CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1 Theoretical Background

Fuel cells are an alternative power source for electric vehicles, electronic devices, household equipment, and military applications. A fuel cell, likes a battery, provides DC electricity from spontaneous electrochemical reactions that occur at two electrodes. Fuel cells are classified according to their electrolyte: proton-exchange membrane, alkaline, phosphoric acid and solid oxide. The general requirements of the proton-exchange membrane (PEM) fuel cell include: high ionic conductivity (with zero electronic conductivity) under cell operating conditions, long term chemical and mechanical stabilities low fuel (hydrogen or methanol) and oxygen gas crossover, interfacial chemical/mechanical compatibility with catalyst layer, and low cost. Fuel cells are operated at relatively low temperatures (at or below about 100 °C), exhibit a high power density. At the present time, there are two common types of PEM fuel cells, which operate on both H_2 and air (oxygen) or methanol and air. The main component in both systems is a "membrane-electrode-assembly" (MEA) that consists of a thin proton conducting polymeric ion-exchange membrane coated on both sides with a layer of metal catalyst powder.

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The basic physical structure or building block of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side (EG&G Services Parsons, Inc. *Fuel Cell Handbook*, 5th edition, 2000). A schematic representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in Figure 2.1

The development of fuel cells as energy sources dates back from the middle of 19th century. The first scientist who invented fuel cells as an electrical conversion is Sir William Grove (Carrette *et al.*, 2001). Fuel cells are one of the oldest electrical energy source technology. However, the development lacked a drive during the first century as new energy sources were discovered. One of the major factor that has influenced the development of fuel cell is the environmental friendly instead the

fossil fuel cells. Fuel cells can help to reduce the amount of fossil fuel cell using and poisonous emission to environment.
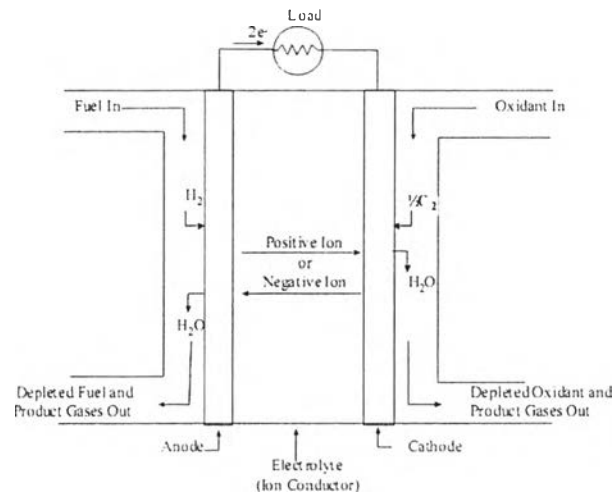

Figure 2.1 Schemetic of an individual fuel cell (EG&G Services Parsons, Inc. *Fuel Cell Handbook*, 5th edition, 2000).

Fuel cells are usually classified by the electrolyte employed in the cell. An exception to this classification is the DMFC (Direct Methanol Fuel Cell) which is a fuel cell in which methanol is directly fed to the anode. The electrolyte of this cell is not determining for the class. A second grouping can be done by looking at the operating temperature for each of the fuel cells. There are, thus, low-temperature and high-temperature fuel cells. Low-temperature fuel cells are the Alkaline Fuel Cell (AFC), the Polymer Electrolyte Fuel Cell (PEMFC), the Direct Methanol Fuel Cell (DMFC) and the Phosphoric Acid Fuel Cell (PAFC). The high-temperature fuel cells operate at temperatures approx. 600 ± 1000 °C and two different types have been developed, the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). All types are presented in this section in order of increasing operating temperature. An overview of the fuel cell types is given in Table 2.1

Table 2.1 The different Fuel Cells that have been realized and are currently in use and development (Carrette *et al.*, 2001)

Fuel Cell System	Temperature Range (°C)	Electrolyte	Charge Carrier	Application Area
AFC	< 100	KOH	OH^-	Space Application
PEMFC	60-120	Polymer Membrane	H^+	Automobile
DMFC	60-120	Polymer Membrane	H^+	Automobile/ Portable Power Generation
PAFC	160-220	Phosphoric Acid	H^+	Stationary Power Generation
MCFC	600-800	Li_2CO_3/Na_2CO_3	CO_3^{2-}	Stationary Power Generation
SOFC	800-1000	ZrO_2/Y_2O_3	O^{2-}	Stationary Power Generation

The Proton exchange membrane fuel cells (PEMFC) are considered to be one of the most promising types of electrochemical device for power generation. Low operation temperature and the wide range of power make them attractive for portable, automotive, and stationary applications.

2.1.1 The Basic Principles of Fuel Cells

The fuel cells are galvanic cells which the free energy from chemical reaction is transformed into electrical energy. The Gibbs free energy change of a chemical reaction is related to the cell voltage via: (Carrette *et al.*, 2001)

$$\Delta G = -nF\Delta u_0, \tag{1}$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, and Δu_0 is the voltage of the cell for thermodynamic equilibrium in the absence of a current flow. The reaction at anode can be either the direct oxidation of hydrogen or methanol or indirect oxidation via a reforming step. The reaction at cathode is oxygen reduction.

