# CHAPTER II
LITERATURE REVIEW

Fuel cells are electrochemical devices that convert the chemical energy (such as hydrogen, natural gas or other hydrocarbon-based fuels) directly into electricity. A fuel cell consists of an electrolyte layer in contact with an anode and a cathode on either side (Sammes *et al.*, 2006). The oxidation reaction occurs on the anode side, whereas the reduction happens on the cathode side. There are numerous types of fuel cells. First, Alkaline Fuel Cell (AFC): the electrolyte in this fuel cell is potassium hydroxide (KOH). The fuel is limited to non-reactive components except for hydrogen. CO is a poison gas, and CO_2 will react with the KOH to form K_2CO_3, even with a small amount of CO_2. Secondly, for the Phosphoric Acid Fuel Cell (PAFC), the electrolyte uses 100% concentrated phosphoric acid (H_3PO_4). At low temperature, H_3PO_4 is a poor ionic conductor, and the poisoning of CO to the Pt catalyst. Thirdly, Molten Carbonate Fuel Cell (MCFC): the electrolyte is in general a combination of alkali carbonates, which is employed in a ceramic matrix of $LiAlO_2$. This fuel cell is able to perform at high temperatures (600-700 °C). Fourth, Tubular Solid Oxide Fuel Cell (TSOFC): a solid is used as the electrolyte. The cell operates at 1000 °C. Fifth, Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC): the electrolyte and electrode materials are the similar to TSOFC, but this fuel cell is operated at a lower temperature. Sixth, Polymer Electrolyte Fuel Cell (PEFC): the electrolyte is an exceptional proton conductor. The liquid in this fuel cell is water; therefore, the corrosion problem is not severe. Water management in the membrane is critical for its efficient performance; the fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced because the membrane must be hydrated (EG&G Service *et al.*, 2000).

For PEFC is also calling PEMFC, PEM stands for Polymer Electrolyte Membrane or Proton Exchange Membrane. They are also called polymer membrane fuel cells, or just membrane fuel cells (Sammes *et al.*, 2006). The heart of a PEM fuel cell is the polymer membrane which has unique capabilities: it is impermeable to gases but it conducts protons. Electrochemical reactions take place at the surface of catalyst at the interface between the electrolyte and the membrane. Hydrogen, which

is fed on anode side of the membrane, splits into protons and electrons. Each hydrogen atom consists of one electron and one proton. Protons pass through the membrane, while the electrons pass through an outside circuit to generate electric current. At the catalyst site between the membrane and the cathode, electrons join with the protons that pass through the membrane, and oxygen fed on the cathode side creates water which is pushed out of the cell by an excess oxygen flow (Sammes *et al.*, 2006). PEMFC by a hydrogen feed shows many advantages: non-corrosive electrolyte, compact and strong; simple mechanical design; high voltage; good tolerance to the difference of pressure of the reaction; and etc. But some disadvantages are also important to consider: very sensitive to impurities of hydrogen (need reforming unit); poor tolerance to sulfur particles; a need for a humidification unit; and etc. To overcome some of the problems of the hydrogen feed fuel cell it is required to employ instead a methanol feed–direct methanol fuel cell (DMFC). This type of fuel cell also uses a polymer electrolyte membrane. DMFC shows at least two advantages over hydrogen feed: it does not need a reforming unit and the deposit size is less due to liquid fuel. However, some drawbacks are a lower efficiency compared to the hydrogen cell and it needs a high amount of catalyst at the anode for the electro-oxidation of methanol. The picture of a proton exchange membrane fuel cell (hydrogen feed) and a direct methanol fuel cell are shown in Figure 2.1 and Figure 2.2, respectively (Andújar *et al.*, 2009). Their reactions are shown in Table 2.1.

