

Polymer Nanocomposites - Fuel Cell Applications

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1. Introduction

“In today’s world, solving environmental problems is an investment and not an expense”. It is our task in our time and in our generation to hand down undiminished to those who come after us, as was handed down to us by those who went before, the natural wealth and beauty which is ours. Throughout the world, environmental protection *via* green power technology is imperative. It has prompted intensive research activities in various aspects of fuel cells (Sopian & Daud, 2006). Fuel cell is an electrochemical device which directly converts chemical energy into an electrical energy by utilizing various fuels such as hydrogen, methanol, ethanol, methylene blue, glucose, natural gas, etc., in a reaction with an oxidant (oxygen) (Haynes, 2001).

Many investigations have been explored on the various components of polymer electrolyte membrane (PEMFC) and direct methanol fuel cells (DMFC) such as gas diffusion layer (GDL), membrane electrode assembly (MEA), bipolar plates, stack, catalysts, and electrolyte membranes (Bazylak, 2006; Ahmed & Sung, 2008). Among the various components of fuel cells, the research and developmental activities are focusing their keen interest towards the development of polymer electrolyte membranes. Electrolyte membranes act as a separator between the electrodes and determine the overall performance of fuel cells. In other words, electrolyte membranes are considered as the basic backbone or heart of the polymer membrane electrolyte fuel cells. High temperature and lower humidity operation of fuel cell is essential for the higher energy performance and it circumvents the reformer which decreases the cost of the entire fuel cell device. In general, acidified polymers have been used as a polymer electrolyte membrane for the applications of fuel cells. The higher extent of acidification leads to a physical infertility and deteriorates the fuel cell performance and durability. So an improvement has to be made on the polymer membrane for the betterment of extended fuel cell performance associated with the durability. Though many efforts have been addressed to gear this issue, synthesis of new proton conducting polymers and modifying the existing polymers with nanometric inorganic filler techniques are very attractive. The difficult molecular and structural parameters of the new polymer synthesis hinder its large scale applications. Whereas easier and controllable synthesis routes

associated with cheap cost and less environmental impact of polymer nanocomposite influences its viable applications in fuel cells.

The polymer nanocomposites are polymer matrices reinforced with nanometric inorganic fillers and are an integral aspect of nanocomposite technology. Polymer nanocomposite materials are remarkable family of isotropic, flexible, amorphous nanocomposite materials, which have been extensively investigated for structural materials and biomedical materials due to their enhanced optical, electrical, thermal, magnetic, physical, chemical, conductive and other smart functionalities (Ahmed & Sung, 2008). Recently, numerous polymer nanocomposite membranes fascinate the fuel cell field (Karen & Richard, 2007). The prerequisites of polymer electrolyte membranes can be effectively satisfied by synergistically combining both organic and inorganic nano materials. The prepared composite materials possess enhanced properties compared with the single organic or inorganic material. Main concept of the development of nanocomposite membranes is to acquire the best properties of the components and trying to eliminate the drawbacks of an individual component by the synergetic interaction. A specific interaction involves between the organic and inorganic components influences the electrochemical stability. The hygroscopic characteristics of the included nanomaterials adsorb water molecules in a greater extent, stores in its voids and has become responsible for the lower humidity operation. The proton transfer takes place on the surface of the inorganic particles and a high surface area of fillers increases surface area of the membrane which in turn improves the surface chemistry. Whereas ceramic property of the nanofillers influence higher temperature applications. Thus the polymer nanocomposite material influences high temperature and lower humidity operation of fuel cells with an extended durability.

Polymer nanocomposite's properties and applications in fuel cell is a valuable reference tool for both the research community and industry professionals. This chapter is aimed to project the efforts carried out, preparation, mechanism and future propsectives of polymer nanocomposites applicable for fuel cells.

2. Requirements of polymer electrolyte membranes

The favorable properties of polymer electrolyte membranes for the efficient fuel cell performances are described as follows:

2.1 Ionic conductivity

Ionic conductivity is defined as the capability of the transportation of ions which determines the power generation of a fuel cell. Catalyst (Pt for PEMFC and Pt-Ru for DMFC) loaded on the electrode splits the fuel (H_2 /methanol) into ions and electrons and the membranes have to conduct ions through its viable channels which are created for the effective passage. Ionic migration includes transportation of protons and other species such as OH^- , H_2O , H_3O^+ , NH_4^+ , HS^- etc., Ionic conductivity effectively determines the over all efficiency of fuel cells. Ionic conductivity of the membranes highly depends on the operating temperature and relative humidity conditions. Increase in the temperature promotes the flexibility of the membrane by the structural reorganization which favors the faster ions migration. If the operating temperature exceeds the membranes dew point, a dramatic drop in the conductivity is observed for the perfluoro sulfonated membranes due to the evaporation of water molecules. Relative humidity also plays a vital role in the determination of ionic conductivity. Increase in the relative humidity humidifies the polymer chains and lowers

the viscosity of the membrane and leads to a higher water content in the electrolyte which presumably raises the ion mobility and conductivity (Li et al. (2003).

2.2 Fuel permeation

Fuel crossover is the major draw back of fuel cells which decreases the fuel cell efficiency by poisoning the cathode catalyst and slows down the electrode chemical reaction. Fuel oxidation kinetics has become sluggish due to the high fuel crossover. It renegades fuel crossing from the anode to the cathode catalytic layer and hampers oxygen reduction at the cathode. The approaches which were made up so far to reduce the fuel cross over were not effective in both PEMFC and DMFC. Though the lowering of temperature and the dilution of fuel (in DMFC) results in diminution of fuel crossover, it considerably decreases the efficiency of fuel cells *via* the minimal ions transportation. Increase in temperature and back pressure enhances the fuel permeation and when it comes with respect to relative humidity fuel crossover has become much more complicated. At lower temperatures increase in relative humidity results in the increment of fuel crossover due to its high level of water content. But sometimes at higher temperatures increase in relative humidity results in a decrement of fuel crossover. Further researches should be applied to analyze this parameter. Low level consumption of fuel is an important factor for the high performance of fuel cells. So fuel crossover should be lowered for the lesser fuel consumption which effectively enhances the performance of fuel cells (Neburchilov et al. 2007).

2.3 Mechanical stability

When the membrane contacts with the fuels especially liquid fuels, swelling ratio of the membrane gets enhanced which diminishes the mechanical stability. For the fabrication of membrane electrode assembly (MEA) and fuel cell applications, the membrane has to be highly strengthened. Hydrophobic property of the membranes supports the mechanical integrity but also hinders the ion transport. The function of hydrophobic phase is to prevent water from "pooling" within the pore volume of the backing layer so that gases can freely contact with the catalyst sites. Furthermore, it facilitates the removal of water molecules on the cathode as it creates a non-wetting surface within the passages of the backing material to avoid mechanical infertility. For the immurement of ionic conductivity and other electrochemical properties, hydrophilic phases are included in the membrane which consequently decreases the mechanical stability. So fuel cell membranes should be designed to contain major hydrophobic part for the betterment of mechanical integrity.

2.4 Thermal stability

Operating conditions of a fuel cell widely depend on the thermal management. Thermal management improves the kinetics of oxidation reaction and tolerates the exhausted carbon monoxide. It controls the cooling system and maintains a good hygrometry level within the fuel cell system. High operational temperature of fuel cells is proximally equal to the methanol reforming and hydrogen desorption which greatly circumvents the need of additional systems such as methanol reformer and hydrogen storage capacitors. The integrated system leads to a higher efficiency, smaller size, high reliability, and simple construction. Though PEMFC and DMFC are being operated at lower temperatures, polymer electrolyte membrane's thermal stability should be opt to be applied in fuel cells. Operational temperature between 120-180°C is necessary to remove the heat from the stack with an adequate temperature difference to cool the air efficiently. Glass transition

temperature of the membranes should be higher than that of operation temperature of fuel cells for the betterment of electrochemical properties.

2.5 Durability (lifetime)

The main advantage of fuel cells over the conventional batteries is as long as fuel supplied to the cell it generates electricity. But the lifetime of commercially available membranes is not adequate for the fuel cell commercialization. Even the operation temperature exceeds 100°C, lifetime of the membranes should be enhanced to a couple of months. Compatibility between the electrode layers and membrane effectively determines the durability of the fuel cells (Cho et al. 2005).