2.1.2 Direct Methanol Fuel Cell (DMFC)

The direct methanol fuel cell is a special form of low temperature fuel cells based on PEM technology. It can operate at slightly higher temperature than polymer electrolyte fuel cell (PEMFC) in order to improve power density. In DMFC, the methanol is directly fed into the cell without intermediate step or reforming the alcohol into hydrogen. Methanol is an attractive fuel source since it can be produced from natural gas or renewable biomass resources. The advantages of methanol are high specific energy density and the fuel storage is more comfortable than hydrogen gas. The liquid DMFC generally uses a diluted methanol in water solution (1-2 M) and a fraction of methanol is used at anode. At present, most DMFC research is concentrated to PEM technology in order to optimizing the proton conductivity first. However these membranes are not advantageous with regard to the methanol blocking. The proton transfer in membranes is due to the water content in the membrane. The similar properties between methanol and water (dipole moment) lead the molecule to transport to cathode by electro-osmotic drag as well as diffusion mechanism. At the cathode, methanol causes a mixed potential due to the interference of methanol oxidation with the reduction of oxygen, resulting in decreasing of cell performance. The methanol crossover depends on many factors such as the membrane permeability, thickness, the concentration of methanol in fuel feed, the operating temperature, and the performance of anode itself. (Carrette *et al*, 2001).

The Direct Methanol Fuel Cell (DMFC) is considered to be a highly promising power source for transportations and portable devices due to its several advantages e.g. no fuel processing unit, low temperature and pressure operation, high energy conversion efficiency, low emission, easy to design compact cell, quiet, clean

and environmental friendly, and etc. The major problems are CO poison of catalyst, the high flux of fuel through the membrane or methanol crossover and the interface resistance between the electrode and the membrane. The selection of DMFC membrane is based on not only high proton conductivity but also good methanol barrier efficiency.

These cells use proton exchange membrane (PEM) as the electrolyte, the liquid methanol is oxidized to form protons, eliminating the need for a fuel reformer.

Anode reaction:

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$$

Cathode reaction:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

Overall:

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$$

DMFC can operate in the temperature range of 50-100 °C that making it attractive for small to medium sized applications such as cellular phones or laptops. However, there are main drawbacks towards commercial value because DMFC is of kinetically slow in the methanol oxidation reaction, resulting in relatively low performance in comparison with the Proton Exchange Membrane fuel cell (PEMFC) which use hydrogen. Another problem is methanol crossover, the permeation of methanol through polymer electrolyte membrane from anode to cathode where it is oxidized reducing the cathode potential. This occurs because the cathode catalyst, normally Pt, is electroactive to methanol oxidation. The interesting challenges for DMFC are to improve methanol oxidative kinetics, cathode kinetics and operation at high temperature with low methanol crossover.
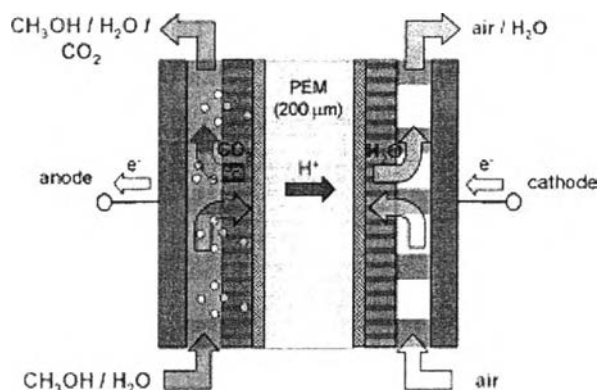
Figure 2.2 Schematic drawing of direct methanol fuel cell (DMFC).

2.1.3 Currently Used Proton Exchange Membrane (Nafion)

Nafion is sulfonated tetrafluoroethylene copolymer discovered by of Dupont in late 1960s (Carrette *et al*, 2001). It is the first class of synthetic polymer which has ionic properties (called ionomers). Because it incorporates perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) chain. Nafion has excellent properties e.g. good thermal and mechanical stability which is suitable to be used as a proton conductor for proton exchange membrane (PEM). The proton transfer mechanism in fuel cells is due to the protons on the SO_3H (sulfonic acid) groups hop from one acid to another (Grotthuss Mechanism) (Agmon *et al.*, 1995). The pores allow a movement of cations or protons but the membranes do not allow anions or electrons to pass through.

The purpose of Proton Exchange Membrane (PEM) in fuel cell are

1. To separate the anode and cathode

2. To prevent mixing of the fuel and oxidant

3. To provide a conductive pathway for protons

The polymer electrolyte membrane must possess some specific properties such as (Rusanov *et al.*, 2005):

- a high ion exchange capacity sufficient to provide a conductivity of the magnitude of 0.1 $S.cm^{-1}$ at operational temperatures;

- low permeability to fuel (hydrogen or methanol) and oxidant (oxygen) to prevent crossover of the membrane;

- substantial water uptake and good swelling to provide efficient dissociation of acids and to form a hydrated ionic phase within the entire volume of the membrane;

- sufficient chemical and mechanical stability for long-term operation under severe conditions (over 5000 h for electric vehicle applications).

