



CHAPTER II LITERATURE REVIEW

2.1 General Information of Fuel Cell

2.1.1 Basic Principle of 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 in between as shown in Figure 2.1 (Haile, 2003). Basic operation of fuel cell is much like that of battery except that, in the case of fuel cell, the reactants and products are continuously flow into and out of the cell (Stambouli *et. al.*, 2002).

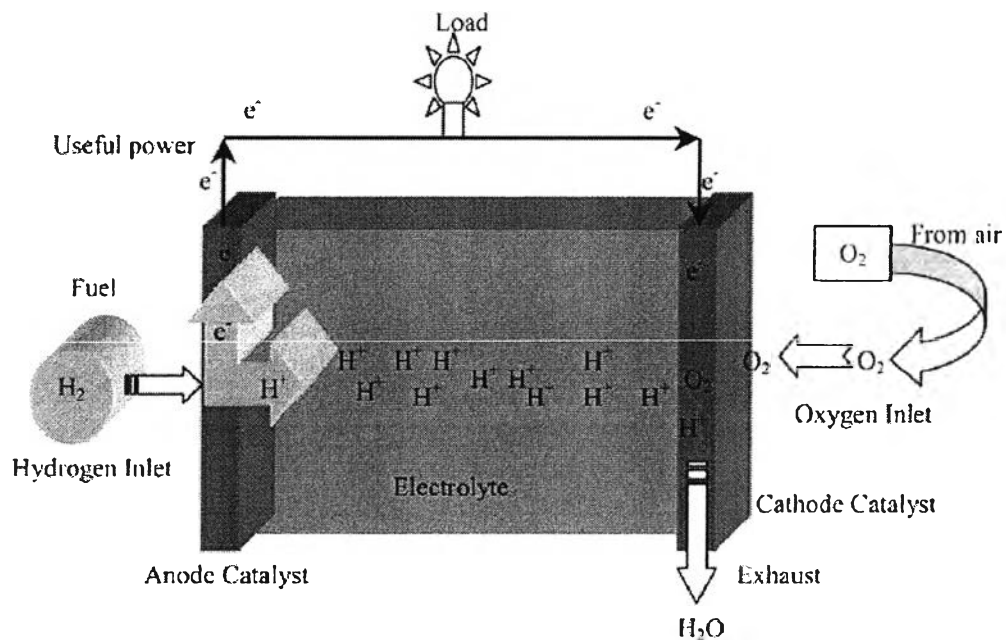


Figure 2.1 Typical operation and component of fuel cell (Stambouli *et. al.*, 2002).

In principle, the fuel is fed to anode where oxidation takes place to split the molecules into ions and electrons. Ions will move through the electrolyte to cathode while electrons are moving out to external circuit resulting in useful electrical energy. Then, at cathode side, ions and electrons will be recombined together with oxidizing agent, i.e., oxygen, by reduction reaction giving the product

which will be removed out from the cell. The process is driven by the positive standard electrical potential of the cell (E^0_{cell}) which finally becomes the electrical potential produced by the fuel cell (Haile, 2003). There are many types of fuel cells classified by the materials used as the electrolytes. At present, the main types of fuel cell are Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel cells (MCFC), Solid Oxide Fuel Cells (SOFC), and Proton Exchange Membrane Fuel Cells (PEMFC) (Sopian *et. al.*, 2006). In addition, a fuel cell type known as Direct Methanol Fuel Cell (DMFC) is similar to PEMFC, but it uses methanol as the fuel instead of hydrogen or hydrogen rich gas. The different electrolytes cause the different operation conditions, advantages, disadvantages and applications to the fuel cell as shown in Appendix A.

2.1.2 Attractive of Fuel Cell

The main advantages of fuel cells over the conventional electrical generating system are recognized in term of higher efficiency, cleaner process, quiet, and more sustainable technology.

