

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

Fuel cell is an electrochemical device that continuously converts a chemical reaction to an electrical energy. The system consists of two electrodes: anode and cathode. The oxidation occurs at the anode side while the reduction occurs at the cathode side. Direct methanol fuel cell (DMFC) has a simple system design because it uses methanol and air at the supply electrode. DMFC is less toxic because its byproducts of reaction are only water vapor (Carrette *et al.*, 2001).

#### 2.1 Direct Methanol Fuel cell (DMFC)

DMFC is a subcategory of the proton exchange membrane fuel cell (PEMFC) family. In the DMFC, methanol is directly fed into the fuel cell without the intermediate step of reforming the alcohol into hydrogen. Methanol is an attractive fuel option because it can be produced from a natural gas or renewable biomass resources. The liquid DMFC generally uses a diluted methanol in water mixture (typically 1-2 molar). The methanol is introduced to the PEMFC to initiate the chemical reaction and to generate the electricity and byproducts as small amounts of water and carbon dioxide. The DMFC has the capability to replace the battery because methanol theoretically has a superior specific energy density in comparison to the best rechargeable batteries (Carrette *et al.*, 2001). These characteristics mean longer operation time for portable mobile phones and laptops, and more power available in these devices to meet consumer demand. DMFCs can also be designed for a quick and easy fuel chamber replacement. For rechargeable batteries, they require many hours for charging a depleted power pack, a DMFC can have its fuel replaced in minutes. The advantage of DMFC is using methanol that can be stored as a liquid. This is easy and safe to install in the system (Kamarudin *et al.*, 2009). At present, most DMFC researches are concentrated on proton exchange membrane (PEM) technology. The membranes used in DMFCs are developed for the PEM application (optimizing the proton conductivity is the priority). However, these membranes have a disadvantage with regard to methanol blocking. The proton

movement in the membrane is associated with the water content in the membrane. Due to the similar properties of methanol as compared to water (e.g., dipole moment), methanol molecules as well as water molecules are transported to the cathode by the electro-osmotic drag as well as diffusion (Carrette *et al.*, 2001). At the cathode, methanol causes a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction. As a consequence, a decrease in cell performance results from the methanol cross-over depending on a number of factors; the most important factors are membrane permeability, thickness, concentration of methanol in the fuel feed, operating temperature, and performance of the anode itself (Carrette *et al.*, 2001).

A major breakthrough in the field of PEMFC is the use of Nafion membranes by Dupont. These membranes are higher acidity, higher conductivity, and more stable than the sulfonated polystyrene membranes. The Nafion membrane consists of a polytetrafluoroethylene (PTFE) as a based structure which is chemically inert in reducing and oxidizing environments. The characteristic value of proton conducting polymer membranes is the equivalent weight which is defined as the weight of polymer that neutralizes one equivalent of base, and is inversely proportional to the ion exchange capacity. However, its high cost, high methanol permeability, and low proton conductivity at lower humidity or higher temperature operating conditions, are the limitation of commercialization in DMFC.

This work is focused on developing two polymer electrolyte membranes to improve DMFC performance. Polysulfone (PSF) is an amorphous structure, a high performance polymer due to excellent thermal and chemical stabilities, a good resistance to inorganic acids and bases, and an outstanding hydrolytic stability against hot water and steam sterilization (Zhu *et al.*, 2011). Poly(vinylidene fluoride) (PVDF) has many unique properties such as an excellent chemical, thermal, and mechanical stabilities, a low surface energy, and a low dielectric constant (Zhu *et al.*, 2011 and Jeon *et al.*, 2009).

Carrette *et al.*, (2001) summarized and classified composites, applications, conditions for fuel cell operation. Fuel cells are galvanic cells, in which the free energy of a chemical reaction is converted into an electrical energy. The basic structure of all fuel cells is similar: the cell consists of two electrodes which are

separated by the electrolyte and which are connected to an external circuit. The electrodes are exposed to gas or liquid as fuel or oxidant (e.g. hydrogen or oxygen). The electrodes have to allow gas or liquid permeation and therefore should possess a porous structure. The structure and content of the gas diffusion electrodes are quite complex and require considerable optimization for the practical application. The electrolyte should also possess gas permeability as low as possible for fuel cells with a proton conducting electrolyte (PEMFC). Hydrogen is oxidized at the anode and protons enter into the electrolyte and are transported to the cathode.

Kamarudin *et al.*, (2007) studied a micro-DMFC system. The micro-DMFC could be replaced with conventional battery without recharging from the electricity. The micro-DMFC could convert the fuel to the electricity and was environmentally safe and could be applied in cell phone. However, methanol crossover was the main problem in micro-DMFC. The methanol crossover affected the self-discharge of methanol, which supplied additional heat instead of electricity, and a severe reduction of the cathode voltage.

