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Organic/Inorganic Nanocomposite Membranes Development for Low Temperature Fuel Cell Applications

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1. Introduction

The criteria that are going to influence the evolution of the world energy system in the present century are complex. The most important new factor is the need to preserve the environment, both locally and globally, through the use of new technologies and sustainable use of existing resources. The Kyoto protocol, which put a limit on greenhouse gas emissions (mainly CO_2) from the industrialized countries, is a turning point in the global energy chain. On the other hand, the fuel specifications to control automotive exhaust gas emission obligate fuel producers to look for different ways of making clean fuel. Automakers are also obligated to look for alternative technology to internal combustion engines. The interest in studies on energy sources alternative to fossil fuels is linked both to the reduction of their availability and the increasing environmental impact caused by their use (Goodstein, 1999). In the energy field, an important cause of pollutant emissions is linked to ground transportation. In the last 40 years, some economic, social and cultural changes have encouraged a wide proliferation of vehicles. For example, in Europe, private cars have increased from 232 to 435 per 1000 inhabitants in the period 1971-1995 (Santarelli *et al.*, 2003). Fuel cells are alternative power sources that can meet global emission regulations, and clean production. Although fuel cells have been used since the 1960's for aerospace and military applications, cost was a strong impediment to terrestrial applications.

2. Fuel cell types

Five major types of fuel cells are available and are defined by their electrolyte. These include alkaline (AFC), phosphoric acid (PAFC), molten carbonate (MCFC), solid oxide (SOFC) and proton exchange membrane fuel cells (PEMFC). Table 1 summarizes some characteristics of these fuel cells. Proton exchange membrane fuel cells are the most attractive candidate for alternative automotive and stationary power sources due to their smaller size and much lower operating temperature compared to other fuel cell systems. Low temperature fuel cells are fuel cells operating at temperature less than 100°C. They are H_2-proton exchange membrane fuel cell (H_2-PEMFC), direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC) and direct DME fuel cell (DDMEFC).

Type	Electrolyte	Charge carrier in the electrolyte	Temperature (°C)
Alkaline fuel cells (AFC)	aqueous KOH solution	OH^-	<100 ,
Proton exchange membrane fuel cells (PEMFC)	proton exchange membrane	H^+	60-120
Phosphoric acid fuel cells (PAFC)	concentrated phosphoric acid	H^+	160-220
Molten carbonate fuel cells (MCFC)	mixture of molten carbonates (Li_2CO_3/K_2CO_3)	CO_3^{2-}	600-650
Solid oxide fuel cells (SOFC)	ceramic solid $ZrO_2(Y_2O_3)$	O_2^-	800-1000

Table 1. Fuel cells systems (Carrette *et al.*, 2001)
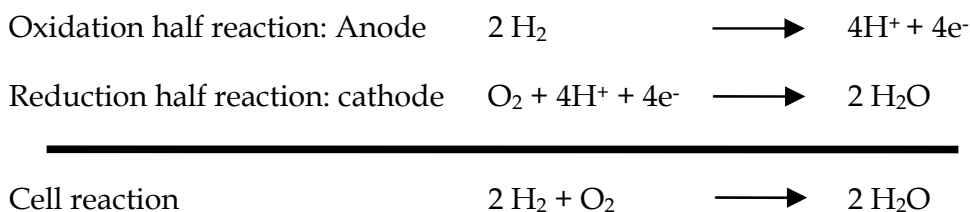
3. Low temperature fuel cells

A fuel cell is an electrochemical system which converts chemical energy to electrical energy. A fuel cell differs from a battery in that fuels are continuously supplied and the products are continuously removed. There are two distinct fuels for low temperature fuel cells: hydrogen as used in a H_2-PEMFC, and methanol as used in a DMFC. These fuel cells consist of six major parts: end plates, current collectors, flow channel blocks, gaskets, gas diffusion layers, and a membrane electrode assembly (MEA). The fuel cell principle enables a separation between power and energy. The maximum power required determines the size of the fuel cell; the energy required determines the amount of fuel to be carried. The specific power (W kg^{-1}) of the H_2-PEMFC is roughly twice that of the DMFC (Raadschelders & Jansen, 2001). Because no mobile electrolyte is employed, corrosion problems in low temperature fuel cells are reduced and cell construction is simplified with few moving parts (Bernardi & Verbrugge, 1991). Also, fuel cells operate very quietly, therefore, reducing noise pollution (Kordesch & Simader, 1995). Since the proton exchange membrane used for the electrolyte is a solid phase, it does not penetrate deeply into the electrode as does a liquid one; therefore the reaction area is limited to the contact surface between the electrode and membrane (Shin *et al.*, 2002). The advantage of using solid electrolyte is that no electrolyte leakage will occur (Uchida *et al.*, 1995; Yi & Nguyen, 1999). To meet the requirements of practical application a large number of single cells are assembled together to form a stack. The performance of a stack is different from that of a single cell. The stack has a much higher operating voltage, a greater power and better fuel-energy efficiency (Chu & Jiang, 1999).

4. Fuels for low temperature fuel cells

4.1 Pure hydrogen

H_2-proton exchange membrane fuel cells have existed since the 1960's; in fact they were used in the Gemini aerospace program of the National Aeronautics and Space Administration (NASA) of the United States. The MEA for H_2-PEMFCs consists of five components namely: a porous backing layer, an anode catalyst layer, a proton exchange membrane, a cathode catalyst layer, and a porous backing layer. Hydrogen is oxidized at the anode. The proton formed migrates through the membrane while the electrons flow through the external circuit. In the cathode reaction water is formed from oxygen, protons and electrons.

The two half reactions for the H_2-PEMFC are as follows:

$$\text{Oxidation half reaction: Anode} \quad 2\,H_2 \quad \longrightarrow \quad 4H^+ + 4e^-$$

$$\text{Reduction half reaction: cathode} \quad O_2 + 4H^+ + 4e^- \quad \longrightarrow \quad 2\,H_2O$$

$$\text{Cell reaction} \quad 2\,H_2 + O_2 \quad \longrightarrow \quad 2\,H_2O$$

H_2-PEMFCs have attracted the most attention due to their high electrochemical reactivity (Gottesfeld & Zawodzinski, 1997; Parthasarathy *et al.*, 1991; Ralph, 1997) and very low noble catalyst loading since the development of a method at Los Alamos National Laboratory (LANL) to reduce the platinum loading to ca. 0.1 mg/cm² (Wilson & Gottesfeld, 1992; Wilson, 1993; Wilson *et al.*, 1995) compared to 35 mg/cm² and 4 mg/cm² used respectively in the Gemini program and at General Electric in the 1970s (Appleby & Yeager, 1986a,1986b). The efficiency achievable is higher than in power plants and internal combustion engines (Dohle *et al.*, 2002) and there is practically zero pollution. However, the H_2-PEMFC has several disadvantages including hydrogen storage and transportation and the public acceptance of hydrogen as fuel. It is well known that hydrogen and air mixtures are explosive (e.g. the Challenger disaster). Hydrogen safety measures are still one of the major implications when it comes to the commercialization of H_2-PEMFCs. Adequate water content of the membranes is essential to maintain the conductivity of the polymeric proton exchange membrane (Anantaraman & Gardner, 1996; Fontanella *et al.*, 1995; Gavach *et al.*, 1989; Zawodzinski *et al.*, 1991, 1993). During fuel cell operation, water molecules migrate through the membrane under electro-osmotic drag, fluid convection, and molecular diffusion, making it difficult to retain a high water content within the membrane. Generally, humidification is applied to the inlets of the anode and/or cathode in order to supply water to the membrane. However, excessive amounts of liquid water could impede mass transport within the electrode structure (Zawodzinski *et al.*, 1991). A thinner membrane is preferred in H_2-PEMFCs because it can provide an improvement in water management due to the enhanced back-diffusion of production water from the cathode to the anode side (Finsterwalder & Hambitzer, 2001). The oxygen reduction reaction (ORR) is very slow compared to the hydrogen reaction; typically hydrogen electro-oxidation on Pt is shown by an exchange current density of 10^{-3} A cm^{-2} Pt at ambient temperature. This is some 10^7 to 10^9 times more facile than the oxygen reduction at the cathode (Ralph & Hogarth, 2002). Thus, oxygen reduction is a rate limiting factor in H_2-PEMFCs (Gloaguen *et al.*, 1998; Paulus *et al.*, 2001).

4.2 Hydrogen reformate

The question of whether customers will be fuelling their vehicles directly with hydrogen or via the hydrogen-rich carrier (e.g. methanol, ethanol, gasoline, diesel, etc.) still seems to be unanswered. This is a very important issue not just from a refueling infrastructure perspective but also from the public perception and from the gearing up of production, and developing guidelines for dealing with safety issues that will need to put in place for the new fuel (Adamson & Pearson, 2000). In principle, any type of liquid fuel may be employed as a hydrogen source, e.g. gasoline, diesel, methanol, ethanol, etc. Hydrogen is produced by a reforming process. Four distinguish fuels are discussed namely methanol, ethanol, dimethylether (DME) and ammonia.
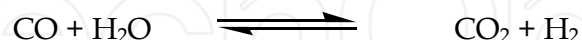
4.2.1 Methanol reforming

Methanol is produced from steam reformed natural gas and carbon dioxide using copper-based catalyst, and also from renewable biomass sources. Methanol is a leading candidate to provide the hydrogen necessary to power a fuel cell, especially in vehicular applications (Ledjeff-Hey *et al.*, 1998; Mokrani & Scurrell, 2009; Olah *et al.*, 2009). Methanol is currently used as a feed stock for a variety of widely used organic chemicals, including formaldehyde, acetic acid, chloromethane, and methyl tert-butyl ether (MTBE). Methanol is the desired fuel to produce hydrogen on-board. Methanol can be reformed to hydrogen by different processes including steam reforming (Amphlett *et al.*, 1985; Breen & Ross, 1999; Duesterwald *et al.*, 1997; Emonts *et al.*, 1998; C.J. Jiang *et al.*, 1993; Takahashi *et al.*, 1982; Takezawa *et al.*, 1982), partial oxidation (Agrell *et al.*, 2001; Cubiero & Fierro, 1998; Velu *et al.*, 1999) and autothermal reforming (Edwards *et al.*, 1998; Höhlein *et al.*, 1996; L. Ma *et al.*, 1996; Mizsey *et al.*, 2001).

Steam reforming of methanol occurs by two different pathways (Emonts *et al.*, 1998). The first one involves the decomposition of methanol into CO and H_2 through the following reaction:
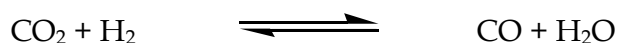
$$CH_3OH \rightleftharpoons CO + 2H_2$$
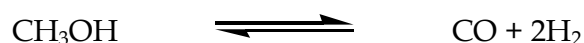
followed by a water gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The second mechanism for methanol steam reforming consists of the reaction of water and methanol to CO_2 and hydrogen:

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2$$
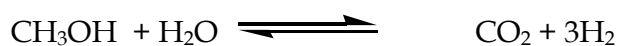
which can be followed by a reverse shift reaction to establish the thermodynamic equilibrium:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Methanol steam reforming is endothermic and therefore requires that external heat, typically 300°C, is supplied. Steam reforming of methanol is usually catalyzed over Cu/ZnO type catalyst and can be performed in fixed-bed reactors (Duesterwald *et al.*, 1997).

4.2.2 Ethanol reforming

Among other candidate liquid fuels, ethanol is a particular case, since it can be easily produced in great quantity by the fermentation of sugar-containing raw materials. In addition, in some countries (e.g. Brazil) ethanol is already distributed in gas stations for use in conventional cars with internal combustion engines. Hydrogen is produced from ethanol in a process unit consisting of either a steam reformer (SR) or a partial oxidation (POX) reactor in series with a water-gas shift (WGS) reactor and a reactor for selective oxidation (PROX) of CO (Ioannides & Neophytides, 2000). Product gas from the reformer or the POX reactor, which operates at an exit temperature higher than 677°C, contains a mixture of H_2, CO, CO_2, CH_4 and H_2O. After cooling, this stream enters the WGS reactor, where a large fraction of CO reacts with H_2O towards CO_2 and H_2 at a temperature of 200°C. The product gas of the WGS reactor contains 0.1-1.5% of residual CO and enters the PROX reactor, where CO is totally oxidized - with the addition of a small amount of air - to CO_2 with residual CO being less than 10 ppm. The CO free, hydrogen rich stream is then fed to the H_2-PEMFC.

