Research Signpost
37/661 (2), Fort P.O., Trivandrum-695 023, Kerala, India

Photo/Electrochemistry & Photobiology in the Environment, Energy and Fuel, 2006: 1-42
ISBN: 81-308-0122-1

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Strategies for the design of membranes for fuel cells

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1. Introduction

Membrane and separation technology have matured and now impact multi million dollar industries. Flamboyant years of high growth rates are ahead. The reach of advanced membrane now extends from food/drug production and separation to pollution, water purification, textile, biotechnology and fuel cell markets. Enthusiasm for membrane applications and research still abounds, with prospects for continued profitability for astute producers and users alike. Membrane science represents a very diverse collection of applications involving such technologies as: reverse osmosis, ultrafiltration, microfiltration, gas separation, electrodialysis, hemodialysis, pervaporation,

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and other business trends. Actually as applications evolve the technology needs to become more precise. Industries continue to consolidate and technology advances become more selective and sophisticated.

In simplest term a membrane can be defined as an interface between two adjacent phases acting as a selective barrier, at the same time organizing a system into compartments and regulating the transport between the two compartments. The main advantage of membrane technology is its unique separation principle, i.e. the transport selectivity of the membrane. Schematic representation of membrane and processes are given in Fig.1. Membranes most often respond to some gradients that they experience between the two sides of the membrane. If concentration is a gradient then dialysis results; if pressure is a gradient then reverse osmosis, ultra filtration, micro filtration or nano filtration results. All these process differ from each other depending on pore diameter of the membrane. If potential is a gradient then electro dialysis or electrophoresis results.

The role of membrane in electrochemical devices is crucial compared to all other process. In the case of reverse osmosis, ultra filtration, micro filtration or nano filtration the role of membrane is to act as a molecular sieve. Whereas in the case of electrochemical devices in spite of acting as a molecular sieve, membrane has to perform certain other, roles like it separates anode and cathode, it prevents mixing of fuel and oxidant and it also provides a conductive path way. In the case of electric field gradient, the membranes have to face some unusual challenges. Normal membranes have to withstand pressure gradients (mechanical stability) as well as exhibit stability under the unfriendly chemical environments (chemical stability). The membranes employed in electrochemical devices have in addition to exhibit electro-chemical stability under the operating conditions of the electrochemical devices as well as have to promote preferential migration of ions in vectorial mode.

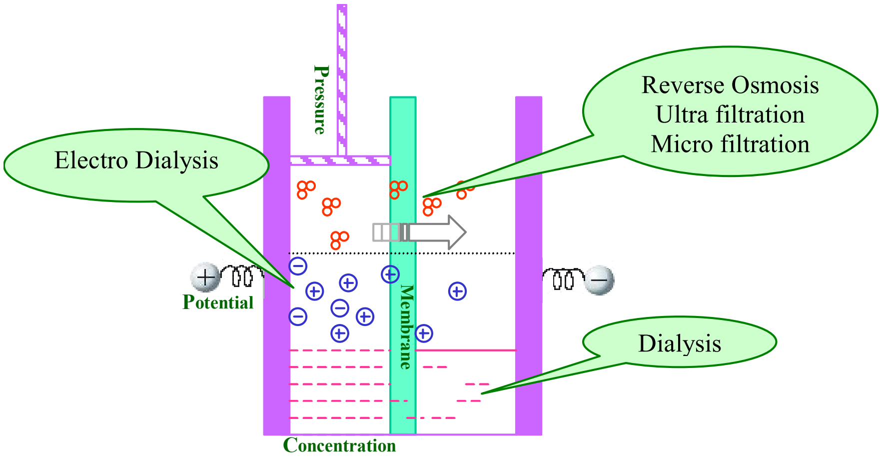


Figure 1. Schematic representation of membrane and processes therein.

Fuel cells are emerging as an alternate energy source for mobile and stationary applications. The successful performance of a fuel cell depends critically on the role played by the membranes. Though Nafion® (a perfluorosulphonated polymer marketed by Ms. Du Pont) has been identified as the preferred membrane for PEM fuel cells, various attempts have gone on in the last decade for the development of alternate, adaptable and acceptable class of membranes for fuel cell applications. The motivation for this review is to examine the conceptual and design strategies that have been formulated and adopted to generate alternate membranes for Nafion®. Conceptually the driving force in these attempts appears to be to design newer class of membranes, which will not demand the exacting experimental conditions and critical management of chemical environments that are necessary for the functioning of Nafion®. In addition the membranes that are developed should also be amenable for control strategies to be implemented in the operation of the fuel cell. This article attempts to examine and to high light the current status of some of the critical aspects of this membrane development studies reported in literature.

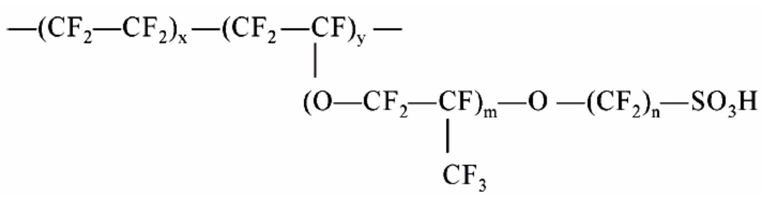
The criteria in choosing a membrane for fuel cell application are listed below.

- It should have high protonic conductivity and zero electronic conductivity
- It should have long-term chemical stability at elevated temperatures in both oxidizing and reducing environments
- It should be stable under the fuel cell potential window
- It should possess good mechanical strength, preferably resistance to solvent swelling
- It should prevent oxidant and fuel cross-over
- It should be cheap and readily available

2. Commercial polymer electrolyte membranes

Commercialized polymer electrolyte membranes can be categorized into two types: fluorinated and non-fluorinated membranes. The Selemion® membrane from Asahi glass Co. is the one of the non-fluorinated type that is the copolymer of styrene and divinylbenzene. This membrane was used in the fuel cell in Gemini project. But this membrane showed degradation during long-term fuel cell operations over 343 K.

The Nafion® membrane, developed by Du Pont de Nemours and Co., is the most famous perfluorosulfonic acid (PFSA) membrane. Dr. Walther developed it in the late 1960; it has been adopted as an electrolyte in production of chlorine from sea water. Later it was applied to the fuel cell. Other PFSA membranes include Aciplex® (Asahi Chemicals), Flemion® (Asahi Glass), and Dow XUS® (Dow Chemical) [1,2]. General structure of PFSA membrane is given in Fig.2.



Nafion 117 m >1, n = 2, x = 5 – 13.5, y = 1000
Flemion m = 0, 1; n = 1 - 5
Aciplex m = 0, 3; n = 2- 5, x = 1.5 - 14
Dow membrane m =0, n = 2, x = 3.6 – 10

Figure 2. General structure of perfluorosulfonic acid membrane.

PFSA consists of three regions: (1) a polytetrafluoroethylene (PTFE, DuPont's Teflon™)-like backbone, (2) side chains of ---O---CF_2---CF---O---CF_2---CF_2--- which connect the molecular backbone to the third region, and (3) ion clusters consisting of sulfonic acid ions. When the membrane becomes hydrated, the hydrogen ions in the third region become mobile by bonding to the water molecules and moving between sulfonic acid sites (Fig 2). There are two advantages to the use of PFSA membranes in PEM fuel cells. First, because the structure is based on PTFE backbone, PFSA membranes are relatively strong and stable in both oxidative and reductive environments. In fact, durability of 60,000 h has been reported [3]. Second, the protonic conductivities achieved in a well-humidified PFSA membrane can be as high as 0.2 Scm^{-1} at PEM fuel cell operating temperatures. The high electronegativity (i.e. electron affinity) of the fluorine atom, bonded to the same carbon atom as the SO_3H group makes the sulfonic acid a superacid (e.g. like the trifluoromethane sulfonic acid).

Important properties of the Nafion® membranes and other commercial membranes are given in Table1 and 2 respectively.

Table 1. Characteristics of Nafion® membranes.

Membrane	**Dry thickness (µm)**	**Equivalent weight ($gmol^{-1}/SO_3^-$)**	**Area resistance (Ωcm^2)**	**Conductivity (Scm^{-1})**	**Water content at 25ºC**
Nafion 105	125	1000	-	-	-
Nafion 112	50	1100	0.07	0.165	20.7 ± 0.5
Nafion 1135	89	1100	0.10	0.11	21.1 ± 0.6
Nafion 115	125	1100	0.12	0.09	21.9 ± 0.6
Nafion 117	175	1100	0.13	0.08	23.2 ± 0.4
Nafion 1110	254	1100	-	-	38

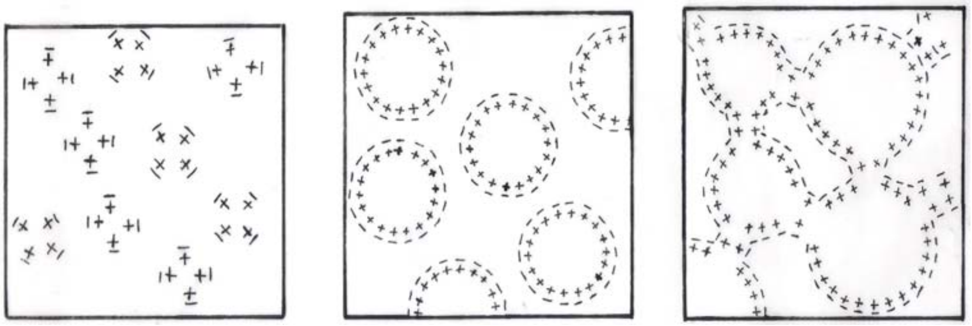
Table 2. Characteristics of other commercial polymer membranes.

Membrane	Dry thickness (μm)	Equivalent weight ($gmol^{-1}/SO_3^-$)	Conductivity (Scm^{-1})	Water content (wt %)	Manufacturer
Dow	125	800	0.114	54	Dow Chemical
Aciplex-S	120	1000	0.108	43	Asahi Chemical
Gore Select	5-20	900-1100	0.028-0.096	32-43	Gore
BAM 3G	140(wet)	375-920	-	87	Ballard
Flemion	50	1000	0.14	38	Asahi Glass

2.1. Structure and properties of PFSA membrane

The most significant feature of PFSA membrane is its high proton conductivity. In dry state, the PFSA membrane does not contain any ion conductive site. As water is absorbed in the membrane, its hydrophilic domain size becomes bigger, the PFSA membrane has the water cluster and finally, swollen in water. As more water is absorbed in the PFSA membrane, the cluster size is connected to each other through the water passage. Water and hydrophilic solvents can penetrate the membrane through water channel and it can also provide the passage of protons. This phenomenon is called percolation [4] and this progress is shown schematically in Fig.3. Its proton conductivity reaches a value as high as 0.083 S cm^{-1}, which is similar to that of 1M sulfuric acid aqueous solution.

