DEVELOPMENT AND CHARACTERIZATION OF SULFONATED POLYSULFONE MEMBRANE FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

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To my beloved husband; Zafizal bin Zolkafli, my family and my eternal friends, Tengku Nur Radiatul Khalilah and Nur Airina Mazlan.

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ABSTRACT

Sulfonated polysulfone membranes with varying degree of sulfonation have been successfully synthesized by electrophilic substitution via sulfonation process in this study. Sulfonated dense membranes were fabricated using locally available pneumatically-controlled casting machine. Characterizations of different degree of sulfonated polysulfone membranes were conducted through swelling effects, ion exchange capacity (IEC), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimeter (DSC), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and proton conductivity measurement. It was observed that an increase in the degree of sulfonation increases the water uptake of the membranes and sulfonic acid group in the polymer membrane. From FTIR, it was clearly confirmed the occurrence of sulfonation in the polymer structure as the evidence of the SO_3 stretching band was noticed at frequency of 1027 cm^{-1}. It was found from TGA that the sulfonic acid group started to decompose at 250ºC and decomposition of the polymer main chain decreases by increasing the degree of sulfonation. The Tg value detected in this study was increased accordingly with the degree of sulfonation though some hindrance was found to decrease the Tg value during the experiments. Proton conductivity measurement of sulfonated polysulfone membrane was found to increase with operating temperature and degree of sulfonation. It was found that at higher temperature (80ºC), SPSU10 membrane exhibits proton conductivity value at par with that of Nafion 117 membrane. It was also observed from XRD analysis that dimethylformamide solvent was prone to form hydrogen bonding with sulfonic groups hence allows formation of a more regular structure which leads to an incipient crystalline character of the material structure. SEM micrographs showed clearly the altered microstructure of polysulfone polymer before and after the sulfonation process.

ABSTRAK

Membran sulfonan polisulfona dengan pelbagai darjah pengsulfonan telah berjaya diperolehi dalam ujikaji ini melalui tindakbalas penukargantian elektrofilik iaitu proses pengsulfonan. Membran pengsulfonan padat disediakan menggunakan mesin penuangan bersistem kawalan pneumatik. Pencirian darjah membran pengsulfonan polisulfona telah dijalankan melalui kesan pembengkakan, kapasiti penukaran ion (IEC), analisis gravimetrik terma (TGA), Pemeteran Kalori Pengimbasan Kebezaan (DSC), X-ray Diffraction (XRD), Kemikroskopan Elektron Imbasan (SEM) dan keberaliran. Diperhatikan bahawa dengan meningkatnya darjah pengsulfonan, tahap pembengkakan dan kumpulan asid sulfonik dalam membran polimer diperolehi meningkat. Daripada analisis Spektroskopi Infra-Merah Penukaran Fourier (FTIR), jelas terbukti bahawa tindakbalas pengsulfonan telah berlaku pada struktur polimer dengan adanya regangan ikatan SO_3 pada frekuensi 1027 cm^{-1}. Daripada analisis terma, didapati bahawa kumpulan asid sulfonik mula menyusut pada suhu 250ºC dan suhu penyusutan rantaian polimer utama menurun dengan peningkatan darjah pengsulfonan. Nilai suhu peralihan kaca (Tg) yang diperolehi dalam ujikaji ini meningkat berkadar terus dengan darjah pengsulfonan walaupun terdapat beberapa faktor yang mempengaruhi penurunan nilai suhu peralihan kaca semasa eksperimen dijalankan. Didapati bahawa nilai keberaliran proton bagi membran pengsulfonan polisulfona meningkat dengan peningkatan suhu operasi dan darjah pengsulfonan. Pada kenaikan suhu 80ºC didapati bahawa membran SPSU10 menunjukkan nilai keberaliran proton pada tahap yang setanding dengan membran Nafion 117. Melalui analisis Belauan Sinar-X (XRD), didapati bahawa larutan dimetilformamida (DMF) berupaya bertindakbalas dengan kumpulan sulfonik dan menghasilkan ikatan hidrogen dimana pembentukan ikatan ini menghasilkan struktur yang lebih tersusun yang menjurus kepada sifat kristal pada struktur bahan. Gambar mikrograf SEM menunjukkan perubahan struktur mikro bagi sulfonan polisulfona sebelum dan selepas proses pengsulfonan.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Energy consumption has increased drastically in the last century due to the increase of human population and activities. World's dependent on hydrocarbon fuel to create power has proven to be the major source for energy production. Nevertheless, high contribution of dangerous toxic and effluent release during the process cause hazardous threat to the environment and human life. This phenomenon has seriously driven research into a new modern technology producing clean energy without harnessing the environment as far as clean fuel is concerned. Fuel cell is the most efficient technology for present and future upcoming life as it shows excellent performance in term of its zero emission contaminate byproduct, high efficiency, flexibility, processability and durability.

