CHAPTER II
LITERATURE REVIEW

2.1 Fuel Cell

Fuel cells are electrochemical devices that convert the chemical energy of a fuel directly into electrical and thermal energy, without combustion as an intermediate conversion of the fuel. Fuel cells consist of two electrodes (anode and cathode) and an electrolyte (usually retained in a matrix). Operation is much like that of battery except that the reactants and product are not continuously feeding to the cell. (Figure 2.1)
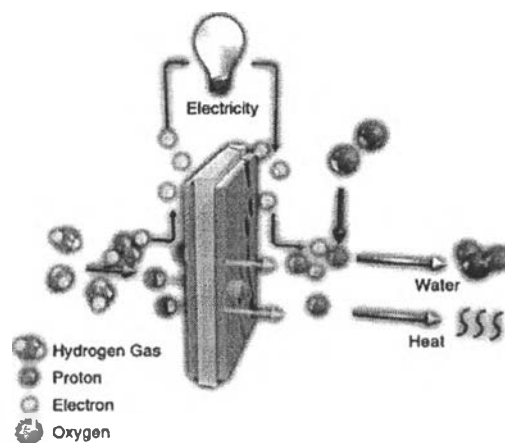

Figure 2.1 Flows and reactions in a simple fuel cell.
(Plug Power: http://www.plugpower.com/)

Fuel cells are 2 - 3 times more efficient than an internal combustion engine in converting fuel to power. Unlike ordinary combustion, fuel (hydrogen rich) and oxidant (typically air or oxygen) are delivered to the fuel cell separately. The fuel and oxidant streams are separated by an electrode-electrolyte system. Fuel is fed continuously to anode (negative electrode) and an oxidant is fed continuously to the cathode (positive electrode). Electrochemical oxidation and reduction take place at the electrodes to produce electrical energy for as long as the fuel and oxidant are fed to electrodes. The primary product of fuel cell reaction is water.

Fuel cell was first invented in 1839 by William Groove, a Welsh judge and amateur physicist, but the technology largely remained dormant until the late 1950s. Originally, fuel cell was consisted of four large cells, each containing dilute sulfuric acid as the electrolyte, hydrogen as the fuel, and oxygen as oxidizing agent, to produce electrical power which was then used to split the water into hydrogen and oxygen. The term "Fuel Cell" was coined in 1889 by L. Mond and C. Langer, who attempted to develop a fuel cell that uses industrial coal gas and air.

The technology had no practical value until the 1930's, when Francis T. Bacon applied the platinum catalysts employed by Mond and Langer in a hydrogen-oxygen fuel cell using less corrosive alkaline electrolyte and nickel electrodes.

In the 1950's, NASA used fuel cells to supply power during space flight. Fuel cells have provided on-board electricity and water to the Gemini, Apollo and space Shuttle missions. During the 1960s, through the expected commercial fuel cells, the technical barriers and high investment were officially started in many of the world-class industries. In this millennium, fuel cell received much attention to develop as a practical energy production pathway of green technology and the indeed energy for lifetime of the earth.

2.2 Attractive Features of Fuel Cell

One of the main attractive features of fuel cell systems is the high efficiency of fuel transformation to electricity. This efficiency, which runs from 40-60% based on the lower heating value (LHV) of the fuel, is higher than that of almost all energy conversion systems. Because fuel cells convert chemical energy directly to electrical energy, this process doesn't involve conversion of heat to mechanical energy. Fuel cell efficiencies can exceed the Carnot limit even when operating at relatively low temperature. In addition, fuel cells operate at near constant efficiency, independent of size, small fuel cells operate nearly as efficiently as large ones.

Though fuel cells are quiet, and operate with virtually no noxious emissions, fuel contaminants, e.g., CO, H_2S, NH_3 and halides, are the points to be concentrated.

The only waste product is the oxidized fuel, which is the water as a consequence from hydrogen fuel. This brings the most attractive features of the fuel cell. Carbon dioxide may be present as well, if a hydrocarbon fuel is used.

Efficient and clean energy production processes making fuel cell becomes another energy for the environment. In addition, fuel cells are expected to be economically viable once the mass production begins, at least in the fields of distributed power generation and remote systems.

