CHAPTER II
LITERATURE REVIEW

2.1 About Fuel Cell
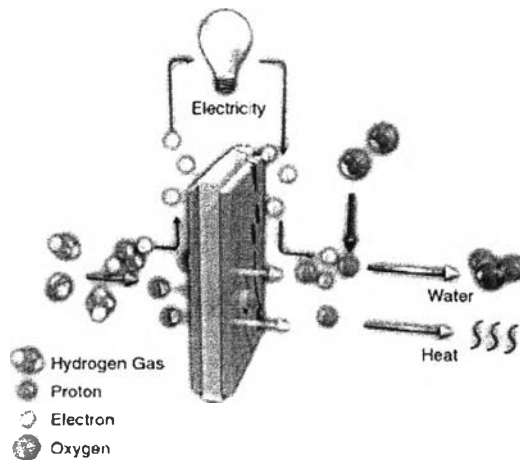

Figure 2.1 Flows and reactions in a simple fuel cell.

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

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 products are not continuously feeding to the cell (see Figure 2.1).

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.

Fuel cells were 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 cells were consisted of four large cells, each containing dilute sulfuric acid as the electrolyte, hydrogen as the fuel, and oxygen as oxidizing agent, to produce electric power which was then used to split the water into hydrogen and oxygen. The term "Fuel Cell" was coined in 1889 by Mond and 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 decided to use 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 as a 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 constant efficiency, independent of size.

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 concerned. Water is the only by- product obtained from the hydrogen fuel. This

brings the most attractive features of the fuel cell. Carbon dioxide may be presented as well, if a hydrocarbon fuel is used.

2.3 Classification of Fuel Cell

The use of electrolyte can vary the operating condition of fuel cell (such as temperature, oxidation condtions, etc.), thus, at present, there are five types of fuel cell classified based on the electrolytes, i.e., Proton Exchange Membrane Fuel Cells (PEMFC), Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel cells (MCFC), and Solid Oxide Fuel Cells (SOFC). In addition, a fuel cell type known as Direct Methanol Fuel Cell (DMFC) is similar to PEMFC, but uses methanol as the fuel instead of hydrogen or hydrogen rich gas (see Table 2.1).

Table 2.1 Fuel cells in currently practical applications and development

	AFC (Alkaline)	PEMFC (Polymer Electrolyte Membrane)	DMFC (Direct Methanol)	PAFC (Phosphoric Acid)	SAFC (Solid Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
Operating temp.(°C)	<100	60-120	60-120	160-220	180-500 (CsH_2PO_4)	600-800	800-1000 low temperature (500-600) possible
Anode reaction	$H_2+2OH^- \rightarrow 2H_2O+2e^-$	$H_2 \rightarrow 2H^++2e^-$	$CH_3OH+H_2O \rightarrow CO_2+6H^++6e^-$	$H_2 \rightarrow 2H^++2e^-$	$H_2 \rightarrow 2H^++2e^-$	$H_2+CO_3^{2-} \rightarrow H_2O+CO_2+2e^-$	$H_2+O^{2-} \rightarrow H_2O+2e^-$
Cathode reaction	$1/2O_2+H_2O+2e^- \rightarrow 2OH^-$	$1/2O_2+2H^++2e^- \rightarrow H_2O$	$3/2O_2+6H^++6e^- \rightarrow 3H_2O$	$1/2O_2+2H^++2e^- \rightarrow H_2O$	$1/2O_2+2H^++2e^- \rightarrow H_2O$	$1/2O_2+CO_2+2e^- \rightarrow CO_3^{2-}$	$1/2O_2+2e^- \rightarrow O^{2-}$
Applications	Transportation Space Military Energy storage systems			Combined heat and power for decentralized stationary power systems	Not yet determined (2004)	Combined heat and power for stationary decentralized systems and for transportation (trains, boats, ...)	
Realized Power	Small plants 5-150 kW modular	Small plants 5-250 kW modular	Small plants 5 kW	Small-medium sized plants 50 kW-11 MW	Small-medium sized plants 50 kW-11 MW	Small power plants 100 kW-2 MW	Small power plants 100-250 kW
Charge Carrier (Electrolyte)	OH^-	H^+	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

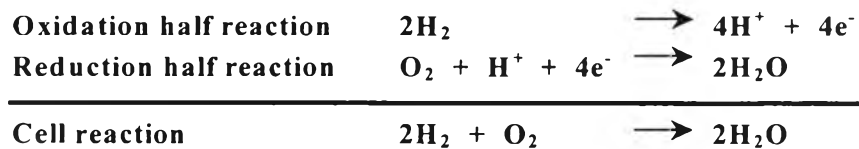Note: Negative ion charge carrier = cathode to anode

Positive ion charge carrier = anode to cathode.

2.4 Solid Electrolyte: Proton Exchange Membrane Fuel Cell (PEMFC)

In PEMFCs, a thin ion-conductive 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 temperature where water is in liquid form. Through, low operating temperature guarantees the quick start up from ambient condition, the requirement of expensive platinum metal catalyst is the limitation.

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 follow.

