CHAPTER II THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel cell

Fuel cell is the device that can convert the chemical energy directly into electricity with the releasing of water and heat as the byproducts. Fuels such as hydrogen, methanol, and etc. have been usually used in fuel cells. The system consists of two electrodes; anode and cathode. The oxidation occurs at the anode side while the reduction occurs at the cathode side. The fuel cell is the efficiency energy with zero pollution (Peighambardoust *et al.*, 2010).



Figure 2.1 The operation of the proton exchange membrane fuel cell (PEMFC) (From http://www.fuelcells.org/fuel-cells-and-hydrogen).

2.1.1 Types of fuel cells

There are many types of fuel cells, fuel cells are generally classified based on the electrolyte used such as PEMFC (Proton exchange membrane fuel cell), DMFC (Direct methanol fuel cell), AFC (Alkaline fuel cell), PAFC (Phosphoric acid fuel cell), MCFC (Molten carbonate fuel cell), SOFC (Solid oxide fuel cell), as shown in table 2.1 (Bozbag *et al.*, 2012).

 Table 2.1 Currently present fuel cells and some typical properties (Bozbag et al.,

 2012)

Fuel cell type	Electrolyte	Charge carrier	Operating temperature range (°C)	Fuel	Potential applications
PEMFC	Solid polymer (Nafion [®])	H⁺	30-130	Pure H ₂	Electicity utility, portable power, transportation vehicle
DMFC	Solid polymer (Nafion [®])	H^+	30-130	Methanol	Portable devices such as cell- phone, laptop
AFC	КОН	OH.	60-120	Pure H ₂	Military, space and residentials pants
PAFC	Phosphoric acid	H^{+}	100-220	Pure H ₂	Electicity utility and transportation
MCFC	Lithium and potassium carbonate	CO ²⁻ 3	650-850	H ₂ , CO, CH ₄ , other hydrocarbon	Electicity utility
SOFC	Solid oxide (yttria, zirconia)	O ²⁻	700-1000	H ₂ , CO, CH ₄ , other hydrocarbon	Electicity utility

A direct methanol fuel cell (DMFC) which is shown in figure 2.2, is a subcategory of the proton exchange membrane fuel cell (PEMFC) family that uses methanol as the fuel without the need for a reformer. The methanol is introduced to the DMFC to initiate the chemical reaction resulting in electricity and byproducts are little amounts of water and carbon dioxide. Commercial DFMC has a longer operating time when compared to lithium-ion battery of similar size and can be instantaneously recharged by refueling in the fuel cartridge. Using methanol as a primary fuel has higher advantages over pure hydrogen. One of the most important is that fact that methanol can be stored as a liquid in a wide temperature range (-97 °C to 64.7 °C). Methanol can be kept in cheap plastic containers, easy to handling, and the most important is an excellent carrier fuel that hydrogen can be extracted from to power fuel cells.



Figure 2.2 The operation of direct methanol fuel cell (DMFC) (From http://www.fuelcelltoday.com/about-fuel-cells/technologies/dmfc).

The methanol solution in which usually around 1 molar is used in DMFC to carry on the reactant into the cell, common operating temperatures are in the range 30 to 130 °C. DMFC are more efficient at high temperature and pressure. Hence, atmospheric pressure configurations are currently preferred. The methanol crossover phenomenon can occur by methanol diffusing through the membrane

without chemical reacting. So, methanol is fed as a weak solution, this decreases efficiency significantly resulting in reduction of the cell efficiency. Methanol crossover is a major factor in loss efficiency, half of the methanol is lost due to crossover (Ahmad *et al.*, 2010).

2.2 Types of proton exchange membrane

The most utilized proton exchange membrane is currently Nafion, which is a perfluorinated polymeric membrane developed by DuPont. Nafion is a perfluorosulfonic membrane consisting of a polytetrafluoroethylene backbone and regularly spaced long perfluorovinyl ether pendant side chains terminated by a sulfonic group as shown in figure 2.3 (Ahmad *et al.*, 2010). Nafion has high proton conductivity, good thermal and chemical stabilities. However, its high cost and high methanol crossover are still limited for its application.



