

**DEVELOPMENT AND CHARACTERIZATION OF SULFONATED
POLYETHERSULFONE MEMBRANE FOR PROTON EXCHANGE
MEMBRANE FUEL CELL APPLICATION**

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ABSTRACT

The objective of this studies is to develop and characterize sulfonated polyethersulfone membrane (SPES) for Proton Exchange Membrane Fuel Cell application. In the experiment, polyethersulfone were sulfonated with different reaction time before continue making the dope solution. The membranes were tested with water uptake, Differential Scanning Calorimeter (DSC) and Scanning Electron Microscopy (SEM) to analyze the membrane performance. The swelling test result showed that the value of water uptake % were directly proportional to the reaction time of sulfonation. Differential Scanning Calorimeter (DSC) result showed that higher reaction time of sulfonation, the higher of the glass transitions temperature (T_g) and melting temperature (T_m) of the SPES. SPES 6 sample gave the best result compared to the other samples with 63.13°C glass transition temperature and 92.87°C melting temperature. Scanning Electron Microscopy (SEM) showed that the membrane has symmetric structure.

ABSTRAK

Projek ini adalah untuk membangunkan dan mengkaji ciri-ciri pengulfonan polyethersulfina membrane (SPES) untuk aplikasi Membrane Ion Balikan Sel Bahan Api. Dalam eksperimen ini, poliethersulfona disulfonan dengan masa reaksi berbeza sebelum membuat cairan 'dope'. Membran diuji melalui kaedah keberaliran, Differential Scanning Calorimeter (DSC) dan Scanning Electron Microscopy (SEM) untuk menganalisa prestasi membrane. Ujian menunjukkan peratus keberaliran membrane adalah berkadar terus dengan masa reaksi. Differential Scanning Calorimeter (DSC) analisa menunjukkan semakin lama masa reaksi semakin tinggi peralihan kaca/transformasi (T_g) dan suhu keburan (T_m). Sampel SPES 6 menunjukkan keputusan yang memberangsangkan dengan memiliki 63.13°C suhu peralihan kaca/transformasi (T_g) dan 92.87°C suhu keburan (T_m). Keratan rentas dan struktur membrane dilihat melalui Scanning Electron Microscopy (SEM) dan pemerhatian mendapati membrane mempunyai struktur simetrik.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

A fuel cell is an electrochemical conversion device. It produces electricity from fuel (on the anode side) and an oxidant (on the cathode side), which react in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. In general, fuel cell convert chemical reaction into electrical.

Proton Exchange Membrane Fuel Cell (PEMFC) are the simplest ones and easy to understand, implement and use. Proton Exchange Membrane Fuel Cell (PEMFC) uses a thin, permeable polymeric membrane as the electrolyte. Membrane in PEMFC needs good proton conductivity, it should conduct only protons, but not electrons and be as thin as possible, so that proton current is affected as little as possible and the voltage drop across the membrane is minimized. The proton exchange membrane (PEM) should survive in a highly acidic environment at elevated temperatures for thousands of hours. The efficiency of a PEM unit usually reaches between 40 to 60 %. For temperatures below 100 °C, Nafion developed by the Du Pont company is most probably widely known and used. However this type of membrane sensitive to contaminants and methanol cannot operate above 80°C its more expensive cost due the complicated production process

In order to get the most efficient system of PEMFC, the membrane develop need to have a good and stable membrane operating at desired temperature and

pressure. The need of developing membrane that satisfies this condition with the minimum cost of production and maintenance are recommended.

1.2 Problem Statement

The increasing of energy and large demand of power generation can cause harmful to the environment. CO₂ will be produce during combustion process and this will lead to increasing CO₂ into our environment and cause the greenhouse effects. In the present of water, CO₂ can cause other problems such as solidification and corrosion.

Currently, common membrane for Proton Exchange Membrane Fuel Cell (PEMFC) is perflourosulfonic acid called Nafion™. Until now Nafion remains as standard for industry but it was very expensive to produce and require heat, high pressure and high level hydration in oder to perform effectively. Thus the main research in membrane fuel cell is to develop cost-effective material and membrane that can operate at low pressure and at high temperature.

