CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

Fuel cell is an electrochemical device that continuously converts chemical reaction to electric energy. The system consists of two electrodes. which are negative electrode (anode) and positive electrode (cathode), and a membrane in between. The oxidation occurs at the anode side while the reduction occurs at the cathode side. Direct methanol fuel cell (DMFC) is the one type of proton exchange membrane fuel cell (PEMFC) which has a simple system design because it uses methanol as a fuel and air to supply electrode. DMFC is less toxic due to the by product from the reaction are water and a very small amount of carbon dioxide.

2.1 Direct Methanol Fuel cell (DMFC)

2.1.1 Principal of DMFC

A direct methanol fuel cell (DMFC) is a special form of low-temperature fuel cells based on PEM technology. It operates at temperature similar to PEMFC although it is usually operated at slightly higher temperatures in order to improve the power density. 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 natural gas or renewable biomass resources. It has the advantage of a high specific energy density since it is liquid at operating conditions. The DMFC generally uses a diluted methanol in water mixture (typically 1-2 molar) and only a fraction of methanol is used at the anode. The methanol is introduced to the PEM fuel cell to initiate the chemical reaction resulting in electricity and by products, which are small amounts of water and carbon dioxide (Carrette *et al.*, 2001). The DMFC has the potential to substitute the battery because methanol has superior specific energy density in comparison to the rechargeable batteries. These characteristics mean longer operation times 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 cartridge replacement. Unlike rechargeable batteries, which require 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 over a wide temperature range (-97 °C to 64.7 °C).

At the present, there are many research works which are concentrated on PEM technologies. The membranes used in DMFCs are being developed for the PEM applications (optimizing the proton conductivity and methanol permeability are the priority). However, these membranes still have shortcomings regarding methanol blocking. Due to the similar properties of methanol as compared to water (e.g., dipole moment), methanol molecules and 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 crossover depending on a number of factors; the membrane permeability, thickness, the concentration of methanol in the fuel feed, the operating temperature, and the performance of the anode itself. On the other hand, the proton movement in the membrane is associated with the water content in the membrane. Therefore, the water content in the membrane is one considerable factor.

2.1.2 Nafion Commercial Membrane

A major discovery in the field of PEM fuel cells comes with the use of Nafion or perfluorosulfonic acid (PFSA) polymer membranes, which were produced by Dupont. The Nafion membrane is relatively durable (long life > 60,000 h in the PEMFC) and has high ionic conductivity. The structure of Nafion is shown in Figure 2.1. The hydrophobic polytetrafluoroethylene (PTFE) backbone of Nafion provides thermal and chemical stability, whereas, the perfluorinated side chains terminating with hydrophilic sulfonic acid (–SO3H) provides the channels for proton transportation. However, its high cost, high methanol permeability, and low proton conductivity or cell performance under low humidity or high temperature operating conditions, have limited its commercialization in DMFC and prevented it from being used in large scale applications (Lufrano *et al.*, 2007 and Choi *et al.*, 2010).

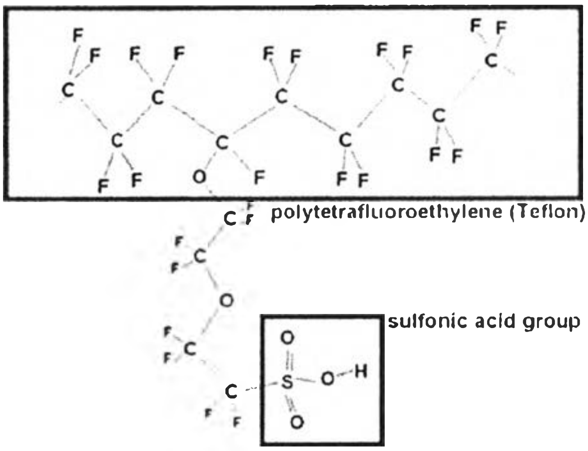

Figure 2.1 Nafion's molecular structure, which is a copolymer of a Teflon backbone and sulfonyl groups (Das, 2013).

Recently, methanol crossover is the biggest challenge faced by DMFC designers as it has the most effect on the cell performance. Several common approaches to prevent it in terms of membrane modifications is currently being studied (Kamarudin *et al.*, 2009).

2.1.3 Modified Polymeric Membrane

There are many researches efforts on the development of alternative membranes, which should be cheaper than Nafion, similar or higher conductivity, and lower methanol crossover in the temperature ranges from 20 to 100 °C (Carrette *et al.*, 2001). The alternative polymeric membranes are currently prepared from non-perfluorinated polymeric materials, such as poly(etheretherketone), poly(vinyl alcohol), poly(vinylidene fluoride), polyimide, polybenzimidazole and polysulfone, for improving DMFC performance.

Sulfonated poly(etheretherketone)s with various degree of sulfonation (DS) values were successfully prepared by using concentrated sulfuric acid. Their water uptake, swelling ratio, ion exchange capacity and absorbed water molecules per sulfonic functional group (λ) were studied. Proton conductivities of the SPEEK membranes generally increased with the increasing of DS (from 0.59 to 0.93) and temperature (from 22 to 90 °C). In addition, SPEEK membranes with higher DS start to lose conductivity at higher temperature. This point suggests that the ability of retaining water was very important at high temperature. Methanol permeabilities of the SPEEK membranes were all lower than that of Nafion 117 membrane. The methanol permeability and swelling ratio were dependent on temperature and the concentration of methanol. The proton conductivities at 22 °C were not higher than that of the Nafion 117 membrane, but higher selectivity values were found for the SPEEK membranes (Xue *et al.*, 2006).

Polymer nanocomposite membranes based on sulphonated poly(ether ether ketone) (SPEEK) containing different weight percentages of synthetic non-spherical nanofillers such as laponite and MCM-41 were prepared and characterized for DMFC. Prior to the preparation of the composite membranes, they were modified using organo silanes. The results showed that there was a decrease in methanol and water permeability with increasing content of modified laponite and MCM-41. While the membranes containing higher (>10) weight percentages of silicates displayed lower proton conductivity values than the plain polymer, which can be related to the permeability, the lower percentages of fillers showed higher selectivity values than the plain (Karthikeyan *et al.*, 2005).

Proton conducting nanoporous membranes based on polyvinylidene fluoride (PVDF) were prepared by re-adapting a procedure used in the lithium battery technology. The performance of the membranes was optimized by the dispersion of SiO_2 ceramic powder at a nano particle size. Indeed, nanoporous composite membranes had promising features, such as high conductivity combined with low methanol permeability. These membranes had a limited thermal stability due to the release of the liquid component. Moreover, the average swelling and methanol crossover of these membranes increased with increasing of SiO_2 due to an increase in porosity. However, the transport and the physical properties made these membranes attractive for some special applications, such as low temperature fuel cells for portable electronics (Croce *et al.*, 2006).