The combination of the perfluorocarbon polymer backbone and the sulfonic acid group provides excellent electrochemical and mechanical properties. The hydrophilic sulfonic acid group makes the water passage as shown in Fig 3c, and the strong matrix originating from the perfluorocarbon backbone prohibits the polymer from dissolution in water. The structure was



a. Dry state of PFSA **b. Water incorporated PFSA** **c. Fully swollen PFSA**

Figure 3. Simplified PFSA structure according to water content [4].

investigated by Gierke et al. [5,6] and reported that the size of the percolation was 4 nm and that of the water passage was 1 nm from the small angle X-ray scattering (SAXS) experiment.

Types of PFSA membranes can be classified according to equivalent weights (EW, molecular weight per sulfonic acid group). The Nafion membrane having EW 900 can be easily dissolved by water or organic solvent due to the short main chain of the polymer backbone. This short polymer backbone restricts the possibility of crystallization, and thus Low EW membrane shows low stability in organic solvent. But, above EW 1000 it is enough for the polymer backbone to crystallize and consequently the PFSA membrane shows high stability in organic solvent [7].

2.2. Proton transport mechanism in PFSA membranes

In order to understand the electrochemical properties of PFSA membrane, the mechanism of proton conduction should be understood. The total proton conductivity of the PFSA membrane is driven by two mechanisms one is Grotthuss hopping mechanism and the other one is vehicular mechanism. Two mechanisms contribute to proton transportation simultaneously in the cluster of the PFSA membrane as shown in Fig. 3. The mechanism dependence of the proton conduction is affected by pK_a value of the sulfonic acid, the equivalent weight, amount of water uptake and size of percolation.

Zawodzinksi *et al.* [8] investigated the water uptake behavior and proton transport of the PFSA membrane. When activity of water vapor reached unity, the Nafion® membrane absorbed 14 water molecules for a sulfonic acid group. First 3 to 5 water molecules were used to hydrate the sulfonic acid group and remaining 9 to11 water molecules were attached to outside of the hydrated shell. As the PFSA membrane was swollen in liquid water, it absorbed around 7 more water molecules per sulfonic acid group and consequently absorbed 21 water molecules in total. These 7 water molecules are called as secondary phase water which has no interaction with the sulfonic acid group. It simply resulted from the polymer-solvent interaction between the PFSA membrane and water molecules. The proton and water diffusion rates diverge with increasing water content. Contribution of Grotthuss mechanism increased with bulk like water (less interacting water with sulfonic acid). Free water molecules at bulk like state can easily form hydrogen bonding like free water molecules outside the membrane and this promotes proton hopping. At lower water content the water molecules were confined in vicinity of the sulfuric acid group.

2.3. Drawbacks of the PFSA membranes

A PFSA membrane exhibits poor ionic conductivity at low humidity and/or elevated temperature, due to chemical degradation at elevated temperatures. For example, the conductivity of Nafion reaches up to 10^{-2} S cm^{-1} in its fully hydrated state but dramatically decreases with temperature above the boiling temperature of water because of the loss of absorbed water in the membranes. Its high preparation cost, lack of safety during its manufacturing and use and methanol permeability are also limitations for PFSA membranes. The price of the commercial Nafion membrane can also be high. The high methanol permeability is related to the structure of the PFSA membrane as already mentioned. Strong sulfonic acid group of PFSA membrane induces considerable phase separation and thus results in big size of the hydrated cluster and water passage. In order to solve these problems numerous approaches have been tried to develop new solid polymer electrolytes, which are cheap materials and possess sufficient electrochemical properties.

3. Modified PFSA membranes

Considerable efforts have been made to modify the PFSA membranes to be suitable for high-temperature operation. Increase in temperature of stability of membranes is attractive for a number of reasons: (1) Kinetics for both electrode reactions will be enhanced. (2) Above the boiling point of water, operation of PEMFCs involves only a single phase of water, i.e., the water vapor, and therefore can be simplified. (3) The required subsystems for cooling, membrane hydration can be eliminated (4) The CO tolerance will be dramatically enhanced, from 10-20 ppm of CO at 80 °C, to 1000 ppm at 130 °C, and up to 30 000 ppm at 200 °C. This high CO tolerance makes it possible for a fuel cell to use hydrogen directly from a reformer, so that the water-gas-shift reactor, the selective oxidizer, and/or the membrane separator for the CO cleanup can be eliminated from the fuel processing system. High reliability, less maintenance, and better transient response capacities can also be expected as the potential features of the high-temperature PEMFC technology.

3.1. Thinner and reinforced PFSA membranes

In order to reduce the internal resistance and cost of the membrane, thinner membranes are preferred. Thinner membranes also improve the water management during PEMFC operation. The reduction in area resistance with decreasing thickness is evident from the data given in Table 1. The challenge in developing thinner membranes is maintaining the required mechanical strength especially at elevated temperatures and under swelling. This has lead to the development of reinforcing PFSA with other polymers. PFSA membranes were reinforced with porous PTFE sheet or by micro PTFE fibril. Nafion-impregnation of other substrates such as porous polypropylene [9], expanded PTFE [10], and polysulfone and microglass fiber fleece [11] has also been investigated. By means of reinforcement, the thickness of PFSA membranes has been successfully reduced down to 5-30 μm with good conducting and mechanical properties [12,13]. Because of the effective back-diffusion of water from the cathode to the anode side through such thin membranes, water management and, therefore, the average conductivity are improved.

3.2. Swelling with low volatile and non aqueous solvents

The attempt to replace water which is acting as a host for proton transport, with non-aqueous and low-volatile solvents leads to membranes for high temperature operation. First attempt was made by Savinell et al., [14] by incorporating phosphoric acid in Nafion and achieved a conductivity of 0.05 S cm^{-1} at 150 °C. The low volatile phosphoric acid acts as a Bronsted base and solvates the proton from the strong sulfonic acid group in the same way as water does [15]. Phosphoric acid (B.P: 158 °C) has a very low volatility and therefore increases the operational temperature up to 200 °C. However, it should be noted that the conductivity obtained for the phosphoric-acid-swollen Nafion is lower than that of pure phosphoric acid. This may indicate that phosphoric acid in pure form is in fact the intrinsic proton conductor. Improved kinetics for oxygen reduction at the cathode has been reported [16] in the Nafion/phosphoric acid electrolyte compared to pure phosphoric acid. However, no fuel cell tests based on Nafion-H_3PO_4 membrane electrolytes have been successfully conducted, because a failure of the anode occurred after a short period of operation. Savinell et al. attributed this failure to the possible anion migration and the consequent electrode flooding. The idea has been extended to impregnation of Nafion membranes with other acids or ionic liquids. Malhotra et al. [17] impregnated Nafion 117 membranes with a phosphotungstic acid (PTA) solution in acetic acid. Fuel cell performance using this membrane at 110 °C (above 110 °C, the acetic acid evaporates) was compared to that with the non impregnated Nafion. A more thermally stable molten salt solvent, tetra-*n*-butylammonium chloride (TBAC), which has a melting point of 58 °C, has also been used for impregnation of PTA into Nafion. In this way the operational temperature of the fuel cell was extended to 120 °C.

Another interesting group of solvents with potential to replace water is the heterocycles (e.g., imidazole, pyrazole, or benzimidazole), containing both proton donor (NH) and acceptor (N). Kreuer et al. reported an increasing conductivity for sulfuric acid mixed with the heterocycles, [18] though no increase in conductivity was observed for a mixture of phosphoric acid with the heterocycles [19]. Sun et al. prepared water-free Nafion 117 membranes by swelling them in imidazole and imidazolium salt (e.g., trifluoroacetate and trifluoromethane sulfonate) solutions [20]. They reported conductivities of about 10^{-3} S cm^{-1} at around 100 °C. No fuel cell test has been reported with PFSA membranes swollen in these ionic or heterocyclic media. The difficulties may arise from (1) the immobilization of the liquids, especially in the presence of water (an attempt has been made to immobilize imidazole as proton solvent [21]), (2) adsorption of the solvent on the catalyst surface and (3) imidazole groups are not as water in solvating acid groups of the membrane.

Other modifications like composite formation with hygroscopic oxides and with solid inorganic proton conductors in order to achieve low-humidity and high-temperature operation PFSA membranes are considered elsewhere. (See section 5).

4. Alternative sulfonated hydrocarbon polymers

Much effort has focused on the development of alternative proton exchange membranes for PEM fuel cells and DMFC, in particular with the aim of increasing the temperature of operation of the fuel cell and to reduce the cost of materials. Some of these sulfonated hydrocarbons, show interesting features for a possible high-temperature operation. The main requisite in choosing polymers for fuel cell application is it should possess high stability in both oxidizing and reducing environment, including thermo-hydrolytic stability. There are three main groups of polymers that were investigated for this purpose. First two groups involve polymers containing inorganic elements, i.e., fluorine in fluoropolymers and silicon in polysiloxanes and the third group is aromatic polymers with phenylene backbones.

4.1. Fluoropolymers

Sulfonated polystyrenes (structure 1 in Figure 4) were investigated in 1960s as the first generation of polymer electrolytes for fuel cells [22,23]. This type of polymer membrane, however, suffers from a short lifetime because the tertiary C-H bonds in the styrene chain are sensitive to oxidation by oxygen and hydrogen peroxide. Because of this limitation, they went for grafting this polymer with partially fluorinated membranes like Poly-(tetrafluoroethylene-hexafluoropropylene) (FEP) and Poly(vinylidene fluoride)- (PVDF) (structure 2 in Figure 4) has been attempted. Poly-(tetrafluoroethylene-hexafluoro-propylene) (FEP) films have been adapted, mainly by Scherer's group [24-27]. The FEP film is first irradiated, and then styrene groups are grafted on with, e.g., divinylbenzene (DVB) as a cross-linker. The proton conductivity is introduced by sulfonating the aryl groups. A recent work reported a fuel cell lifetime over 5000 hours at 358 K based on this type of membrane [28]. Poly(vinylidene fluoride)- (PVDF) based polymer membranes have also been prepared by grafting and then sulfonating the styrene groups, mainly by Sundholm's group [29-37]. The combination of the good physical stability and chemical resistance of PVDF with the good conductive properties of sulfonated polystyrene seems to be responsible for high water uptake [34] and high proton conductivity [30-32].

A novel family of sulphonated co-polymers incorporating the α,β,β-trifluorostyrene monomer and a series of substituted α,β,β-trifluorostyrene co-monomers have been referred as Ballard Advanced Materials 3rd Generation (BAM3G) membranes for PEMFC applications [38,39]. They are partially per-fluoro-sulphonic acid (PFSA) membranes with an equivalent weight (EW) in the range of 320–920. Due to its low EW, it was shown that its water retention capacity is higher than that of the conventional perfluorinated membranes. It was also shown that the fuel cell performance based on these membranes is superior to that of conventional perfluorinated membranes [38,39]. This membrane should provide further improvement to its mechanical strength in the dry state and its dimensional stability in the wet state. Full cell performance at low temperatures shows promising results [40] but there was no fuel cell performance at temperatures above 300 K.

Poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) films were made proton conductive by means of irradiation treatment followed by sulfonation. These membranes have exceptionally low water uptake capacity and excellent dimensional stability. The membrane was tested in direct methanol fuel cell (DMFC). The temperature range used in the fuel cell tests was 303–368 K and

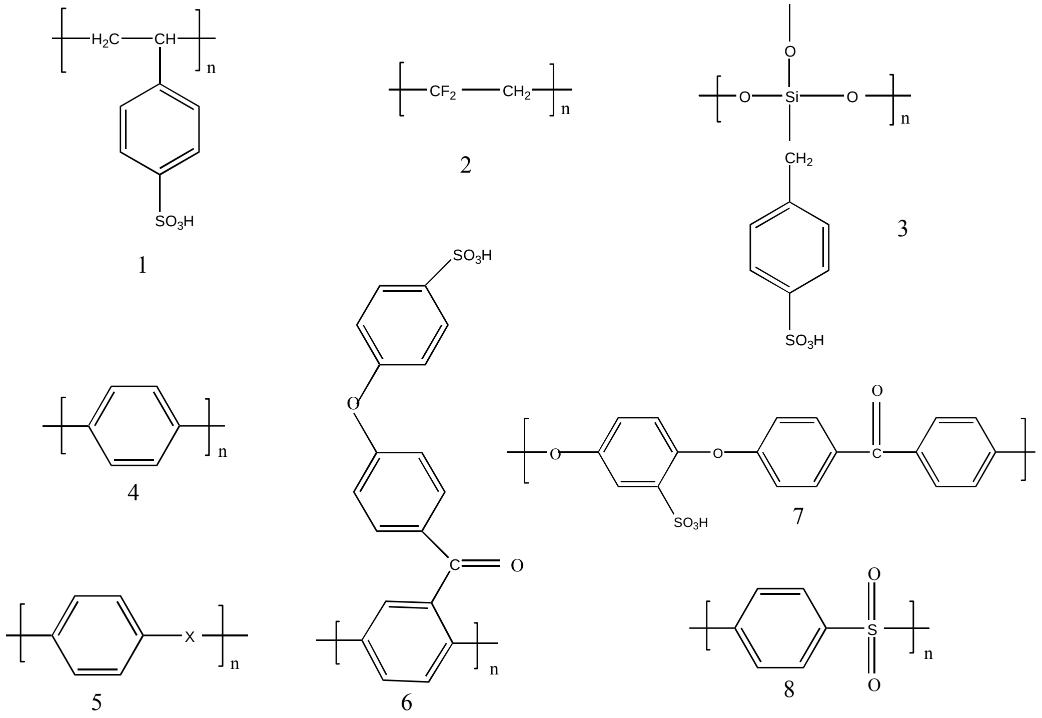


Figure 4. Chemical structures of polymers.

the measurement results were compared with those of the Nafion®115 membrane (41). Methanol crossover was reported to decrease when the thickness of the membrane increases, so the ETFE-based membrane compares favourably to Nafion® membranes. The maximum power densities achieved with the experimental ETFE-based membrane were about 40–65% lower than the corresponding values of the Nafion®115 membrane, because of the lower conductivity and noticeably higher IR-losses. Chemical and mechanical stability of the ETFE-based membrane appeared to be promising since it was tested over 2000 h in the DMFC without any performance loss.

4.2. Polysiloxanes

The development of stable polymer electrolytes having good proton conductivity, low cost and operating at medium temperature represents a crucial step in the evolution of polymer electrolyte fuel cells. Siloxanic proton-conducting membranes are another type of temperature resistant polymers of interest for fuel cell application. In particular, inorganic Si-O-Si networks have been formed by sol–gel processing using precursors characterized by an organic-polymerizable unit (methacrylic or epoxy groups), proton donor and acceptor functionalities (SO_3H, SO_2NH_2), and inorganic condensable units ($Si(OR)_3$) [42,43].

In this way, organic groups can be chemically bonded to the silica matrix. The products obtained are termed as organic-modified silicates (ORMOSIL) or organic-modified ceramics (ORMOCER) [44]. By functionalizing the inserted organic group, a large family of polymer electrolytes have been prepared, sometimes named organic modified silicate electrolyte (ORMOLYTE) and used primarily as electrolytic membranes for lithium batteries [45-47]. Attempts have been made to develop proton-conducting membranes for fuel cell applications by using arylsulfonic anions [48] or alkylsulfonic anions [43,49] grafted to the benzyl group. The poly(benzylsulfonic acid siloxane) (structure 3, Figure 4) membranes can be cross-linked via hydrosilylation, and they have been reported to exhibit a proton conductivity of 10^{-2} S cm^{-1} at room temperature and a thermal stability of the amorphous network up to 473 K with optical transparency and chemical stability. Two new siloxanic proton-conducting membranes were prepared by sol-gel method. The proton conductivities at 388 K of ca. 1.9×10^{-3} and 1.8×10^{-4} S cm^{-1} of fully hydrated membranes, classify these silicone networks as good proton conductors [50]. No report on fuel cell tests based on the silicone polymer membranes seems to be available so far.

4.3. Aromatic hydrocarbons

Aromatic hydrocarbons represent a large group of polymers that are low in cost and available commercially and from the chemical point of view, it exhibits good oxidation resistance. Polymers consisting entirely of linked benzene rings, e.g., poly-*p*-phenylene (PP) (structure 4, Figure 4), are resistant to oxidation and stiff rigid-rod polymers. Commercial polymers from the aromatic family are more often of the type shown in structure 5 in Figure 4, where X is an atom or group of atoms, giving the polymer chains a certain degree of flexibility. Ether links provide a good choice of functional groups as the -C-O-C- link itself is flexible and also is highly resistant to thermal oxidation. An example is poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP), (structure 6, Figure 4). Aromatic polymers containing ether links like polyetheretherketones (Victrex PEEK, structure 7, Figure 4) are widely investigated. Being fully aromatic, this polymer has excellent thermal oxidation resistance with a glass transition temperature of 416 K. More commonly, X is a simple functional group such as $-SO_2-$ in polysulfone, -NHCO- in polyamides, -COO- in polyesters, and -CO- in polyketones. Poly-*p*-phenylene sulfone (structure 8, Figure 4) itself has too high a softening point (about 793 K) to be processable. A few other well established polymers are sulfonated poly arylene ethersulfone (PES) and poly benzimidazole (PBI).

To create the proton conductivity, charged units can be introduced into the polymer structures. This can be done by sulfonating the hydrocarbons. Usually sulfonation is carried out in one of the following ways:

- By direct sulfonation in concentrated sulfuric acid, chlorosulfonic acid or sulfur trioxide
- By lithiation-sulfonation-oxidation
- By chemically grafting a group containing a sulfonic acid onto a polymer
- By graft copolymerization using high energy radiation followed by sulfonation of the aromatic component
- By synthesis from monomers bearing sulfonic acid groups

Sulfonation of thermostable polymers is generally accompanied by an increase in glass transition temperature, T_g. For example the T_g increases from 423 K (PEEK) to around 503 K in s-PEEK of 60% sulphonation. The presence of pendant SO_3H groups produces steric hindrance to intersegmental motion and reduces mobility and flexibility, and the sulfonic acid groups interact and form strong hydrogen bonds that increase chain rigidity.

Polyether-etherketones are thermoplastic polymers with an aromatic non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by a number of linkages, –O– and –CO–. The oxidation stability is expected to increase with increasing content of ketone segments, and with a decrease in ether segments.

Sulfonation of polyetherketones can be carried out directly in concentrated sulfuric acid or oleum, the extent of sulfonation being controlled by the reaction time and temperature [51-53], although it has been reported that this method is not appropriate for the preparation of polymers with a low degree of sulfonation (<30%) since the sulfonation reaction takes place at the same time as polymer dissolution; the resulting sulfonation is heterogeneous and the polymer microstructure is difficult to reproduce [51].

Sulphonated polyether-etherketone (*s*-PEEK) with 100% sulphonation corresponds to one sulphonic acid group per repeat unit. It was claimed that the conductivity of s-PEEK membrane with equivalent weight 625 g mol^{-1} undergoes shrinkage of 1.5% up to 413 K and a reversible elongation of 0.6% occurs at 453 K. The conductivity of s-PEEK was 0.05 S cm^{-2} at 100 % RH and at 373 K and increased to 0.11 S cm^{-2} at 423 K. It looses water at 423 K and sulphonic group degrades at 513 K. This limits the use of this membrane above 423 K in fuel cell where severe oxidative and reductive environment exits. The stability of *S*-PEEK depends on the solvent used to cast it [54,55]. It was found that when dimethylformamide (DMF) was used as the casting solvent, the amide function forms a hydrogen-bonding complex with the sulphonic acid group starting at 333 K [54]. But, when dimethyl acetamide (DMAc) was used, this hydrogen bonding occurs at 413 K. The solvent interaction with s-PEEK reduces the proton conductivity of the membrane. The decrease in proton conductivity was more pronounced with membrane cast in DMF. It is also found that for highly sulphonated PEEK, the excess of sulfuric acid degrades DMF or DMAc, resulting in formation of dimethylaminium sulphate and corresponding carboxylic acids. This results in a decrease in the proton conductivity of the membrane due to decrease in sulphonic acid concentration [55]. Accordingly, it is important to understand the relations between these results and the performances of PEFC in low and high temperatures operating conditions when these membranes are used. As it is not well established that *s*-PEEK can be used in high temperature operating conditions, it is necessary to develop composite membranes based on *s*-PEEK.

High-surface amorphous silica, was used as a filler of sulfonated poly(ether ether ketone) (s-PEEK) having 1.6 mequiv g^{-1} ion-exchange capacity [56]. Membranes containing up to 20 wt% silica were prepared by bulk mixing of the finely ground powder with the polymer solution. The membrane containing 10 wt% silica exhibited the best electrical and mechanical characteristics. Its conductivity at 373 K rises from 8 x 10^{-3} to 9 x 10^{-2} S cm^{-1} for relative humidity increasing in the range of 75–100%, and is up to two times higher than that of the unmodified polymer. At 100% relative humidity, the conductivity is nearly independent of temperature between 80 and 130ºC, but it decreases down to 3 x 10^{-2} S cm^{-1} at 433 K.

4.3.1. Polymer blends

Polymer blending is an effective way of tuning the properties to those desirable for fuel cell application. The miscibility between two polymers can be effectively improved by favoring specific interactions between the polymer chains, such as hydrogen bonding, ionic interaction, or ion-dipole interactions, which also act to crosslink the blend and modify mechanical and swelling properties. Sulfonated polysulfone (s-PSU) and PEEK have been used in blends with PBI, as well as with more weakly basic components such as polyetherimine, poly(4-vinylpyridine), diaminated PSU [57,58], and other modified PSUs containing pendant basic aromatic groups [59]. The ionic interaction increases the glass transition temperature, T_g, of the blend membranes compared with that of either of the components by 15 to 50 K in sPSU-PBI. Such effects depend upon the relative proportion of sulfonated and basic polymer and the base strength of the latter. Swelling in water and brittleness in the dry state are both lower than that for the corresponding non-blended sulfonated polymer membrane to the extent that a water-soluble sPEEK becomes virtually insoluble on blending with PBI. These advantages are lost at higher temperatures as the degree of ionic crosslinking is severely reduced above 343 K for sulfonated polymer-aminated PSU and above 383 K for sulfonated polymer-PBI; above these temperatures, reverse proton transfer occurs with an associated increase in solubility of the sulfonated component. Therefore, a challenge remains to associate both covalent and ionic crosslinking in order to combine the reduced swelling of the former with the flexibility and mechanical stability of the latter. Fuel cell performance using sPEEK-PBI membrane exhibited a current density of 300 mA cm^{-2} at 500 mV and at 383 K with low methanol crossover [60].