The new alternative PEM materials such as sulfonated polybenzimidazole, sulfonated polysulfone, sulfonated poly(phenylene oxide), sulfonated polyimides, sulfonated polyphosphazene have been studied. Poly(aryl ketone)s such as poly(ether ether ketone) has several desired properties such as excellent thermal stability, high electrical and mechanical performance even at high temperature, high chemical resistance, and the ease to modify the chemical structure (Hickner *et al.*, 2004) The glass transition temperature of nonsulfonates PEEK is 146°C. However, this polymer has low ion exchange property due to hydrophobic character. Sulfonation is a powerful method to introduce sulfonic acid group functionallity which can increase hydrophilicity and transportation of protons due to increase acidity. In sulfonated PEEK (S-PEEK), the intermolecular interaction through hydrogen bonding increase with increasing degree of sulfonation (DS). Further, PEEK membranes show higher thermal degradation temperature than Nafion and hence are expected to show higher thermal stability at elevated temperature. The three principle methods for sulfonation of polymer are: the sulfonation of the polymer backbone, the radiation grafting of monomer groups onto the polymer backbone and then sulfonation, and the chemical grafting of sulfonated monomer groups. The sulfonated poly(ether ether ketone) (S-PEEK) has good thermal stability, appropriate proton conductivity at high degree of sulfonation (DS), and water uptake increases with increase DS. However, if the water uptake is too much, there are loss of mechanical strength and high methanol permeation. These problems can be solved by polymer blending, composite, and cross-linking. These materials were often prepared by post-sulfonating the polymer which not only decreases the mechanical and thermal stabilities, but also lack the control of sulfonation (e.g. the position and amount of sulfonate group in polymer structure).

There are side reactions such as degradation and cross-linking via the intermolecular condensation of sulfonic acid and a phenyl groups to form an intermolecular sulfone link. The new method to the direct synthesis of S-PEEK from sulfonated monomer has been studied (Gil *et al.*, 2004).

2.2 Literature Survey

The synthesized poly(ether ether ketone) with degree of sulfonation above 1.0 for the first time (Wang *et al.*, 2003). There were 1.2 sodium sulfonate groups per repeating unit. The sulfonated polymer were prepared directly from 5,5'-carbonylbis(2-fluorobenzenesulfonate), 4,4'-difluorobenzophenone and phenolph-thalein via aromatic nucleophilic substitution reaction. The sulfonated poly(ether ether ketone) (S-PEEK) showed excellent thermal stability, high diffusion of water vapour, high permselectivity of water vapour over nitrogen, and high permselectivity of anions.

Two main types of aromatic polymer: polybenzimidazole (PBI) and poly(ether ketone) (PEK) were studied (Jones *et al.*, 2001). The increases in their proton conductivities were accomplished by the complexation of PBI with acids, the grafting of groups containing sulfonic acid moieties on to PBI by N-substitution, and the direct sulfonation of PEK. These PEK were "ether rich" such as PEEK and PEEKK, or "ketone rich" such as PEK and PEKEKK. The improvement in their proton conductivity by direct sulfonation leads to an increase in the density of mobile protons and the water uptake due to the presence of the protogenic groups. The degree of sulfonation was controlled, resulting in enhanced hydrophilicity which led to enhance softness of the polymer, irreversible swelling, and water soluble in extreme cases. S-PEEK exceeds 10^{-2} Scm^{-1} at the respective potential operating temperature and showed excellent polarization characteristic in H_2-O_2 (air) fuel cells.

The modified PEEKs sulfonation at different temperatures (22, 36, 45, and 55 °C) were synthesized and varied the period of sulfonation time with concentrated H_2SO_4 used as solvent (Huang *et al.*, 2001). The sulfonation reaction took place in aromatic ring between the two ether (-O-) links which was the only one substitutent

attached to each repeating unit before the complete substitution of this preferred aromatic ring. The degree of sulfonation (DS) could be controlled by reaction time and temperature. At high temperature above 55 °C, DS could be reached to more than 100%. The solubility of S-PEEK after sulfonation was strongly dependent on DS and type of counter-ion. S-PEEK-Na with more than 55% of DS dissolved in dimethylformamide (DMF) and dimethylacetamide (DMAc) at room temperature. Whereas high DS S-PEEK-Na can be dissolved in water.

The effect of casting solvent types between DMF and DMAc on S-PEEK membrane conductivity was investigated (Robertson *et al.*, 2003). These solvents exhibited strong interactions with sulfonic acid groups of S-PEEK. The difference between these two solvents was that DMF readily interacted with the polymer to form a hydrogen-bonding complex even at 60 °C, whereas DMAc was less susceptible to undergo this reaction and exhibited such bonding only at high temperature (140 °C).

S-PEEK membranes with various DS were prepared (Li *et al.*, 2003). The post-sulfonation took by dissolving PEEK in concentrated H_2SO_4 (95-98%). DS was controlled by reaction time. With increasing of DS, the proton conductivity and methanol permeability S-PEEK increased at room temperature. The S-PEEK membranes with DS 39% and 47% were tested in single cell, the proton conductivity exceeded 10^{-2} Scm^{-1} above 80 °C, a value close to that of Nafion 115. The methanol permeability was lower than Nafion 115 over 25-80 °C.

