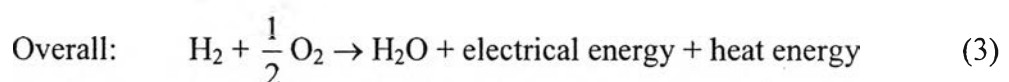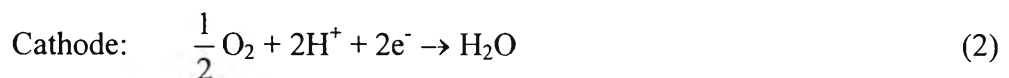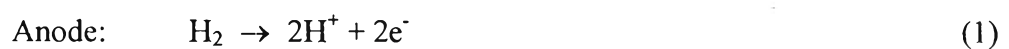# CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 General Principle of Fuel Cell

Fuel cell is an electrochemical device which directly converts chemical energy into electricity through a redox process. Due to its ease of operation and clean renewable sources make fuel cell becomes the most promising and attractive candidate for a wide variety of power applications ranging form portable and transportation to large-scale stationary power system.

In the operating system, hydrogen gas is electrocatalytically oxidized to hydrogen ions at the anode composed of Pt deposited on a conductive carbon. The protons pass through an electrolyte membrane. The cathode is Pt on carbon in which O_2 from air is electrocatalytically reduced which combines with the proton producing H_2O and heat. The electrons flow through the external circuit (Farrauto, 2005) to generate electricity (Figure 2.1). Even though the open circuit voltage or theoretical maximum voltage is $E_0 = 1.16$ Volt but in the case of a real system, it can generate only about 0.7 volt/cell. Therefore, a number of individual cells are combined to form a fuel cell stack to obtain the voltage up to a reasonable level (Figure 2.2).
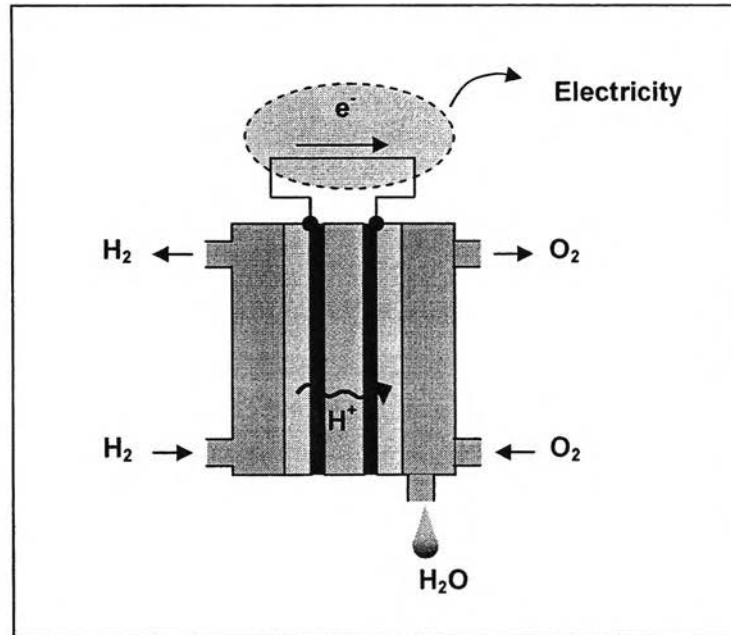
Anode: $H_2 \rightarrow 2H^+ + 2e^-$ (1)

Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (2)

Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ + electrical energy + heat energy   (3)
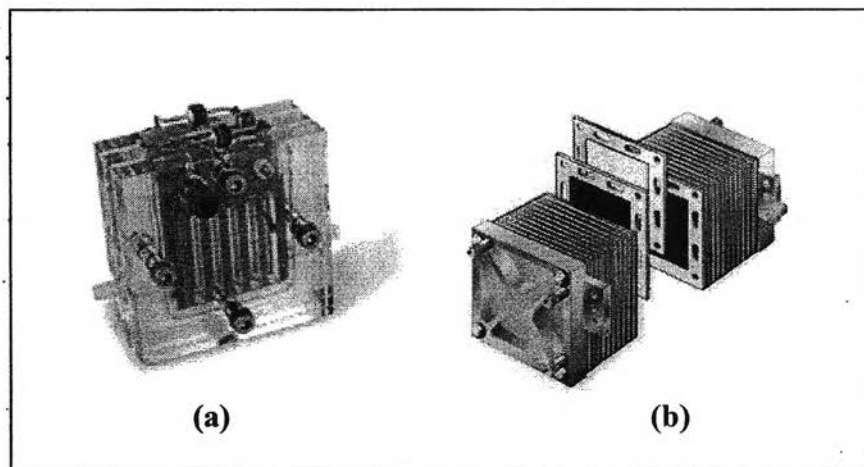
Figure 2.1 Schematic of fuel cell.

