CHAPTER II

LITERATURE REVIEW

2.1 Fuel Cell

Fuel cells are electrochemical devices for electrical energy production by the conversion of chemical energy of reactants both fuels i.e., hydrogen, natural gas or other hydrocarbon-based fuels and oxidant. Fuel cell has been considered to be one of the most promising power generations not only due to low pollutant emissions but also high efficiency of the energy system for a wide range of applications including stationary power sources, automobiles, and portable electronic devices. The increasing concerns about environmental problems are the major factors that have motivated the development of fuel cell.

The main components of a single fuel cell consist of an electrolyte sandwiched between two electrodes which are anode and cathode as shown an example of hydrogen/oxygen fuel cell in Figure 2.1. In principle, the operation of fuel cell is similar to battery. They produce electrical energy directly from electrochemical reactions. However lifetime of battery is limited depending on reactants containing inside the cell. Since fuel and oxidant are stored outside fuel cell it can produce electrical power as long as the reactants are supplied.
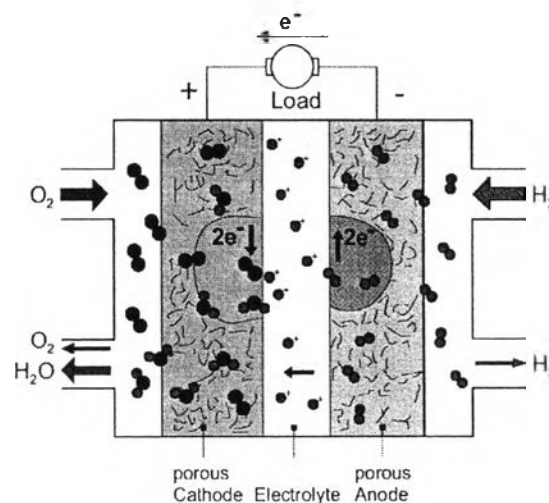

Figure 2.1 Schematic draw of a single fuel cell components and operations based on hydrogen/oxygen fuel cell (Carrette *et al.*, 2001).

In principle, fuel cells are classified into six main types based on electrolyte and fuel used in the cell which are alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), and direct methanol fuel cell (DMFC). An overview of the fuel cell types is given in Table 2.1.

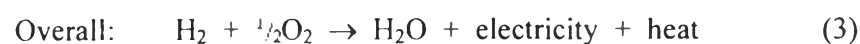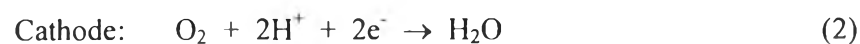**Table 2.1** Characteristics of different types of fuel cell (Stamboul *et. al.*, 2002 and Carrette *et. al.*, 2001)

Fuel Cell type	Fuel	Electrolyte	Charge carrier	Operating Temperature ($^{\circ}$C)	Realised Power	Applications
Alkaline fuel cell (AFC)	pure H_2, or hydrazine	Potassium hydroxide (KOH)	OH$^-$	< 100	Small plants 5-150kW modular	Transportation, space, military, energy storage systems
Polymer electrolyte membrane fuel cell (PEMFC)	H_2	Polymer, proton exchange membrane	H$^+$	60-120	Small plants 5-250kW modular	
Direct methanol fuel cell (DMFC)	CH_3OH	Polymer, Proton exchange membrane	H$^+$	60-120	Small plants 5kW	
Solid oxide fuel cell (SOFC)	CH_4, H_2, CO	Stabilised zirconia and doped perovskite	O^{2-}	800-1000	Small power plants 100-250kW	Combined heat and power for stationary decentralised systems and for transportation (trains, boats, etc)
Molten carbonate fuel cell (MCFC)	CH_4, H_2, CO	Malten salts such as nitrate, sulphate, carbonates	CO$_3^{2-}$	600-800	Small power plants 100kW-2MW	
Phosphoric acid fuel cell (PAFC)	H_2	Phosphoric acid	H$^+$	160-220	Small - medium sized plants 50kW-11MW	Combined heat and power for decentralized stationary power systems

2.2 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Among the various types of fuel cell, PEMFC is the most promising candidate fuel cell system because (Andújar $et.$ $al.$, 2009);

- the simple and compact cell structure and operation lead to relatively uncomplicated design and easy for manufacture compared with other fuel cell types
- the use of non-corrosive solid and dry electrolyte reduces the handling of corrosive material and the problems of resupply
- high current and power density are given
- its tolerance to CO_2 makes possible to use the atmospheric air as an oxidant.