DMFC technology is a further development of the PEMFC that is particularly promising for portable electronics and vehicular applications due to the advantages of a liquid fuel. This technology uses methanol as the source of energy. DMFC consists of an anode which promotes the electro-oxidized of methanol to produce  $\text{CO}_2$  at the anode, and through the reaction with oxygen (usually air) to produce water or steam at the cathode. The DMFC has the potential to replace the battery because methanol theoretically has better specific energy density in comparative relation to the best rechargeable batteries. These characteristics mean longer operation times for portable mobile devices and laptops and more power available in these devices to meet consumer demands. DMFCs can also be designed for a quick and easy fuel chamber replacement. However, methanol crossover is currently the biggest challenge facing DMFC designers because it has the most adverse effect on the cell performance. Several common approaches to prevent it in terms of membrane modifications and novel cell/stack designs are currently being studied (Kamarudin *et al.*, 2009).

Seo *et al.* (2009) focused on the methanol crossover and performance of DMFC under various operating conditions such as; methanol flow rate, temperature

at operation, and methanol concentration. The crossover current density in an open circuit was determined with methanol crossover under applied voltage. The Nafion 117 was used as the membrane in DMFC to test the effects of methanol flow rate, temperature operating, and methanol concentration. The temperature and methanol concentration influenced methanol crossover. The methanol crossover increased with increasing temperature operating, methanol concentration, and methanol flow rate (Seo *et al.*, 2009).

DMFC could be adapted for powering portable electronic devices because DMFC possesses a high power density, long life time, and requires no recharging (Kamarudin *et al.*, 2012). The main problem came from the generated carbon dioxide and methanol permeation. However, an operating system design of DMFC and fabrication DMFC system were employed to solve these problems. This work presented a description of diverse fuel-field design for DMFC and showed its advantages (Kamarudin *et al.*, 2012).

This review was focused on discussing hybrid membranes of two main types; Nafion-based and non-Nafion-based membranes. The Nafion based membranes included organic-inorganic membranes, acid-base membranes, and Nafion plus bio-component membranes. The non-Nafion-based membranes included organic-inorganic membranes, salt-based membranes, and acid-base membranes. A membrane with desirable characteristics such as low methanol permeability, high proton conductivity, high mechanical and thermal stabilities would lead to excellent performances in DMFC (Ahmad *et al.*, 2010).

Higashihara *et al.*, (2009) reviewed recent studies on proton exchange membrane (PEM) materials for fuel cell. The candidates for the breakthrough in PEM application were divided into four parts: 1) sulfonated/non-sulfonated multiblock copolymers which contained hydrophobic and hydrophilic oligomers; 2) branched polymers in which the inner hydrophilic domains were surrounded by outer hydrophobic domains; 3) locally and densely sulfonated polymers with multiple sulfonic acid moieties along the main chains and; 4) high -ion exchange capacity (IEC) polymers with a highly hydrophobic main chain skeleton.

Souzy *et al.*, 2005 showed a synthesis of a fluoropolymer to be used as the membrane in a fuel cell. The synthesis of the fluoropolymer was divided three main

parts; the first was related to the direct radical copolymerization of fluoroalkenes with a fluorinate monomer. The second was the chemical modification of hydrogenated polymer with sulfonated fluoropolymer. The last was the synthesis by grafting the fluoropolymer with a monomer (Souzy et al., 2005).

Many technical ways are possible to improve the polymer membrane in fuel cell such as: grafted copolymer, irradiation, and composite membrane with porous material. To increase the proton conductivity and decrease the methanol cross-over of the electrolyte membrane, this work was focused on the sulfonation process in the sulfonation process, this polymer was sulfonated with sulfuric acid which was easy and safer than previous work.

The cation-exchange membranes (CEM) and alkali-doped polybenzimidazole membrane (APM) were studied for the alkaline direct ethanol fuel cell (DEFC). Three types of membrane were studied for the alkaline DEFCs and the membrane properties were compared: ionic conductivity; permeability; thermal properties and mechanical properties. The three types of membrane were: (1) the AEM was required to improve its thermal stability; (2) the CEM was another choice for using in the alkaline DEFC operation at high temperatures ( $<90\text{ }^{\circ}\text{C}$ ) when compared with the AEM; and (3) the APM was required to improve the mechanical properties and to decrease the permeability. The APM could operate at high temperatures in the alkaline DEFC (An *et al.*, 2012).

