CHAPTER II
LITERATURE REVIEW

2.1 Fuel Cell Systems

A fuel cell is an electrochemical conversion device. It produces electricity from fuel (on the anode side) and an oxidant (on the cathode side), which react in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate virtually continuously as long as the necessary flows are maintained.

Fuel cells are different from electrochemical cell batteries in that they consume reactant from an external source, which must be replenished a thermodynamically open system. By contrast batteries store electrical energy chemically and hence represent a thermodynamically closed system.

Many combinations of fuel and oxidant are possible. A hydrogen cell uses hydrogen as fuel and oxygen (usually from air) as oxidant. Other fuels include hydrocarbons and alcohols. Other oxidants include chlorine and chlorine dioxide.

Table 2.1 Types of fuel cells

Fuel Cell Name	Electrolyte	Working Temperature (°C)	Electrical Efficiency
Alkaline fuel cell	Aqueous alkaline solution (e.g., potassium hydroxide)	under 80	Cell: 60–70% System: 62%
Direct methanol fuel cell	Polymer membrane (ionomer)	90–120	Cell: 20–30% System: 10–20%
Proton exchange membrane fuel cell	Polymer membrane (ionomer) (e.g., Nafion or Polybenzimidazole fiber)	(Nafion)50–120 (PBI)125–220	Cell: 50–70% System: 30–50%
Phosphoric acid fuel cell	Molten phosphoric acid (H_3PO_4)	150-200	Cell: 55% System: 40% Co-Gen: 90%
Molten carbonate fuel cell	Molten alkaline carbonate (e.g., sodium bicarbonate $NaHCO_3$)	600-650	Cell: 55% System: 47%

2.1.1 Proton Exchange Membrane Fuel Cells (PEMFCs)

Proton exchange membrane fuel cells, also known as polymer electrolyte membrane fuel cells (PEMFC), are a type of fuel cell being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications. Their distinguishing features include lower temperature/pressure ranges (50-100 °C) and a special polymer electrolyte membrane.
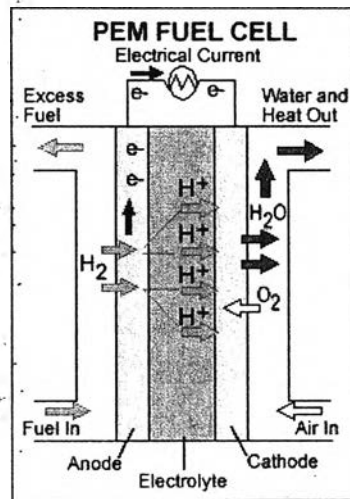

**Figure 2.1** Diagram of a PEM fuel cell.

A proton exchange membrane fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, as opposed to the direct combustion of hydrogen and oxygen gases to produce thermal energy.

A stream of hydrogen is delivered to the anode side of the membrane electrode assembly (MEA). At the anode side it is catalytically split into protons and electrons. This oxidation half-cell reaction is represented by:

$$2H_2 \rightarrow 4H^+ + 4e^- \qquad E^o = 0V$$
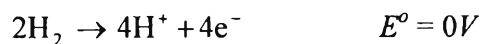
The newly formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side of the MEA, thus creating the current output of the fuel cell.

Meanwhile, a stream of oxygen is delivered to the cathode side of the MEA. At the cathode side oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This reduction half-cell reaction is represented by:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^o = 1.229V$$
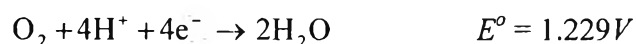
In addition to this pure hydrogen type, there are hydrocarbon fuels for fuel cells, including diesel, methanol and chemical hydrides. The waste products with these types of fuel are carbon dioxide and water.