The effect of two solvents on proton conductivities and mechanical strength of S-PEEK were evaluated (Kaliaguine *et al.*, 2003). DMF and DMAc were used, the result demonstrated that DMF entered in strong hydrogen bonding with sulfonic acid groups of S-PEEK, decreasing the amount of protons available for charge transfer. DMF and DMAc could react with residual sulfuric acid during high temperature treatment, resulting in formation of dimethylaminium sulfate and carboxylic acid. The electrical conductivity decreased due to decreasing in sulfonic acid concentration.

The PEEK was modified by using concentrated H_2SO_4 (97.4%) to produced proton conducting polymers containing HSO_3 groups (Javaid Zaidi *et al.*, 2003). The

sulfonation reaction was carried out at room temperature and at difference reaction times to produce polymers of various DS. The sulfonation decreased crystallinity of PEEK and increased the solubility in organic solvent due to presence of sulfonic acid groups. These groups could facilitate the transport of protons needed for high proton conduction in polymer. Increasing sulfonic groups could also increase the water uptake. DS of S-PEEKs was varied from 40-80 mol%. The S-PEEK became amorphous after sulfonation which enhanced solubility in DMF. The glass-transition temperature (T_g) increased from 151 °C for pure PEEK to 217 °C upon sulfonation due to increasing in $-SO_3H$. The increasing of T_g reflected an increased intermolecular association through the polar ionic site. The water uptake also increased with DS.

The new method for preparation cross-linked S-PEEK was used (Mikhailenko *et al.*, 2004). The cross-linking involved thermally activated bridging of polymer chains with polyatomic alcohol; e.g., ethylene glycol, glycerine, and meso-erythitol, which made polymer mechanical strongly and reduced water swelling. The cross-linkings were obtained by intra/inter chain condensation of sulfonic acid functionalities by thermal treatment. However, the cross-linking decreased the number of sulfonic groups available for proton transfer, the conductivities of S-PEEK membranes were slightly reduced. Some of the membranes exhibited conductivity above 2×10^{-2} Scm^{-1} at room temperature.

Gil *et al.*, (2004) synthesized S-PEEK directly by sulfonated monomer, sodium 5,5′-carbonylbis(2-fluorobenzene-sulfonate) were prepared. Then, the reaction between them with 4,4′-difluorobenzophenone and 3,3′-5,5′-tetramethyl-4,4′-biphenol took place, resulting in S-PEEK. It exhibited conductivities from 0.02 to 0.07 S.cm^{-1} at 25 °C, water swelling from 13 to 54%, ion-exchange capacity (IEC) from 0.7 to 1.5 meq/g, and methanol diffusion coefficient from 3×10^{-7} to 5×10^{-8} cm^2/s at 25 °C. These coefficients ware much lower than of Nafion (2×10^{-6} cm^2/s), thus the S-PEEK membrane could reduce the amount of methanol crossover in DMFC.

A series of sulfonated poly(ether ether ketone ketone) (PEEKK) was prepared (Li *et al.*, 2004) through aromatic nucleophilic substitution poly-

condensation of bisphenol-A with different ratios of 1,4-bi(3-sodium sulfonate-4-fluorobenzoyl)-benzene to 1,4-bi(4-fluorobenzoyl)benzene. All sulfoanted PEEKKs were easily dissolved in dimethylformamide (DMF), dimethylsulfoxide (DMSO), and 1-methyl-2-pyrrolidone (NMP) due to the sodium sulfonate groups in the polymerhad excellent hydrophilic properties. Thermal properties were investigated by TGA and DTA, no T_g and crystalline peaks were observed. Therefore, they were amorphous polymers. The temperature of 10% weight loss was greater than 300 °C which showed that the polymer had high thermal stabilities. And this temperature decreased with increasing concentration of sodium sulfonate groups in polymer backbone. The swelling of the membranes (6.02-16.02%) were lower than Nafion, IECs (0.67-1.44) were higher than Nafion, and proton conductivities were 0.022-0.125 Scm^{-1}.

Sulfonation and product characterization of both commercial Victrex and Gatone PEEK were studied (Xing *et al.*, 2004). The mass average molecular weights (M_w) pf both PEEKs were estimated from the intrinsic viscosity measured in H_2SO_4 solution. It was verified that the higher temperature sulfonation (55 °C) did not induce any chain degradation. A new method for determining DS directly in H_2SO_4 (non-deuterated) reaction solution was accomplished by ^{1}H-NMR using a solvent suppression technique. This technique gave DS values higher than that obtained by what might be considered the more accurate method of ^{1}H-NMR analysis of recovered samples in DMSO-d6 solution. The new method was useful to evaluate the sulfonation kinetics and obtained a desired target DS for S-PEEK. Both Victrex and Gatone derived S-PEEK showed a high first thermal degradation temperature (~ 250 °C). The conductivities of S-PEEK increased with increasing DS. The S-PEEK films were cast from DMAc and showed higher proton conductivity than DMF due to the formation of strong complexes between the decomposed product of the solvent and sulfonic groups.