Efficiency

Because fuel cells convert chemical energy directly to electrical energy without involving the conversion of heat to mechanical energy, this brings one of the main attractive features, which is the high efficiency of fuel energy conversion to electricity, to fuel cell systems. This efficiency, which runs from 40-60% based on the lower heating value (LHV) of the fuel, is higher than that of almost all conventional electrical production systems as seen from Table 2.1 (Stambouli *et. al.*, 2002).

Table 2.1 Fuel efficiency (Stambouli *et. al.*, 2002)

Means	Gas-electric	Micro-turbine	Diesel-electric	Fuel cell
Efficiency	20%	24%	32%	50% (90% with heat recovery)

Fuel cell efficiencies exceed the Carnot limit even when operating at relatively low temperature. In addition, fuel cells operate at constant efficiency, independent of size.

Clean Technology

As mentioned, fuel cell operation does not involve combustion process resulting in no NO_x and SO_x being released to environment. In addition, other harmful exhausted compounds observed in combustion system, e.g., CO, H₂S, NH₃, halides, particles and organic compounds, are also not the point to be concerned. Carbon dioxide (CO₂) may be presented, if a hydrocarbon fuel is used, but the emission is much lower than that of the conventional system (Table 2.2). (Stambouli *et. al.*, 2002; Sopian *et. al.*, 2006) This provides the significant benefits when we consider about the global warming situation, which is becoming the national concerns worldwide nowadays.

Table 2.2 Exhausted compounds in air emissions from a year of operation (Stambouli *et. al.*, 2002)

Air emission ^a	SO _x	NO _x	CO	Particles	Organic compounds	CO ₂
Fossil fuelled plant	28,000	41,427	28,125	500	468	4,044,000
Fuel cell	0	0	72	0	0	1,860,000

^aPounds of emission per 1650 MWh from one year full operation.

Moreover, because there is no moving part required for operating fuel cell, thus, this technology is quiet resulting in no sound pollution to people.

Sustainable Technology

It has been noticed that fossil fuel reserves will be shortage in next few decades. In contrast, the fossil fuel demand is increasing every year as seen from Figure 2.2 (Song, 2002). Therefore, the development of sustainable alternative energy resources is essential. There are numbers of energy production systems have been studied, i.e., solar cell, wind and tidal power, nuclear technology, and fuel cell. However, when considering about capacity, reliability and environmental

friendliness, fuel cell comes up the only one technology that satisfies all the concerns. In addition, the fuels such as ethanol, methanol, hydrogen, or light hydrocarbon compounds can be produced from biomass, which is a reliable renewable energy resource.