Fuel cells are the latest promising energy producers for the future century. Countries like 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. In addition, fuel cell research activities in Asian region especially in Japan, China and Taiwan (Lee *et al.*, 2002) are now accelerating, as they are in progress to demonstrate the fuel cell bus and scooters for future application in the region.

Malaysia as one of the rapid emergence countries has also embarked into fuel cell technology since 1998 under Intensify Research in Priority Area (IRPA) grant, which focusing on the Proton Exchange Membrane Fuel Cell for transportation application. This project was the pioneered project in Malaysia, and the second phase of the project is now underway to further develop the upcoming technology in the region. From this effort, Malaysia has emerged to be one of the possible contributors to this viable technology and probably will be ready to joint others as an active participant in this future technology.

Concern with the environment and earth limited resources has led to introduction of commercial application of fuel cells, mainly in the field of ground transport and distributed power generation. General Motors, Daimler Chrysler, Ford, Ballard, Honda, Toyota and other big companies in the world are seriously concentrating on polymer electrolyte membrane fuel cell (PEMFC) into car and buses and several prototype has been demonstrated to verify the performance and to upgrade the current performance of fuel cell system. Meanwhile for high capacity power generation, Solid Oxide Fuel Cell (SOFC) has made their marked success in the fuel cell field as they have been verified to achieve high performance and efficiency in high capacity grid power supply and distributed generation (Casanova and Veyo, 2001).

According to a study performed by Business Communications Co., Inc. (US) (www.bccresearch.com), the fuel cell market is estimated at about $218 million in 2000. With commercialization of most of the fuel cell technologies rapidly falling in place, this market is expected to have a steep increase to an estimated $2.4 billion by 2005, an AAGR (average annual growth rate) of more than 61.7%. With the technology's extensive use in the vehicle market, proton exchange membrane fuel cell sales have become the dominant version in the market, bringing 2000 sales of $104 million up to $1.6 billion by 2005. Research on the fuel cells R&D and intellectual property (IP) studies have found that PEMFC was the highest amount for patent disclosure in fuel cell field and membrane was the most area being studied in PEMFC. This suggests that fundamental research is still playing a critical role in fuel cell development, even while much of the industrial emphasis is on commercialization and manufacturing processes (Barrett, 2002).

Table 1.1: U.S. sales of fuel cell by type, 2000-2005 ($ Millions)

	2000	**2005**	**AAGR % 2000-2005**
Proton exchange membrane	104.0	1640.0	73.6
Solid Oxide	54.0	260.0	36.9
Molten carbonate	25.0	450.0	78.3
Phosphoric acid	20.4	35.6	11.8
Alkaline	15.0	30.0	14.9
Total	**218.4**	**2415.6**	**61.7**