Polymer blends of poly(vinyl alcohol)-poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PVAPAMPS) family membranes have been prepared and evaluated as novel proton-conducting materials on the basis of a new concept of binary chemical cross-linking. Chemical cross-linking in pristine PVAPAMPS with terephthalaldehyde as a cross-linker to form the main chain gives the polymer membrane a good mechanical property. In addition, by forming the side chains using aldehydes with different spacer lengths as auxiliary cross-linkers, the membranes prepared gain excellent flexibility. PAMPS is “trapped” in the membrane, and provides high proton conductivity (0.12 S cm^{-1}, 298 K) due to the sulfonic acid groups in its chemical structure. The membranes show a larger sorption of nonfreezing water and display an isotropic membrane swelling. Despite their high ion exchange capacity (IEC=1.68) and high water uptake, the membranes show good water stability. This can be attributed to the high flexibility of the side chains provided by the auxiliary cross-linkers, which allows easy relaxation of the polymer chains

[61]. Two types of sulfonated co-polyimides (co-SPIs) with ion exchange capacities of 1.83–2.32 meq g^{-1} were prepared from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), two types of sulfonated diamines, namely, 4,4′-bis(4-sulfophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) and bis(3-sulfopropoxy)benzidines (BSPBs), and common non-sulfonated diamines via statistical polycondensation reaction. The BSPB-based co-SPI membrane had a clear microphase-separated structure composed of hydrophilic and hydrophobic domains but the connection of hydrophilic domains was rather poor. On the other hand, the BAPBDS-based co-SPI membranes did not show such a clear microphase separation. The co-SPI membranes except for a few ones showed high proton conductivities of 0.10–0.16 S cm^{-1} in water at 323 K, which was comparable to that of Nafion 112 (0.13 S cm^{-1}). The methanol permeabilities of the co-SPI membranes hardly depended on feed composition up to 50 wt% of methanol and were in the range of 0.5×10^{-6} to 1.8×10^{-6} cm^2/s at 323 K, which was more than two times smaller than those of Nafion 112. As a result, the co-SPI membranes showed more than two times larger ratios of proton conductivity over methanol permeability than Nafion, suggesting high potential for direct methanol fuel cell application [62]. Other blends like sPEK-PBI-aminated PSU, sPEK-PBI exhibited high power density compared to sPEEK-PBI but methanol crossover is high. Sulfonated bisphenol-A-polysulfone (SPSU) or sulphonated polyethylene oxide (SPPO) and their derivatives could be the choice of membrane and it can be cross linked with a polybase such as poly(ethyleneimine) (PEI) or poly(benzimidazole) (PBI). They are expected to offer good mechanical, thermal and chemical stability with good proton conductivity.

4.4. Microstructures

Properties and structure of the sulfonated PEEK have been thoroughly investigated and the results provide the fundamental understanding of hydrocarbon based polymer electrolyte membrane. Sulfonated polyaromatic polymers have different microstructures from those of PFSA membranes. The schematic feature and significant properties of the hydrated PEEK is illustrated in Figure 5 and Table 3 respectively along with the hydrated Nafion® membrane, according to Kreuer [63].

It can be seen that the sizes of hydrated ion cluster and water passage significantly reduced, when compared with those of the Nafion® membrane. While the acidity of sulfonic acid group in the Nafion® membrane is very high (pKa = -6), that in the S-PEEK membrane is relatively low (pKa = -1), and consequently its polarity is lower than that of the Nafion®. Weak polarity of the sulfonic group induces less phase separation between polymer backbone and the sulfonic acid group. Moreover, the polymer backbone is more rigid than that of Nafion®.

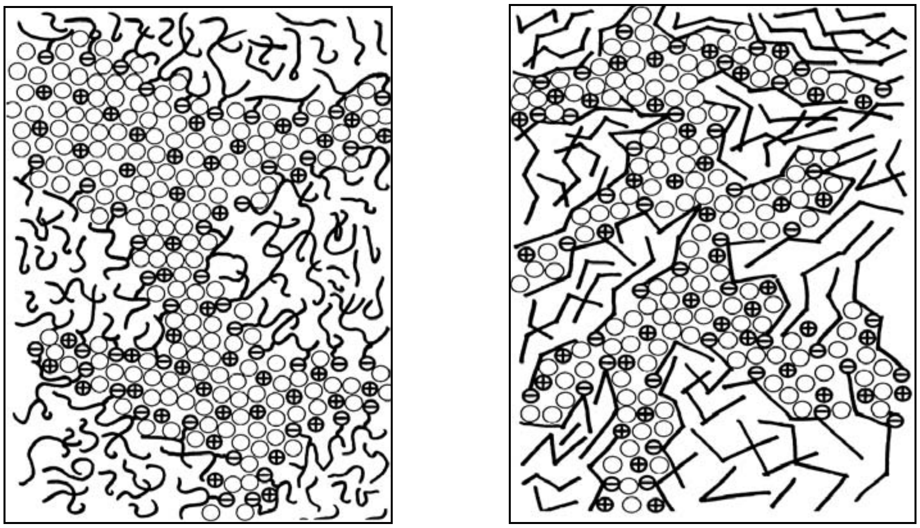


Figure 5. Schematic representation of the microstructures of Nafion 117 and SPEEK [63].

Table 3. Significant properties of Nafion 117 and SPEEK – A comparison.

PFSA membrane (Nafion)	Sulfonated polyaromatic membranes (S-PEEK)
Wide channels	Narrow channels
Good connectivity between channels	Dead-end channels
More separated	Less separated
Less branched	Highly branched
Small $-SO_3^-/-SO_3^-$ separation	Large $-SO_3^-/-SO_3^-$ separation
pKa ~ -6	pKa ~ -1
$D_{MeOH} = 2.91 \times 10^{-6}$ cm^2/s	$D_{MeOH} = 6.57 \times 10^{-8}$ cm^2/s
High water uptake	Less water uptake

4.5. Conductivity and water uptake

The unique structure of the S-PEEK induces quite different transport properties such as methanol permeability and proton conductivity. Weaker acidity of the sulfonic acid group decreases both degree of dissociation of the protons and dielectric screening of the sulfonic acid group, and thus protons tend to be localized in adjacent anion. This lowers proton conductivity severely with decreasing water content. In order to have comparable proton conductivity to that of Nafion, it shoud have more water content about 30 water molecules per sulfonic acid group. In spite of higher water content, less pronounced phase separation leads to low solvent permeation and low electro osmotic drag, which is the advantage of the S-PEEK in the DMFC application.

Remaining problem, however is brittleness of the membranes at dried state. It can be solved by blending with PBI membranes.

For PFSA membranes, the extreme hydrophobicity of the perfluorinated polymer backbones provide mechanical strength and the extreme hydrophilicity of the terminal sulfonic acid groups maintain the proton conductivity. The water uptake by the PFSA membranes is high but extremely sensitive to the relative humidity. Generally speaking, PFSA and sulfonated hydrocarbon membranes have similar water uptakes at low water activities, whereas at high relative humidity (100%) PFSA membranes have a higher water uptake due to the more polar character of the sulfonic acid functional groups. Consequently, the sulfonated polyaromatic membranes in general need more humidification during fuel cell operation in order to maintain the high level of conductivity.

The length of alkyl chains and chain branching were found to have tremendous effects on the water uptake and proton conductivity (and its temperature dependence), as well as the thermal stability of the obtained polymer membranes [64]. High conductivity can be obtained at high sulfonation degree, but high sulfonation results in high swelling and therefore poor mechanical properties, especially at higher operating temperatures [65].

4.6. Fuel cell performance

The evaluation of sulfonated hydrocarbon polymers in fuel cells is still in an early stage. Sulfonated S-PEEK membranes have been tested in both hydrogen and oxygen (air) and in direct methanol fuel cells. A membrane 18 μm thickness with ion exchange capacity 1.6 meq g^{-1}, exhibited a cell voltage of 0.8 V at 0.5 mA cm^{-2} at 363 K and 0.72 V with oxygen and air, respectively [66]. S-PEEK membranes of 70 μm thickness gave higher performance at 358 K than Nafion-115 under the same test conditions, in particular at high current densities when the membrane can dehydrate [66]. Patent reports claim 4000 h of functioning of S-PEEK with IEC 1.47 meq g^{-1} at a modest cell temperature of 323 K [67], giving a maximum power density of 0.386 W cm^{-2} at 0.52 V, whereas at 363 K at constant current density of 0.5 mA cm^{-2}, S-PEEK has attained 1000 h of functioning without failure. At 343 K in an H_2-O_2 fuel cell, naphthalenic sPI with IEC 1.26 and 1.98 meq g^{-1} provided 0.5 and 0.6V, respectively, at 0.5 mA cm^{-2} [76], and a lifetime of 3000 h has been obtained at 333 K, 0.25 mA cm^{-2}, with an output of about 0.63 V [69]. However, membranes of high IEC are hydrolytically unstable. In DMFC, the most promising fuel cell performance is being obtained with membranes based on sulfonated poly(ether ketone)s and their blends, and recent results indicate power density as good as that given by Nafion. Thus non-blended S-PEEK (60 μm thickness) gives a power density of 150 mW cm^{-2} at 120ºC, whereas an

S-PEEK-PBI-PSU-NH_2 blend has given 250 mW cm^{-2} at 383 K [70]. The DMFC operating at 393 K with S-PEEK membranes can be shut down and started up without a change in performance over a period of more than two months. Bilayer membrane prepared from S-PEEK of two different ion-exchange capacities (IECs) with layers of EW 770 and 900 g/mol, 50 and 20 μm, respectively exhibited current density of 1.5 A cm^{-2} at 600 mV at 363 K [71].

4.7. Limitations of sulfonated polymers

Sulfonated polymers are highly deliquescent and hard to recover from solution; this is circumvented by preparing mixed derivatives where the sulfonated groups are replaced by non-sulfonated groups. It is also of importance to realise that sulfonated materials are likely to have a temperature limit at 473 K where in some instances decaying of the proton conductivity has been attributed to the decomposition of the SO_3H groups. Particularly aggressive environment in a PEMFC or DMFC can initiate different types of degradation mechanisms and aging processes that result in either chemical or morphological/textural alteration. Such modification might arise from desulfonation, chain scission caused thermohydrolytically, or by free radicals generated at the electrodes or loss of mechanical properties owing to excessive swelling. Species such as $HO\cdot$ and $HO_2\cdot$ could arise from oxygen diffusion through the membrane and incomplete reduction at the anode, and possible degradation mechanisms involving oxidizing species and hydroxy radicals occurs. All these limitation paved way to inorganic organic composite membranes.

