CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Fuel Cell Systems

A fuel cell is an electrochemical energy conversion device. It produces electricity from external supplies of fuel (on the anode side) and oxidant (on the cathode side). These react in the electrolyte. H_2/O_2-fuel cell systems are distinguished by the types of electrolytes used and following names and abbreviations are now frequently used in publications, following as table below.

Table 2.1 H_2/O_2-fuel cell types

Fuel Cell System	Temperature Range (°C)	Efficiency (cell) (%)	Electrolyte
Alkaline Fuel cell (AFC)	60-90	50 – 60	35- 50% KOH
Proton Exchange Fuel Cell (PEFC)	50-80	50 – 60	Polymer Membrane (Nafion/Dow)
Phosphoric Acid Fuel Cell (PAFC)	160-220	55	Concentrated Phosphoric Acid
Molten Oxide Fuel Cell (SORC)	620-660	60 -65	Molten Carbonate Melts (Li_2CO_3/Na_2CO_3)
Solid Oxide Fuel cell (SOFC)	800-1000	55-65	Yttrium-stabilized Zirkondioxide (ZrO_2/Y_2O_3)

2.1.2 Proton Exchange Membrane Fuel Cells (PEMFCs)

2.1.2.1 Operating Principle of PEMFCs

As the most practical fuel cell candidate, PEMFCs have been attracted because of their low operating temperature, non-production of CO_2, and suitability for electric vehicles. Therefore, this present work focuses on PEMFCs. In a H_2/O_2 proton exchange membrane fuel cell (PEMFCs), a proton-conducting polymer membrane, as the electrolyte, separates the anode and cathode sides.

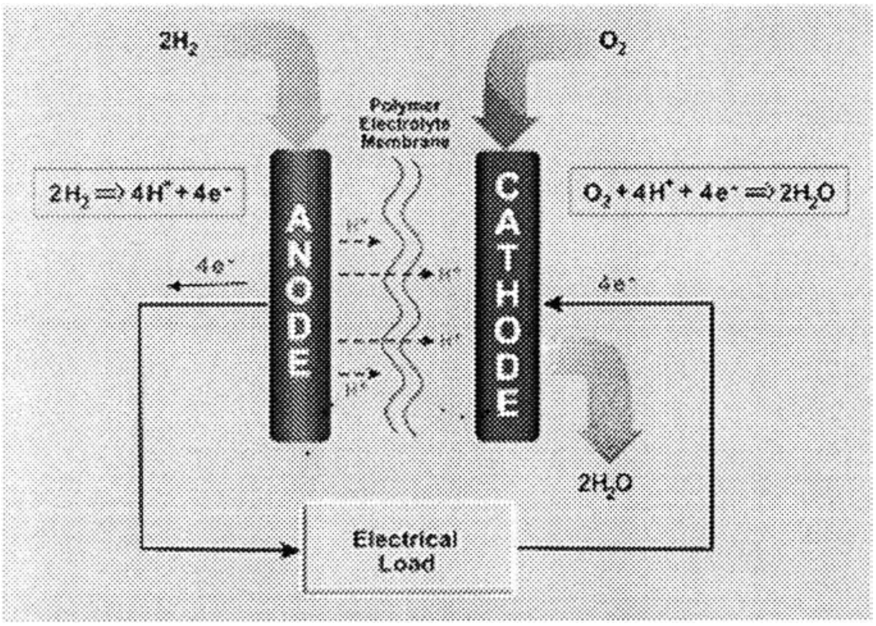

Figure 2.1 Principle of the proton exchange membrane fuel cells (PEMFCs).

At the anode, hydrogen diffuses to the anode catalyst, yielding protons and electrons. The protons enter through the membrane to the cathode, but the electrons are forced to travel in an external circuit (supplying power) due to the electrical insulating property of the membrane. On the cathode side, oxygen combines with electrons from the cathode and protons from the membrane to produce water.