The electrochemical reactions in PEMFC take place simultaneously on both anode and cathode of the cell by applying hydrogen as a fuel and oxygen or air as an oxidant. At the anode, hydrogen is oxidized at a catalyst surface to generate protons and electrons. The protons move through the polymer electrolyte membrane and enter to the cathode whereas the electrons flow through the electrical circuit consequently electricity generating. At the cathode, the oxygen is reduced by recombining with protons and electrons providing water and heat as by-products. The reactions are as following:

Anode: $\quad \frac{1}{2}H_2 \rightarrow 2H^+ + 2e^-$ $\qquad$ (1)

Cathode: $\quad O_2 + 2H^+ + 2e^- \rightarrow H_2O$ $\qquad$ (2)

Overall: $\quad H_2 + \frac{1}{2}O_2 \rightarrow H_2O + electricity + heat$ $\qquad$ (3)

In addition, PEMFC is similar to direct methanol fuel cell (DMFC) that uses solid polymers as an electrolyte but DMFC employs methanol as the fuel instead of hydrogen. The basic electrochemical reactions of DMFC are:

Anode: $\quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ $\qquad$ (4)

Cathode: $\quad \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ $\qquad$ (5)

Overall: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$ (6)

Theoretically, the electrical potential difference between cathode and anode is equal to 1.229 V (at 25 °C and 1 atm) when pure hydrogen and pure oxygen are used as fuel and oxidant, respectively. In practice, the energy losses are always found in the fuel cell, as a consequence, the cell potential difference is not ideal and diminishes to be ~ 0.7-0.8 V for the optimal fuel cell performance (Li, 2006). The voltage loss in fuel cell is often called over-voltage or over-potential and the phenomena that cause voltage loss is termed to polarization, thus a plot of voltage change as a function of current density is referred to polarization curve. As shown the typical polarization curve of PEMFC in Figure 2.2, the decrease of cell voltage with the increasing of current density is due to (i) the diffusion of H_2/O_2 through the electrolyte and slow kinetic reactions of the electrodes mainly from oxygen-reduction kinetics, (ii) ohmic resistance usually contributed to the resistance of the electrolyte to ionic current, and (iii) slow mass diffusion at the certain level of current density.
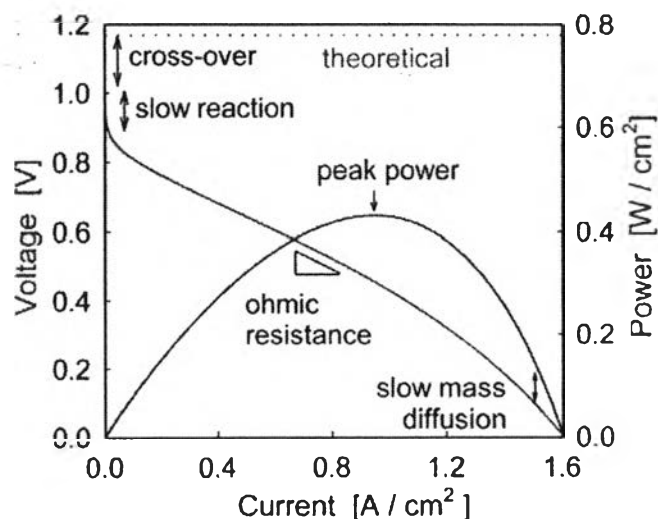

Figure 2.2 Typical fuel cell polarization curves (voltage vs. current density) and power density curves (Haile, S.M., 2003).

2.3 High Temperature PEMFC

In the real situation, working temperature of PEMFC is depending on polymer electrolyte membrane material used (typically lower than 100 °C). Although, PEMFC has been developed for decades, many limitations including high cost of the materials, inadequate water and heat management, durability of each component, intolerant to impurities of hydrogen such as CO, and slow kinetic reaction of the cathode are necessary to be improved. To overcome those shortcomings, PEMFC operated at high temperature is raised according to following reasons;

2.2.1 Improvement of Reaction Kinetics

The over-voltage is mainly due to the slow oxidation reduction reaction (ORR) therefore the enhancement of reaction kinetics will improve the performance of the cell. It is found that the reaction kinetics especially ORR will be enhanced at high temperature (Zhang *et. al.*, 2006).

2.2.2 Improvement of CO Poisoning on Catalyst Surface

In general, high purity hydrogen is needed for PEMFC operation because platinum (Pt) catalyst is very sensitive to fuel contaminants e.g. carbon monoxide (CO). Usually, hydrogen produced by reforming of carbon-containing fuels such as methanol, ethanol and diesel etc. is contaminated with trace amount of CO. The absorption of CO on the Pt surfaces reduces the catalyst surface area available for hydrogen oxidation reactions resulting in depressing the PEMFC performance. The CO coverage on the catalyst surface is diminished at elevated temperature as reported by Yang *et. al.* (Figure 2.3) thus high temperature operation enhances CO tolerance of PEMFC to be used with reformed hydrogen.