Jung *et al.*, (2007) prepared the polymer blends based on SPEEK/PVDF with different compositions for the membrane in DMFC. The blends were only compatible in the limited range of composition due to the high hydrophobic characteristic of PVDF in the blend. The blend membranes showed good compatibility within a limited composition range of less than around 10 wt% of PVDF. 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 to direct methanol fuel cell.

Lin *et al.*, (2009) studied the nitrated SPEEK membranes that were prepared by simple substitute reaction with the incorporation of nitro groups into SPEEK. They found that the nitrated SPEEKs had a lower glass transition temperature and thermal decomposition temperature and a lower water uptake than SPEEK. This provided sufficient mechanical strength without swelling in the DMFC as they had more hydrophobic nitro groups and the formation of ionic clusters. Furthermore, the methanol permeability was suppressed without loss of conductivity as compared with the SPEEK membranes because the addition of nitro groups caused a different distribution of ion channels in membranes that provided more effective phase separation morphology. The nitrated SPEEK membranes also showed superior single-cell performance owning to the relatively low methanol permeability and the higher maximum power density. Thus, the nitrated SPEEK membranes are satisfactory as the PEM for the DMFC.

Blend membranes consisting of SPEEK (an acidic polymer) and polysulfone-4-nitrobenzimidazole (PSF-NBIm) (a basic polymer) were prepared with various PSF-NBIm contents (0-5 wt %). The blend membranes exhibited better electrochemical performances and lower methanol crossover in DMFC than pure SPEEK due to an enhancement in proton conductivity through acid-base interactions and an insertion of benzimidazole side groups into the ionic cluster of SPEEK, leading to larger ionic cluster size which assisted the proton transfer. They also showed lower liquid uptake in water and water/methanol solutions resulting from the hydrophobicity and methanol blocking of the PSF-NBIm groups. Finally, they suggested that the pK_a may play an important role in tuning the properties and performances of acid-base blend membranes (Li *et al.*, 2009).

PVA membrane for DMFC was modified for the chemical structure by sulfonation, using sulfosuccinic acid as a sulfonating agent which induced the proton conductivity. The PEM was prepared through the mixing of PVA with various amounts (2, 4, and 5% w/w) of sodium montmorillonite layered silicate nanoclay. The water uptake, proton conductivity, and methanol permeability initially decreased after the 2 wt% of layered silicate was added. This was related to the mobility of sulfonated PVA the light of interaction between clay and sulfonated PVA, the steric effect providing the exfoliation of nanoclay, and change in the degree of crystallinity of polymer with the nanoclay content. The tensile strength of the membrane increased remarkably after the nanoclay was added because of the reinforce effect. The elongation at break of the membrane also increased with the clay content, which could be related to the decrease in the crystallinity of polymer. The best membrane with respect to the maximum selectivity was obtained from the membrane containing 2% (w/w) nanoclay (Duangkaew *et al.*, 2008).

Yang *et al.*, (2009) synthesized a novel composite PEM composed of a PVA and montmorillanite (MMT) ceramic fillers by using solution casting method and then crosslinked by an immersion in a solution of 5 wt% of glutaradehyde (GA) and acetone at 40 °C for 12 h. The PVA/MMT composite polymer membrane showed good thermal and mechanical properties due to the additive effect of the MMT fillers and chemical crosslinking reaction between the –OH group on the PVA and –CHO group on the GA and also showed high ionic conductivity. The permeability values and swelling ratio of all membranes were lower than those of the Nafion 117 membrane. Therefore the addition of the hydrophilic MMT filler to the PVA polymer matrix not only facilitated a reduction of the Tg but also increased its ionic conductivity as the MMT in the polymer matrix created some defects or amorphous domains at the interface between the ceramic particle and polymer chain, an increase in ionic conductivity occurred.

The proton conducting composite membranes based on the PVA, titanium oxide nanotube (nt-TiO_2), and poly(styrene sulfonic acid) (PSSA) blends were prepared by a solution casting method. It was found that the methanol permeability of the PVA/nt-TiO_2/PSSA composite membranes was lower than that of the Nafion 117 membrane. The storage modulus of the PVA/nt-TiO_2/PSSA composite membranes increased with increasing nt-TiO_2 filler loading up to 5wt%. At the higher nt-TiO_2 filler loading (10wt %), the storage modulus decreased due to the poor dispersion of nt-TiO_2 which indirectly resulting in poor physiochemical properties. The highest peaks# power density of the DMFC was realized with 2M methanol fuel. Moreover, the peak power densities at ambient temperature conditions were in this order of 2M methanol > 1M methanol > 4M methanol. The electrochemical performances of DMFC with PVA/5wt%nt-TiO_2/20wt%PSSA composite membrane were several times greater than that of the DMFC with Nafion 117 membrane, both with 2M methanol fuel and at ambient conditions. However, the electrochemical performance of the DMFC with 4M methanol fuel was poor due to the higher methanol crossover rate (Yang *et al.*, 2010).

The titania submicrospheres with sulfonic acid groups (TiO_2-SO_3H) on their surfaces were synthesized through a facile and fast surface-functionalization via chelation reaction. After that the sulfonated titania submicrospheres were incorporated into SPEEK matrix to get a series of SPEEK/TiO_2–SO_3H hybrid membranes. The modification TiO_2 with sulfonic acid groups improved the interfacial compatibility between the inorganic filler and the polymer matrix, which was confirmed by FESEM images which showed that no obvious TiO_2–SO_3H agglomeration occurred and fillers were homogeneously distributed within the SPEEK matrix. It was found that the hybrid membranes showed an increase in mechanical strength with increasing TiO_2–SO_3H content. The SPEEK/TiO_2–SO_3H hybrid membranes also displayed higher proton conductivity and lower methanol permeability, resulting in a higher selectivity in comparison to the pristine SPEEK membrane and the SPEEK/TiO_2 membrane (Xu *et al.*, 2011).

A S-PEEK membrane with DS of 63% was modified by adding various amounts of Cloisite15A® clay. The S-PEEK mixed with 2.5 wt% of Cloisite15A® (SP63/2.5Cl) was identified as the best composite formulation in this study because of its high selectivity. Subsequently, various amounts of 2,4,6-triaminopyrimidine (TAP) as a compatibilizer were further incorporated into SP63/2.5Cl formulation. A complete exfoliated nanocomposite structure of SP63/2.5Cl/5.0TAP was confirmed by X-ray diffraction (XRD). The increase of Cloisite15A® content in the S-PEEK membrane dramatically improved the swelling behavior and methanol barrier properties. Furthermore, SP63/2.5Cl/5.0TAP membrane showed superior performances in DMFC when compared to the Nafion 112. It was suggested that to overcome dispersion problem normally found in commonly used clay, a compatibilizer was recommended for better adhesion between the polymer matrix and the clay in order to get good dispersion (Jaafar *et al.*, 2011).