Anode: $2H_2 \xrightarrow{\qquad} 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \xrightarrow{\qquad} 2H_2O$

In addition to pure hydrogen, hydrocarbon fuels such as diesel, methanol, and chemical hydrides can be used for fuel cells. The waste products of these fuel types are carbon dioxide and water.

The materials used in fuel cells differ by type. The electrode/bipolar plates are usually made of metal, nickel or carbon nanotubes, and are coated with a catalyst, platinum or palladium, in order to increase efficiency. Carbon paper separates them from the electrolyte. The electrolyte could be ceramic or a membrane.

Typically, a single fuel cell produces about 0.86 volt. The cells are layered and combined in series and parallel circuits to form a fuel cell stack in order to create enough voltage. The number of cells used is usually greater than 45 but varies with design.

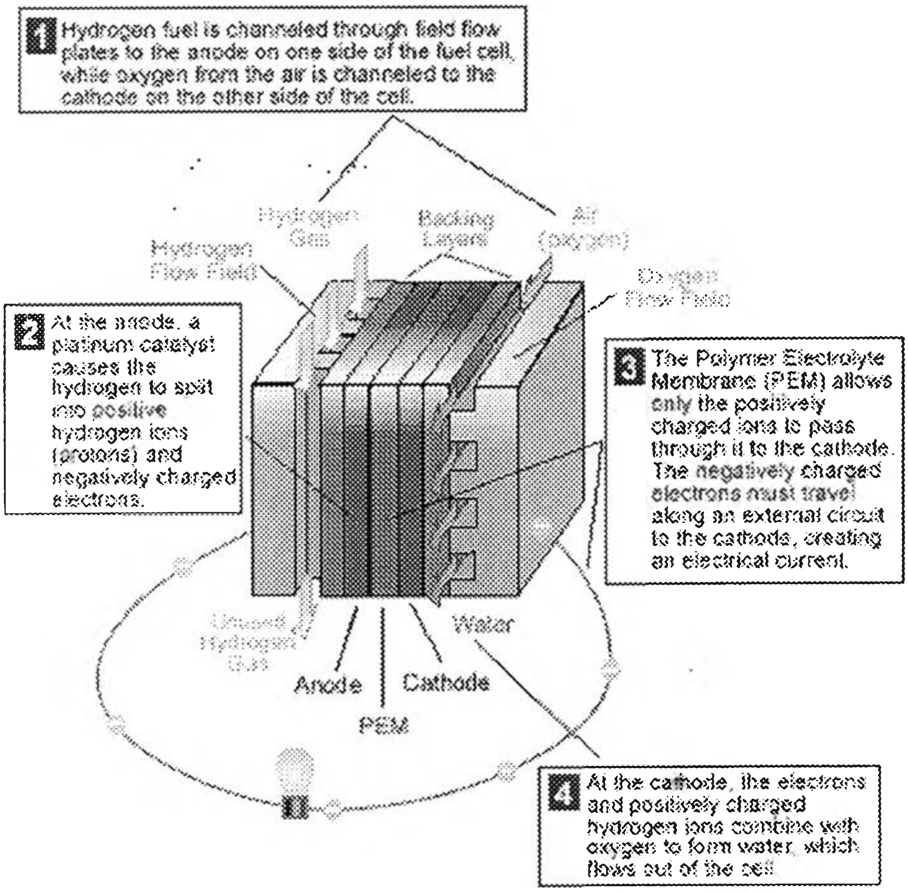

Figure 2.2 The construction of the proton exchange membrane fuel cells (PEMFCs).

Bipolar plate as electrode with in-milled gas channel structure, is fabricated from conductive plastics (enhanced with carbon nanotubes for more conductivity); Porous carbon papers; Reactive layer, usually on the polymer membrane applied; Polymer membrane.