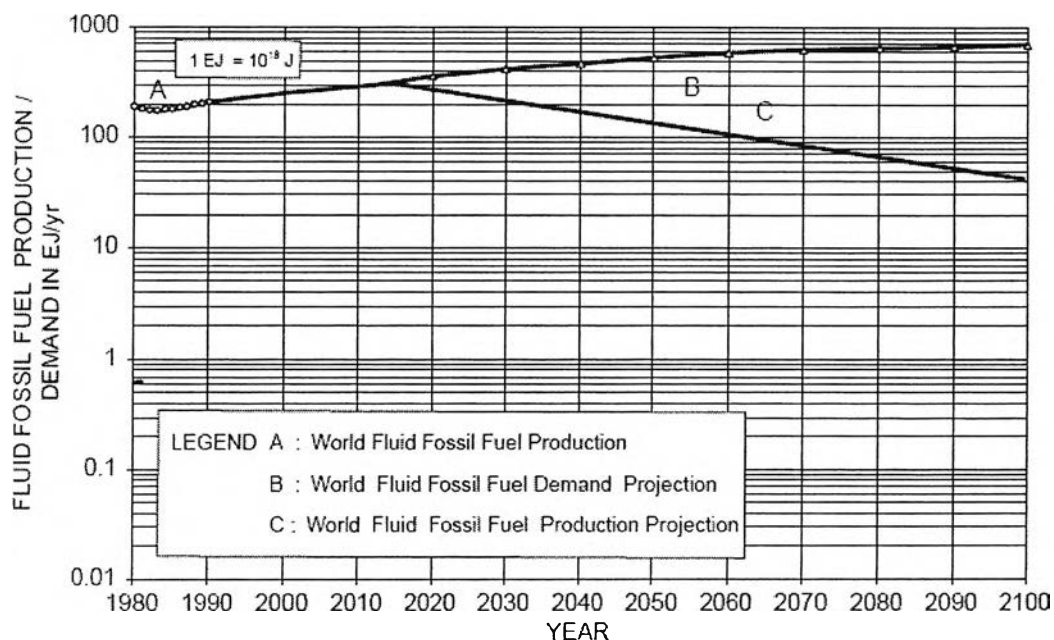


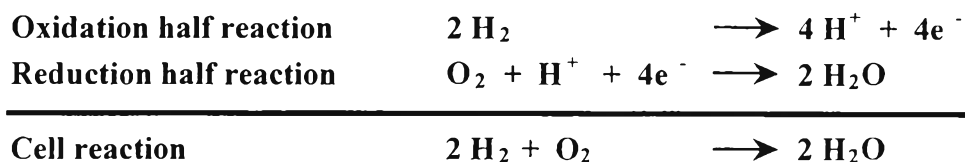
Figure 2.2 Fluid fossil fuel (petroleum and natural gas) world production/demand estimates (Sopian *et. al.*, 2006).

2.2 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

In PEMFCs, a thin proton-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 (Kerres, 2001). Through, low operating temperature guarantees the quick start up from ambient condition. However, the requirement of expensive platinum metal catalyst is the limitation (Beuschem *et. al.*, 2005).

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 (Song, 2002).

Electrochemistry of Fuel Cells



Hydrogen is oxidized on the anode whereas 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 anode and 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 (Yang *et al.*, 2001). The final products of the overall reaction are electrical power, water, and heat (Figure 2.1). 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. 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 (Haile, 2003). An exploded view of a PEMFC and a PEMFC stack are presented in Figure 2.3.

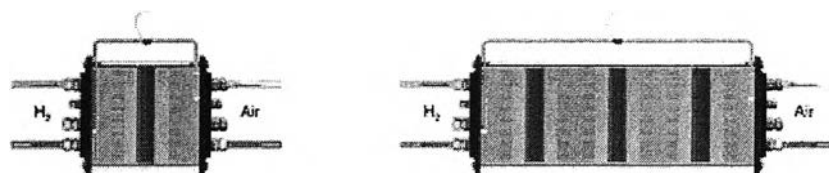


Figure 2.3 Single fuel cell and fuel cell stack (<http://www.plugpower.com>).

2.2.1 Applications and Expectations

PEMFCs are considered to be attractive and alternative systems for power generation of vehicles and moving electronic products (Cropper, 2004). 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.

2.2.2 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 (Kerres, 2001). 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.

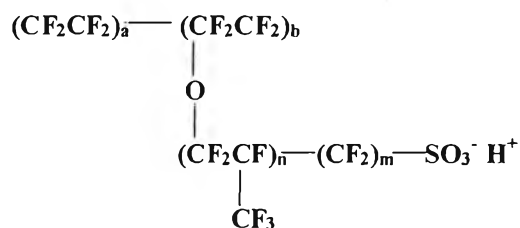
The polymer electrolyte membrane allows positive ions (are hydrogen ions, or protons) from anode side to pass through to the cathode side, in one direction, but separates hydrogen and oxygen molecules and therefore prevents direct combustion. Only the hydrogen ions contained within the membrane are mobile 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.

2.3 Conventional Polymer Electrolyte Membrane

Historically, proton conductive materials for fuel cell have been developed for more than 50 years, starting from cross-linked polystyrene-divinyl benzene-sulfonic acid and sulfonated phenol-formaldehyde which was conducted in 1950. However, the major scientific breakthrough of electrolyte material development was introduced in the early 1970s based on the perfluorinated, sulfonic acid polymer, Nafion[®], produced by DuPont (see chemical structure in Scheme 2.1) (Kerres, 2001).