Table 2.1 Reaction of polymer electrolyte membrane of hydrogen and methanol feed

Reaction	Hydrogen feed	Methanol feed
At the anode	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$
At the cathode	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Overall	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$2CH_3OH + 3O_2 \rightarrow 2H_2O + 4CO_2$
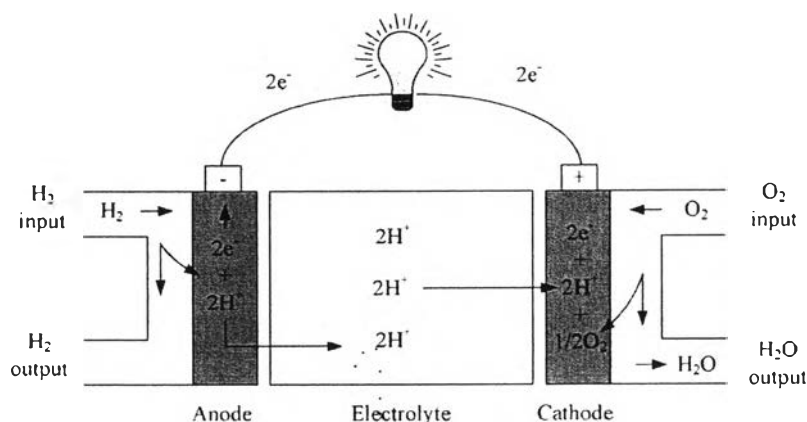
Figure 2.1 Operation principle of proton exchange membrane fuel cell (hydrogen feed).
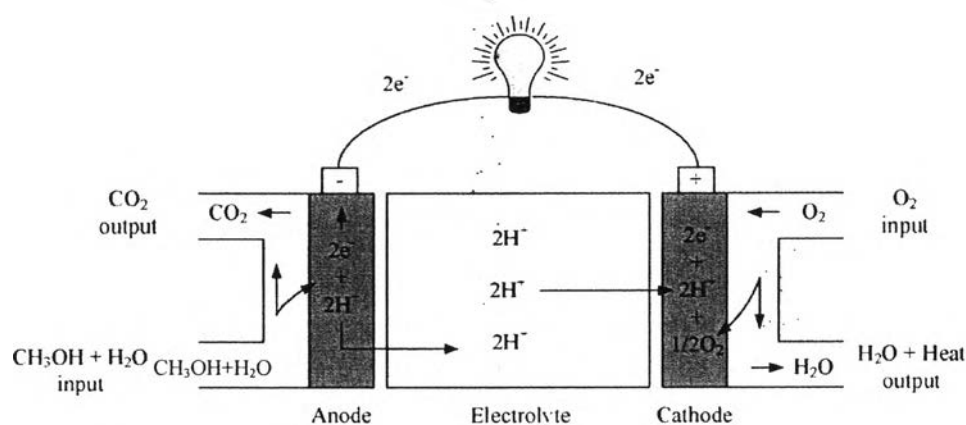
Figure 2.2 Operation principle of direct methanol fuel cell.

PEM fuel cells are the most attractive of all the fuel cell types for many applications due to their simplicity, quick start-up, loading capabilities, efficiency, modularity, and versatility (Sammes *et al.*, 2006). There are many chemical functional groups that can be introduced in to a polymer chain in the support of mechanical and thermal properties, electrical properties and for reducing permeability of methanol for use as direct methanol fuel cell (DMFC). All of these properties can be accomplished with aromatic imide functional groups. Fang *et al.* (2003) suggested that aromatic polyimides are a class of high performance polymers that have excellence thermal, electrical and mechanical properties, in agreement with

Zhu *et al.* (2008) who claimed that aromatic polyimides are excellent chemical and oxidative stabilities. However, aromatic polyimides are difficult to dissolve in organic solvents and possess a high melting temperature (Fang *et al.*, 2003) resulting in a difficult processing. The four common methods in modifying the properties of a polymer are: (I) Surface modification; (II) Plasma treatment; (III) Grafting functional groups; and (IV) Blending. Blending of polymer in membrane casting solution is useful and a manageable technique for modifying the properties of the prepared membrane (Rahimpour *et al*, 2008).

The common methods to determine the polymer structure are Fourier Transform Infrared Spectroscopy (FTIR) and ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR). Characterizations of cast films are the water uptake and the swelling ratio, the proton conductivity, the methanol permeability, the differential scanning calorimetry (DSC), the thermo gravimetric analysis (TGA), the dynamic mechanical analysis (DMA), and several other methods. The literature reviews about the polyimide copolymer are given below.