Figure 2.3 Nafion (perfluorinated polymeric membrane) (Peighambardoust *et al.*, 2010).

To achieve high efficiency in fuel cell applications, the polymer electrolyte as membrane (proton exchange membrane) must possess the following desirable properties: high proton conductivity to support high currents with minimal resistive losses, zero electronic conductivity, adequate mechanical strength and stability, chemical and electrochemical stability under operating conditions (Peighambardoust *et al.*, 2010). The methanol permeability of the membrane should be low for keeping efficiency in the DMFC application. One of the potential types of the proton exchange membrane is the sulfonated polymer membrane.



Figure 2.4 The chemical structures of sulfonated (a) poly(4-phenoxybenzoyl-1,4-phenylene) (S-PPBP), (b) poly(p-xylylene) (S-PPX), (c) poly(phenylene sulfide) (S-PPS), (d) poly(phenylene oxide) (S-PPO), (e) poly(ether ether ketone) (S-PEEK), (f) poly(ether ether sulfone) (S-PEES), (g) arylsulfonated poly(benzimidazole) (S-PBI) (h) sulfonated polyphenylquinoxaline (S-PPQ), and (i) phenoxy polyperyleneimide (PSPPI) (Rusanov *et al.*, 2005).

2.2.1 Polyether-Ketones

Kobayashi *et al.*, (1998) prepared poly(oxy-1,4-phenylene-oxy-1,4phenylene-carbonyl-1,4-phenylene), (PEEK) and poly(4-phenoxybenzoyl-1,4-phenylene), (PPBP) that were sulfonated with sulfuric acid by incorporating sulfonic acid moieties. The sulfonated polymers containing 65 mol% sulfonic acid showed a high proton conductivity of 10^{-2} – 10^{-4} S/cm at room temperature. S-PPBP could absorb water to much higher levels than S-PEEK, and the proton conductivities of S-PPBP were much higher than those of S-PEEK for the same sulfonation levels.



Figure 2.5 (a) Proton conductivities of S-PEEK and S-PPBP with 65 mol% sulfonation level under 100% relative humidity as a function of temperature. (b) Water absorption of S-PEEK and S-PPBP (Kobayashi *et al.*, 1998).

2.2.2 Polysulfones

Fu *et al.*, (2006) synthesized sulfonated polysulfones (SPSf) with different degrees of sulfonation for direct methanol fuel cell (DMFC). The ion exchange capacity (IEC), proton conductivity, water uptake, and single DMFC polarization were measured. SPSf membranes with 50–70% sulfonation exhibited performances comparable to that of Nafion 115 due to lower methanol crossover. However, the performance at high current densities with high concentrations of

methanol (2 M) are lower than that of Nafion 115 due to the lower proton conductivity.



Figure 2.6 Comparison of the polarization curves of the SPSf membrane with that of Nafion 115 in DMFC (Fu *et al.*, 2006).

2.2.3 Polybenzimidazoles

Kang *et al.* (2009) synthesized sulfonated polybenzimidazoles with various degrees of sulfonation. Sulfonated polybenzimidazoles exhibited distinct properties: transparent, tough, flexible and resistant to high temperature. Water uptake and proton conductivity also increased with increasing degree of sulfonation.



Figure 2.7 Proton conductivity of sulfonated polybenzimidazoles as a function of temperature (Kang *et al.*, 2009).

2.2.4 Polyimide

Woo *et al.* (2003) studied the relationship between the sulfonation level of 2,2'-diamino 4,4'-biphenylsulfonic acid, 3,3',4,4' benzophenonetetracarboxylic dianhydride and a non sulfonated diamine. When increasing the sulfonation level up to 30-35 mol%, the proton conductivity, the methanol permeability, and the amount of water uptake were increased. The synthesized sulfonated polyimide membrane exhibited thermal stability up to 300 °C and absorbed five times less water than Nafion.



Figure 2.8 (a) Water uptake as a function of ion exchange capacity of sulfonated polyimide; and (b) Proton conductivity and methanol permeability as a function of sulfonation level (Woo *et al.*, 2003).