5. Composite membranes

The term “composite membranes” can be used to describe any membrane made from organic and inorganic components (at least one of each of the organic and inorganic components). Some percentage of an organic or inorganic component is dispersed into an organic or inorganic electrolyte support, producing a composite membrane. A composite membrane may be defined as one in which a mixed membrane is more effective for at least one property (water uptake, conductivity, mechanical properties, etc.) than either material of the composite system alone.

The addition of an inorganic material into a polymer membrane can alter and improve physical and chemical polymer properties of interest (such as elastic modulus, proton conductivity, solvent permeation rate, tensile strength, hydrophilicity, and glass transition temperature) while retaining its important polymer properties to enable operation in the fuel cell. Their use in fuel-cell systems is attractive because they will enhance the efficiency of the cell significantly. The development of composite membranes must be the most important aspect to be considered if we want to get membranes suitable for high temperature PEFC applications. Below, we will consider the various types of composite membranes under development for these applications.

5.1. Composites with hygroscopic oxides

An effective way to achieve low-humidity and high-temperature operation of PFSA membranes is to recast per-fluoro sulfonic acid (PFSA) membranes with mixed hygroscopic oxides (e.g., SiO_2 TiO_2 and ZrO_2). The first nano-composite Nafion-SiO_2 membranes were obtained by growing the silica particles inside a preformed membrane [72,73-78]. *In situ* hydrolysis of metal alkoxides was also used to prepare a number of nanocomposite Nafion membranes containing zirconium oxide [79], mixed silicon-titanium oxide, and mixed silicon-aluminium oxide [80-83, 98]. Thereafter a number of patents have been granted [81]. It has been shown that the water uptake by the oxide-containing membrane is higher than that of the pristine Nafion. For recast Nafion membranes predried at 353 K, the water absorbing ability by humidification with water vapor at 333 K was found to be 17 wt %, whereas for membranes containing 3 wt % SiO_2 of 7-nm size, the water absorbing ability was increased to as high as 43 wt % [102]. This is because of water absorption on the particles of the hygroscopic oxide. As a result of the water adsorption, the back-diffusion of the cathode-produced water is enhanced and the water electro-osmotic drag from anode to cathode is reduced. These modified Nafion membranes were developed with aims at an internal (self) humidification at low operational temperatures [84]. High-temperature operation has also been demonstrated using a recast Nafion membrane containing 3 wt % SiO_2. Antonucci et al. [97] tested a DMFC at 418 K under pressures of 4.5 atm (methanol-water)/5.5 atm (air). The performance obtained was about 350 mA cm^{-2} at 0.5 V. Mauritz et al. [75] developed a sol-gel technique to introduce SiO_2 into the fine hydrophilic channels (ca. 50 Å diam.) of PFSA membranes. Detailed investigations on microstructures and fundamental properties of the obtained composite membranes have been carried out [85-90]. A modification of the method is proposed by using a Nafion solution, instead of the preformed PFSA membranes, mixed with tetraethyl orthosilicate (TEOS) (and TMDES) [91,92]. High SiO_2 content in Nafion has been reached up to 54%. Conductivity in the range of 10^{-7} to 10^{-5} S cm^{-1} was reported at 373 K under dry argon atmosphere. Attempts were made to test these composite membranes in an H_2/O_2 PEMFC at temperatures above 100 °C [93-96]. By processing tetraethoxysilane in the Nafion acidic medium, a mixture of SiO_2/siloxane polymer is formed within the PFSA membrane, with SiO_2 contents of up to 10 wt %. At 403 K under a pressure of 3 atm, a

PEMFC based on such a membrane delivered 4 times the current density (at 0.4 V) as obtained with unmodified Nafion 115 membranes [95].

Thermal treatment of Nafion 3-wt% SiO_2 nano-composite membranes by hot pressing up to 433 K was shown to increase the polymer crystalline fraction [97,98]. Direct methanol fuel cells based on this type of membrane and fed with 2 M methanol were characterized by low methanol crossover and were able to work up to 418 K with open circuit voltages of 0.82–0.95 V and power density peaks of 150–240 mW/cm^2 in air and oxygen, respectively. Kim et al., exploited plasma enhanced chemical vapor deposition (PECVD) technique to deposit nano-scale films of silica (10, 32, 68 nm) on Nafion membrane [99]. The ion conductivity of the composite membrane containing silica film with 10 nm thickness was similar to the unmodified Nafion membrane, but its methanol permeability was reduced to an extent of 40%. Cell performance of the composite membrane with 10 nm silica was higher than that of the bare Nafion membrane by about 20%. Nafion®-MO_2 (M = Zr, Si, Ti) nanocomposite membranes were synthesized by sol–gel method [100]. The membranes synthesized by this approach were completely transparent and homogeneous. At 363 K and 393 K, all Nafion®-MO_2 composites exhibited higher water sorption than Nafion® membrane. However, at 90 ºC and 120 ºC, the conductivity was enhanced only in Nafion®-ZrO_2 composite with a 10% enhancement at 40% RH over Nafion®. This can be attributed to the increase in acidity of zirconia based membranes shown by a decrease in equivalent weight in comparison to other nanocomposites based on Ti and Si. An organic species bearing an organic sulfonic acid (HSO_3^-) was grafted onto the surface of montmorillonite (MMT) by silane condensation, and the composite membranes were cast together with Nafion [101]. The methanol permeability of the composite membrane decreased by 90% relative to pristine Nafion 115. By rendering proton conductivity to MMT by functionalization with an organic sulfonic acid, the proton conductivity of the composite membrane was lowered only slightly from that of pristine Nafion 115. The combination of these effects led to a significant improvement in the performance of a DMFC made with Nafion/HSO_3^-MMT composite membranes. From the point of view of practical applications, it must be pointed out that Pt- loaded Nafion membranes are very expensive and that, in the absence of platinum, silica-loaded membranes show a poor fuel cell performance when fed with anhydrous gases [102].

High-surface amorphous silica, was used as a filler of sulfonated poly(ether ether ketone) (s-PEEK). The membrane containing 10 wt % silica exhibited the best electrical and mechanical characteristics. Its conductivity at 273 K increases from 8 x 10^{-3} to 9 x 10^{-2} S cm^{-1} for relative humidity increasing in the range of 75–100%, and is up to two times higher than that of the unmodified polymer. At 100% relative humidity, the conductivity is nearly independent of temperature between 353 K and 403 K, but it decreases down to 3 x 10^{-2} S cm^{-1} at 433 K [56]. Similarly composite membranes loaded with SiO_2, TiO_2 and ZrO_2 were prepared by hydrolysis of silanes and metal alkoxides in solutions of s-PEEK and s-PEK [103]. While homogeneous dispersions of TiO_2 and ZrO_2 particles were obtained starting from $Ti(OEt)_4$ and $Zr(OPr)_4$, the hydrolysis of $Si(OEt)_4$ led to the formation of larger particles and cavities in the polymeric matrix. However, smaller and better-dispersed silica particles (~100nm size) were formed by using either silanes covalently bonded to the polymer chain or organically modified silanes bearing imidazole groups. A good balance of low permeability and high conductivity (3.5–4.5 x 10^{-3} S cm^{-1} against 5 x 10^{-3} S cm^{-1} for the unmodified polymer) was achieved by incorporation of a mixture of 10–15 wt% ZrO_2 in s-PEEK.

5.2. Composites with solid inorganic proton conductors

Solid inorganic proton conductors have dual role being both hydrophilic and proton conducting unlike hygroscopic oxides which have primarily a single function i.e. water retention**.** Among the inorganic solid proton conductors, zirconium phosphates, heteropolyacids, metal hydrogen sulfate are of special interest for developing high temperature composite membranes for PEMFC.

5.2.1. Zirconium phosphates

These are water-insoluble, layered compounds containing intercalated hydronium ions and have reasonable conductivity at room temperature. However, the proton transport properties are highly dependent on the humidity level of the atmosphere and thus for fuel cell applications water management remains a challenge.

There are two predominate structures of zirconium hydrogen phosphate α- $Zr(HPO_4)2\cdot H_2O$ and γ-($ZrPO_4[O_2P(OH)_2]\cdot\ nH_2O$) as illustrated in Fig. 6. The pendant OH group which extends into the interlayer structure of α-ZrP leads to proton transport by forming hydrogen bonded network with water. The γ-ZrP does have the advantage of having an extra water molecule per formula unit and is more acidic than the α-ZrP [104].

The transport mechanism in α-ZrP at room temperature is dominated by surface transport than the bulk transport; four orders of magnitude greater than the bulk transport, however the crystallinity also plays an important role [105]. In addition, conductivity in α-ZrP is highly dependant on the hydration, varying by two orders of magnitude as the relative humidity is increased form 5 to 90% [106]. Recent research has confirmed the dominance of the surface transport and demonstrated enhancements that can be made through modification

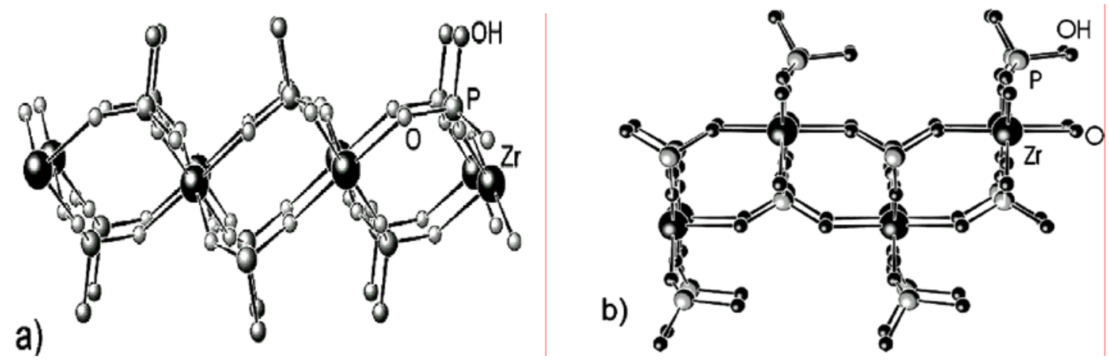


Figure 6. Schematic representation of α- and γ-layers of Zr-phosphonates [107].

of the P–OH groups [108]. Based on this understanding of α-ZrP, attempts to enhance the proton conductivity have been made in the following directions:

- By forming composite membranes with α-ZrP.
- By intercalating functional groups.
- By maximizing the internal surface area using sol–gel synthesis and pillaring.
- By maximizing the external surface area by mechanical and colloidal synthesis.