4.2.3 DME reforming

DME (dimethylether) has become a promising candidate as a hydrogen source for the reforming process, because it has a high hydrogen-to-carbon ratio and a high energy density. DME can be easily handled, stored and transported. Furthermore, the infrastructure of LPG can readily be adapted for DME due to their similar physical properties. Furthermore, DME is not toxic and less explosive. DME can be catalytically reformed at relatively lower temperatures than ethanol and methane. DME can be reformed through three ways, namely steam reforming (SR), partial oxidation (POX) and authothermal reforming (ATR). DME SR proceeds via two moderately endothermic reactions in sequence; hydrolysis of DME to MeOH and steam reforming of MeOH to hydrogen and carbon dioxide. Hydrolysis of DME takes place over acid catalysis, e.g. zeolite and alumina, while MeOH SR proceeds over Cu-, Pt-, or Pd based catalyst. Therefore, bi-functional catalyst containing both acidic and metallic sites are generally needed for DME SR (Faungnawakij *et al.*, 2010; Ledesma & Llorca, 2009; Nishiguchi *et al.*, 2006; Takeishi & Suzuki, 2004). DME POX has been investigated over various metal catalysts such as Pt, Ni, Co and Rh supported on different oxide. Supports such as Al_2O_3, YSZ, $LaGaO_3$-based and MgO were used at a high reaction temperature ranging from 400 to 700°C (S. Wang *et al.*, 2002; Q. Zhang *et al.*, 2005). ATR also can be used to produce hydrogen from DME. ATR is a combination of SR and POX, and catalysis such as $CuFe_2O_4$-Al_2O_3 (Faungnawakij & Viriya-empikul, 2010) and Pd-based (Nilsson *et al.*, 2007, 2009) were investigated.

4.2.4 Ammonia reforming

Anhydrous ammonia is a widely used commodity and is available worldwide in liquid form in low pressure tanks. Procedures for safe handling have been developed in every country. Facilities for storage and transport by barges, trucks and pipelines from producer to ultimate consumer are available throughout the world. Therefore, liquid anhydrous ammonia is an excellent storage medium for hydrogen (Hacker & Kordesch, 2003). Studies demonstrate that hydrogen derived from anhydrous liquid ammonia, via a dissociation and followed by hydrogen purifier, offers an alternative to conventional methods of obtaining
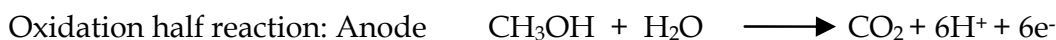
pure hydrogen for small scale use (Strickland, 1984). The dissociation rate depends on temperature, pressure and the catalyst being used. An almost complete decomposition of ammonia can take place at approximately 430°C at atmospheric pressure. The influence and kinetic data of materials like porcelain or silica glass, metals like ion, tungsten, molybdenum, nickel, etc. especially noble metals and metal oxides, have been investigated for the dissociation of ammonia. The most used catalysts are nickel oxide and iron oxide (Papapolymerou & Bontozoglou, 1997) and the better cracking efficiencies were obtained with catalysts based on Zr, Mn, Fe and Al/alloys (Boffito, 1999; Rosenblatt & Cohn, 1952; Shikada *et al.*, 1991).

4.3 Direct methanol fuel cell

DMFC technology is relatively new compared to the H_2-PEMFC. However, the direct oxidation of methanol in a DMFC has been investigated over many years and some prototypes were built in the 1960's and early 1970's by the Shell Research Center in England (Glazebrook, 1982; Schatter, 1983) and by Hitachi Research Laboratories in Japan (Tamura *et al.*, 1984; Williams, 1966). These studies were abandoned in the mid-1980's due to the low performance (25 mW cm^{-2} at best) resulting from the use of a liquid acid electrolyte (Glazebrook, 1982; Kordesch & Simader, 1996; Lamy *et al.*, 2001). An alkaline electrolyte was also used, but evolved CO_2 caused carbonation of the electrolyte resulting in decreased efficiency by reducing the electrolyte conductivity and de-polarizing the cathode (Verma, 2000). Currently all the research in DMFCs focuses on using solid proton exchange membranes as electrolyte, largely due to its proliferation in H_2-PEMFCs. The structure of the DMFC is similar to the H_2-PEMFC. At the anode methanol is directly oxidized to carbon dioxide, and the reaction at the cathode is similar to the H_2-PEMFC.

The two main half reactions for the DMFC can be summarized as follows:

Oxidation half reaction: Anode $\quad CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Reduction half reaction: cathode $\quad {}^3/_2 O_2 + 6H^+ + 6e^- \longrightarrow 3 H_2O$

Cell reaction $\quad\quad\quad\quad\quad\quad CH_3OH + {}^3/_2 O_2 \longrightarrow CO_2 + 2 H_2O$

The thermodynamic reversible potential for a DMFC is 1.21V at 25°C (Larminie & Dicks, 2000). This value is comparable to that for a H_2-PEMFC, which is 1.23V (Chu & Gilman, 1994; Léger, 2001; Qi & Kaufman, 2002; Scott *et al.*, 1998). In practice, a DMFC has a much lower open circuit voltage (OCV) (Qi & Kaufman, 2002) and electrochemical losses at both electrodes lead to a significant reduction in overall performance from the theoretical thermodynamic maximum (Argyropoulos *et al.*, 1999a). Since methanol is used directly at the anode, and as a consequence, a DMFC requires less auxiliary equipment and is therefore a more simplified system compared to a H_2-PEMFC. Methanol is a liquid made from natural gas or renewable biomass sources, which is relatively cheap. Methanol is also easy to store, transport, and distribute, where advantage can be taken of the existing gasoline infrastructure (Mokrani & Scurrell, 2009; Olah *et al.*, 2009). The anodic reaction is exothermic for both the H_2-PEMFC and the DMFC; heat management is a problem in H_2-PEMFC stacks. In contrast, aqueous methanol acts as a coolant in DMFCs (Hogarth *et al.*, 1997; Hogarth & Ralph, 2002; Lim & C.Y. Wang, 2003; Surampudi *et al.*, 1994).

However, as the DMFC is still in its infancy, many problems need to be overcome to reach the commercialization stage. This includes the very sluggish methanol oxidation reaction, methanol crossover through the polymeric proton exchange membrane, CO_2 evolvement at the anode (Argyropoulos et al., 1999a,1999b; Nordlund et al., 2002; Scott et al., 1998), and cathode flooding (Amphlett et al., 2001; M. Mench et al., 2001; X. Ren & Gottesfeld, 2001; Z.H. Wang et al., 2001). The methanol crossover through the polymer electrolyte leads to a mixed potential at the cathode, which results from the ORR and the methanol oxidation occurring simultaneously. This effect causes a negative potential shift at the cathode and a significant decrease of performance in the DMFC. Methanol crossover also causes fuel loses; it had been found that over 40% of methanol can be wasted in a DMFC across Nafion® membranes (Narayanan et al., 1996). In a DMFC, cathode flooding, which typically occurs unless high cathode stoichiometries are used, can determine to a great extent overall cell performance (Amphlett et al., 2001; M. Mench et al., 2001; X. Ren & Gottesfeld, 2001; Z.H. Wang et al., 2001). Water management in the DMFC is especially critical because anode water activity is near unity due to contact with liquid methanol solution (M.W. Mench & C.Y. Wang, 2003). Thus, unlike a H_2-PEMFC, no back-diffusive flux of water from cathode to anode will occur, and as a result, vapourization into dry cathode flow is the only pathway for removal of excess cathode-side water accumulation from electro-osmotic drag, ORR, and diffusion (M.W. Mench & C.Y. Wang, 2003).

4.4 Direct ethanol fuel cell

Direct fuel utilization will be of interest. Besides methanol, other alcohols, particularly those coming from biomass resources, are being considered as alternative fuels. Ethanol as an attractive fuel for electrical vehicles was investigated in direct ethanol fuel cells (Fujiwara et al., 1999; Gong et al., 2001; Lamy et al., 2001; W.J. Zhou et al., 2004). However, multimetallic catalysts are necessary to orientate the oxidation reaction selectively in the direction of complete combustion to carbon dioxide (Lamy et al., 2001). The reaction mechanisms of anodic oxidation of ethanol are more difficult to elucidate than methanol oxidation, since the number of electrons exchanged greatly increases (12 electrons per ethanol molecule versus 6 electrons for methanol), thus many adsorbed intermediates and products are involved (Lamy et al., 2001). Direct ethanol fuel cell was the second most studied fuel cell after methanol. The proton conductor membranes used are mainly Nafion® membranes. However some investigators used high temperature membrane such as Nafion®/Silica by Aricò et al. (1998), and also by J. Wang et al. (1995) using a phosphoric acid doped polybenzimidazol (PBI) membrane.

4.5 Direct DME fuel cell

Serov and Kwak (2009) have summarized the recent progress in development of direct DME fuel cell (DDMEFC). DDMEFC could be a valuable direct liquid fuel cell candidate for commercialization. However, compared with PEMFC and DMFC, DDMEFC show poor performances under ambient conditions due to the poor electrooxidation reactivity of DME (Colbow et al., 2000; Kerangueven et al., 2006; Mench et al., 2004; Mizutani et al., 2006; Ueda et al., 2006). On the anode side of DDMEFC, the following oxidation reaction takes place:

$$CH_3OCH_3 + 3H_2O \longrightarrow 2CO_2 + 12\,H^+ + 12\,e^-$$
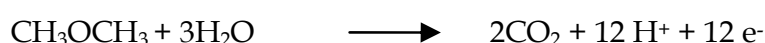
The number of electron transferred for complete oxidation is 12, this result in a reduced theoretical fuel requirement of DME, when compared to methanol with 6 electrons transferred, and hydrogen with 2 electrons (Mench *et al.*, 2004; Serov & Kwak, 2009; K. Xu *et al.*, 2010). Furthermore, DME has the advantage over methanol in that crossover is much less pronounced (Mench *et al.*, 2004; Serov & Kwak, 2009). DDMEFC performance increase with increasing temperature, since DME electrooxidation is favored at high temperature. Furthermore, increasing the temperature will enhance also oxygen reduction reaction (ORR) (K. Xu *et al.*, 2010). Compared with hydrogen as the fuel for PEMFC, more water is needed for DME electrooxidation reaction and H^+ migration from anode side to cathode side due to the elctro osmotic force of water (Ferrell *et al.*, 2010; K. Xu *et al.*, 2010; Yu *et al.*, 2005).

5. Organic proton conductor membranes

Proton exchange membranes or proton conductor membranes are the most important component of low temperature fuel cells. Since the development of a solid polymer electrolyte, all the research on fuel cells focuses on the use of these types of electrolyte.

5.1 Perfluorinated membranes

The first commercially available perfluorinated membrane material from DuPont was Nafion® 120 (1200 equivalent weight (EW), 250 µm thick) followed by Nafion® 117 (1100 EW, 175 µm thick). These high equivalent weight materials were found to have limited use in fuel cells. In 1988, The Dow Chemical Company developed their own perfluorinated polymer membrane with low equivalent weight, typically in the range of 800-850. Nafion® of DuPont and Dow® membranes have identical backbones and are structurally and morphologically similar, but the side chain is shorter in the Dow polymer. Since the success of Dow Chemical, where it was found that the Dow® membrane performed better than the DuPont membrane in H_2/O_2 fuel cells, DuPont has been active in further developing their membranes with respect to durability and continuous improvement. They increased power densities by further decreasing the equivalent weight from 1100 to 1000 EW and membrane thickness from 175 to 25 µm. Table 2 shows the latest DuPont membranes with some characteristics. Nafion® 117 is the preferred membrane for DMFCs. In the 1990's, Aciplex® perfluorinated ion exchange membranes were introduced by the Asahi Chemical Industry, and the Flemion® series were introduced by Asahi Glass Co. (Yoshida *et al.*, 1998). In general these membranes are in the category of long chain perfluorinated membranes, like Nafion®. Some characteristics of these perfluorinated membranes are summarized in Table 2.

Nafion® membranes are chemically synthesized in four steps according to the DuPont de Nemours process (Grot, 1978): 1) The reaction of tetrafluoroethylene with SO_3 to form the sulfone cycle; 2) The condensation of these products with sodium carbonate followed by co-polymerization with tetrafluoroethylene to form an insoluble resin; 3) The hydrolysis of this resin to form a perfluorosulfonic polymer and 4) The chemical exchange of the counter ion Na^+ with the proton in an appropriate electrolyte. The Dow® membrane is prepared by the co-polymerisation of tetrafluoroethylene with vinylether monomer. The polymer can be described as having a Teflon-like backbone structure with a side chain attached via an ether group. This side chain is characterized by a terminal sulfonate functional group (Savadogo, 1998).