Scheme 2.1 Chemical structure of Nafion[®] ($n = 6-10$ and $m \geq 1$).

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 H₂O and alkaline hydroxide electrolysis cells.

The Nafion[®] membranes, fully fluorinated polymers, exhibit exceptionally high chemical stability in strong bases, strong oxidizing, and reducing acids, H₂O₂, Cl₂, H₂, and O₂ at temperature up to 125°C (Kreuer, 2001). 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% H₂SO₄ solution, in a hydrated membrane.

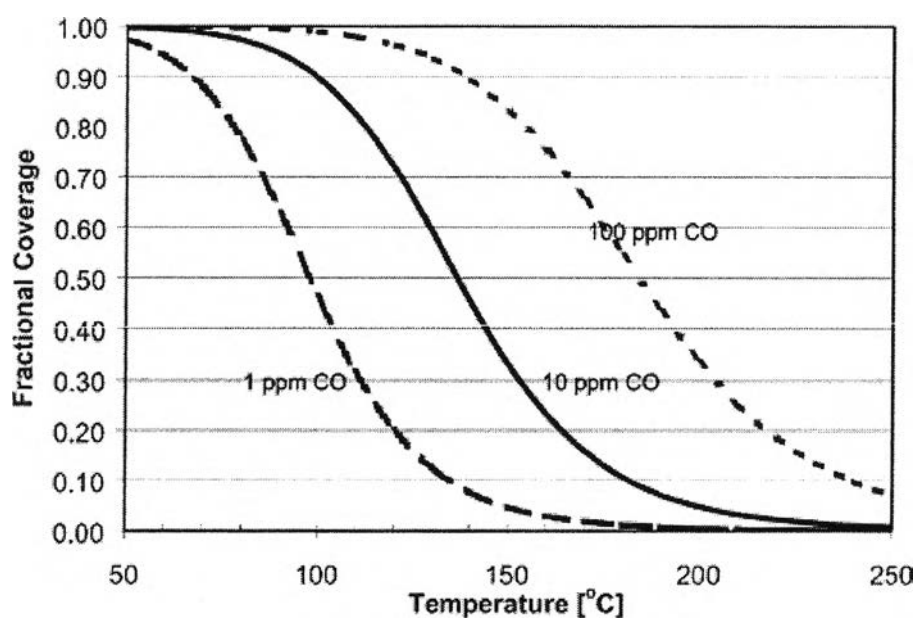


Figure 2.4 CO tolerant of catalyst at various temperatures. (Yang *et al.*, 2001)

Although, Nafion[®] satisfies the requirements of high proton conductivity, good chemical inertness, low H₂ and O₂ permeability, and good mechanical properties. The main drawbacks of this membrane are expensiveness and the need of complicated water management system. Moreover, it had been studied that the

increase of operating temperature to more than 120 °C led to the significantly improvement in CO tolerant of electrode catalysts, i.e., platinum, resulting in the applicability of hydrogen gas obtained from reforming process (Figure 2.4). (Yang *et al.*, 2001) Thermal acceleration of proton movement at higher temperature also provides the higher proton conductivity to the cell. However, the evaporation of water inside to membrane limits the temperature of the cell at lower than 100 °C. This brings to the deadlock of using Nafion® and initiates many scientists to develop the alternative polymers for PEMFC, especially the membranes functioned in water-free condition (Beuscher *et al.*, 2005).