Electrochemistry of Fuel Cells

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

Cell reaction	$2H_2 + O_2$	$\longrightarrow$ $2H_2O$

Hydrogen is oxidized on the anode and oxygen is reduced on 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 of the half-reaction 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 electrical power, water, and heat (see Figure 2.2).
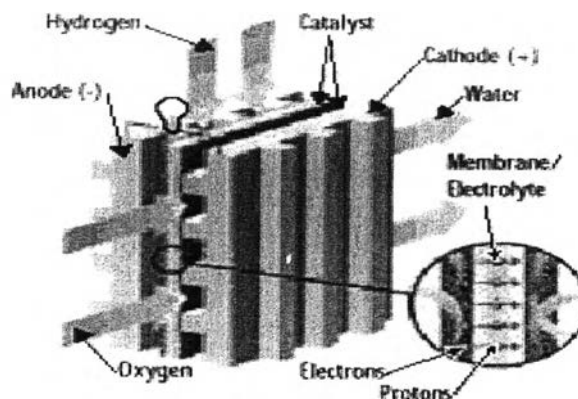

Figure 2.2 Flows and reactions in Proton Exchange Membrane Fuel Cell.

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

The electrical energy and heat 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. Single fuel cell produces a limited voltage, usually less than one volt. In order to produce a level of voltage for practical applications, the cells are connected in 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.
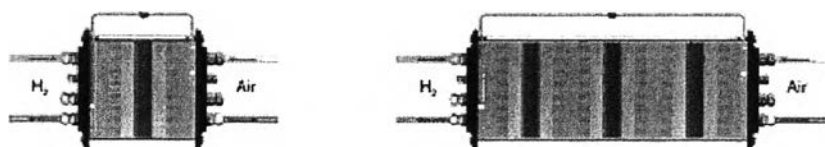

Figure 2.3 Single fuel cell and fuel cell stack.
(Plug Power: http://www.plugpower.com/)

2.5 Applications and Expectations

PEMFCs are considered to be attractive and alternative systems for power generation of vehicles and moving electronic products. At this moment 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 Membranes

In general, electrolyte is a substance that dissociates into positively charged and negatively charged ions in the presence of water, thereby making the water solution electrically conducting. 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 (are 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 Requirements 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 °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.

In order to develop new alternative membranes with better fuel cell performance, four elements of the polymer electrolyte membrane can be varied. Those are primary structure of the polymer, morphology of the polymer, nature of the acid group used, and nature of the medium such as water. The function of the medium is to be proton transportation 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 for 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, see chemical structure in Scheme 2.1), as the polymer electrolyte membrane, which the structure consists of the ionomer units shown below where n = 6-10 and $m \geq 1$.

Scheme 2.1 Chemical structure of Nafion®

$$(CF_2CF_2)_a \text{---} (CF_2CF_2)_b$$
$$|$$
$$O$$
$$|$$
$$(CF_2CF)_n \text{---} (CF_2)_m \text{---} SO_3^- H^+$$
$$|$$
$$CF_3$$
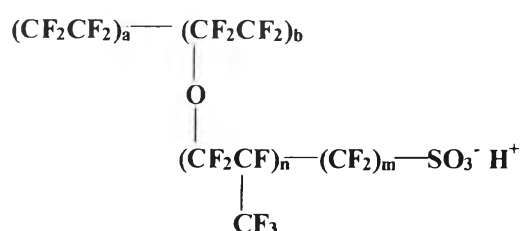
Nafion® was first applied in the fuel cells in 1966 and still be the most widely used as ion-exchange membrane in PEMFCs prototypes. Nafion and its derivatives have three features in common. The polymer chains consist mainly of a poly (tetrafluoroethylene) (PTFE) backbone, which statistically forms segments 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 pendant to the main perfluoro-chain and carries a terminal acidic group providing the ion clusters for 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 keeping 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, 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 $OCF_2-CF_2-SO_3H$ (where $n=0$ and $m=2$). 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 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) utilizes 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.

A number of research group developed ionomers produced by soaking of polybenzimidazole foils with phosphoric acid, where the phosphoric acid acted as the proton-conducting species (1994). These blend membranes had the disadvantage that the phosphoric acid gradually diffused out of the membrane together with the water formed within action of the fuel cell so that the membrane lost its initial ionic conductivity. Ledjeff (1993) proposed the application of cross-linked sulfonated poly

(ethersulfone) ionomers, produced via electrophilic sulfonation as protonic conductors in PEFCs. However, no PEFC application data were provided in this article. In a patent paper, sulfonated PEEK (polyether ether ketone) membranes were proposed as proton conductor in a PEFC (Helmer-Metzmann et al., 1993). In this patent a good chemical stability of the sulfonated PEEK membranes was reported. A new publication of Ledjeff et al. suggested the application of organic solvent-soluble, thermally and chemically stable polyphenylenes as protonic conductors in PEFC (Matejcek, 1995). However, no PEFC application data of these membranes have been reported to date. Recently, the BALLARD Company announced the development of a non-fluorinated proton-conducting membrane based on an arylic main-chain polymer which showed a good performance in a PEFC (Steck, 1995). However, the chemical nature of the base polymer was not disclosed, as was to be expected.