Membrane	Thickness (μm)	Equivalent Weight
Nafion® series (DuPont)		
Nafion® 117	175	1100
Nafion® 115	125	1100
Nafion® 112	50	1100
Nafion® 111	25	1100
Nafion® 1135	87	1100
Nafion® 1035	87	960
Nafion® 105	125	960
Dow Chemicals Co.		
Dow® XUS 13204.10	127	800–850
Flemion® series (Asahi Glass Co.)		
Flemion® R	50	900
Flemion® S	80	900
Flemion® T	120	900
Aciplex® series (Asahi Chemicals Industry)		
Aciplex® 1004	100	1000

Table 2. Perfluorinated membranes

5.2 Partially fluorinated ionomer membranes

5.2.1 Sulfonated copolymer based on the α,β,β-trifluorostyrene monomer membranes

The Canadian Ballard company developed proton conductor membranes based on trifluorostyrene monomer, under the trade name BAM1G and BAM2G (Ballard Advanced Materials first and second generation, respectively). The longevity of these polymers was limited to approximately 500 hours under practical fuel cell operating conditions (Savadogo, 1998). Based on the above work, Ballard developed third generation membranes under the trade name BAM3G (Steck, 1995; Steck & Stone, 1997; Wei *et al.*, 1995a,1995b). The BAM3G membranes consist of sulfonated copolymers incorporating α,β,β-trifluorostyrene and a series of substituted α,β,β-trifluorostyrene co-monomers. These membranes have an equivalent weight ranging between 375 and 920. The water content of the sulfonated BAM3G is much higher than that of Nafion® and Dow membranes. BAM3G membranes demonstrated a lifetime approaching 15,000 hours when tested in a Ballard MK5 single cell and also exhibited performances superior to Nafion® and Dow® membranes in a H_2/O_2 fuel cell. Disadvantages of these membranes include the complicated production process for the monomer α,β,β-trifluorostyrene (Livingston *et al.*, 1956) and the difficult sulfonation procedure (Kerres, 2001; Wei *et al.*, 1995b).

5.2.2 Grafted ionomer membranes

Partially fluorinated membranes can be obtained by using a simultaneous and pre-radiation grafting of monomers onto a base polymer film, and subsequent sulfonation of the grafted component (Brack *et al.*, 2003; Büchi *et al.*, 1995a,1995b; Gode *et al.*, 2003; Gupta *et al.*, 1993; Hatanaka *et al.*, 2002; W. Lee *et al.*, 1996; Lehtinen *et al.*, 1998; Scherer, 1990). These membranes were prepared by pre-irradiation of fluoropolymer films, such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) or poly(ethylene-*alt*-tetrafluoro-ethylene) (ETFE), using an electron beam or gamma irradiation source. The pre-irradiated films were grafted by exposing them to solutions of styrene and other radically polymerizable monomers. The grafted films are sulfonated using chlorosulfonic acid. The grafting mixture was crosslinked with divinylbenzene (DVB) and tri-allyl cyamirate (TAC) (Gupta *et al.*, 1994; Gupta & Scherer, 1994) or poly(vinylidene fluoride) (Sundholm, 1998). A disadvantage of membranes using styrene and divinylbenzene monomers is that their oxidation stability is limited, due to the tertiary C-H bonds which are sensitive to O_2 and hydrogen peroxide attack (Kerres, 2001).

5.3 Non-perfluorinated membranes

5.3.1 Polybenzimidazole (PBI)

PBI is synthesized from aromatic bis-o-diamines and dicarboxylates (acids, esters, amides), either in the molten state or in solution (Jones & Rozière, 2001). PBI is relatively low cost and is a commercially available polymer known to have excellent oxidation and thermal stability. The commercially available polybenzimidazol is poly-[2,2`-(*m*-phenylene)-5,5`-bibenzimidazole], which is synthesized from diphenyl-iso-phthalate and tetra-aminobiphenyl. Hoel and Grunwald (1977) reported on proton conductivity values of PBI in the range of 2×10^{-4} – 8×10^{-4} S/cm at relative humidities (RH) between 0 and 100%. Other authors observed proton conductivity some two to three orders of magnitude lower (Aharoni & Litt, 1974; Glipa *et al.*, 1997; Powers & Serad, 1986). PBI is a suitable basic polymer which can readily be complexed with strong acids (Jones & Rozière, 2001; Glipa *et al.*, 1997; Y.L. Ma *et al.*, 2004; Powers & Serad, 1986; Samms *et al.*, 1996; Savadogo & B. Xing, 2000; Wainright *et al.*, 1995, 1997; J.T. Wang *et al.*, 1996a,1996b; B. Xing & Savadogo, 1999). The immersion of PBI film in aqueous phosphoric acid leads to an increase in both its conductivity and thermal stability (Powers & Serad, 1986). Savinell and co-workers prepared PBI/H_3PO_4 via two different routes: a) directly casting a film of PBI from a solution containing phosphoric acid; b) preparation by immersion of a preformed PBI membrane in 11M phosphoric acid for several days (Samms *et al.*, 1996; Wainright *et al.*, 1997). The typical thickness for different films was 75 μm. The conductivity depends on the quantity of phosphoric acid in the membrane. Conductivity in the range 5×10^{-3} to 2×10^{-2} S/cm at 130°C and 5×10^{-2} S/cm at 190°C have been reported (Wainright *et al.*, 1995). The conductivity for type "a" membranes is higher than those of type "b" membranes. At a temperature above 150°C, the conductivity of type "a" membranes is similar to that of Nafion® at 80 °C and 100% RH. It was shown that the methanol crossover through doped PBI type "a" membrane, was at least ten times less than that observed with Nafion®. The disadvantage of these membranes is that the H_3PO_4 molecules can diffuse out of the membrane towards basic polymer sites because they are in excess. PBI/H_3PO_4 membranes are suitable for direct methanol fuel cell application at a temperature >100°C. However, they

can only be used with a feed of vapourized methanol, because when a liquid contacts the membrane, the phosphoric acid leaches out of the membrane and the proton conductivity drops considerably (Kerres, 2001).

5.3.2 Sulfonated polyimide membranes

The sulfonated polyimide (SPI) membranes were obtained by casting on a glass plate the polymer solution and evaporating the solvent (Cornet *et al.,* 2000; Fan *et al.,* 2002; Faure *et al.,* 1996, 1997; Gebel *et al.,* 1993; Genies *et al.,* 2001; Woo *et al.,* 2003). The polymer solution synthesis was achieved in different ways: The first way was based on the phthalimide-five member imide (4,4′-diamino-biphenyl 2,2′ disulfonic acid (BDSA), 4,4′ oxy-diphthalic dianhydride (ODPA) and 4,4′–oxydianiline (ODA)) at 200°C. The second way was based on the naphthalimide-six member imide ring (BDSA, 1,4, 5,8-naphthalene tetracarboxylic dianhydride (NTDA) and ODA) at 160°C (Faure *et al.,* 1996, 1997; Gebel *et al.,* 1993). The third way was based on the 3,3`,4,4`-benzophenone-tetracarboxylic dianhydride (BTDA), BDSA and ODA (D`Alelio, 1944). The fourth way was based on BDSA/NTDA/mAPI (bis-[3-(Aminophenoxy)-4-phenyl]isopropylidene) (Genies *et al.,* 2001). The water content of membranes at 25°C for the phthalic and naphthalenic sulfonated polyimide membranes is 26% and 30%, respectively. The water content obtained for Nafion® membranes under the same conditions was 20% (Faure *et al.,* 1997; Gebel *et al.,* 1993). It was also claimed that the sulfonated polyimide membranes were 3 times less permeable to hydrogen gas than Nafion® membranes. The lifetime measurements were performed on a 175 μm phthalic polyimide and a 70 μm naphthalenic sulfonated polyimide film at 60°C, 3 bar pressure for H_2 and O_2 and under a constant current density. It was found that the membrane based on the phthalic structure broke after 70 hours whereas the membrane based on the naphthalic polyimide was stable over 3000 hours (D`Alelio, 1944). The proton conductivity of SPI was found to be half of Nafion® 117, typically 4.1×10^{-2} S/cm, and methanol permeability was found to be 7.34×10^{-8} compared to 2.38×10^{-6} cm²/s for Nafion® 117 (Woo *et al.,* 2003).

5.3.3 Phosphazene-based cation-exchange membranes

It was shown that polyphosphazene-based cation-exchange membranes have a low methanol permeability, low water swelling ratios, satisfactory mechanical properties, and a conductivity comparable to that of Nafion® 117 (Allcock *et al.,* 2002a,2002b; Guo *et al.,* 1999; Tang *et al.,* 1999; Wycisk & Pintauro, 1996; X. Zhou *et al.,* 2003). Polyphosphazene-based membranes have been fabricated from poly[bis(3-methylphenoxy)phosphazene] by first sulfonating the base polymer with SO_3 and then solution-casting a thin film (Tang *et al.,* 1999; Wycisk & Pintauro, 1996; X. Zhou *et al.,* 2003). Polymer crosslinking was carried out by dissolving benzophenone photoinitiator in the membrane casting solution and then exposing the resulting films after solvent evaporation to UV light (Guo *et al.,* 1999). The conductivity of the polyphosphazene membranes were either similar to or lower than that of Nafion® 117 membranes (Guo *et al.,* 1999; X. Zhou *et al.,* 2003). However, methanol permeability of a sulfonated membrane was about 8 times lower than that of the Nafion® 117 membrane (X. Zhou *et al.,* 2003). Sulfonated/crosslinked polyphosphazene films showed no signs of mechanical failure (softening) up to 173°C and a pressure of 800 kPa (Guo *et al.,* 1999).

5.3.4 Sulfonated poly(arylethersulfone) membranes

Polysulfone (PSU) is a low cost, commercially available polymer (e.g. PSU Udel™ from Amoco) which has very good chemical stability. The synthesis and characterization of sulfonated polysulfone (SPSU) has been achieved by Johnson *et al.* (1984) and Nolte *et al.* (1993). It was found that membranes cast from SPSU (Udel™ P-1700) solutions were completely water soluble (Nolte *et al.,* 1993) and become very brittle when drying out which can happen in the fuel cell application under intermittent conditions (Kerres *et al.,* 1999).

There are two new but different procedures for the sulfonation of polysulfone. In one procedure, the sodium-sulfonated group was introduced in the base polysulfone via the metalation-sulfination-oxidation process (Kerres *et al.,* 1996, 1998a). In the other procedure, trimethylsilyl chlorosulfonate was used as the sulfonating agent (Baradie *et al.,* 1998). Lufrano *et al.* (2000,2001) prepared SPSU via trimethylsilyl chlorosulfonate with different degrees of sulfonation (DS). Different membranes with sulfonation degree from 23% to 53% (Lufrano *et al.,* 2000) on the one hand and 49%, 61% and 77% (Lufrano *et al.,* 2001) on the other hand were prepared. With a 61% sulfonation degree a proton conductivity for SPSU of 2.7×10^{-2} S/cm at 25°C was reported (Lufrano *et al.,* 2001). This conductivity was 3.5 times lower than Nafion® 117, but was compensated by the lower thickness, 90 μm vs. 210 μm for Nafion® 117. The cell performance obtained by Lufrano *et al.* (2001) was almost the same for SPSU and Nafion® in a H_2/O_2 fuel cell. This is higher than that reported previously by Kerres *et al.* (1998a) and Baradie *et al.* (1998). Y.S. Kim *et al.* (2003) prepared sulfonated poly(arylether sulfone) membranes.

Promising alternatives suggested by Kerres and co-workers, include composite membranes made from blends of acidic and basic polymers (Cui *et al.,* 1998; Jörissen *et al.,* 2002; Kerres *et al.,* 1999, 2000; Walker *et al.,* 1999) or modified PSU via the metalation-sulfochlorination and the metalation-amination routes (W. Zhang *et al.,* 2001) or crosslinked SPSU (Kerres *et al.,* 1997, 1998b,1998c). These alternatives are made by blending acidic polymers such as SPSU with basic polymers such as poly(4-vinylpyridine) (P4VP), polybenzimidazole (PBI) or a basically substituted polysulfone. Crosslinked SPSU blend membranes have been produced via a new crosslinking process. The blends have been obtained by mixing PSU Udel™ Na-sulfonate and PSU Udel™ Li-sulfinate in *N*-methyl pyrrolidone. The membranes have been crosslinked by S-alkylation of PSU sulfinate groups with di-halogenoalkanes. These membranes show very good performance in H_2/O_2 fuel cells and DMFCs (Kerres *et al.,* 2000; Kerres, 2001). These membranes also show a markedly reduced methanol permeability (Kerres, 2001; Walker *et al.,* 1999).