2.4 Development of Alternative Materials for Anhydrous PEMFC

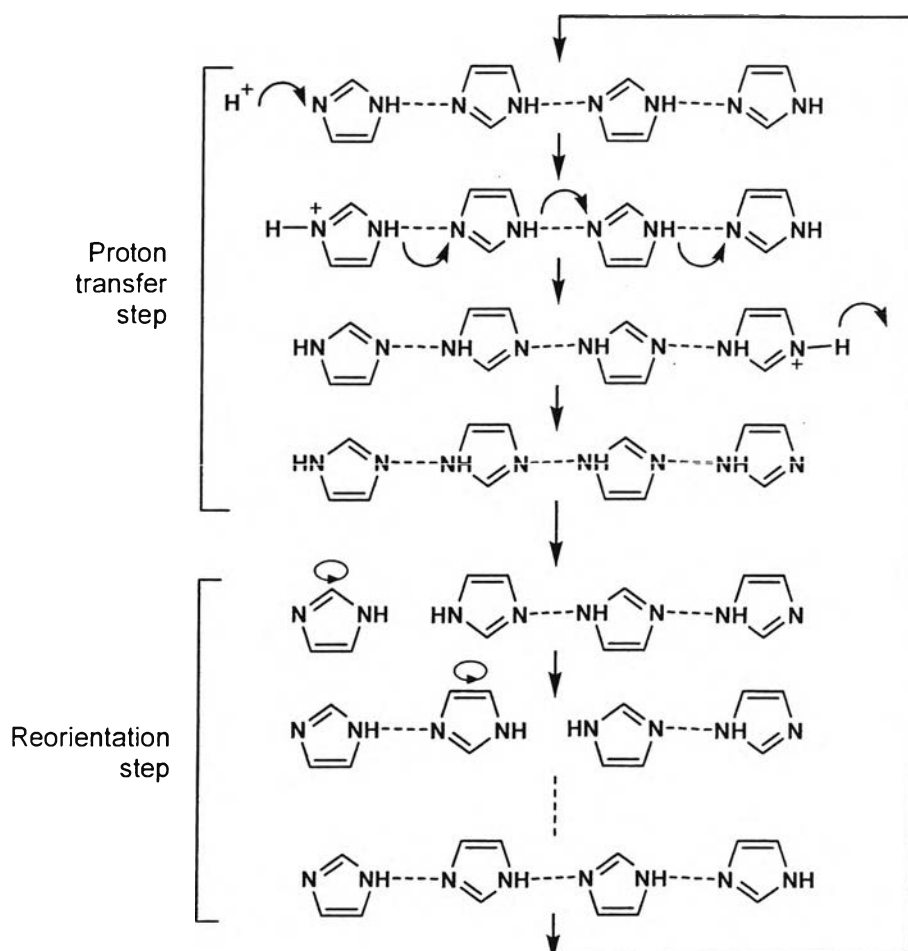


Figure 2.5 Proton transfer mechanism of pure imidazole reported by Münch *et al.*(2001).

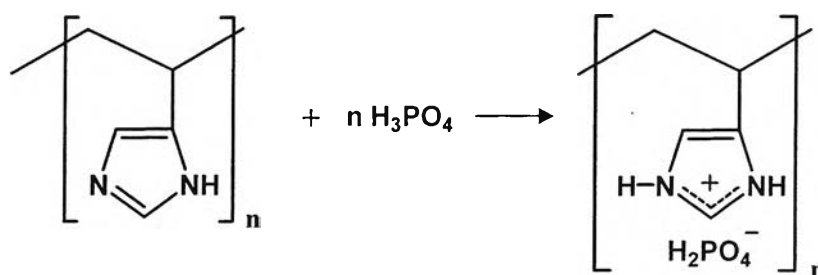
To overcome the limitation of PEMFC operating temperature, which is defined by the boiling point of water, the alternative proton carriers that have higher evaporating temperature have been proposed, i.e., heterocyclic-resonance structure compounds. Imidazole is one of the simplest structures of heteroaromatic compounds that has been successively studied as proton conductive materials because its has proton conductivity as high as $\sim 7 \times 10^{-3} \text{ S/cm}^{-1}$ at 120 °C with the melting point and boiling point of 90 and 256 °C, respectively. (Kreuer *et. al.*, 1998) Proton transferring mechanism of the neat imidazole was reported by Münch *et. al.* (2001). The mechanism was proposed to be involved with proton transfer- and reorientation process (Figure 2.5). Consequently, the works on imidazole-based PEMFCs have been published in every aspect such as mixing with other small molecules, incorporating in to polymer matrix, functionalizing on to polymeric structure, and modifying to imidazole derivative compounds. The example of each aspect is summarized in table 2.3.