A new PEM composite membrane comprising of PVA, sulfonaic acid functionalized CNT and fluorinated MMT was prepared by simple solution casting method with sulfosuccinic acid as a crosslinking agent. The polymer membrane showed good thermal properties as T_d increased from 285 to 410 °C with the chemical crosslinking and addition of the inorganic nano filler. The proton conductivity increased with increasing temperature and the content of crosslinking agent but was still low when compared to other membranes due to low level of sulfonic group in MWCNT and crosslinking agent in the membrane. The water content was in the range of 35-45 %, which exhibited higher water uptake owing to the high hydrophilic nature of the crosslinking agent. Especially, it was found that the fluorinates MMT used in this study played an important role in water uptake and acts as a hydrophilic surface for controlling the swelling. The methanol permeability was rather high compared to other type of PVA membrane because of the crack on the surface, as shown on the SEM image. MMT did not act as a blocking material for methanol transport in this study owing to their agglomeration (Maiti *et al.*, 2011).

The sulfonated PEEK and poly(1,4-phenylene ether ether sulfone) (PPEES) samples were prepared from 98 % sulfuric acid at different reaction times to fabricate S-PEEK and S-PPEES membranes at various DS for vanadium redox flow batteries. 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 because the membrane became more hydrophilicity which absorbed more water and increased the proton transfer through the membrane. On the other hand, an increase in DS also induced a decrease in the mechanical properties of the membranes, as the increase in the water uptake led to a decrease in mechanical strength. The S-PEEK and S-PPEES membranes showed lower vanadium ion permeability values than that of the Nafion 117 membrane (Macksasitorn *et al.*, 2012).

2.2 Polysulfone

2.2.1 Polysulfone (PSF)

PSF is an amorphous high-performance polymer with excellent thermal and chemical stabilities, good resistance to inorganic acids and bases, and outstanding hydrolytic stability against hot water and steam sterilization. Membrane based on polysulfone was preferred for applications involving water purification and gas separation (Zhu *et al.*, 2011).

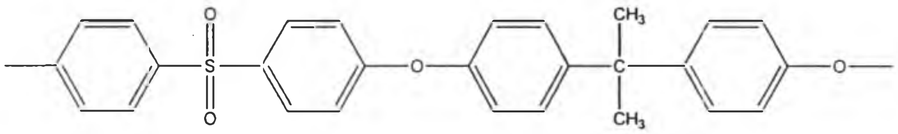

Figure 2.2 Structure of polysulfone (PSF).

2.2.2 Applications of PSF

The ultrafiltration membrane was prepared as a composite of spray dried silica granule blended with polysulfone, where N-methyl-2-pyrrolidone (NMP) or N, N-dimethyl formamide (DMF) was used as a solvent for the composite material. The polymer-nanocomposite membrane showed significant enhancement of water permeability due to the available interstitial pore channels in spray dried granules present in the composite membranes and kept the separation characteristics intact or even marginally improved at the same time. This is because of the fact that wherever spray dried granules were exposed at the surface; they induced a lower contact angle compared to only PSF. The another reason was the granules remained deeper inside the surface in case of PSF-NMP compared to that of PSF-DMF case which increased the permeability (Sen *et al.*, 2014).

Liu *et al.*, (2014) prepared PSF ultra filtration membranes by incorporating specific zeolite 4A to break through the tradeoff between permeability and selectivity including the pure water flux and protein rejection. The results showed that zeolite 4A were precisely embedded in the selective layer and offered abundant fast nano-scale water flow paths (0.5-0.8 nm) in both nano channels and free volumes. The embedding of zeolite 4A caused a denser, rougher, negatively charged surface with smaller pore size, which ensured the high protein rejection. Furthermore, all modified membranes showed good thermal and mechanical stability. The hydrophilicity and fouling resistance were also improved for some extents.

Junaidi *et al.*, (2013) synthesized the asymmetric PSF mixed matrix membranes incorporated with SAPO-34 zeolite, which had a small pore size, for CO_2 separation in natural gas industry due to high CO_2 adsorption of SAPO-34. The asymmetric mixed matrix membranes were prepared by using the phase inversion method. The results showed that the prepared MMMs showed gas permeation in the order of $CO_2 > CH_4 > N_2$ and hence the PSF/SAPO-34 membrane with 10 wt% SAPO-34 loading showed the highest separation performance enhancement on CO_2/N_2 and CO_2/CH_4 gas pair, when compared to the pure PSF membrane. For the higher SAPO-34 loadings (20 wt% and above), the gas permeation properties of MMMs were disturbed by the large interfacial voids across the membrane surface due to the agglomeration of zeolite particles. The resistance of larger molecule gasses was greatly reduced, which was confirmed by SEM images and TGA curves. The reduction of thermal stability of all membranes exposed the poor interfacial interaction between PSF matrix and SAPO-34 zeolite.

2.2.3 Sulfonation of PSF Membranes

Although much effort has been focused on modified PSF to suit fuel cell applications, most of them involved direct sulfonation of the backbone. Sulfonation process is a method for the introduction of sulfonic acid functionality to the polymer backbone in order to aid the polymer to be more hydrophilic resulting in an increase in the transport of protons or proton conductivity (Fu *et al.*, 2006). The sulfonated PSF (S-PSF) will have improved properties suitable for use in DMFC such as ion exchange capacity (IEC), proton conductivity, and water uptake.

PSF was modified by attaching flexible sulfoalkyl side chains of varying lengths in order to achieve higher proton conducting polymers. Even though the reactions were straightforward to carry out, the limited conversions in the sulfoalkylation step decreased the precision in the degree of substitution. The polymers were prepared through lithiation and sulfonation of PSF, followed by grafting of sulfoethyl, sulfopropyl, or sulfobutyl chains into the sulfonate units of polymer. The results also implied that the PSF with the sulfoethyl side chains in addition had some sulfonic acid groups directly attached to the PSF backbone. These limitations may be overcome by optimizing the reaction conditions by, for example investigating the influences of the reaction medium and temperature. The onset of thermal decomposition of the sulfoalkylated PSFs occurred slightly above 300 °C. The spacing of the sulfonic acid groups from the PSF backbone seemed to improve the swelling properties, as compared to directly S-PSF. 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 passed (Karlsson *et al.*, 2004).