Merle *et al.*, 2011 studied the preparation and properties of anion exchange membranes. This work showed classifications based on the nature and the properties of anion exchange membranes for alkaline fuel cells and included descriptions for many topics such as characterization, transport mechanisms in anion exchange membranes, and stability of alkaline anion exchange membranes at high pH. This work identified three different categories; heterogeneous membranes, interpenetrating polymer network, and homogeneous AEMs (Merle *et al.*, 2011).

The composite membrane was made from phosphate based alkylimidazolium ionic liquid in sulfonated poly(ether ether ketone) polymer matrix. The composite membrane was confirmed and characterized by FTIR and TGA. The maximum proton conductivity was 3.16 mS/cm at 145  $^{\circ}\text{C}$  in fully anhydrate conditions. The

maximum power density of composite membrane was  $203 \text{ mW/cm}^2$  at  $145 \text{ }^\circ\text{C}$  under dry state (Jothi *et al.*, 2013).

The sulfonated PEEK and PPEES samples were prepared from 98% sulfuric acid at different reaction times to fabricate S-PEEK and S-PPEES membranes at various degree of sulfonation (DS). The S-PPEES could only be sulfonated at the DS value of 80% due to the poor solubility of PPEES and a short reaction time. The properties of S-PEEK and S-PPEES membranes depended on the DS. An increase in DS induced increases in the water uptake, IEC, proton conductivity, and vanadium ion permeability. On the other hand, an increase in DS also induced a decrease in the mechanical properties, as the increase in the water uptake led to low mechanical strength. The S-PEEK and S-PPEES membranes showed lower vanadium ion permeability values than that of the Nafion117 membrane (Macksasitorn *et al.*, 2012).

Sulfonated poly(ether ether ketone)s at various DS values were successfully prepared. Proton conductivities of the SPEEK membranes were increased with increasing DS and reaction temperature. Methanol permeability of the SPEEK membranes was all lower than that of Nafion117 membrane. The methanol permeability was dependent on temperature and the concentration of methanol. The proton conductivities at  $22 \text{ }^\circ\text{C}$  were not higher than that of Nafion117 membrane, but higher selectivity values were found for SPEEK membranes (Xue *et al.*, 2006).

The proton-conducting sulfonated poly(1,4-phenylene sulfide)(SPPS) was prepared by the sulfonation of PPS. SPPS was blended in solutions of various concentrations of zeolite to form different composite polymer electrolyte membranes. SEM micrograph showed no void in the membranes, which referred to a good interaction between the zeolite particles and the polymer matrix. The proton conductivity of the composite membrane was reduced from  $0.075$  to  $0.02 \text{ Scm}^{-1}$  with 10 wt% zeolite at room temperature. The composite membranes showed higher thermal stability than the pure polymer membrane that might come from the strong specific interaction between the sulfonic groups of the matrix membrane and the zeolite (Choi *et al.*, 2010).

Tricoli *et al.*, (2003) tried to exploit the molecular sieving properties of two zeolites (Chabazite and Clinoptilolite) to improve selectivity of Nafion ion

conducting membranes. The performances of the Chabazite-Nafion and Clinoptilolite-Nafion composite membranes were lower than that of the Nafion membranes in terms of ion conductivity and transport selectivity. However, this result was due to the properties of the chosen zeolites. The incorporation of semi-permeable particles in a polymer matrix was the best method to notably vary transport properties. Such method was simple and allowed a decrease in defects of membranes.

Proton conducting nanoporous membranes were made by re-adapting a procedure for using in the lithium battery technology (Croce *et al.*, 2006). The performance of the membranes was modified with SiO<sub>2</sub> ceramic powder at a nano particle size. The nanoporous composite membranes showed better features, such as a high conductivity and low methanol permeability. The membranes had a limitation in term of thermal stability due to the release of the liquid component. However, the transport and the physical properties, associated with a prospective very low cost, made these membranes attractive for some special applications, such as low temperature fuel cells for portable electronics (Croce *et al.*, 2006).

Nafion/H-ZSM-5 composite membranes were prepared by mixing H-ZSM-5 zeolites with Nafion (DE2020). All composite membranes have a lower methanol permeabilities and higher proton conductivities than pure DE2020 membrane. Two of the membranes: (DEZ X-Y, where DE, Z, X and Y stands for DE2020 Nafion, ZSM-5 zeolite, Si/Al ratio of the zeolite and the weight percentage of the zeolite) DEZ25-5 and DEZ50-1 were tested in DMFC due to their lower ethanol cross-over and higher proton conductivity, respectively. The DEZ25-5 membrane showed the best DMFC results. Its maximum power density was more stable throughout the measurement and it reached the highest MPD at the end of the 5<sup>th</sup> day (Yildirim *et al.*, 2009).