Figure 2.2 Types of fuel cell; (a) single cell of fuel cell, and (b) fuel cell stack. (www.ecorete.it and www.machinedesign.com)

2.2 Classification of fuel cell

Currently, fuel cells are devided into five types base on the material of the electrolyte.

    1. Polymer Electrolyte Membrane Fuel Cell (PEMFC)

2. Alkaline Fuel Cell (AFC)
3. Phosphoric acid Fuel Cell (PAFC)
4. Molten Carbonate Fuel Cell (MCFC)
5. Solid Oxide Fuel Cell (SOFC)

These fuel cells operate at different temperatures and each is best suited to particular applications. Comparison of such fuel cells are summarized in Table 1.

Table 2.1 Comparison of different fuel cells

Fuel cell	Electrolyte	Conducting ion	Operating Temperature (°C)	Efficiency (Cell)	Applications	Advantages	Disadvantages
PEM	- Solid organic polymer - Poly perfluoro sulfonic acid	H^+	50-80	50-60%	- Electric Utility - portable power - Transportation	- Solid electrolyte reduce corrosion & management problems - Low temperature - Quick start-up - High power density	- Low temperature requires expensive catalysts - High sensitivity to fuel impurities
AFC	Aqueous solution of potassium hydroxide soaked in matrix	OH^-	60-90	50-60%	- space - underwater	- High performance based on cathode reaction in alkaline electrolyte	- Expensive removal of CO_2 from fuel and air streams required
PAFC	Liquid phosphoric acid soaked in matrix	H^+	160-220	55%	- Electric Utility - Transportation	- Up to 85% efficiency in co-generation of electric and heat - Impure H_2 as fuel	- Pt catalyst - Low current & power - Large size/weight

Table 2.1 Comparison of different fuel cells (continue)

Fuel cell	Electrolyte	Conducting ion	Operating Temperature (°C)	Efficiency (Cell)	Applications	Advantages	Disadvantages
MCFC	Liquid solution of lithium, sodium and/or potassium carbonates soaked in matrix	CO_3^{2-}	620-660	60-65%	- Electric Utility	- High efficiency - Fuel flexibility - Internal reforming - High temperature waste heat	- High temperature enhances corrosion and breakdown of cell components
SOFC	Solid zirconium oxide to which a small amount of yttria is added	O^{2-}	800-1000	55-65%	- Electric Utility	- High efficiency - Fuel flexibility - Internal reforming - High temperature waste heat - Solid electrolyte reduce corrosion & management problems	- High temperature enhances breakdown of cell components

2.3 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Among various types of fuel cells, polymer electrolyte membrane fuel cell (PEMFC) is the most attractive fuel cell type for portable electrical devices and automotives due to its simplicity in compact size as well as high power density with fuel flexibility.