5.3.5 Sulfonated poly(aryletherketone) membranes

The poly(arylether ketones) are a class of non-fluorinated polymers consisting of sequences of ether and carbonyl linkages between phenyl rings, that can either "ether-rich" like PEEK and PEEKK, or "ketone-rich" like PEK and PEKEKK. The most common material is polyetheretherketone (PEEK) which is commercially available under the name Victrex™ PEEK from ICI Advanced Materials. A number of groups are developing proton conducting polymer materials based on this classification of materials including ICI Victrex, Fuma-Tech and Axiva/Aventis/Hoechst. Sulfonated-PEEK (SPEEK) membranes were prepared as proton conductors in PEMFCs by Schneller *et al.* (1993). Sulfonation of polyetherketones can

be carried out directly in concentrated sulfonic acid or oleum - the extent of sulfonation being controlled by the reaction time and temperature (Bailly *et al.,* 1987; B. Bauer *et al.,* 1994, 1995). Direct sulfonation of PEEK can give materials with a wide range of equivalent weights to form SPEEK. However, the complete sulfonation of the polymer results in a fully water-soluble product. A sulfonation level of around 60% was found to be a good compromise between the conductivity and mechanical properties of membranes. The backbone of SPEEK is less hydrophobic than the backbone of Nafion®, and the sulfonic acid functional group is less acidic (Kreuer, 2001). Various studies have been made on the conductivity of SPEEK (Alberti *et al.,* 2001; B. Bauer *et al.,* 2000; Kobayashi *et al.,* 1998; Kreuer, 1997, 2001; Linkous *et al.,* 1998; P. Xing *et al.,* 2004; Zaidi *et al.,* 2000). The conductivity increases as a function of the degree of sulfonation, the ambient relative humidity, temperature and thermal history. The conductivity of these materials was found to be high at room temperature (Soczka-Guth *et al.,* 1999). In SPEEK with 65% sites sulfonated, the conductivity was higher than that of Nafion® 117 measured under the same conditions - the conductivity reaching 4×10^{-2} S/cm at 100°C and 100% RH (Linkous *et al.,* 1998). SPEEK membranes exhibit at 160°C and 75% RH, sufficiently high values of protonic conductivity - typically 5×10^{-2} – 6×10^{-2} S/cm - for possible applications in low temperature fuel cells (Alberti *et al.,* 2001). The dependence of the conductivity on RH is more marked for SPEEK than for Nafion® under the same conditions (B. Bauer *et al.,* 2000). Sulfonated polyaryls have been demonstrated to suffer from hydroxyl radical initiated degradation (Hubner & Roduner, 1999). In contrast, SPEEK was found to be durable under fuel cell conditions over several thousand hours by Kreuer (2001). The brittleness of SPEEK makes their handling difficult and may lead to mechanical membrane failure during operation. These types of membranes become very brittle when drying out. SPEEK can also be chemically cross-linked to reduce membrane swelling and increase its mechanical strength. Materials prepared by cross-linking are comparable to commercial Nafion® in terms of their mechanical strength and proton conductivity (Yen *et al.,* 1998). Kerres and co-workers prepared novel acid-base polymer blend membranes composed of SPEEK as the acidic compound, and of P4VP or PBI as the basic compounds (Kerres *et al.,* 1999; Jörissen *et al.,* 2002).

6. Organic/inorganic nanocomposite membranes

Membrane electrode assembly (MEA) is the basic component of the single cell of a stack. The proton exchange membrane (PEM) is the key element of this component, which separates the electrode structure to prevent the mixing of reactant gases and the formation of an electrical short. This makes its properties, functionality, cost and reliability very important for real cell operations. Up to now perfluorinated sulfonic acid (PFSA) membranes have been the best choice for commercial low temperature polymer products (<80°C). The advantages of PFSA membranes are:

i.   Their strong stability in oxidative and reduction media due to the structure of the polytetrafluoroethylene backbone; and
ii.   Their proton conductivity, which can be as high as 0.2 S cm^{-1} in full hydrated polymer electrolyte fuel cell.

When used at elevated temperatures, however, PEMFC performances decrease. This decrease is related to: dehydration of the membrane; reduction of ionic conductivity;

decreases in affinity with water; loss of mechanical strength through a softening of the polymer backbone; and parasitic losses (the high level of gas permeation). There are several reasons for the development of high temperature membranes (Savadogo, 2004):

i.   The operation of PEMFC at temperature above 140°C is receiving world-wide attention because fuel selection remains straightforward, and a number of fuels, including reformed hydrogen with high CO content and light hydrocarbons (alcohol, natural gas, propane, etc.) are still being considered for PEMFC application. Accordingly, cell temperature operation at temperatures above 140°C is of great interest because, in this temperature range, anode catalyst poisoning by CO is less important and the kinetics of fuel oxidation will be improved and the efficiency of the cell significantly enhanced. High temperature cell operation will contribute to reducing the complexity of the hydrocarbon fuel cell system. Some other advantages of operating PEMFC at high temperature are: a reduction in the use of expensive catalysts; and minimization of the problems related to electrode flooding. Light hydrocarbons may be potential energy vectors for PEMFC, which may lead to the development of suitable membranes that are stable in high temperature operating conditions and prevent fuel crossover.

ii. Enhancement of gas transport in the electrode layers is also expected because no liquid water will be present in the cell at these temperatures. Membrane proton conductivity should be dependent on water content at these temperatures; consequently, it is not necessary to humidify the gas before it enters the stack. This may help improve the kinetics of mass transport and simplify the fuel cell system. In particular, the kinetics of oxygen reduction reaction could be improved, by at least three orders of magnitude, if we increase the operating temperature from 25 to 130°C. PFSA membranes cannot be used in PEMFC operating above temperatures around 100°C, because at these temperatures they will lose their mechanical properties and their swelling properties will be lowered. They do not perform well above 90°C in a hydrocarbon PEMFC and above 85°C in hydrogen PEMFC. The boiling point of water can be raised by increasing the operating pressure above 3 bar, which may correspond to a boiling point of water of about 135°C. But raising the pressure of PEMFC is undesirable from an efficiency point of view.

One of the main drawbacks of DMFC (direct methanol fuel cell) is the slow methanol oxidation kinetics. An increase in the operating temperature of the DMFC from 90 to about 140°C is highly desirable. Also operation at high temperature will enhanced CO tolerant when a reformate hydrogen is used in H_2-PEMFC. One approach to achieve water retention at high temperature is to fabricate a composite membrane constituted of organic proton conductor and inorganic materials. The organic/inorganic composite proton conductors are developed to overcome the breakdown of the actual state-of-the-art membranes (i.e. PFSA membranes: Nafion® (DuPont), Dow, Flemion® (Asahi Glass Corporation) and Aciplex® (Asahi Chemicals)). Thus, increasing the operating temperature above 100°C, reduced methanol permeability (methanol crossover), increasing the water retention and also increasing the mechanical and thermal stability of the composite membranes.

The method of inclusion of inorganic proton conductor or inorganic particle has involved a bulk powder dispersed in a polymer solution, leading specifically to particles of highly dispersed inorganic fillers of particle size in the sub-micronic range. These methods make use of mild chemistry technique, including intercalation/exfoliation, sol-gel chemistry, and

ion-exchange (Bonnet *et al.*, 2000; Jones & Rozière, 2001). Such approach generally avoid any sedimentation of the inorganic component, intimacy of contact between the inorganic and organic components at the molecular level assures the greatest possible interface and, at such small particle size, the mechanical properties can be improved compared with those of a polymer-only membrane (Jones & Rozière, 2001, 2003). In addition, since in many proton conductors of conductivity suitable for electrochemical applications the proton transfer process takes place on the surface of the particles, increase in surface area (small particle size) will increase the conductivity (Jones & Rozière, 2001).

This concept was suggested by Watanabe *et al.* (1995, 1996) and is based on the development of self-humidifying composite membranes. The membranes are fabricated from the dispersion of nano-particles of Pt in a thin Nafion® film ($\approx$ 50 μm). Membranes fabricated based on this concept should not require external humidification and should suppress the crossover of H_2 and O_2. The dispersed particles should catalyze the oxidation and the reduction of the crossover H_2 and O_2 respectively. Water from this reaction is directly used to humidify the membrane. This is supposed to result in a more stable operation of the cell at 80°C without any external humidification of the membrane (Watanabe *et al.*, 1998).

6.1 Organic/silica nanocomposite membranes

Silica as an additive to Nafion® was widely studies. Both recast Nafion® (Adjemian *et al.*, 2002a,2002b; Antonucci *et al.*, 1999; Arimura *et al.*, 1999; Dimitrova *et al.*, 2002a,2002b) and Nafion® film (e.g. Nafion® 117) (Adjemian *et al.*, 2002b; Baradie *et al.*, 2000; Jung *et al.*, 2002) are used in the fabrication of the composite membrane. Organic–silica composite membranes have been prepared according to several methods by casting mixtures such as: using silicon dioxide particles (e.g. Aerosil A380 from Degussa) (Antonucci *et al.*, 1999; Aricò *et al.*, 1998; Arimura *et al.*, 1999; Dimitrova *et al.*, 2002a,2002b), diphenylsilicate (DPS) (Liang *et al.*, 2006), the other one is to introduce silica oxide incorporated via *in situ* sol-gel reaction of tetraethoxysilane (TEOS) (Adjemian *et al.*, 2002b; Baradie *et al.*, 2000; Deng *et al.*, 1998; R.C. R.C. Jiang *et al.*, 2006b; Jung *et al.*, 2002; Mauritz *et al.*, 1995, 1998). Nafion®–silica membranes shows good performance at T > 100°C due to low levels of dehydration. Nafion®–silica membranes were prepared by mixing Nafion® ionomer (5 wt.%) with 3 wt.% SiO_2 followed by a regular membrane casting procedure. In the final stage, the membranes were heat treated at 160°C for 10 min to achieve both a high crystallinity and high mechanical stability (Antonucci *et al.*, 1999). A DMFC utilizing these membranes was tested under galvanostatic conditions at 500 mA cm^{-2}. The voltage initially decreased from 0.42 to 0.36 V but then remained stable for 8 h. The performance decrease is due to adsorption of poisoning species, which appears to be a reversible process at 145°C (removed by short circuit discharging in the presence of water). These membranes demonstrated higher performance with increasing temperature. A nano-particles possessed a core-shell structure consisting of silica core (< 10 nm) and a densely grafted oligometric ionomer layer was incorporated into Nafion® matrix to form a composite membrane. The polyelectrolyte-grafted silica particles [P(SPA)-SiO$_2$] was dispersed in Nafion® solution and a composite membrane was formed by recasting process. The proton conductivity of Nafion® membrane containing P(SPA)-SiO$_2$ (4 wt.%) is significantly higher than that of unmodified recast Nafion® in the range 25 to 80°C. The composite membrane offers superior cell performance over unmodified recast Nafion® at both operating temperature of 50 and 80°C. At 50°C, the

maximum power output of the composite membrane is about 1.8 times greater than of the Nafion® membrane and at 80°C, the ratio becomes 1.5 (Tay *et al.*, 2008).

Adjemian *et al.* (2002b) prepared composite membranes by either impregnating an extruded film via sol-gel processing of tetraethoxysilane (TEOS), or by preparing a recast film, using solubilized PFSA and silicon oxide polymer/gel. TEOS when reacted with water in an acidic medium undergoes polymerization to form a mixture of silicas (SiO_x) and siloxane polymer with terminal hydroxide and ethoxide groups(SiO_x/-OH/-OEt). When PFSAs are used as the acidic medium, the SiO_x/siloxane polymer forms within the membrane. Composite membranes were tested in fuel cell operating with pre-humidified reactant gases at temperature of 130°C and a pressure of 3 atm. The PFSA/silicon oxide composite membranes shows resistivities 50% lower than their respective unmodified PFSA under the same operating conditions. The observed resistivity trend from best to worst is as follows: Aciplex® 1004/silicon oxide > Nafion® 112/silicon oxide > Nafion® 105/silicon oxide > Aciplex® recast/silicon oxide > Nafion® recast/silicon oxide > Nafion® 115/silicon oxide.

Recently a new approach to make composite membrane was introduced, where a functionalized silica is used as a filler to make the composite membranes (Li *et al.*, 2006; Y.F. Lin *et al.*, 2007; Sambandam & Ramani, 2007 ; Su *et al.*, 2007; Tung & Hwang, 2007). Sol-gel derived sulfonated diphenyldimethoxysilane (SDDS) with hydrophilic –SO_3H functional groups were used as the additive to reduce the methanol permeability of Nafion® (Li *et al.*, 2006). The Nafion®-SDDS nanocomposite membranes were prepared by mixing Nafion® – dimethyl formamide (DMF) solutions with SDDS sol and casting to membranes. The proton conductivity of composite membrane decreased compared with commercial Nafion® membranes. This is partly because (i) the relative low conductivity of organosilica, (ii) the slightly tortuous path through the membrane which is caused by the embedding of the organosilica into the hydrophilic clusters, (iii) and the hydrophobic phenyl groups of the organosilica which change the distribution of the hydrophilic/hydrophobic phases therefore reduce the water content of the membrane. The proton conductivity decreases with the increase of the fillers. On the other hand, the methanol permeability is reduced with the increase of the SDDS content. The methanol permeability drops by a factor of 0.41, 0.61, 0.67 and 0.71 times for nanocomposite with loading of 5, 10, 20 and 25 wt.%, respectively as compared to bare recast Nafion® (Li *et al.*, 2006).

Sulfonic acid functionalized silica was synthesized by condensation of MPTMS (3-mercaptopropyltrimethoxy silane) precursor through a sol-gel approach. Sulfonated poly(ether ether ketone) composite with sulfonic acid functionalized silica were prepared by casting (Sambandam & Ramani, 2007). At 80°C and 75% RH (relative humidity) the measured conductivity was 0.05 S cm^{-1} for SPEEK containing 10% sulfonic acid functionalized silica and 0.02 S cm^{-1} for the plain SPEEK membrane. At 80°C and 50% RH the measured conductivity was 0.018 S cm^{-1} for SPEEK containing 10% sulfonic acid functionalized silica and 0.004 S cm^{-1} for the plain SPEEK membrane.