Han *et al.* (2012) explored the use of zeolites for proton conducting membranes for PEMFC. The high proton mobility in HZSM-5 was exploited as a zeolite proton conducting membrane. Micro-fabrication and micromachining techniques were used to prepare the freestanding HZSM-5 micromembranes on a silicon support and the unit was assembled into a working MEA. It compared well with Nafion117 MEA under room temperature operation and a lower feed rate

common in micro fuel cell. The limitation of the membrane design and the relative brittleness of zeolites remained important obstacles. Alternatively, HZSM-5 was employed in the structured composite membrane for water regulation in PFSA (the proton transport in perfluorosulfonic acid). A rational approach was used to bring the various elements together to optimize their forms and functions. They successfully demonstrated that it was possible to achieve enhanced PEMFC performance even under harsh operating conditions, simultaneously to strengthen the membrane, and to reduce the PFSA amount in the composite membrane.

## 2.2 Polysulfone (PSF)

Nafion is widely used as the membrane material at present for both (PEMFC) and (DMFC) due to its high proton conductivity and good thermal and chemical stabilities. However, the high cost and the crossover of liquid methanol fuel from the anode to the cathode through the Nafion membrane have created interest in other non-fluorinated polymeric materials such as poly(ether ether ketone), polyimidazole, polyimide, and polysulfone as membranes for PEMFC and DMFC. These materials are easier to synthesize and less expensive compared to Nafion. More importantly, they usually exhibit lower methanol permeability than that found with Nafion.

Polysulfone (PSF) has many applications such as printed circuit boards, tubing, and battery separator (Fu *et al.*, 2006). It has excellent mechanical, thermal, and chemical stabilities. The sulfonated polysulfone have improved properties suitable for using in DMFC namely IEC, proton conductivity, and water uptake. Sulfonation is a method for the introduction of sulfonic acid functionality into the polymer backbone aiding the polymer to be more hydrophilic resulting in an increase in the transport of protons or proton conductivity (Fu *et al.*, 2006).



**Table 2.1** Proton conductivity and methanol permeability of polysulfone compared with Nafion in previous work

Polymer	25 °C RH100%	80 °C RH100%	25°C	Water uptake (%) at 25 °C	Water uptake (%) at 80 °C	References
	Proton Conductivity (S/cm)	Proton Conductivity (S/cm)	Methanol (cm <sup>2</sup> /s)			
PSf-sph-63	8.00E-03	2.20E-02	2.92E-07	6.6	12.8	(Zhu <i>et al.</i> , 2011)
PSf-sph-82	1.90E-02	4.50E-02	7.41E-07	12.1	24.5	
PSf-sph-100	4.40E-02	8.90E-02	1.15E-06	22.4	55.3	
PSf-sph-122	6.50E-02	1.43E-01	1.49E-06	25.9	76.6	
PSf-sna-32	1.10E-02	2.50E-02	3.60E-08	4.59	10.3	
PSf-sna-39	2.20E-02	5.10E-02	1.79E-07	9.29	19.8	
PSf-sna-49	4.10E-02	7.50E-02	3.01E-07	16.5	35.7	
PSf-sna-58	5.70E-02	1.17E-01	5.23E-07	20.3	45.7	
Nafion 115	9.00E-02	1.51E-01	1.68E-06	28.6	42.7	
SPSU-3	5.50E-03	-	1.50E-07	9.1	-	
SPSU-4	1.50E-02	-	2.50E-07	13.2	-	
SPSU-5	2.20E-02	-	3.30E-07	17.1	-	
SPSU-6	5.00E-02	-	6.00E-07	24.4	-	
SPSU-7	7.00E-02	-	7.50E-07	58.1	-	
SPSU-3-t	1.30E-03	-	5.00E-08	8.3	-	

SPSU-4-t	5.50E-03	-	1.00E-07	11.2	-	
SPSU-5-t	2.20E-02	-	1.25E-07	15.1	-	
SPSU-6-t	5.00E+02	-	2.25E-07	21.2	-	
SPSU-7-t	6.00E-02	-	4.55E-07	52.4	-	
PPSU-A-0.75	2.00E-04	1.40E-03	3.98E-08	27	28	(Abu-Thabit <i>et al.</i> , 2010)
PPSU-A-1.5	5.00E-05	6.00E-03	9.12E-08	52	55	
Nafion 117	5.00E-02	8.00E-02	6.80E-06			
SPSf57	8.30E-03	-	-	24.3		(Lufrano <i>et al.</i> , 2009)
SPSF66	2.80E-02	-	-	27.2		
SPSU 87	-	9.00E-02	-			(Chen <i>et al.</i> , 2005)
SPSU 127	-	1.40E-01	-			
sPS-15	4.00E-03	2.10E-02	-			(Devrim <i>et al.</i> , 2009)
sPS-25	7.00E-03	4.60E-02	-			
sPS-40	1.40E-02	1.20E-01	-			
SPSf90 *at 60 °C	0.5	-	-			(Lufrano <i>et al.</i> , 2011.)
SPSf *at 60 °C	2.4E-04	-	-			(Fu <i>et al.</i> , 2008)