Bhuvana *et al.* (2006) studied a series of polyamide-imide with high thermal stability. The series were synthesized by the polycondensation of diamine and aromatic diacid using polar protic solvents. The diamine was modified by allowing diamine to react with BPTDA (3,3',4,4'-benzophenone tetracarboxylic acid anhydride) and imide rings to diacid by the reaction between aromatic diol and 2,4-dichlorobenzoic acid. Then, the two new monomers were allowed to react together. The series exhibited T_g values in the range of 207-234 °C but the char yields were only 48 - 66%.

Wang *et al.* (2007) studied a miscible (Torlon® polyamide-imide with Matrimid® 5218 polyimide and polybenzimidazole) polymer blend system. Miscibility was studied by DSC, MDSC, FTIR and MDA. The results showed better performances than those of pure Torlon® film.

Rahimpour *et al.* (2008) used a polycondensation reaction for the synthesis of poly(amide-imide) containing a flexible group and blended with a polyethersulfone (PES) membrane. Trimellitc anhydride, 2-[2-(2-Amino-ethoxy)-ethoxy]-ethylamine and *p*-phenylene diamine were selected as the monomers for the imide and the amide groups. The blend was of a higher tensile strength and an

elongation strength, but thermal stability was lower compared to that of the PES membrane.

Hsiao *et al.* (2005) worked on a series of poly(amide-imide)s by the synthesis of a diacid monomer from the reaction of trimellitic anhydride and 2,4-diaminotriphenylamine in 2:1 mole equivalence. Then the polymers were synthesized with the diacid monomer and the aromatic diamine at various amounts of aromatic groups. The series had good thermal stability and moderately high glass transition temperatures in range of 259 - 314 °C and at 530 °C it showed a 10% weight loss.

Cheng *et al.* (2004) considered the unsymetrical extended diamine of various aromatic bis(trimellitimide)s to generate a series of new aromatic poly(amide imide)s. The introduction of unsymmetrical extention in the aromatic polymer backbone gave excellent solubility in common organic solvents (DMF, DMAc, NMP, Pyridine, *m*-cresol) and a high thermal stability.

Pan *et al.* (2010) synthesized a series of six-member sulfonated copolyimides, as they were prepared by the one-step solution copolycondensation. All of three monomers (1,4,5,8-naphthalenetetracarboxylic dianhydride, 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)-phenyl](2*H*)phthalazin-1-one, 4,4'-Bis(4-aminophenoxy) biphenyl) were reacted together. Due to the polymer structures containing a lot of aromatic rings in the main chain, they showed an excellent thermal stability, high thermal property, and also low methanol permeability (lower than Nafion[®]117) as well as solubility in aprotic solvents like m-cresol and NMP, because they introduced an ether group or diamine into the main chain.

Jonquières et al. (2005) synthesized a new family of polyamide imides containing hard blocks and soft blocks differing in chemical structures. The family was in the form of poly(urethane-amide-imide).

Sung *et al.* (2010) used a Nafion dispersion (5 wt.% 1100 E.W., sulfonic acid form) to prepare Nafion-based electrode to study the interface between the sulfonated polyimide and the electrode by the introduction a crosslinkable layer that reduced methanol cross over where the crosslinked layer maintained the stable interface of longer operation compared to that without the crosslinkable layer.

Pinto *et al.* (2007) dealt with the reaction of poly(ether imide) (PEI) sulfonated by a sulfonating agent which was prepared from a concentrated sulfuric acid and acetic anhydride dissolved in NMP and compared to a crude PEI obtained from a commercial (Nafion[TM] 117). The percentages of sulfonation varied in the range of 0.02 - 0.8%. The modified polymers (PEI-SO$_3$H) were of better thermal and good mechanical stabilities but became swollen by water at a high level of the sulfonation.