L64 copolymer-templated mesoporous SiO_2, functionalized with perfluoroalkylsulfonic acid was prepared (Y.F. Lin *et al.*, 2007). A condensation reaction between the surface silanol groups of the mesoporous silicas and 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid Beta-sultone was conducted. Nafion®/functionalized mesoporous silica composite membranes were prepared via homogeneous dispersive mixing and the solvent

casting method. The room temperature proton conductivity of full hydration composite membrane was increased from 0.10 to 0.12 S cm^{-1} as the M-SiO$_2$-SO$_3$H content increased from 0 to 3 wt.%. Methanol permeability decreases with increasing the content of M-SiO$_2$-SO$_3$H, where methanol permeability was 4.5×10^{-6} cm^2 s^{-1}, which was 30% lower than unmodified Nafion®. The current densities measured with composite membranes containing 0, 1, 3 and 5 wt.% M-SiO$_2$-SO$_3$H, were 51, 66, 80 and 70 mA cm^{-2}, respectively, at a potential of 0.2 V. Moreover, all composite membranes containing M-SiO$_2$-SO$_3$H performed better at high current density than did unmodified Nafion®.

Nanocomposite proton exchange membranes were prepared from sulfonated poly(phtalazinone ether ketone) (SPPEK) and various amounts of sulfonated silica nanoparticles (silica-SO$_3$H) (Su *et al.*, 2007). The use of silica-SO$_3$H compensates for the decrease in ion exchange capacity of membranes observed when no-sulfonated nano-fillers are utilized. The strong –SO$_3$H/-SO$_3$H interaction between SPPEK chains and silica-SO$_3$H particles leads to ionic cross-linking in the membrane structure, which increases both the thermal stability and methanol resistance of the membranes. The membrane with 7.5 phr of silica-SO$_3$H (phr = g of silica-SO$_3$H / 100 g of SPPEK in membranes) exhibits low methanol crossover, high bound-water content, and a proton conductivity of 3.6 fold increase to that of the unmodified SPPEK membrane. Nafion®/hydrated phosphor-silicate composite membrane was synthesis by Tung and Hwang (2007). The phosphor-silicate glass, with a nominal composition of 30% P$_2$O$_5$ and 70% SiO$_2$ (molar ratio) (called 30P70Si), was prepared by the accelerated sol-gel process, where tetraethylorthosolicate and trimethyl phosphate are used as precursors. It was found that the methanol permeability decreases dramatically with increased SiO$_2$-P$_2$O$_5$ content and the proton conductivity only decreases slightly , as a consequence the selectivity of the hybrid membranes are higher than unmodified Nafion® membrane.

6.2 Organic/heteropolyacid (HPA) nanocomposite membranes

Perfluorosulfonic acid based organic/ inorganic composite membranes with different heteropolyacid (HPA) additives have been investigated as alternate materials for low humidity PEMFC operation (Giordano *et al.*, 1996; Ramani *et al.*, 2004, 2005a,2005b; Tazi & Savadogo, 2000, 2001). Two major factors limiting the performance of Nafion®/HPA composite membranes are (Ramani *et al.*, 2005b): (i) the high solubility of the HPA additive and (ii) the large particle size of the inorganic additive within the membrane matrix (Ramani *et al.*, 2004, 2005a). Stabilization technique have been developed (Ramani *et al.*, 2005a) to limit the solubility of the HPA additive. Recast Nafion® with phosphotungstic acid (PTA) as HPA fillers were prepared by Ramani *et al.* (2005b). Three types of fillers were used PTA with 30-50 nm particle size, PTA with 1-2 μm particle size and TiO$_2$ with 1-2 μm particle size. The composite membranes had hydrogen crossover currents on the order of 1-5 mA cm^{-2}, with the crossover flux decreasing and approaching the value for recast Nafion® as the particle size was reduced. A 25 μm thick composite membrane with PTA (1-2 μm particle size) had an area-specific resistance of 0.22 Ω cm^{-2} at 120°C and 35% RH, while the corresponding value for a 25 μm thick composite membrane with PTA (30-50 nm) was 0.16 Ω cm^{-2}. The latter membrane compared favorably with recast Nafion®, which had an area-specific resistance of 0.19 Ω cm^{-2} under the same conditions. Savadogo and co-workers (Savadogo, 2004; Tazi & Savadogo, 2000, 2001; Tian & Savadogo, 2005) prepared composite

membranes constituted of recast Nafion®and mixed with appropriate concentration of HPA, namely, silicotungstic acid (STA), phosphotungstic acid (PTA) and phosphomolybdic acid (PMA). It was shown that the water uptake of the various membranes increases in this order: Nafion®117 (27%) < Nafion®/STA (60%) < Nafion®/PTA (70%) < Nafion®/PMA (95%). The ionic conductivity increases in the order Nafion®117 (1.3 × 10^{-2} S cm^{-1})) < Nafion®/PMA (1.5 × 10^{-2} S cm^{-1}) < Nafion®/PTA (2.5 × 10^{-2} S cm^{-1}) < Nafion®/STA (9.5 × 10^{-2} S cm^{-1}). The tensile strength of the membranes decreases in the order: Nafion®117 (15000 Pa) < Nafion®/STA (14000 Pa) < Nafion®/PMA (8000 Pa) < Nafion®/PTA (3000 Pa), while their deformation (ε_{max}) changes in the order : Nafion®/STA (45%) < Nafion®/PMA (70%) < Nafion®/PTA (170%) < Nafion®117 (384%). The current density at 0.600 V of the PEMFCs based on the various membranes varies in the order: Nafion®117 (640 mA cm^{-2}) < Nafion®/STA (695 mA cm^{-2}) < Nafion®/PTA (810 mA cm^{-2}) < Nafion®/PMA (940 mA cm^{-2}).

Tazi and Savadogo (2000) fabricated Nafion® membranes containing silicotungstic acid and thiophene. They reported an increase of up to 60% of water uptake and a considerable improvement in the fuel cell current density, when compared to the plain Nafion® membrane. Dimitrova *et al.* (2002a) prepared a recast Nafion®-based composite membrane containing molybdophosphoric acid. This composite membrane exhibit significantly higher conductivity in comparison to Nafion® 117 and pure recast Nafion®. An enhancement of a factor of 3 in the conductivity at 90°C was observed. Zaidi *et al.* (2000) prepared a series of composite membranes using SPEEK as polymer matrix and tungstophosphoric acid (TPA), its sodium salt (Na-TPA) and molybdophosphoric acid (MoPA) as inorganic fillers. The conductivity of the composite membranes exceeded 10^{-2} S/cm at room temperature and reached values of about 10^{-1} S/cm above 100°C. From the DSC (Differential Scanning Calorimeter) studies, it was indicated that the glass transition temperature of the SPEEK/HPA composite membrane increases due to the incorporation of solid HPA into SPEEK membrane. This increase in the glass transition temperature was attributed to an intermolecular interaction between SPEEK and HPA. Staiti *et al.* (2001) prepared Nafion®(recast)-silica composite membranes doped with phosphotungstic (PWA) and silicotungstic (SiWA) acids for application in direct methanol fuel cell at high temperature (145°C). The phosphotungstic acid-based membrane showed better electrochemical characteristics at high current densities with respect to both silicotungstic acid-modified membrane and silica- Nafion® membrane. The best electrochemical performance is obtained with the PWA-based membrane, which gives a maximum power density of 400 mW cm^{-2} at current density of about 1.4 A cm^{-2} under oxygen feed operation at 145°C. Maximum power density of 340 mW cm^{-2} is obtained from the fuel cell which uses the silica-modified membrane, whereas a lower performance was achieved with the SiWA-based membrane. The maximum power density obtained in air with the PWA-based membrane is 250 mW cm^{-2} at 145°C, and 210 mW cm^{-2} with the Nafion-SiO$_2$ membrane at the same temperature.

Shao *et al.* (2004) prepared Nafion®/silicon oxide (SiO$_2$)/phosphotungstic acid (PWA) and Nafion®/silicon oxide composite membranes for H$_2$/O$_2$ proton exchange membrane fuel cells operated above 100°C. It was found that the composite membranes showed a higher water uptake compared with the Nafion® recast membrane. The proton conductivity of the composite membranes appeared to be similar to that of the native Nafion® membrane at high temperatures and 100% relative humidity (RH), however, it was much higher at low RH. When the composite membranes viz. Nafion®/SiO$_2$/PWA and Nafion®/SiO$_2$ were

employed as an electrolyte in H_2/O_2 PEMFC, the higher current density values (540 and 320 mA cm^{-2} at 0.4 V, respectively) were obtained than that of the Nafion®115 membrane (95 mA cm^{-2}), under the operating conditions of 110°C and 70% RH. A similar membrane was prepared by Aricò *et al.* (2003a,2003b). Sulfonic-functionalized heteropolyacid-SiO_2 nanoparticles were synthesized by grafting and oxidizing of a thiol-silane compound onto the heteropolyacid-SiO_2 nanoparticle surface (H.J. Kim *et al.*, 2006). The composite membrane containing the sulfonic-functionalized heteropolyacid-SiO_2 nanoparticles was prepared by blending with Nafion® ionomer. TG-DTA analysis showed that the composite membrane was thermally stable up to 290°C. The DMFC performance of the composite membrane increased the operating temperature from 80 to 200°C. The function of the sulfonic-functionalized heteropolyacid-SiO_2 nanoparticles was to provide a proton carrier and act as a water reservoir in the composite membrane at elevated temperature. The power density was 33 mW cm^{-2} at 80°C, 39 mW cm^{-2} at 160°C, 44 mW cm^{-2} at 200°C, respectively.

SPEEK-silica membranes doped with phosphotungstic acid (PWA) was synthesized by Colicchio *et al.* (2009). The silica is generated *insitu* via the water free sol-gel process of polyethoxysiloxane (PEOS), a liquid hyperbranched inorganic polymer of low viscosity. PEOS was used as silica precursor instead of the corresponding monomeric tetraethoxysilane (TEOS). At 100°C and 90% RH the membrane prepared with PEOS (silica content = 20 wt.%) shows two times higher conductivity than the pure SPEEK. The addition of small amount of PWA (2 wt.% of the total solid content) introduce in the early stage of membrane preparation brings to a further increase in conductivity (more than three times the pure SPEEK). Different classes of composite membranes containing HPA and silica were developed, namely, phosphomolybdic acid (PMA)/phosphotungstic acid (PWA)- P_2O_5-SiO_2 glass electrolyte (Uma & Nogami, 2007), poly(vinyl alcohol) (PVA)/sulfosuccinic acid (SSA)/silica hybrid membrane (D.S. Kim *et al.*, 2004), PVA/SiO_2/ SiW (silicotungstic acid) (Shanmugam *et al.*, 2006), PVA/PWA/SiO_2 (W. Xu *et al.*, 2004), polyethylene oxide (PEO)/PWA/SiO_2 (Honma *et al.*, 2002), polyethylene glycol (PEG)/4-dodecylbenzene sulfonic acid (DBSA)/SiO_2 (H.Y. Chang *et al.*, 2003), PWA-doped PEG/SiO_2 (C.W. Lin *et al.*, 2005).

6.3 Organic/TiO$_2$ nanocomposite membranes

Nanosized titanium oxide was synthesized by sol-gel hydrolyzing an alcoholic solution of Ti(OiPr)$_4$ by Baglio *et al.* (2005). Thermal treatments at different temperature, namely 500, 650 and 800°C, were performed to tailor the oxide powder properties. The crystallite size for the three sample was found to be 12, 22 and 39 nm, respectively. A composite membrane Nafion®/ 5 wt.% TiO_2 was prepared by using the recast procedure. The composite membrane thickness was about 100 μm. A maximum power density of 350 mW cm^{-2} was obtained at 145°C with the cell equipped with the composite membrane containing TiO_2 calcined at 500°C. Sacca *et al.* (2005) synthesized TiO_2 powder by the sol-gel method starting with a Ti(OiPr)$_4$ and calcined a 400°C. This powder was made of spherical particles with a grain size between 5 and 20 nm. A recast Nafion® with 3 wt.% TiO_2 composite membrane was prepared, the thickness of the membrane was 100 μm. The proton conductivity of different membranes were measured at two different values of relative humidity (RH), 100 and 85% RH, respectively, and simulating the cell operating conditions in the temperature range from 80 to 130°C. Nafion® recast (70 μm thickness) has the lower conductivity ranging

from 0.12 to 0.14 S cm^{-1}, while the composite Nafion®/TiO$_2$ showed highest value than Nafion® 115 (125 μm) were value in the range 0.15-0.18 S cm^{-1} . A power density of 0.514 W cm^{-2} for Nafion® / 3 wt.% TiO$_2$ composite against 0.354 W cm^{-2} for Nafion® 115 at 0.56 V and at T = 110°C was recorded. At 120°C, Nafion® 115 was damaged while the composite Nafion®/TiO$_2$ membrane continued to work up to 130°C by reaching a power density of about 0.254 W cm^{-2} at 0.5 V.