Nafion 115	0.144	-	-			(Furtado Filho <i>et</i> <i>al.</i> , 2011)
Nafion 117	0.143	-	-			*At 65 °C

Polysulfone (PSU) was modified by attaching flexible sulfoalkyl side chains of various lengths in order to achieve higher-proton conducting polymers (Karlsson *et al.*, 2004). Even though the reactions were straight forward to carry out, the limited conversions in the sulfoalkylation step decreased the precision in the degree of substitution. The onset of thermal decomposition of the sulfoalkylated PSUs occurred slightly above 300 °C. The size of the sulfonic acid groups from the PSU backbone seemed to improve the swelling properties, as compared to directly sulfonated PSU. The sulfoalkylated polymers kept their dimensional stability when equilibrated in water up to temperatures ( $T_{crit}$ ) between 70 and 100 °C. This was believed to be a result of the hydrophilic–hydrophobic separation in these materials. The level of proton conductivity increased dramatically when  $T_{crit}$  was reached (Karlsson *et al.*, 2004).

Sulfonated polysulfone (SPSU) showed IEC more than twice that of Nafion-115. SPSFU was made with a sulfonation process using the trimethylsilylchlorosulfonate as the sulfonating agent. The silicon-containing compound formed during the synthesis of SPSU was completely removed from the SPSU by a simple evaporation. The proton conductivity of the SPSU increased with the relative humidity (RH) and exceeded the conductivity of Nafion-115 above 80% RH. The higher IEC promoted the conductivity of SPSU. Through pressing thin Nafion-115 layers on to both sides of SPSU membrane, a PEM fuel cell composite membrane—Nafion-layered SPSU was prepared. The Nafion layers on the SPSU served as a shield preventing the water-soluble SPSU from being washed out of MEA, and the membrane was stable during the fuel cell operation up to 120 °C (Chen *et al.*, 2005).

The characterization of sulfophenylated PSUs and PPSUs were shown in this work (Karlsson *et al.*, 2005). The thermal stability of these new ionomers were satisfactory, with the onset of degradation temperatures occurring between 300 and 350 °C. Equilibration of the membranes immersed in water at temperatures between 20 and 150 °C showed that these materials were improved in swelling properties as compared to other sulfonated aromatic polymers. The sulfophenylated PSUs and PPSUs showed a much higher degree of interaction with the water than Nafion, as shown by the differential scanning calorimetry (DSC) measurement. In addition, the more rigid molecular structure of the aromatic polymers probably also resulted in narrow channels in the membrane which confined the water to a higher degree than in Nafion. The conductivity of some of the sulfophenylated ionomers was retained at a constant high level at temperatures between 90 and 150 °C. Although the conductivity of the sulfophenylated ionomers was lower than for the Nafion 117 membrane under the same conditions, the latter membrane absorbed excessive amounts of water and lost its mechanical integrity at temperatures above 100 °C (Karlsson *et al.*, 2005).

The proton and methanol transport properties were investigated before and after annealing of SPSU membranes at sub- $T_g$ . The annealing of SPSU membranes led to the decreasing of water content, proton conductivity, and methanol permeability, as compared with SPSU membranes prepared at a lower temperature. This might be due to denser structure in the annealed SPSU membranes than in the untreated SPSU membranes. The annealing below  $T_g$  accelerated the stability of SPSU membranes and subsequently induced a more compact structure, which also affected the methanol permeability as well as the proton conductivity. This result exhibited the importance of a physical aging in the amorphous sulfonated glassy polymers on the proton conduction and the methanol transport (Park *et al.*, 2005).

Fu *et al.*, (2006) synthesized sulfonated polysulfones (SPSf) with different degrees of DS for 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 those of Nafion 115 due to a lower methanol crossover. The performances at high current density with high

concentration of methanol (2 M) were lower than those of Nafion 115 due to the lower proton conductivity.