2.6 Fabrication cost

For the commercialization of fuel cells, cost of the electrolyte membranes has to be controlled. So far, cost of the commercially available membranes is consuming almost the cost of an entire fuel cells device (Tricoli & Nannetti, 2003). Nafion membrane remains quite expensive with production costs of about US\$800/m². Though the membranes are commercially available in the market, to bring forth fuel cells in a global level more significant efforts should be devoted in this area. A short version of the aforementioned favorable properties for the efficient fuel cell performance is depicted in Table. 1.

Properties	Increase in operating conditions			
	Thickness	Temperature	Relative humidity	Fuel concentration
Water content	↓	↓	↑	↑
IEC	↓	↑	↑	----
Mechanical stability	↑	↓	↓	↓
Conductivity	↓	↑	↑	↑
Fuel permeability	↓	↑	↑	↑
Cell performance	↓	↑	↑	↑
Life time	↑	↓	↑	↓
Emission of gases	----	↓	----	↑

Table 1. Favorable properties of the polymer electrolyte membranes for the efficient fuel cell performances.

3. Criteria for the selection of inorganic nanomaterial

i. Hygroscopic characteristics

Hygroscopic characteristic is one of the most influential property for the polymer nanocomposite which effectively determines ion transportation of the membrane. Though the acidified polymer influences water adsorption characteristic, structural, bonded and

adsorbed water molecules of nanometric fillers alone can effectively influence the aforementioned property. Since the water molecules present in the membrane determines the ion mobility, fillers have to be chosen based on their strong hygroscopic properties.

ii. Ceramic property

As aforementioned, the fuel cells have to be operated at higher temperatures. A higher acidification degree of a polymer obliterated the thermal stability which in turn lowers the fuel cell operation temperature. Nanoparticle's ceramic effort influences the thermal stability of a polymeric backbone which in turn promotes the operational temperature. So a higher ceramic effort of nanoparticle may influence its viable applications.

iii. Porosity and pore connectivity

The water molecules adsorbed by the inorganic fillers have to be stored in the surface of the nanofillers. Since porosity is directly proportional to the water adsorption, extended porosity is essential for the higher water adsorption. In addition, a strong interconnection between the pores facilitates the continuous ion transportation.

iv. Surface area

The electrochemical performance of a system is purely dependent upon the surface area of the constituted materials. Though the host polymeric material may have surface area, a further increment in the surface area of the material *via* nanofillers may influence the system's electrochemical performance. So the inorganic fillers should be prepared to possess higher surface area.

v. Additional ions

The additional ions given *via* surface of the nanomaterial promote the number of ion migration which in turn influences ionic conductivity of the membrane. This criteria is effectively done by the acidified hygroscopic fillers and protonic conductors.

4. Preparation of polymer nanocomposite techniques

The polymer nanocomposite membranes which are applicable for fuel cells have been prepared by the following techniques.

i. Casting of polymeric nanocomposite solution

Solution casting is one of the simplest methods for the preparation of nanocomposite membranes. A few microlitres of a dilute solution containing the dissolved polymer and nanofillers are cast as a film followed by the evaporation of a solvent. It enables direct incorporation of nanosized inorganic materials into a polymer matrix and a number of nanocomposite membranes have been prepared using this procedure. In a typical experimental procedure, appropriate amount of nanoparticles are first mixed with the polymer solution under vigorous stirring. The membrane is then obtained by film casting and dried until all the solvent gets evaporated (Gnana kumar et al. 2007). For bulk mixing, the inorganic components should be prepared in the form of powders or dispersions. It is an easier process and the thickness of the membrane could be easily controlled. But a physical interaction exists between the polymer and nanomaterial has left few questions such as inhomogeneities of the composite membrane and the formation of pores around the oxide particles and may leach out under the repetitive cycles.

ii. Sol-Gel

Sol-gel process is a versatile technique for the preparation of proton-conducting nanocomposite materials. Direct mixing of precursor solution with the organic polymer leads to the formation of proton conducting membranes. A hybrid structure is obtained at the molecular level with entirely different properties by co-polymerization of inorganic monomer in the presence of organic polymeric solution under the proper solvent and catalyst. The general methodology used to prepare these membranes is coined as a sol-gel process (Nagarale et al. 2005).

e.g.: Mixing of organic polymer solution with organometallic precursors such as Tetramethoxysilane (TMOS), Tetraethyl orthosilicate (TEOS), Zr(IV)-propoxide, Ti(IV)-butoxide, etc. by hydrolysis and condensation in presence of suitable catalysts, acid or base.

iii. Insitu impregnation process

Insitu impregnation process is a versatile technique for the preparation of low cost proton-conducting nanocomposite materials. A homogeneous natured membranes obtained at lower temperature from this technique influences its potential application. The membranes are impregnated in the inorganic material's precursor solution and the process begins with its incorporation. The nucleophilic attack of the water present in the membrane on the inorganic atoms leads to the hydrolysis of the infiltrated inorganic precursor and membranes have to be treated with necessary reactants for the condensation process. If the reaction is an acid-catalyzed hydrolysis, and the acidified polymer which possesses the pendant $\text{SO}_3\text{-H}^+$ group will itself act as a catalyst, and the need for external reactants has been circumvented. The impregnation of polymer membranes with inorganic precursors experienced a difficulty in maintaining concentration gradient of precursor solutions which virtually limits the incorporation of inorganic components into the polymer matrix to a certain level.

e.g.: Nafion membrane modified with tetra ethyl orthosilicate (TEOS) (Kelarakis et al. 2010).

iv. Covalent Binding

Synthesis of polymer nanocomposites *via* the formation of covalent bonds between aromatic polymers and inorganic clusters is an effective approach in the development of proton-conducting membranes for fuel cell applications. This approach requires molecular precursors that contain a hydrolytically stable chemical bond between the element that will form the inorganic network during sol-gel processing and the organic moieties.

Organic components can be chemically modified to covalently attach the inorganic network, e. g. silylation. The organic components after silylation are easily accessible to common hydrolysis and polycondensation reactions. The primary aim is to synthesize a polymer containing both $\text{-SO}_3\text{H}$ functions and silicon moieties. The order of the synthesis steps is (i) Sulfonation, (ii) Silylation and (iii) Sol-gel process

A novel, efficient and experimentally simple method for the introduction of silicon functional groups into polymeric carbon frameworks is to combine the features of a cross-linked polymer and the presence of covalent organic-inorganic, C-Si, bonds in one macromolecule (Vona et al. 2006). Cross-linking can be obtained during the sulfonation step by formation of SO_2 bridges among the repeating unit of PEEK.

The synthesis route follows the given steps :

Step 1. Direct sulfonation of PEEK with chlorosulfonic acid (ClSO_3H); this will result in SOPEEK

- sulfochlorinated PEEK

- Step 2. Silylation – this will introduce covalently linked silicon moieties in SOPEEK
- Step 3. Hydrolysis of sulfochlorinated PEEK in order to obtain the desired $-\text{SO}_3\text{H}$ functions (SOSiPEEK)

v. Polymerization process

For the ideal ionic membrane, hierarchically ordered ionic channels/particles should orient vertical to the membrane surface. This can be achieved only *via* surface-initiated atom transfer radical polymerization (ATRP). Ordered two-dimensional macroporous silicon renders proton conducting membrane by growing a thick uniform polyelectrolyte brush using surface initiated atom transfer radical polymerization throughout the porous matrix (Yameen et al. 2009).

e.g. : Firstly, a macroporous silicon scaffold is modified with the self-assembled monolayers of 2-bromo-2-methyl-N-(3-triethoxysilylpropyl)propionamide. Then the macroporous membranes with polymer brushes were copolymerized by sulfopropyl methacrylate (SPM) and monomethoxy oligo- (ethylene glycol) methacrylate (MeOEGMA) and the membrane channels were completely filled with polySPM-co-MeOEGMA brushes, thus indicating that the surface-initiated copolymerization proceeded smoothly in the confined environment of the membrane channels. It has been demonstrated that the synthesis of hybrid membranes by pore-filling surface polymerization is a new approach to create proton-conducting channels with tailor-made and finely tuned physicochemical characteristics.