Hybride membranes based on highly sulfonated poly(ether ether ketone) (SPEEK, DS = 0.9) where titania network was dispersed by *insitu* sol-gel reactions were prepared by Di Vona *et al.* (2007). Titania network was introduced following two routes: route 1 using titanium tetrabutoxide (Ti(OBu)$_4$) and pyridine, and route 2 uses Ti(OBu)$_4$ and 2,4-pentandione. Composite membranes prepared by route 2 showed a good conductivity property that can be attributed to the structural characteristics of the inorganic network generated in the presence of a chelating agent. This membrane shows a stable value (σ = 5.8 × 10^{-2} S cm^{-1}) at 120°C in fully hydrated conditions. Jian-hua *et al.* (2008) prepared a composite Nafion®/TiO$_2$ membranes by carrying out *insitu* sol-gel reaction of Ti (OC$_4$H$_9$)$_4$ followed by hydrolyzation-condensation in Nafion® 112, 1135 and 115. TiO$_2$ prepared with this method was found to be 4 nm. TiO$_2$ contents were 1.23, 2.47 and 3.16 wt.% for Nafion® 112/TiO$_2$, Nafion® 1135/TiO$_2$ and Nafion® 115/TiO$_2$, respectively. The polarization characteristics of all three MEAs with the membranes containing TiO$_2$ were improved significantly comparing with those of pure Nafion® film. A mixture of titanium tetraisopropoxide (TTIP) and PEG 1000 were used to prepare the titania sol by Liu *et al.* (2006). The average particle size of 20 nm was reported. The formed sol was deposited on the surface of Nafion® 112 membranes by spin coating. The TiO$_2$ film is dense and well attached to the membrane, but some cracks in the membrane coated with diluted titania sol (e.g. 0.002 mg cm^{-2}), while the membrane coated with thick titania sol (e.g. 0.021 mg cm^{-2}) are very dense and cracks free. The proton conductivity of nano-TiO$_2$-coated Nafion® membranes at 25 and 80°C were recorded with different TiO$_2$ content. It was found that the maximum conductivity was with uncoated Nafion® 112, with values of 0.027 and 0.041 S cm^{-1} for 25 and 80°C, respectively. The conductivity of coated Nafion® decreases with increasing titania content. On the other hand, methanol permeability of the coated membranes decreases with increasing TiO$_2$ content, namely from 3.2 × 10^{-6} to 1.7 × 10^{-6} cm^2 s^{-1} at 25°C, and from 12.5 × 10^{-6} to 4.6 × 10^{-6} cm^2 s^{-1} at 85°C. Thus the rise in temperature leads to a strong increase in permeation by a factor of about 3. The methanol permeability of the unmodified Nafion® 112 membrane was found to be 3.6 × 10^{-6} and 13 × 10^{-6} cm^2 s^{-1} at 25 and 85°C, respectively. The cell performance with titania coated membrane with a content of 0.009 mg cm^{-2} exhibits a higher voltage than cells with Nafion® membrane or with the other coated membranes. Nafion® 112 delivered a maximum power density of 37 mV cm^{-2} at a current density of 200 mA cm^{-2}. A maximum power density of 44 mW cm^{-2} is obtained from a fuel cell that employs the titania-coated membrane with 0.009 mg cm^{-2} content.

6.4 Organic/zirconia and sulfated zirconia nanocomposite membranes

Zirconia as an inorganic filler was added to polymeric proton conductor membranes (Aricò *et al.*, 2003b, 2004; Nunes *et al.*, 2002; Sacca *et al.*, 2006; Silva *et al.*, 2005a, 2005b). The incorporation of zirconia should increase the working temperature, water retention and mechanical stability of the composite membrane. Organic / inorganic composite membranes

based on SPEK and SPEEK for application in direct methanol fuel cell were synthesized by Nunes and co-workers (Nunes *et al.*, 2002). The inorganic fillers were introduced via *in situ* generation of SiO_2, TiO_2 or ZrO_2. The modification with ZrO_2 led to a 60-fold reduction of the methanol flux. However, a 13-fold reduction of conductivity was also observed.

Recast Nafion® composite membranes containing three different percentages (5%, 10% and 20%, w/w) of commercial ZrO_2 as an inorganic filler were tested in fuel cell in a temperature range of 80-130°C in humidified H_2/air gases at 3.0 bar abs by Sacca *et al.* (2006). The introduction of 5 wt.% ZrO_2 in Nafion® produces no evidence changes in the cell performance, while a better performance with 10 wt.% ZrO_2 in Nafion® was obtained with a power density greater than 600 mW cm^{-2} at 0.6 V both at 80°C and 110°C. The good performance of 10 wt.% ZrO_2 in Nafion® was maintained at 130°C with gas humidification of 85% RH, with a maximum power density of about 400 mW cm^{-2} was obtained in the potential range of 0.5-0.6 V. Silva *et al.* (2005a,2005b) prepared SPEEK/ZrO_2 composite membranes using *insitu* formation of zirconia with zirconium tetrapropylate as alkoxide and acetyl acetone as chelating agent. The water/alkoxide ratio was always maintained higher than 1 to ensure the formation of a finely dispersed inorganic phase in the polymer solution. The thickness of the prepared membranes with 0.0, 2.5, 5.0, 7.5, 10.0, 12.5 wt.% of zirconium oxide were 188, 175, 133, 146, 128, 106 μm, respectively. The proton conductivity of the composite membranes was measured at 25°C and it was found that it decreases continuously with the ZrO_2 content. Pervaporation experiments at 55°C showed that the membrane permeability towards methanol decreases with the amount of ZrO_2. Composite SPEEK with 5.0, 7.5, 10.0 wt.% of ZrO_2 were tested in fuel cell. The performance of 12.5 wt.% ZrO_2 composite was very low due to the high ohmic resistance of the corresponding MEA. The membrane 5 wt.% ZrO_2 presents the best DMFC performance among all the studied MEAs. Three types of superacidic sulfated zirconia (S-ZrO_2) were prepared by different methods using hydrated zirconia and sulfuric acid by Hara and Miyayama (2004). Their proton conductivities were evaluated at 20-150°C under saturated water vapor pressure. It was found that the concentration on S-ZrO_2 varied largely depending on the method of preparation. The S/Zr atomic ratio changed from 0.046 for the sample prepared through a mixture of hydrated zirconia powder and sulfuric acid to 0.35 for sample prepared through a mixture of hydrated zirconia sol and sulfuric acid. A powder compact of the former S-ZrO_2 showed a proton conductivity of 4 × 10^{-2} S cm^{-1} at 70°C and 8 × 10^{-3} S cm^{-1} at 150°C, whereas that of the latter S-ZrO_2 exhibited a high conductivity of 5 × 10^{-2} S cm^{-1} at 60-150°C.

S. Ren *et al.* (2006) prepared sulfated zirconia/ Nafion® 115 nanocomposite membrane by ion exchange of zirconium ions into the Nafion® followed by precipitation of sulphated ZrO_2 by treatment in H_2SO_4. The incorporation of sulfated zirconia increases water uptake by the Nafion® membrane, and more water is absorbed than an unmodified membrane at high temperatures. The membrane proton conductivity is decreased slightly by ZrO_2 impregnation. The proton conductivity of Nafion® 115 membrane was found to be 1.5 × 10^{-2} S cm^{-1} at 25°C, while that of S-ZrO_2/ Nafion® 115 membrane is decreased to 5.0 × 10^{-3} S cm^{-1} at 25°C. At 110°C and above, the proton conductivity of S-ZrO_2/ Nafion® 115 membrane is more than one-half that of the Nafion® 115 membrane. Fine particle superacidic sulfated zirconia (S-ZrO_2) was synthesized by ameliorated method, and composite membranes with different S-ZrO_2 contents were prepared by a recasting procedure from a suspension of S-

ZrO_2 powder and Nafion® solution (Zhai *et al.,* 2006). The results showed that the IEC (Ion Exchange Capacity) of composite membrane increased with the content of S-ZrO_2 and S-ZrO_2 was found to be compatible with the Nafion® matrix. The incorporation of the S-ZrO_2 increased the crystallinity and also improved the initial degradation temperature of the composite membrane. The performance of single cell was the best when the S-ZrO_2 content was 15 wt.% and achieved 1.35 W cm^{-2} at 80°C and 0.99 W cm^{-2} at 120°C based on H_2/O_2 and at a pressure of 2 atm, the performance of the single cell with optimized S-ZrO_2 was far more than that of the Nafion® at the same condition (e.g. 1.28 W cm^{-2} at 80°C and 0.75 W cm^{-2} at 120°C). A self-humidifying composite membrane based on Nafion® hybrid with SiO_2 supported sulfated zirconia particles (SiO_2-SZ) was fabricated and investigated for fuel cell application by Bi *et al.* (2008). The bi-functional SiO_2-SZ particles, possessing hygroscopic property and high proton conductivity, was incorporated in recast Nafion® membrane. The proton conductivity of Nafion®/SiO_2-SZ, Nafion®/SiO_2 and recast Nafion® under dry and wet H_2/O_2 conditions at 60°C were compared. The two composite membranes showed higher proton conductivity in contrast to the recast Nafion® membrane under 0% RH mode with the order Nafion®/SiO_2-SZ > Nafion®/SiO_2 > recast Nafion®. Under 100% RH mode, the Nafion®/SiO_2-SZ composite membrane also exhibited the highest proton conductivity values among the three membranes. The proton conductivity of Nafion®/SiO_2-SZ membrane was 6.95 × 10^{-2} S cm^{-1} and the value was higher than Nafion®/ SiO_2 membrane of 5.54 × 10^{-2} S cm^{-1} and recast Nafion® membrane of 6.55 × 10^{-2} S cm^{-1}. Single cell performance of these composite membranes were tested with wet H_2 and O_2 at 60°C. Nafion®/ SiO_2 composite membrane exhibited the worst output performance (0.864 W cm^{-2}) due to the increased proton conductive resistance caused by incorporated less proton conductivity of SiO_2 particles. In contrast, Nafion®/SiO_2-SZ composite membrane showed similar cell performance to recast Nafion® (1.045 W cm^{-2} vs. 1.014 W cm^{-2}). However, the single cell performance of Nafion®/SiO_2-SZ and Nafion®/SiO_2 membranes with dry H_2 and O_2 at 60°C were 0.980 and 0.742 W cm^{-2}, respectively. These results shows that the composite membrane perform better than unmodified Nafion® (i.e 0.635 W cm^{-2}) under dry condition and the composite membranes manifested a good water retention.

6.5 Organic/zirconium phosphate nanocomposite membranes

Layered zirconium phosphate (ZrP) and phosphonates were used as inorganic fillers of proton conducting polymeric membranes because they are proton conductors with good chemical and thermal stability. Under the most favourable conditions, their conductivity is around 10^{-2} S cm^{-1} for high surface ZrP (Alberti *et al.,* 1978; F. Bauer & Willert-Porada, 2005) and 10^{-1} S cm^{-1} for zirconium phosphate sulfophenylenphosphonates (Alberti *et al.,* 2004,2005a). ZrP can be added to Nafion® (Alberti *et al.,* 2007; F. Bauer & Willert-Porada, 2004,2005,2006a; Casiola *et al.,* 2008; Costamagna *et al.,* 2002; Grot & Rajendran, 1999; Helen *et al.,* 2006,2007; Hou *et al.,* 2008; R. Jiang *et al.,* 2006a; Kuan *et al.,* 2006; H.K. Lee *et al.,* 2004; Mitov *et al.,* 2006; Yang *et al.,* 2001a,2001b,2004), SPEEK (Bonnet *et al.,* 2000; Nunes *et al.,* 2002; Silva *et al.,* 2005b; Tchicaya-Bouckary *et al.,* 2002; Triphathi *et al.,* 2007,2009), SPEK (Nunes *et al.,* 2002; Ruffmann *et al.,* 2003) and difulfonated poly(arulene ether sulfone) (Hill *et al.,* 2006). A similar inorganic material derived from ZrP, named zirconium phosphate sulfophenylen-phophonate was also used as a filler with Nafion® (Y.T. Kim *et al.,* 2004), SPEEK (Krishnan *et al.,* 2006) and PVDF (polyvinyl -lidene fluoride) (Casiola *et al.,* 2005).

F. Bauer & Willert-Porada (2004,2005,2006a) impregnated Nafion® with different ZrP contents. The proton conductivity of unmodified Nafion® 117 and Nafion® 117/ZrP (21 wt.%) was measured at three different temperatures, 80, 100 and 130°C. It was found that the presence of ZrP decreased the proton conductivity in all cases. At high humidity the conductivity first increased from 80 to 100°C and decreased at 130°. The conductivity decrease is more pronounced in case of the unmodified Nafion®. DMFC performance was conducted with Nafion® 117 and Nafion® 117/ZrP composite membrane at 130°C and 4.6 bar at the anode and cathode. It was found that the power output of Nafion® was higher than that of the composite membranes (Nafion® 117/13 wt.% ZrP and Nafion® 117/26 wt.% ZrP). At 0.2 A cm^{-2}, a values of 420, 370 and 370 mV were measured for Nafion® 117, Nafion® 117/13 wt.% ZrP and Nafion® 117/26 wt.% ZrP, respectively. The crossover current was reduced by a factor of two as compared to the unmodified Nafion®. Also the two composite membranes tested exhibited a higher OCV than unmodified Nafion®, which also indicates lower methanol permeability. A values of 725, 768 and 760 mV were reported for Nafion® 117, Nafion® 117/13 wt.% ZrP and Nafion® 117/26 wt.% ZrP, respectively.