The characterization of sulfophenylated PSFs and polyphenylsulfones (PPSFs) were synthesized by lithiation, followed by reaction with 2-sulfobenzoic acid cyclic anhydride. The resulting ionomers were cast into the membrane. The thermal stability of these new ionomers was satisfactory, with the onset of degradation temperatures occurring between 300 and 350°C. These membranes showed the improvement in swelling properties as compared to other sulfonated aromatic polymers because of these membranes endured immersion in water at temperatures between 20 and 150 °C without swelling and kept their mechanical stability. Furthermore, the sulfophenylated PSFs and PPSFs showed a much higher degree of interaction with the water than Nafion, as shown by the DSC measurements. The more rigid molecular structure of these aromatic polymers also resulted in narrow channels in the membrane which confined the water to a higher degree than in Nafion; this led to increasing proton conductivity up to 90 °C. 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. Therefore, the latter membrane absorbed largely amounts of water and lost its mechanical at temperatures above 100 °C (Karlsson *et al.*, 2005).

Fu *et al.*, (2006) synthesized S-PSF with different degrees of sulfonation (DS) for DMFC by using a mild sulfonation process. The ion exchange capacity (IEC), proton conductivity, water uptake, and single DMFC polarization were measured. The results showed that the proton conductivity and methanol crossover increased with increasing DS but the former?? was still lower than that of Nafion 115. The conductivity of the S-PSF membrane also increases with increasing temperature. The liquid uptake increased with the DS, temperature, and methanol concentration increase. S-PSF membranes within the range of 50–70% DS exhibited better performances comparable to those of Nafion 115 at lower methanol concentrations (1 M) due to lower methanol crossover. The performances at high current densities with high concentrations of methanol (2 M) were lower than that of Nafion 115 as the reduction in methanol crossover could not compensate for the lower proton conductivity.

Vernersson *et al.*, (2006) synthesized the sulfophenylated polysulfone (PSU-SPH), carrying 0.8 sulfonaic acid units per repeating unit of the polymer;it was evaluated as a membrane electrolyte for DMFC applications. The PSU-SPH membrane showed superior methanol crossover, with a methanol permeability of only 25% of Nafion 117 under similar conditions. The liquid uptake was about one third that of Nafion 117. However, it has been reported that water in sulfonated aromatic polymer membrane was confined in more narrow channels, thus lowering the water transport by lowering electro-osmotic drag. Moreover, the PSU-SPH membrane showed a significant lower conductivity than Nafion 117. When the methanol feed concentration increased, the conductivity would be decreased as methanol has lower ion conduction properties than water. In contrast, the higher degree of PSU-SPH sulfonation should have a significantly positive effect on cell performance, as the conductivity increases with increased ion exchange capacity. The stability of the PSU-SPH membrane showed the promising results with very low degradation over a period of 72 h. It was concluded that although the mass transport properties of PSU-SPH membrane were superior, but it could not match the performance of Nafion 117 in DMFC application.

Kim *et al.*, (2008) studied the polymer blend membranes of sulfonated poly(arylene ether sulfone) copolymer, with a sulfonation of 60 mol% (SPAES-60), and nonsulfonated poly(ether sulfone) copolymer (RH-2000). Transport properties of blend membranes with various morphologies induced by different drying conditions were measured and analyzed on basis of absorbed water molecules. It was explained that both proton conductivity and methanol permeability could be related with the number of free water molecules. The well-developed structure was a co-continuous morphology (Group IV) could be obtained. SPAES-60 and RH-2000 were three-dimensionally connected and hydrophilic and hydrophobic channels were also connected. Although the methanol permeability increased, hydrophilic channels facilitated proton movement and a hydrophobic network also restricted the free flow of large size methanol molecules through the membrane. When the highly sulfonated copolymer (SPAES-60) formed a co-continuous morphology with nonsulfonated hydrophobic copolymer (RH-2000), the selectivity was maximized, and even at high temperature excellent selectivity was maintained by the restriction of hydrophilic channels by neighboring continuous hydrophobic phase. Thus, in order to enhance the blend effect, co-continuous morphology is considered to be good alternative membrane in DMFC applications.

Two series of PSF-based ionomers with sulfonic acid groups in the side chains have been synthesized by a facile two-step process and characterized. The S-PSF was obtained by using 4-hydroxybenzenesulfonic acid sodium salt and 2-naphthol-6,8-disulfonic acid dipotassium salt were designated, respectively, as PSF-SPH-Y or PSF-SNA-Z (where Y or Z refers to the value of DS) after chloromethylation of PSF. The DS could be easily adjusted by controlling the degree of chloromethylation, which determined how many sulfonated group can be located, in the first step. The presence of sulfonic acid groups increased the intermolecular interactions and molecular bulkiness, which hindered the rotation of high molecular chain segments, leading to increased T_g. The water sorption increased with increasing IEC, DS, and temperature. Optimized polymer compositions such as PSF-SNA-58 exhibited 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 such as low cost, high thermal and oxidative stabilities, low water uptake, and low methanol permeability make it an attractive alternate for DMFC (Zhu *et al.*, 2011).

2.2.4 Modified PSF Membrane

Despite offering much strength, the DMFC also has some limitations, including poor adhesion between the membrane and electrodes, low activity of the electrodes, and crossover of unreacted methanol through the membrane. Methanol crossover induces an unexpected drop in the open circuit voltage because performance losses at the cathode due to the mixed potential effect and catalytic poisoning, and therefore the overall efficiency of the system decreases. Various solutions of these problems have been proposed, such as synthesis of cost-effective alternative polymers and blending of organic-inorganic compounds (Kim *et al.*, 2008).

Lufrano *et al.*, (2006) developed the composite membranes modified with silica filler. The S-PSF samples were synthesized by a mild sulfonation process using trimethylsilylchlorosulfonate as a sulfonating agent. The composite membranes with 5 wt% of silica filler tested in DMFC gave a maximum power density of about 180 mW cm^{-2} at 120 °C. Thermal analysis measurements showed an increase in T_g with the increasing DS of polymer. Moreover, it also was found that at about 220-250 °C the desulfonation process started. Proton conductivities of the membranes were about 5×10^{-2} S cm^{-1} at 90 °C suitable for use in DMFC applications.