2.2.3 Improvement of Heat and Water Managements

About 40–50% of the energy produced by a PEMFC is lost as heat. Heat is always generated during the cell operation however it is necessary to remove agglomerated heat in order to maintain the working temperature. Since, operating at high temperatures or at less humidity requirement would not require pressurization and complicated cooling system, these make high temperature and anhydrous PEMFC system be more simple and practical.
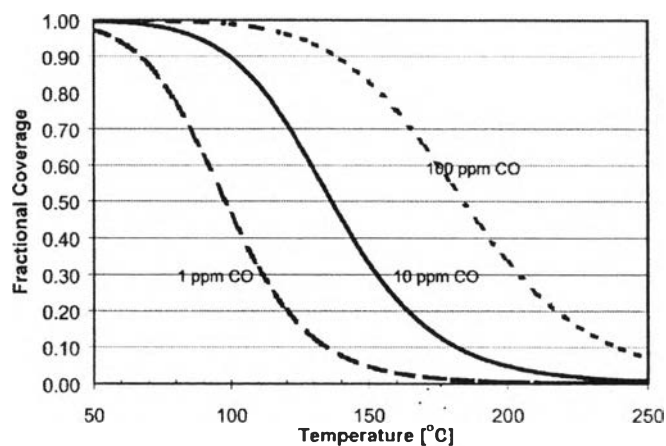
Figure 2.3 CO coverage on a platinum surface as a function of temperature and CO concentration. H_2 partial pressure is 0.5 bar (Yang *et. al.*, 2001).

2.4 Polymer Electrolyte Membrane

Polymer electrolyte membrane (PEM) is one of the most important parts of PEMFC because it plays the important roles as; (i) proton conductor to migrate proton from anode to cathode for oxygen reduction (ii) gas barrier to avoid explosion by the crossover of the reactants (iii) electron insulator to force the transfer of electrons through the external circuit for electric power output. Therefore, the good features of the PEM are; high proton conductivity, excellent electronic insulator, low gas permeability, and good chemical and mechanical stability in the fuel cell environment. There are several polymer membranes reported for the use as electrolytes in PEMFC. Typically, polymer electrolyte membranes are classified into four main types which are perfluorinated ionomer, non-fluorinated hydrocarbon, heterocyclic based polymer and acid–base blended membranes.

2.4.1 Perfluorinated Ionomer Based Membranes

Up to now, the most widely used membranes for PEMFC are perfluorosulfonic acid based polymers. The best known is Nafion® by DuPont. Similar polymers have been developed as a commercial product by other manufacturers such as Asahi Glass (Flemion®), Asahi Chemicals (Aciplex®), and

Dow Chemical (Dow). Nafion® is considered to be a standard membrane material due to its high proton conductivity (~0.1 S/cm in the fully hydrated state) (Ahmad *et. al.*, 2010), good chemical stability and mechanical properties. The Nafion® structure consists of non-polar domain of tetrafluoroethylene polymer backbone and polar domain of perfluoro vinyl ether side chain ended with perfluorosulfonic acid moiety. The chemical structure of Nafion® is illustrated in Figure 2.4.

Figure 2.4 Chemical structure of Nafion®: $m=1$; $n=2$; $x=5-13.5$; $y=1$.

The difference in polarity of these two domains results in nanophase-segregated structure formation (Figure 2.5) which hydrophilic domain of water phase surrounded by sulfonic groups separates from the hydrophobic fluorinated polymer backbone formed into approximately spherical clusters connected by short narrow channels (Hsu *et.al.*, 1983).

Figure 2.5 Cluster-network model of Nafion® membranes proposed by Hsu *et.al*, (1983).

The proton transport in Nafion® is based on hydrogen-bond of water cluster network in the hydrophilic region therefore the performance of such membrane is strongly influenced by water content. For example, the proton conductivity of the hydrous-based membrane of Nafion® and Krytox-Si–Nafion® hybrid membranes significantly decreases when the temperature is up to 80 °C due to the water evaporation as shown in Figure 2.6 (Gosalawit *et. al.*, 2006). This drawback of Nafion® limits its use in high temperature PEMFC.
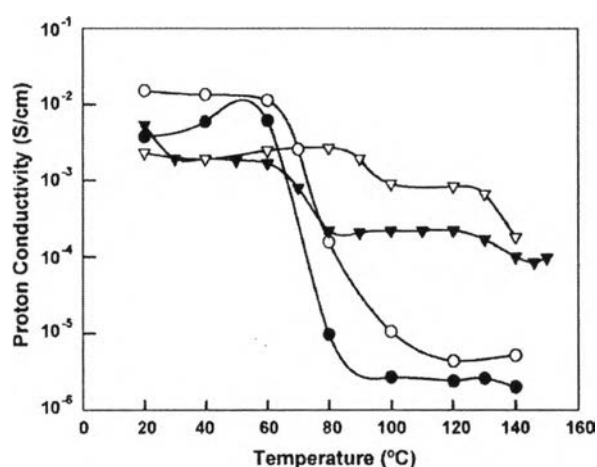
Figure 2.6 Proton conductivity of Nafion® (●), 1.5wt.%Krytox-Si–Nafion® (○) , 2.5wt.% Krytox-Si–Nafion® (▼), and 5.0 wt.%Krytox-Si–Nafion® (▽) hybrid membranes (Gosalawit *et. al.*, 2006).