Yang and coworkers (Yang *et al.*, 2001a,2001b,2004; Costamagna *et al.*, 2002) introduced ZrP into Nafion® 115 through ion exchange of Zr^{4+} followed by precipitation of ZrP by treatment with phosphoric acid as described by Grot and Rajendran (1999). An MEA employing Nafion® 115/23 wt.% ZrP gave a H_2/O_2 PEMFC performance of about 1000 mA cm^{-2} at 0.45 V at a temperature of 130°C and a pressure of 3 bar, while unmodified Nafion® 115 gave 250 mA cm^{-2} at 0.45 V when operated under the same conditions of temperature and pressure. Similar experiment performed with recast Nafion® and recast Nafion®/36 wt.% ZrP composite confirmed an analogous improvement of performance of the composite membrane over the unmodified ones. The composite recast Nafion®/36 wt.% ZrP gave about 1500 mA cm^{-2} at 0.45 V at a temperature of 130°C and a pressure of 3 bar.

Alberti *et al.* (2005b,2007) prepared a recast Nafion® filled with ZrP according to the procedure described in the patent (Alberti *et al.*, 2005b). Zirconyl propionate was used instead of zirconyl oxychloride and the solutions were dissolved in DMF. The IEC (ion exchange capacity) of the prepared composite membrane was found to be higher than those previously reported for Nafion®/ZrP membranes prepared according to the exchange method (F. Bauer & Willert-Porada, 2006b; Yang *et al.*, 2004). The proton conductivity was found to decrease with increasing the filler loading, which is in agreement with the trend found for Nafion®/ZrP prepared by the exchange method (F. Bauer & Willert-Porada, 2005; Casiola *et al.*, 2008; Yang *et al.*, 2004). At constant RH, the logarithm of conductivity shows approximately the same linear dependence on ZrP loading in the RH range 50-90%. However, at 35% RH, the increase in the ZrP loading results in a larger conductivity decrease than that observed in the above RH range. A similar behavior was also reported for Nafion®/ZrP membranes obtained by the exchange method already at 50% RH (Yang *et al.*, 2004), thus confirming that the same type of filler prepared by using different procedures gives rise to different membrane properties. It was concluded that the main difference between pure Nafion® and composite membranes appear at low RH and high filler loading. It was reported that the Nafion® conductivity undergoes an irreversible decay above certain values of temperature and RH, which was attributed to an anisotropic swelling of the membrane, pressed between the electrodes, in the direction parallel to the membrane surface (Alberti *et al.*, 2001; Casiola *et al.*, 2006). It was also found that, at a given RH value,

the decay temperature for composite Nafion®/ZrP membranes was higher than for pure recast Nafion® membranes prepared and thermally treated under the same conditions used for the composite sample. The conductivity of the pure Nafion® starts to decay at temperatures higher than 130°C, while the conductivity of the composite membrane is stable up to 140°C. Nafion® 115/23 wt.% ZrP was prepared by ion exchange and tested for DMFC by Hou *et al.* (2008). It was found that the liquid uptakes of Nafion® 115 and Nafion® 115/23 wt.% ZrP membranes increased linearly with increasing methanol concentration. The slope of the plot for Nafion® 115 was larger than for the composite membrane i.e. the liquid uptake of Nafion® 115 increased from 34.3% in 0M methanol solution to 58.6% in 10M methanol solution, while that of the composite membrane increased from 28.3% to 37.5% in the corresponding methanol solution. When 23 wt.% of ZrP was incorporated into Nafion® 115, the IEC of the resulting membrane increased significantly to 1.93 meq/g from a value of 0.909 meq/g for pure Nafion® 115. The proton conductivity at room temperature of Nafion® 115 and Nafion® 115/23 wt.% ZrP was found to be 0.10 and 0.084 S cm^{-1}, respectively. Also it was found that the methanol crossover through the composite membrane was suppressed. The DMFC test at 75°C and 5M methanol solution shows that the composite membrane performed better that the pure Nafion® 115, with a peak power density of 96.3 and 91.6 mW cm^{-2}, respectively. When the methanol concentration was further increase to 10M, the peak power density of DMFC with composite membrane was 76.19 mW cm^{-2}, which is higher than that for Nafion® (42.4 mW cm^{-2}). However, Bonnet *et al.* (2000) investigated the incorporation of ZrP in SPEEK. It was found that the conductivity of the composite membrane exceeded that of the polymer-only membrane, and increases with the amount of the filler (from 0-30 wt.%) up to 0.08 S cm^{-1} when measured at 100°C and 100% RH. A similar trend was also observed, when the RH varied from 50 to 100%. At all value of RH, the composite membrane SPEEK/20 wt.% ZrP conductivity was higher than that of non-modified SPEEK. A similar membrane was prepared by Tchicaya-Bouckary *et al.* (2002). The conductivity of SPEEK/25 wt.% ZrP was found to be weakly temperature dependence, the conductivity increases from 2×10^{-2} to 5×10^{-2} S cm^{-1} between 20 and 100°C at 100% RH. This composite membrane was tested in H_2/O_2 fuel cell at 100°C at an oxygen pressure of 3.6 bars absolute. A value of 1 A cm^{-2} at 0.6 V was reported. These results are much better than that reported for Nafion® 115/ ZrP (Costamagna *et al.,* 2002) which provided ca. 0.7 A cm^{-2} at 0.6 V, 130°C and 3 bars pressure. Nunes and co-workers studied the incorporation of ZrP in SPEEK and SPEK (Nunes *et al.,* 2002; Ruffmann *et al.,* 2003; Silva *et al.,* 2005c). ZrP was prepared according to the procedure described by Belyakov & Linkov (1999). It was reported that the incorporation of ZrP did not lead to a particular reduction of water and methanol permeability, and the proton conductivity at 25°C was decreased to the same extent (44 mS cm^{-1} for a SPEK/ 20 wt.% ZrP and 50 mS cm^{-1} for a pure SPEK membranes). A good values of proton conductivities were measured for membranes with 70/20/10 and 69/17/14 wt.% SPEK/ZrP/ZrO$_2$ where a conductivities of 45 and 35 mS cm^{-1} were measured, respectively (Nunes *et al.,* 2002). ZrP pretreated with *n*-propylamine and PBI was incorporated with SPEEK (Silva *et al.,* 2005c), the proton conductivity of the composite membranes decreases with the amount of inorganic incorporation. On the other hand, methanol and water permeability in the pervaporation experiments at 55°C showed that it decrease with the amount of inorganic incorporation. Similar trend was found for the composite membranes permeability towards nitrogen, oxygen and carbon dioxide. The SPEEK composite membranes were tested in a DMFC at 110°C, it was found that the

unmodified SPEEK (SD = 42%) membrane presented the maximum power density output. It achieved an output power density value of 10.4 mW cm^{-1} for 51.8 mA cm^{-2}. The unmodified membrane with SD = 68% could not be characterized due to its instability (high swelling or even solubility). However, the SPEEK (SD=68%)/20 wt.% ZrP/11.2 wt.% PBI had even higher power density than the membrane with SD = 42% for current density lower than 25 mA cm^{-2}. When the relative humidity at the cathode feed was increased to 138%, the SPEEK (SD=68%)/20 wt.% ZrP/11.2 wt.% PBI membrane had the best performance, with an output power density value of 14.7 mW cm^{-1} for 58.8 mA cm^{-2} (Silva *et al.*, 2005c). However, the filler addition to SPEEK (SD = 42%) besides reducing the crossover had an excessive (negative) effect on the proton conductivity.

Zirconium phosphate sulfophenylphosphate, a functionalized ZrP, was incorporated in Nafion® (Casiola *et al.*, 2008; Y.T. Kim *et al.*, 2004), SPEEK (Bonnet *et al.*, 2000; Krishnan *et al.*, 2006) and PVA (Casiola *et al.*, 2005). ZrP sulfophenylphosphates (ZrSPP) are a class of layered materials exhibiting proton conductivity comparable with that of Nafion membranes (i.e. 0.07-0.1 S cm^{-1} at 100°C and 100% RH) due to the presence of the –SO$_3$H groups in the interlayer region (Alberti *et al.*, 2005a). The functionalization of the ZrP nanoparticles with SPP is therefore expected to increase the conductivity of the Nafion®/ZrP membranes. These phosphonates are ideally obtained by partial replacement of SPP groups for the phosphate groups of ZrP (Casiola *et al.*, 2008). Nafion® 117/ZrSPP composite membranes was found to have a higher conductivity than the parent Nafion® 117/ 20 wt.% ZrP and pure Nafion® 117 membrane at 100°C and RH between 30-90%, with highest value approaching 0.1 S cm^{-1} at RH = 90% (Casiola *et al.*, 2008), while appreciable dehydration of Nafion® 117 resulted in drastic reduction of proton conductivity above 100°C (Y.T. Kim *et al.*, 2004). However, the proton conductivity of Nafion®/12.5 wt.% ZrSPP composite membrane slightly increased up to 70°C and remained constant until 140°C, with a conductivity of 0.07 S cm^{-1} (Y.T. Kim *et al.*, 2004).

6.6 Organic/palladium nanocomposite membranes

This approach is to utilize the unique properties of palladium which is permeable to protons, but very resistant to methanol transport. It was suggested first by Pu *et al.* (1995) where they used a palladium foil of 25 μm thick sandwiched between two Nafion® 115 sheets. They proved that with this approach methanol crossover can be reduced, but the cell performance will be lower due to the increase of the membrane thickness.

Choi *et al.* (2001) used the same approach by sputtering metallic palladium on the surface of a Nafion® 117 to plug the pores of Nafion®. The palladium film was found to be 20 nm. Methanol permeability was reduced from 2.392 × 10^{-6} cm^2 s^{-1} in unmodified Nafion® 117 to 1.7 × 10^{-6} cm^2 s^{-1} in Pd-sputtered membrane and the cell performance at 95°C was improved compared to the unmodified Nafion® 117 membrane. The methanol permeability reduction was confirmed by the high OCV obtained with the modified membranes. Similarly, Yoon *et al.* (2002) used sputtering technique to deposit Pd film on the surface of Nafion® 117. It was found that the Pd films thinner than 300 Å were dense and appeared to be well attached to the membrane, but there were many cracks in the 1000 Å films. The 1000 Å films were very unstable and were easily delaminated from the membrane surface. When the composite membrane is immersed in water, the Nafion® membrane swells very much, but the Pd film can not expand as much as the membrane (Yoon *et al.*, 2002). The proton conductivity was

found to decrease with increasing Pd thickness. For the Pd-1000 Å film, 30% reduction in conductivity was observed. Methanol permeability at 25°C decreased with increasing Pd thickness and they varied from 2.90×10^{-6} to 2.23×10^{-6} cm^2 s^{-1} by deposition of Pd film of 1000 Å on the Nafion® 117 membrane. For the Pd-1000 Å-Nafion® 115 membrane, permeability decreased as much as 44% from 2.97×10^{-6} to 1.67×10^{-6} cm^2 s^{-1}. The cell performance at 90°C exhibited a slight decrease with the Pd layered Nafion® 115 membranes. The methanol crossover through an MEA is inversely proportional to current density and thus, its effect on the performance is more prominent at low current densities. It was found that at low current densities cell performance increased in Pd film of 1000 Å on the Nafion® 115, where the Pd film act as a barrier to methanol crossover. However, these results are different of that of Choi *et al.* who observed significant increase in DMFC performance in Pd-20 nm film on Nafion® 117.