Generally, PEMFC consists of two electhodes which are anode and cathode, and a solid polymer membrane, which act as an electrolyte. The polymer electrolyte membrane is sandwiched between two platinum porous electrodes such as carbon paper and mesh. Some single cell assemblies can be mechanically compressed across electrically conductive separators to fabricate electrochemical stacks as shown in Figure 2.3.
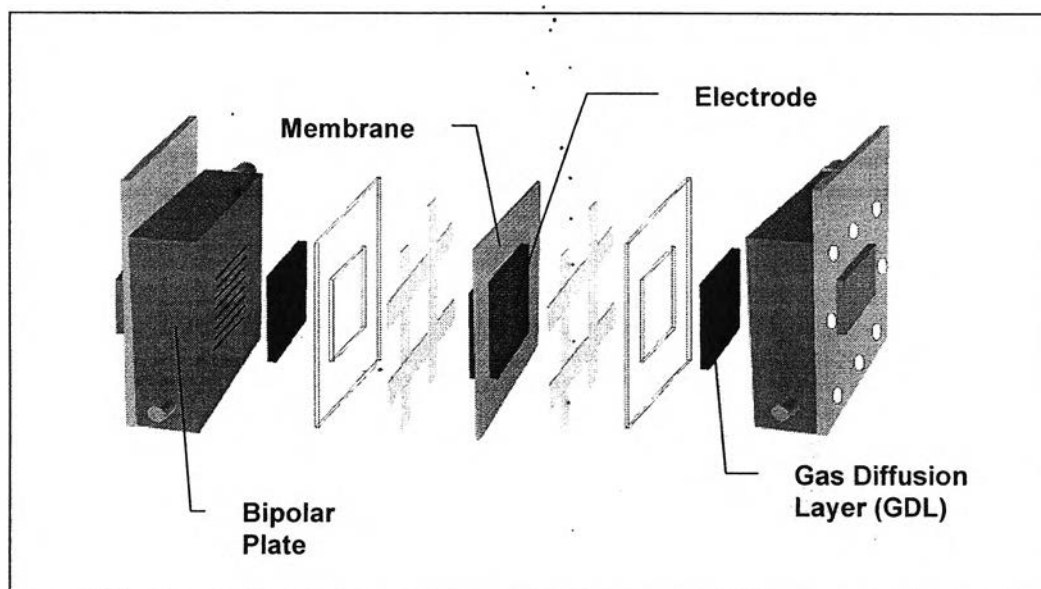

Figure 2.3 Components of PEMFC.

2.4 Polymer Electrolyte Membrane (PEM)

The most important part of PEMFC is the polymer membrane which acts as an electrolyte with some unique capabilities. These polymers are electronic insulator, but excellent conductors of hydrogen ions. High proton conductivity, sufficient

barrier to mixing of fuel and reactant gases, chemically and mechanically stable in the fuel cell environment are required in PEM. Up to now, membranes have been developed based on two systems; water based and water free system.

2.4.1 Water-based System

Conventional membranes are tetrafluoroethylene with sulfonic acid modified side chain polymers commercially available under the commercial name of Nafion®(Du Pont), Flemion®, Aciplex® and Dow as shown in Figure 2.4. Each regions provide the different performance; the main chain is the Teflon-like, fluorocarbon backbone whereas the side chain is connected to the molecular backbone. At the side chain, the ion clusters consisting of sulfonic acid ions, SO_3^-, H^+ are dopped.
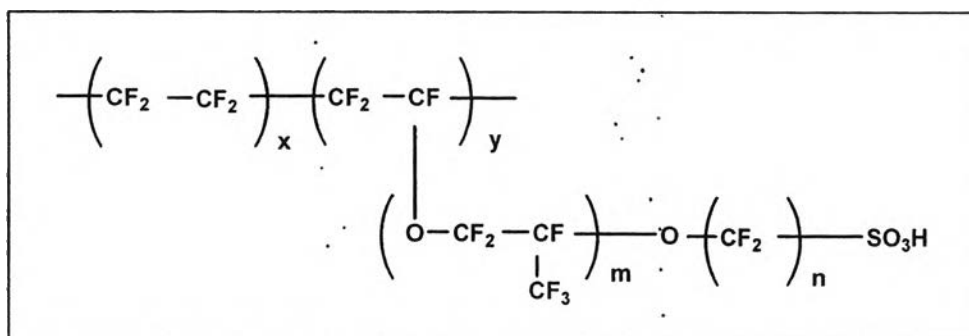

Figure 2.4 Chemical structure of perfluorinated polymer electrolyte membranes (Nafion®117; m≥1, n=2, x=5-13.5,y=1000, Flemion®; m=0, 1, n=1-5, Aciplex®; m=0, 3, n=2-5, x=1.5-14, Dow; m=0, n=2, x=3.6-10) (Rikukawa *et al.*, 2000).

