, in this study, SP63 was chosen to be modified by adding various amounts of Cloisite15A®. The effect of clay loading on the physical properties of SPEEK nanocomposite membranes was studied. From the results, SPEEK mixed with 2.5 wt. % of Cloisite15A® (SP63/2.5CL) has been identified as the best composite formulation. Subsequently, various amounts of TAP were further incorporated into SP63/2.5CL formulation. The effect of TAP incorporation was characterized based on their thermal and physico-chemical properties such as thermal stability, ion exchange capacity (IEC), water uptake, methanol uptake, mechanical stability, proton conductivity and methanol permeability. A complete exfoliated nanocomposite structure of resultant nanocomposite membrane was confirmed by x-ray diffraction (XRD) and was supported by field emission scanning electron microscopy (FESEM). The resultant SPEEK/Cloisite15A®/TAP nanocomposite membranes characteristics were compared with the parent SPEEK and commercially Nafion®112 membranes. The highest power density of SPEEK nanocomposite membrane achieved was 39.4 mWcm^{-2}, which is 46% higher compared to commercial Nafion®112 membrane. Due to its promising improved characteristics and performance, SP63/2.5CL/5.0TAP nanocomposite membrane could be chosen as the best polymer electrolyte membrane to be applied for DMFC application.

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ABSTRAK

Masalah aliran silang metanol yang berlaku pada bahan api metanol terus (DMFC) menggunakan membran komersil Nafion®, mendorong kepada kajian pembangunan membran pertukaran proton (PEM). Penyelidikan ini dijalankan untuk mensintesis dan mencirikan polimer-bukan organik membran nanokomposit sulfona poli (eter eter kiton) (SPEEK) diisi dengan tanah liat *Cloisite15A®* dengan memasukkan *2,4,6-triaminopyrimidine* (TAP) sebagai penserasi untuk aplikasi bahan api metanol terus (DMFC). Kesan pelbagai darjah pengsulfonan (DS) bagi SPEEK dan kesan penambahan *Cloisite15A®* dan TAP terhadap sifat-sifat membran tersebut telah dikaji. Berdasarkan hasil kajian, SPEEK dengan DS 63 % (SP63) telah dikenalpasti sebagai membran yang optimum berdasarkan kepada ciri-ciri kesuluruhan membran yang lebih tinggi berbanding membran dengan DS yang lain. Oleh itu, dalam kajian ini, membran SP63 dipilih untuk diperbaiki dengan memasukkan pelbagai amaun tanah liat *Cloisite15A®*. Kesan penambahan tanah liat terhadap sifat-sifat fizikal untuk membran nanokomposit SPEEK telah dikaji. SPEEK yang ditambah dengan 2.5 % berat tanah liat *Cloisite15A* (SP63/2.5CL) telah dikenalpasti sebagai formulasi komposit yang terbaik. Seterusnya, pelbagai amaun TAP ditambah ke dalam formulasi SP63/2.5CL. Kesan penyatuan TAP telah dicirikan berdasarkan kepada sifat-sifat haba dan kimia-fizik seperti kestabilan haba, kapasiti penukaran ion (IEC), ambilan air, ambilan metanol, kestabilan mekanikal, keberaliran proton dan kebolehtelapan metanol. Stuktur nanokomposit yang terkelupas secara sempurna daripada membran nanokomposit yang terhasil telah disahkan oleh pembelauan x-ray (XRD) dan disokong oleh medan pemancaran mikroskopi pengimbas elektron (FESEM). Ciri-ciri membran nanokomposit SPEEK/Cloisite15A®/TAP dibandingkan dengan membran SPEEK induk dan membran komersil Nafion®112. Kuasa ketumpatan tertinggi yang dicapai oleh membran nanokomposit SPEEK ialah 39.4 $mWcm^{-2}$, yang mana 46% lebih tinggi berbanding membran komersil Nafion®112. Disebabkan pencirian dan prestasi yang menjanjikan peningkatan, membran nanokomposit SP63/2.5CL/5.0TAP boleh dipilih sebagai membran polimer eletrolit yang terbaik untuk aplikasi DMFC.