Z.Q. Ma *et al.* (2003) followed a different approach, where Nafion® membrane was modified by sputtering a thin layer of Pt/Pd-Ag/Pt on its surface. The methanol crossover can be reduced by sputtering Pd-Ag alloys over the polymer electrolyte, furthermore, when hydrogen is absorbed and dissolved in the membrane, the palladium-silver alloy membrane not only reduces the possibility of embrittling due to $\alpha \rightarrow \beta$ phase transition at low temperatures (< 150°C) but also leads to a higher permeability for hydrogen than pure palladium membrane. The composite membranes were prepared as follows: on one side of the Nafion® 117 membrane, a 2 nm Pt film was first deposited. This was followed by a Pd-Ag film with three different thicknesses (0.1, 0.2 and 1 μm). On the top of the Pd-Ag, it was coated with another 2 nm Pt film. Before a MEA was manufactured, a 4-5 μm layer of Nafion® polymer was recast over the surface of the sputtered Pt/Pd-Ag/Pt layer with Nafion® solution. The final membrane prepared was in the form of Nafion®117/Pt/Pd-Ag/Pt/Nafion®, containing 0.0086 mg cm^{-2} Pt, 0.90 mg cm^{-2} Pd, and 0.27 mg cm^{-2} Ag. The cell performance and the OCV increased with increasing the sputtering alloy layer thickness and the best performance and the highest OCV were found with the 1 μm Pd-Ag film. Also it was showed that the performance with the 1 μm Pd-Ag film is higher than that of cell with a Nafion® membrane having catalyst loading twice as high. Palladinized Nafion® composite membrane was prepared via ion-exchange and chemical reduction method (Y.J. Kim *et al.*, 2004). Palladium(II) acetylacetonate and tetraammine-palladium(II) chloride hydride were used as palladium precursors. Nafion® 117 samples were immersed in palladium precursor solutions followed by chemical reduction of palladium precursors by sodium borohydride. The use of tetraamminepalladium(II) chloride hydride formed 40-50 nm of palladium particles while palladium(II) acetylacetonate formed 5-10 nm of particles. For all palladinized samples, water uptake was higher than for unfilled Nafion® whereas above a certain amount of incorporated palladium, methanol uptake was lower than for unfilled Nafion®. Incorporating Pd nanoparticles decreases the proton conductivity and methanol permeability, compared to bare Nafion®, simultaneously. However, the conductivity increased and methanol permeability decreased as the amount of incorporated Pd increased, and above a certain amount the rapid increase of conductivity and permeability appeared. The DMFC performance at 40°C was improved by incorporating Pd.

Different approach for the incorporation of Pd in Nafion® membranes was suggested by Tang *et al.* (2005). Multi-layer self-assembly Nafion® membranes (MLSA Nafion® membranes) were prepared by alternately assembling charged Pd particles and Nafion®

ionomer onto Nafion® 112 membranes. The Pd particles, size of about 1.8 nm in average, are charged by PDDA (polydiallyldimethylammonium chloride) ionomers. The Pd loading of the first-layer MLSA Nafion® membranes was 0.63 µg cm^{-2}, and the surface coverage of the Pd nanoparticles on the Nafion® membrane was estimated as 22%. After 5-double-layer Pd particles/Nafion® ionomers assembling, the Pd loading reached to 2.86 µg cm^{-2}. The methanol crossover current of the original Nafion® membranes and 1-double-layer, 2-double-layer, 3-double-layer, 4-double-layer, 5-double-layer MLSA Nafion® membrane were 0.0495, 3.87 × 10^{-3}, 1.38 × 10^{-3}, 7.32 × 10^{-4}, 5.16 × 10^{-4} and 4.25 × 10^{-3} A cm^{-2}, respectively, corresponding conductivities of 0.112, 0.110, 0.105, 0.094, 0.087 and 0.081 S cm^{-2}. No DMFC data were provided, however, it was suggested that the 3-double-layer self-assembly membrane is the best suited for DMFC application, since it has a methanol crossover decreased to 0.86%, and a conductivity remaining at 83.9% comparing to original Nafion® membrane. Electroless plating was also used to deposit Pd layer on Nafion® membranes (Hejze et al., 2005; Sun et al., 2005). Palladium layer can reduce methanol crossover when coated on the surface of Nafion®, i.e. limiting current from methanol permeation through a membrane electrode assembly was reduce from 64 to 57 mA cm^{-2} for 1M methanol, and from 267 to 170 mA cm^{-2} for 5M methanol, for Nafion® 115 and Pd/Nafion® 115 membranes respectively (Sun et al., 2005). Also it was demonstrated that the DMFC performance increase with the incorporation of Pd in Nafion® 115. When 1M methanol was used, the power density increased from 36 to 45 mW cm^{-2}, for Nafion® 115 and Pd/Nafion® 115, respectively. When 5M methanol was used, the maximum power density on Pd/Nafion® 115 was 72 mW cm^{-2}, while the performance of MEA with pure Nafion® 115 membranes was only 32 mW cm^{-2}.

6.7 Organic/montmorillonite nanocomposite membranes

Montmorillonite (MMT) is a type of layered silicate composed of silica tetrahedral and alumina octahedral sheets (J. Chang et al., 2003) and its intercalation into Nafion® membrane can decrease successfully the methanol permeability and improve mechanical property (Jung et al., 2003; Song et al., 2004). Research by J. Chang et al. (2003) has showed that layered silicates incorporated into SPEEK membranes helped to reduce swelling significantly in hot water and decrease the methanol crossover without a serious reduction of the proton conductivity. Gaowen and Zhentao (2005) prepared organically modified MMT (OMMT) through ion exchange reaction between alkylammonium cations and metal cations. The nanocomposite membranes (SPEEK/OMMT) were prepared using the solution intercalation technique. The water uptake of SPEEK membrane increased rapidly above 50°C, while the SPEEK/OMMT composite membranes posses of rather constant water uptake up to 80°C. This indicates that MMT layers incorporated into SPEEK matrix prevent extreme swelling of the composite membranes due to the cohesion of the functional groups between SPEEK matrix and MMT layers. The proton conductivity of the membrane was measured at temperature ranging from 22 to 110°C. It was found that the conductivity of SPEEK/OMMT composite is lower than that of the pristine SPEEK and decreases sequentially as the content of OMMT increases, which is due to prolonging the transfer route of proton. The conductivity of SPEEK/OMMT (5 wt.%) approaches the value of Nafion® 115 at 90°C and reaches 1.2 × 10^{-2} S cm^{-1}. The activation energies of SPEEK/OMMT are higher than that of Nafion® 115, where the value of 32.08 kJ/mol and 10.8 kJ/mol, respectively, were found. Methanol permeability was found to be in the

following order: Nafion® 115> SPEEK > SPEEK/OMMT. Therefore, incorporating nano-sized dispersion of OMMT prevents methanol from migrating through the membrane. Song *et al.* (2004) prepared recast Nafion®/MMT nanocomposite membranes at a loading of 3 wt.% clay. It was found that the strength increased more than 35% and the tensile elongation almost doubled. The thermal decomposition behavior of Nafion®/MMT nanocomposite was similar to that of pristine Nafion®, but the major decomposition temperature of polymer main chain shifted to much higher temperature region. The proton conductivity of pristine recast Nafion® with thickness of ca. 100 μm and dry state reached about 0.08 S/cm at room temperature. For Nafion®/MMT nanocomposite membranes, the room temperature conductivity was almost similar to that of neat Nafion® below MMT loading of 2 wt. % and then decreased gradually with the increase in filler content. The methanol permeability of pristine recast Nafion® was 2.3×10^{-6} cm^3 cm/ cm^2 s, while for Nafion®/MMT composite membranes with a thickness of 50 μm significantly decreases to 1.6×10^{-7} cm^3 cm/ cm^2 s by only 1 wt.% organo clay loading, which amounted to more than 90% reduction. Jung *et al.* (2003) prepared dodecylamine-exchanged montmorllonite (m-MMT) by a cation exchange reaction. The thermal resistance of Nafion®/MMT composite was found to be lower than that of the pristine Nafion®. Also the thermal resistance of 5 and 7 wt.% MMT was lower than that of 3 wt.% MMT. On the other hand, Nafion®/MMT displayed higher thermal resistance than that of pristine Nafion®. The thermal resistance of the Nafion®/m-MMT nanocomposite was also increased slightly with increasing the contents of m-MMT in the composite membrane. The methanol permeability of pristine Nafion® was found to be 0.13 mol/l at 1 h. By adding MMT and m-MMT, the methanol permeability decreased to 0.045 and 0.042 mol/l at 1 h, respectively. The proton conductivity of Nafion®/MMT was found to be 8.9×10^{-2}, 7×10^{-2}, 7.2×10^{-2} and 6.7×10^{-2} S/cm at 110°C for a content of MMT of 0, 3, 5 and 7 wt.%, respectively. However, the conductivity of Nafion®/m-MMT was found to be 8.9×10^{-2}, 7.72×10^{-2}, 7.57×10^{-2} and 7.4×10^{-2} S/cm at 110°C for a content of m-MMT of 0, 3, 5 and 7 wt.%, respectively. In general the proton conductivity of the composite membranes decreased slightly with increasing the contents of MMT and m-MMT and lower than pristine Nafion®. Pristine Nafion® performances were 385, 410 and 138.1 mA/cm^2 (at a potential of 0.4 V) at 90, 110 and 125°C, respectively. For Nafion®/3 wt.% MMT performances were 370, 452.6 and 282.86 mA/cm^2 (at a potential of 0.4 V) at 90, 110 and 125°C, respectively. Finally, for Nafion®/3 wt.% m-MMT performances were 367.1, 440 and 290 mA/cm^2 (at a potential of 0.4 V) at 90, 110 and 125°C, respectively. Gosalawit *et al.* (2008) prepared sulfonated montmorillonite (SMMT) with SPEEK. It was found that the inorganic aggregation in SPEEK increased with SMMT loading. The stability in water and in methanol aqueous solution as well as the mechanical stability were enhanced with SMMT loading. Whereas thermal stability improvement did not exist significantly. The methanol permeability was reduced when the SMMT loading increased. The proton conductivity was improved with the incorporation of SMMT. SMMT/SPEEK nanocomposite membranes showed significant cell performance for DMFC as compared to pristine SPEEK and Nafion® 117 membranes.

6.8 Organic/zeolites nanocomposite membranes

Mordenite crystals dispersed in poly(acrylic acid) was prepared by Rao *et al.* (1994) and Libby *et al.* (2001), while mordenite dispersed in Nafion® was prepared by Arimura *et al.* (1999). These membranes displayed proton conductivity about two orders of magnitude

lower than that of pristine Nafion®. A study of using ZSM5 as a filler in Nafion® was study by Byun *et al.* (2006). These composite membranes show higher water uptake than Nafion® 115, while methanol permeability has decrease with increasing zeolite contents. The selectivity of nanocomposite membranes was higher than that of Nafion® 115. Zeolite beta was incorporated in Nafion® (Holmberg *et al.*, 2008) and Chitosan (Y. Wang *et al.*, 2008) membranes. Zeolite beta/ Nafion® nanocomposite membranes with loading of 2.5 and 5 wt.% posses proton conductivity/methanol permeability (selectivity) ratios as much as 93% higher than commercial Nafion® 117 at 21°C, and 63% higher at 80°C. These composite membranes outperform Nafion® 117 in DMFC (Holmberg *et al.*, 2008). The incorporation of zeolite beta in Chitosan reduces the methanol permeability. Furthermore, zeolite beta was sulfonated, therefore the methanol permeability was further reduced as a result of the enhanced interfacial interaction between zeolite beta and Chitosan matrix. The cell performance of the composite membrane were comparable to Nafion® 117 at low methanol concentration (2M) and much better at high methanol concentration (12M) (Y. Wang *et al.*, 2008). Other zeolite based nanocomposite membranes investigated are MCM-41 (Bello *et al.*, 2008; Gomes *et al.*, 2008; Karthikeyan *et al.*, 2005; Marschall *et al.*, 2007), zeolite Y (Ahmad *et al.*, 2006), zeolite BEA (Holmberg *et al.*, 2005) and Chabazite and clinoptilolite (Tricoli & Nannetti, 2003). These membranes can maintained the proton conductivity at temperature above 100°C, also methanol permeability is reduced by incorporating these zeolites.

7. Conclusion

High temperature operating fuel cell enhanced the performance, especially for methanol, DME and ethanol fuel cells. Incorporating nano inorganic materials in the organic matrix has several advantages, namely increase membrane thermal and mechanical stabilities, increase the working temperature and water retention. Some inorganic fillers are proton conductor which can increase the conductivity of the composite membrane or at least keep the same conductivity of the pristine organic membrane. Fuel crossover also can be reduced by incorporating these inorganic nano materials.

From all the investigated inorganic fillers, the nano size played a major role to enhance the compatibility and the interaction of the inorganic fillers with the polymeric matrix. Also the optimal inorganic loading was found to be around 5 wt.%, with the majority around 3 wt.%.

However, for commercialization of these nanocomposite membranes, more R&D needed to be done, which include:

- Systematic study of these nanocomposite, especially inorganic loading;
- The interaction between the nano-inorganic materials with the organic matrix need to be understood;
- High temperature fuel cell performance needed to be done with very little or no humidification and no pressure;
- Long term fuel cell performance;
- Long term membrane stability (thermal and mechanical) and also long term membrane leaching; and
- A comprehensive comparative study between all the investigated inorganic materials and the interaction with different organic materials.

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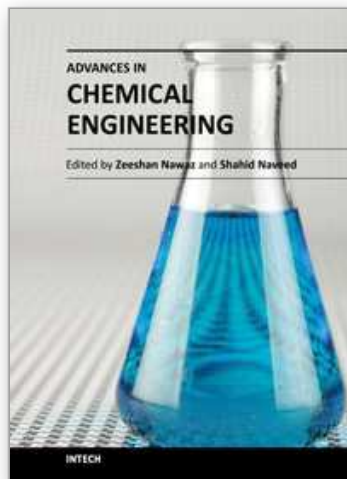
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Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the sate of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic molding. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided in to two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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