CHAPTER I
INTRODUCTION

The Direct Methanol Fuel Cell (DMFC) is considered to be a highly promising power source for transportations and portable devices due to its several advantages e.g. no fuel processing unit, low temperature and pressure operation, high energy conversion efficiency, low emission, easy to design compact cell, quiet, clean and environmental friendly, and etc. The major problems are CO poison of catalyst, the high flux of fuel through the membrane or methanol crossover and the interface resistance between the electrode and the membrane. The selection of DMFC membrane is based on not only high proton conductivity but also good methanol barrier efficiency.

The materials commonly used for Polymer Electrolyte Membrane (PEM) in DMFC are perfluorosulfonic acid ionomers (e.g. Nafion produced by Dupont) because their good chemical and physical stability as well as excellent proton conductivity especially in fully hydrated membrane can provide high conductivity in order of 10^{-3}-10^{-2} Scm^{-1} at room temperature, high hydrolytic and oxidative stability, and good mechanical stability even in the presence of water. However, the three majors drawback are very high cost, high methanol permeability which leads to poisoning of the catalyst and reduction of the fuel cell electrical efficiency, and the loss of proton conductivity at low humidity and high temperature ($>$ 80 °C) due to lack of absorbed water in the membrane. The proton exchange membrane should have these characteristics: high proton conductivity, minimal water and methanol transport, excellent mechanical properties, good thermal and chemical stability, high resistance to dehydration, low gas permeability, low swelling, high resistance to oxidation, reduction and hydrolysis, and low cost. The PEM is a key component in DMFC system because it functions as an electrolyte for conducting protons from the anode to the cathode as well as providing a barrier for the transporting of electron, methanol, and gas cross-leaks between the two electrodes.

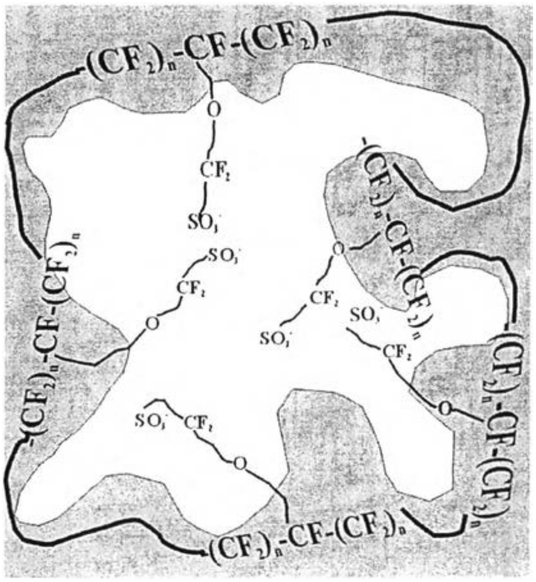

Figure 1.1 Nafion chemical structure (Carrette *et al.*, 2001).

The operation at high temperature (>120°C, preferably >150°C) and very low humidity levels are desirable. There are several advantages such as enhance catalyst stability towards the fuel impurities by reduced poisoning effect of the catalyst from CO which is very temperature-dependent (The CO adsorption is less pronounced with increasing temperature), faster electrode kinetics, chiefly a simplified water management design, increase in catalyst activity. Presently, Nafion which has been studied for more than 20 years, is still widely accepted and used.

The new alternative PEM materials such as sulfonated polybenzimidazole, sulfonated polysulfone, sulfonated poly(phenylene oxide), sulfonated polyimides, sulfonated polyphosphazene have been studied. Poly(aryl ketone)s such as poly(ether ether ketone) has several desired properties such as excellent thermal stability, high electrical and mechanical performance even at high temperature, high chemical resistance, and the ease to modify the chemical structure (Hickner *et al.*, 2004). The glass transition temperature of nonsulfonates PEEK is 146 °C. However, this polymer has low ion exchange property due to hydrophobic character. Sulfonation is a powerful method to introduce sulfonic acid group functionallity which can increase hydrophilicity and transportation of protons due to increase acidity. In sulfonated

PEEK (S-PEEK), the intermolecular interaction through hydrogen bonding increase with increasing degree of sulfonation (DS). Further, PEEK membranes show higher thermal degradation temperature than Nafion and hence are expected to show higher thermal stability at elevated temperature. The three principle methods for sulfonation of polymer are: the sulfonation of the polymer backbone, the radiation grafting of monomer groups onto the polymer backbone and then sulfonation, and the chemical grafting of sulfonated monomer groups. The sulfonated poly(ether ether ketone) (S-PEEK) has good thermal stability, appropriate proton conductivity at high degree of sulfonation (DS), and water uptake increases with increasing DS. However, if the water uptake is too much, there are loss of mechanical strength and high methanol permeation. These problems can be solved by polymer blending, composite, and cross-linking. These materials were often prepared by post-sulfonating the polymer which were not only degraded the mechanical and thermal stabilities, but also lack the control of sulfonation (e.g. the position and amount of sulfonate group in polymer structure). There are side reactions such as degradation and cross-linking via the intermolecular condensation of sulfonic acid and a phenyl groups to form an intermolecular sulfone link. The new method to the direct synthesis of S-PEEK from sulfonated monomer has been studied (Gil *et al.*, 2004). This method provides a more advantage than the post-sulfonation method. Because it is possible to control DS and position of sulfonate groups, to prevent cross-linking and other side reactions. It is also possible to incorporate two sulfonic acid group per polymer repeating unit. The synthesis of S-PEEK has been carried out by the nucleophilic substitution of fluorine through the reaction with the hydroxyl groups of biphenols. Sulfonation takes place only on the phenyl flanked by two ether groups of PEEK repeating units. This phenyl ring has four equivalent ortho positions for sulfonation, but only one of these four positions on the ring can be substituted in concentrated sulfuric acid. The other two phenyl rings which connect an ether group and a carbonyl group, are deactivated for the electrophilic sulfonation by the electron withdrawing effect of the carbonyl group. Further sulfonation (i.e. $DS > 1$) on the same phenyl ring does not take place because the sulfonic acid group ($-SO_3H$) exhibits electron withdrawing effect.