In an operating fuel cell, proton transport is believed to occur by two competing mechanisms: the vehicle mechanism and the Grotthuss or hopping mechanism (Kreuer, 1996). The vehicle mechanism occurs by the movement of the hydrated proton aggregate through the aqueous environment, in a process similar to molecular diffusion. The Grotthuss mechanism involves the 'hopping' of a proton along a chain of hydrogen bonded water molecules. The hops are followed by reorientation of the water molecules (Pivovar, 2006) (Figure 2.5).
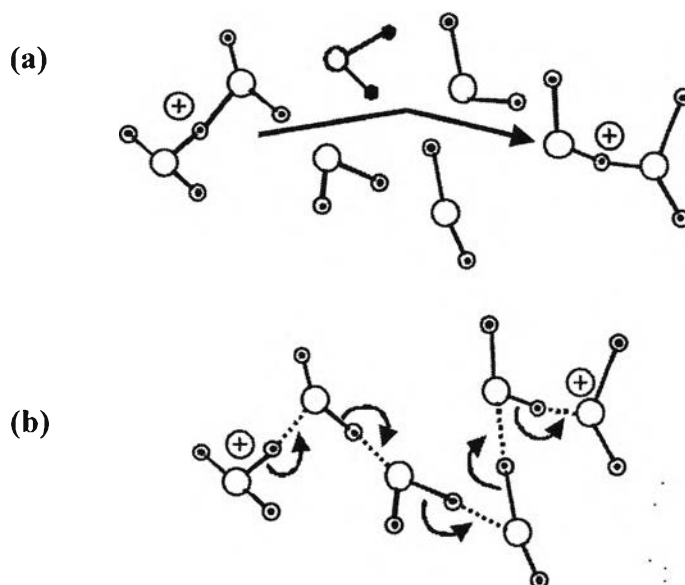
Figure 2.5 Schematic of proton transport mechanisms; (a) vehicle mechanism, (b) Grotthuss or hopping mechanism (Pivovar, 2006).

As the structure and mechanism of proton transport of Nafion, the cluster of water molecules induces the proton movement through the irregular hydrogen network resulting in an increase in proton conductivity when increasing the temperature (Figure 2.6(a)). At that time, the significant movement of proton conductivity according to thermodynamics can be expected. Moreover, at high operating temperature, we can overcome the poisoning of expensive Pt catalyst with a trace amount of CO impurity in hydrogen fuel. In addition, about half of the theoretical electricity is lost as an heat. Therefore, the membrane that can be used at elevated operating temperature is an ideal. Nafion shows , however, on this viewpoint the performance is poor. When the temperature is increased, the shrinkage of water cluster (Figure 2.6(b)) brings the limitation to nafion. At present, the water free membrane is expected as an alternative choice for PEMFC.

2.4.2 Water-free System

In order to overcome the limitation of nafion, the use of non-aqueous, low volatile solvent to replace water as the proton acceptor within membranes has received much attention. Heterocycles (e.g. imidazole, benzimidazole, pyrazole) which have resonance structure are involved in proton transport of water free system. They form similar hydrogen bond networks to water and transport properties in the