Currently, the research on Nafion® deals with the transport phenomena within the membrane as well as the polymer modifications to increase its performance in addition to an improvement of water retention capacity of the membrane (Smitha *et. al.*, 2005).

2.4.2 Non-fluorinated Hydrocarbons

For decades, many types of hydrocarbon membranes either aliphatic or aromatic polymers have been developed to be used as polymer electrolytes in PEMFC because they are less expensive and easy to modify with various functional groups. Moreover, the proper molecular design for hydrocarbon polymer synthesis

can depress the degradation of the materials for example the incorporating of aromatic ring into polymer structures for the use of membranes at elevated temperature (Peighambardoust *et. al.*, 2010).

Aliphatic hydrocarbon polymers containing appropriate functional groups for initiating proton transfer i.e., sulfonic acid, carboxylic acid, phosphoric acid, amine, and hydroxyl group have been investigated, for example, poly(vinylphosphoric acid) [PVPA] (Yamada *et. al.*, 2005), polyacrylic acid [PAA] (Bozkurt *et. al.*, 2003), polyethylenimine (Yang *et. al.*, 2008), Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid (Rhim *et. al.*, 2004), and polysaccharide-alginic acid (Yamada *et. al.*, 2003). The structures of the aliphatic hydrocarbon polymer are shown in Figure. 2.7.
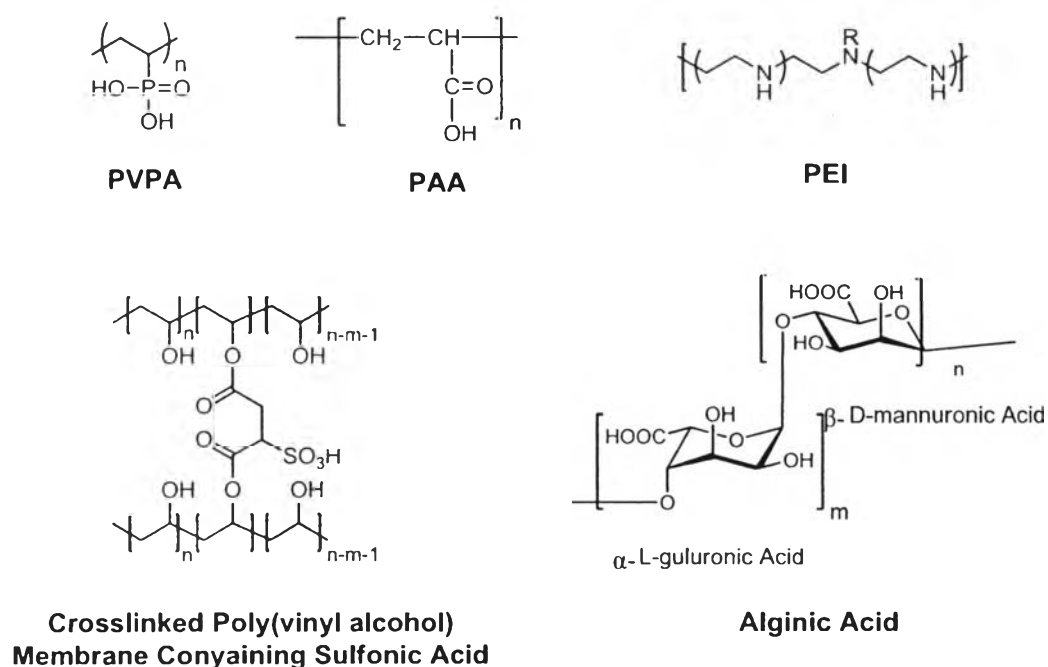
PVPA   **PAA**   **PEI**

Crosslinked Poly(vinyl alcohol)   **Alginic Acid**
Membrane Conyaining Sulfonic Acid

Figure 2.7 Chemical structures of PEMs based on aliphatic hydrocarbon polymers.