2.1.2.2 Electrolytes-membranes

The PEMFCs (originally refer to as the solid polymer electrolyte fuel cell) use several ion-exchange polymers as its electrolyte. These polymers are electronic insulators, but excellent conductors of hydrogen ions. Hydrocarbon-type polymers such as crosslinked, polystyrene-divinylbenzene sulfonic acids and sulfonated phenolformaldehyde are not suitable for this application because they are unstable due to C-H bond cleavage, particularly at the α-H sites where the functional groups are attached. Therefore, these polystyrenes were replaced with fluorine-substituted polystyrenes (e.g. polytrifluorostyrene sulfonic acid). The most used electrolyte is a hydrated perfluorosulfonic acid polymer such as Nafion, which is still used to date, consists of a fluorocarbon polymer backbone and sulfonic acid group have been chemically bonded. The acid molecules are fixed to the polymer and cannot be leached out, but the protons on these acid groups are free to migrate through the electrolyte.

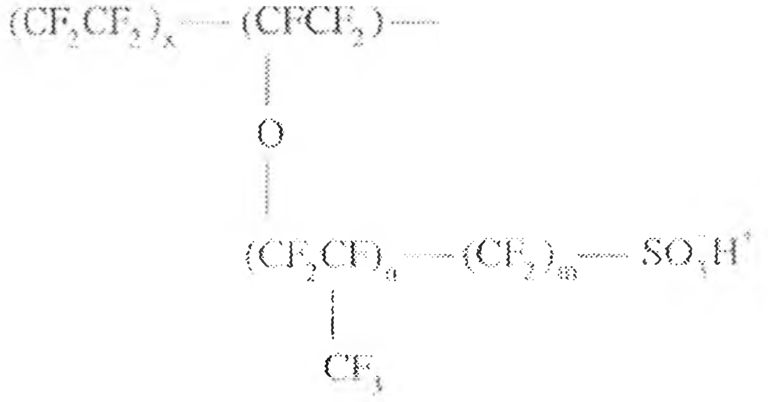

Figure 2.3 Structure of perfluorocarbon ion exchange polymers.

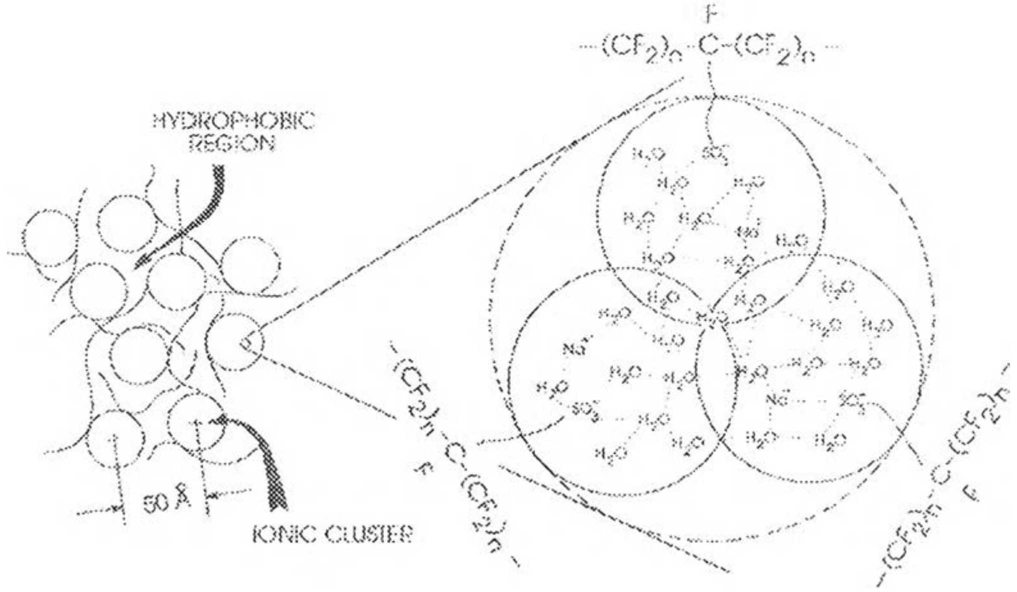

Figure 2.4 Schematic representation of ion clustering in Nafion.