2.3 Classifications of Fuel Cell

The use of electrolyte can vary the operating condition of fuel cell (such as temperature, oxidation conditions, etc.), thus, at present, the electrolyte defines the key properties, particularly operating temperature, of the fuel cell. For this reason, fuel cells are usually classified to five types according to the electrolyte used in the cells as follows.

- Polymer Electrolyte Membrane Fuel Cells (PEMFC)
- Alkaline Fuel Cells (AFC)
- Phosphoric Acid Fuel Cells (PAFC)
- Molten Carbonate Fuel cells (MCFC)
- Solid Oxide Fuel Cells (SOFC)

In addition, a fuel cell type known as Direct Methanol Fuel Cell (DMFC) is similar to PEMFC, which uses methanol as the fuel instead of hydrogen or hydrogen rich gas.
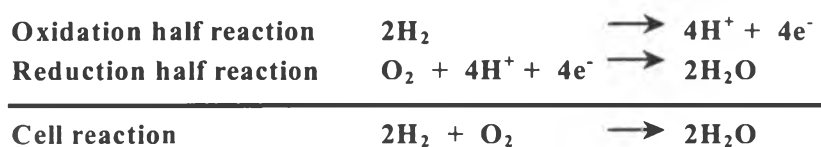
2.4 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

In PEMFCs, a thin ion-conducting polymer membrane is utilized as the electrolyte. Advantages of solid electrolyte are high power density, with less corrosion and electrolyte management problems compared to liquid electrolytes. The PEMFCs operate in temperatures where water is in liquid form. Through, low operating

temperature guarantees the quick start up from ambient conditions, the requirement of expensive platinum metal catalysts are the problems.

The PEMFC consists of a negatively charged electrode (cathode), a positively charged electrode (anode), and an electrolyte membrane. The half-cell reactions and the total reaction of the PEMFC are presented as below.

Electrochemistry of Fuel Cells

Oxidation half reaction	$2H_2$	$\longrightarrow$ $4H^+ + 4e^-$
Reduction half reaction	$O_2 + 4H^+ + 4e^-$	$\longrightarrow$ $2H_2O$
Cell reaction	$2H_2 + O_2$	$\longrightarrow$ $2H_2O$

Here, the oxidation of hydrogen is occurred at the anode where as the reduction of oxygen is occurred at the cathode. Protons are transported from the anode to the cathode through the electrolyte membrane and electrons are carried to the cathode over an external circuit. On the cathode, oxygen reacts with protons and electrons forming water and producing heat. Both the anode and the cathode contain a catalyst to speed up the electrochemical processes. These two half-reactions occur very slowly at the low operating temperature of PEMFC, so catalysts are used on both electrodes to increase the rates of each half-reaction. The final products of the overall reaction are electric power, water, and excess heat (Figure 2.2).
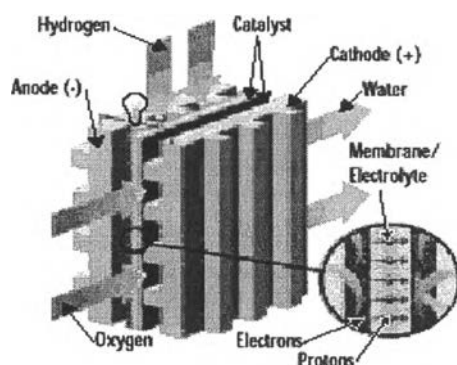

Figure 2.2 Flows and reactions in polymer electrolyte membrane fuel cell.

(Los Alamos National Laboratory: http://www.lanl.gov/)

The electrical and heat energy are produced by the cathode reaction. Theoretically, the Gibbs energy of the reaction is available as electrical energy and the rest of the reaction enthalpy is released as heat. In practice, a part of the Gibbs energy is also converted into heat via the loss mechanisms.