Some novel aromatic hydrocarbon polymers such as sulfonated poly(ether ether ketone) [PEEK] (Gosalawit *et. al.*, 2008), star-shaped sulfonated block copoly(ether ketone)s (Matsumoto *et. al.*, 2008), hyperbranched polymers with both diethyl phosphate and acryloyl groups at the chain ends [HBP-PE-Ac]

(Itoh *et. al.,* 2008), polysulfones grafted with poly(vinylphosphonic acid) (Parvole *et. al.,* 2008), sulfonated polyimide copolymers containing fluorenyl groups (Miyatake *et. al.,* 2004), and densely sulfonated poly(ether sulfone)s bearing 10 sulfonic acid moieties (Matsumoto *et. al.,* 2009) are summarized in Figure 2.8.
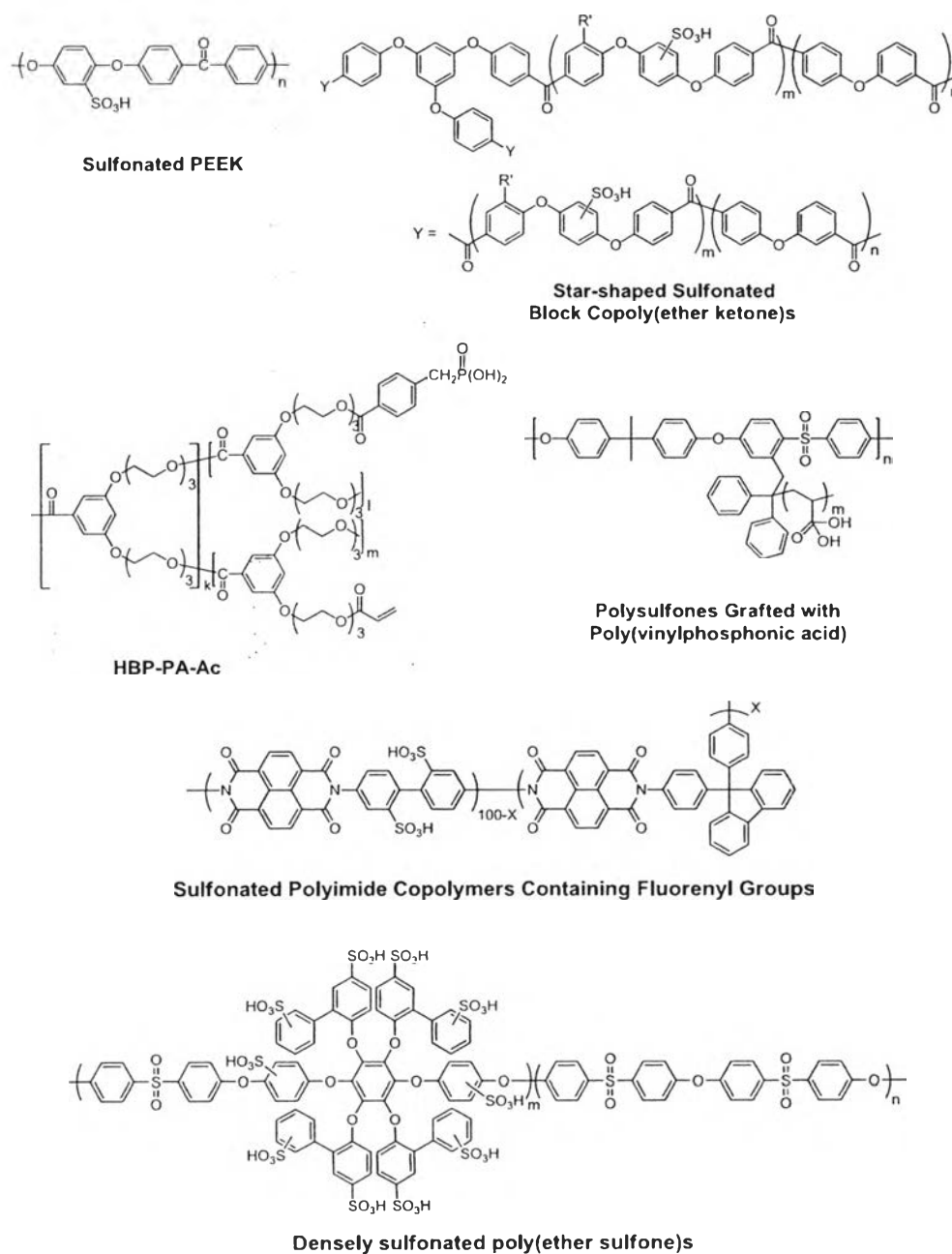

Figure 2.8 Chemical structures of PEMs based on aromatic hydrocarbon polymers.