The performance of S-PEEK/PBI blend membranes was developed by introducing the inorganic proton conducting material, Boron phosphate (BPO$_4$) (Javaid *et al.*, 2005). The contents of solid BPO$_4$ in the composite membrane varied from 10 to 40%(w/w). The proton conductivity was measured by Impedance

spectroscopy at room temperature. The conductivity of composite membrane was increased with increasing BPO_4 particles. The highest conductivity was 6 mS/cm for composite membrane containing 40%(w/w) of BPO_4 at room temperature. The membranes showed very good thermal stabilities, moderate swelling, and good proton conductivities. The T_g decreased with the incorporation of BPO_4 which indicated that blends of S-PEEK/PBI with BPO_4 were not compatible. The composite membranes showed T_g higher than 220 °C, whereas Nafion showed at 80 °C, and they were mechanically stronger than Nafion.

The the new type PEM based on sulfonated poly(ether ether ketone ketone) (S-PEEKK) was studied (Li et al., 2005). The polymer was prepared directly by nucleophilic polycondensation of 3,3',5,5'-tetramethyl diphenyl-4,4'-diol with different rations of 1,4-bi-(3-sodiumsulfonate-4-fluorobenzoyl)-benzene to 1,4-bi(4-fluorobenzoyl)-ben-zene. The thermal properties from DTA showed no T_g in temperature range of 100-400 °C and no crystalline peaks. From TGA data, the polymer had excellent thermal stability at about 400 °C. The 10% weight loss temperature of the polymerdecreased as the content of sodium sulfonated groups increased. The S-PEEKK membranes showed an increase in ion exchange capacity (IEC) with increasing DS (DS values of 0.8, 1.0, and 1.2 exhibited IECs of 1.01, 1.36, and 1.57, respectively). With increasing DS, the S-PEEKK membranes showed water contents varying from 16.08 to 26.71% and the water content in the membranes increased that could provide more channels for cationic transport and led to membrane structure loosening.

S-PEEKs via using concentrated H_2SO_4 at different reaction conditions were prepared (Muthu Lakshmi et al., 2005). The reaction times were varied from 3-5 hours, polymer concentration 4–10% (w/v) and temperature 35-50 °C. The DS was found to be 50–80% by a calculation from ^{1}H-NMRand elemental analysis (S-content). The TGA presented multi-step mass loss, the first step at 50-225±25 °C was due to loss of moisture (1-10%), and second step at 250-425±25 °C was attributed to volatilization of SO_3 from sulfonic groups. The polymer backbone degradation took place above 450 °C. The proton conductivity was varied from 0.034×10^{-2}-0.235×10^{-2}

Scm^{-1} according to increasing in extent of sulfonation. However, the mechanical properties decreased with increasing DS.

Their other work involved novel S-PEEK copolymer with controlled DS. The S-PEEK copolymers were synthesized by polycondensation reaction of silylated phenolphthalein, silylated biphenol, 5,5'-carbonyl-bis(2-fluorobenzene sulfonate) (sulfonated 4,4'-difluorobenzophenone) and 4,4'-difluorobenzophenone at various the molar ratio. The DSC analysis showed that T_g of S-PEEK was higher than 230 °C and TGA analysis demonstrated that the polymer backbone was broken down at temperature above 450 °C. The value of water uptake of S-PEEK membrane was similar to Nafion. The proton conductivity of membranes at 25-27 °C were found to be 10^{-5}-10^{-3} Scm^{-1} and methanol diffusion coefficients were in range 6.57×10^{-8} to 2.5×10^{-6} cm^2/S.

S-PEEK was synthesized via nucleophilic substitution reaction with the following monomers: 4,4'-difluorobenzophenone (monomer k), sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (monomer m), and 3,3',5,5'-tetramethyl diphenyl-4,4'-diol (monomer l) in DMSO/toluene system (Li et al., 2005). They used small angle X-ray scattering (SAXS) to study internal structures of S-PEEK membranes which showed that after swelling in water, the size of ion clusters in membranes increased and DS of S-PEEK increased with increasing size of cluster and provided a larger proton transfer channel.

Sulfonated poly(ether ketone ketone)s (S-PEKK)s with varying DS were studied (Vetter et al., 2005), the performance of these S-PEEK membranes were comparable to Nafion with the same pretreatment conditions and better than S-PEEK membranes with similar functionalization. The sulfonation of PEKK and PEEK involved the reaction between aromatic rings and electrophilic agents. The presence of more ketone groups in PEKK deactivated aromatic ring, made their sulfonation more difficult than in PEEK. The PEEK could be easily sulfonated by reacting with H$_2$SO$_4$ even in the more severe conditions (during 4 days at 60 °C). The difference temperatures and reaction times led the DS up to about 38-70%. The polymer started to be brittle at 80 °C. The TGA analysis showed that the first degradation of S-PEKK started at 207–220 °C according to decomposition of segments substituted by

sulfonic acid groups. The second decomposition was performed at 440–460 °C due to random chain scission and transfer reactions. The highly sulfonated membranes could swell and take a large amount of acid solution and obtain high conductivity. The polymer with 70% DS had a conductivity near that of Nafion and for DS higher than 50%, the membranes started to swell in water and water/methanol forming a gel. DS at 43—48% was the best choice, whereas at 70% have a performance worse than 48%. Although the conductivity was higher due to swelling of polymer.