1.3 Objective of Study

To develop and characterize sulfonated polyethersulfone (SPES) membrane for Proton Exchange Membrane Fuel Cell (PEMFC) application.

1.4 Scope of Study

In order to accomplish the objective of study, the following scope of study has been drawn:

- a) Development and fabrication the sulfonated polyethersulfone as a membrane for proton exchange membrane fuel cell.
- b) Study the physical and chemical characteristic of sulfonated polyethersulfone membrane using water uptake, scanning electron microscopy (SEM), and differential scanning calorimeter (DSC).

CHAPTER 2

LITERATURE REVIEW

2.1 Fuel Cell History

As early as 1839, Sir William Grove (often referred to as the "Father of the Fuel Cell") discovered that it may be possible to generate electricity by reversing the electrolysis of water. It was not until 1889 that two researchers, Charles Langer and Ludwig Mond, coined the term "fuel cell" as they were trying to engineer the first practical fuel cell using air and coal gas. While further attempts were made in the early 1900's to develop fuel cells that could convert coal or carbon into electricity, the advent of the internal combustion engine temporarily quashed any hopes of further development of the fledgling technology. (Gasik, 2008)

2.2 Fuel Cell Definition

A fuel cell is an electrochemical device (a galvanic cell) which converts free energy of a chemical reaction into electrical energy, the byproducts are water and carbon dioxide depending on reactants fossil fuel used. A fuel cell produces electricity on demand continuously as long as the fuel and oxidant supplied. The components of a fuel cell are anode, anodic catalyst layer, electrolyte, cathode catalyst layer, cathode, bipolar plates and gasket (Basu and Shah, 1993).

Ramani (2007) explained in a combustion engine, fuel is mixed with air in appropriate stoichiometric ratios to initiate a combustion reaction that further creates work. In a combustion reaction, the gas species are not spatially separated, but in proton exchange membrane fuel cell (PEMFC), these combustion reactions are split into two half-cell reactions, namely, fuel oxidation and oxygen reduction, that occurs in two separate chambers called anode and cathode, respectively.

2.3 Types Of Fuel Cell

The different types of fuel cell technologies offer special features that may favor specific applications, but their full product potential will only be understood after commercial introduction. High conversion efficiencies, low pollution, low noise, modular construction and potential for low costs are critical parameters to open up large market segment (Basu and Shah, 1993). Table 2.1 shows comparison between different types of fuel cell.

Table 2.1 : Comparison between different types of fuel cell

| | PEMFC | DMFC | AFC | PAFC | MCFC | SOFC |
|-----------------------------|---------------------------------|---------------------|---|-----------------------------------|---|----------------------------------|
| Primary applications | Automotive and stationary power | Portable power | Space vehicles | Stationary power | Stationary power | Vehicle auxiliary power |
| Electrolyte | Polymer membrane | Polymer membrane | Concentrated (30-50%) KOH in H ₂ O | Concentrated 100% phosphoric acid | Molten Carbonate retained in a ceramic matrix of LiAlO ₂ | yttrium stabilized Zirkondioxide |
| Operating temperature range | 50-100 ⁰ C | 0-60 ⁰ C | 50-200 ⁰ C | 150-220 ⁰ C | 600-700 ⁰ C | 700-1000 ⁰ C |