2.2.5 Poly(phenylene oxide)

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) can meet most of the requirements for application in PEMFC because it is a hydrophobic polymer with high glass transition temperature, high mechanical strength, and excellent hydrolytic stability. Although the structure of PPO is simple as compared to other aromatic polymers, it allows many modifications in both aryl and benzyl positions:

electrophilic substitution on the benzene ring, radical substitution of the hydrogen from the methyl groups, and metalation of PPO with organometallic compounds. These modifications can provide PPO with desired charge density for proton conduction (Xu *et al.*, 2008).

Sulfonation is a conventional electrophilic substitution reaction, but it can be used to prepare the sulfonated PPO (SPPO) with variable charge density, which is a good matrix. As an aromatic polymer, PPO can be sulfonated using concentrated sulfuric acid, chlorosulfonic acid, pure or complex sulfur trioxide, or acetylsulfate. The sulfonation can be easily controlled by adjusting time, temperature, concentration, and solvents. The SPPO has been considered as a good proton conductive material with high thermal stability for practical applications in fuel cells (Xu *et al.*, 2008).

Yang *et al.*, (2006) studied about sulfanated poly(phenylene oxide) membrane as proton exchange membrane. PPO was sulfonated to different ion exchange capacities (IECs) using chlorosulfonic acid as the sulfonating agent. The thermogravimetric analysis (TGA) was used to investigate thermal stability. With DS increasing, the hydrophilicity, water uptake, and IEC values of SPPO membranes increased when compared with PPO. The proton conductivity of these SPPO membranes was measured and found to be 1.16×10^{-2} S/cm at ambient temperature.



Figure 2.9 Thermogravimetric and the first derivative curves for pure PPO and SPPO (Yang *et al.*, 2006).



Figure 2.10 Conductivity of SPPO membranes as a function of IEC values (Yang *et al.*, 2006).

Li *et al.*, (2007) prepared sulfonated poly(phenylene oxide) (SPPO). The obtained membrane of SPPO was heat-treated and stretched with different forces by thermal mechanical analyzer under its glass transition temperature. In addition, the effects of stretching and heating on conductivity of SPPO were investigated. FTIR was used to investigate chemical structure. It was shown that the highest conductivities achieved were about 10 times that of the original membranes and reached 0.0983 S/cm.



Figure 2.11 FTIR spectra of PPO and SPPO (Li et al., 2007).



Figure 2.12 Conductivities of SPPO with three kinds of sulfonation degree after being stretched (Li *et al.*, 2007).

Petreanu *et al.*, (2012) prepared sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with different sulfonation degrees. Thermal behaviors of sulfonated PPO were tested by differential scanning calorimetry and thermogravimetry. The sulfonation degrees were correlated with the glass transition temperature (Tg) and the percent of weight loss. One notices a good fitting between sulfonation degree and the percent of weight loss related to sulfonic moieties.



Figure 2.13 Conductivities of SPPO with three kinds of sulfonation degree after being stretched (Petreanu *et al.*, 2012).

2.3 Composite proton exchange membranes

Hybrid organic/inorganic composite membranes are being usually developed for elevated temperature fuel cell applications. Because of many of the inorganic materials are capable of operating at a much higher temperature than a pure polymer membrane. The addition of inorganic compounds into the polymer membrane matrix enhances proton conductivity, water retention, and mechanical strength while reduces fuel permeability at high temperatures (Unveren *et al.*, 2010). Zeolite is used as an inorganic additive in polymer electrolyte membranes. Zeolite has very high water retention ability, which can only be eliminated at around 200 °C, and zeolite has molecular sieving properties, which is suitable for selective separations based on molecular size and shape (Yildirim *et al.*, 2009).

2.3.1 Polyether-Ketones

Ahmad *et al.*, (2006) prepared composite membranes of a sulfonated polyether ether ketone (SPEEK) polymer and a novel solid proton conductor, namely heteropolyacid-loaded Y-zeolite. The novel solid proton conductor has high proton conductivity, high thermal because of the presence of Y-zeolite. The conductivity of the composite membranes at room temperature as well as at higher temperatures was found to increase with the incorporation of solid conducting material particles into the SPEEK. The conductivity increased by 3–4 times at room temperature.