5. How does the polymernanocomposite satisfy the requirements of electrolyte membrane applicable for fuel cell?

Polymer nanocomposite has already been proved as an effective technique for the empowerment of higher temperature and lower humidity fuel cell applications. The significant improvements which have been made on the polymeric membranes to support /empower the higher temperature and lower humidity fuel cell applications are given as follows:

5.1 Water adsorption and retention

The nanometric inorganic fillers present in a composite bind larger amount of water molecules with the membrane *via* its hygroscopic effort. The voids or cavities which are present in the inorganic fillers influence higher amount of water adsorption and tightly pack the water molecules in its voids. The higher amount of water molecules present in the membrane humidifies the polymeric units or channels which in turn favors the lower humidity operation and also circumvents the usage of a humidifier. Though the operational temperature of fuel cells exceeds 100°C , a tight packing of water molecules achieved *via* nanofiller influences water retention of the composite membrane. Thus it declines the major drawback of Nafion membrane's protonic conductivity decrement at high temperatures and facilitate the higher temperature fuel cell applications.

5.2 Ionic conductivity

The most trifling case in ionic conductivity mechanism is the assistance of proton migration by the translational dynamics of bigger species. The proton diffuses together with a vehicle (*e.g.*, as H_3O^+) where the counter diffusion of unprotonated vehicles (*e.g.*, H_2O) allows the net transportation of protons. The relevant mechanism is called as vehicle mechanism.

Increase in the temperature diminishes the hydrogen bonding between water molecules which distinctly reduces the proton jump in Grothus mechanism. In many cases, Grothus type mechanism is progressively dominated by vehicle-type mechanisms at increasing temperature, i.e. there is a gradual transition from Grothus to vehicle type conductivity (Lorrain et al. 1996). The higher amount of water molecules adsorbed by the nanofillers promote the aforementioned mechanisms. A higher amount of absorbed water molecules solvate the acid moieties of a polymer in a greater extent and facilitate the hydrogen bonding among/between water molecules and has become responsible for the higher ionic conductivity. In addition, protonic conductor added swollen membrane induces additional protons *via* its surface which promotes ionic conductivity of the membrane further.

5.3 Fuel cross over

As aforementioned, fuel permeation is a major drawback of fuel cells. A high protonic conductivity-methanol permeability selectivity ratio is an effective parameter for the efficient fuel cell performances. But higher fuel permeation decreases the selectivity ratio and there by fuel cell efficiency by poisoning the cathode catalyst and slows down the electrode chemical reaction. The addition of fillers effectively blocks the molecular passage (Fig. 1). For the filler free membrane, methanol molecule can be easily transported without any hindrances. But the fillers (ceramic and protonic conductors) create tortuous path ways for the molecular transportation, reduces the electro osmotic drag which effectively dries the membrane at the anode side and suppresses the flooding. It has been observed that the cross over current measured with the modified membrane in an order of magnitude lower than that of the unmodified polymer membranes (Ahmad et al. 2010; Gnana kumar et al. 2007).

5.4 Thermo and mechanical properties

Though ionic conductivity and fuel permeation play a decisive role in the determination of fuel cell efficiency, thermal and mechanical stabilities have also to be considered. Though higher acidification degree of a polymer is responsible for the higher ionic conductivity, it deteriorates the thermal and physical stabilities. So a compromise has always to be taken between the mechanical and electrochemical properties. In order to increase the thermal and mechanical stabilities, acidification degree has to be lowered. But it leads to a lower ionic conductivity and lower electrochemical performances. By keeping the high ionic conductivity of a polymeric membrane, physical and mechanical stabilities have to be strengthened. Thermal stability of the polymeric membrane is influenced by the nanofiller *via* its ceramic effort (Neburchilov et al. 2007). It is also evidenced that the T_g and Young's modulus of the polymer are improved by the incorporation of inorganic additives.

5.5 Fuel cell performance

Due to the increased water retention, high ionic conductivity associated with the lower fuel permeability of the polymer nanocomposite electrolyte membrane results in better electrode performance at high temperatures and lower humidities. Thus it has been reported that nanocomposite membrane exhibited 5-10 magnitude greater performance than that of bare polymer membrane.

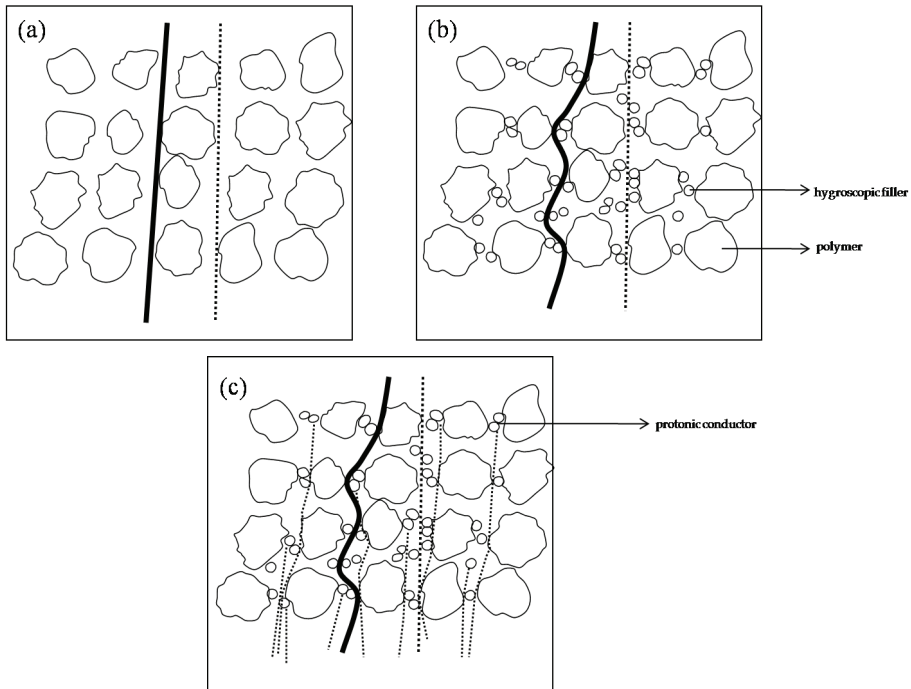


Fig. 1. Proposed ion transportation and fuel cross over mechanisms of (a) bare polymer, (b) polymer-ceramic filler nanocomposite and (c) polymer-nanoprotonic conductor composite membranes [(—) methanol, (•••••) ions and (.....) additional ions]

5.6 Durability

Incorporation of hygroscopic oxides improves lifetime of the membrane by enhancing the corresponding membrane’s physical stability. Hygroscopic oxides fix the acid functional group within the membrane and do not allow the electrolyte to leach out and thus ensure the durability of the polymer membranes (Neburchilov et al. 2007). The nanocomposite membrane extended the durability of bare polymeric membranes for a couple of months.

5.7 Easier fabrication techniques

Complex synthesis methods are the major hindrances for the preparation of new polymers. It has directed the researchers to work on the modification of existing polymers. Among the various techniques proposed, polymer nanocomposite has well known for its easier and controllable fabrication methods.

6. Polymer nanocomposite membranes

6.1 Perfluorinated nanocomposite membranes

The concept perfluorinated polymer nanocomposite for fuel cell applications was developed by Watanabe et.al (Watanabe et al. 1994). Though Nafion membrane is considered as a standard bench mark of all kind of fuel cell membranes due to its elevated chemical, thermal

and physical stabilities, it exhibits few limitations such as high temperature and lower humidity operation difficulties. Various efforts have been explored on the development of new polymer electrolyte membranes. But none of them can compete with the Nafion membrane at a large scale level. Instead of developing a new kind of polymeric membranes, the modification of commercially available membranes can create wonders. Perfluorinated polymer nanocomposite membranes can be prepared either by (1) casting a bulk mixture of powder or colloidal inorganic components with a polymer solution, or (2) *in-situ* formation of inorganic components in a polymer membrane or in a polymer solution. Inorganic components are prepared in the form of powders or dispersions for bulk mixing. Transfer of this colloidal suspension into a polymer solution should enable inorganic particles of nanometer size to be dispersed in a formulated membrane. Sometimes colloidal suspensions can also be utilized for bulk mixing. Other techniques such as exchange-precipitation and sol-gel reactions are also effective for the preparation of composite membranes.

i. with hygroscopic oxides

As discussed, high ionic conductivity of Nafion membranes has been facilitated by the high retention of water molecules in the membrane. The water molecules retention is facilitated by the hygroscopic oxides such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), and zirconia (ZrO_2). Water adsorbed on the surface of the oxides effectively decreases the electro-osmotic drag by enhancing the back diffusion of the cathode produced water. Hygroscopic oxides can act as self-humidifying agents. The humidification of Nafion membrane is effectively done by the hygroscopic oxides and inclines the utilization of a separate humidifier.