2.10 Proton Transport Phenomena

Proton transfer mechanism within the membrane is crucial phenomena to understand the transportation of proton donors and acceptors, such as sulphonic acid and water or imidazole groups, respectively. Microscopic models of the membranes have been studied by using molecular modeling either molecular dynamics or quantum mechanics. Overall process in proton transfer of membranes is occurred in following steps: (i) dissociation of protons, (ii) reaction, (iii) complex reforming step, and (iv) diffusion The classical theory for proton transfer mechanism at low temperature is the *Grotthuss mechanism* (Kreuer et al., 2004) (see Figure 2.4). Firstly, SO_3H group dissociates into proton, as a consequence of irreversible proton transfer through water molecules. The rate determining step depends on the breaking and forming of hydrogen bond in the ion clusters.
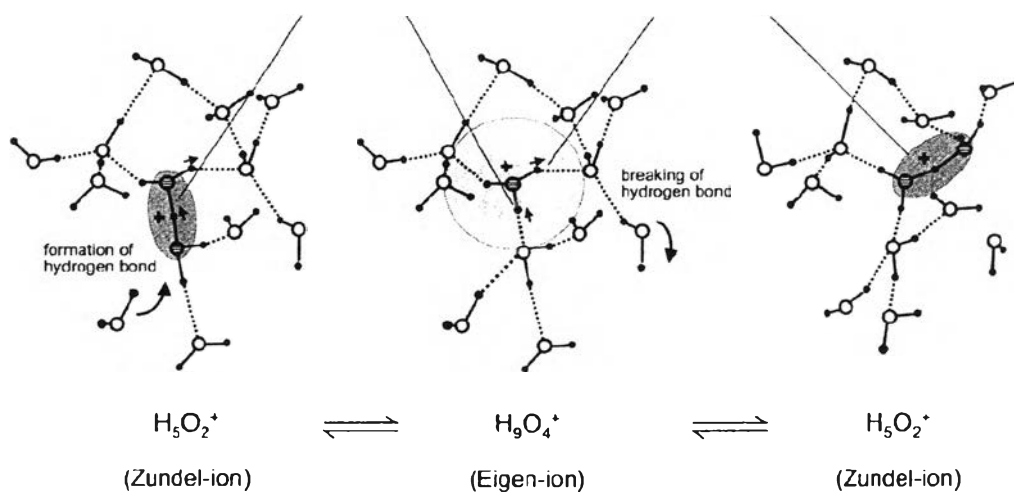
$H_5O_2^+$ ⇌ $H_9O_4^+$ ⇌ $H_5O_2^+$

(Zundel-ion)   (Eigen-ion)   (Zundel-ion)

Figure 2.4 Proton conduction in water. The protonic defect follows the center of symmetry of the hydrogen-bond pattern, which diffuses by hydrogen-bond breaking and forming processes; therefore, the mechanism is frequently termed "Grothuss" or structural mechanism.

The second theory is the *Vehicle mechanism* (Kreuer, 1996). The formation of protonic charge carriers is from the water itself. In other words, protons are transferred in bulk waters by defect protons. It should be noted that the *Grotthuss* (rotational) mechanism are progressively dominated by the *Vehicle* (translational) mechanism at higher temperature.

The third theory is the surface transport mechanism which is not frequently mentioned as shown in Figure 2.5. The concept indicated the mobility of protons at polymer interface. When protons are –on average- located close to the pore surface, transport occurs along the aqueous/polymer interface in the membrane network at low water content (Seeliger *et al.*, 2005).
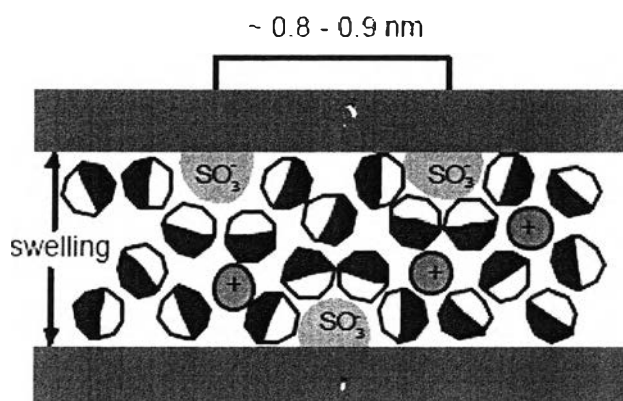
Figure 2.5 Proton transfer in bulk water by defect protons. (Kreuer *et al.*, 2004)

2.11 Alternative Membranes for PEMFC

Conventional Nafion® is currently chosen for a polymer membrane in the most PEMFC and DMFC applications, despite its shortcoming. Many researchers have been developing alternative membranes to overcome the limitation of Nafion®, such as, low operating temperature < 100 °C, high methanol crossover for Direct Methanol Fuel Cell (DMFC), and high cost of membranes. Rikukawa and Sanui (2000) suggested that in order to produce the material that are less expensive than Nafion®, material lifetime and mechanical properties should be fairly considered, which provides the cost factor to be commercially realistic. Even though hydrocarbon polymers have low thermal and chemical stability, they have attracted much interest for further development.
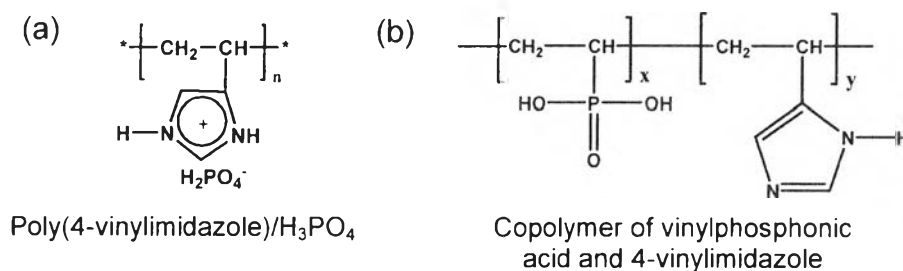
2.11.1 Alternative Hydrocarbon Polymer Membranes