The electrical conductivity of polyvinylidene fluoride (PVDF)–polysulfone (PSF) blend films was measured by studying the I–V characteristics in the temperature range of 298–398 K. The results showed the dependence of current on electric field, temperature, and blending compositions in the form of I–V characteristics. The analysis was made by the interpretations of the Poole–Frenkel plots, the Schottkyln ( $J$ ) vs.  $T$  plots, and the Richardson and Arrhenius plots. For individual polymers, the conduction mechanism was observed to be of a Poole–Frenkel type. On blending, the charge conduction appears to be the Schottky emission at lower temperature and the Poole–Frenkel mechanism at higher temperature. The results suggested that the Pool–Frenkel mechanism was mainly responsible for the observed conduction. The conductivity was found to increase with an increase in the polysulfone concentration in the blend (Saxena *et al.*, 2009).

Sulfonated polysulfones were obtained by employing 4-hydroxybenzenesulfonic acid sodium salt and 2-naphthol-6,8-disulfonic acid dipotassium salt and designated, respectively, as PSf-sph- $y$  or PSf-sna- $z$  (where  $y$  or  $z$  refers to the value of DS). Two series of polysulfone-based ionomers with sulfonic acid groups in the side chains had been synthesized by a facile two step process and characterized. The degree of sulfonation could be easily adjusted by controlling the degree of chloromethylation in the first step (the value of DS was calculated from  $^1\text{H}$  NMR data). Optimized polymer compositions exhibited a better performance in DMFC compared to Nafion 115 membrane despite lower proton conductivity because of lower methanol crossover. The various advantages associated with polymer composites namely low cost, high thermal and oxidative stabilities, low water uptake, and low methanol permeability made it an attractive alternate for DMFC (Zhu *et al.*, 2011).

PSF was sulfonated and fabricated as proton conducting polymer composite membranes based on sPS/TiO<sub>2</sub>. The degree of sulfonation was controlled by varying the molar ratio of the polymer to a sulfonating agent. Composite membranes were prepared using DMAC as the casting solvent and TiO<sub>2</sub> as the inorganic filler. TGA results showed the composite membranes had good thermal properties. The

introduction of the inorganic filler supplied the composite membrane with a good thermal resistance and improved the water uptake. Single fuel cell tests performed at different operating temperatures indicated that sPS/TiO<sub>2</sub> composite membrane was more stable hydrodynamically and also performed better than the sPS membranes. Membrane electrode assemblies (MEAs) were prepared by the gas diffusion layer (GDL) spraying method (Devrim *et al.*, 2009).

SPSU was successfully prepared using chlorosulfonic acid and trimethylsilylchlorosulfonate as sulfonating agents. SPSU with moderate water uptake, IEC, and proton conductivity values was prepared and the effect of reaction time on DS was studied (Unnikrishnan *et al.*, 2012). Sulfonation process significantly improved the water uptake and proton conductivity. As DS increased, the proton conductivity was also found to increase. Nanocomposite membranes were prepared using NMP as the casting solvent and C30B (porous material) as the inorganic nano-filler. TGA showed that the nanocomposite membranes have higher thermal stability than SPSU. It was noticed that, the increase in DS increased the T<sub>g</sub> value by the DSC analysis. The introduction of nanofiller improved the thermal resistance, water uptake, and proton conductivity of virgin and sulfonated PSU. The incorporation of C30B had a positive effect on the proton conductivity of the nanocomposite membranes. SEM micrographs confirmed homogeneous dispersion of C30B in SPSU thus leading to improved properties as observed in other studies. XRD studies also revealed that the complete exfoliation of the C30B in the polymer matrix (Unnikrishnan *et al.*, 2012).

Sulfonation process could improve the performance of polysulfonemembrane indicated by the contact angle, T<sub>g</sub>; and swelling (Chen *et al.*, 2001). The degree of sulfonation was improved with the increasing mole ratio of chlorosulfonic acid and the maximum degree of sulfonation was two sulfonic acid groups when the mole ratio was larger than 10. The contact angle decreased as the degree of sulfonate of membranes increased. The decrease of contact angle of membranes indicated that the hydrophilic of polysulfone was improved. The glass transition temperature of the membranes decreased with increasing degree of sulfonation. The result showed that the free volume of membrane increased with

increasing degree of sulfonation. The degree of swelling increased as the degree of sulfonation increased. That mean, the free volume was increased with the degree of sulfonation (Chen *et al.*, 2001).

The polysulfone was improved by various 1,3-dipolar cyclo addition of alkyne sulfonated, 1,7 octadiyne as a crosslinker and copper catalyst(Norris *et al.*). The methanol permeability decreased with increasing concentration of crosslinker while the proton conductivity increased. The MEA containing improved polysulfone showed a high power density ( $130\text{mW}/\text{cm}^2$ ) at  $25\text{ }^\circ\text{C}$ , when compared the power density of improved polysulfone and Nafion 117. The result showed the power densities of Nafion 117 and improved polysulfone were nearly the same(Norris *et al.*).