2.4.3 Heterocyclic based polymers

Kreuer *et. al.*, started to investigate the use of heterocycles i.e., imidazole, pyrazole and benzimidazole as proton reservoir in the solid polymer electrolyte for fuel cell (Kreuer *et. al.*, 2004). So far, heterocyclic based polymer electrolytes have been widely studied for using in high temperature PEMFC. Due to the characteristic features of heterocycles which are (i) amphoteric structure which can either donate or accept protons (ii) high thermal stability leading to a development of heterocycles to use as proton conductive species instead of water in anhydrous PEM. The proton transfer in heterocycles is generated by the transport of excess proton through proton transfer- and reorientation steps under hydrogen bond network (Münch *et. al.*, 2001). The proton transfer of imidazole molecules is shown in Figure 2.9.
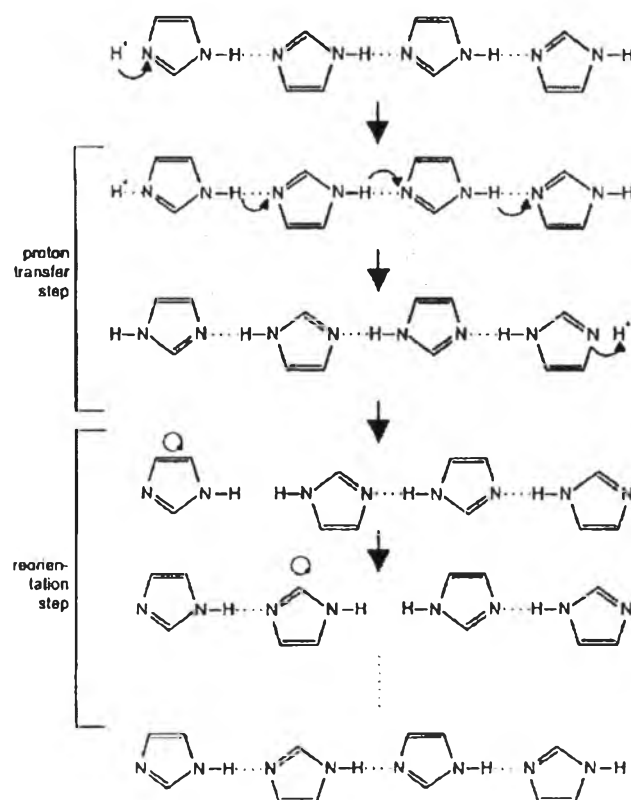

Figure 2.9 Proton transfer mechanism of imidazole.

The modification of heterocyclic polymers can be classified into two main types which are the incorporation of the heterocycles in the polymer backbone

and in the pendent groups. Examples of polymer containing heterocycle as a polymer main chain are polybenzimidazole [PBI] (Bouchet *et. al.*, 1999), benzimidazol-2-yl substituted PBI [BPBI] (Leykin *et. al.*, 2010), hyperbranched polybenzimidazoles [HBPBIs] (Xu *et. al.*, 2007), and poly(benzimidazole-co-aniline) [PBIANI] (Bhadra *et. al.*, 2010) (Figure 2.10). However, most of these polymers required protonic sources for initiating proton transfer of the systems such as strong oxo acid.
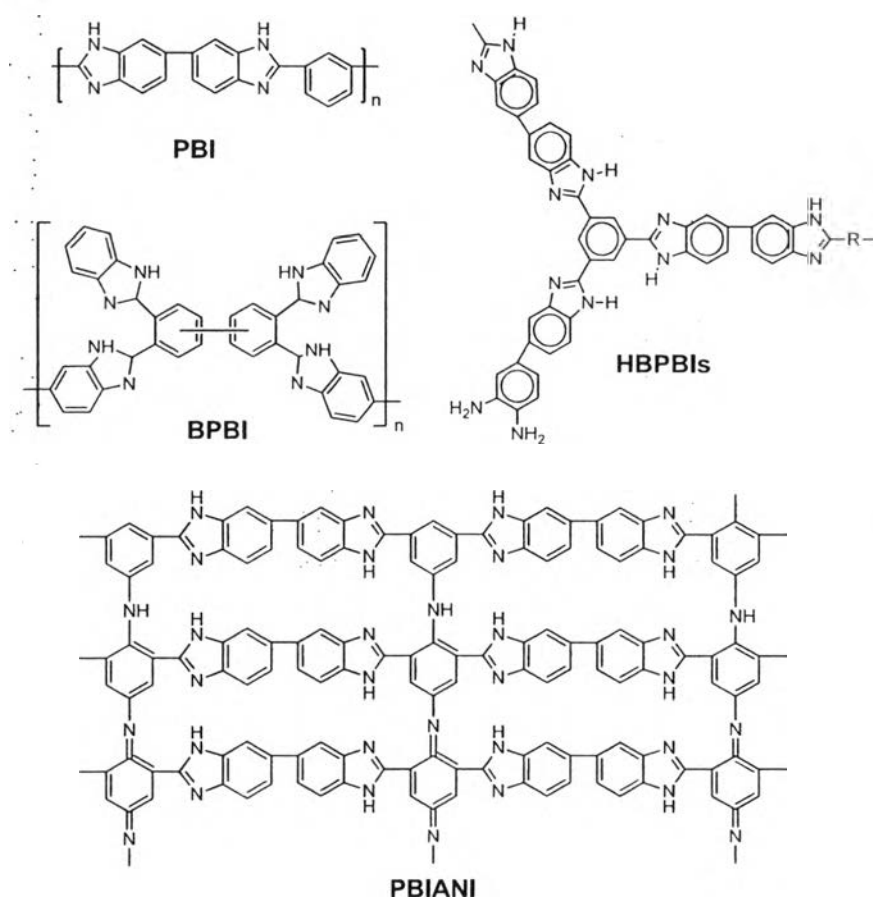

Figure 2.10 Chemical structures of PEMs based on heterocycle main chains.