The synthesis of S-PSF was also prepared by a post sulfonation method using trimethylsilyl chlorosulfonate as a mild sulfonating agent, with two different degrees of sulfonation (60%, S-PSF-60 and 70%, S-PSF-70). A composite membrane of S-PSF-60 was prepared with 5 wt% silica filler. These membranes were investigated for DMFC operating at low (30-40 °C) and high temperatures

(100-120 °C). The thermal analysis measurement of S-PSF showed an increasing in T_g with increasing DS while the thermal stability of S-PSF showed lower thermal stability than pure PSF due to the introduction of bulky sulfonic acid groups in polymer. When silica filler was added, the desulfonation peak of composite membrane was slightly increased. It was attributed to the interaction of silica particles with the polymer matrix. The increase in cell temperature produced a decrease in cell performance and unstable behavior due to dehydration of the membrane. This can also increased the methanol crossover in the membrane because as the temperature increased, the methanol oxidation kinetics were enhanced but they were generally associated with higher power density (Lufrano *et al.*, 2008).

PSF was sulfonated with trimethylsilyl chlorosulfonate in 1,2-dichloroethane at ambient temperatures and fabricated as proton conducting polymer composite membranes with TiO_2 (SPSF/TiO_2) by solution casting process. The DS was controlled by varying the molar ratio of the polymer to a sulfonating agent. The thermal analysis results showed the composite membranes to have good thermal properties. The introduction of the inorganic filler supplied the composite membrane with a good thermal resistance because the introduction of SO_3 groups increased the intermolecular interactions by hydrogen bonding and molecular bulkiness. The interactions hindered the inter rotation of high molecular chain segments and led to increased T_g of SPSF, and improved the water uptake because the presence of TiO_2 in the membrane reduced the membrane free volume and swelling ability. Proton transfer was enhanced by increasing the number of acid sites or DS. Single fuel cell tests performed at different operating temperatures indicated that SPSF/TiO_2 composite membrane was more stable hydrodynamically and also performed better than the SPSF membranes because TiO_2 reduced fuel crossover and ionic resistance. Also, TiO_2 actsed both as a mechanical reinforcement and kept water necessary to proton conduction (Devrim *et al.*, 2009).

The electrical conductivity of polyvinylidene fluoride (PVDF) – 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 electrical field, temperature, and blending compositions in the form of I–V characteristics. The analysis was made by the interpretation of the Poole–Frenkel, Schottkyln (J) vs. T plots, Richardson and Arrhenius plots. For individual polymers, the conduction mechanism was observed to be of a Poole–Frenkel type. For blending, the charge conduction appeared to be the Schottky emission at lower temperature and the Poole–Frenkel mechanism at higher temperature. The analysis of these results suggested that the Pool–Frenkel mechanism was mainly responsible for the observed conduction. The SEM images of its blend showed the amorphous phase of PSF which was partially filling the original porous space of the pure PVDF, affecting the size or the perfection of the polymer crystal. The conductivity increased with an increasing in the PSF concentration of the blend sample due to the releasing of charge carriers from traps, or better mobility through amorphous PSF regions (Saxena *et al.*, 2009).

The composite membranes, based on S-PSF and acidic silica filler, reacted with chlorosulfonic acid under stirring at room temperature for 30 min before solution casting. The composite membranes, based on S-PSF and modified silica, showed satisfactory proton conductivity, low methanol crossover and low swelling compared to the composite membranes based on S-PSF and bare silica and prisitne S-PSF membrane. This was attributed to a better distribution of acidic silica than bare silica as well as a higher ionic conductivity of acidic silica. The highest performance of 60 mW cm^{-2} in single cell at 60 °C with air feed was obtained with the composite membranes based on S-PSF and acidic silica. Therefore, this membrane could be considered as a new highly promising material to be used as a PEM in DMFC applications (Lufrano *et al.*, 2012).

The effects of chlorosulfonic acid and trimethylsilyl chlorosulfonate, used as sulfonating agents, on the performance of PSF were investigated. Both sulfonating agents showed a similar trend in the results. They found that the proton conductivity increased with increasing DS. The water uptake also increased with increasing of DS due to the hydrophilic domains had become continuous and formed large channels resulting in increased water uptake capacity. It was noticed that, both the effects of hinder the internal rotation of molecules and secondly increased molecular bulkiness led to an increase in T_g for the sulfonated polymers. Nanocomposite membranes were prepared using NMP as the casting solvent and C30B as the inorganic nanofiller. Thermalgravimetric analysis (TGA) showed a decrease in decomposition temperature after sulfonation, and the nanocomposite membranes had higher thermal stability than S-PSF. The introduction of nanofiller improved the thermal resistance, water uptake, and proton conductivity of virgin and S-PSF. The incorporation of C30B had a positive effect on the proton conductivity of the nanocomposite membranes because of increasing pore size and pore density, creating sufficient the number of channels for proton conductivity. SEM micrograph confirmed homogeneous dispersion of C30B in S-PSF thus led to improve their properties. XRD studies also revealed that the complete exfoliation of the C30B in the polymer matrix (Unnikrishnan *et al.*, 2012).

Herrero *et al.*, (2013) prepared the composite membranes consisting of S-PSF and layered double hydroxide (LDH) for use in PEMFC. PSF was sulfonated with trimethylsilylchlorosulfonate in 1,2-dichloroethane at room temperature for different DS, and the membranes were prepared by casting method. The sulfonation process was confirmed by FTIR spectra. It showed the characteristic peaks at 3400 cm^{-1} and 1014 cm^{-1} which can be assigned to the stretching O-H vibration of the $-SO_3H$ group and symmetric stretching O=S=O vibration of $-SO_3H$ group. The sulfonation of PSF reduced the thermal stability of the polymer, which showed the onset temperature of each loss weight taking place at lower temperature, indicating that increase in DS led to lower thermal stability. However, the introduction of LDH powders improved the thermal behavior, especially in the samples with higher DS and also clearly affected the properties of S-PSF membranes, particularly their water uptake, electrical and transport parameters.

PSF is not only used as PEM in DMFC but also can be used in alkaline fuel cells (AFCs). Nonjola *et al.*, (2013) synthesized quaternary PSF/titanium dioxide (QPSF/TiO_2) nanocomposite membranes by using DMAc as the casting solvent in a recasting process. The nanocomposite membranes were characterized by TGA, SEM, XRD, AFM, water uptake and ionic conductivity. Thermal analysis results showed that the composite membranes had good thermal properties because the introduction of the inorganic filler with good thermal resistance. But it showed lesser improvement in thermal degradation temperature as compared to pure QPSF. The physic-chemical properties as studied by means of SEM and XRD techniques suggested the uniform and homogeneous distribution of

TiO_2 at 2.5 wt% loading, and negligible agglomeration at 10 wt% loading, also indicated enhancement of crystalline character of these membranes. Besides, the energy dispersive X-ray spectra (EDX) analysis gave proportional percentages that the distribution of titania element on the surface of the composite membrane was uniform.