Nafion is modeled typically by three-zone pore model. Interconnecting channels within the polymer contain (i) a low dielectric region with the hydrophobic fluorocarbon polymer matrix, (ii) a high dielectric region containing ion clusters with the sulfonate exchange sites, courterions, and sorbed water, and (iii) an interfacial region containing the pendant side chains of the sulfonate groups and a small amount of water. The hydration water is composed of three water molecules per sulfonic acid group that form the primary hydration shell. A second phase is located in the nanopores between the hydrated, sulfonated polymeric backbone. The structure is showen schematically in Fig. 2.4. (Klein *et al.*, 2005)

This material is suitable for serving as electrolytes in PEMFCs because of their high proton conductivity at low temperature, and they have chemical and mechanical properties to perform as a good PEM.

2.2 Literature Review

2.2.1 Organic/Inorganic Hybrid Membranes

In 2001, Costamagna and coworker have synthesized Nafion/zirconium phosphate composite membranes (using either commercial

Nafion115 or recast Nafion). A Nafion115/23wt%zirconium phosphate MEA operated with H_2/O_2 shows a fourfold increase in current density at 0.4V over an MEA based on commercial Nafion and recast Nafion/zirconium phosphate composite giving higher current density than commercial Nafion/zirconium phosphate. The composite membranes are stable during time when maintained at 130°C, while irreversible degradation affects Nafion under the same conditions.

Ramini (2003) improved proton conductivity over pure Nafion by adding different inorganic heteropolyacid (HPA) such as phosphotungstic acid, silicotungstic acid, phosphomolybdic acid and silicomolybdic acid to Nafion. The composite membranes can slightly improve conductivity at low humidities because the HPA additives have much larger particle size than the cluster size. The thermal stability of the composite membranes is improved by casting in the NA^+ form, using a high boiling solvent, which permit a more stringent heat treatment process on the MEA. The membranes show 1 mA/cm^2 of crossover currents. The MEAs made using membranes containing molybdenum-based HPA additives are less stable in the membrane environment than those containing tungsten because of redox transitions of the additive in the fuel cell operating range. These MEAs also present poorer performance at all conditions.

Damay and Klein (2003) have studied transport of Nafion composite membranes such as a Nafion, Nafion/$7SiO_2$-$2P_2O_5$-ZrO_2 (SPZ), Nafion/SiO_2+H_3PO_4 (iHPO), Nafion/SiO_2+$H_3PW_{12}O_{40}$ (iHPW) and Nafion/ZrP composites. These membranes were investigated using water desorption measurements and ac impedance spectroscopy as a function of time, relative humidity and temperature. These membranes except Nafion/ZrP indicate higher conductivity than Nafion at high temperature. The Nafion/ZrP membrane exhibits reduced proton mobility because the ZrP particles block part of the hydrophilic polymer channels through which protons migrate. This implied that the structure of the composite plays a much more important role (than previously thought).

Sacca (2004) also reported the preparation and characterization of Nafion - TiO_2 hybrid membranes. The incorporation of nanometer TiO_2 power leads to the composite membrane with a good mechanical and thermal resistance and improves the water uptake and IEC values, compared to the commercial Nafion membrane. The composite membrane give a power density of 0.514 Wcm^{-2} at T=110°C.

Moreover, Sacca and coworker (2005) have prepared recast ZrO_2-Nafion composite membranes with three different percentages (5%, 10% and 20% w/w) of zirconium (IV) oxide by Doctor-Blade casting technique for PEMFCs at temperature about 120-130°C. The water uptake increases by increasing of the inorganic content since that is a hydrophilic compound, whereas the IEC value decreases due to the presence of ZrO_2. The membranes were tested in a single cell in the temperature around 80-130°C with 100% R.H., the OCV is decreased when cell temperature increases. The 10% (w/w) ZrO_2-Nafion membranes obtain power density values of 604 $mWcm^{-2}$ and of 387 $mWcm^{-2}$ at 0.6 V and at 110°C (100% RH) and 130°C (85% RH), respectively.