Single fuel cell produces a limited voltage, usually less than one volt. In order to produce a useful voltage for practical applications, the cells are connected in a series to form a fuel cell stack to increase the voltage multiplied by the number of unit cells stacked. An exploded view of a PEMFC and a PEMFC stack are presented in Figure 2.3.
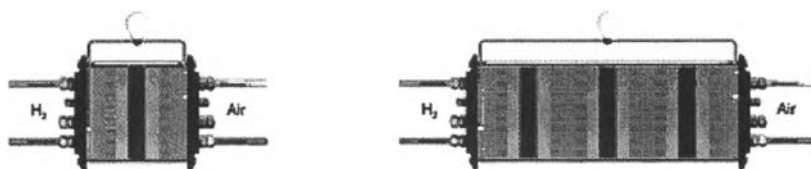

Figure 2.3 Single fuel cell and fuel cell stack.

(Plug Power: http://www.plugpower.com/)

2.5 Applications and Expectations

PEMFCs are considered to be attractive and alternative systems for power generation of vehicle and moving electronic products. At present, automotive industry is the largest investor in the PEMFC development. PEMFCs are well suited to transportation applications owing to a continuous electrical energy supply from fuel at high levels of efficiency and power density with minimal maintenance without any moving part in the power generating stacks.

Applications in stationary power generation both large-scale utility plants and small scale systems for distributed electricity and heat generation in buildings and individual homes are also on expectation. Fuel cells are considered to be an alternative for power generation in areas where no existing power grid or the power supply is available or reliable.

New applications are emerging in the field of portable power generation, where fuel cell systems may offer benefits compared to primary and rechargeable batteries in portable electronics. Major drawbacks of batteries are limited in capacity and slow recharging. With a suitable hydrogen storage method, fuel cell systems are quick to recharge and will achieve high power and energy densities.

2.6 Electrolyte Membrane

In general, electrolyte is a substance that dissociates into positively charged and negatively charged ions in the presence of water. When membrane absorbs water, the negative ions are rigidly held within the matrix of membrane. The electrolyte in the polymer electrolyte membrane fuel cell is a polymer, usually referred to as an ion-exchange membrane.

The polymer electrolyte membrane allows positive ions (hydrogen ions, or protons) from anode side to pass through to the cathode side, in one direction, but separates hydrogen and oxygen molecules and therefore prevents direct combustion. Only the hydrogen ions contained within the membrane are mobile and are free to carry positive charge through the membrane. However, the polymer electrolyte membrane also acts as an electronic insulator as part of the organic polymer. The electrons produced at one side of the cell must proceed, through an external wire, to the other side of the cell to complete the circuit.

The conductivity of the membrane is sensitive to contamination. For example, if the membrane is exposed to metallic impurities, metal ions diffuse into the membrane and displace protons as charge carriers, which lower the membrane conductivity.

2.7 Characteristics of the Traditional PEM and the Requirement for Development

The basic characteristics of membrane for fuel cell are required for high conductivity, good barrier properties, high mechanical strength, thermal and chemical stability, and electronic insulation properties. The membrane should have interaction

with water, provide good conductivity under a range of hydration conditions, and allow adequate transport of water to prevent polarization.

Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation. The membrane must remain hydration in order to be proton conductive. Therefore, the membrane must contain water so that the hydrogen ions can carry the charge within the membrane. This limits the operating temperature range of PEMFCs to be under the boiling point of water, and the water management system is the point to be concerned in PEMFC development. Operating PEMFCs at temperature exceeding $100^{\circ}C$ is possible only if under pressure conditions are set up. As a result, water is kept in a liquid state, but the shelf life of the cell will be short. Dehydration of the membrane reduces proton conductivity and excess of water can lead to flooding of the electrodes. Both conditions result in poor cell performance.

To develop new alternative membranes and improve polymer electrolyte fuel cell performance, four elements of the polymer electrolyte membrane can be varied:

- Primary structure of the polymer
- Morphology of the polymer
- Nature of the acid group used
- Nature of the medium, such as water, used to foster dissociation and transport of protons within the polymer phase.

2.8 Development of PEMFCs

The use of organic cation-exchange membrane polymers in fuel cells was conceived in the 1950s. The early membrane includes the hydrocarbon-type polymers such as cross-linked polystyrene-divinyl benzene-sulfonic acid and sulfonated phenol-formaldehyde tested in PEMFCs.