Antonucci et al. (1999) improved the power density of Nafion up to 240 W cm^{-2} at 145°C by the incorporation of silica. Though the fuel cell operation temperature exceeds 100°C , performance decay was not observed for the modified Nafion membrane due to the inclination of membrane dehydration phenomenon (Antonucci et al. 1999). Dimitrova et.al. modified Nafion with a high boiling point solvent (dimethylsulfoxide or 1-methyl-2-pyrrolidone) and silica. The incorporation of hydrophilic inorganic particles retained more water content and influences the water transfer to the cathode. The higher water uptake brings about a size growth of the ionic clusters and pores which effectively determined the transport properties of the membrane. The modified membrane structure consists of the broader water filled channels with more separated and less branched channels and pores which correspond to a smaller hydrophilic-hydrophobic interface and smaller average separation of sulfonic groups. It leads to an increased ionic conductivity even under higher temperatures (Dimitrova et al. 2002). Miyake et.al. modified Nafion 117 membrane with silica *via* sol-gel technique (Miyake et.al. 2001). The enhanced water uptake of the modified hybrid membranes than that of pure Nafion is attributed to the strong hygroscopic effort of silica. The tensile strength of the silica modified membrane was 5.4×10^3 psi which is much higher than unmodified membrane whose tensile strength was 3.2×10^3 psi. By the simple hydrolysis and condensation of alkoxysilanes, inorganic phase has grown inside the organic matrix based on the sol-gel process. The condensation and hydrolysis of TEOS promoted the growth of a silicon oxide phase inside the Nafion clusters. TEOS included in Nafion through sol-gel process influences water uptake which favors ionomer structure, cluster and channel size. The modified Nafion membrane exhibited four times higher current density than that of unmodified Nafion at 130°C under 3 atm pressure (Miyake et.al. 2001). Jiang et al. modified the Nafion membrane by silica through sol-gel technique. Though the conductivities achieved for the composite

membranes are inferior to the Nafion membrane, lower methanol permeability in the range of $4.17 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ achieved for the 5 wt.% silica loaded membrane with the higher thermal stability influence its viable application (Jiang et al. 2006). At lower silica loadings, the hydrophilic silica particles may mainly exist around the hydrophilic ion-cluster and the ion channels. Addition of silica particles increases tortuous nature of the methanol transport channels by changing the microstructure of Nafion. The cell voltage of 5 wt.% silica composite membrane was increased due to the lower methanol crossover (Jiang et al. 2006). There after number of efforts and patents (Adjemian et al. 2006) has been filed on the modification of Nafion with hygroscopic oxides. Other hygroscopic oxides such as titania, alumina and zirconia were also extensively utilized for the modification of Nafion. Incorporation of hygroscopic oxides to the Nafion membrane, leads to a self- humidification, reduces the fuel permeation and eventually enhances the fuel cell performance. The size of polar ionic clusters of Nafion membrane is about 3-5 nm. So the hygroscopic filler size which have to be incorporated in to the polar matrix should be lesser than the nafion membrane's polar cluster size. The effectively panned hygroscopic fillers in the Nafion polar clusters alone can influence the electrochemical properties.

ii. with protonic conductors

The purpose of the inclusion of hygroscopic oxides into the Nafion membrane is only/mainly to retain the water molecules. But the incorporation of protonic conductors effectively satisfies both high water retention and provision of additional ion sites in a greater extent. Nafion membranes modified by the proton conductors exhibited excellent properties and are described as follows:

A simple method for the preparation of inorganic proton conductor-PFSA composite membranes is obtained from the casting of an ionomer solution containing proton conductor compounds. This is a well known method and adopted by many researchers in general. On the other hand, exchange precipitation method is under the rapid subject enrollment in the Nafion membrane modification field. For this process, Nafion membrane is first swollen in a boiling methanol-water mixture and then soaked in a zirconyl chloride solution at 80°C. In this way Zr^{4+} ions are introduced into the ionic sites of the membranes by ion exchange method. Then according to the desirable functionality, membranes can be activated either with phosphoric acid or sulfuric acid (Grot & Rajendran, 1999). The pores of Nafion membrane trap the proton conductors for the plausible ionic conduction. Proton conductors enhance the water retention characteristics and increase the operational temperature of fuel cells. A strong influence of the protonic filler concentration on mechanical properties as well as the thermal properties was also observed.

The surface area of Nafion membrane was increased two orders of magnitude by the inclusion of zirconium phosphate. C. Yang et.al modified the Nafion 115 membrane *via* an exchange reaction involving Zr^{4+} ions followed by precipitation of zirconium phosphate. Under the low humidification conditions, the maximum power densities achieved at 145°C with these MEAs were 375 and 260 mW cm^{-2} in the presence of oxygen and air, respectively. The best fuel cell performances were observed for the composite membranes under the lower methanol preheating temperature and lower humidification cathode gas feed conditions. It simplifies the auxiliary systems and eliminating the requirement to vaporize the necessary quantities of water for humidification, as required by conventional systems with the improvement of water retention (Yang et al. 2001). Bauer et al. modified Nafion 117

membranes with zirconium phosphate. The ionic interaction between the filler and the hydrophilic clusters was very strong which reduced the ability of the back-bone regions of Nafion to align into crystallites. It leads to a strong influence on both the mechanical properties and glass transition temperature of the corresponding hybrid membranes. When the operation temperature exceeds the glass transition temperature of a Nafion membrane, a significant damage occurs usually in the membrane, and was successfully prevented by the addition of protonic conductors (Bauer et al. 2004). A decrease in the methanol permeation leads to a high ionic conductivity-fuel permeability selectivity ratio which eventually promoted its viable application in DMFC.

iii. with carbon nanotubes

As aforementioned, high cost of the Nafion membrane hinders its commercial application in a large amount. Thinner membranes have been introduced to reduce the cost of electrolyte membrane. Decrease in the thickness not only leads to a reduction in the cost but also escorts to a reduction in the resistance of a membrane. However a decrement in the thickness facilitates a mechanical infertility which eventually lowers the durability. To endure the thinner membrane's stability, Nafion membranes were modified with carbon nano tubes. Carbon nanotubes (CNT) are considered as the ideal reinforcing fibers due to their unique one-dimensional structure and a range of fascinating properties such as exceptional mechanical properties, low density, high aspect ratio, unique nano porous structure, high specific surface area, and tunable properties etc.,. But the main drawback of CNT inclusion in Nafion matrix is the high risk of short-circuit caused by a non electrically isolated electrolyte. But it can be tackled by keeping the lower content of carbon nanotubes than the percolation threshold.

Liu et al. developed Nafion-multi walled carbon nano tube composite for the PEMFC applications. It has been reported that an inclusion of carbon nano tubes with the Nafion ionomer increases the mechanical strength from 22.08 to 37.08 MPa. A good compatibility exhibited between CNT and Nafion matrix results in restraining the swelling of a membrane and improved the mechanical strength. At the mean while, a low content of CNT doesn't affect the ionic conductivity of the membranes. A low CNT content neglects the short circuit and results in a comparable fuel cell performance as that of pure Nafion membrane (Liu et al. 2006). Thomassin et al. reported that an inclusion of MWCNT decreases the methanol permeability due to its better dispersion. An increase in the length of the CNT reduces methanol permeability in a large amount and also accounts for the higher mechanical strength. Though a decrease in the ionic conductivity was observed for the composite membranes, a larger reduction in methanol permeability accounts for the high conductivity-fuel permeability selectivity ratio and ensures its appliances (Thomassin et al. 2007). Kannan et al. observed that the acidified single walled carbon nano tubes enhanced ionic conductivity and activation energy of the Nafion membrane. The extra sulfonic acid moieties anchored on the surface of the CNTs could facilitate the hopping of protons, which in turn would help to increase the proton mobility and accounts for the high ionic conductivity. An increase in the acid-water clusters of the recast Nafion membrane decreases the charge-transfer resistance which in turn enhances a power density of 260 mW cm⁻² at 0.42 V which is far ahead of pure recast Nafion membrane. Though high ionic conductivity was facilitated for the composite membrane, physical yield point was also improved (mechanical stability) through the governance of CNT features (Kannan et al. 2008).