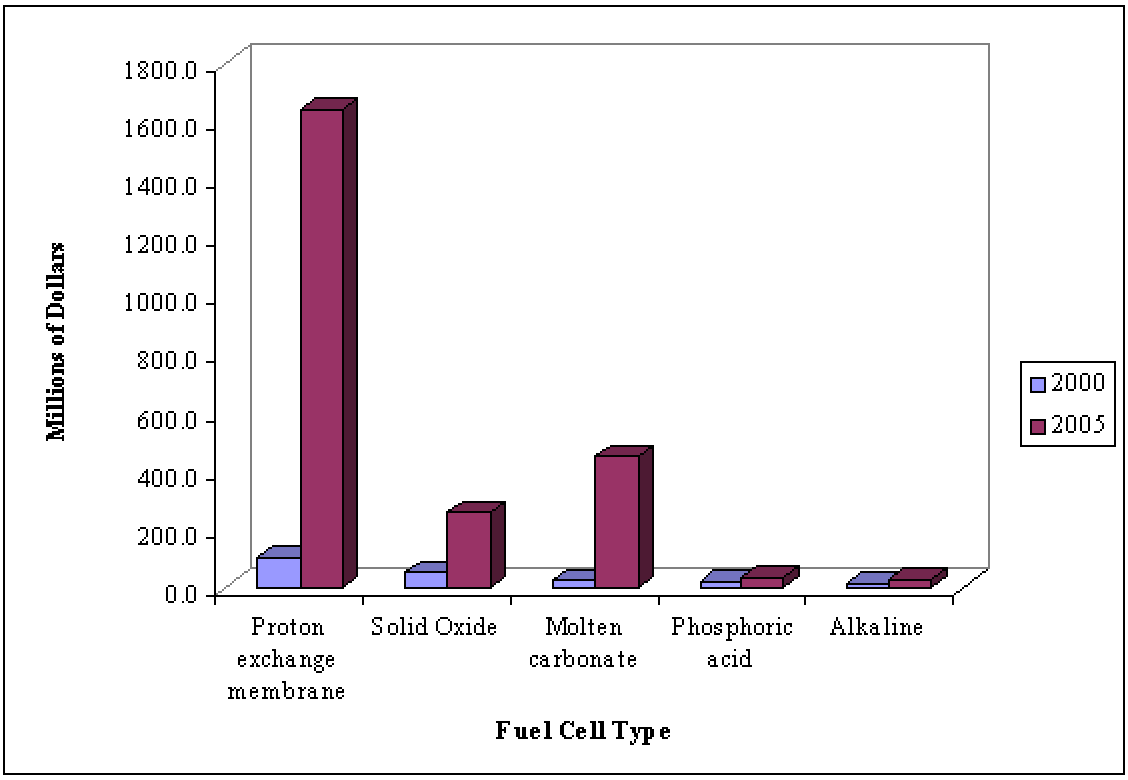

Figure 1.1: U.S. sales of fuel cell by type, 2000-2005

Fuel cells are distinguished primarily by the type of electrolyte and the operating temperature used. There are five types of fuel cell, which include: Alkaline Fuel Cell (AFC), Proton Exchange Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). However, Proton Exchange Membrane Fuel Cell (PEMFC) has received numerous attentions from world automotive producers due to its high power density and high flexibility in operation.

Membranes used in fuel cell applications are basically a proton exchange membrane type that is capable of transporting the proton within the membrane structure. The proton exchange membrane is a solid, organic polymer usually poly (perflourosulfonic acid) which was used as an electrolyte in Proton Exchange Membrane Fuel Cell (PEMFC) (which also can be known as Polymer Electrolyte Membrane Fuel Cell). The existence of PEMFC has been long acknowledged back in 1960s but it did not perform reliably in space fuel cell projects due to the high cost of the membranes and expensive auxiliary system for heat and water removal. A surprising technology turn over occurred in 1990's when PEMFC appeared as the most attractive object for development especially in fleet and vehicles application. This is driven by significant high power densities obtained as a result of new development of membrane types in recent years (Kordesch and Simadar, 1996; Carretta *et al.*, 2001).

Although the US General Electric Company (GE) initiated the development of PEMFC in 1950s, it was the introduction of Nafion by DuPont that ensured continuing interest in these systems. Initially Nafion was manufactured for membrane cells used in the production of chlorine (chlor-alkali cells). By 1990, Ballard had overcome many of the engineering problems associated with PEMFC systems and this had stimulated many groups in the United States and Japan to improve the properties of the original Nafion material (Steele and Heinzel, 2001).

The material generally used up to now, a sulfonated fluoropolymer first developed by US space scientists in the early 1970s, is effective but expensive.