Composite membranes with α-ZrP

Due to the insolubility of these layered compounds, the first composite membranes were prepared by mixing of the finely ground filler with the ionomer solution s-PEEK membranes containing 40 wt% amorphous zirconium phosphate sulfophenylenphosphonate ($Zr(O_3P\text{-}OH)_{2-x}(O_3P\text{-}C_6H_4SO_3H)_x.nH_2O$, with x =1, 1.5). The conductivity of these membranes lies between those of the two components and reaches a maximum value of 0.04 S cm^{-1} at 423 K and 100 % RH [56]. Experiments [109] showed that composite Nafion/ZrP membranes can be produced with a conductivity of 0.64 S cm^{-1} compared to pure Nafion 0.40 S cm^{-1} at the same conditions, while halving the methanol permeability (100% RH, conditioned in boiling water for 1 h). Furthermore, composite membranes of dispersed α-ZrP in SPEEK, have been demonstrated to show a three-fold improvement in conductivity with composites loaded with 10 wt.% α-ZrP [110]. Experiments varying the inorganic species (silica, zirconium phosphate sulfophenyl-phosphonate or α-ZrP) have also been conducted [56], however only slight improvements in the conductivity were realised, falling short of pure zirconium phosphate sulfophenylphosphonate.

Intercalation of functional groups

Attempts to improve the conductivity of solid acid membranes have included the synthesis of new layered compounds, where Brønsted bases are intercalated in the interlayer region or functionalised organic radicals replace the hydroxyl of the phosphate group [104]. When the organic moieties contain a proton-generating function such as -COOH, $-PO_3H$, $-SO_3H$, or NH_3^+, these compounds become proton conductors. Zirconium alkyl sulfophenyl-phosphonates or the variety $(Zr(O_3PC_6H_4SO_3H)_{0.85}(O_3PC_2H_5)_{1.15}\cdot nH_2O)$ and $(Zr(O_3PC_6H_4SO_3H)x\ (O_3PCH_2OH)_{2}.x\cdot nH_2O)$ have been investigated for their conductivity under different temperature and relative humidity regimes [111]. The results of conductivity measurements at 373 K and 95% RH are given in Table 4.

Table 4. Conductivity of Zirconium Phosphates and Phosphonates.

Layered ZrP and phosphonates	**σ (S cm^{-1}) at 100°C, 95% RH**
α-$Zr(O_3P\text{-}OH)_2 \,.\, H_2O$ *	1.8×10^{-5}
γ-$ZrPO_4[O_2P(OH)_2].\ 2H_2O$*	2×10^{-4}
$Zr(O_3P\text{-}OH)_2 \,.\, nH_2O$ ¶	1–5 x 10^{-3}
$Zr(O_3P\text{-}OH)_{1.5}(O_3P\text{-}C_6H_4SO_3H)_{0.5}$ ¶	0.9–1.1 x 10^{-2}
$Zr(O_3P\text{-}OH)(O_3P\text{-}C_6H_4SO_3H)\ nH_2O$ §	0.8–1.1 x 10^{-1}

* Crystalline; § Semicrystal: ¶ Amorphous

Unfortunately the sulfophenylphosphonates, when compared to standard α-ZrP exhibit increased dependance on relative humidity at humidities less than 50%. They are however, still capable of conducting with a value of 0.01 S cm^{-1} at 65% RH at 373 K [112]. One of the other significant advantages of the sulfophenyl-phosphonates is that as the temperature is increased from ambient conditions up 373 K there is no drop in conductivity, indicating that the hygroscopic nature is not affected.

Titanium phosphates are also very good at conducting protons [113,114]. Mesoporous MCM type zirconium and titanium phosphates synthesised by the sol–gel route using surfactant templates have surface areas 240–330 m^{2}g^{-1} [114]. All conductivities recorded were very low < 5 x 10^{-7} S cm^{-1}.

Internal surface area maximization

Sol–gel processing is indeed a versatile synthesis route to the tailoring of nanostructure of solid acids. This is one of the methods of creating mesoporous solid acids. The dominant proton transport mechanisms of α-ZrP is surface transport. Alberti et al. [115] investigated the conductivity of mesoporous zirconium phosphate pyrophosphate to examine the effect of increasing the surface area. Conductivity at 293 K reduced from 1.3×10^{-3} to 4×10^{-7} S cm^{-1} as the humidity was reduced from 90 to 20%, approximately a 350-fold increase over crystalline α-ZrP. Contrary to expectations the evidence suggested that there was as increase in bulk –POH groups as the conductivity rose implying that when hydrated, the proton conductivity is a bulk property. Increases in the conductivity over α-ZrP were attributed to a reduction in the activation energy of the sample (4.6 kcal mol^{-1} at 293 K and 90% RH). Long term observations of the materials lead to the discovery that the interlayer phosphate groups tend to rehydrate and the mesopores disappear (the surface area had reduced to < 10m^{2}g^{-1}). This is a disconcerting result as it raises questions as to the stability of this structure in near fuel cell conditions.

External surface area maximization

Ball-milling of standard α-ZrP for 6 h caused the proton conductivity to increase from 3×10^{-6} to 6×10^{-4} S cm^{-1}, due to the reduction in crystallinity and increase in exposed surface. Investigation of the proton conductivity of modified ZrO_2 have demonstrated the applicability of surface modification techniques to metal oxides [108,116]. Surface modification of nanometre sized zirconia (ZrO_2) particles by reaction with phosphoric acid was able to produce pseudo zirconium phosphate particles with a conductivity of 5.0×10^{-3} S cm^{-1} at 90% RH [108]. Processes of this nature give a clear example of how the surface transport mechanism can be exploited to increase surface area and develop proton conductivity.

5.2.2. Heteropolyacids

The heteropolyacids(HPA) ($H_3PMo_{12}O_{40}.nH_2O$ and $H_3PW_{12}O_{40}.nH_2O$) in addition to being electro-catalytically active, exhibit exceptionally high conductivities at room temperature, ~0.17 S cm^{-1}, when 29 waters of hydration are present (n=29) [117]. Owing to these characteristics, a series of composite membranes have been prepared by incorporating HPA into polymer matrix.

Composite Nafion membranes containing heteropolyacids were obtained by two simple methods either by mixing a Nafion solution with an appropriate amount of a heteropolyacid followed by casting [118,119] or by impregnating the preformed membranes with a heteropolyacid solution [120]. Nafion recast membranes loaded with silicotungstic acid (STA), phosphotungstic acid (PTA), and phosphomolybdic acid (PMA) were systematically investigated by ionic conductivity, water uptake, tensile strength, and thermal behavior. In comparison with Nafion 117, all these membranes exhibited higher proton conductivity (0.012 – 0.015 S cm^{-1} at 35 % RH) and greater water uptake, but decreased tensile strength (~14 kPa whereas Pristine Nafion ~ 40 MPa). Water uptake, increased from 27% for pristine Nafion 117 to a maximum of 95% for the PMA-based membrane.

Composite PTA-Nafion 117 membranes, prepared by impregnation with PTA solutions in acetic acid or in molten tetra-*n*-butylammonium chloride, were tested in H_2/O_2 fuel cells working at 1 atm up to 383 K [120]. In comparison with unmodified Nafion 117, these membranes showed a strong performance enhancement that increased with increasing temperature.

Upon slight heating, the HPA dehydrate and the conductivity drops precipitously. Moreover these materials are water soluble. As such, use of these materials in fuel cells implies the impossible requirements of retaining hydration to ensure high conductivity and removing by-product water to prevent dissolution. Although these compounds are of little value as solid state electrolytes, they may provide benefits with respect to rapid oxygen reduction kinetics when implemented as aqueous electrolytes. HPA is highly water soluble eventually leaches out from the polymer electrolyte membrane.

A series of composite membranes has been prepared by incorporation of tungstophosphoric acid, and molybdophosphoric acid into a partially sulphonated PEEK polymer. In comparison with the pure sulfonated polymers, the composite membranes are characterized by a higher glass transition temperature, probably because of the intermolecular interaction between the sulfonic groups and the heteropolyacids, and by greater water uptake at room temperature (up to five times for TPA-loaded s-PEEK with 80% sulfonation degree). They also exhibited the following performances: (i) thermal stability up to 548 K; (ii) good flexibility and strong mechanical properties; (iii) high conductivity during storage in water for several months; and (iv) easy preparation.

Despite these claims of interesting properties, the following drawbacks are observed. The high content of the HPA (60 wt %) may have an important impact on the mechanical properties (high HPA content may lead to a brittle composite) and high cost (HPAs are very costly) of the composite membrane. Composite membranes based on low content of HPA are an interesting approach to decrease the high cost of the HPA. The methods of preparation of these composite membranes are based on dispersion of an inorganic solid in the polymer. Accordingly, the particle size of the inorganic solid, the method and parameters of dispersion may, of course, have important effect on the properties of the composite membrane.

5.2.3. Metal hydrogen sulfate

Another group of inorganic solid proton conductors is *hydrogen sulfates*, $MHXO_4$, where M is Rb, Cs, or $NH4^+$, and X is S, Se, P, or As. In general, such compounds are comprised of oxyanions, for example SO_4, SeO_4, PO_4, AsO_4, or even PO_3H etc., which are linked together via O–H...O hydrogen bonds. At room temperature, the structures are typically ordered and the transport properties are rather conventional. Upon slight heating, however, many in the $MHXO_4$ and $M_3H(XO_4)$ families of solid acids, transform into a disordered structure and exhibit conductivities as high as 10^{-2} S cm^{-1}. Proton transport is facilitated by the rapid reorientation of XO_4 groups in the disordered structure [121,122]. These materials are true proton conductors; no water molecules are required to serve as hosts for a vehicular transport mechanism, and the electrolyte need not be hydrated. Among these compounds is $CsHSO_4$, the most interesting. It undergoes several phase transitions and the high temperature phase above 414 K exhibits high proton conductivity about 10^{-2} S cm^{-1} due to the dynamically disordered network of hydrogen bonds. Compared with other low-temperature hydrate proton conductors, this compound has relatively high thermal (decomposition temperature 485 K) and electrochemical stability, as it does not contain water molecules in its structure. Its conductivity does not depend on atmospheric humidity. The proton transport properties of this solid acid is attractive for fuel cell applications.

Several challenges must be addressed before they reach technological relevance. The most important of these is the tendency of sulfate and selenate based materials to become reduced under hydrogen in the presence of typical anode catalysts such as Pt [123]. The by-product of this reduction reaction, H_2S (or H_2Se), is an exceptional poison for the electrocatalyst, and even if membrane degradation is only slight, the impact on fuel cell performance is devastating. They also suffer from poor mechanical properties and water solubility, as well as extreme ductility and volume expansion at raised temperatures; however, these compounds have not yet found practical applications, though an attempt was made to assemble an H_2/O_2 fuel cell with a solid $CsHSO_4$ acid electrolyte [124].