Another challenge of heterocyclic based membranes is a modification of heterocycle in the polymer structure as a pending group. There are some reports showing that these kinds of material can act as self-proton conductive polymers for example benzimidazole tethered ethylene oxide oligomers [bimi-EO]

(Persson *et. al.*, 2003), benzimidazole tethered on linear poly(ethylene glycol) [bimiPEOAGE] (Persson *et. al.*, 2006), and benzimidazole-grafted polydimethylsiloxane [bimiPVMS] (Persson *et. al.*, 2005) with the highest proton conductivity of 70 µS/cm at 110 °C, 80 µS/cm at 160 °C, and 7 µS/cm at 140 °C, respectively (Figure 2.11).

bimi-EO

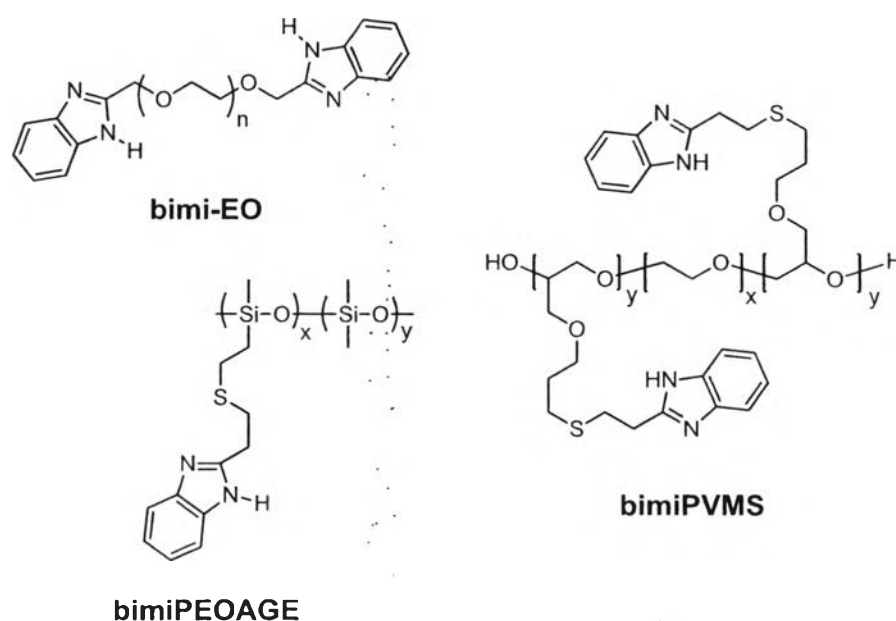**bimiPVMS**

bimiPEOAGE

Figure 2.11 Chemical structures of self conductive polymers based on heterocycle pendent group.