The materials used in fuel cells differ by type. In a typical membrane electrode assembly (MEA), the electrode–bipolar plates are usually made of metal, nickel or carbon nanotubes, and are coated with a catalyst (like platinum, nano iron powders or palladium) for higher efficiency. Carbon paper separates them from the electrolyte. The electrolyte could be ceramic or a membrane.
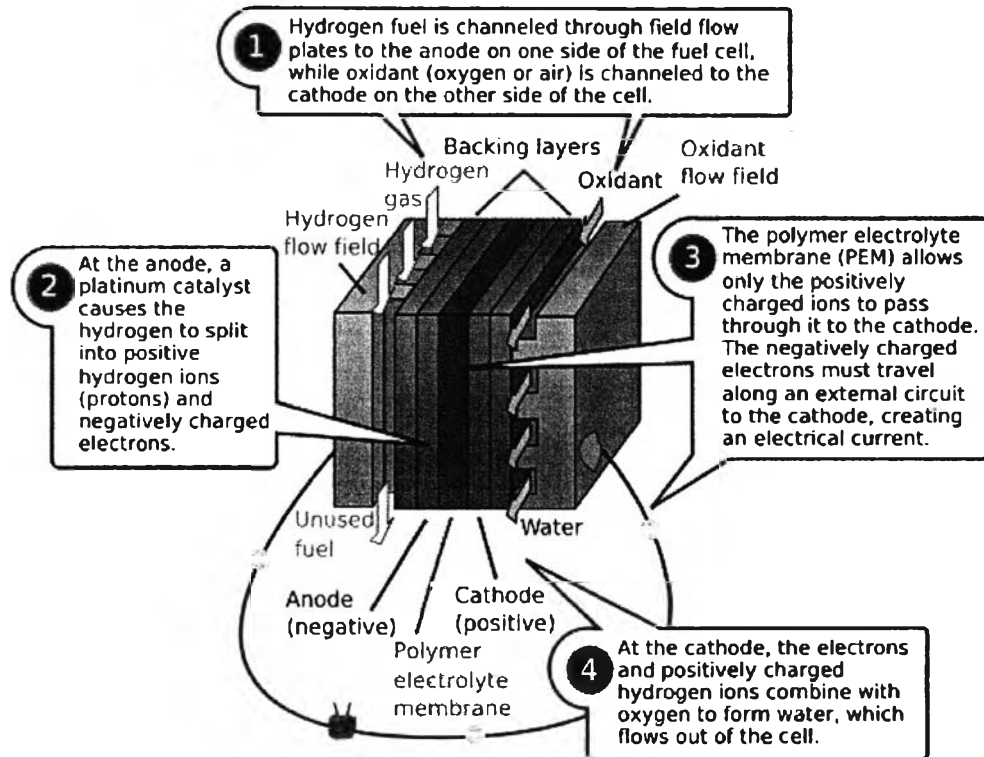
Figure 2.2 The construction of the proton exchange membrane fuel cells.

2.2 Poly(vinylidene fluoride) (PVDF)

The discovery of piezoelectric in PVDF by Kawai in 1969 has attracted much attention to this polymer. They found that the poly(vinylidene fluoride) exhibited large piezoelectric effect after poling. Due to PVDF has a $-(CH_2-CF_2)_n-$ repeat unit occupies a half-way point in the homologous series of fluorinated vinyl monomers stretching from polyethylene (PE) to poly(tetrafluoroethylene) (PTFE). The PVDF is typically 50–70% crystalline with at least four different crystals including form II (α-phase), form I (β-phase), form III (γ-phase) and from IV (δ-phase), which could transform from one to the other under certain conditions.

The common polymorph of PVDF was α (TG^+TG^-) conformation, which could be produced during crystallization from the melt. The most important polymorph with outstanding piezoelectric and pyroelectric properties is β form that has a TTT conformation (all-trans) as show in Figure 7. The γ form has a GTTT conformation while δ corresponds to the polar form of α.
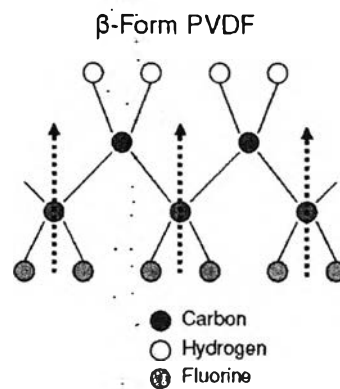

Figure 2.3 The β form of PVDF.

When PVDF is in β form structure, the dipole is strongest. This structure aligns all of dipoles throughout the polymer chain creating polarization that extends to the boundaries of the PVDF. These dipoles are allowing PVDF to act as a sensor or transducer. The β crystal in PVDF could be obtained from a modification by various processes such as mechanical deformation, poling under large electric fields, crystallization from the melt under high pressure very high cooling rates [Nalwa, Hari Singh, (1995)].