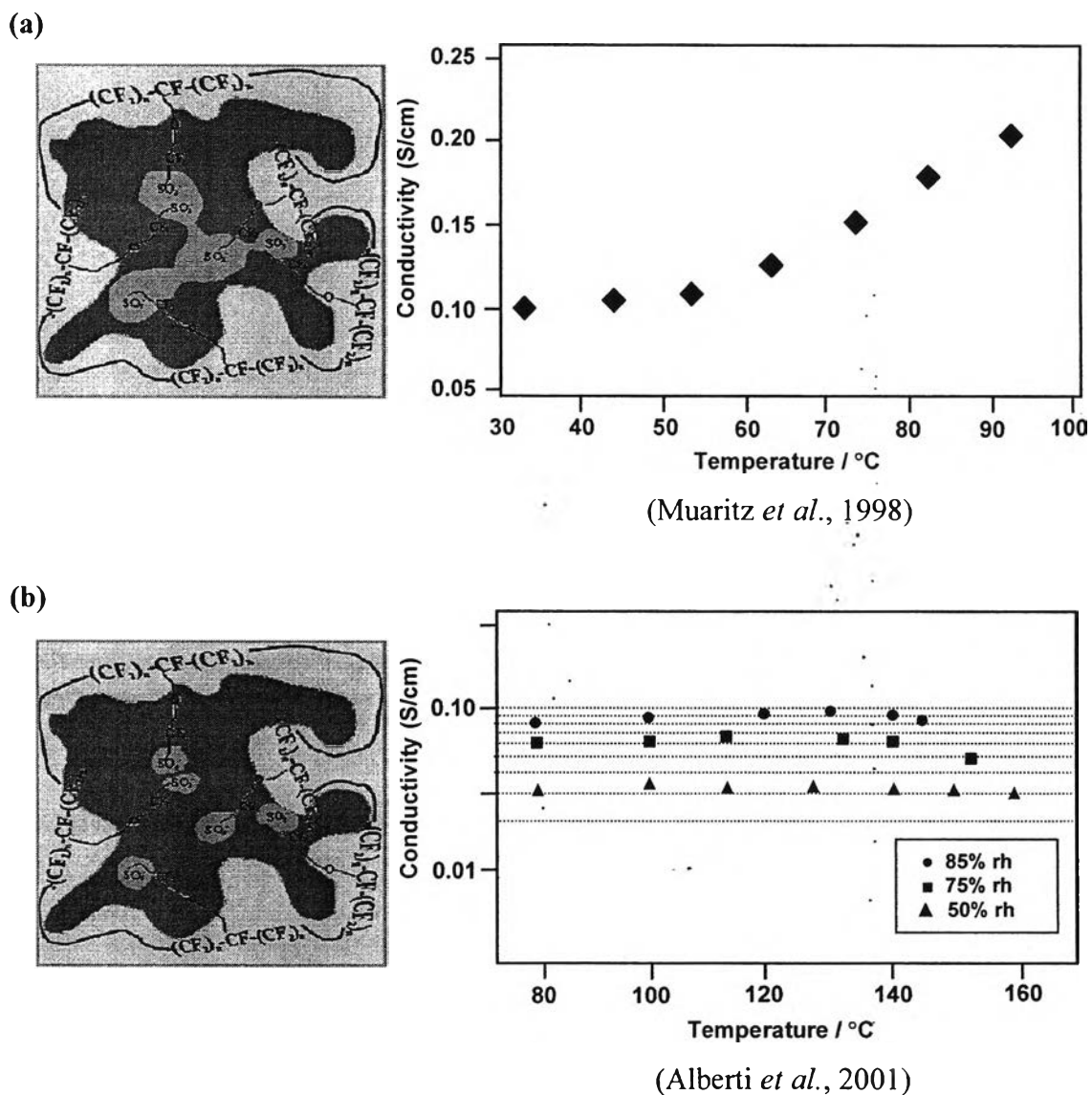liquid state are similar to water for a given temperature relative to the melting point (Kreuer, 2001).

(a)

(Muaritz *et al.*, 1998)

(b)

(Alberti *et al.*, 2001)

Figure 2.6 Morphologies and the relation between conductivity and temperture of Nafion membrane at; (a) < 80°C, and (b) > 80°C.

Although the proton transferring mechanism of heterocyclic molecules have remained obscure, the existence of a Grotthuss-type mechanism (structure diffusion) for pure-imidazole has been established experimentally (Munch *et al.*, 2001). The proton movement in an environment of immobilized heterocycles