S-PEEKs with different DS via varying the sulfonation reaction temperature were prepared (Carbone *et al.*, 2006). The membranes were prepared by using different solvents (DMSO, DMAc, DMF, and DMAc/DMF mixture). Structural and chemical-physical properties of the film were characterized by TGA and X-ray analysis. The direct sulfonation of PEEK produced a copolymer with ion rich and poor regions. The presence of sulfonic groups increased DS, and also T_g too. The WAXS and SAXS data showed that there were very low crystalline structure with sulfonic groups randomly distributed inside the polymer matrix. In a casting process, DMSO was used and it induced ion poor segment crystallization due to a lower solubility of a polymer at high solvent concentration. The membranes prepared by DMAc and DMF were amorphous. All membranes are tested in H_2/air single cell at 100 °C, the DMSO membranes has poorer performance than any membranes. The S-PEEK membranes were prepared by using DMAc/DMF solvent, were tested at 130 °C and had maximum power density about 400 mWcm^{-2}.

S-PEEK was synthesized via reduction of sulfochlorinated PEEK (Zhang *et al.*, 2006). The partial reduction of sulfochlorinated PEEK could achieve SO_2Cl and sulfinate groups. The covalent cross-linking membranes were prepared by a reaction with the cross-linker diiodobutane and then hydrolysis of the sulfochloride groups by aqueous post-treatment. The IEC of the starting-water-soluble S-PEEK was 2.68 meqg^{-1} which was due to 98.24% DS. DS could be determined by ^{1}H-NMR, yielding DS around 94% (0.94 per group/repeating unit). From an elemental analysis, the sulfochlorination conversion of S-PEEK was about 100%. The TGA analysis showed that the un-modified PEEK was very stable and degradation only at high temperature (580 °C) due to main chain scission. The pyrolysis products were CO, phenol, and

CO_2. The swelling was lower than 40% for low IEC at room temperature (25 °C) and showed a slight increased to about 1.5 $meqg^{-1}$. High IEC at 2.0 $meqg^{-1}$, the swelling was more than 170% at 25 °C, resulting in the decrease of mechanical stability. The swelling only slightly increased at low IEC (< 1.26), that was advantageous for fuel cell applications. The new cross-linked membranes were thermally stable, low resistance, and reduced water uptake which only moderately increased with temperature, and stable performance under air condition at elevated temperature up to 130 °C.

Poly(amide imide) (PAI) was synthesized by using 1,2,4-benzentricarboxylic anhydride (BTBA) and 4,4'-methylenebis(phenylene isocyanate) (MBPI) (Wu *et al.*, 2006). Then PAI was blended with S-PEEK and characterized for DMFC application. All blended membranes were strong and homogeneous. The intrinsic viscosity of S-PEEK and PAI were 4.68 dLg^{-1} and 0.55 dLg^{-1}, respectively. The weight average molecular weights were 256,122 g/mol and 241,857 g/mol, respectively. The water uptake of S-PEEK decreased by blending with PAI. However, the adsorption in concentrated methanol was high. The water diffusion decreased with increasing PAI. The S-PEEK/PAI 70/30%(w/w) had properties similar to Nafion and low methanol permeability.

Regina *et al.*, (2006) prepared S-PEEK with a cardo group (WC) by varying a wide range of DS. And they prepared composite membranes that incorporate an amorphous zirconium phosphate sulfophenylene phosphonate $(Zr(HPO_4)$-$(O_3PC_6H_4SO_3H))$, hereafter Zr(SPP) in a S-PEEK-WC matrix. The composition of composite membranes was fixed at 20 wt% of Zr(SPP). For comparison, a commercial Nafion 117 membrane was characterized under same condition. The composite membranes exhibited decreasing water uptake when compared with polymeric membranes at high DS values and temperature higher than 50 °C. The water uptake in composite membranes remained constant at 20-70 °C. The methanol permeability of both polymeric and composite membranes was always lower than that of Nafion 117. At 22 °C and 100% RH, the proton conductivity of the polymeric membranes increased from 6×10^{-4} to 1×10^{-2} Scm^{-1} with increasing of DS from 0.1 to

1.04. The higher conductivity was comparable to that of with Nafion 117 (3×10^{-2} Scm^{-1}).

A series of cross-linked S-PEEKs containing propenyl groups were synthasized via aromatic nucleophilic substitution reaction (Zhong *et al.*, 2006). These kinds of S-PEEKs had reactive double bonds which could be cross-linked and grafted by UV radiation. The aromatic nucleophilic substitution polycondensation with 5,5′-carbonylbis(2-fluorobenzene sulfonate) and 4,4′-difluorobenzophenone at various ratios were synthesized and cast into membranes. The proton conductivity of S-PEEK membranes with IEC from 0.624 to 1.700 ranged from 0.008 to 0.025 Scm^{-1} at 25 °C and from 0.028 to 0.072 Scm^{-1} at 85 °C. The S-PEEK membranes exhibited much lower methanol diffusion coefficients compared with Nafion membranes.