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LIST OF SYMBOLS

A	-	Membrane area, cm^2.
d	-	Thickness membrane sample/ spacing between layers in XRD measurement, nm.
d_{dry}	-	thickness of the dry membrane, cm.
d_{wet}	-	thickness of the wet membrane, cm.
e^-	-	electron.
W_w	-	Weight of the wet membranes, g.
W_d	-	Weight of the dry membranes, g.
L_{dry}	-	length of the dry membrane, cm.
L_{wet}	-	length of the wet membrane, cm.
M	-	Molar concentration, mol/L.
P	-	Membrane permeability, cm^2s^{-1}.
S	-	Face area of the membrane, cm^2.
T_d	-	Thermal degradation temperature, °C.
T_g	-	Glass transition temperature, °C.
wt. %	-	Weight percentage.
σ	-	Proton conductivity, Scm^{-1}.
θ	-	Angle at the maximum point of the first peak in XRD spectra, (°).
n	-	Order of diffraction.
λ	-	Wave length of X-ray, nm.

LIST OF ABBREVIATIONS

AFC	-	Alkaline fuel cell
CL	-	Cloisite15A®
DMFC	-	Direct methanol fuel cell
DS	-	Degree of sulfonation
DSC	-	Differential scanning calorimetry
DTG	-	Derivative thermogravimetry
ED	-	Electrodialysis
FC	-	Fuel cell
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
^{1}H-NMR	-	Hydrogen nuclear magnetic resonance
IEC	-	Ion exchange capacity
MCFC	-	Molten carbonate fuel cell
MEA	-	Membrane electrode assembly
MeOH	-	Methanol
MMT	-	Montmorillonite
NA	-	Not available
NMP	-	N-methylprrolidone
OCV	-	open circuit voltage
PAFC	-	Phosphoric acid fuel cell
PBI	-	Polybenzimidazole
PEEK	-	Poly (ether ether ketone)
PEFC	-	Polymer electrolyte fuel cell

PEM	-	Proton exchange membrane/polymer electrolyte membrane
PEMFC	-	Proton exchange membrane fuel cell
PES	-	Polyethersulfone
PFI	-	Perfluorinated
PI	-	Polyimide
PPBP	-	Poly4-phenoxybenzoyl-1,4-phenylene,Ply-X2000)
PS	-	Polysulfone
Pt	-	Platinum
PVA	-	polyvenylalcohol
RH	-	Relative humidity
RT	-	Room temperature
SEM	-	Scanning electron microscopy
SFC	-	Solid oxide fuel cell
SO_3H	-	sulfonic acid
SPEEK	-	sulfonated poly (ether ether ketone)
SP48	-	sulfonated poly (ether ether ketone) with 48% degree of sulfonation
SP50	-	Sulfonated poly (ether ether ketone) with 50% degree of sulfonation
SP63	-	Sulfonated poly (ether ether ketone) with 63% degree of sulfonation
SP77	-	Sulfonated poly (ether ether ketone) with 77% degree of sulfonation
SP88	-	Sulfonated poly (ether ether ketone) with 88% degree of sulfonation
TAP	-	2,4,6-triaminopyrimidine
TGA	-	Thermal gravimetric analysis
XRD	-	X-Ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Current energy production chains are mostly based on oil, coal and natural gas which have negative impacts on environment in terms of carbon dioxide (CO_2) emission and other greenhouse gases thereby contributing to global warming, acid rain and photochemical oxidants. These atmosphere changes are considered as the most serious environmental threats throughout the world because of its potential impact on food production and processes essential to a productive environment (Pimentel *et al*., 1994). Furthermore, the limited availability of fossil fuel-based conventional energy sources compared with the dramatic increase of world population even further burden this situation (Kheshgi and Prince, 2000). This energy crisis can cause an increase of oil prices and burden the world's community. Therefore, concerns about CO_2 emissions and energy crisis may discourage widespread dependence on the use of coal and encourage the development and use of a reliable alternative energy production chains based on clean and renewable energy technologies (Gabbar, 2009).