has been suspected to Grotthuss-type mechanism involving proton transfer between heterocycles and hydrogen bond breaking and forming process (reorientation) (Herz *et al.*, 2003) (Figure 2.7).
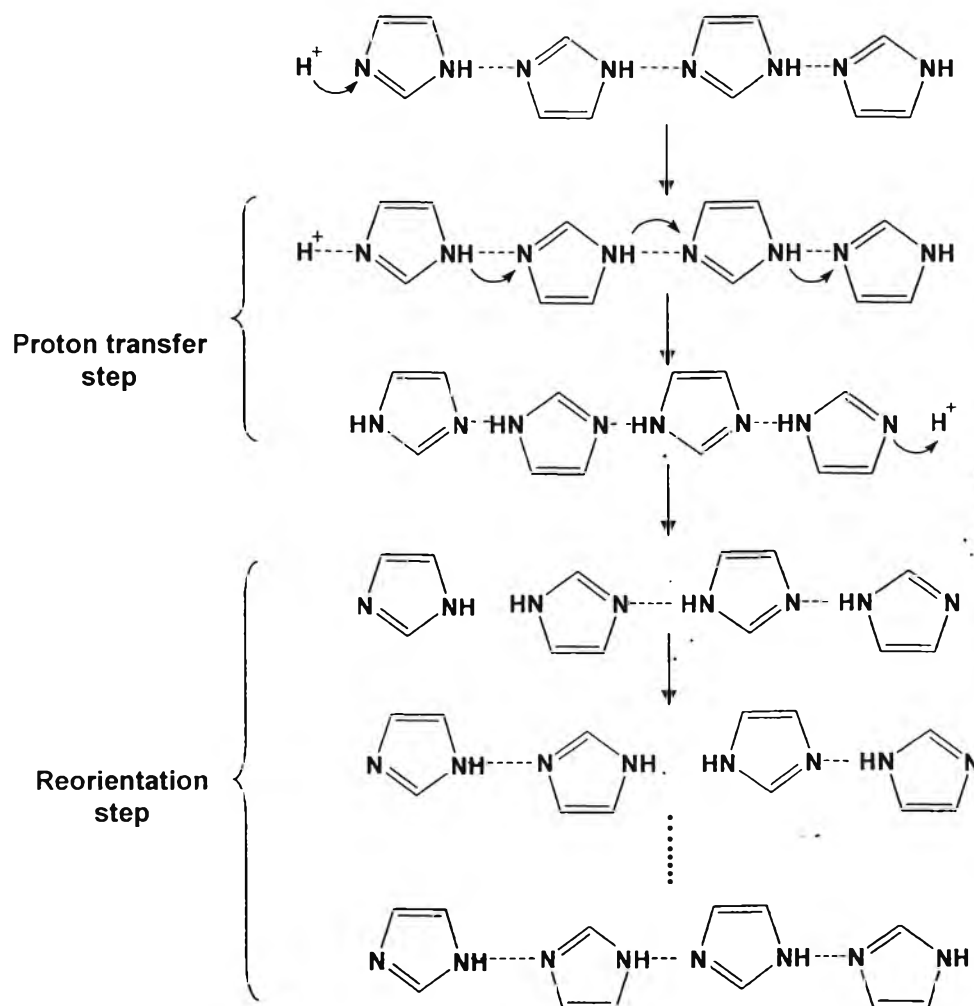
Figure 2.7 Proton transfer process as proposed by Daycock *et al.*

For the past several years, many approaches have focused on the development of new materials which incorporating the heteocyclic molecule into the main chain, side chain or even blending with polymer.

2.4.2.1 Incorporated Heterocylic Molecule into the Main Chain

Xiao *et al.* (2005) prepared a series of polybenzimidazoles (PBIs) incorporating main chain pyridine groups. It showed the high proton

conductivities of 0.1 to 0.2 S/cm at 160°C (Figure 2.8). The mechanical property measurements showed that the pyridine-based PBl membranes were thermally stable and maintained mechanical integrity even at high PA doping levels. Moreover, preliminary fuel cell tests demonstrated the feasibility of the novel pyriding-based PBI(PPBI) membranes from the PPA process for operating fuel cells at temperatures in excess of 120°C without any external humidification.
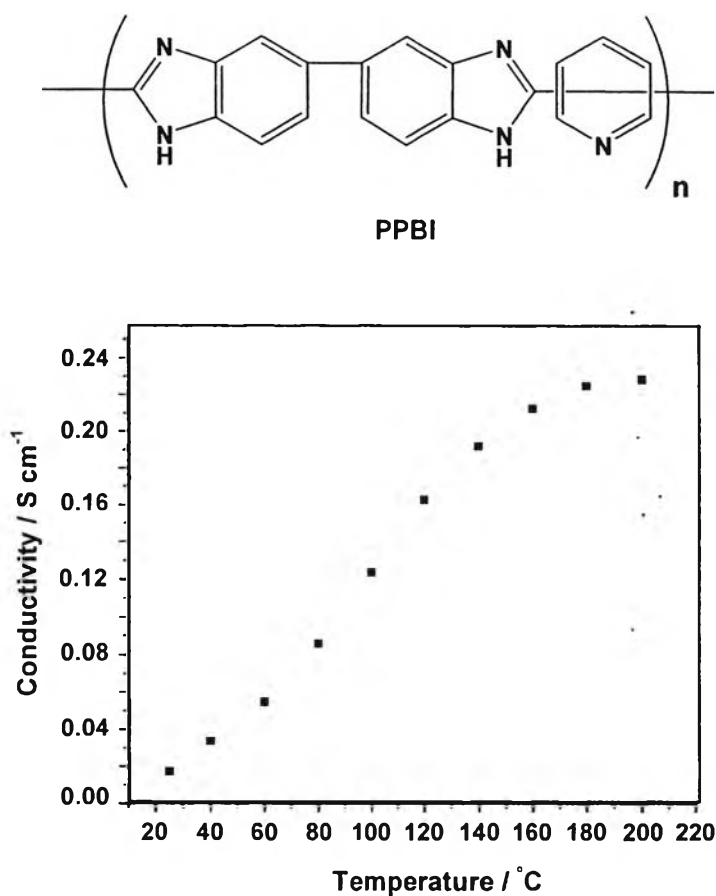