Sulfonate groups, introduced by complexing the perfluorinated polymer with sulfonic acid, turned out to be good ionic conductors, particularly when associated with water molecules. Dupont has long dominated the market with its Nafion^{TM} brand, though Asahi Chemicals and others have introduced similar thermoplastic copolymers subsequently. These materials conduct well, resist attack by acids, bases and oxidants and have good mechanical properties, which are retained over time. On the downside, they are sensitive to contaminants and methanol, upset by over or under-hydration, lose performance in prolonged operation above about 80˚C, and cost hundreds of dollars per square meter.

Research groups have sought to improve the existing material or find alternative polymer that possess similar performance as standard Nafion. For low cost, however, a more radical approach is needed and the search has been on for alternative polymer backbones, including 'disposable' hydracarbon. One possibility to introduce the sulfonate group into the polymer structure is by sulfonation. This is due to its simple processing and reaction, which depends mainly on the properties of the sulfonating agent and polymer base unit.

In order to achieve higher performance and efficient system, PEMFC needs to have a good and stable membrane operating at desired temperature and pressure. Thus, it is essential to identify the economical and effective ways to produce and manufacture the ideal membrane with desirable properties.

1.2 Problem Statement

As mentioned above, the development of fuel cells was driven by the space industry in the 1960s. At that time the PEM materials were crosslinked, sulphonated polystyrenes. Sulphonated fluorocarbon membranes such as Nafion TM, which was introduced by DuPont in the early 1970s, then superseded sulfonate polystyrenes as the preferred membrane materials for PEMFC. Since then, Nafion remains the industry standard until today, but this material has the downside of being very costly to produce and require heat, high pressure and a high level of hydration to perform effectively (Johnstone, 2001).

The development of low cost membranes materials for fuel cells has gained wide attention and turned to be the most challenging in the field of membrane community in the last few years. Many hydrocarbon polymers such as polysulfones, polyethersulfones, polyetherketones, polyether etherketones, polyimides, polybenzimidazole, polyoxadiazole, polyphosphazenes have been claimed to be possible substitutes for perflourinated ionomers provided that a charge group (sulfonic) is introduced into the structural unit (Kopitzke, 1999; Lufrano *et al.*, 2000; 2001; Hogarth and Glipa, 2001). Among the aforementioned polymers, the polysulfone is considered to be the most interesting polymer due to its low cost, commercial availability and ease of processing. Though this study on sulfonated polysulfone might not be the first in the world but however it can be considered as a landmark for the research in fuel cell membrane in the Asian region by using sulfonation process.

Based on the latest purchase pricing of the Nafion membrane material (which is PTFE polymer) and polysulfone polymer (Amoco Udel P1700), it was found that 1 kg of PTFE flouro polymer worth RM 690 meanwhile polysulfone polymer price is RM 198 for 1 kg of polymer. It was clearly seen that the price of PTFE polymer is five times higher than the of polysulfone polymer. If the production and manufacturing cost of modifying PTFE membrane were to be included in the comparison with modifying polysulfone polymer, it is expected that this gap of difference would be much more higher. Therefore, in order to minimize the overall cost of PEMFC system; search on the cost-effective polymer is very crucial in PEMFC research and development. Thus the main drivers of research into fuel cell membrane materials is the development of cost-effective material that can operate at low pressure and high temperature conditions and possess the performance at par with Nafion (Wnek *et al.*, 1999; Marsh, 2001).

1.3 Research Objectives

As described in the research background and problem statement section, therefore the objectives of this research are:

(a) to develop and characterize the sulfonated polysulfone membrane for polymer electrolyte membrane fuel cell (PEMFC) application.

(b) to study and compare the performance of SPSU membrane with that state of the art Nafion membrane.

1.4 Scope of the Research

In order to accomplish the set objectives, the following scope of works has been drawn.

(a) Performing the sulfonation reaction at ambient temperature.

(b) Development of a sulfonated polymer solution making and fabrication of sulfonated dense membranes.

(c) Physical and chemical characterization of the produced sulfonated membranes.

(d) Studies of effects of sulfonation process on polysulfone polymer by swelling (water uptake), thermal stability, proton conductivity measurement and membrane microstructure.