There are wide ranges of renewable energy sources available, such as biomass, wind power, solar thermal systems, geothermal, hydroelectric, nuclear, photovoltaics, hydrogen fuel, etc. where they have less, or zero, impacts on environment (Sestoa and Casaleb, 1998; Nfaoui *et al.,* 2004). However, these technologies also have some drawbacks such as limited availability of main sources, high cost due to costly manufacturing process, complexity of its conversion system, high risks technology and etc. (Hall *et al.,* 1986; Wolfson 1991; DeMeo *et al.,* 1991; David *et al.,* 1994; Flavin and Lenssen*,* 1994).

Apart from these renewable energy sources, fuel cells have also received much attention as promising alternative energy sources where electrical energy is obtained by direct conversion of combustible. Fuel cells need no particular environment to work well and are highly efficient both in electrical and physical performance (De Francesco *et al.,* 2002).

Currently, there are six types of fuel cells, which include: alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC) and direct methanol fuel cell (DMFC). Among them, the PEMFC using hydrogen as a fuel has been already commercialized (Woo *et al.,* 2003). The PEMFC is attractive for automotive and portable applications because of its low operating temperature (Dohle *et al.,* 2003). However, hydrogen is flammable and hard to store. As an alternative, some researchers invented a steam reformer system to produce hydrogen from methanol fuel. This process however dramatically increases the fuel cell's weight and complexity (Libby *et al*., 2003).

Therefore, direct methanol fuel cell (DMFC) has become more attractive, as DMFC utilize gaseous or liquid methanol as fuel, thus avoiding the use of an expensive reforming system. DMFC provide for a simpler proton exchange membrane (PEM) cell system, lower weight, streamlined production, and thus lower costs (Chen *et al*., 2007). Other advantages offer by DMFC including high efficiency, high power density, low or zero emissions and reliable. However, there are some limitations that may restrict the advantages of using DMFC for power generation. The most crucial issue that should be highlight is the drawbacks that involved the PEM of DMFC system.

1.2 Problem Statement

Polymer electrolyte membrane (PEM) is the heart of the DMFC system, which acts as an electrolyte for proton transfer from anode to cathode as well as providing a barrier to the pathway of electrons between the electrodes (Xing *et al.,* 2004). Perfluorinated (PFI) proton exchange membranes from DuPont, Dow Chemical, Asahi Glass, and Asahi Chemical companies, which have been used as electrolyte membranes in proton exchange membrane fuel cell (PEMFC), possess outstanding chemical and mechanical stability. They perform excellently not only in PEMFC but also in DMFC (Zaidi *et al*., 2000; Chang *et al.,* 2003).

However, PFI membranes have two shortcomings: (1) very expensive due to the complicated production process; and (2) high methanol permeability in DMFCs (Li *et al*., 2003; Chang *et al*., 2003; Dillon *et al*., 2004). The methanol permeation across the PFI membranes in DMFC limits their performances. Methanol crossover is particularly troublesome because it leads to: (1) cathode depolarization (i.e., a loss of fuel cell power) when methanol contacts the cathode catalyst and oxidation occurs, (2) excessive water production and possible electrode flooding when methanol is chemically oxidized in the air at cathode, and (3) a reduction in the fuel efficiency of the entire system (Carter, 2003).

Due to these problems, a number of works on the development of alternative PEM have been carried out to minimize the shortcoming. The developments in preparing new membranes can be classified into three different branches such as 1) synthesizing new polymers of non-fluorinated backbones based (Antonucci *et al.,* 1999; Jones and Roziere, 2008), 2) incorporating inorganic fillers such as montmorillonite (Jung *et al.,* 2003), Palladium alloy (Ma *et al*., 2003), silicon (Jung *et al*., 2002), titanium oxide (Yoon *et al*., 2002) and zeolite (Libby *et al*., 2003) into parent polymer matrices and 3) sulfonated polymers (Roelofs *et al*., 2010; Tian *et al*., 2010).