Intaraprasit *et al.*, (2011) fabricated sulfonated poly(ether ether ketone) (SPEEK)/Analcime composite membranes. Composite membranes led to a decrease in the ion exchange capacity (IEC) and water uptake of the membranes. It was found that the composite membranes conducted the proton higher than that of Nafion 115. However, having Analcime above 10 wt%, the proton conductivity of the composite membrane decreased to be lower than that of the SPEEK as the result of agglomeration of solid particles. The maximum value of conductivity 0.4016 S/cm was achieved at 90 °C from SPEEK/10 wt% Analcime.



Figure 2.14 Water uptake and ion exchange membrane of SPEEK/Analcime composite membranes as a function of Analcime loading (Petreanu *et al.*, 2012).

Zaidi *et al.*, (2007) prepared composite membranes from inorganic proton conducting material (tungstophosphoric acid (TPA)/Y-zeolite) with sulfonated polyether ether ketone (SPEEK) polymer. The composite membranes were prepared by embedding different proportions (10-40 wt%) of conducting material (TPA/Yzeolite) into SPEEK polymer matrix. The membrane with low loading of inorganic conducting material showed better reduction in methanol crossover. The membranes were thermally stable up to around 160 °C.

2.3.2 Polysulfones

Lufrano *et al.*, (2006) prepared composite polysulfone membranes modified with silica filler. The synthesis of sulfonate polysulfone samples was carried out by using trimethyl silyl chlorosulfonate as sulfonating agent. Composite membranes with 5 wt% of silica filler were prepared and characterized. A composite membrane tested in direct methanol/oxygen fuel cell provided a maximum power density of about 180 mW/cm² at 120 °C.

Wen *et al.*, (2009) prepared a series of sulfonated poly(ether sulfone) (SPES)/boron phosphate (BPO₄) composite membranes, with a BPO₄ content up to 40 wt%. Water uptake and oxidative stability were significantly increased by increasing the content of BPO₄. However, even when the content of BPO₄ was as high as 30%, the composite membrane still possessed strength similar to the Nafion 112 membrane. Proton conductivities increased from 0.0065 to 0.022 S/cm at room

temperature as BPO_4 increased from 0 to 40%. The conductivities also increased with the temperature.



Figure 2.15 Proton conductivities of the membranes at different temperatures (Wen *et al.*, 2009).

2.3.3 Chitosan

Wu *et al.*, (2007) prepared hybrid membranes composed of chitosan (CS) as organic matrix and surface-modified Y zeolite as inorganic filler. Y zeolite was modified using silane coupling agents, 3-aminopropyl-triethoxysilane (APTES) and 3-mercaptopropyl-trimethoxysilane (MPTMS), to improve the organic–inorganic interfacial morphology. The transitional phase generated between chitosan matrix and zeolite filler reduced or even eliminated the nonselective voids. The hybrid membranes exhibited a significant reduction in methanol permeability compared with pure chitosan and Nafion 117 membranes. By introducing $-SO_3H$ groups on zeolite surface, the conductivity of hybrid membranes was increased up to 2.58×10^{-2} S/cm. In terms of the selectivity, the hybrid membrane was comparable with Nafion 117 at low methanol concentration (2 mol/L) and much better (three times) at high methanol concentration (12 mol/L).



Figure 2.16 Methanol permeability of membranes vs. methanol concentration (Wu *et al.*, 2009).

Wang *et al.*, (2008) synthesized zeolite beta particles with different sizes and narrow size distribution. Then, zeolite beta was incorporated into chitosan (CS) matrix to prepare CS/zeolite beta hybrid membranes. The chitosan membrane filled by zeolite beta particles about 800 nm in size exhibited the lowest methanol permeability, which can be described to their optimum free volume and methanol diffusion characteristics. To further improve the performances of CS/zeolite beta hybrid membranes, zeolite beta particles about 800 nm in size were sulfonated. The introduction of sulfonic groups could reduce the methanol permeability further as a result of the enhanced interfacial interaction between zeolite beta and chitosan matrix. Furthermore, the selectivity index, CS/zeolite beta hybrid membranes were comparable to Nafion 117 membrane at low methanol concentration (2 M) and much better at high methanol concentration (12 M).