Hydrocarbon polymers provide some advantages over PFSA polymers, i.e., they are less expensive, commercially available and their structures permits the introduction of polar sites as a pendant group for increasing water uptake (see Scheme 2.2). Hydrocarbon membranes based on polystyrene have received much attention for fuel cell systems. For example, sulfonated polystyrene (ethylene-butadiene) polystyrene (SEBS) triblock copolymer was reported by Sangeeth (2005). The membrane revealed excellent conductivity in the order of 10^{-1} S/cm in fully hydrated state at room temperature. Afterthat, Mokrini and Honeault (2006) blended

this SEBS with polyvinylidine chloride (PVDF). The SEBS part offer good proton conductivity while PVDF insures good dimensional stability and chemical resistant to the film.

Poly (vinyl alcohol) (PVA) membranes are well known as methanol barriers and water soluble polymer; thus, a swelling of PVA could be controlled by crosslink degree. It is important to note that the high water permeability should give high proton conductivity at least when the membranes are equilibrated with phosphoric acid (Bryan *et al.*, 1999). Besides, Nikolic *et al.* (2007) reported the cross-linked PVA membranes prepared by gamma irradiation. The proton conductivity was measured from the 6 M KOH-impregnated membranes at certain time and temperature. The cross-linked PVA membranes showed the comparable polarization curve to Nafion® membrane.

Scheme 2.2 An example of hydrocarbon polymer membranes: (a) Bozkurt *et al.*, 2001, and (b) Bozkurt *et al.*, 2003.

(a) Poly(4-vinylimidazole)/H_3PO_4

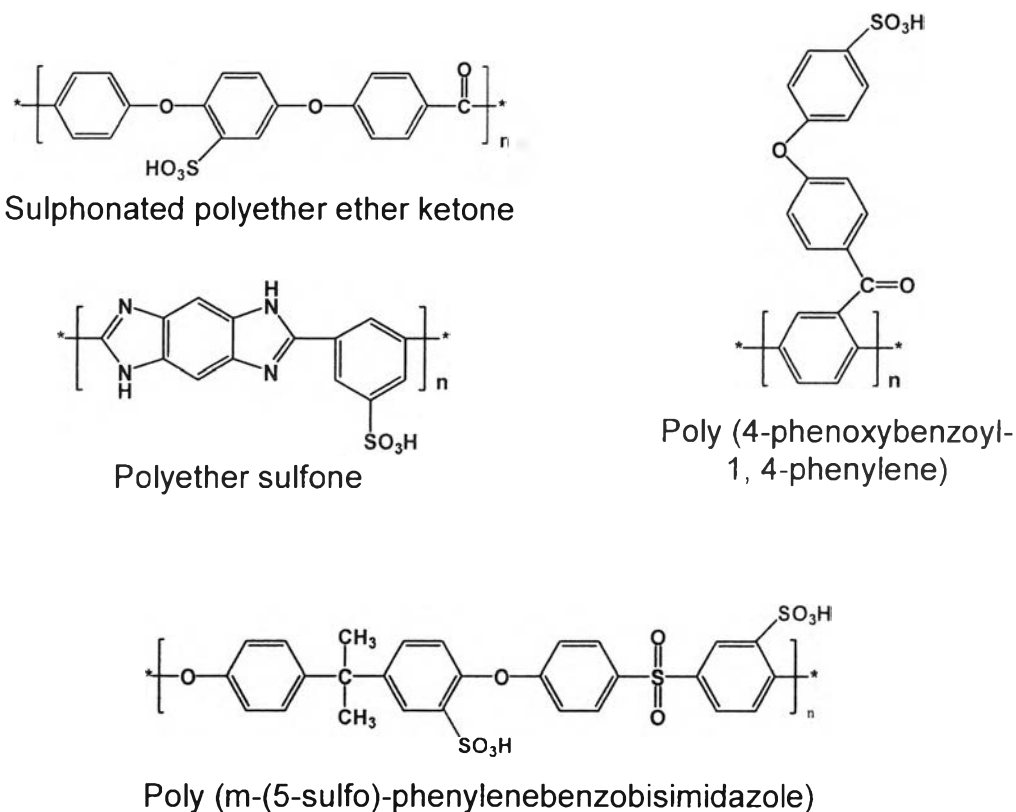(b) Copolymer of vinylphosphonic acid and 4-vinylimidazole

2.11.2 Alternative Sulphonated Aromatic Polymer Membranes

Aromatic hydrocarbons posses a superior property over hydrocarbon polymers: e.g. chemical resistance, thermal and mechanical stabilities at elevated temperature (see Scheme 2.3). Sulfonated polybenzimidazole exhibited excellent performance compared to Nafion® membrane at high temperature (Bae *et al.*, 2002). Radiations of blended cross-linked polyphosphazenes were also prepared for the reduction of water swelling (Carter et al., 2002). Polyarylenes are rigid polymers with T_g > 200 °C due to the presence of inflexible and bulky aromatic

groups (Guth *et al.*, 1999). The aromatic rings offer the possibility of both electrophilic and nucleophelic substitutions. The sulfonation of polyarylenes, e.g., polyethersulfone (PESF) (Kice and Puls. 1977), polyetherketone (PEK) with varying number of ether and ketone functionalities (such as PEEK (Kobayashi *et al.*, 1998), PEKK (Gasa *et al.*, 2007), etc.), poly (arylene ethers) (Hong *et al.*, 2008, Wang *et al.*, 2006), polyester (Zou *et al.*, 2004) and polyimide (Vallejo *et al.*, 1999) are some of the relevant examples for polyaromatic membranes in PEMFC.