Non-fluorinated polymers such as sulfonated polyimides, polystyrene sulfonic acid, sulfonated poly(arylene ether sulfones), polyphosphazene, polybenzimidazole, sulfonated polysulfone, sulfonated poly(phthala-zinone ether ketone) and sulfonated poly (ether ether ketone) have been developed as a potential electrolyte membrane for DMFC (Glipa *et al.,* 1997; Hasiotis *et al.*, 2001; Lufrano *et al*., 2001; Woo *et al*., 2003; Smitha *et al*., 2003; Kaliaguine *et al*., 2003; Li *et al*., 2003; Carter *et al*., 2003; Lee *et al*., 2004; Gil *et al*., 2004).

Among the potential polymers, sulfonated poly (ether ether ketone) (SPEEK) was considered as the most intensively studied alternative PEM for DMFC (Nunes *et al*., 2002). This is because SPEEK can offer adjustable proton conductivity and excellent chemical and thermal stability (Xing *et al*., 2004). Frequently, SPEEK is prepared by sulfonating of poly (ether ether ketone) (PEEK) base polymer with concentrated sulfuric acid (Yang, 2008). The introduction of sulfonic acid groups into PEEK polymer structure increase the negative functionalities and thus improve proton conductivity (Zaidi *et al*., 2000; Huang *et al*., 2001; Hasani-Sadrabadi *et al.,* 2010a). The smaller gap of hydrophobic-hydrophilic nano-phase domain of SPEEK than that of PFI polymers results in less interconnected hydrophilic domains and accordingly reduced electro-osmotic drag as well as the methanol crossover (Kreuer 2001; Hasani-Sadrabadi *et al.,* 2010a). However, methanol permeability varied largely with degree of sulfonation (DS) in which it is hard to maintain high methanol barrier at high DS (Yang, 2008). This behavior consequently causes an excessive swelling and low mechanical stability (Li *et al*., 2003). Therefore, a modification approach on highly potential SPEEK PEM is crucial to maintain or even increase its proton conductivity and provide high barrier properties towards methanol for better performance for DMFC applications.

Recently, great interest has been paid to the preparation of polymer-inorganic nanocomposite materials in order to overcome the high methanol permeability problem in SPEEK membranes comprising high surface area nano-structured particles (Staiti *et al.,* 2001). The exclusive characteristics of polymer-inorganic nanocomposites rely on the dispersion of nano-scale clay layers in the polymer matrix, which strongly depends on the interfacial structural properties (Thomassin *et al*., 2006; Hasani-Sadrabadi *et al.,* 2010a). From the morphological point of view, exfoliated/delaminated polymer-inorganic nanocomposite rather than intercalated or ordinary nanocomposites was considered as the promising structures having great potential to exhibit high performance nanocomposites (Villaluenga *et al*., 2007; Hasani-Sadrabadi *et al.,* 2010a).

Therefore, many studies are now focused on the interfacial voids issue due to the poor adhesion of the hydrophobic polymer and the hydrophilic inorganic filler surface. There are numbers of works introducing new polymer-inorganic electrolyte membrane by modifying the external surface of the inorganic filler itself to produce homogeneous polymer-inorganic membrane (Thomassin *et al.,* 2005; Thomassin *et al.,* 2006; Kim *et al.,* 2006; Lin *et al.,* 2007a; Lin *et al.,* 2007b; Chuang *et al.,* 2007). However, studies on the particular issue by filling the interface spacing between the polymer-inorganic with a kind of compatibilizer are scarcely reported (Villaluenga *et al.,* 2007; Yong *et al.,* 2001).

Therefore, in this study, the work aims at developing and characterizing polymer-clay nanocomposite based on the dispersion of nano-scaled clays into SPEEK matrices assist by a compatibilizer. Due to its high length to width ratio, i.e., 70-150, that is crucial to significantly reduce the methanol crossover and good conductivity value, i.e., 10^{-4} at room temperature, the commercially available organically modified montmorillonite (MMT) clay namely Cloisite15A® and 2,4,6-triaminopyrimidine (TAP) as a compatibilizer were selected to developed new PEM with enhance of physico-chemical properties, mechanical properties, thermal stability and performance in DMFC.