Table 2.1 : Continue

| | PEMFC | DMFC | AFC | PAFC | MCFC | SOFC |
|-------------------------------------|----------------|------------------------------|-----------------|----------------|--------------------------------------|---------------------|
| Charge carrier | H ⁺ | H ⁺ | OH ⁻ | H ⁺ | CO ₃ | O ⁻ |
| Prime cell components | Carbon-based | Carbon-based | Carbon-based | Graphite-based | Stainless steel | Ceramic |
| Catalyst | Platinum | Pt-Pt/Ru | Platinum | Platinum | Nickel | Perovskites |
| Primary fuel | H ₂ | Methanol | H ₂ | H ₂ | H ₂ , CO, CH ₄ | H ₂ , CO |
| Start-up time | Sec-min | Sec-min | | Hours | Hours | Hours |
| Power density (kW/m ³) | 3.8-6.5 | ~0.6 | ~1 | 0.8-1.9 | 1.5-2.6 | 0.1-1.5 |
| Combined cycle fuel cell efficiency | 50-60% | 30-40% (no combine cycle) | 50-60% | 55% | 55-65% | 55-65% |

Fuel cell types are generally characterized by electrolyte material. The electrolyte is the substance between the positive and negative terminals, serving as the bridge for the ion exchange that generates electrical current.

While there are dozens of types of fuel cells, there are six principle kinds in various stages of commercial availability, or undergoing research, development and demonstration. These six fuel cell types are significantly different from each other in many respects; however, the key distinguishing feature is the electrolyte material.

2.3.1 Alkaline Fuel Cells (AFCs)

Alkaline Fuel Cells (AFCs) were the first type of fuel cell to be widely used for manned space applications. AFCs contain a potassium hydroxide (KOH) solution as the electrolyte. AFCs operate at temperatures between 100°C and 250°C (211°F

and 482°F). Higher temperature AFCs use a concentrated (85wt%) KOH solution while lower temperature AFCs use a more dilute KOH solution (35-50wt%). The electrolyte is contained in and/or supported by a matrix (usually asbestos) which wicks the electrolyte over the entire surface of the electrodes. A wide range of electro-catalysts can be used in the electrodes (e.g., Ni, Ag, spinels, metal oxides, and noble metals). The fuel supplied to an AFC must be pure hydrogen. Carbon monoxide (CO) poisons an AFC and carbon dioxide (CO₂) reacts with the electrolyte to form potassium carbonate (K₂CO₃). Even the small amount of CO₂ in the atmosphere (about 370 ppm) must be accounted for operation of an AFC (Hirschenhofer et al., 1998).

2.3.2 Molten Carbonate Fuel Cell (MCFC)

The electrolyte in an MCFC is an alkali carbonate (sodium, potassium, or lithium salts, i.e., Na₂CO₃, K₂CO₂, or Li₂CO₃) or a combination of alkali carbonates that is retained in a ceramic matrix of lithium aluminum oxide (LiAlO₂). An MCFC operates at 600 to 700°C where the alkali carbonates form a highly conductive molten salt with carbonate ions providing ionic conduction through the electrolyte matrix. Relatively inexpensive nickel (Ni) and nickel oxide (NiO) are adequate to promote reaction on the anode and cathode respectively at the high operating temperatures of an MCFC (Baker, 1997).

2.3.3 Phosphoric Acid Fuel Cell (PAFC)

Phosphoric Acid Fuel Cell (PAFC) technology is the most mature of the types in use today. PAFCs use a concentrated 100% phosphoric acid (H₃PO₄) electrolyte retained on a silicon carbide matrix and operate at temperatures between 150 and 220°C. Concentrated H₃PO₄ is a relatively stable acid, which allows operation at these temperatures. At lower temperatures, CO poisoning of the anode electro-catalyst (usually platinum) and poor ionic conduction in the electrolyte become problems (Hirschenhofer et al., 1998).

2.3.4 Solid Oxide Fuel Cells (SOFC)

Solid Oxide Fuel Cells (SOFCs) offer the stability and reliability of all-solid-state ceramic construction. High-temperature operation, up to 1,000°C, allows more flexibility in the choice of fuels and can produce very good performance in combined-cycle applications. SOFCs approach 60 % electrical efficiency in the simple cycle system, and 85 % total thermal efficiency in co-generation applications (Singhal, 1997).

