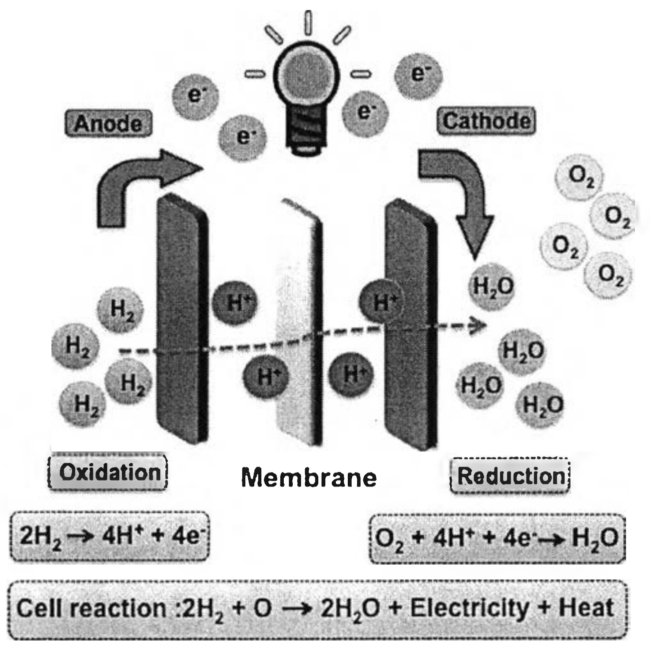
CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Basic Principle of Polymer Electrolyte Membrane (PEM)



Scheme 2.1

Polymer Electrolyte Membrane (PEM) is a solid thin film, which is located between cathode and anode side. It is used as electrolyte to transfer hydrogen ion (proton) and gas separator to prevent gas crossover. The operation of the polymer electrolyte membrane fuel cell (PEMFC) starts from the hydrogen gas was purged into the system and reacted with catalyst via oxidation reaction to generate free electrons and protons. For free electrons, they move along the external circuit to generate electricity. In the case of protons, the membrane allows the proton to transfer from anode side to cathode side, and at that time the protons need to move through the membrane as fast as possible if we want to enhance the efficiency of electrical production. The material used as a membrane has to meet the requirements such as adequate mechanical property, high proton conductivity, low gas permeability, and low cost.

2.2 Proton Conductive Polymer

2.2.1 Nafion® Membrane

Nafion®, a perfluorosulfonated membrane, is a commercial material widely used as PEM. Nafion® membrane is a solid polymer electrolyte which exhibits high proton conductivity, high chemical and high thermal stability. The chemical structure of polymer consists of a linear backbone of fluorocarbon chains and pendant groups with sulfonyl group at the end of the side chain (Neburchilov *et al.*, 2007). The sulfonyl group in the structure of Nafion® membrane can form water cluster to transfer proton via hydrogen bond. The proton conductive property of Nafion® membrane is about 10^{-2} -10^{-1} S/cm at low temperature (less than 80 °C) under fully hydrated condition. In contrast, Nafion® membrane demonstrates a significant decrease (more than 50%) of proton conductivity when it is operated at high temperature (above 80 °C) because of evaporation of water cluster (Kim *et al.*, 2006). In addition, other drawbacks of Nafion® membrane are low resistance to methanol permeability and high cost of the material.

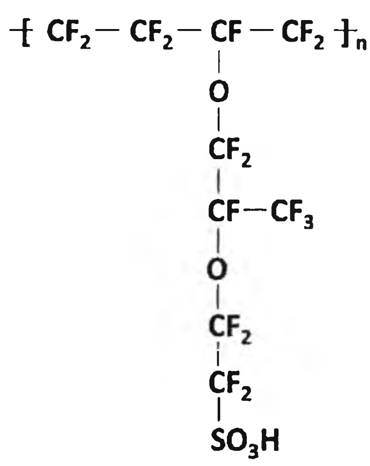


Figure 2.1 Chemical structure of perfluoro sulfonic acid polymers (Nafion®).

2.2.2 Sulfonated Poly (Ether Ether Ketone), SPEEK

There are many researchers studied about development of membrane efficiency for compensating a variety of drawbacks occurring from Nafion® membrane. Sulfonated poly (ether ether ketone) (SPEEK) is a kind of PEM based on hydrocarbon polymer. It demonstrates good properties to be used as PEM such as high thermal stability, chemical resistance, proton conductive and mechanical properties. The chemical structure of SPEEK membrane consists of aromatic ring and carbonyl group. Aromatic ring is substituted with sulfonyl group on the backbone by reacting with concentrated sulfuric acid (96%). The ability of SPEEK membrane to transfer proton relies on the degree of sulfonation substituted on the backbone. The sulfonyl group can form water cluster to transfer proton via hydrogen bond network. The sulfonation rate of SPEEK can be controlled by changing reaction time, temperature, and acid concentration (Mikhailenko *et al.*, 2004).