Scheme 2.3 An example of sulphonated aromatic polymer membranes (Smitha *et al.*, 2005).

Sulphonated polyether ether ketone

Polyether sulfone

Poly (4-phenoxybenzoyl-1, 4-phenylene)

Poly (m-(5-sulfo)-phenylenebenzobisimidazole)

2.11.3 Acid-base Polymer Complex Membranes

Acid-base complexes have been demonstrated to maintain high proton conductivity at elevated temperature without suffering from dehydration effect. In general, acid-base complexes are considered as an acid component into an alkaline polymer base for proton conductivity (see Scheme 2.4). For example, the phosphoric acid (H_3PO_4) doped polybenzimidazole (PBI) showed a comparable

proton conductivity under anhydrous system with Nafion® (Qinfeng et al., 2001). These H_3PO_4 doped PBI complexes are sensitive to the doping level and operating temperature, i.e., at the doping level changing from 450 to 1600 % at 165 °C, the proton conductivity increased from about 4.6×10^{-2} S/cm to 0.13 S/cm. A fuel cell was operated with such complexes at 190 °C yielding the power density and current density of 0.55 W/cm^2 and 1.2 A/cm^2, respectively. This might be due to the improvement of the poisoned-electrode catalyst at elevated temperature (Steiner and Sandor, 1999).

Scheme 2.4 An example of acid-base polymer complex membranes.

PBI/H_3PO_4

SPEEK/PBI

PAAM/strong acid

PEI/strong acid

PEO/strong acid
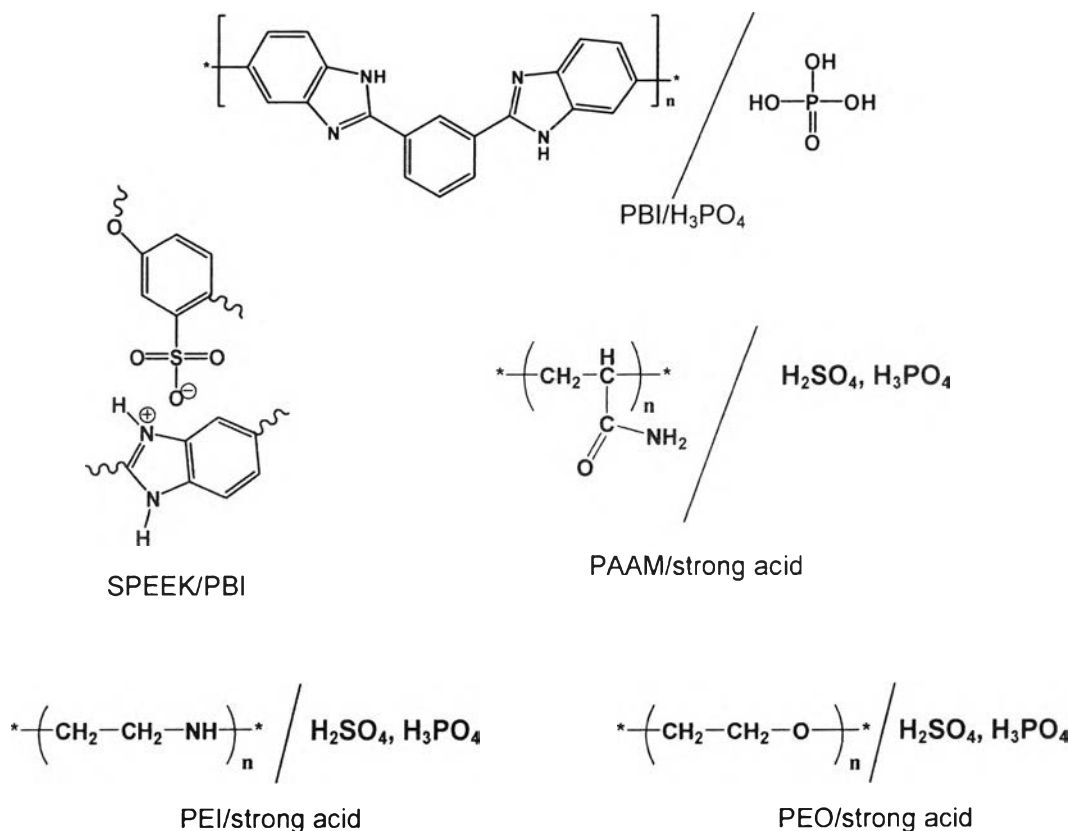
2.12 Evaluations of PEM

2.12.1 % Water Uptake

Water uptake through the Nafion® and other sulfonated non-perfluorinated membranes are based on the molecular structure of the membrane, i.e., ion cluster size (Kreuer, 2001). The water uptake in the membrane is generally

evaluated as follows: (i) immersing the membrane in distilled water at room temperature for 48 h and weighted to obtain W_w; (ii) drying the wet membrane under vacuum at 80 °C for 24 h to obtain dry membrane (W_d); and (iii) calculating the water uptake from the weight differences between wet and dry membranes using following equation:

$$Water\ Uptake = \left(\frac{W_w - W_d}{W_w} \right) \times 100\% \qquad ; W = weight$$

In addition, the water uptake is also evaluated by thermogravimetric analysis. The water content in the membrane is considered as the percent weight loss of the hydrated membrane at the temperature range of 60-150 °C which is the water evaporation temperature.