2.3.5 The Direct-Methanol Fuel Cell (DMFC)

The direct-methanol fuel cell (DMFC) is similar to the PEM cell in that it uses a polymer membrane as an electrolyte. However, a catalyst on the DMFC anode draws hydrogen from liquid methanol, eliminating the need for a fuel reformer. While potentially a very attractive solution to the issues of hydrogen storage and transportation (particularly for portable applications), the principal problem facing the commercial application of the DMFC today stems from its relatively low performance in comparison to hydrogen fueled PEMFCs.

2.3.6 The proton exchange membrane fuel cell (PEMFC)

The proton exchange membrane fuel cell (PEMFC) is also known as the solid polymer or polymer electrolyte fuel cell. A PEMFC contains an electrolyte that is a layer of solid polymer (usually a sulfonic acid polymer, whose commercial name is Nafion™) that allows protons to be transmitted from one face to the other (Gottesfeld and Zawadinski, 1998). PEMFCs require hydrogen and oxygen as inputs, though the oxidant may also be ambient air, and these gases must be humidified. PEMFCs operate at a temperature much lower than other fuel cells, because of the limitations imposed by the thermal properties of the membrane itself. The operating temperatures are around 90°C. The PEMFC can be contaminated by CO, reducing

the performance and damaging catalytic materials within the cell. A PEMFC requires cooling and management of the exhaust water to function properly (Gottesfeld and Zawadinski, 1998).

2.4 Fuel Cell Benefit

The fuel cell benefits include high efficiency, environmental friendly, fuel flexibility and reliability. This makes fuel cell an excellent choice of good power generation.

2.4.1 High Efficiency

Depending upon fuel cell type and design, fuel-to-electricity efficiency ranges from 30 to 60% (LHV). For hybrid fuel cell/gas turbine systems, electrical conversion efficiencies are expected to achieve over 70% (LHV). When byproduct heat is utilized, the total energy efficiency of fuel cell systems approaches (Basu and Shah, 1993)

2.4.2 Environmental Friendly

The environmental benefits of fuel cells are some of the main motivating forces in their development. These benefits include the zero- or near-zero-emission of criteria pollutants (NO_x, SO_x, CO, and hydrocarbons) and very low noise emissions.

Environmentally friendly fuel cell properties could eliminate consumer contempt for power generation close to their houses and businesses. While most consumers probably would prefer to have conventional electricity generated at a

location far from their homes due to the noise and pollution, the benign nature of fuel cells makes them non-offensive even if placed in residential communities.

2.4.3 Reliability

Fuel cells are assumed to be superior to the grid because they are on site and subject to fewer disruptions with availability of 35%. With no moving parts, fuel cells will have less instances of failure than mechanical systems. (Barbir, 2005)

2.4.4 Fuel Flexibility

The primary fuels that can be directly utilized within fuel cell stacks today are hydrogen, carbon monoxide, methanol, and dilute light hydrocarbons like methane, depending upon the fuel cell type. Hydrogen is the optimal fuel for all types of fuel cells. Methanol can be used directly in a certain type of PEMFC called a direct methanol fuel cell.

2.5 Membrane for Proton Exchange Membrane Fuel Cell

Fuel cell used solid polymer as a membrane of the fuel cell. This membrane must have negative charge ion to allow the proton or mobile cation (H^+) migrate through the membrane. To achieve high efficiency, the membrane must possess the following desirable properties:

- a) High proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity.
- b) Adequate mechanical strength and stability
- c) Chemical and electrochemical stability under operating conditions
- d) Moisture control in stack

- e) Extremely low fuel or oxygen by-pass to maximize coulombic efficiency
- f) Production costs compatible with intended application

Nafion™ produced by Dupont is an example of good polymer membrane that satisfied the desirable properties above.

2.5.1 Perflourinated Polymer (Nafion™)

Nafion™ or perflourinated polymer produced by Dupont is widely used because of its high proton conductivity, good chemical stability and mechanical strength. However there are some limitations of the Nafion™ membrane. The high cost of producing this membrane and limitation of temperature is the main disadvantages of this membrane (Johnstone *et al*, 2001).