2.4.4 Acid-base Blended Membranes

Acid-base blended membrane is a type of proton conductive membranes which show the high proton conductivity, high thermal stability and good mechanical strength. Generally, polymers having basic functional groups such as ether, alcohol, imine, amide, or imide perform their reaction with polymers having acid such as phosphoric acid, sulfuric acid or carboxylic acid functional groups to form hydrogen bond interaction between acid and base by which the basic polymers act as solvent for acid dissociation (Li *et. al.*, 2003). Figure 2.12 show some examples of acid-base blended membranes.
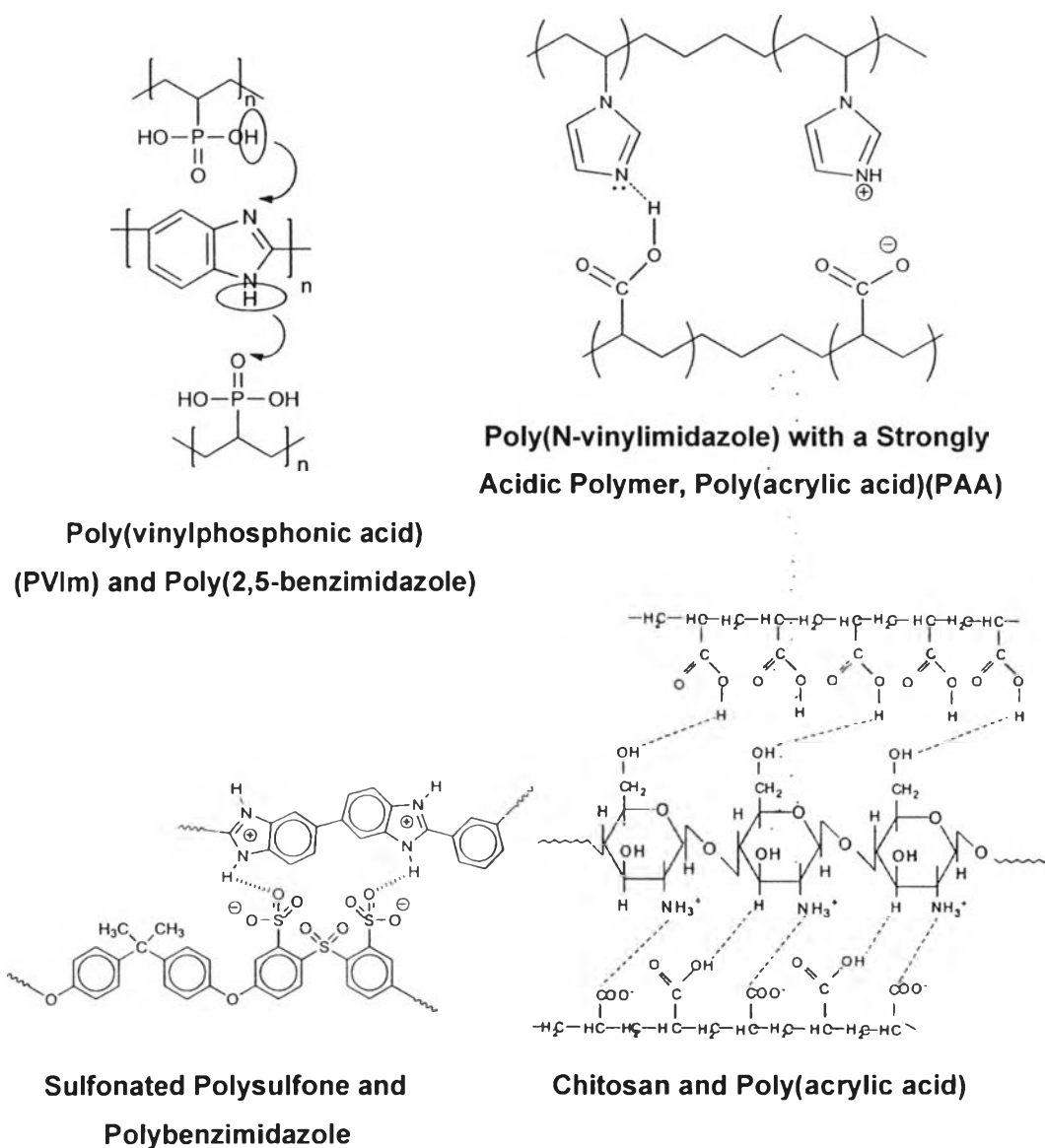
Poly(vinylphosphonic acid)
(PVIm) and Poly(2,5-benzimidazole)

Poly(N-vinylimidazole) with a Strongly
Acidic Polymer, Poly(acrylic acid)(PAA)

Sulfonated Polysulfone and
Polybenzimidazole

Chitosan and Poly(acrylic acid)

Figure 2.12 Examples of acid-based blended membrane.

2.5 Points of Study

Heterocycles are attractive for using as electrolyte membranes under high temperature or relatively low humidity not only due to their proton conductive behavior and high boiling point compared with water but also ease of molecular design and modification. Although many types of heterocyclic based membranes

have been developed for several decades, their conductive properties are still limited for the practical use.

Based on our viewpoint, an understanding of the molecular structures of the materials as well as the factors related to the proton transfer efficiency would lead us to a fundamental knowledge for PEM development. The present work proposes a molecular design containing multifunctional-benzimidazole with an ultimate goal to enhance the proton conductivity of the heterocyclic membrane with the high order structure of the benzimidazole molecules (Chapter III). In this work, a series of benzimidazole model compounds are developed and the factors of molecular packing structure and hydrogen bond network formation related to the proton conductivity are clarified. Moreover, we extend our work to the multi-benzimidazole branching with an expectation to enhance the proton conductivity of the heterocyclic membrane with a proper level of multi-direction proton transfer groups along with chain mobility of the polymers (Chapter IV). In this work, a varied multi-benzimidazole branchings are prepared and the factors of chain mobility and hydrogen bond interaction correlated with proton transfer effectiveness are investigated. Based on the studies of hydrogen bonding-molecular packing structure-chain mobility with proton conductivity relationship, tri-benzimidazole compound of aminotris[2-(benzimidazol-2-yl)ethyl]methane is designed to enhance proton transfer effectiveness with its lots of proton conductive species and flexible chain mobility. The synthesis method is presented in Chapter V.