6.2 Hydrocarbon membranes

In addition to the modification of commercially available membrane Nafion, various efforts have also been addressed on the several kinds of polymers. Poly ether ether ketone (PEEK) based membranes were developed to contain hetero poly acids and an oxide phase. It was either produced by hydrolysis of amino-modified silanes or by dispersion of surface modified fumed silica. Though hetero poly acid possesses good proton conductivity, it has shown degradation in the DMFC applications due to its dissolution in water. The stability has usually been increased through silica modification which increases the strength of the covalent bonds or columbic interactions but reduces the acid strength. By the addition of silanes and the dispersion of surface-modified silica, leach out of hetero poly acid can be effectively reduced.

Karthikeyan et.al. modified the SPEEK membrane with different forms of silica such as laponite (a synthetic layered silicate), aerosol (spherical nano particle), and MCM-41 (acid silicate with mesoporous structure). The 10% MCM-41 included membrane exhibited better conductivity and reasonable fuel permeability among the studied membranes. This was achieved by the effective formation of pathways between the filler and polymer matrix due to its high compatibility. In general, the polymer chain strongly interacts with silica or silanol through hydrogen bonding. It results in the enhanced mechanical stability of the hybrid membranes (Karthikeyan et al. 2007). Kalappa et al. developed SPEEK/TiO₂ membrane with reduced methanol permeability. The weaker hydrophilicity of the polymer, higher concentration of rigid backscattering sites, and increased tortuous pathways for the molecules to encounter during permeation were created by the TiO₂ inorganic particles. It blocks the molecular passage and resulted in the lower fuel permeability. The included inorganic particles prevent the reactant loss, enhance the power density, and guaranteed the long-term membrane stability (Kalappa et al. 2007).

The most extensively studied protonic conductor in the fuel cell field is zirconium phosphate (ZrP). Two predominate structures of α -zirconium hydrogen phosphate and γ -zirconium hydrogen phosphate are available. The hydrogen bonded network of water is achieved due to the pendant OH group and the interlayer region of α -ZrP. At the mean while, the γ -ZrP has the advantage of having an extra water molecule per formula unit and is more acidic than the α -ZrP. Inclusion of protonic conductors enhances the water content of the membrane and also provides the additional ions. A three fold improvement in conductivity was achieved for the 10 wt.% α -ZrP loaded SPEEK membrane. Using the bulk mixing method, composite SPEEK membranes were prepared with zirconium phosphate and sulfophenyl phosphonate. Conductivities of 0.09 S cm⁻¹ at 100°C and 0.04 S cm⁻¹ at 150°C under 100% RH were reported for these membranes (Bonnet et al. 2000).

Silva et al. synthesized hybrid SPEEK membrane with ZrP/PBI. The inorganic incorporation of pretreated zirconium phosphate decreases the membrane proton conductivity, aqueous methanol swelling, and methanol permeability. But the high proton conductivity-methanol permeability selectivity ratio obtained in these membranes resulted a maximum power density and current density of 50.1 mW cm⁻², 250 mA cm⁻², respectively under 130°C (Silva et al., 2005). Hickner et al. developed sulfonated polysulfone phosphotungstic acid hybrid membrane and the ionic conductivity and mechanical modulus of the material was improved by the addition of inorganic particles (Hickner et al. 2001). Dimitrova et al. incorporated phosphate antimonite acid particles into sulfonated polysulfone. The fabricated membranes exhibited the improved mechanical properties and conductivities close to Nafion were obtained with the absence of excessive water swelling at 80°C (Dimitrova et al.

2001). Cesiumphosphate is a promising protonic conductor that has a bulk conduction mechanism. Increase in the temperature beyond 140°C changes the monoclinic structure of cesiumphosphate into a tetragonal structure which leads to an increase in the conductivity by 2–3 orders of magnitude and is often referred to as a “superprotonic” transition (Haile et al. 2001). Recently, Sunarso et.al. blended titanium zirconium phosphate into the polyvinyl alcohol and ethylene glycol matrix. 50 wt.% of titanium zirconium phosphate content enhances the ionic conductivity up to 0.25 S cm⁻¹ which is three orders magnitude greater than the PVA membranes (Sunarso et al. 2008). The functionalized inorganic phase dominated proton conduction which may be attributed to a higher freedom of charge carriers due to the acidic groups of the inorganic phase, instead of just relying on the polymer bonds.

6.3 Acid-base membranes

In general, acid-base membranes involve the incorporation of an acid with the alkaline material. For the immurement of electrochemical properties, most of the polymer electrolyte membranes possess acidic functional groups. The high ionic conductivity of the sulfonic acid group is achieved by their strong attractive forces with hydrogen ions. In order to improve its affinity towards water than methanol, it is being incorporated with the basic polymers such as polyvinylalcohol, polyethyleneoxide, polyacrylamide polybenziimidazole, polyaryleneether, and polyether ketone. The polymers contain functional groups such as alcohol, amide/imide, ether, ketone which are purely meant as the basic sites. The basic functional group reacts with acidic functional group by the establishment of hydrogen bonds. In other words, acid dissociates in the basic polymer which acts as a solvent. The polymer electrolyte membranes which are made up of acidic functional groups possess high ionic conductivity due to their strong attractive forces with hydrogen ions. Because of phosphoric and sulfuric acid’s unique proton conduction mechanism by self-ionization and self-dehydration, it exhibits the effective proton conductivity even in their anhydrous form. Though ionic conductivity of the acid-base membranes are ensured by the sulfonic acid attachment, higher ionic conductivity and improved mechanical properties are under crisis for the acid-base membranes.

The sulfonic acid functionalized polymer nanocomposites based on PVA/SiO₂/sulfosuccinic acid (SSA) were reported. In the hybrid membranes, sulfosuccinic acid served as both sulfonating as well as cross-linking agent. The proton conductivity and methanol permeability of the hybrid membranes were studied with changing SSA content from 5 to 25 wt% and found very much depends on SSA content. They found proton conductivities in the range of 10⁻³ to 10⁻² S cm⁻¹, and the methanol permeability 10⁻⁸ and 10⁻⁷ cm² s⁻¹ range. They claimed the decrement in methanol permeability in the presence of silica particles. In course of finding, inclusion of SSA decreases the crystallinity of the membrane and an inclusion of silica decrease the crystallinity further. The segmental mobility of polymer chains is much higher in amorphous regions than the crystalline. The amorphous nature produces greater ionic diffusivity in accordance with the high ionic conductivity which can be obtained in amorphous membranes that have a fully flexible backbone (Kim et al. 2004). In general, a decrease in the crystalline nature effectively increases the flexibility of the polymeric backbone and promotes the ion transfer. Gnana kumar et.al studied the particle size effect on the ionic conductivity properties. A decrease in the nanometric size of silica filler enhanced the ionic conductivity of the polymer nanocomposite. The critical nucleation radii of nanoparticles are larger than the particle diameter. But the structural transitions can occur only with the larger particle radius than the critical nucleation radius. These transitions can easily occur with the smaller size

particles and yields to the structural changes (Gnana kumar et al. 2009). With an account of surface tension, the unique properties are so strong in the vicinity of surface (shell region), while they are in bulk it is strong enough in the central part of a particle (core region). Since the ratio of the shell to the core contribution increases with the decrease in the particles size which allowed to increase the ionic conductivity of the prepared composite membranes. Decrease in the filler size enhances the surface area which effectively creates a new route for polymer–filler interface and yielded the high ionic conductivity. Among the hybrid membranes, 90 nm silica filler incorporated hybrid membrane exhibited the high ionic conductivity. This study has directed the polymer nanocomposite researchers to study the influence of size, shape and phase of the nanomaterials on electrochemical and physical properties.