From the literatures of S-PSF membranes, it could be summarized the proton conductivity and methanol permeability values as in the following Table 2.1.

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

Polymer	Proton Conductivity (S/cm)	Proton Conductivity (S/cm)	Methanol (cm^2/s) at 25°C	Water Uptake (%) at 25 °C	Water Uptake (%) at 80 °C	References
	25 °C RH100%	80 °C RH100%				
PSF-sph-63	8.00E-03	2.20E-02	2.92E-07	6.6	12.8	(Zhu *et al.*, 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	
S-PSF-3	5.50E-03	-	1.50E-07	9.1	-	(Park *et al.*, 2006)
S-PSF-4	1.50E-02	-	2.50E-07	13.2	-	
S-PSF-5	2.20E-02	-	3.30E-07	17.1	-	
S-PSF-6	5.00E-02	-	6.00E-07	24.4	-	
S-PSF-7	7.00E-02	-	7.50E-07	58.1	-	
S-PSF-3-t	1.30E-03	-	5.00E-08	8.3	-	

Table 2.1 (Cont.) Proton conductivity and methanol permeability of PSF compared with Nafion in previous work

Polymer	**Proton Conductivity (S/cm)**	**Proton Conductivity (S/cm)**	**Methanol (cm^2/s) at 25°C**	**Water Uptake (%) at 25 °C**	**Water Uptake (%) at 80 °C**	**References**
	25 °C RH100%	**80 °C RH100%**				
S-PSF-4-t	5.50E-03	-	1.00E-07	11.2	-	(Park *et al.*, 2005)
S-PSF-5-t	2.20E-02	-	1.25E-07	15.1	-	
S-PSF-6-t	5.00E+02	-	2.25E-07	21.2	-	
S-PSF-7-t	6.00E-02	-	4.55E-07	52.4	-	
PPSF-A-0.75	2.00E-04	1.40E-03	3.98E-08	27	28	(Abu-Thabit *et al.*, 2010)
PPSF-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 *et al.*, 2009)
SPSF66	2.80E-02	-	-	27.2		
S-PSF 87	-	9.00E-02	-	-	-	(Chen *et al.*, 2005)
S-PSF 127	-	1.40E-01	-	-	-	
S-PSF-15	4.00E-03	2.10E-02	-	-	-	(Devrim *et al.*, 2009)
SPSF-25	7.00E-03	4.60E-02	-	-	-	
S-PSF-40	1.40E-02	1.20E-01	-	-	-	
SPSf90 *at 60 °C	0.5	-	-	-	-	(Lufrano *et al.*, 2012.)
SPSf *at 60 °C	2.4E-04	-	-	-	-	(Fu *et al.*, 2008)
Nafion115 at 65 °C	0.144	-	-	-	-	(Furtado Filho *et al.*, 2011)

2.3 Zeolite

Many kinds of polymer can be used in the PEM, such as Nafion and PSF, which provide high performance such as high proton conductivity, mechanical strength, chemical resistance, and lifetime. The modification of these polymers is for improving their properties. But sometime polymer membranes still have poor selectivity, which is a low ratio of proton conductivity to methanol permeability, because these membranes have low proton conductivity or high methanol permeability due to the modification of chemical structure of polymer. However, the poor selectivity of polymer membranes can be improved by mixing with some other materials. One of popular research areas in composite membranes is the use of inorganic fillers embedded in polymer matrix to minimize the loss of proton conductivity caused by the fillers while reducing the methanol permeability.

2.3.1 Introduction of Zeolite

Zeolites are a class of microporous crystalline aluminosilicate composed of interconnected SiO_4 and TiO_4 tetrahedron. They contain cations electrostatically bound to the host framework to compensate the negative charge introduced by Al(III). These cations can move freely along the diffusion path formed by voids and channels in the zeolite structure, and are responsible for the ion conducting properties of zeolite. Zeolite are highly hydrophilic solids and have a high water sorption capacity because of the charged anionic framework and the extra-framework cations in addition to their open structure, high pore volume and surface area. Zeolites' strong affinity to water, which acts as a vehicle for proton migration, and their sieving properties are the reasons for proposing zeolites as additives to polymer membranes to reduce methanol permeability (Zhang *et al.*, 2011).

Several works have been studied in chemical and physical processes, such as gas separation and heterogeneous catalysis. From the regular pore size of zeolites, on a sub-nanometer scale, it makes these materials high performance for separations based on molecular size and shape. Zeolites membrane can also separate components based on preferential adsorption, in which the strong adsorption of one component blocks or hinders the passage of the other components. However, membranes made of pure zeolites are plagued by defects such as cracks or gaps, exhibit poor mechanical properties such as brittleness and fragility, and are expensive to manufacture (Libby *et al.*, 2001).

In this work, a composite polymer membrane composes of zeolite as a dispersed phase and polymer matrix was prepared in order to increase the proton conductivity and decrease the methanol permeability of the PEM. Zeolite has two important properties:

1. Very high water retention ability, which can only be eliminated at around 200 °C.
2. Molecular sieving property, making them suitable for selective separations based on molecular size and shape.

2.3.2 Modified Composite Membrane with Zeolite

Unfortunately, membranes made of pure zeolites are brittle, fragile, and often have defects. Composite membranes can be made using zeolites as fillers and a polymeric matrix as a host. If the zeolites are well dispersed in the matrix, they can serve as extra route for proton transport in the membrane in addition to the already existing water channels. This leads to the increase in the membrane conductivity, whereas the tortuous pathways created by the zeolites can decrease the methanol permeability (Yildirim *et al.*, 2009).

This research is most easily organized as measurements of methanol permeability, determinations of proton conductivity, and selectivity values. The selectivities are the ratios of conductivity and permeability. Some heat treatment is important to insure that the membranes are insoluble in water. The longer heat treatment retards transport in the PVA component of the membrane and increases selectivity. The PVA/Mordenite composite membranes have fulfilled their potential. In particular, a PVA/Mordenite membrane containing 50 % Mordenite by volume, heat-treated for 27 h to make it insoluble, demonstrated a 20-fold improvement in selectivity over Nafion. This successful resulted contrasts the lack of selectivity improvement seen for the short heat treatment composites, thus demonstrating the importance of tailoring the transport properties between the polymer and zeolite phases in order to achieve selectivity gains (Libby *et al.*, 2003).