Table 2.3 Example of imidazole-base compounds for fuel cell membrane

Type	Compounds	Conductivity (S/cm)/ Temperature (°C)	Reference
Mixing with other small molecule	Imidazole and sulfanilic acid	$5 \times 10^{-2} / 130$	Kreuer <i>et. al.</i> , 1998
Blending with Polymer	Poly(acrylic acid) doped with imidazole	$1 \times 10^{-3} / 120$	Bozkurt <i>et. al.</i> , 2003
Functionalization onto polymer chain	Poly(4-vinylimidazole) doped with phosphoric acid	$1 \times 10^{-3} / 150$	Bozkurt <i>et. al.</i> , 2001
Modifying the structure	Imidazole-terminated ethyleneoxide oligomer doped with triflic acid	$1 \times 10^{-3} / 120$	Schuster <i>et. al.</i> , 2001

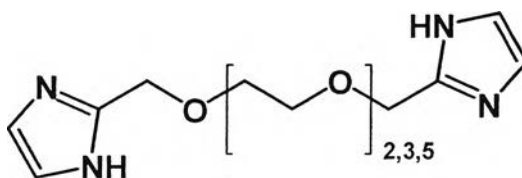
Because we are focusing on the application of fuel cell at temperature higher than 100 °C, using of imidazole molecules directly may cause the leakage since its melting point is 90 °C. Thus, the approaches of imidazole immobilization onto polymer chain or modifying the structure of imidazole are more important for us. For the case of immobilization of imidazole with polymer, poly (4-vinylimidazole) doped with phosphoric acid, reported by Bozkert *et. al.* (2001) is found to be the simplest one (Scheme 2.2). They showed that the 1.0 molar ratio doped of phosphoric acid with the polymer exhibit the proton conductivity of 1×10^{-3} at 150 °C.

Scheme 2.2 Poly (4-vinylimidazole) doped with phosphoric acid.



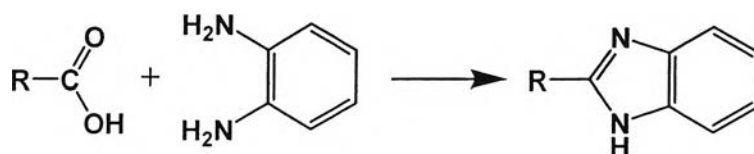
The speculation of proton hopping from one imidazole side chain to the adjacent imidazole unit was proposed as the reason of high proton conductivity, while, phosphoric acid was used as a proton source. However, there was no concrete evidence to prove their idea of such proton hopping system. Moreover, the orientation of imidazole groups which is the most important factor for proton hopping along the chain was not be touched upon. The studies about favoring proton transfer property by inducing orientation of imidazole unit have been rarely found. One of the examples is the development of imidazole-terminated ethyleneoxide oligomer proposed by Schuster *et. al.* (2001) (Scheme 2.3). There, the ethyleneoxide spacers were aimed to offer both immobilization of imidazole groups and flexibility of oligomers. They expected that the flexible chain will not obstruct the arrangement of imidazole units which is generated by hydrogen bond formation. They showed that the conductivity of the mixture between the oligomers and trifluoromethanesulfonic acid (triflic acid) is in the level of 10^{-3} S/cm at 120 °C. However, they could not prove their expectation of imidazole unit-arrangement in the system.

Scheme 2.3. Imidazole-terminated ethyleneoxide oligomer.