Historically, the first major application of fuel cell systems was in the Gemini space flights, for which the solid-polymer electrolyte fuel cell system of the General

Electric Company was chosen. The U.S. Gemini space program in the 1960s used a fuel cell module which membranes were polystyrene-divinylbenzene-sulfonic acid cross-linked within an inert fluorocarbon film. Though the fuel cells performed quite well for space missions of 1-2 weeks duration, there were some problems about the power densities (<50 mW/cm^2) and the unstability under the electrical environment of polystyrene sulfonate ion-exchange membrane. The life of PEMFCs was limited by oxidative degradation of the polymer electrolyte. For these reasons, the alkaline fuel cell system was chosen for the later Apollo program and the space shuttle flights.

When these polystyrenes were replaced with fluorine-substituted polystyrene, e.g. polytrifluorostyrene sulfonic acid. The shelf life of PEMFCs was extended by four to five times. However, the operating temperature of PEMFCs using fluorinated polystyrenes was limited to less than 75°C.

2.9 Nafion®: A Commercialized PEMFC

The General Electric Company pursued the development of solid polymer electrolyte fuel cells after the use in the Gemini space flights. The major breakthrough was the material development of the perfluorinated, sulfonic acid polymer, Nafion® (produced by DuPont in the early 1970s), as the polymer electrolyte membrane, which the structure consists of the ionomer units shown below where $n = 6$-10 and $m \geq 1$.

$$(CF_2CF_2)_a \text{---} (CF_2CF_2)_b$$
$$|$$
$$O$$
$$|$$
$$(CF_2CF)_n\text{---}(CF_2)_m\text{---}SO_3^- H^+$$
$$|$$
$$CF_3$$
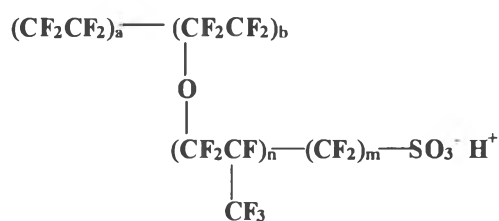
Scheme 2.1 Chemical structure of Nafion®

Nafion®, was first applied in the fuel cells in 1966 and still be the most widely used ion-exchange membrane in PEMFCs prototypes. Nafion® and its derivatives have

three features in common. The polymer chains consist mainly of a poly(tetrafluoroethylene) (PTFE) backbone, which statistically forms segments of several units in length, and a few ether linkage of perfluorinated vinyl polyether. The latter joints the PTFE segments to form a flexible branch pendent to the main perfluoro-chain and carries a terminal acidic group which is the ion clusters to provide the cation-exchange capacity. The acid molecules are fixed to the polymer and will not be leaked out, but the protons on these acid groups are free to migrate through the membrane. These perfluorinated ionomer membranes with sulfonic acid groups meet all the required characteristics of ion-exchange membranes for using in fuel cells as well as for using in H_2O and alkaline hydroxide electrolysis cells.

The Nafion® membranes, fully fluorinated polymers, exhibit exceptionally high chemical stability in strong bases, strong oxidizing, and reducing acids, H_2O_2, Cl_2, H_2, and O_2 at temperature up to 125°C. A high degree of dissociation and a high concentration of mobile H^+ ions ensure good ionic conductivity in Nafion®. A conductivity of > 0.05 (ohm.cm)$^{-1}$ at 25°C is considered to be acceptable for use in fuel cells. The range of equivalent weights for Nafion® that is of greatest interest in PEMFCs is 1100 to 1350. This provides a highly acidic environment, i.e., comparable to a 10 wt% H_2SO_4 solution, in a hydrated membrane.

The main advantages of Nafion® over polystyrene sulfonic-acid membranes are high acidity because of the presence of fluorocarbon rather than hydrocarbon groups (the fluorine atom is electrophilic), and higher stability of the C-F compared with the C-H bond in the electrochemical environment that membranes yielded electrochemical stability in PEMFCs at temperatures up to about 100°C.