The sulfonated block copolymers of polysulfone, poly phenylene sulfide sulfone(PSf-co-PPSS) and polyether ether ketone (PEEK) were blended with tungstic acid to phosphoric acid (TPA) for reducing swelling form water at high temperature (Jang *et al.*, 2008) The result showed decreasing water uptake with the influence of TPA concentration in SPEEK/TPA and SPSf-co-PPSS/TPA membrane. The TPA content decreased the number of water absorption site and removed the hydrogen-bonded water molecules in the composite membranes. The proton conductivity of SPSf-co-PPSS/TPA membrane increased with increasing the TPA content, but the proton conductivity of SPEEK/TPA increased from 4 to 16% of TPA(Jang *et al.*, 2008).

Polytetrafluoroethylene (PTFE)/quaternized polysulfone composite membrane was made by immobilizing a quaternized polysulfone solution into a hydrophobic porous PTFE membrane(Li *et al.*). The conductivity of the composite membrane showed the highest value of  $0.3\text{ S cm}^{-1}$  with 400%  $\text{H}_3\text{PO}_4$  as doping level at  $180\text{ }^\circ\text{C}$ . The performances of the composite membrane increased with increasing temperature and oxygen partial pressure (Li *et al.*).

### 2.3 Polyvinylidene Fluoride (PVDF)

PVDF is used in many applications such as acid storage tanks, cables, tubing, and membrane. PVDF has been used due to its excellent mechanical properties, high chemical and weathering resistance, high temperature capabilities,

and good flexibility (Wootthikanokkhan *et al.*, 2006). PVDF can be fabricated as membranes. The methanol permeability values of PVDF are lower than that of Nafion because of the hydrophobic nature of PVDF. The aim of this work was to fabricate PVDF as membranes by sulfonation and to improve properties such as water uptake, ion exchange capacity, proton conductivity, methanol permeability, and the thermal properties of membranes (Wootthikanokkhan *et al.*, 2006).

Lehtinen *et al.*, (1998) compared the commercial Nafion 117 membrane to the PVDF-g-PSSA membranes which showed higher proton conductivity (at high degrees of grafting), a higher oxygen diffusion coefficient, and lower solubility of oxygen in the membrane. The PVDF-based membranes also absorbed water much more than that of Nafion, which might be a disadvantage because of the change in the membrane surface area and thickness during drying and swelling. On the other hand, a high water uptake from the vapor phase was beneficial as it might prevent the membrane from drying out during the operation of the fuel cell.

The strong hydrophilic sulfonate groups were introduced into the hydrophobic PVDF membrane with the binary monomers (AA/SSS) by high energy electron beam pre-irradiation (Liu *et al.*, 2006). AA was grafted into the membrane prior to SSS due to the better compatibility with the PVDF. Reaction conditions including binary monomer ratio and pH of reaction solution could regulate the degree of grafting. The surface chemical composition changes were confirmed by FT-IR-ATR and XPS, and the results were also supported by the SEM and AFM surface morphology. The contact angle decreased revealed the improvement of the hydrophilicity, indicating that the surface was well grafted by hydrophilic polymers (Liu *et al.*, 2006).

The PVDF-based composite PEM was prepared by an addition of ceramic powders and doping of PAMPS (prepared by spontaneous polymerization of AMPS aqueous solution). Using of a polymeric water-insoluble ionomer, likes PAMPS, in the membrane solved the problem of ionomer loss from the membrane and made it applicable in a DMFC. This composite membrane showed high thermal stability, high conductivity at room temperature, and low methanol permeability. The water uptake and proton conductivity increased with the content of alumina filler. Methanol permeation was reduced at high alumina filler contents. The membranes



with high alumina filler contents were shown to be promising for using in the DMFC due to their high  $\Phi$  values (Shen *et al.*, 2006).

The methanol crossover of a sulfonated polymer such as SPEEK could be effectively reduced by blending with PVDF. The methanol resistance of the SPEEK/PVDF membranes increased with the PVDF content at the expense of their ion exchange capacities and proton conductivities. The optimum blending ratios for SPEEK/PVDF membranes, which provided compromised proton conductivity and methanol permeability, ranging between 50/50 and 90/10% w/w (Wootthikanokkhan *et al.*, 2006).