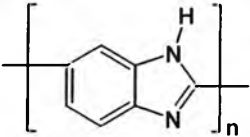
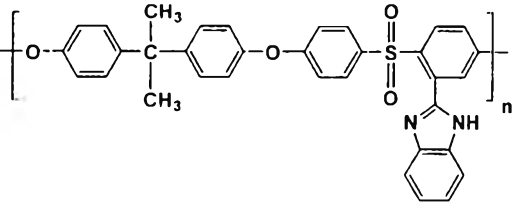
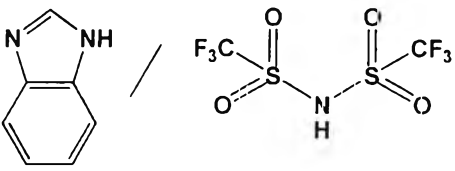
Not only imidazole but also benzimidazole have been applied for being proton carrier in PEMFCs. Despite the lack of studies on proton conducting mechanism of benzimidazole, the more flexible preparation and stiffer structure of benzimidazole than imidazole make it more preferable for scientists to do researches on benzimidazole-based polymer electrolyte membranes than the imidazole ones. Incorporation of benzimidazole in proton conductive polymers was carried out through (i) main chain structure, (ii) side chain structure, and (iii) free molecule as shown in Table 2.4. Most of the works on benzimidazole-based compounds for PEMFCs are concentrated on incorporating benzimidazole units as the main chain or as the side chain of polymer through the reaction between carboxylic acid and diamine as illustrated in Scheme 2.4.

Scheme 2.4. General reaction of benzimidazole formation.



However, those kind of structures are difficult to develop the effective arrangement of benzimidazole unit which is the key factor for proton hopping mechanism of heterocyclic resonance-structured compounds. Thus, specific structures that favor the orientation or packing of heteroaromatic groups together with the formation of hydrogen bond network, which suppose to be the most effective condition for proton transfer, are still needed to be concerned (Scheme 2.5).

Table 2.4 Example of benzimidazole-base compounds for fuel cell membrane

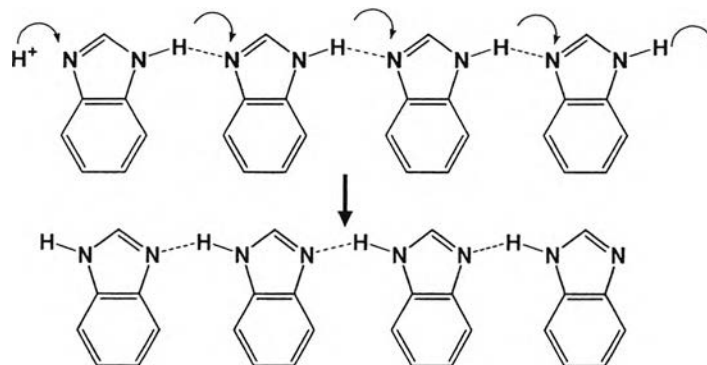
Approach	Structure	Conductivity / Temperature	Reference
Main chain	 <p>Poly (2,5-benzimidazole) doped with phosphoric acid</p>	$6 \times 10^{-3} \text{ S.cm}^{-1}$ / 110 °C	Kim <i>et. al.</i> , 2004
Side chain	 <p>Benzimidazole functionalized polyether sulfone blend with SPEEK</p>	$2.5 \times 10^{-4} \text{ S.cm}^{-1}$ / 130 °C	Fu <i>et. al.</i> , 2006
Free molecule	 <p>Ionic liquid of Benzimidazole / Bis (trifluoromethanesulfonyl) imide</p>	$2 \times 10^{-2} \text{ S.cm}^{-1}$ / 150 °C	Nakamoto <i>et. al.</i> , 2007

2.5 Points of Research

Taking the proton hopping mechanism of heteroaromatic structures to our account, we would like to challenge the development of the model compounds which might be able to induce the well-defined molecular arrangement governed by hydrogen bond networks. The formation of this packing structure will function as a

specific route for proton movement resulting in the effective proton transferability of the compounds.

Scheme 2.5 Ideal system for the most effective proton transfer of benzimidazole compound.



Here, we consider the development of model compounds based on the small molecules of the benzimidazole derivatives. The structures are designed to favor the molecular packing structure of the compounds through the formation of hydrogen bond networks between heteroaromatic functional groups, at the same time, exclude all the complicated factors existed in the polymeric system. Various characterization techniques were applied to clarify the structures, properties and molecular orientations of the compounds. Proton conductivity measurement was performed by using the impedance meter.