2.12.2 % Swelling Ratio

Membranes are cut with area size of 10 mm × 50 mm and weighed before measurement (Xing *et al.*, 2004). After that, the membranes were immersed in distilled water at room temperature for 24 h. The weight and dimensional change of films were measured. Swelling ratio is calculated by using following equation:

$$Swelling\ ratio = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \qquad ; L = length$$

It should be noted that when a swelling ratio of the membrane is high, higher membrane resistance will be obtained, resulting in poorer proton conductivity.

2.12.3 Ion Exchange Capacity

Ion exchange capacity (IEC) of the membrane is an important factor to indicate the efficiency of proton transferring through the membrane. The membrane is immersed in 1M NaCl for 48 h at ambient temperature. By titration of

NaCl solution with 0.01 M NaOH solution using phenolphthalein as indicator, IEC can be varied depending on the number proton exchangeable groups. The volume of NaOH solution titrated is expressed it in term of milliequivalent of exchanged proton per dry polymer weight (meq$_{H+}$/g) (Basile *et al.*, 2006).

$$\text{IEC (mmol/g)} = \frac{\Delta V_{NaOH} \times C_{NaOH}}{\text{Sample dry weight}}$$

2.12.4 Proton Conductivity

The complex impedance spectroscopy is used in order to evaluate the electrical property of the membrane by applying alternating current with various frequencies. The typical impedance response (Z_{im}-Z_{re} plot) is achieved (see Figure 2.6). The impedance (Z) is defined as the ratio of the voltage to the current at a given frequency which has a complex quantity of real (Z') and imaginary (Z") parts with phase angle (θ) as shown in the equation 1-3.

$$Z' = |Z| \cos \theta \tag{1}$$

$$Z'' = |Z| \sin \theta \tag{2}$$

$$\theta = \tan^{-1}(Z'/Z'') \tag{3}$$

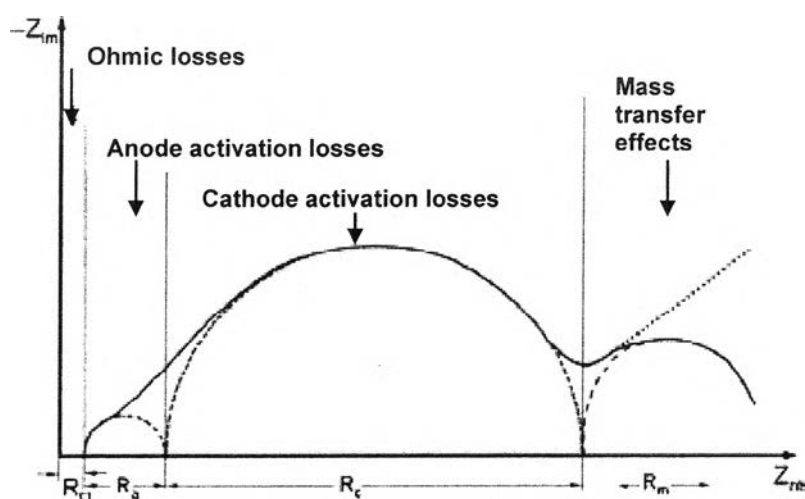**Figure 2.6** Nyquist (impedance) plot (Z_{im}-Z_{re}) of a hypothetical PEM fuel cell stack and four losses in the system (Zhang *et al.*, 2007).

Ohmic loss is a key driving performance of fuel cell. There are three potential causes of ohmic voltage loss: (a) resistance to ion migration in the electrolyte, (b) resistance to electron transport in the cell components, and (c) contact resistances. Only small amounts of ohmic resistance (on the order of milliohms) have a drastically effect on overall efficiency. This brings to the smaller current densities in fuel cell. However, the internal resistance of the cell during operation consists of a complex function of many parameters, e.g., temperature, hydration, current densities, etc (Cooper *et al.*, 2006).

Generally, proton conductivity (σ) at various temperatures is calculated by σ = L/RA, where L and A are the thickness and surface area of the membrane, respectively. The ohmic resistance of the membrane, R, is obtained from the extrapolation of (Z_{re}) x axis intercept.
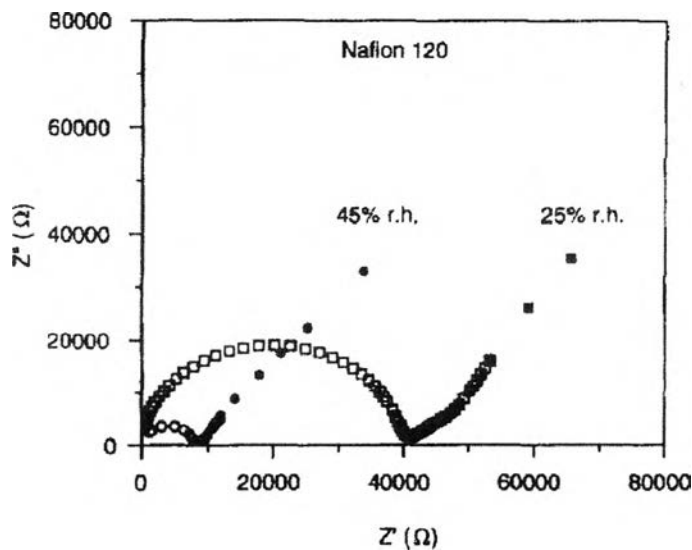

Figure 2.7 Complex impedance plots (Z_{im}-Z_{re}) of Nafion® 120 at different relative humidities, 25% and 45% (Wintersgill *et al.*, 1998).