1.3 Research Objectives

Based on the research background and the problem statement, the objectives of this research have been identified as:

1. To develop sulfonated poly (ether ether ketone) (SPEEK)/Cloisite15A®/ 2, 4, 6-triaminopyrimidine (TAP) nanocomposite polymer electrolyte membranes.
2. To characterize the developed SPEEK/Cloisite15A®/ TAP nanocomposite membranes in terms of physico-chemical properties, mechanical stability, thermal stability and membrane structural morphologies.
3. To evaluate the performance of the developed membrane electrolyte assembly (MEA) from SPEEK/Cloisite15A®/TAP nanocomposite membranes in a DMFC single cell.

1.4 Research Scopes

In order to achieve the aforementioned objectives, the following scopes are covered:

1st stage

1) Synthesizing SPEEK polymer by sulfonation process.

2) Determining the degree of sulfonation (DS) of the synthesized SPEEK polymer by using proton nuclear magnetic resonance (^{1}H-NMR).

2nd stage

3) Identifying the suitable compositions for preliminary polymer solution formulation based on data available in the open literatures.

4) Preparing SPEEK/Cloisite15A®/TAP membrane solution for flat sheet membrane module.

3rd stage

5) Determining Cloisite15A® dispersion state in SPEEK polymer matrices using X-Ray Diffraction (XRD), scanning electron microscopy (SEM) or field emission scanning electron microscopy (FESEM) and Fourier transform infrared (FTIR).

6) Characterizing the physico-chemical properties of the developed membranes such as methanol and/or water uptake, contact angle, proton conductivity and methanol permeability.

7) Conducting the mechanical stability test on the developed membranes in terms of tensile strength and tensile stretch.

8) Conducting the thermal stability study by using thermal gravimetric analysis (TGA).

4th stage

9) Preparing Membrane Electrode Assembly (MEA) from the developed membranes.

10) Evaluating the performance of the developed membranes by incorporating into an electronic load of single DMFC system.

5th stage

11) Performing the abovementioned characterization studies on:
   a) SPEEK membrane with 1.0 wt. % loading of Cloisite15A® and TAP.
   b) SPEEK with various degree of sulfonation incorporated with 1.0 wt. % of Cloisite15A® and TAP.
   c) SPEEK with various amount of Cloisite15A® loaded.
   d) SPEEK/Cloisite15A® with various amount of TAP loaded.

1.5 Thesis Outline

In **Chapter 2** a literature overview of polymer electrolyte membranes is presented. The focus lies on polymer-inorganic based membranes. **Chapter 3** describes the methodology which is used to characterize the developed membranes. The used and developed methods in base polymer analysis and membrane characterization are presented. Finally direct methanol fuel cell tests are described. A preliminary study of the introduction of minute amount of Cloisite15A® and TAP in SPEEK polymer matrices and characterization of the prepared membrane is given in **Chapter 4**. The influence on the addition of small amount of Cloisite15A® and TAP on membrane properties such as liquid uptake, proton conductivity and methanol permeability is studied. In **Chapter 5**, an in-depth study of the effect of degree of sulfonation on membrane properties is presented. The study emphasizes on the swelling behavior of the polymer-inorganic nanocomposite membranes such as liquid uptake as a function of temperature and methanol concentration and membrane dimensional changes. In **Chapter 6**, polymer-inorganic nanocomposite membranes with various inorganic loading are presented. The focus lies on the obtaining appropriate amount of inorganic amount to produce a polymer-inorganic nanocomposite membrane with promising physicochemical properties, particularly proton conductivity and methanol permeability. **Chapter 7** focuses on preparation of polymer-inorganic membrane containing various amount of TAP. The main objective of this chapter is to obtain the best amount of TAP to be loaded into appropriate amount of inorganic filler as obtained in Chapter 6. The membrane electrode assembly (MEA) developed from polymer-inorganic membranes containing different amount of TAP loading was then undergo the performance test in a single direct methanol fuel cell. All developed polymer-inorganic nanocomposite membranes were characterized and compared with Nafion®112 membrane. Finally, in **Chapter 8** conclusions on the developed membranes are presented. Recommendations for further research are given as well as other directions for the use of this kind of membranes.

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