5.3. Hybrid inorganic organic composite membranes

A remarkable family of inorgano-organic polymers was developed by reacting polyethers such as PFSA, PVA, PEO, PPO, PTMO with alkoxysilanes (49, 50) and doping with inorganic proton conductor like HPA. The organic moiety adds flexibility, the inorganic moiety silica, adds stability and the active moiety (HPA), increases the conductivity of the system. The synthetic procedure consists of two main steps: (*i*) Organic polymer is end-capped with alkoxysilanes through isocyanato coupling and (*ii*) subsequent hydrolysis condensation of these precursors. The resulting jelly materials consist of nanosized silica domains interconnected by polymer chains. In the presence of water vapor, membranes made of these hybrids become proton conducting when doped with HPA, which probably is entrapped within the silica domains.

These hybrid membranes are isotropic, homogeneous and flexible. Material properties can be widely controlled. They possess excellent thermal stability.

Silica-immobilized phosphotungstic acid (PTA/SiO_2), or silicotungstic acid, (STA/SiO_2) [125], were used as fillers of recast Nafion [126], 3-glycidoxypropyltrimethoxysilane (GPTS) [127], and polybenzimidazole (PBI) [128-130].

Nafion recast membranes filled with PTA/SiO_2 (30/70 weight ratio) and STA/SiO_2 (45/65 weight ratio), so that the silica content was in all cases 3 wt%, were prepared by bulk mixing of a 5% Nafion solution with the powdered filler and then thermally treated at 433 K [126]. Tests in direct methanol fuel cells at 418 K showed that the PTA/SiO_2 membrane had better electrochemical characteristics at high current densities compared with membranes loaded with STA/SiO_2 or only 3 wt% SiO_2. Peaks of power density of 400 mW/cm^2 and 250 mW/cm^2 were reached by feeding the cell with oxygen and air.

Nafion/silicon oxide (SiO_2)/phosphotungstic acid (PWA) and Nafion/ silicon oxide composite membranes were studied for the H_2/O_2 fuel cells operated above 373 K. The incorporation of the SiO_2 and PWA into the Nafion membrane could increase the crystallinity of the Nafion recast membrane. It was found that the composite membrane showed a higher uptake of water compared with the Nafion recast membrane. The proton conductivity of the composite membranes appeared to be similar to that of the pristine Nafion membrane at high temperatures and at 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 0.4V, respectively) were obtained than that of the Nafion 115 membrane (95 mA/cm^2), under the operating condition of 383 K and at the humidified temperature of 373 K [131].

Nafion/silica/phosphotungstic acid (PWA) composite membranes were studied for low temperature (<373 K) direct methanol fuel cells (DMFCs). The composite membranes were prepared by sol–gel reaction of tetraethoxysilane (TEOS) within the nanophase of hydrated perfluorosulfonic acid membranes (Nafion 117) and the subsequent treatment in phosphotungstic acid (PWA) solution. The silica content in membranes decreased the methanol diffusion coefficient within appropriate silica content range. The proton conductivities (σ) of these composite membranes are higher than those of commercial Nafion 117. The data from single direct methanol fuel cell using these two membranes of commercial Nafion without treatment and Nafion/silica/PWA composite membranes with optimal silica content as polymer–electrolyte show that the cell with composite membrane has higher open circuit voltage (OCV = 0.75 V) and maximal power density of 70 mW/cm^2 than those of commercial Nafion without treatment (OCV = 0.68V, maximal power density of 62 mW/cm^2) at 353 K [132].

Hybrid organic–inorganic composites consisting of silicotungstic acid and poly(vinyl alcohol) were prepared by a sol–gel method. The silicotungstic acid present in the composite acts as acid catalyst to hydrolyze/condense the silica precursor that leads to isotropic composite. The conductivity is found to increase with increase in temperature Fig. 7. Conductivity measurements performed at higher temperatures, in the range from 80 to 100ºC, give almost stable values of (4.13–8.31) $\times 10^{-3}$ S cm^{-1} at 100 % RH. The conductivity and thermal stability of the composite membrane can be fine tuned by altering the individual components at the molecular levels. The activation energy for the proton migration in the composite film is reported to be 10 kJ/mol [133].

PPO thin films with PMA (PPO-PMA films) have been prepared by using the solvent mixture. PPO-PMA solutions were cast onto a glass plate. The composite membranes were prepared by casting Nafion mixture on porous PPO-PMA films. The composite membranes are tested as electrolytes in direct methanol fuel cells (DMFCs). The performance tests have shown that they have a good perspective in DMFCs. The methanol cross-over in the DMFC can be reduced by composite membranes containing PPO-PMA barrier films [134].

Novel fast proton-conducting GPTS–STA–SiO_2 and GPTS–STA–ZrP composites were successfully fabricated. The polymer matrix obtained through hydrolysis and condensation reaction of 3-glycidoxypropyltrimethoxysilane (GPTS) showed apparent proton conduction at high relative humidity with conductivity from 1.0 x 10^{-7} to 3.6 x 10^{-6} S cm^{-1}, although no proton donor was incorporated. The proton conductivities of the fabricated composites were high, and increased up to 1.9 x 10^{-2} S cm^{-1} by addition of 30 wt% silicotungstic acid (STA). By incorporating a-zirconium phosphate ZrP into the GPTS–STA

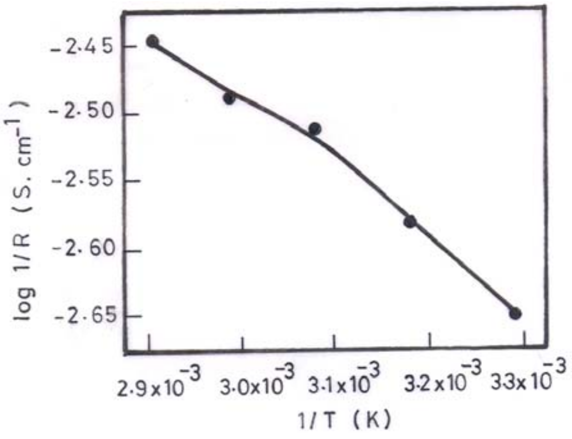


Figure 7. Conductivity as a function of inverse temperature for PVA–SiO_2–SiW [133].

polymer matrix, the composite showed increased conductivity at low temperature ~80ºC, indicating weak dependence on humidity by molecular water in ZrP. The high proton conductivity of the composites is due to the proton conducting path through the GPTS-derived 'pseudo-polyethylene oxide pseudo-PEO' networks, which also contains trapped solid acid silicotungstic acid as a proton donor [127].

PBI-PTA/SiO_2 membranes, containing from 40 to 68 wt% filler, were characterized by conductivity measurements as a function of temperature up to 423 K at fixed relative humidity and as a function of relative humidity at 373 K [128]. For a PTA/SiO_2 weight ratio of 30/70, the conductivity increases with the filler content reaching a maximum for 60 wt% PTA/SiO_2. The highest conductivity (1.2×10^{-3} S cm^{-1} at 433 K and 100% relative humidity) was observed for STA/SiO_2 weight ratio of 45/65. On the other hand, the conductivity of a membrane loaded with only 50 wt% STA was five orders of magnitude lower, thus indicating that hydrated silica provides the main pathway for proton conduction. It is interesting to observe that the conductivity of these heteropolyacid/SiO_2 membranes, although still too low for fuel cell applications, is only weakly dependent on relative humidity in the range 40–100%.

5.4. Proton transport mechanism

Proton transport in composite membranes is the result of a complex process dominated by the surface and chemical properties of both the polymer membranes and composite. There are three general approaches [135] to increase the proton transport through the use of nanocomposite membranes:

(i) Hygroscopic composites: In this case the introduced material (e.g. silica, titania and zirconia) is hydroscopic. This effectively increases the swelling of the membranes at lower relative humidities while at the same time increasing the resistance to fuel crossover by creating more resistance in the flow channels. This increases the proton transport through the water phase and reduces methanol permeability (e.g. Fig. 8a).

(ii) Conductive composites: Generally a second proton conducting species is introduced into the polymer to reduce the methanol and water permeability of the membranes. The aim is to constrict the pores in the polymer matrix and hence create greater resistance to molecular migration of the unwanted species. The introduced conductive species (e.g. α-ZrP) is assumed to make up for conduction losses due to the reduced water within the membrane (Fig 8b).

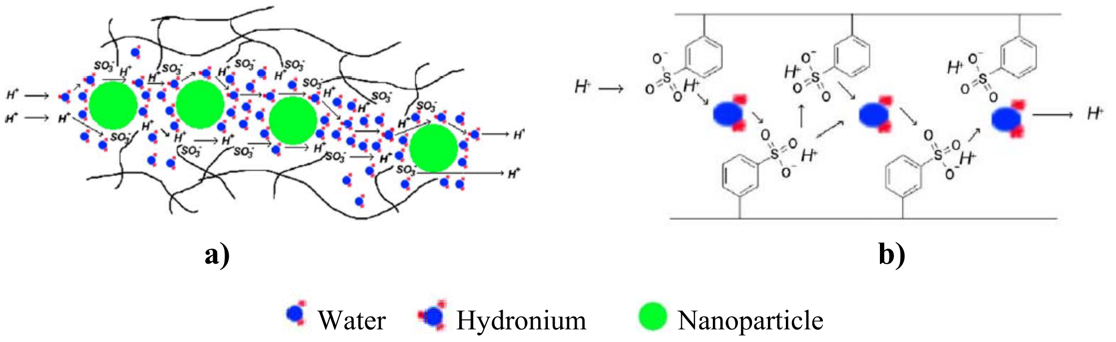


Figure 8. Proton transport in (a) hygroscopic composite membranes (b) surface functionalised solid acid membranes.

(iii) Water substituted composites: These composites consist of the polymer matrix to which an alternative proton transporter is added (e.g. hetropolyacids). The aim is to immobilise a highly conductive acid in the matrix so that the proton conductivity is independent of hydration and electro-osmotic drag is reduced. These membranes have had some success; however the substituted composite tends to leach from the membrane over time.

5.5. Perspectives

Ionomers of very-high-proton conductivity, such as perfluorinated polymers bearing -SO_3H groups, filled with silica, ZrP or heteropolyacid has a positive effect on fuel cell performance at temperatures higher than 363–373 K, even for relative humidity considerably lower than 100%. This effect cannot be simply connected to an increasing number of proton carriers or to specific proton acceptor properties of the inorganic particles, since silica particles have negligible proton conductivity, whereas -Si-O-Si- and -Si-OH groups are expected to be better proton acceptors than -O_3POH groups. In addition, the mechanical reinforcement of the membrane, and hence the reduction of the swelling properties, could also play an important role, especially in the temperature range 363–383 K, where high humidification conditions can be still obtained at acceptable pressures of the cell. Although many insoluble and stable inorganic particles dispersed in a variety of ionomeric matrices have been considered, the structure, crystallinity degree, shape and dimensions of the particles, as well as their distribution in the various domains of the hydrated ionomers, are not thoroughly investigated. The goal of preparing more economical membranes than Nafion for hydrogen fuel cells operating at temperatures lower than 373 K, the attention should be directed to low-cost ionomers filled with high contents of particles exhibiting high conductivity.