However, progress in this technology was slow due to the "drying out" of the membrane during system operation. The major problem encountered with the General Electric fuel cell was to keep the membrane wet under operating conditions. Proper humidification of the reactant gases is necessary. The General Electric Company solved the water management problem by:

(i) internal humidification of the reactant gases in a separate chamber, and

(ii) differential pressurization, i.e. using a higher pressure on the cathode side (10 atm with air) than on the anode side (2 atm with hydrogen).

In 1987, Ballard made a breakthrough in PEMFC performance by using a new, sulfonated fluorocarbon polymer membrane from Dow Chemical, similar to that developed by DuPont (Nafion®). It produces four times the current at the same operating voltages as the Nafion® membrane.

A newer series of perfluorinated ionomers (qv), developed by Dow Chemical Co., provides an attractive alternative to Nafion® in PEMFCs. This newer polymer has a PTFE-like backbone similar to those of Nafion®, but the pendent side chain containing the sulfonic acid group is shorter. Instead of the long side chain of Nafion®, the side chain of the Dow polymer consists of $OCF_2\text{-}CF_2\text{-}SO_3H$ (where $n=0$ and $m=2$, Scheme 2.1). This polymer possesses ion-exchange properties similar to that of Nafion, and is also available with higher acid strength and lower equivalent weights, i.e., 600-950. Even at these low equivalent weights, the Dow membrane has a good mechanical strength and does not hydrate excessively, whereas Nafion® of comparable equivalent weight would form a highly gelled polymer, having poor or no mechanical integrity. The physical and transport properties of ion-exchange membranes are largely determined by the amount of absorbed H_2O. For a given equivalent weight, the Dow polymer membrane absorbs less water (~50%) than Nafion®, but it has comparable ionic conductivity and lower permeability. As comparing to Nafion®, PEMFCs contained Dow polymer membrane give advantages about operating temperature (above 100°C), less CO poisoning of the electrocatalyst, including increase the kinetics electrode.

The Fuel cell Group at the Paul Scherrer Institute (PSI) utilize the radiation-grafting method for membrane preparation, in particular concerning the development of low cost alternatives to the perfluorinated proton-conducting membranes, by the radiation grafting of monomers onto various trunk polymers and subsequent sulfonation of the grafted side chains. Highly crosslinked membranes of the system FEP (perfluoroethylene-perfluoropropylene copolymer)-styrene/divinylbenzene and

membranes with triallyl cynurate in addition to divinylbenzene as crosslinkers were previously reported (Scherer *et al.*, 1997). The research group at PSI found the crosslinker combination of divinylbenzene (DVB) and triallyl cyanurate (TAC) that provides a good stability, a high flexibility and a low resistance.

2.10 Motivation of the Present Work

Kreuer *et al.* (1998) reported the properties of imidazole and pyrazole as a solvent for acidic protons in polymers and liquids. The creation of protonic defects and the mobility of protons in these environments are found to be similar to the situation in corresponding water containing systems. It is also reported that imidazole and pyrazole enhance the thermal stability. Like water, these heterocyclic molecules form similar hydrogen bond networks and the transport properties in the liquid state. They act as proton donor and acceptor in proton conduction processes. The chemical properties of imidazole or pyrazole based molecules may extend the application range for proton conducting solids and liquids.


Imidazole   **Pyrazole**

Scheme 2.2 Chemical structure of imidazole and pyrazole

Schuster *et al.* (2001) presented imidazole-terminated ethyleneoxide oligomers as model materials. Conductivity of materials showed the structure diffusion (intermolecular proton transfer and structural reorganization by hydrogen bond breaking and forming processes) to be dominant conduction process, which gave rise to proton conductivities of up to 5×10^{-3} S cm^{-1} at 120°C in completely water free materials. Heterocyclics (imidazole) may be bound to soft oligomer chains (ethyleneoxide) in such a way that the heterocycle aggregates allow the local dynamics for rapid long range transport of 'excess' protons via structure diffusion, involving proton transfer between

heterocyclics with the corresponding reorganization of the hydrogen bond pattern. This mechanism may be the basic for fast proton transport in fully polymeric systems comprising similar soft spacers as part of their architecture.