Wang *et al.*, (2010) synthesized zeolite beta particles about 800 nm in diameter, and functionalized by γ -glycidoxypropyltrimethoxysilane (GPTMS). Afterward, chitosan (CS) membranes filled by GPTMS-modified zeolite beta particles were prepared. These CS/zeolite beta hybrid membranes showed the lower methanol permeability, which could be assigned to the better interfacial morphology

and compatibility between the GPTMS-modified zeolite beta particles and chitosan matrix. The CS membrane filled by 10 wt% GPTMS-modified zeolite beta particles exhibited the lowest methanol permeability, which was 4.4×10^{-7} and 2.2×10^{-7} cm²/s at 2 and 12 M methanol concentration, respectively. The proton conductivity of this hybrid membrane was 1.31×10^{-2} S/cm, which was slightly lower than that of the pure CS membrane.



Figure 2.17 Selectivity of the Nafion117, pure CS, CS/Beta and CS/Beta-GPTMS hybrid membranes at 2M (a) and 12M (b) methanol concentration (Wang *et al.*, 2010).

2.3.4 Polyvinyl alcohol

Uctug *et al.*, (2011) synthesized Polyvinylalcohol-mordenite (PVA-MOR) mixed matrix membranes. Zeolite distribution within the polymer matrix was found to be homogeneous. The composition of 60–40 wt% PVA-MOR membranes were found to give the optimum transport properties. Proton conductivity of these membranes was found to be slightly lower than that of Nafion117 whereas their methanol permeability was at least two orders of magnitude lower than Nafion 117.



Figure 2.18 SEM images of PVA–MOR membrane samples (surface), (a) 50/50 wt% PVA–MOR membrane – magnification: 1200 times, (b) 50/50 wt% PVA–MOR membrane – magnification: 2000 times, (c) 50/50 wt% PVA–MOR membrane – magnification: 5000 times, (d) 50/50 wt% PVA–MOR membrane – magnification: 10,000 times (Uctug *et al.*, 2011).

2.3.5 Nafion

Zhang *et al.*, (2011) prepared Nafion–Faujasite composite membranes by solution casting. Faujasite was found to undergo severe dealumination during the membrane activation, but its structure remained intact. The zeolite interacted with Nafion probably through hydrogen bonding between Si–OH and SO₃H groups, which combined with the increase of the water uptake and the water mobility, and the addition of a less conductive phase (the zeolite) led to optimum proton conductivity between 0.98 and 2 wt% of zeolite.

Yildirim *et al.*, (2009) prepared composite membranes (DEZ) based on DE2020 Nafion incorporated via H-ZSM-5 zeolites with different Si/Al ratios. All composite membranes had lower methanol permeability and higher proton conductivity than pure DE2020 membrane. The composite membranes with Si/Al ratio 25 and 5 wt% of zeolites (DEZ25-5) had the lowest methanol permeability and the membrane with Si/Al ratio 50 and 1 wt% of zeolites (DEZ50-1) had the highest proton conductivity as tested in the DMFC.

Yang *et al.*, (2011) prepared a Zeolite/Nafion composite membrane by using microporous titanosilicate, H-ETS-10. Various H-ETS-10s with different percentage of ion exchange rate were obtained through ion-exchange process using 0.02, 0.04 and 0.05 N HCl solutions, respectively. In cases of H-ETS-10s with 80 % and 90 % of ion exchange rate, the proton conductivities became higher than of Nafion 115 and recasting membrane while the methanol permeability was lower than of Nafion 115, indicating the blocking effect against methanol permeation through membrane exerted by zeolite particles. In cases of incorporating H-ETS-10s with 80% and 90% of percentage of ion exchange rates, the MEA fabricated with composite membrane with 5.0 wt% of zeolite content showed the best cell performance.



Figure 2.19 Proton conductivities of Nafion 115, recasting Nafion membrane and various H-ETS-10/Nafion composite membranes with zeolite content measured at room temperature (Yang *et al.*, 2011).