Proton conducting inorganic-organic composites based on 3-glycidoxypropyl trimethoxysilane (GPTS) as a matrix and silicotungstic acid as a proton donor by introduction of SiO_2 and/or Al_2O_3 as a dispersoid were fabricated by Nagai and Chiba in 2005. The sample derived from SiO_2 sol (SG) shows a conductivity of 10^{-2} s/cm at 100°C whereas those derived from Al_2O_3 (AG) and SiO_2/Al_2O_3 (SAG) show slightly lower values. The enhanced mechanical strength is obtained for AG while SG is rather fragile. The chemical durability against water and methanol exhibited that SAG are superior to SG and AG. As whole SAG is suitable material as a membrane for PEMFC.

Bebin *et al.* (2005) have studied the preparation of nanocomposite membranes by a recasting procedure using a Nafion solution mixed with surface-modified Laponite particles. The surface modification of the clay particles occur via plasma activation, leading to sulfonic acid groups bonded to clay's surface. The dispersion of these clay particles in Nafion enhances both the water retention of the membrane and its proton conductivity. At temperature close to 100°C, a dehydration delay of the membrane is taken place due to the hydrophilic properties of the inorganic particles. Fuel cell tests have shown a significant increase of the power density of the cell using a hybrid membrane, especially in dehydration working conditions.

Nafion-MO_2 (M = Zr,Si,Ti) nanocomposite membranes using in situ sol-gel methods were investigated the characterization of a proton conducting membrane (Jalani, 2005) SEM images implied that these membranes have nano-sized inorganic particles within the pores of the membrane. At 90°C and 120°C, all Nafion- MO_2 nanocomposites are better water uptake than Nafion membrane. These results can be attributed to the increased acidity and surface areas of nanoparticles. Nafion-ZrO_2 sol-gel is the most acidic membrane so it exhibits highest water uptake and consequently it shows higher conductivity than Nafion. Further, the degradation temperatures and Tg of all nanocomposites are improved so all of them are better thermomechanical properties than Nafion.

The hybrid Nafion115-inorganic oxide such as SiO_2, TiO_2, WO_2 and SiO_2/phosphotungstic acid (PWA) membranes have been prepared by the recasting proceduce. The impregnation of these additives increases crystallinity and mechanical strength of the membranes due to a good interaction between these inorganic particles and the membranes. The composite membranes give higher water uptake values than Nafion membranes. The proton conductivity of the composite membranes except Nafion/TiO_2 is close to that of the Nafion membrane at high temperature and at 100% R.H., however, it is much higher at low R.H. The performance of these composite membranes in the PEMFC operated at 110°C and 70% RH is better than that of Nafion membrane and is found in the order of Nafion/SiO_2/PWA> Nafion/SiO_2> Nafion/WO_3> Nafion/TiO_2 (Shao *et al*, 2005).

In 2007, Henrik Ekstrom demonstrated the electrochemical characterization of 0-18 nm-thick titanium, zirconium and tantalum oxide/Nafion117 films, acting as electrolyte in PEMFCS. TiO_2 films with thickness up to 18nm are shown to conduct protons, while ZrO_2 and Ta_2O_5 block proton transport at a thickness of 1.5nm. TiO_2 in combination with pure platinum increases the oxygen reduction activity because of a larger surface area of platinum. From the results, TiO_2 can be used as electrolyte in fuel cell electrodes and low-temperature proton exchange fuel cells.

2.2.2 Inorganic Membranes

Vichi (2000) has described the effect of pore-wall chemistry on proton conductivity in mesoporous TiO_2. The surface site density changes from 5.5 to 5.7, causing an increase in conductivity from $8.00\text{x}10^{-3}$ to $1.005\text{x}10^{-2}$ $\Omega^{-1}cm^{-1}$ at 25°C and 81% R.H. The state of surface protonation results found that the conductivities of the samples increase with decreasing the equilibration pH. Surface modification by adsorbing phosphate anions from solution with different pH showed that a very small degree of phosphate loading yields an increase in conductivity from 8.27 $\text{x}10^{-3}$ to 9.66 $\text{x}10^{-2}$ $\Omega^{-1}cm^{-1}$ at pH 2.5. Therefore, the lower cost and higher hydrophilicity of these materials make them effective substitutes for Nafion in fuel cells.