In order to develop novel PEM material, complex impedance measurements of commercial Nafion® have been demonstrated frequently in many research papers. Theoretically, dry polymer membrane shows the dielectric relaxation, so-called insulator, especially in low temperatures. The dielectric

relaxation is the reorientation of electrical dipoles where the centers are fixed in position. It is fascinating that even dry Nafion® has significantly high ion mobility. In fact, it is extremely difficult to remove all traces of water from the material. Figure 2.7 shows a complex impedance diagram of Nafion® 120 which frequencies increase from right to left. The intercept of arc is shifted from high to low resistance as water content increases significantly. The electrical conductivity data can be easily replotted in term of proton conductivity with temperature as shown in Figure 2.8.
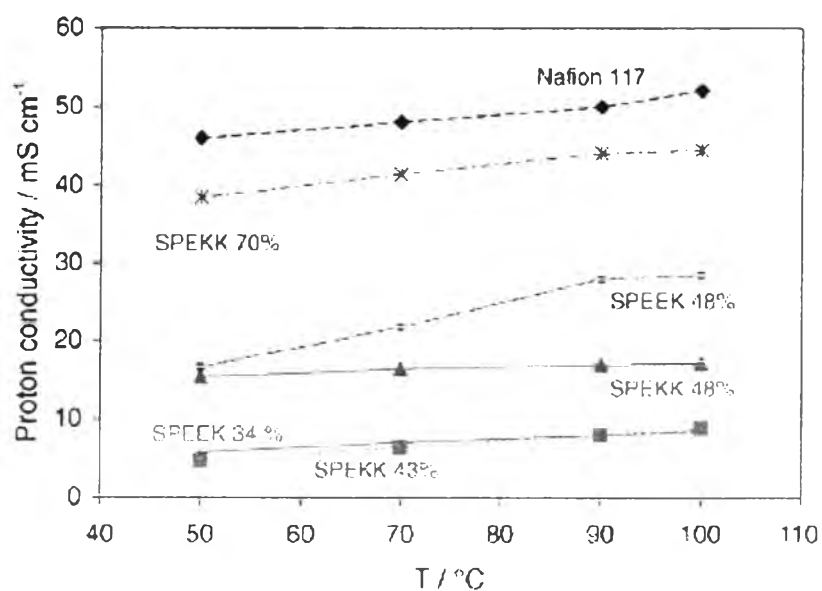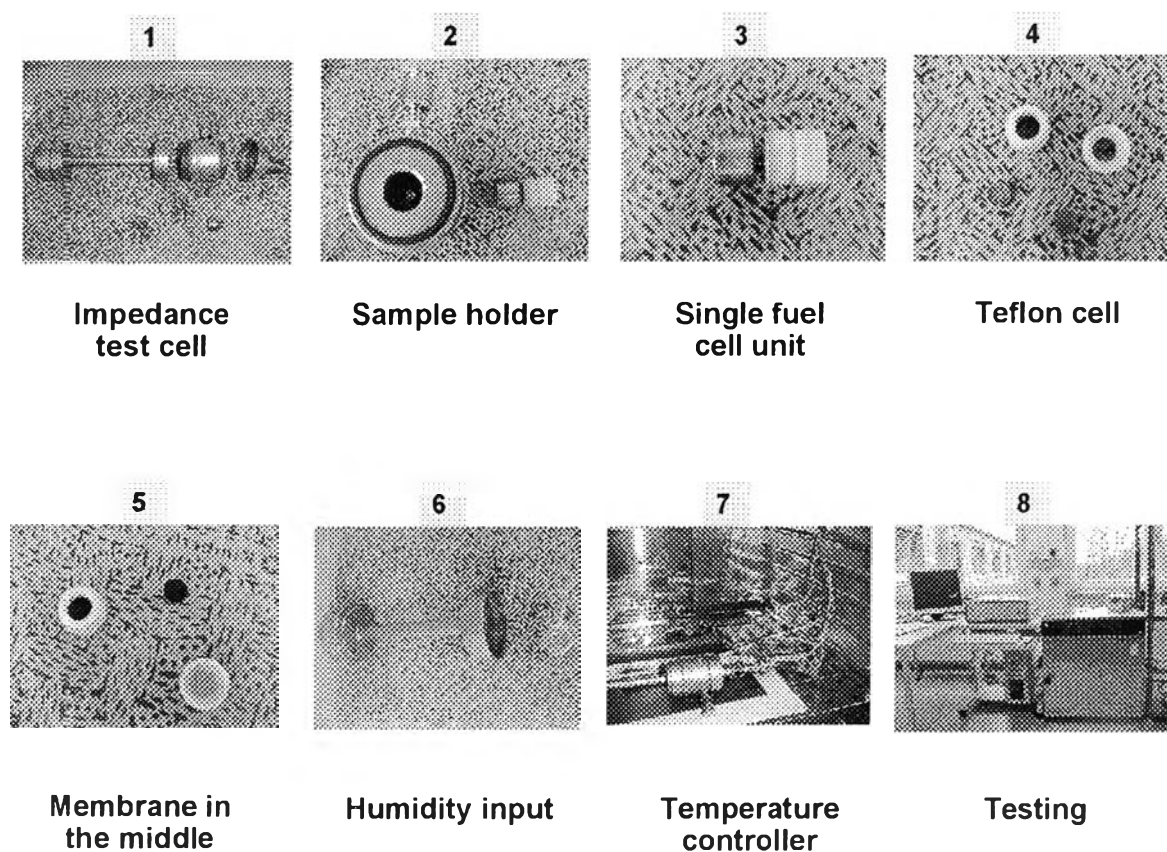