Different methods for generation of the β conformation from the melt or from other PVDF conformations are shown in Figure 2.4.
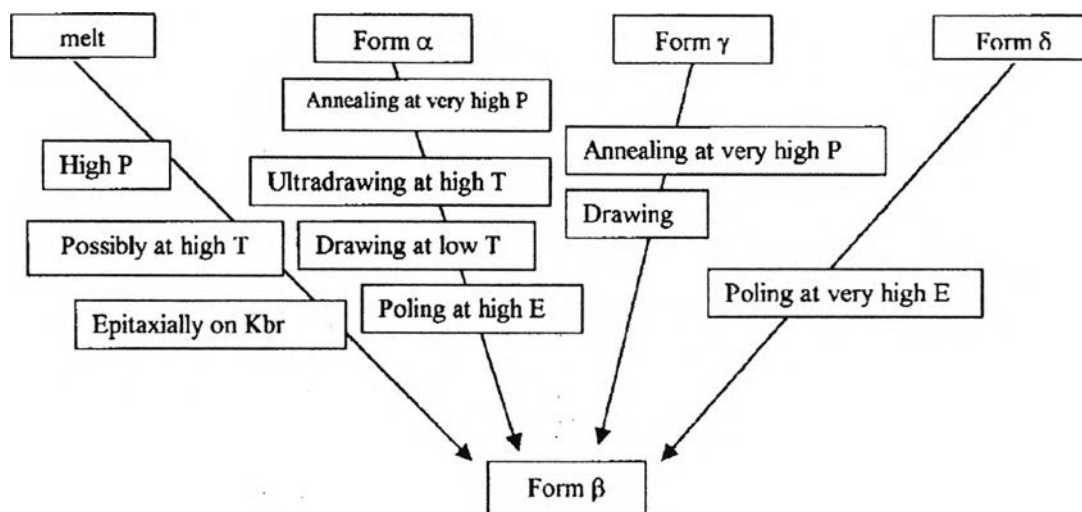
Figure 2.4 Transitions from different conformations of PVDF to β-phase.

2.3 Organic Membranes

In 1997, the electrochemical characterization of proton-conducting membranes prepared by irradiation-induced grafting and subsequent sulfonation of PVDF films had been performed. In particular, measurements of the ionic conductivity, oxygen solubility and diffusion in the membranes were presented, as well as kinetic data for the oxygen reduction reaction in a membrane-platinum system and a simulation of the performance of these PVDF-g-PSSA membranes in a solid polymer electrolyte fuel cell using a microcathode technique. At sufficient degrees of grafting (>40%) the conductivity reached 0.1 Scm^{-1}, well above that of Nafion 117 (DuPont). The PVDF-g-PSSA membranes showed lower solubility and higher diffusion coefficients of oxygen and a higher water uptake than Nafion 117. The microcathode measurements indicated that those PVDF-g-PSSA membranes which had conductivity higher than that of Nafion 117 may also give improved performance in fuel cell conditions provided that they had the necessary mechanical and chemical stability [Lehtinen et al., 1998].

In Soresi's work [Soresi et al., 2004], it was shown that PVDF can be an interesting alternative to Nafion for the fabrication of proton-conducting membranes for polymer fuel cells. To this aim, PVDF (which is hydrophobic in nature) can be structurally modified by radiation grafting with styrene comonomers, which allow to link sulfonic groups. Membranes obtained from the P(VdF-5 mol% HFP) copolymer and from commercial porous and dense PVDF homopolymer films were compared together. High grafting degrees and water uptake had been reached depending on the nature of the polymer matrix. Room temperature conductivity exceeding 60 mS/cm at 90% RH had been observed in the case of the sulfonated membrane obtained from the PVDF-based copolymer. In this case, the conduction mechanism and the uptake process had been investigated at different humidity conditions and compared with the data reported for Nafion 117.

In Mokrini's work [Mokrini et al., 2006], Proton-conductive polymer membranes were used as an electrolyte in the so-called proton exchange membrane fuel cells. Current commercially available membranes were perfluorosulfonic acid polymers, a class of high-cost ionomers. The potential of polymer blends, namely those of styrene–(ethylene-butylene)–styrene block copolymer (SEBS) and polyvinylidene fluoride (PVDF), in the proton exchange membrane application was examined. SEBS/PVDF blends were prepared by twin-screw extrusion and the membranes were formed by calendering. SEBS is a phase-segregated material where the polystyrene blocks can be selectively functionalized offering high ionic conductivity, while PVDF insures good dimensional stability and chemical resistance to the films. Proton conductivity of the films was obtained by solid-state grafting of sulfonic acid moieties. The obtained membranes were characterized in terms of conductivity, ionic exchange capacity and water uptake. Modification of interfacial properties between SEBS and PVDF was found to be a key to optimize the blends performance. Addition of a methyl methacrylate–butyl acrylate–methyl methacrylate block copolymer (MMA–BA–MMA) was found to compatibilize the blend by reducing the segregation scale and improving the blend homogeneity. Mechanical resistance of the membranes was also improved through the

addition of this compatibilizer. As little as 2 wt.% compatibilizer was sufficient for complete interfacial coverage and lead to improved mechanical properties. Compatibilized blend membranes also showed higher conductivities, 1.9×10^{-2} to 5.5×10^{-3} S cm^{-1}, and improved water management.