Tricoli *et al.*, (2003) exploited the molecular sieving properties of two natural zeolites (Chabazite and Clinoptilolite) to improve selectivity of Nafion membranes. The performances of Chabazite-Nafion and Clinoptilolite-Nafion composite membranes were inferior to that of zeolite-free recast Nafion membranes with regard to both ion conductivity and transport selectivity. The composite membranes with zeolite content up to 40 vol% exhibited uniform distribution of zeolite throughout the thickness. Although these membranes have more brittle than Nafion, these composite sheets retain when hydrated. However, this result was due to the properties of the chosen zeolites. This work showed that incorporating semi-permeable particles into a polymer matrix was an effective method to composite membrane materials with notably varied transport properties with respect to the sole polymer. Such method was a simple one and afforded to form defects-free membranes, which could exhibit mass transport properties close to those of the filler while retaining the plasticity of the polymer matrix. If adequately selective particles were utilized as the filler, composite membranes with suitable transport selectivity could be obtained.

The type of solvent appeared to be much more significant positive effect on methanol permeability than proton conductivity, leading to a higher characteristic factor. Regarding the characteristic factor and mechanical strength, the composite membrane fabricated with high boiling point DMF as the solvent would be superior to that fabricated with low boiling point propanol as the solvent. This suggested that in case of using high boiling point DMF as the solvent in fabrication of composite membrane, the hydrophilic parts of Nafion micelles should have tightened up with hydrophilic zeolite particles and have led to higher mechanical strength of the composite membrane. Therefore, it was concluded that the type of solvent was of the most critical regarding the arrangement of perfluoro polymeric micelle and mechanical strength, depending on the boiling point of solvent, thus heat treatment temperature. The result showed that silica/Nafion composite membrane was not as effective as that of zeolite/Nafion composite membrane due to the absence of pore system and less hydrophilicity. The characteristics of water uptake of zeolite composite membrane were quite consistent with the result of proton conductivity. These composite membranes show higher water uptake than Nafion 115, strongly suggesting better water retention ability of zeolite. The proton conductivity slightly dropped with increasing zeolite contents due to blocking effect of zeolite particles surrounded by inversely oriented hydrophilic micelles of Nafion. However, the proton conductivity of most composite membranes was significantly higher than that of Nafion 115. The result regarding the size effect showed that the methanol permeability of large-sized H-and Na-ZSM-5/Nafion composite membranes tended to increase with increasing zeolite content due to the leak through void fractions between large zeolite crystals and Nafion. It was concluded that the smaller crystal size had less methanol permeability (Byun *et al.*, 2006).

Zeolite beta synthesized from gels containing tetraethylammonium hydroxide as the structure directing agent was known to have high density of internal hydroxyl group nests and the removal of aluminium framework only increased this density. The incorporation of phenyl sulfonic acid groups into the pores of zeolite beta was more important for enhanced proton conductivity than the alumina framework (in either the proton or the ammonium exchanged form) and that the conductivity observed in these samples did not arise from a cooperative effect between the bound organic sulfonic acid groups and the aluminum acid sites. Furthermore, the presence of framework hydroxyl groups was necessary for increasing the proton conductivity through the formation of better hydrogen bonded water network in the pores with many dangling –OH and better water retention inside the molecular sieve leading to a faster Grotthüss transport of the mobile protons (McKeen *et al.*, 2008).

Nafion/H-ZSM-5 composite membranes based on DE2020 Nafion dispersion and H-ZSM-5 zeolites with different Si/Al ratios were prepared. All composite membranes had lower methanol permeability and higher proton conductivity than pure DE2020 membrane. The lower methanol permeability of the membrane might be due to the aggregation of the particles, or phase separation occurs, causing change in the membrane morphology. Two of the membranes: (DEZ X-Y, where DE, Z, X and Y stand for DE2020 Nafion, ZSM-5 zeolite, Si/Al ratio of the zeolite and the weight percentage of the zeolite, respectively) DEZ25-5 and

DEZ50-1 were tested in DMFC due to their lower methanol permeability and high proton conductivity, respectively. The DEZ25-5 membrane showed the best DMFC performance. Its maximum power density was more stable throughout the measurements and it reached the highest MPD at the end of the 5 day (Yildirim *et al.*, 2009).

The PEMs were prepared by the sulfonation of poly(1,4-phenylene sulfide) (PPS) and zeolite with various concentrations to form different composite polymer electrolyte membranes. SEM micrograph showed no interfacial void implying there was good interaction between the zeolite particles and the polymer matrix. The water uptake decreased with increasing zeolite concentration because of the decreasing the number of water absorption sites. In addition, the proton conductivity of the composite membrane was reduced from 0.075 to 0.02 $S.cm^{-1}$ with 10 wt% zeolite at room temperature resulting from the loss of sulfonic groups in wet membrane due to specific interaction between sulfonic acid group and zeolite. The ion exchange capacity of the composite membrane decreased from 1.5 to 1.03 $meq.g^{-1}$ with 10 wt% zeolite. The composite membranes showed higher thermal stability than the pristine polymer membrane, this was due to the strong specific interaction between the sulfonic groups of the matrix membrane and zeolite particles (Choi *et al.*, 2010).

Zhang *et al.*, (2011) prepared a Nafion–Faujasite composite membrane by using solution casting technique. Faujasite was found to undergo severe de-alumination in acid medium during the membrane activation, but its structure remained intact that confirmed by XRD patterns, which showed no other crystalline phases were detected. The zeolite interacted with Nafion probably through the hydrogen bonding between Si–OH and SO_3H groups. Combining with the increase of the water uptake and the water mobility, and the addition of a less conductive phase (zeolite) led to optimum proton conductivity between 0.98 and 2 wt% of zeolite. In addition, SEM observations highlighted the porosity of composite membranes, and the large number of defects and voids which can accommodate a significant amount of water.

Poly(ether ether ketone) (PEEK) was sulfonated with concentrated sulfonic acid (98%) at various DS using sulfonation times between 2 and 5 h at a constant temperature of 50 °C. The methanol permeability, thermal and mechanical properties, and proton conductivity of composite membranes were measured for the effect of ferrierite zeolite as inorganic filler at various amounts (5, 10, 15, 17, and 20% v/v). The properties of the S-PEEK membrane depended on DS; a higher DS value tended to increase water uptake, IEC and proton conductivity of the membranes. The presence of the Ferrierite zeolite filler in the composite membrane exhibited higher proton conductivity relative to the pure S-PEEK membranes due to the characteristics of the zeolite, a hygroscopic material that could retain water within its pores, thus leading to the enhancement of proton transfer through the membrane. The methanol permeability was lower compared to that of Nafion 117. However, at high zeolite content, the addition of zeolite tended to increase the methanol permeability, whereas the conductivity of the composite membrane and mechanical properties decreased due to the poorer distribution of zeolite and the agglomeration of the zeolite particles, which resulted in resultant voids in the polymer membrane (Auimviriyavat *et al.*, 2011).