Similarly, composite membranes of PVA/SiO₂ with copolymer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and 2-hydroxyethyl methacrylate (HEMA) crosslinked by poly(ethylene glycol) dimethacrylate (PEGDMA) has been reported. They found proton conductivities of 0.02–0.11 S cm⁻¹ with significantly lower fuel permeabilities than that of Nafion (Fu et al. 2009). Sulfonic acid functionalized silica/PVA composite membranes have been reported, created by a sol-gel method, where -SO₃H groups were introduced by oxidation of -SH group present in mercaptopropylmethyldimethoxysilane (MPDMS) (Nagarale et al. 2004). The resulting membrane had good thermal and electrochemical properties. The phosphonic acid functionalized silica/PVA composite proton exchange membrane has also been reported. The phosphonic acid functionalisation was carried by phosphomethylation of aminopropyltriethoxysilane in aqueous medium. The resulting composite membrane had an excellent methanol barrier capability with good hydrophilicity and proton conductivity at higher temperatures. From selectivity parameter, they found, 50% silica loaded PVA composite with 3 h of phosphorylation resulted best proton-exchange membrane. It was about 20% more suitability in comparison to Nafion 117 membrane for direct methanol fuel cell applications (Binsu et al. 2005). Apart from the silica composites, heteropolyacid and zirconium phosphate composite membranes have also been reported with good proton conductivity and lower methanol permeability.

Basic polymers can be doped with an amphoteric acid, which acts both as a donor and an acceptor in proton transfer and therefore allows for the proton migration. Phosphoric acid (H₃PO₄) doped polybenzimidazole (PBI) has received much attention in the past few years. The proton hopping from one N-H site to another contributes little to the conductivity, as pure PBI is not conducting. Proton hopping from one N-H site to phosphoric acid, anions contributes significantly to the conductivity. At a doping level of 2 mol H₃PO₄ per repeat unit, the conductivity of the membrane is about 2.5 × 10⁻² S cm⁻¹ at 200 °C. The presence of the free or unbounded acid is necessary to improve the conductivity. At an acid-doping level of 5.7 mol H₃PO₄, the measured conductivity is 4.6 × 10⁻³ S cm⁻¹ at room temperature, 4.8 × 10⁻² S cm⁻¹ at 170 °C, and 7.9 × 10⁻² S cm⁻¹ at 200 °C. However the ionic conductivities of PBI doped membranes could be further enhanced if it is doped with nanometric inorganic fillers. Though high acid doping levels result in higher conductivity, it deteriorates the mechanical properties of the acid doped polymer membranes, especially at temperatures above 100°C. This has been a critical issue for development of the acid doped polymer membranes. The use of thermally stable polymers like PBI allows for good mechanical strength at reasonably high acid doping levels. Further introduction of inorganic solid components into the polymer is expected to improve the mechanical behavior as well as the thermal stability, water adsorption and other properties. He et.al reported the PBI based ZrP nanocomposite membranes. It is known that ZrP is a surface proton conductor, the surface area and its

capacity for surface adsorption have a significant effect on the conductivity. For the acid doped ZrP/PBI membrane, there is a large variety of hydrogen bonding around each particle of ZrP, involving H_3O^+ , PO_4 , H_2O , P-O and P-OH groups. The fine ZrP particles in the membrane therefore attract the protonated active ions or groups associated with the proton transfer, which might cause an improvement in the conductivity. The ZrP incorporated PBI membranes exhibited high ionic conductivity around 0.10 S cm^{-1} even at 200°C . It also exhibited prompt ionic conductivity even at lower relative humidities. From this it is clear that included nanoparticles played a decisive role in the determination of ions transportation *via* their additional ion sites and strong water adsorption tendencies (He et al. 2003). The significant efforts which have been made on the polymer nanocomposite membranes and its important properties are given in Table 2.

6.4 Miscellaneous nanocomposite membranes

Apart from the normal blending techniques, efforts have been made on the irradiated membranes to identify the impact of nanocomposite technology. Gnanakumar et al. (2010) doped tin oxide particles with the PVdF-HFP copolymer before the grafting reaction. In course of finding, included nanoparticles reduced the polymeric content volume which has been available for the irradiation technique and decreased the grafting degree value and there by acidification degree value. In general, water adsorption is directly proportional to the acidification degree values. But a different trend was followed by the prepared nanocomposite membrane. Though the acidification values are lower, inclusion of hygroscopic fillers induces higher amount of water adsorption.

It has been reported that the hydrated tin oxide particles exhibit structural, bonded, and adsorbed water molecules. The structural, bonded, and adsorbed water molecules represent the condensed hydroxyl groups, hydrogen bonded water, and physisorbed water molecules, respectively. The structural and adsorbed water molecules are stored inside the micro-pores of tin oxide particles and are not released even at the higher temperatures. The adsorbed water molecules influence the ion transportation of the membrane. This suggests that the ionic conductivity is not only proportional to the number of attached acid molecules and also relates with the number of sorbed water molecules which act as proton sources and ion conduction paths. Though high ionic conductivity was achieved for the tin oxide included membrane, methanol permeability was much inferior to the bare PVdF-HFP membrane and attributed to the tortuous nature of the included tin oxide particles. Thus by the aforementioned efforts, PVdF-HFP-PSSA-SnO₂ membrane exhibited higher direct methanol performance than that of bare PVdF-HFP membrane (Gnana Kumar et al. 2010). Shen et al. reported the influence of nanometric alumina on the irradiated PVdF-PSSA membrane and the impact of nanocomposite technology has been clearly understood (Shen et al. 2006).

7. Future prospectives

The new nanoscale fillers has been a major contributor to the rapid development of polymer nanocomposites, robust structure–property–processing relationships with the polymers are critical to further market infiltration. Though the development of polymer nanocomposite membrane for fuel cell applications has been well developed, a specific nanoscale filler (or fillers), and a particular spatial arrangement of the filler are still in their infancy stage. The underlying mechanisms and compatibility between the nanofillers and polymers have to be clearly understood. It will bring forth a high durability of fuel cells.

Polymer	Nanofiller	Conductivity	Fuel cross over	Fuel cell performance	Reference
Nafion 117	—	90 - 120 mScm ⁻¹	14.1 - 17.2 cm ² s ⁻¹ at 60°C; 3.48 and 0.78 mol min ⁻¹ cm ⁻² (65 and 25°C, 1.5 M, and OCV)	50 mA cm ⁻² (80°C and 1M)	Saarinen et al., 2007
Nafion 115	—	41 - 61 mS cm ⁻¹	19.8 cm ² s ⁻¹ (25°C and 2M) & 4.66 mol min ⁻¹ cm ⁻² (25°C and 1M)		Yang et al., 2001
Nafion®	SiO ₂		4 mol min ⁻¹ cm ⁻²	120 mA cm ⁻² , 240 mW cm ⁻²	Antonucci et al., 1999
Nafion®	ZrP	24 - 60 mS cm ⁻¹ (25°C, 100% RH)		12 mA cm ⁻² (80°C and 1M)	Yang et al., 2001
Nafion®	Sulfonated CNT	0.015 cm ⁻¹		260 mW cm ⁻²	Kannan et al., 2008
SPEEK	Silanes/silica	5 mS cm ⁻¹ (90°C and 100% RH)	0.8 × 10 ¹⁶ m ³ m m ⁻² s ⁻¹ Pa ⁻¹		Ponce et al., 2004
SPEEK	SiO ₂ /ZrP/Zr SPP	0.095 cm ⁻¹			Bonnet et al., 2000
PBI	ZrP + H ₃ PO ₄ SiWA + SiO ₂	9 × 10 ⁻² S cm ⁻¹ at 200°C, 5% RH 2.2 × 10 ⁻⁸ S cm ⁻¹ at 160°C, 100% RH			He et al., 2003 Staiti et al., 2001
PVA/SSA	SiO ₂	10 ³ to 10 ² S cm ⁻¹	10 ⁸ and 10 ⁷ cm ² s ⁻¹		Kim et al., 2004
PVA/glycerin	ZrP + AA	10 ³ to 10 ⁴ S cm ⁻¹ at 25°C			Vaivars et al., 1999

Table 2. Summary of polymer nanocomposite membranes under development.