Although heterocyclic molecules such as imidazole group shows an important feature to contribute the proton connection route in PEM membrane without using water as a media, up to now, there is no report about functionalization of polymer chain with heterocyclic molecules for the objectives of PEM. Considering the up-to-date PEM, there are some requirements to produce membrane to overcome the present stage, especially the use in high temperature and the water required in the membrane. On this viewpoint, the present project considers a state-of-the-art PEM by designing the polymer chain with engineering polymer backbone functionalized with heterocyclic molecules such as imidazole group as a proton transferring part. The key of the success should also relate to a well-defined structure to let the proton transfer in a regular manner. As shown in Scheme 2.2, the present project proposes a concept of polymer chain to satisfy the requirements at molecular level.
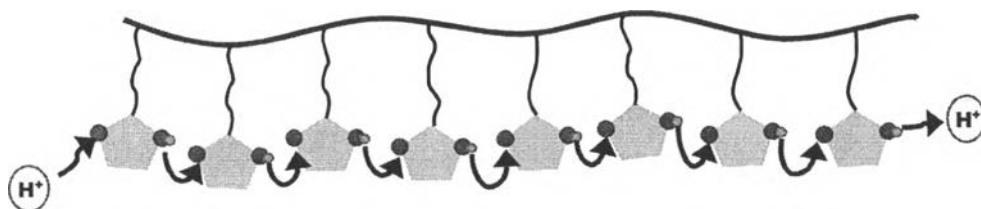
Scheme 2.3 Schematic draw of the functionalized polymer for PEM and
the proton connection route obtained.

Here, a type of polyamide functionalized with heterocyclic molecules such as adenine is proposed as a concrete example (Scheme 2.3). It is important to note that, there are aza-methylene phenol molecules related to the structure since it is our own successful result (Laubuthee *et al.*, 2001) to produce the open-ring structure of benzoxazine monomer at dimerization step. This molecule will be a spacer to conjugate heterocyclic molecules such as imidazole group onto polymer backbone. To achieve the

polymer membrane as designed, the project is divided into three parts, i.e. Heterocyclic Derivatives of Polymeric chain, Polymer Electrolyte Membrane, and Polymer Electrolyte Membrane Characterization. The present work focuses on the Part I: Heterocyclic Derivatives of Polymeric chain and aims to develop heterocyclic molecules appropriate for polymerization in the Part II. The achievement of this work will be a guideline to develop a novel material for PEMFC in the next stage.
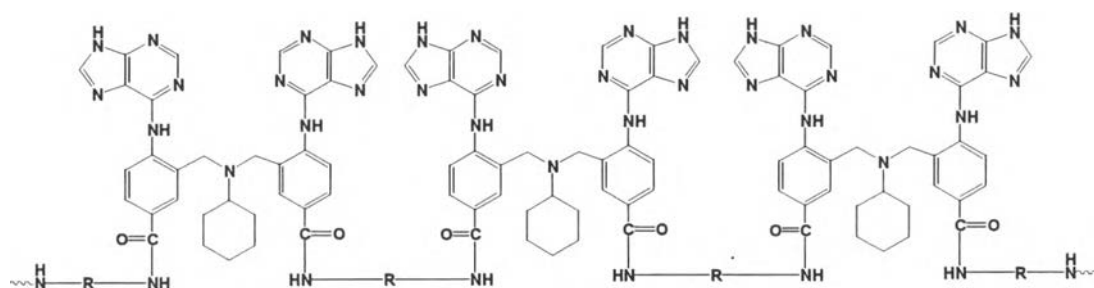
Scheme 2.4 Schematic draw of bis(hydroxybenzyl)amine based

proton transfer polymer system.

Another important point in the present project (Part II: Polymer electrolyte membrane) to produce membrane is that the polyamide chain will be produced at the aza-methylene phenol molecules by amidation. The compound, then, will be cast for membrane. The next stage is to evaluate the proton conductivity and other properties related to the properties of PEMs (Part III: Polymer electrolyte membrane characterization). Through studies in these parts, the final goal should bring a novel type of polymer chain satisfied the requirements of the PEM.