Vora *et al.* (2006) synthesized a series of amorphous fluoro-poly(ether-imide) (6f-PEI) and the series of fluoro-copoly(ether-imide) (6F-CoPEI). The thermal degradation was below or close to the glass transition temperature of neat polyimides and this method was effective at upper operating temperature. These polymers can dissolve in almost organic solvents but some swelling occurred when curing at a high temperature.

García *et al.* (2009) set out the review, the design, the preparation, and the potential applications of aromatic polyamides and related polymers from the past decade. In line with commercial aromatic polyamides, the aromatic polyamide synthesis, the polyamide with controlled structures, the applications of the aromatic polyamides were expanded. They introduced heterocyclic rings in the main chain such as polyesters, polyamide-imide, polyureas, polycyanurate, polyazomethines, and polyamides, which provided an excellent thermal property with an improved solubility.

Bhuvana *et al.* (2007) synthesized poly (amide-imide-imide)s based on diacids with bulky m-chloro phenyl and rigid pyridine. The polymers showed an excellent thermal stability, solubility and mechanical properties. They can be accepted as new materials of engineering plastics.

Zhu *et al.* (2008) studied six-membered sulfonated polyimides containing phthalazinone. The monomer was successfully sulfonated by using a concentrated sulfuric acid and fuming sulfuric acid. The polymers had an excellent dimension and thermal stability, the decomposition temperatures were over 318 °C. The proton conductivity of the membranes ranged from 2.3×10^{-3} to 3.8×10^{-3}S cm^{-1} depending on their sulfonation degrees; the degree of sulfonation was obtained from calculating the mole ratio of sulfonated monomer.

Li *et al.* (2008) synthesized sulfonated poly (arylene-co-imide)s by using Ni(0) catalytic copolymerization. Because of the introduction of electron donating phenoxy groups, the hydrolysis of the imide rings was decreased, resulting in copolymers which exhibited an excellent water stability. The proton conductivities of copolymer membranes were above 3.2×10^{-1} S cm^{-1} at 80 °C and the methanol permeability was lower than Nafion$^®$ 117.

Meyer *et al.* (2006) studied the stability of sulfonated polyimide (sPI) membranes in fuel cell conditions. They found that the synthesized sulfonated polyimides which contained higher IEC values led to an excessive water uptake and poor mechanical properties. In the ageing study, sPI presented a limited lifetime which strongly depended on both IEC and temperature. The chemical analysis revealed that the hydrolysis of the imide rings was the main process of degradation during operation. However, the extrapolated lifetime at room temperatures was larger than 3000 h which could be sufficient for portable applications.

Ng *et al.* (2010) dealt with poly(arylene ether benzimidazole) in which the degree of sulfonation and sulfonation site was controlled by the reaction conditions. The most highly sulfonated material exhibited a degree of sulfonation of 430% which corresponded to an IEC of 4.91 meq g^{-1}. The side chain was activated for sulfonation in oleum and concentrated sulfuric acid when reaction was carried above 70 °C, but if temperature was above 130 °C this led to a main chain degradation.

Woo *et al.* (2003) worked on the sulfonated polyimide membranes in different sulfonation levels by controlling the molar ratio of benzidinedisulfonic acid and oxydianiline. The amount of water uptakes increased with the sulfonation level, but the size of water cluster was not altered by the sulfonation levels. The films showed: a relatively high proton conductivity when sulfonation level was over about 30 - 35 mol% because micro-separated ionic water cluster began to be connected like a percolated network structure; low methanol permeability, as 63% of sulfonated group in polymer membrane exhibited methanol permeability only 3% of Nafion$^®$ 117 membrane; and they were thermally stable up to 300 °C which is suitable for direct methanol fuel cell.

Shang *et al.* (2006) prepared a series of proton conductive membranes from aromatic diamine monomer with a flexible structure, non-sulfonated diamine and

naphthalene tetracarboxylic dianhydride via the high-temperature polymerization method. The proton conductivity of the membranes ranged from 7.9×10^{-3} to 7.2×10^{-2} S cm^{-1}. The methanol permeability was much lower than Nafion$^{\text{®}}$ and the membranes exhibited a high hydrolysis stability.