The cost of the nanoparticles and the environmental hazardous methods has to be decreased further. Nanoparticle synthesis *via* biological methods is an innovative field on now a days. A proper attention on the in-situ nanoparticle synthesis in the membranes *via* bio methods will bring a glory to this field.

Nanoscale multicomponent polymer blends is an innovative trend in the fuel cell field in which the nanoparticles should be arranged in between the two polymer layers. The nanoparticles embedded between the two polymeric layers may promote the thermal and mechanical behaviors and decreases fuel permeation of the membrane. In addition, new processing tools have to be developed to uniformly distribute nanofiller to produce homogeneous bulk properties or spatially vary the nanofiller concentration to meet specific design criteria.

Incorporation of nanometric metal(IV) phosphates such as zirconium phosphate (ZrP) and tin phosphate (SnP) in polymer matrices may result in an increased proton conductivity of the polymers. For this purpose, precipitation from a solution containing M(IV) ions, within an appropriate polymer matrix has to be carried out. With the appropriate amount of metal particles, appreciable degree of improvements in proton conductivity especially at high temperature and lower humidity fuel cell operation could be done.

By drawing inspiration from biology and engineered fiber reinforced composites, polymer nanocomposites with spatially controlled morphology are beginning to provide viable options to critical components of active devices. Polymer nanocomposites have recently become a part of established modern technologies, but the most significant

accomplishments of these materials are still ahead of us. As an increasing number of scientists contribute to the understanding of polymer nanocomposites, what remains to be seen is which products will be critically enhanced and enabled by this broad and evolving class of materials.

8. Conclusion

Though we in the consumer society will have to live a technologically sophisticated version of the lifestyle currently practiced on the economic ladder, we have to hand over a pollution free environment to the next generation for their social and economical welfare. Fuel cells are the correct option for the above need. Many hurdles stand in the way of their ascendance however. Applications of PEMFC and DMFC have well developed but the recent development is polymer electrolyte membranes for the efficient fuel cell operation. Required parameters, commercially available membranes and its modifications, and recent trend towards the development of polymer nanocomposite electrolyte membranes have been reviewed in detail. Though the limitations of commercially available membranes have been cured to some extent so far, it has to overcome few more drawbacks. Improved, less expensive conducting materials now allow the newest fuel cells to work at higher temperatures, and generate more power per volume, both of which lower costs. The polymer nanocomposite membrane resulted in the enhanced thermal, mechanical, ionic conductivity associated with the lower fuel drag than that of bare polymeric materials. The significant improvement has been achieved *via* the synergetic combination of organic and inorganic phases. Polymeric membranes applicable for fuel cells have been classified into various types such as perfluorinated, hydrocarbon and acid-base membranes. Irrespective of the aforementioned types, nanocomposite technology has been applied in all the aforementioned processes and make the polymer membrane suitable for fuel cell applications. According to the fuel cell experts, the commercialization of fuel cells is not far off. Both industrial and academic level activities should be triggered on the development of polymer nanocomposite electrolyte membranes to bring forth the commercialization of fuel cells one step ahead.

9. References

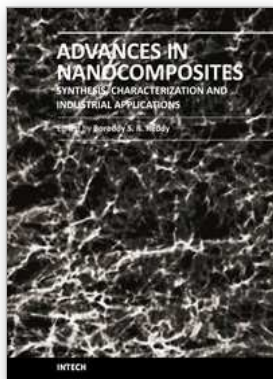
- Adjemian, K.; Dominey, R.; Krishnan, L.; Ota, H.; Majsztrik, P.; Zhang, T.; Mann, J.; Kirby, B.; Gatto, L.; Simpson, M.; Leahy, J.; Srinivasan, S.; Benziger, J. & Bocarsly, A. (2006) Function and characterization of metal Oxide-Nafion composite membranes for elevated-temperature H₂/O₂ PEM fuel cells. *Chemistry of Materials*, 18, 2238-2248, 0897-4756.
- Ahmed, D. & Sung, H. (2008) Design of a deflected membrane electrode assembly for PEMFCs. *International Journal of Heat Mass Transfer*, 51, 5443-5453, 0017-9310.
- Ahmad, H.; Kamarudin, S.; Hasran, U. & Daud, W. (2010) Overview of hybrid membranes for direct-methanol fuel-cell applications, *International Journal of Hydrogen Energy*, 35, 2160-2175, 0360-3199.
- Antonucci, P.; Arico, A.; Creti, P.; Ramunni, E. & Antonucci, V. (1999) Investigation of a direct methanol fuel cell based on a composite Nafion-silica electrolyte for high temperature operation. *Solid State Ionics* 125, 431-37, 0167-2738.

- Bauer, F. & Porada, M. (2004) Microstructural characterization of Zr-phosphate-Nafion® membranes for direct methanol fuel cell (DMFC) applications. *Journal of Membrane Science*, 233, 141–149, 0376-7388.
- Bazylak, A.; Berejnov, V.; Markicevic, B.; Sinton, D. & Djilali, N. (2006) Numerical and microfluidic pore networks: Towards designs for directed water transport in GDLs. *Electrochimica Acta*, 53, 7630–7637, 0013-4686.
- Binsu, V.; Nagarale, R. & Shahi, V. (2005) Phosphonic acid functionalized aminopropyl triethoxysilane-PVA composite material: organic-inorganic hybrid proton-exchange membranes in aqueous media. *Journal of Materials Chemistry*, 15, 4823-4831, 0959-9428.
- Bonnet, B.; Jones, D.; Rozière, J.; Tchicaya, L.; Alberti, G.; Casciol, M.; Massinelli, L.; Bauer, B.; Peraio, A. & Ramunni, E. (2000) Hybrid organic-inorganic membranes for a medium temperature fuel cell. *Journal of New Material Electrochemical System*, 3, 87-92, 1480-2422.
- Cho, K.; Jung, H.; Choi, N.; Sung, S.; Park, J.; Ho, J. & Sung, Y.; (2005) A coated Nafion membrane with a PVdF copolymer/Nafion blend for direct methanol fuel cells (DMFCs). *Solid State Ionics*, 176, 3027–3030, 0167-2738.
- Dimitrova, G.; Baradie, B.; Foscallo, D.; Poinsignon, C. & Sanchez, J. (2001) Ionomeric membranes for proton exchange membrane fuel cell (PEMFC): sulfonated polysulfone associated with phosphoantimonic acid. *Journal of Membrane Science*, 185, 59-71, 0376-7388.
- Dimitrova, P.; Friedrich, K.; Vogt, B. & Stimming, U. (2002) Transport properties of ionomer composite membranes for direct methanol fuel cells. *Journal of Electroanalytical Chemistry*, 532, 75-83, 1572-6657.
- Fu, R.; Hong, L. & Lee, J. 2008, Membrane design for direct ethanol fuel cells: A hybrid proton-conducting interpenetrating polymer network. *Fuel Cells*, 8, 52-61, 1615-6846.
- Gnana kumar, G.; Kim, P.; Nahm, K. & Elizabeth, R. (2007) Structural characterization of PVdF-HFP/PEG/Al₂O₃ proton conducting membranes for fuel cells. *Journal of Membrane Science*, 303, 126–131, 0376-7388.
- Gnana kumar, G.; Lee, D.; Kim, A.; Kim, P.; Nahm, K. & Elizabeth, R. (2007) Structural and transport properties of porous PVdF-HFP electrolyte membranes modified with an inorganic filler. *Composite Interfaces*, 15, 731–746, 0927-6440.
- Gnana Kumar, G.; Kim, P.; Kim, A.; Nahm, K. & Elizabeth, R. (2009) Structural, thermal and ion transport studies of different particle size nanocomposite fillers incorporated PVdF-HFP hybrid membranes. *Materials Chemistry and Physics*, 115, 40–46, 0254-0584.
- Gnana Kumar, G.; Shin, J.; Nho, Y.; Hwang, I.; Fei, G.; Kim, A. & Nahm, K. (2010) Irradiated PVdF-HFP-tin oxide composite membranes for the applications of direct methanol fuel cells. *Journal of Membrane Science*, 350, 92–100, 0376-7388.
- Grot, W. & Rajendran, G. U.S. Pat. 5,919,583 (1999).
- Haile, S.; Boysen, D.; Chisholm, C. & Merle, R. (2001) Solid acids as fuel cell electrolytes. *Nature*, 410 (6831), 910–913, 0028-0836.