2.5.2 Sulfonated Polyethersulfone

To overcome the high producing cost of perflourinated polymer problems, studies have been conducted on non-fluorinated, hydrocarbon-based, polymer electrolyte membranes such as sulfonated polyethersulfone. The monomers for polymerization are commercially available and relatively cheap. The hydrocarbon-based polymer electrolyte membrane offers the possibility of the wide-scale commercialization of PEMFCs for future power generation systems.

2.6 Factors Affecting Membrane Performance

There are several factors that affecting membrane performances that is including hydration and thickness of the membrane.

2.6.1 Hydration

Proton conductivity is relies on water level in the membrane, the level of hydration of the membrane is crucial in determining the membrane efficiency. Higher conductivity is supported by higher level of hydration However, for operations with wet membranes, there is a possibility of the cathode being flooded which slows down the oxidation reaction. This is in particular a problem with Nafion™ because of a phenomenon known as electro-osmotic drag. The electroosmotic drag coefficient (EODC), which is a quantitative measure of hydration, is defined as the number of water molecules transported per proton (Wang *et al*, 2002).

2.6.2 Thickness

Lowering the membrane thickness is one of the methods to improve the membrane performance. Reduced membrane thickness also results in lower membrane resistance, higher membrane conductivity, lower production cost and rapid hydration. However, there is a limit to the extent to which membrane thickness can be reduced because of difficulties with durability and fuel by-pass.

2.6.3 Temperature

Membrane such as Nafion™ has high conductivity, excellent chemical stability, mechanical strength and flexibility, and potentially long-term durability. However, it functions only in a highly hydrated state and therefore it is limited to operation at temperatures up to around 80 °C under ambient pressure in order to maintain a high water content in the membrane. Generally, at high temperature, the performances of membrane will drop.

2.7 Membrane Testing Result Review

Table 2.2 shows the previous study of membrane characteristic

Table 2.2 : Results of membrane characteristic and performance

| Author/Year | Result |
|--|--|
| Wang <i>et al</i> (2002) | <ul style="list-style-type: none"> • Based on the phase images of SPES, it was concluded that the SPES has a percolation limit at about 40% of sulfonation degree. This percolation limit can explain the sudden increase of water uptake. |
| Rong Guan <i>et al</i> (2005) | <ul style="list-style-type: none"> • As the degree of sulfonation of SPES increased, the decomposition temperature of polymer chains decreased. • Showed a decrease in tensile strength as degree of sulfonation increased. • AFM phase images showed hydrophilic ionic domains connected to produce a co-continuous morphology at higher DS. |
| Ahmad Rahimpour <i>et al</i> (2008) | <ul style="list-style-type: none"> • Morphological studies results in porous membranes with larger surface pore size and higher sub-layer porosity. |
| Sheng Wen <i>et al</i> (2009) | <ul style="list-style-type: none"> • Composite membranes had higher T_g and thermal stability than the pure SPES membranes. |

Sheng Wen *et al* The composite membranes had higher T_g and thermal stability than the pure SPES membranes. Oxidative stability also increased with BPO_4 content, because of the cohesion of functional groups between SPES matrix and boron phosphate, which resisted the excessive swelling of the composite membranes under wet conditions. Increased proton conductivity was measured in response to increased BPO_4 content and increased temperature. The improved membrane properties were mainly due to the uniform distribution of embedded BPO_4

particles within the membrane matrix. The above facts make that the SPES/BPO₄ composite membranes are attractive candidates for high-temperature PEMFCs applications.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Material Selection

3.1.1 Polyethersulfone (PES)

Polyethersulfone (PES) is one of the materials which has been most widely used in the manufacture of synthetic polymer membranes due to its toughness and rigid resin similar to conventional engineering plastics, such as polycarbonate, at room temperature. Figure 3.1 shows structure of polyethersulfone.

