CHAPTER I
INTRODUCTION

In recent years, the world energy consumption has been increasing because of the world economic growth which affects energy cost. However, fuel energies pose several problems towards environment; for example, they can generate greenhouse gases such as carbon dioxide (CO_2), water vapor, and methane, which have effects on human health. Therefore, it is logical to find an alternative energy and to develop its performances to replace the current energy sources. Many researchers have found useful and less toxic alternative energy sources. Solar, water, wind, and biomass are possible candidates to be used instead of the petroleum fuel and coal. Fuel cell is one of the efficient alternative energy sources. A fuel cell is an electrochemical device, which continuously converts chemical reaction to electric energy. A fuel cell is clean because its by product is water vapor. Fuel cell is usually classified by the electrolyte employed in the cell such as Alkaline Fuel Cell (AFC), Polymer Electrolyte Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell (DMFC), and Phosphoric Acid Fuel Cell (PAFC).

This work focuses on DMFC. Methanol is a possible candidate as a liquid fuel due to its high energy density. It would simply enable safe handling, and low cost distribution system. DMFC consists of an anode, a cathode, and a membrane. The membrane is the proton exchange membrane employed as an electrolyte. The membrane should have the required properties such as high proton conductivity, which is the most important, good mechanical and chemical stabilities under the operating temperature. The membrane should be able to resist swelling, has good interface with the catalyst layer, has a low methanol crossover, and relatively low cost compared to the commercial membranes (Carrette*et al.*, 2001).

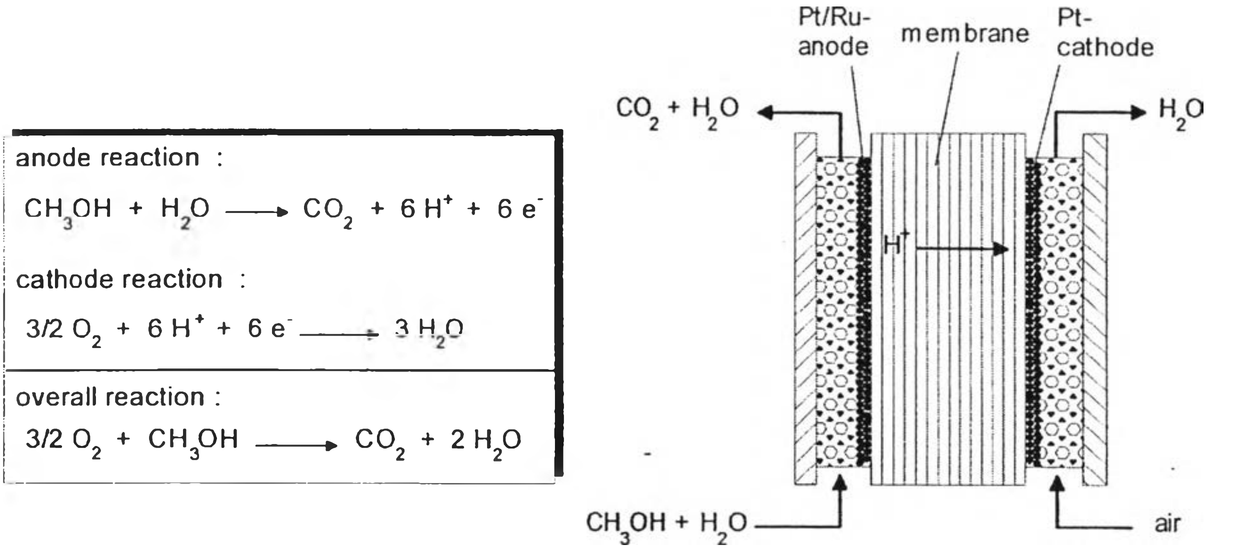

Figure 1.1 Schematic principle of a DMFC single cell (Baldauf and Preidel, 1999).

The basic structures of all fuel cells are similar: the cell consists of two electrodes, separated by the electrolyte, which are connected to an external circuit. Water is actually consumed at the anode in the oxidation, which produces carbon dioxide and a set of protons and electrons. The protons (H^+) pass through the proton exchange membrane and the electrons transport from the anode to the cathode through an external circuit to supply power to external devices. The air combines with the protons and electrons to form water molecules.

The equations (1.1), (1.2), (1.3) show the oxidation, reduction and overall reactions respectively

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)

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

The goal of this work is to develop a membrane as the polymer electrolyte for a direct methanol fuel cell. The membrane supports proton transport and separates the fuel between cathode and anode. In 2009, Higashihara *et al.*, studied (PEM) materials for improving the polymer electrolyte in fuel cell. The goal of this work was to adjust and develop a method of the sulfonation process to increase performances of PEMs. The method was categorized into four parts; 1) sulfonated/non-sulfonated multiblock copolymers, 2) branched polymers, 3) locally and densely sulfonated polymers with multiple sulfonic acids along the backbone polymer, and 4) high – IEC polymers with a highly hydrophobic backbone polymer.

Nafion is widely used as the membrane in DMFC because its high proton conductivity and mechanical strength. However, it has high price and high methanol permeability. High methanol permeability leads to a decrease in the DMFC performance. Therefore, alternate polymer membranes were developed for replacing commercial Nafion. The polymers selected were polysulfone and polyvinylidene fluoride as polymer membranes. Polysulfone is widely used in many utilizations such as tubing, printed circuit boards, and battery separator. Polysulfone could improve DMFC performance by sulfonation process. The hydrophilic of polysulfone was improved by a sulfonation process for pervaporation separation system (Shih-Hsiung *et al.*, 2000). The methanol crossover of sulfonated polysulfones (S-PSF) with different degrees of DS was lower when compared with Nafion 115 (Fu *et al.*, 2006).The methanol permeability of polyvinylidene fluoride was found to be lower than Nafion because it is a hydrophobic polymer (Wootthikanokkhan *et al.*, 2006).

In this work, the polymers were sulfonated at various ratios of acid per polymer. The sulfonated membranes were prepared and characterized in terms of proton conductivity, mechanical and thermal stability, and methanol permeability based on the effect of degree of sulfonation. FTIR and TGA techniques were employed to confirm the sulfonic group attachments on the polymer backbones.