- Haynes, C. (2001) Clarifying reversible efficiency misconceptions of high temperature fuel cells in relation to reversible heat engines. *Journal of power sources*, 92,199-203, 0378-7753.
- He, R.; Li, Q.; Xiao, G.; Bjerrum, N. J. (2003) Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors *Journal of Membrane Science*, 226, 169-184, 0376-7388.
- Hickner, M.; Kim, Y.; Wang, F.; Zawodzinski, T. & McGrath, J. (2001) Proton exchange membrane nanocomposites for fuel cells. *International SAMPE Technical Conference*, 33, 1519-1532.
- Jiang, R.; Kunz, H. & Fenton, J.(2006)Composite silica/Nafion membranes prepared by tetraethylorthosilicate sol-gel reaction and solution casting for direct methanol fuel cells. *Journal of Membrane Science*, 272,116-124, 0376-7388.
- Kalappa, P.& Lee, J. (2007) Proton conducting membranes based on sulfonated poly(ether ether ketone)/TiO₂ nanocomposites for a direct methanol fuel cell. *Polymer International*, 56, 371-375, 0959-8103.
- Kannan, R.; Kakade, B. & Pillai, V. (2008) Polymer electrolyte fuel cells using Nafion-based composite membranes with functionalized carbon nanotubes. *Angewandte Chemie International*, 120,2693-2696, 1433-7851.
- Karen, I. & Richard, A. (2007) Polymer nanocomposites. *MRS bulletin*, 32, 314-322, 0883-7694.
- Karthikeyan, C.;Nunes, S.; Prado, L.; Ponce, M.; Silva, H.; Ruffmann, B. & Schulte, K. (2005) Polymer nanocomposite membranes for DMFC application. *Journal of Membrane Science*, 254,139-146,0376-7388.
- Kelarakis,A.; Alonso,R.; Lian, H.; Burgaz , E.; Estevez, L. & Giannelis, E. (2010) *Functional polymer nanocomposites for energy storage and conversion*, American Chemical Society, 171-185, 9780841225435, New York, United States of America.
- Kim, D.; Park, H.; Rhim, J. & Lee, Y. (2004) Preparation and characterization of crosslinked PVA/SiO₂ hybrid membranes containing sulfonic acid groups for direct methanol fuel cell applications. *Journal of Membrane Science*, 240, 37-48, 0376-7388.
- Li, Q.; He, R.; Jensen, J. & Bjerrum, N. (2003) Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C -Review. *Chemistry of Materials*, 15,4896-4915, 0897-4756.
- Liu, Y.; Yi, B.; Shao, Z.; Xing, D.& Zhanga, H. (2006) Carbon nanotubes reinforced Nafion composite membrane for fuel cell applications. *Electrochemical Solid-State Letters*, 9(7),A356-A359, 1099-0062.
- Lorrain, Y.; Pourcelly, G. & Gavach, C. (1996) Influence of cations on the proton leakage through anion-exchange membranes. *Journal of Membrane Science*, 110,181-190, 0376-7388.
- Miyake, N.; Wainright, J. & Savinell, R. (2001) Evaluation of a sol-gel derived Nafion silica hybrid membrane for proton electrolyte membrane fuel cell applications-I. proton conductivity and water content. *Journal of Electrochemical Society*, 148, A898-A904, 0013-4651.
- Nagarale, R.; Gohil, G.; Shahi, V. & Rangarajan, R. (2004) *Organic-inorganic hybrid membrane: Thermally stable cation-exchange membrane prepared by the sol-gel method*, *Macromolecules*, 37, 10023-10030, 0024-9297.

- Nagarale, R.; Shahi, V. & Rangarajan, R. (2005) Preparation of polyvinyl alcohol-silica hybrid heterogeneous anion-exchange membranes by sol-gel method and their characterization, *Journal of Membrane Science*, 248, 37-44, 0376-7388.
- Neburchilov, V.; Martin, J.; Wang, H. & Zhang, J. (2007) A review of polymer electrolyte membranes for direct methanol fuel cells- Review. *Journal of power sources*, 169, 221-238, 0378-7753.
- Park, Y.; Moon, J. & Kim, H. (2005) Proton conducting organic-inorganic nanocomposite membranes from MPTS and GPTS. *Electrochemical Solid State Letters*, 8, A191- 194, 1099-0062.
- Ponce, M.; Prado, L.; Silva, V. & Nunes, S. (2004) Membranes for direct methanol fuel cell based on modified heteropolyacids, *Desalination*, 162, 383-391. 0011-9164.
- Saarinen V. (2007) Studies on the direct methanol fuel cell: Characterization of proton conducting polymer membranes and investigations of current distribution at the cathode. PhD Thesis, Helsinki University of Technology (Espoo, Finland).
- Shen, Y.; Qiu, X.; Shen, J.; Xi, J. & Zhu, W. (2006) PVDF-g-PSSA and Al₂O₃ composite proton exchange membranes, *Journal of Power Sources*, 161,54-60, 0378-7753.
- Silva, V.; Ruffmann, B.; Vetter, S.; Mendes, A.; Madeira, L. & Nunes, S. (2005) characterization and application of composite membrane in DMFC. *Catalysis Today*, 104, 205-212, 0920-5861.
- Sopian, K. & Daud, W. (2006) Challenges and future developments in proton exchange membrane fuel cells. *Renewable Energy*, 31,719-727, 0960-1481.
- Staiti, P. & Minutoli, M. (2001) Influence of composition and acid treatment on proton conduction of composite polybenzimidazole membranes, *Journal of Power Sources*, 94,9-13, 0378-7753.
- Sunarso, J.; Chen, C.; Wang, L.; Dalla, R.; Lu, G. & Costa, J. (2008) Characterization of hybrid organic and inorganic functionalized membranes for proton conduction. *Solid State Ionics*, 179,477-482, 0167-2738.
- Thomassin, J.; Kollar, J.; Caldarella, G.; Germain, A.; Jerome, R. & Detrembleur, C. (2007) Beneficial effect of carbon nanotubes on the performances of Nafion membranes in fuel cell applications. *Journal of Membrane Science*, 303, 252-257,0376-7388.
- Tricoli, V. & Nannetti, F. (2003) Zeolite-/Nafion composites as ion conducting membrane materials. *Electrochimica Acta*, 48, 2625-2633, 0013-4686.
- Vaivars, G.; Azens, A. & Grangvist, C. G. (1999) Proton conducting polymer composites for electrochromic devices, *Solid State Ionics*, 119, 269-273, 0167-2738.
- Vona, M.; Marani, D.; D'Ottavi, C.; Trombetta, M.; Traversa, E.; Beurroies, I.; Knauth, P. & Licocchia, S. (2006) A simple new route to covalent organic/inorganic hybrid proton exchange polymeric membranes. *Chemistry of Materials*, 18 (1), 69-75, 0897-4756.
- Watanabe, M.; Uchida, H. & Emori, M. (1998) Analyses of self-humidification and suppression of gas crossover in Pt-dispersed polymer electrolyte membranes for fuel Cells. *Journal of Electrochemical Society*, 145 (4),1137-1141, 0013-4651.
- Yameen, B.; Kaltbeitzel, A.; Langer, A.; Muller, F.; Gosele, U.; Knoll, W. & Azzaroni, O. (2009) Highly proton-conducting self-humidifying microchannels generated by copolymer brushes on a scaffold, *Angewandte Chemie International*, 48, 3124-3128, 1433-7851.

- Yang, C.; Srinivasan, S.; Aric`o, A.; Cret`, P.; Baglio, V.; Antonucci, V. (2001) Composite Nafion/zirconium phosphate membranes for direct methanol fuel cell operation at high temperature, *Electrochemical Solid State Letters*, 4 (4), A31-A34, 1099-0062.
- Young, S.& Mauritz, K. (1998) Nafion®/(organically modified silicate) nanocomposites via polymer in situ sol-gel reactions: Mechanical tensile properties, *Journal of Polymer Science Part B: Polymer Physics*, 40, 2237- 2247, 0887-6266.



Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications

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Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

How to reference

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