2.4 Organic/Inorganic Hybrid Membranes

In Chen-Yang's work [Chen-Yang et al., 2002], a series of novel solid-type α-Al$_2$O$_3$-containing polyacrylonitrile (PAN)-based composite polymer electrolytes (CPE) with high conductivity and high mechanical property at room temperature was prepared. The effect of the addition of α-Al$_2$O$_3$ on the properties of the PAN-based composite polymer electrolyte was analyzed. The best conductivities obtained at room temperature is 5.7×10^{-4} S cm^{-1} from the CPE with 7.5 wt% α-Al$_2$O$_3$ and 0.6 LiClO$_4$ per PAN repeat unit. The stress–strain test result indicated that the membranes prepared possessed high yield stress (73 kg cm^{-2}) suitable for serving as separators in the solid-state lithium and lithium ion batteries and high yield elongation (225%) pliable to form good interface with electrodes. Also discussed were the effects of the addition of the ceramics on the interactions in the system and the possible conduction mechanism.

In 2003 and 2004, Navarra's research [Navarra et al., 2003; 2004; 2005] reported on the synthesis and the properties of a new microporous, composite proton-conducting gel membrane, formed by swelling a poly(vinylidene)fluoride-poly(acrylonitrile), PVdF/PAN blend-based matrix containing a dispersed Al$_2$O$_3$ ceramic filler with aqueous acid solutions. It was shown that this membrane had a high and stable conductivity, a proton transport not critically influenced by the relative humidity level, and a projected low cost. Tests in a methanol-air laboratory cell also demonstrated that the membrane was basically suitable for application in direct methanol fuel cells. Furthermore, new poly-vinylidene fluoride/poly-acrylonitrile (PVdF/PAN) based proton conducting membranes by means of vibrational spectroscopy was investigated in 2005. It was found that a complete phase inversion occured during the preparation procedure,

when the gelling solvents were replaced by an acidic solution, providing the proton conducting property. The uptake of acid was promoted both by the presence of PAN and the ceramic filler, Al_2O_3. No particular interaction between the polymer matrix and the acidic solution could be detected, supporting the picture of an inert matrix entrapping a liquid component. However, the dissociation degree of the acid was decreased due to the spatial confinement in the membrane. By comparing the dissociation degree and the actual amount of acid in the membrane to the conductivity, it was concluded that the limiting factor for the conductivity was the long-range mobility of the protons, which was governed by the morphology of the membrane.

Nafion/zirconium sulphophenyl phosphate (ZrSPP) composite membranes were prepared to maintain proton conductivity at elevated temperatures by Young-Taek Kim [Young-Taek Kim et al., 2004]. ZrSPP was precipitated by the reaction of Zr^{4+} ion and m-sulphophenyl phosphonic (SPP) acid with a stoichiometric ratio P/Zr = 2. The synthesis of ZrSPP was confirmed by phosphonate (P-O) stretching band, assigned at $900-1300$ cm^{-1} in FTIR spectra. The sharp diffraction pattern at $2\theta = 5°$ indicated crystalline α-layered structure of ZrSPP. The proton conductivity of Nafion/ZrSPP (12.5 wt %) composite membrane reached ca. 0.07 S/cm at 140 °C without extra humidification.

In Jalani's work [Jalani et al., 2005], Nafion®-MO_2 (M = Zr, Si, Ti) nanocomposite membranes were synthesized with the goal of increasing the proton conductivity and water retention at higher temperatures and lower relative humidities (120 °C, 40% RHs) as well as to improve the thermo-mechanical properties. The sol–gel approach was utilized to incorporate inorganic oxide nanoparticles within the pores of Nafion® membrane. The membranes synthesized by this approach were completely transparent and homogeneous as compared to membranes prepared by alternate casting methods which are cloudy due to the larger particle size. At 90 °C and 120 °C, all Nafion®-MO_2 sol–gel composites exhibited higher water sorption than Nafion® membrane. However, at 90 °C and 120 °C, the conductivity was enhanced in only Nafion®-ZrO_2 sol–gel composite with a 10% enhancement at 40% RH over Nafion®.