PPBI

Figure 2.8 Chemical structure and temperature dependence of ionic conductivity of PA-doped 2,5-PPBI membranes.

2.4.2.2 Incorporated Heterocylic Molecule into the Side Chain

        Persson *et al.* (2006) synthesized the comb-like copolymers with benzimidazole units tethered to the side chains and found that the benzimidazole-tethered copolymers showed T_g at 50-60°C. This might be a

consequence of the strong hydrogen bond between the benzimidazole units. The proton conductivity exhibited a non-arrhenius behavior and a maximum conductivity of 6.6μS/cm was reached at 160°C under anhydrous conditions (Figure 2.9).
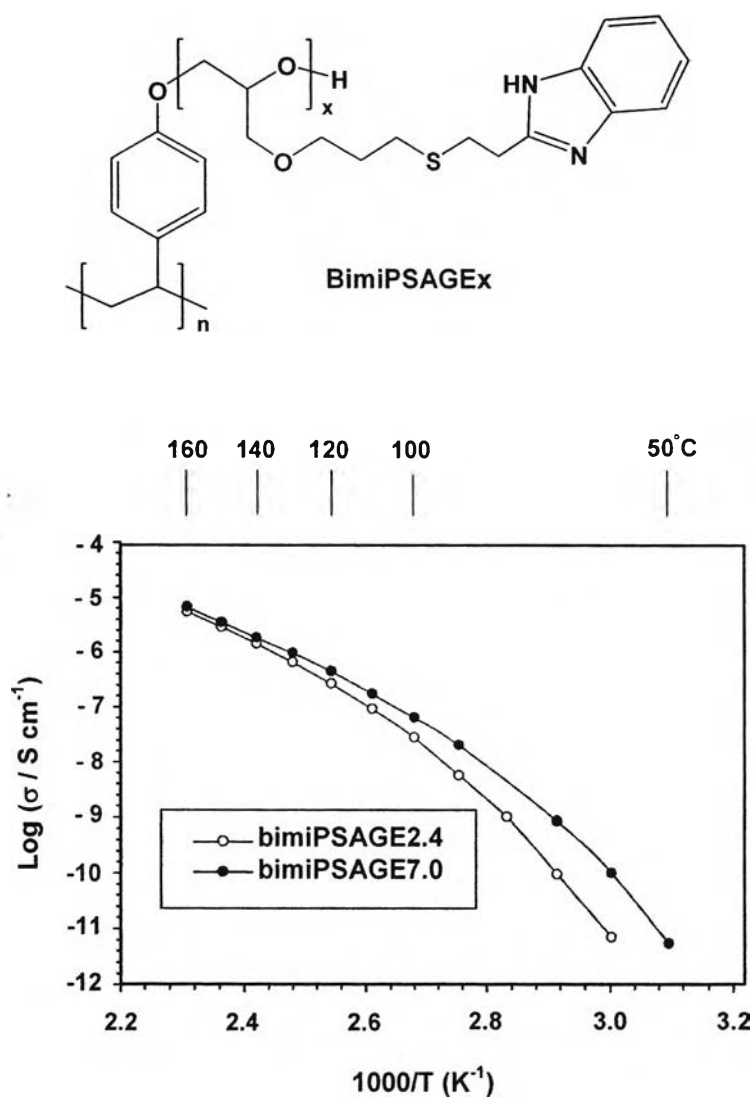

Figure 2.9 Chemical structure and Arrhenius conductivity plots of the bimiPSAGEx samples.