Mika (2003) has prepared antimony-phosphate glass and characterized its proton conductivity property. Its conductivity exhibits 1 to 10 S/m at low relative humidity. The increased temperature can cause the increasing of its conductivity at R.H. less than 30%. The glass samples are not hygroscopic and are stable in reduction condition. Therefore, such membranes can be useful in the fuel cell operating at temperatures from 90 to roughly 150°C because ions have more energy and a higher probability to overcome energy barriers as they migrate.

Proton-conducting materials, which were zirconiumphosphates; sulfunic acids based on triethoxy silane compounds, can be used as active materials for infiltrating CREAFILTER membrane. To immobilize these acids, an inorganic sol is prepared which contains the acids. Typical working conditions for Nafion are 80°C and a R.H. of up to 100%, whereas the CREAFILTER membrane works at temperatures of at least 90°C and R.H. of about 30%. The power densities of Nafion are more than $50mW/cm^2$, while the CREAFILTER PEM with other proton conducting membranes reaches power densities of up to 200 mW/cm^2 under the same condition (Augustin *et al*, 2002).

A fast proton-conducting silicophosphate-$HClO_4$ (SiP-$HClO_4$) gel glass and SiP-$HClO_4$-alumina composite were fabricated by Park and coworker in 2004. The inorganic composite has high thermal stability and stable conductivity up to 140°C, which shows a high proton conductivity of over $2.6\text{x}10^{-2}$ Scm^{-1} because of the nanostructure, which contain both trapped solid acids ($HClO_4$) as a proton source and strongly hydrogen-bonded hydroxyl groups combined to P-O-Si oxide bonds as proton conduction paths. Moreover, an increase of proton conductivity can be occurred due to the molecular water contained in a gel structure, also.

Vichi and coworker (2004) have prepared 5% antimony(Sb)-modified titania and 5% tungsten(W)-modified titania by sol-gel method. The antimony-modified titania is also treated with H_2O_2 in order to obtain antimonic acid. At 25 °C, the electrical conductivity of the 5%Sb/TiO_2 varies from 2.02×10^{-5} to 1.12×10^{-2} Scm^{-1} and that of the material treated with H_2O_2 varies from 1.56×10^{-5} to 2.37×10^{-2} Scm^{-1} in the R.H. range from 33% to 81%. For the 5%W/TiO_2, the conductivity varies from 1.02×10^{-5} to 2.66×10^{-3} Scm^{-1}. The conductivity values of the 5%Sb/TiO_2 are superior to those reported previously for antimonic acid films and Nafion, leading to be a potential material for application as electrolyte in fuel cells.

Colomer (2005) has described the characteristic of nanoporous anatase TiO_2 ceramic membranes, which are prepared via sol-gel processes. Proton conductivity of membranes depends on relative humidity and follows an Arrhenius-like dependence on the temperature. The highest value of proton conductivity is 0.015 S/cm at 90 °C and 81% R.H., for HNO_3 acid treated membranes. An increase of the surface site density of the calcined xerogels enhances their electrical conductivity since the distance between water molecules will be lower and the proton hopping along the channels will be easier. Moreover, the treated materials will have a more positive surface charge than the untreated membranes, resulting in the effect of proton mobility. The similar values of proton conductivity, lower cost and higher hydrophilicity of nanoporous anatase membranes make them potential substitutes for Nafion membranes in PEMFCs.

SiO_2-P_2O_5-ZrO_2 inorganic membrane has the proton conductivity 10^{-2} S/cm at 130°C and 100%R.H. The introduction of phosphorous to the membranes can enhance proton conductivity at lower R.H. due to the increase of points for proton conduction (Aparicio *et al.*, 2006).