This can be attributed to the increase in acidity of zirconia based sol–gel membranes shown by a decrease in equivalent weight in comparison to other nanocomposites based on Ti and Si. In addition, the TGA and DMA analyses showed improvement in degradation and glass transition temperature for nanocomposite membranes over Nafion®.

2.5 Inorganic Membranes

In 2000, Vichi and Tejedor-Tejedor [Vichi et al., 2000] described how the proton conductivity of a mesoporous TiO_2 membrane was strongly affected by the chemistry of the pore walls. We had studied the effect of site density, state of surface protonation, and surface modification in samples with a fixed pore structure. Pore structure was kept fixed by firing all samples at the same temperature. Changing the surface site density (number of water molecules per square nanometer) from 5.5 to 5.7 leads to an increase in proton conductivity from 8.00×10^{-3} to 1.00×10^{-2} S/cm at 25 °C and 81% relative humidity (RH). The effect of the state of protonation was studied by pretreating wafers at pH 1.5 and equilibrating them with solutions at pH 2.5 and 4.0. This variable (protonation state of the material) was found to have an even stronger effect on conductivity. Surface modification was achieved by adsorbing phosphate anions from solutions with different pH. It was observed that even a very small degree of phosphate loading (0.71 ions/nm^2) leads to an increase in conductivity from 8.27×10^{-3} to 9.66×10^{-3} S/cm at pH 2.5. The conductivity of our materials, especially those treated at pH 1.5, is very close to that of Nafion, a polymeric material used as a proton conducting membrane in fuel cell systems. The lower cost and higher hydrophilicity of our materials make them potential substitutes for costlier hydrophobic polymeric membranes in fuel cells.

In 2005, Colomer [M.T. Colomer, 2005] prepared nanoporous anatase ceramic membranes via particulate sol–gel processes. The calcined xerogels were mesoporous, with a BET surface area of 121 m^2/g, an average pore diameter of 5.8 nm and a pore

volume of 0.236 cm^3/g. Proton conductivity of the membranes was measured as a function of temperature and relative humidity, R.H. When anatase membranes are treated at pH 1.5, the proton conductivity increased in the whole range of temperature and R.H. It indicates that the surface site density (number of water molecules per square nanometer) of these materials has a strong effect on conductivity. The proton conductivity of the studied anatase membranes followed an Arrhenius-like dependence on the temperature (from room temperature to 90 °C), in both treated and untreated membranes. A sigmoidal dependence of the conductivity on the R.H. was observed with the greatest increase noted between 58 and 81% R.H. in both treated and untreated anatase membranes. The highest value of proton conductivity was found to be 0.015 S/cm at 90 °C and 81% R.H., for treated anatase ceramic membranes. An increase of the conductivity could be achieved by means of longer times of treatment. According to the activation energy values, proton migration in this kind of materials could be dominated by the Grotthuss mechanism in the whole range of R.H. The similar values of proton conductivity, lower cost and higher hydrophilicity of these membranes make them potential substitutes for perfluorosulfonic polymeric membranes in proton exchange membrane fuel cells (PEMFCs).

In Tanita's work [Kuanchaitrakul et al., 2008], niobium-modified titania and antimony/niobium-modified titania ceramic were prepared via the sol-gel technique. The various contents of antimony, 0 to 3 wt%, and 3% niobium are incorporated into titania to improve the porous surface condition of the ceramic particles. Inorganic membranes were fabricated by using the spin-coating technique using epoxy resin as a binder. The physical, chemical, and electrical properties of these membranes were investigated. The XRD and Raman results showed that pure TiO_2 and doped TiO_2 nanoparticles obtained possess an anatase structure with mesoporosity. The specific surface area of the doped TiO_2 was higher than that of pure TiO_2 and it is worth pointing out that the doping of antimony affected the surface areas more than the doping of niobium in TiO_2. Moreover, these membranes were also tested to evaluate their potential use as an electrolyte in PEMFCs by using impedance spectroscopy, TGA, universal testing machine and water

uptake. The results showed that the proton conductivity value of TiO_2/epoxy membrane was enhanced by doping niobium and antimony into TiO_2 matrix and all of the nano-composite films present good thermal and mechanical properties.