2.4.2.3 Blended Heterocylic Molecule with Polymer Matrix

Karadedeli *et at.* (2005) prepared anhydrous proton conducting organic eletrolytes by doping of adipic acid (AA) with benzimidazole

tetrahydrofuran, dissolved in methanol, and purified by using a column with basic Al$_2$O$_3$, and finally dried in a vacuum for several days (Scheme 2.1).

n=2 (bimi-2EO) or 10 (bimi-10EO)
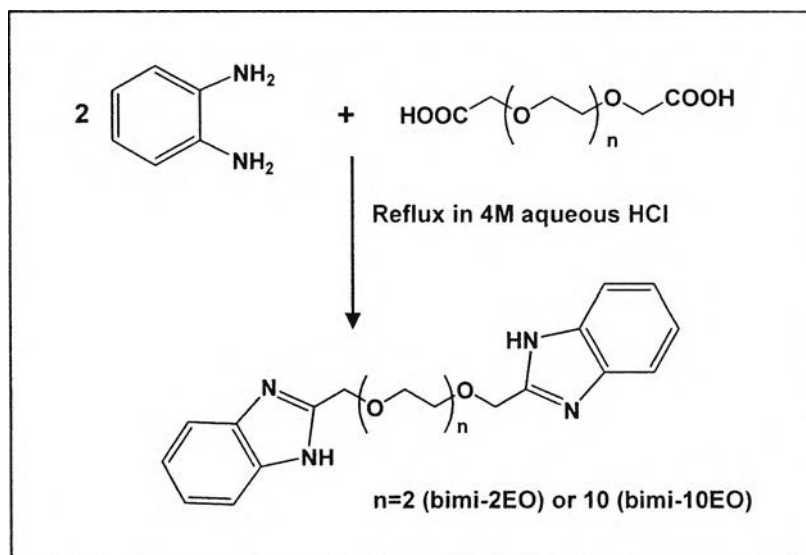
Scheme 2.1 Preparation of benzimidazole oligomers (Presson *et al.*, 2003).

Vinodkumar *et al.* (2007) synthesized 2-(4-bromophenyl)-1*H*-benzimidazole by the condensation of *O*-phenylenediamine and 4-bromobenzoic acid as shown in Scheme 2.2 . The product was carried out from polyphosphoric acid (PPA) at 180°C for 4 h (Scheme 2.2).

1,2-phenylene diamine   4-bromobenzoic acid   2-(4-bromophenyl)-1*H*-benzimidazole
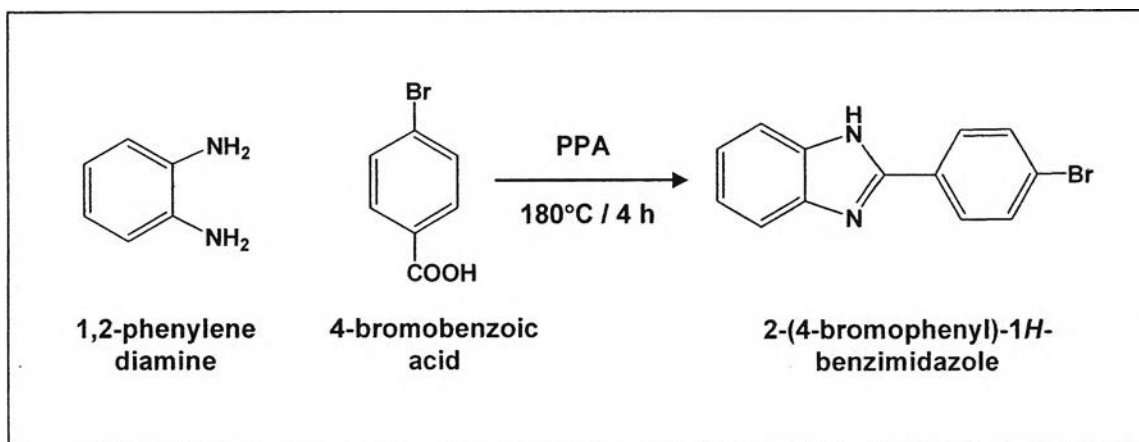
Scheme 2.2 Preparation of 2-(4-bromophenyl)-1*H*-benzimidazole (Vinodkumar *et al.*, 2007).