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 micro-machining techniques were used to prepare the freestanding HZSM-5 micro-membranes of different Si/Al ratios on a silicon support and the unit was assembled into a working MEA. It compared well with Nafion 117 MEA under room temperature operation and low feed rates common in micro fuel cell. HZSM-5 with high aluminum content (low Si/Al ratios) exhibited good proton conductivity and better performance that approached that of Nafion MEA. The limitation of the membrane was brittleness of zeolites. Alternatively, HZSM-5 was employed in the structured composite membrane for water regulation in PFSA. A rational approach was used to bring the various elements together to optimize their forms and functions. They successfully demonstrated that it was possible through confinement to achieve enhanced PEMFC performance even under harsh operating conditions. PFSA was confined in zeolite sleeves to induce self-humidifying and to enhance performance at high temperature and dry conditions.

The research involving PEM is focused on hybrid membranes of two main types; Nafion-based and non-Nafion-based membranes. The Nafion based membranes include organic–inorganic membranes, acid–base membranes and Nafion plus bio-component membranes. The non-Nafion-based membranes include 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 will lead to excellent performance in a DMFC (Ahmad *et al.*, 2010)

Zeolites are promising membrane materials for DMFCs but the type of zeolite has to be carefully chosen and the composite membranes extensively characterized due to the large number of variables that can affect the characteristics of the composite membranes.

2.4 Graphene oxide

2.4.1 Introduction of Graphene Oxide (GO)

Graphene oxide (GO) is a compound of carbon, oxygen, and hydrogen in various ratio. GO is one of the most important derivatives of graphene, which is obtained from graphite by treating with strong oxidizer. The layered structure of GO is identified with hydroxyl, carbonyl, and epoxy groups on the plane and edge (He *et al.*, 2014). GO is a pivotal importance as an ampliphilic soft material due to the strong interfacial interactions to oxygen-containing functional groups, large surface area, excellent physical properties, and chemical stability (Heo *et al.*, 2013). By now graphene-based hybrid materials are used for polymer composites, electrochemical sensor and biosensors, fillers in composite materials for engineering application, supercapacitors, energy storage and environmental applications (Nicotera *et al.*, 2014).

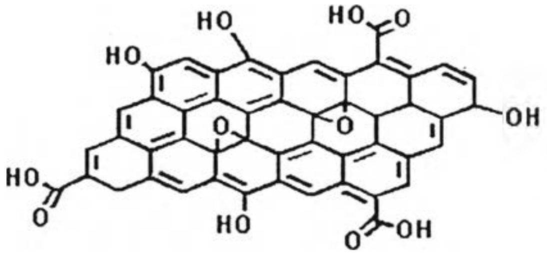

Figure 2.2 Structure of graphene oxide (He *et al.*, 2014).

2.4.2 Polymer Membrane based on GO

Currently, polymer membranes based on graphene oxide as an inorganic fillers have been attracting attention for application in electronics and nanocomposites (Choi *et al.*, 2012). The polymer/GO composite membranes are expected to provide high DMFC performance owing to the large surface area, barrier effect, and chemical stability of GO. Moreover, polymer/GO composite membranes have shown better capacitance and long cycle life (Chien *et al.*, 2013).

Tseng *et al.*, (2011) fabricated and characterized the composite membrane composing of sulfonated polyimide (S-PI) and GO. The S-PI/GO membranes with low GO loading (0.3 and 0.5 wt %) showed higher proton conductivity than Nafion117, being achieved at 90 °C. The content of GO not only promoted proton conductivity, but also resulted in positive effect on mechanical and blocking properties. From the results, the S-PI/GO membrane could retain the water at high temperature and low humidity condition resulting in a good proton conductivity, while the methanol permeability could be restricted. Therefore, its good performance makes it an excellent candidate for fuel cell applications.

Choi *et al.*, (2012) synthesized the Nafion/GO composite membranes (NG) for use in DMFC. The NG composite membranes showed obviously an enhancement of thermal and mechanical properties because of the interaction between GO sheet and Nafion. Furthermore, the incorporation of GO sheet (0.5 wt %) in the ionic clusters of Nafion resulted in selective transport, decreasing methanol permeability (40% less than Nafion) while maintaining the proton conductivity (98.1% of that in Nafion). NG composite membrane at 5 wt % GO loading also showed the highest selectivity, 150% higher than that of Nafion membrane. Especially, they exploited the NG composite membranes that exhibited much higher power density at severe operating conditions (5 M of methanol concentration).

He *et al.*, (2014) synthesized a various sizes (mean radius of 60 nm – 1 μm) of GO by the modified Hummers method. Different sizes of GO were incorporated into the S-PI to investigate the effect of size on DMFC performance. The composite membrane with 0.5 wt % of the smallest size GO exhibited highly uniform microstructure and showed the best results; high conductivity at 80 °C and 100 %RH, low methanol permeability, and excellent DMFC performance compared to that of pristine S-PI and other S-PI/GO membranes. These results could be attributed to the well-connected proton transport channels due to strong hydrogen interaction between the smallest size of GO and S-PI.

2.4.3 Polymer Membrane based on Sulfonated Graphene Oxide (S-GO)

GO is highly attractive for many applications. Nevertheless, the advantage of using GO to improve the DMFC performance have not been realized because the DMFC performance and non-homogeneous distribution of the GO (Choi *et al.*, 2012). To overcome this matter, one of the challenges is sulfonation of GO in order to enhance proton conductivity using GO without agglomeration in polymer matrix.

Heo *et al.*, (2013) prepared a novel composite membrane using S-GO and S-PEEK. The proton conductivity of S-GO/S-PEEK membrane increased significantly due to an increase in the number of SO_3H groups in both S-GO and S-PEEK and formed the proton transport networks in membrane. The incorporation of S-GO in membrane not only improved proton conductivity, but also positively influenced the mechanical properties because of the interaction between S-GO and S-PEEK, and blocking methanol passing through the membrane. Consequently, the S-GO/S-PEEK membranes have increased the selectivity of the membrane. Therefore, this composite membrane showed good potential for usage in DMFCs.

Chien *et al.*, (2013) developed the membrane by dispersing S-GO into a Nafion matrix. S-GO/Nafion membrane with a low S-GO content showed the better S-GO dispersion in Nafion. The composite membranes exhibited lower methanol and water uptake resulting in lower methanol permeability, reduced swelling ratio, and improved proton conductivity in low humidity. This was attributed to better water retention ability, as well as high selectivity by steric hindrance and shrinkage of the ionic clusters. These results can be implemented in DMFCs and demonstrated superior DMFC performance over the commercial Nafion.