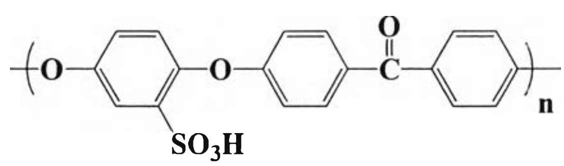


Figure 2.2 Chemical structure of sulfonated poly (ether ether ketone), SPEEK.

For example, Yi *et al.*, (2010) prepared SPEEK membrane doped with ionic liquid instead of water to transfer proton because of the unique properties of the ionic liquid i.e., high thermal stability, good chemical stability and non-volatility. The maximum ionic conductivity of the membrane was 8.3×10^{-3} S cm^{-1} at 170 °C under anhydrous conditions; however, the membrane was swelled due to the ionic liquid addition leading to a decrease in tensile strength of the membrane.

2.3 Heterocyclic Molecules

Because of the reduction of humidity at the temperature above 80 °C, the proton conductivity of membrane using water molecules to transfer proton is inefficient. In order to solve this problem, the proton transfer under anhydrous system is proposed. Heterocycles are the promising molecule for conductive species. The proton is transferred via their resonance structure. Moreover, it demonstrates good properties such as high thermal stability and hydrogen bond network.

M. Schuster *et al.*, (2001) reported about imidazole immobilization via flexible spacer. It was found that the heterocyclic molecule can transfer proton via resonance structure. The highest proton conductivity based on imidazole molecule is about 5×10^{-3} S cm^{-1} at 120 °C under water-fee condition.

Moreover, M. Yamada *et al.*, (2005) conducted the research on anhydrous proton conducting polymer electrolyte based on poly (vinylphosphonic acid)-heterocycle composite material. This research had investigated about acid-base hybrid materials by mixing of strong phosphonic acid polymer of poly (vinylphosphonic acid) (PVPA) with the heterocycles such as imidazole and pyrazole. As a result, PVPA-heterocycle composite material showed the high proton conductivity of approximately 10^{-3} S cm^{-1} at 150 °C under anhydrous system.

2.4 Proton Transfer Mechanisms

In general, proton conduction occurs in both hydrous and anhydrous states. In hydrous state, water is used as proton carrier for proton transferring. Water molecule (H_2O) carries a proton in the form of hydronium ion (H_3O^+) followed by proton hopping through hydrogen bond network of water cluster. This manner for proton movement is called vehicle mechanism. For anhydrous system, heterocycles e.g., imidazole, benzimidazole, and pyrazole are alternative molecules, which act as proton carrier in water-free polymer electrolyte. The heterocyclic compounds perform amphoteric behavior for proton transferring via Grotthuss mechanism that proton moves from one molecule to another through proton transfer and reorient under hydrogen bond network.

Yamada *et al.*, (2003) proposed self-assembled acid-base composite of hybrid acidic surfactant of monododecyl phosphate (MDP) and basic surfactant of 2-undecylimidzole (UI) molecules with highly ordered structure to enhance proton conductivity in heterocycles. It was found that the proton conductive route is effectively controlled by an appropriate molecular arrangement between acidic and basic moieties. The highest proton conductivity was observed at 1×10^{-3} S cm^{-1} at 150 °C under anhydrous condition.

2.5 Layered-by-Layered Assembly Technique

Layered-by-Layered (LBL) technique is a simple technique of multilayer assembly construction by alternating adsorption of anionic and cationic solution. The advantages of the adsorption processes are independent of the membrane size and shape. LBL deposition between sodium salt of poly (styrene sulfonate) and poly (ally amine hydrochloride) leads to multilayer film formation based on electrostatic attraction between opposite charges as a driving force to maintain its layers (Decher, 1997). In addition, the forming forces of LBL films are not only limited to electrostatic interaction but also based on hydrogen bonding and stereo complex formation.

LBL assembly is a promising approach for applying in various applications such as biosensors, biocompatibilizations and implants (Dech *et al.*, 2003). For instance, Serizawa *et al.*, (2002) investigated the formation of alternating ultrathin film of poly (vinyl alcohol) (PVA) and poly (methyl methacrylate) (PMMA) by using LBL assembly technique. The multilayer film was achieved, based on physical adsorption, when two polymers did not mutually dissolve.

2.6 Motivation of Research

It is known that the hydrogen bond is the key factor playing an important role in transferring proton. To enhance proton conductive performance of membrane, the membrane is focused to develop the proton transfer channel efficiency. Currently, we found that the benzimidazole model compound with varied number of benzimidazole unites has an effect on the increment of proton conductivity owning to the strong hydrogen bond interaction. Furthermore, the membrane containing acid as a proton donor and base as a proton acceptor can also enhance proton transfer efficiency.

As mentioned above, this work combines the concepts of proton donor-acceptor with uniform molecular arrangement of heterocycles to enhance proton transfer efficiency of membrane in anhydrous system.