S-PEEK membranes was prepared and crosslinking via polyols (ethylene glycol and glycerol) (Mikhailenko *et al.*, 2006). The membranes were found to be stable in hot water and highly proton conductive. The best mechanical properties (flexibility, little brittleness) were possessed by the membranes with cross-linker/S-PEEK mole ration about 3. Lower ratio led to a non-complete cross-linking, whereas higher ratio led to brittleness. The membranes were stable up to temperature above 200 °C. The ethylene glycol and glycerol molecule did not link neighboring main chains via sulfonic acid functions but rather formed alcohol-ether oligomers, bonded to $-SO_3-$ group and generating an interpenetrating network which interacted with the main chains.

A series of block S-PEEK copolymers was synthesized with high IEC consisting of hydrophobic and hydrophilic blocks (Zhao *et al.*, 2006). The membranes with different IECs for the same block chain length or with different block chain lengths at the same IEC were focus on the structure-properties in terms of water uptake and proton conductivity. The membranes exhibited conductivities from 0.027 to 0.068 Scm^{-1} at 30 °C and from 0.049 to 0.11 Scm^{-1} at 80 °C, water uptake from 34% to 54% and IEC from 1.25 to 1.48 $meqg^{-1}$. The SAXS profiles of block S-PEEK ionomers exhibited a well-defined ionomer peaks due to the phase separation between ionic and hydrophobic domains. The block S-PEEK membranes

showed increased water uptake and proton conductivity compared to the random S-PEEK membranes at the similar IEC.

A a series of cross-linked S-PEEK membranes were studied (Zhong *et al.*, 2007), which were prepared via photochemical cross-linking of S-PEEK membranes by dissolving benzophenone and triethylamine photo-initiator in membrane casting solution. Then, the membranes were exposed to UV light after solvent evaporation. The S-PEEK was synthesized by a reaction between diallyl bisphonol A, 4,4'-difluorobenzophenone and 5,5'-carbonyl-bis(2-fluorobenzene sulfonate). The cross-linked S-PEEK membranes were compared with a non-cross-linked membrane. The cross-linked membranes exhibited higher thermal stabilities, mechanical strength, hydrolytic and oxidative stabilities as well as lower water uptake and methanol diffusion coefficients with increasing photo-irradiation time. The photo-irradiation time at 10 min could improve those kinds of properties with only slightly reduction of elongation at break and proton conductivity. Therefore, this condition could be used in DMFC application.

The sulfonation selectivities of seven PEEKs were investigated (Liu *et al.*, 2007). The S-PEEKs contained various side substituents such as phenol, methylphenyl, trifluoromethylphenyl, and phenoxylphenyl groups. Two series of sulfonated PEKs based on methylphentlated and phenylated PEKs (Me-SPEKs and Ph-SPEKs) with stereo-controlled sites and high sulfonation were prepared by post-sulfonation method under mild conditions. A family of both homo- and copolymers with IEC 0.84-2.23 meqg^{-1}could prepared by controlling the unsulfonated segments length. These side group sulfonated polymer exhibited excellent dimension stability in hot water.

The phenyl phosphonic acid functionalized poly[aryloxyphosphazene] membranes was prepared (Allcock *et al.*, 2001). Membranes were cast from *N,N*-dimethyl-formamide and found to have proton conductivities between 10^{-2} and 10^{-1} S/cm, total ion exchange capacities between 1.17 and 1.43 meq/g. Equilibrium water swelling values were determined to be between 11 and 32% depending on the polymer structure. Methanol diffusion coefficients for both radiation cross-linked and non-cross-linked membranes in 3 M aqueous methanol at 80 °C and 2.8 bar were

found to be at least 12 times lower than for Nafion 117, and 6 times lower than for a radiation cross-linked sulfonated polyphosphazene membrane.

The blends of sulfonated poly[bis(phenoxy)phosphazene] (SPOP) and polybenzimidazole (PBI), where the latter was used as a cross-linking component (Wycisk *et al.*, 2005). The membranes were evaluated in term of room-temperature water swelling and proton conductivity, methanol permeability at 60 °C, and direct methanol fuel cell (DMFC) performance at 60 °C with a 1.0 M methanol and air at atmospheric pressure. Initial screening of membranes was carried out using a "sandwich" membrane electrode assembly (MEA) design, where a polyphosphazene film was inserted between two half-MEAs made with Nafion 117. MEAs were also prepared by hot-pressing catalyst electrodes directly onto SPOP-PBI blended films. Comparable current-voltage data were obtained with the two MEA configurations. Membrane performance in a DMFC was dependent on the blend composition (ion exchange capacity (IEC), of the SPOP and wt% of added PBI). For an 82 μm thick membrane composed of 1.2 mmol/g IEC SPOP with 3 wt% PBI, the maximum power density was 89 mW/cm^2 (vs. 96 mW/cm^2 with Nafion 117), while the methanol crossover was 2.6 times lower than that with Nafion 117.

