CHAPTER I
INTRODUCTION

The limited energy sources such as petroleum fuels and coal are short while the consumption increases steadily. Internal and external problems of exporting fuel countries lead to the higher price of fuels. Moreover the toxic byproducts of petroleum and coal are released and stay as pollutions in the environment. Many scientists have found useful and less toxic alternative energy sources. Wind, water, and biomass, and etc. are used instead of the petroleum fuels and coal. Fuel cell is one of the efficient alternative energy sources (Stambouli *et al.*, 2002). Fuel cell is clean and a lesser toxic energy source and the byproduct from the reaction is only water vapor. Many kinds of fuel cell are used with various advantages. Solid oxide fuel cell has been developed for power generation applications: residential power, automobile auxiliary power, and gas turbine hybrid system. Alkaline fuel cells are used in certain applications such as the Apollo space missions and automobiles (Vielstich *et al.*, 2003).

Direct methanol fuel cells (DMFC) are proton exchange membrane fuel cells which use methanol as the fuel. The main applications of DMFC are energy sources of small vehicles such as a forklift, a tugger, consumer goods like laptop, a mobile phone, and a digital camera.

The heart of direct methanol fuel cell is the polymer electrolyte membrane. The main application of polymer electrolyte membrane is to conduct protons. The protons from oxidized methanol migrate through this electrolyte membrane. To obtain a good membrane for the direct methanol fuel cell, the membrane should have the required properties. High proton conductivity is the most important. Chemical and mechanical stabilize under the operating temperature are also expected properties. The membrane should be able to resist swelling, have good interface with the catalyst layer, and a low methanol cross over. The last but also important is low cost.

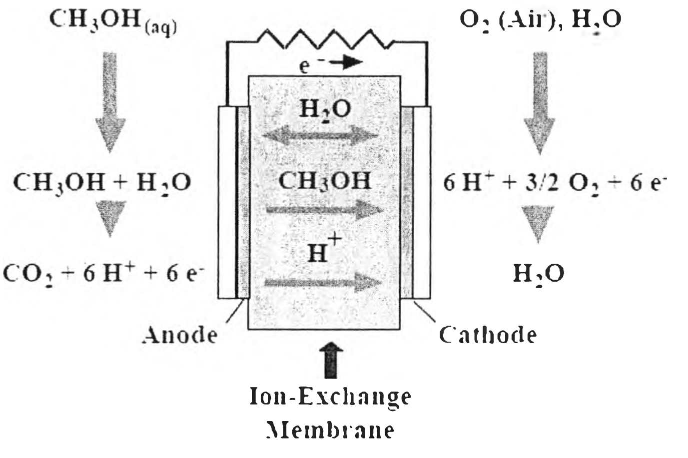

Figure 1.1 The operation of fuel cell.

Oxidation: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (1.1)

Reduction: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (1.2)

Cell reaction: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$ (1.3)

From Figure 1.1, the direct methanol fuel cell generates electricity by separating the methanol oxidation and the oxygen reduction. The methanol oxidation occurs on the anode side. Methanol is fed to the anode and reacts with water to produce carbon dioxide, protons, and electrons. These protons and electrons react with the oxygen on the cathode side to produce water. The electron from the methanol reaction is directed to the external circuit. While the protons that are generated pass through the membrane between the electrodes to complete the overall reaction.

One of the commercial proton exchange membrane is Nafion®. Nafion® possesses many advantageous properties as a proton exchange membrane. It has high proton conductivity, good mechanical and chemical properties, and also has high thermal stability. But Nafion® still has some weak points. The conductivity of Nafion® is low at a high operating temperature, high methanol crossover, and high cost.

Recently, the sulfonated polyether ketone has been synthesized as are placement candidate for Nafion® (Mikhailenka *et al.*, 2001). Because of the hydrophilic property, the sulfonated polyether ketone is suitable be the membrane for the direct methanol fuel cell. The sulfonated degree controls hydrophilic and hydrophobic characteristics of the membrane. Increasing the sulfonation degree induces higher conductivity but also increases the methanol permeability. It is well known that an aromatic polyimide has the thermal stability and high mechanical strength. The trend of modifying a membrane for the direct methanol fuel cell tends towards sulfonated aromatic polyimide with improved proton conductivity and reduced methanol permeability.

In this work, sulfonated poly(aromatic imide-co-aliphatic imide) membranes were synthesized at various degrees of sulfonation. The polyimide membranes were synthesized from 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid, hexamethylenediamine (SDDM) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride using dimethylsulfoxide as a solvent. The membrane was obtained by casting the mixture solution on in a petri dish. The effect of the degree of sulfonation to the properties of the membrane was investigated. The chemical structure of SDDM and SPI were characterized by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR). Degradation temperature of SPI was analyzed by the thermogravimetry analysis (TGA). The membrane required properties for the fuel cell were obtained: the proton conductivity, the methanol permeability, the ion exchange capacity, the water uptake and mechanical properties obtained from dynamic mechanical analyst (DMA).