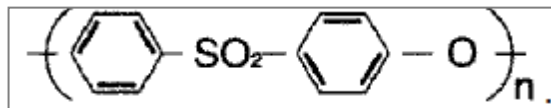


Figure 3.1: Polyethersulfone (PES) Structure

The greatest characteristic of PES is that it has by far better high-temperature properties than conventional engineering plastics. Specifically, PES remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200°C.

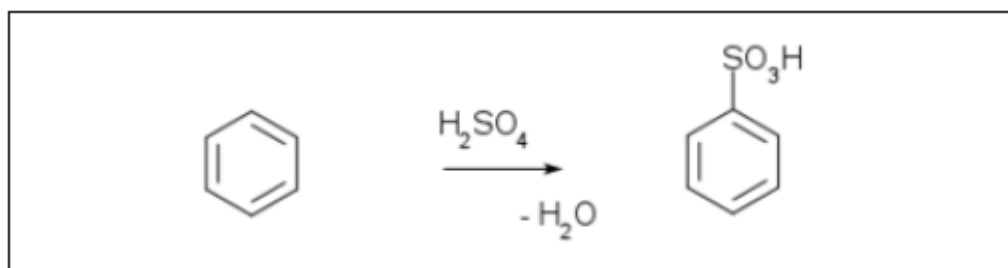
PES has excellent resistance to aqueous chemicals such as hot water, steam, acid and alkali, oils, grease, gasoline, alcohols, and aliphatic hydrocarbons. However, like almost all other organic compounds, PES is attacked by concentrated sulfuric acid and concentrated nitric acid. Table 3.1 shows of polyethersulfone properties.

Table 3.1: Polyethersulfone properties.

| Properties | Values |
|------------------------------|---------------------|
| Heat resistance (°C) | 200 |
| Water absorption (%) | 1.5-2.1 |
| Tensile strength (Mpa) | 127 |
| Volume resistivity, (ohm.cm) | 10×10^{16} |

3.1.2 Sulphuric Acid (H₂SO₄)

Sulphuric acid (H₂SO₄) was a sulfonating agent that has been utilized widely in sulfonation process. The ability to preserve the chain length of the starting polymer had made H₂SO₄ among the preferred choice of sulfonating agent. Figure 3.2 shows the Electrophilic Aromatic Substitution by H₂SO₄ and table 3.2 is the summaries of sulphuric acid properties.

**Figure 3.2 :** Electrophilic Aromatic Substitution by H₂SO₄ (Lufrano *et al*, 2001)**Table 3.2:** Properties of sulphuric acid

| Properties | Value |
|----------------------------|----------|
| Density, g/cm ₃ | 1.84 |
| Molecular weight, g/mol | 98.08 |
| Melting point, °C | 10 |
| Boiling point, °C | 290 |
| Soluble in water | miscible |
| Acidity | -3 |

3.1.3 Sodium Methoxide

To yield the desired sulfonated product, a solution of base is essential to cleave the trimethylsilyl group into the polymer backbone. In this study, sodium methoxide (CH_3ONa) was used. Table 3.3 shows the properties of sodium methoxide

Table 3.3: Properties of sodium methoxide

| Properties | Value |
|---|-------|
| Density, (g/cm_3) | 0.994 |
| Molecular weight, (g/mol) | 54 |
| Flash point, ($^{\circ}\text{C}$) | 29 |
| Viscosity, (cPs) | 28 |
| Boiling point, ($^{\circ}\text{C}$) | 85 |
| pH | 14 |
| Vapor pressure, (kPa) | 4.6 |

3.1.4 Dimethylacetamide (DMAc)

Dimethylacetamide, DMAc, is a colorless, high boiling, polar, hygroscopic liquid. DMAc is a good solvent for a wide range of organic and inorganic compounds and it is miscible with water, ethers, esters, ketones and aromatics compounds. It is used in the production of polyacrylonitrile and polyurethane based fibers, films and coatings. The polar nature of DMAc enables it to act as a combined solvent and reaction catalyst in many reactions producing high yields and pure product in short time periods. Table 3.4 shows the properties of Dimethylacetamide (DMAc)