The sulfonated poly[bis(phenoxy) phosphazene] (S-BPP) with an interprenatrating hydrophilic network was synthesized (Burjanadze *et al.*, 2006). The S-BPP can be trapped in a crosslinked interprenetrating hydrophilic network of hexa(vinyloxy- ethoxyethoxy)cyclotriphosphazene (CVEEP). Membranes with good mechanical and thermal stabilities were obtained exhibiting high ion exchange capacities in the range of 1.62-1.79 mmol/g. The proton conductivity was measured as a function of water partial pressure in nitrogen (0 mbar to 25 mbar) in the temperature range 25°C to 75 °C. At 25 mbar water partial pressure and 75 °C, a conductivity of 2.2×10^{-4} S/cm was obtained for s-BPP with a network made of 50 wt% CVEEP. After immersion in water, the conductivity increased up to 0.013 S/cm at 25 °C. The hydrophilic nature of the CVEEP network stabilizes the water content and enhances the proton conductivity at elevated temperatures.

A series of sulfonated poly(arylene ether nitriles ketone) (SPAENK) copolymers with controlled degree of sulfonation (DS) were synthesized by direct

copolymerization of 4,4'-(hexafluoroisopropylidene)diphenol with 2,6-difluoro-benzonitrile and sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) at various molar ratio (Zhang *et al.*, 2005). The heteropolyacids (HPA)/SPAENK composite membranes were also prepared by solvent casting of the SPAENK with various concentrations of phosphotungstic acid. The properties of pristine SPAENK membranes were compared with the composite membranes, which showed lower water uptake but higher proton conductivity.

The proton conductivity was improved by addition of an aluminosilicate; zeolite beta, into the sulfonated poly(ether ether ketone) (SPEEK) matrix (Sengul *et al.*, 2009). The proton conductivity of the original SPEEK membrane (DS 68%) was 0.06 S/cm at 60 °C and that of the composite membrane containing of zeolite beta filled SPEEK was found to increase to 0.13 S/cm. The best conductivity results belong to zeolite beta having a SiO_2/Al_2O_3 ratio of 50 at 10 wt% loading.

A novel polyelectrolyte complex (PEC) membrane for direct methanol fuel cells (DMFCs) was prepared by blending a cationic polyelectrolyte, chitosan (CS), with an anionic polyelectrolyte, acrylic acid-2-acrylamido-2-methylpropane sulfonic acid copolymer (P(AA-AMPS)) (Jiang *et al.*, 2008). The proton conductivity and methanol permeability were measured and compared with the Nafion 117 membrane. The dual function of P(AA-AMPS) as both an ionic crosslinker and a proton conductor led to not only a decreasing in methanol permeability but also an increasing in proton conductivity. The overall selectivity increased with the increase of P(AA-AMPS) concentration.

The inorganic proton conductors, phosphomolybdic acid (PMA), phosphotungstic acid (PWA) and silicotungstic acid (SiWA) were mixed with chitosan (CS) solution (Cui *et al.*, 2009). The heteropolyacids (HPAs) leads to strong electrostatic interaction to form insoluble complexes. Among these membranes, CS/PMA membrane was identified as ideal for proton exchange membrane as it exhibited low methanol permeability (2.7×10^{-7} $cm^2.s^{-1}$) and comparatively high proton conductivity (0.015 $S.cm^{-1}$ at 25 °C).

Hybrid organic/inorganic composite proton exchange membranes based on a poly(vinylidene fluorideco-chlorotrifluoroethylene) grafted membrane and varying

amounts of zeolite were investigated (Patel *et al.*, 2009) When the weight percent of zeolite 5A is above 7%, the proton conductivity at room temperature was decreased to 0.011 S/cm. The water uptake of the composite membranes decreased from 234 to 125% with an increase of the zeolite 5A weight percent to 10 wt%. The decrease in water uptake is a result of the decrease in the number of available water absorption sites because of the hydrogen bonding interactions between the zeolite particles and the graft copolymer matrix.

The series of Nafion membranes modified with silica and tetrapropylammonium (TPA) and tetrabutylammonium (TBA) cations were fabricated (Krivobokov *et al.*, 2010). The Fe-silicalite/Nafion composite membranes showed the highest relative selectivity (as defined by the proton conductivity to methanol permeability ratio) of 5.4 and proton conductivity of 11 mS.cm^{-1}. The selectivity of the composite membranes increases in the order: SiO_2/Nafion < TAA/Nafion < Fe-silicalite/Nafion.

Novel hybrid organic/inorganic composite proton exchange membranes based on sulfonated poly(1,4-phenylene sulfide) membrane with varying amounts of zeolite were synthesized (Choi *et al.*, 2010). Increasing of zeolite concentration to 10 wt%, the proton conductivity of composite membrane decreased from 0.075 to 0.02 S.cm^{-1} at room temperature which may be due to strong interaction between sulfonic group of SPPS and the zeolite particles. The water uptake of the composite membrane also decreased from 255% to 150% with the increasing of the zeolite content to 10 wt%. The thermogravimetric analysis showed the increment of thermal stability of the composite membranes with increasing concentration of zeolite.

Nafion–Faujasite composite membranes were prepared by Zhang *et al.*, 2011. The zeolite interacts with Nafion probably through hydrogen bonding between SO3H and Si–OH groups, which combined with the increase of the water uptake and the water mobility.