Membranes of sPEEK/PVDF blends with different compositions were prepared by casting solutions (Jung *et al.*, 2007). The blends were only compatible in the limited range of composition due to the high hydrophobic characteristic of PVDF in the blend. The blend could produce good ion conduction channels, leading to the high-proton conductivity. The dimensional stability of the membrane could be also enhanced by introducing PVDF with high hydrophobic character. These could contribute to high performance of the cell based on the blended membrane. This simple hydrocarbon blend membrane with the advantage of lower cost is suggested to be very promising for practical applications in direct methanol fuel cell (Jung *et al.*, 2007).

Biomimetic electro-active polymers were based on the SPEEK and the SPEEK/PVDF (Jeon *et al.*, 2009). The SPEEK/PVDF-blend film was better than the pure SPEEK membrane with respect to their chemical, mechanical, and electrical properties. The straightening-back phenomenon did not appear in the step responses of the SPEEK/PVDF actuator. Both the step and harmonic responses of the SPEEK/PVDF actuator showed much larger displacements than those of the pure SPEEK actuator. Also, the blocking force of the SPEEK/PVDF actuator was larger than that of the SPEEK actuator. The results validated the use of SPEEK and SPEEK/PVDF as electro-active polymers and confirmed that the SPEEK/PVDF-blend could be adjusted to give better actuation performances by controlling the swelling ratio through the compositions of SPEEK and PVDF (Jeon *et al.*, 2009).

PVDF nanofibers were prepared by using the electrospinning method. In order to improve the capacity performance of the membrane, the PS/PVDF

membranes were prepared by pored filling and the SPS/PVDF membranes were then manufactured successfully by introducing sulfonate ( $-\text{SO}_3\text{H}$ ) groups using sulfuric acid. Sulfonate groups in the network could be confirmed through EDS, FTIR, and SEM. By controlling the concentration of PS, characteristics were comparable to those of Nafion, which had water uptake, IEC, and electrical conductivity values suited for the PEMFC application, could be observed in the modified membranes. In particular, not only water uptake values (90–550%) were much higher than that of Nafion 115, but also IEC values were more than double that of Nafion 115. In MEA tests, for the SPS/PVDF membranes pore-filled with 15 wt% PS, the results were almost similar to those of Nafion (Jang *et al.*, 2011).

Thermal polymerization of styrene adsorbed into PVDF films from a styrene solution at 90 °C was shown to be a simple method of introducing and fixing a polymer dopant in a fluoro polymer matrix, whose subsequent sulfonation made the film a proton conducting membrane (Abdrashitov *et al.*, 2011). The water, methanol, and hydrogen permeability coefficients and their dependences on the introduced PS content, ion exchange capacity, and membrane water uptake were measured. According to the main transport characteristics, the synthesized membranes were comparable to Nafion type perfluorinated membranes, but methanol permeability was 1.5–1.8 times lower than that of Nafion type perfluorinated membranes (Abdrashitov *et al.*, 2011).

The proton exchange membrane (PEM) was prepared with PVDF and perfluorosulfonic acid (PFSA) as precursors for semi-interpenetrating polymer network (IPN) with 1, 3-benzenedisulfonyl azide (1, 3-BDSA) as crossing agent. The crossing structure of PVDF was formed, and semi-IPN was constructed at PFSA with hydrogen abstraction reaction of 1,3-DBSA and recombination together. The performance of semi-IPN membranes was characterized and compared with pure PFSA membrane. The result showed the tensile strength of composite membrane was much higher than pure PFSA membrane. The power density of composite membrane was improved to maximum at 382 mW cm<sup>-2</sup> at 940 mA cm<sup>-2</sup> (Zhao *et al.*).

Direct blending of polyvinylidene fluoride-hexafluoro propylene with silica sulfuric acid was made for using as proton exchange membrane in DMFC (Gnana kumar *et al.*). The silica sulfuric acid with the PVdF- HEP polymer made a porous

structure in the composite membrane. The porosity was introduced from the steric repulsion of hydrophilic silica sulfuric acid and hydrophobic PVdF-HEP in the composite membrane. PVdF-HEP hydrophilicity was improved silica sulfuric acid. The hydrophilicity of the composite membrane was made from ion channels which increases ion conductivity but introduced devious pathways for methanol to transport (Gnana kumar *et al.*).

Nafion and PVDF were mixed to fabricate blend membranes and to decrease water affinity. The PVDF was modified by adding various Nafion content. The proton conductivity of Nafion/PVDF blend membrane was lower than pure Nafion from non-conducting of PVDF component. The value of proton conductivity depended on the water retention. The water uptake of blend membranes showed an increase with increasing Nafion fraction. The maximum power of blend membrane was  $440 \text{ mWcm}^{-2}$  at  $900 \text{ mAcm}^{-2}$  without any auxiliary conductive filler (Song *et al.*, 2003).