Figure 2.8 Proton conductivity at 100% relative humidity as a function of temperature of SPEEK, SPEKK, and Nafion® 117 (Vetter *et al.*, 2005).

The proton conductivity measurements of the present work are based on anhydrous system. In other words, the membranes are measured without moisture feeding in the case of anhydrous system as shown in Scheme 2.5.

Scheme 2.5 Instrument and equipment for proton conductivity measurement under anhydrous system

| **Impedance test cell** | **Sample holder** | **Single fuel cell unit** | **Teflon cell** |

| **Membrane in the middle** | **Humidity input** | **Temperature controller** | **Testing** |

2.13 Motivation of the Present Work

On this viewpoint, the present project considers a state-of-the art PEM by designing the polymer chain with engineering polymer backbone functionalized with imidazole group as a proton transferring part.

2.13.1 Copolymer Membranes of Acrylic acid and 4-Vinylimidazole and Their Structural Relationships for PEMFCs.

At present, perfluorosulfonic acid (PFSA)-based membranes have long been the standard membranes based on sulfonic acid moieties, e.g. sulfonated Teflon (Nafion®), and sulfonated poly (trifluorostyrenes). Up to now mainly Nafion®

shows an outstanding property in chemical stability. Considering the PEMFC system, the membrane (materials and fabrications) including the membrane electrode assembly is more than half of the total PEMFC cost. Although for the past few years, the cost of Nafion is reduced about 30%, the price is still expensive ($100 for a 12×12 inch^2). The success of the project will favor the use of PEMFC in the country under reasonable price.

Available PFSAs have almost all of the necessary properties for a good fuel cell membrane. The most significant drawbacks of the PFSA membranes are their relatively high cost, their dependence on water for conduction, and their limited stability at temperatures substantially in excess of 100 °C. The latter properties are particularly unfortunate because recent work has suggested that substantial improvements in fuel cell performance in the presence of CO or for direct methanol fuel cells can be achieved by operating at temperatures above 120 °C. It should be noted that in some cases, CO is existed as a contamination in hydrogen and this also obstruct the function of the membrane.

Much of the development of aromatic-based membranes has focused on the improvement in thermal stability of the membranes. However, these membranes are still vulnerable to the loss of conductivity upon loss of water. Since the acid sites on sulfonated aromatics are less acidic than those of PFSAs, both water and hydronium ions are tightly held at the sulfonate site. This results in an especially severe conductivity drop with decreasing water content for aromatic sulfonate membranes.

The present work was inspired from the following results. 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 at 120°C in completely water free materials. Here, 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.

Yang *et al.* prepared Nafion[®]/imidazole samples. The imidazole impregnated recast Nafion[®] membrane was tested in a fuel cell but was not able to generate any current. Although, the imidazole-based membrane was promising with respect to its proton conductivity at elevated temperatures, its chemical incompatibility with the platinum catalyst makes it necessary to search for new materials with the desired electrochemical properties.

Although 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 imidazole groups 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. 4-Vinylimidazole will be synthesized to copolymerize with acrylic acid monomer. Acrylic acid served as proton donor, whereas 4-vinylimidazole served as proton acceptor. We expect to achieve polymer membrane with low price and fairly proton conductivity, compared with Nafion[®]. Moreover, proton hopping mechanism of copolymer membranes was further investigated in order to obtain the proton transfer model of this alternative membrane. The proton transfer mechanism might give an idea for the polymer chemist to understand and design the polymer electrolyte membrane in the next step.

2.13.2 SPEEK Blended with Poly (AA-co-4VIm) for PEMFCs.

Aromatic sulfonated poly (ether ether ketone) (SPEEK) has both good thermal stability and mechanical strength (Li et al., 2007 and Karthikeyan et al., 2005). The proton conductivity of SPEEK depends on a sulfonation degree controlled by time and temperature of sulfonation process. However, the proton conductivity of the SPEEK membrane will be drastically decreased when the temperature is above 80 °C due to the loss of water hydration. Therefore, Poly (AA-

co-4Vim) is designed to maintain the proton conductivity by blending into SPEEK. This membrane system might provide fairly good thermal and physical properties with maintaining the proton conductivity above 80 °C.

2.13.3 Benzoxazine-based Model Compound

Benzoxazine-based family of phenolic resins has good thermal properties and flame retardance of phenolics. Our research group succeeded in the synthesis of a series of the controlled structured benzoxazine dimers. Here, the modification of the dimers with adenine group and the amidization bring the polymer chains with the imidazole-containing pendant group. To be a model compound, the key of the success should also relate to a well-defined structure to let the proton transfer in a regular manner.