Baglio *et al.*, (2005) prepared composite Nafion membranes containing three natural zeolites (Mordenite, Chabazite and Clinoptilolite) by using a

recast procedure for application in high temperature Direct Methanol Fuel Cells (DMFCs). The Nafion-zeolite membranes showed good properties for high temperature DMFC application, due to their improved water retention characteristics. A maximum power density of 390 mW/cm² was achieved at 140 °C with the mordenite-based composite membranes.

2.3.6 Poly(phenylene oxide)

Sadrabadi *et al.*, (2008) prepared sulfonated poly(2,6-dimethyl-1,4phenylene oxide) (sulfonated PPO) with various degrees of sulfonation. The solutions were mixed with organically modified montmorillonite (MMT) to prepare membranes. FTIR was used to investigate chemical structure. A sulfonated PPO/MMT membrane with 27% sulfonation and 2.0 wt% MMT loading showed a membrane selectivity of approximately 63,500 compared to 40,500 for Nafion 117.



Figure 2.20 FTIR spectra of PPO and sulfonated PPO (Sadrabadi et al., 2008).



Figure 2.21 (a) Water uptake and proton conductivity of membranes as a function of sulfonation degree (b) Effect of particles loading weights on the proton conductivity and methanol permeability of sulfonated PPO membranes (27% degree of sulfonation) (Sadrabadi *et al.*, 2008).

Sadrabadi *et al.*, (2009) prepared a series of sulfonated poly(2,6dimethyl-1,4-phenylene oxide) (S-PPO) and sulfonated poly(ether ether ketone) (S-PEEK) at various sulfonation degrees and characterized for their degree of sulfonation, water uptake, ion exchange capacity, proton conductivity and methanol permeability. According to the membrane selectivity and hydrolytic stability measurements, 75 wt% of S-PPO and 25 wt% of S-PEEK was selected as the optimum composition. Afterwards, different amounts of an organically modified montmorillonite (MMT) were incorporated into the predetermined optimum composition matrices. Transport property measurements of nanohybrid membranes were shown that the maximum selectivity parameter of 75wt% S-PPO/25wt% S-PEEK composition appeared in the presence of 1.5 wt% of MMT, which is 1.53 times higher than the corresponding value for Nafion 117.



Figure 2.22 (a) Proton conductivity of the pristine and nanocomposite membranes as a function of S-PPO composition and MMT loading weight (b) Methanol permeability of the fabricated membranes (comprising 0, 1.5 and 3.0 wt% MMT) at various S-PPO compositions (Sadrabadi *et al.*, 2009).

Aliabadi *et al.*, (2011) prepared a series of composite membranes based on sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) comprising phosphotungstic acid (PWA). PPO matrices were first sulfonated to different extents to determine the maximum possible sulfonation degree. Afterwards, 20 wt% of PWA was added into sulfonated polymeric matrices. The results of conductivity measurements revealed that in the presence of PWA molecules the proton conductivity of SPPO membranes with sulfonation degree of 40% was improved from 1.82×10^{-2} S/cm to 2.57×10^{-2} S/cm at 25 °C.



■ SPPO-15 PWA - △ SPPO-18:PWA - ◆ SPPO-27:PWA - * \$PPO-35:PWA - ○ SPPO-40:PWA

Figure 2.23 Proton conductivity of the SPPO-based membranes with various sulfonation degrees containing 20 wt% of PWA, at different temperatures (Aliabadi *et al.*, 2011).

Haghighi *et al.*, (2011) studied the sulfonated poly (2,6-dimethyl-1,4phenylene oxide) (SPPO)-polybenzimidazole (PBI) blend membranes with increasing PBI content and investigated as proton exchange membranes (PEMs) for direct methanol fuel cell (DMFC) applications. Among various SPPO-PBI blend membranes, 80:20 wt% was found as the optimum composition, which showed the highest membrane selectivity. Direct methanol-air single fuel cell tests revealed a higher cell efficiency of 11.6 % for SPPO80-PBI20 than 10.9% for Nafion 117 at 5 M methanol feed, and also a higher power density of 57.6 mW/cm² compared to 39.4 mW/cm² for Nafion 117.



Figure 2.24 Methanol permeability and membrane selectivity of SPPO-PBI blend membrans as a function of PBI loading (Haghighi *et al.*, 2011).