S-PEEK can dissolve in some organic solvents that allow it for casting to be a membrane. This solubility property offers a more convenient and less expensive process when compared with fabricating perfluorosulfonic acid membrane. In this study, the direct sulfonated poly(ether ether ketone)s are synthesized by varying the degree of sulfonation. Then, the S-PEEK membranes are prepared and characterized in terms of electronic, mechanical, thermal, hydrolytic, barrier properties, and morphology. Further study, the modification of S-PEEK membranes will take place in order to enhance the performance for practical use in DMFC, it can be modified by incorporate the conductive fillers, blended with another polymer, cross-linking to improve durability and so on.

In order to improve the performance of PEM, it is possible to modify the membrane composition by adding various proton conductors to form different types of membrane: adding plasticizers and/or crosslinking agent to the polymer matrix, polymer blended membrane, and inorganic/polymer composite membrane. The latter is of interest towards the increase in proton conductivity, the maintenance of water at high temperatures, and the increased mechanical support (Ramirez-Salgado *et al.*, 2007).

In our work, we are interested in developing sulfonated poly(aryl ketone)s for using as proton exchange membrane (PEM). The sulfonated poly(ether ketone ether sulfone) (S-PEKES) membranes were synthesized and characterized. The effect of degree of sulfonation (DS) on the important properties such as the proton conductivity, the methanol permeability, the water uptake (%), the thermal and mechanical stability, etc., were investigated by suitable techniques. The properties of the pure S-PEKES membrane were compared with S-PEEK 150XF and commercial Nafion 117 mambranes.

Furthermore, the incorporation of inorganic substance such as zeolites, into the polymer matrix, has been developed to form composite proton exchange membranes. The incorporation of various types of zeolites, within polymer matrix, can offer several advantages: proper mixing of inorganic and polymer at a molecular level provides good mechanical stability compared with a pristine polymer membrane; since proton conductivity is the effect of proton transporting on the surface of the proton conductor particles, an increase in surface area is expected to increase the proton conductivity obtained for a composite membrane (Smitha *et al.*, 2005).

Scope of Research Work

Research Work 1: Synthesis and Properties of Sulfonated Poly(ether ketone ether sulfone) (S-PEKES) via Biphenol S: Effect of Sulfonation

To synthesize the sulfonated poly(ether ketone ether sulfone) (S-PEKES) system A and B. The poly(ether ketone ether sulfone) (PEKES) was synthesized by nucleophilic aromatic substitution polycondensation between bisphenol S and 4,4'-difluoro-benzophenone (system A), and between bisphenol S and 4,4'-dichlorobenzophenone (system B). The resulting polymer was sulfonated by using concentrated sulfuric acid. The sulfonated membrane was fabricated by solvent casting. The sulfonated polymer samples were characterized by FTIR, ^{1}H-NMR, TGA, and LCR meter, and the degree of sulfonation (DS) was determined. The effect of sulfonation degree on these properties were evaluated.

Research Work 2: Polymer Electrolyte Membrane based on Sulfonated Poly(ether ketone ether sulfone) (S-PEKES) with Low Methanol Permeability for direct Methanol Fuel Cell Application

The proton conductivities and methanol permeabilities of S-PEKES-A, S-PEKES-B, S-PEEK 150XF, and Nafion 117 were determined. The effect of sulfonation degree, humidity, and temperature on these properties were evaluated. The thermal and mechanical stabilities of all membranes were characterized.

Research Work 3: Composite Proton Exchange Membranes of Sulfonated Poly(ether ketone ether sulfone) (S-PEKES) and Molecular Sieve with High Mechanical Strength for Direct Methanol Fuel Cell

Various concentrations of the molecular sieve 3A, 4A, and 5A were incorporated into the S-PEKES (DS = 0.66) to form the composite membranes. The effects of molecular sieve type and concentration on various properties of composite membranes were investigated and compared with Nafion 117 membrane.

Research Work 4: Solid Polymer Electrolyte based on ZSM-5/Sulfonated Poly(Ether Ketone Ether Sulfone) (S-PEKES) Composite Membranes with High Proton Conductivity

Various concentrations of the ZSM-5 zeolite with different Si/Al ratio were incorporated into the S-PEKES (DS = 0.66) to form the composite membranes. The effects of ZSM-5 concentration and Si/Al ratio on various properties of composite membranes were investigated and compared with Nafion 117 membrane.