6. Acid-base polymer membranes

Acid–base complexes have been considered as a viable alternative for membranes that can maintain high conductivity at elevated temperatures without suffering from dehydration effects. In general, the acid–base complexes considered for fuel cell membranes involve incorporation of an acid component into an alkaline polymer base to promote proton conduction or incorporation of excess base in to an acidic polymer (sulfonated polymer with absorbed imidazole, benzimidazole or another appropriate proton acceptor).

6.1. Complexation with acids

Polymers bearing basic sites such as imine, amide, imide, ether or alcohol groups react with strong acids such as phosphoric acid or sulfuric acid. The basicity of polymers enables the establishment of hydrogen bonds with the acid. In other words, the basic polymers act as a solvent in which the acid undergoes to some extent dissociation. A number of basic polymers have been investigated for preparing acid-base electrolytes, such as PBI [136-144], PEO [145,146] PVA [147], polyacrylamide (PAAM) [145,147-150] and polyethylenimine (PEI) [151]. Recently Nylon [152] and poly(diallyldimethylammonium- dihydrogen phosphate, $PAMA^+$-$H_2PO_4^-$) [153]. Among these PBI doped with H_3PO_4 and H_2SO_4 are well investigated because of their unique proton conduction mechanism by self-ionization and self-dehydration [154] H_3PO_4 and H_2SO_4 exhibit effective proton conductivity even in an anhydrous (100%) form.

Polybenzimidazoles are synthesised from aromatic bis-*o*-diamines and dicarboxylates (acids, esters, amides), either in the molten state or in solution. The repeat unit, benzimidazole, has remarkable thermal properties [155]. Thus, it melts at 443 K and boils at >633 K. The thermal properties of polybenzimidazoles, which depend on the nature of the component tetraamine and dicarboxylic acids, have been largely reported in the early literature [156]. The commercially available polybenzimidazole is poly-[2,20-(*m*-phenylene)-5,50-bibenzimidazole], which is synthesised from diphenyl-*iso*-phthalate and tetraaminobiphenyl, and this will be referred to hereafter simply as “PBI”. It is characterised by excellent thermal and mechanical stability. Under conditions relevant to fuel cell use viz. oxidising and reducing environments at elevated temperature and in the presence of water, no weight gain/loss for PBI in either H_2/H_2O or O_2/H_2O at 473 K was observed [157], although its stability at 573 K in oxidizing conditions was not satisfactory. It was concluded that at 573 K, the imidazole ring is susceptible to hydrolysis, and that the products of this hydrolysis are more readily oxidisable.

Early reports of the proton conductivity of PBI are conflicting. Thus, whereas values in the range 2×10^{-4}– 8×10^{-4} S cm^{-1} at relative humidities between 0 and 100% were published [158], other authors [155,159,160] observed proton conductivity of magnitude some two to three orders of magnitude lower. These latter values are those generally accepted for non-modified PBI, and are clearly too low for any use of PBI membranes in fuel cell applications. Two principal routes have been developed to improve the proton conduction properties, and these repose upon the particular reactivity of PBI, which is twofold, and arises from the –N= and –NH-groups of the imidazole ring. Due to its basic character (pK_a value of -5.5) PBI complexes with inorganic and organic acids [141,161]. In addition however, the –NH-group is reactive; hydrogen can be abstracted, and functional groups then grafted on to the anionic PBI polymer backbone [162,163]. It should be mentioned also that unlike for other polyaromatic polymers, the direct sulfonation of PBI using sulfuric or sulfonic acid is not appropriate for the preparation of proton conducting polymers for fuel cell membranes, since it tends to lead to a polymer of low degree of sulfonation and increased brittleness [164].

Acid "doped" is the term generally used to describe the homogeneous polymer electrolyte system formed by dissolution of phosphoric [141,161,165-168] (sulfuric [165-168], hydrochloric [168], hydrobromic [165,166], nitric [168], perchloric [168]) acid in PBI. The basic character of the PBI polymer allows doping levels of up to ca. 50 wt.%. Two routes to the complexation of H_3PO_4 by PBI have been reported, the first in which PBI films are immersed in an acid solution of molarity M for time t, [136,142,168,161,165-169] and the second where films are cast directly from a solution of the polymer and phosphoric acid in a suitable solvent [141]. This second manner produces doped films directly, and so reduces the preparation time. Depending on the quantity of acid in the complex PBI/H_3PO_4, such systems have a conductivity between 5×10^{-3} and 2×10^{-2} S cm^{-1} at room temperature [141,167,168] and even 3.5×10^{-2} S cm^{-1} at 463 K [136,161]. The nature of the acid influences the conductivity of doped PBI, and after contact with acid of high concentration (11 mol dm^{-3}) the conductivity follows the order $H_2SO_4 > H_3PO_4 > HNO_3 > HClO_4 > HCl$ [168]. Importantly, for the functioning of a fuel cell at temperatures above 373 K, the electro-osmotic drag number of PBI/H_3PO_4 is almost zero [144]. A low level of gas hydration can therefore be used without drying out of the membrane, which may also assist in reducing reactant crossover, a point of particular importance in the context of the search for membranes suitable for direct methanol fuel cells (DMFC). Polybenzimidazoles are known for their vapour barrier properties. The permeability of PBI complexed by H_3PO_4 is considerably lower than that of Nafion®, in particular, with respect to methanol, reflecting the dense, non-porous character of PBI films [161]. A direct methanol fuel cell using such a phosphoric acid doped membrane and operating on a 50/50 methanol/water feed to the anode at 423 K would have a methanol crossover equivalent to less than 10 $mAcm^{-2}$, [161] which can be compared with crossover rates in excess of 100 $mAcm^{-2}$ when Nafion® is employed.

Highly doped (highly conducting) and slightly doped PBI membranes also differ in their textural properties. Qualitatively, in the higher conductivity regime, membranes are more swollen and flexible than unmodified PBI. Quantitatively, dynamic mechanical testing of a PBI film doped with 320 mol% H_3PO_4 shows that in the range of interest for a medium temperature fuel cell (373–473 K), the modulus is relatively constant and is extremely high (ca.109 Pa) [160]. For comparison, the storage modulus of Nafion® is roughly 1000 times lower (ca.106 Pa at 423 K) than the modulus of the PBI film.

PBI can be derivatised by replacing the imidazole hydrogen with alkyl or aryl substituents [159,162,163]. This method was developed as a route for further improving the chemical stability of PBI by introduction into the imidazole ring of groups less reactive than the imidazole hydrogen, and provides the opportunity of tuning the properties of the polymer by the choice of substituent. The synthesis [159,170] and electrochemical characterization [159] of benzylsulfonate N-substituted PBI was recently described.

The extent of sulfonation directly affects the water uptake and the conductivity. The conductivity of a sulfonated PBI membrane is closely related to the amount of water it contains, and this water uptake corresponds to 4, 7, 9 and 11 water molecules/PBI repeat unit with degrees of sulfonation of 0, 50, 65 and 75%, respectively [158]. This leads to a hydration number (i.e. number of water molecules associated with each sulfonic acid group) of ca. 7, lower by at least a factor 2 than in Nafion® or sulfonated polyetherketone membranes [171]. Fig. 9 shows the conductivity of benzylsulfonate-grafted PBI, pristine

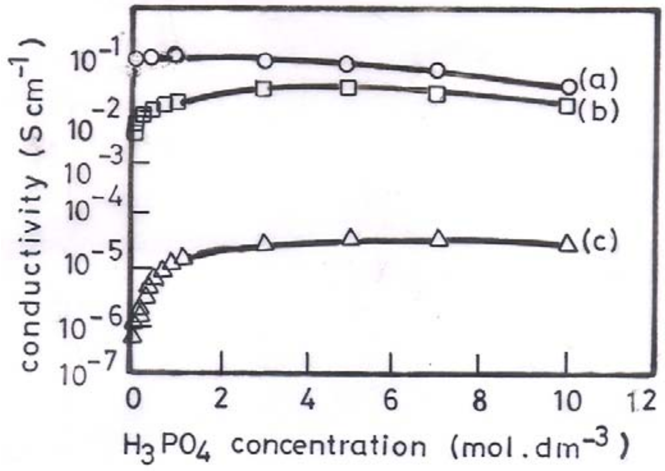


Figure 9. Conductivity at 25ºC of: (a) NafionTM-117; (b) benzylsulfonate-grafted PBI and (c) PBI as a function of the H_3PO_4 concentration (immersion time 8 h) [173].

PBI and Nafion®-117 derived from membrane resistance measurements at 298 K in aqueous phosphoric acid. The conductivity of the benzylsulfonate grafted PBI ranges from 3 x 10^{-3} to 2 x 10^{-2} S cm^{-1}, lower than that of Nafion® (1 x 10^{-1} to 3 x 10^{-2} S cm^{-1} under these conditions of measurement) and is significantly higher than that of PBI (ca. 10^{-5} S cm^{-1}), which is slightly doped by phosphoric acid under these conditions. Benzylsulfonate grafted PBI displays a high conductivity as long as the corresponding polymer films are maintained in an environment of high relative humidity [172]. To an extent which increases with the initial degree of sulfonation, they shrink and become brittle if left to dry and their initial flexibility cannot be recovered by simply soaking in water [159 and 173]. Partial loss of conductivity (to ca. 10^{-4} S cm^{-1}) accompanies this textural change.

6.2. Doping with organic and inorganic bases

Immersion of pristine PBI in aqueous inorganic bases has been reported to increase its conductivity by almost an order of magnitude [174]. However, the kinetics of this reaction is slow (immersion for 10 days), and the concentration of base is (e.g. 8M NaOH) high compared with the conditions required to complex PBI with acids. Uptake of base is faster by benzylsulfonate-grafted PBI [172]; it has been observed that after a short contact time (15–60 min) with an aqueous solution of an organic or inorganic base, shrunken benzylsulfonate grafted PBI membranes achieve satisfactory textural and proton transport properties. In each case, the conductivity is close to 10^{-2} S cm^{-1} at 298 K and 100% RH. In addition, if such base-treated membranes are exposed to a dry atmosphere, they will dry and wrinkle but recover their flexibility after a few seconds immersion in water. The conductivity values of sulfonated PBI after dehydration, and after immersion in basic solution are summarized in Table 5.

Table 5. Conductivity 25ºC, 100% relative humidity of benzylsulfonate grafted PBI after dehydration and immersion in basic aqueous solutions (1 M, 15 min, 298 K) [172].

Membrane	**Conductivity (S cm^{-1})**
PBI-S	4.2 x 10^{-4}
PBI-S/NH_4OH	1.5 x 10^{-2}
PBI-S/imidazole	7.9 x 10^{-3}
PBI-S/DABCO	1.2 x 10^{-2}
PBI-S/LiOH	1.2 x 10^{-2}
PBI-S/NaOH	1.2 x 10^{-2}
PBI-S/KOH	1.7 x 10^{-2}
PBI-S/CsOH	1.7 x 10^{-2}

Doped PBI membranes show considerable potential for fuel cells operating at moderate temperatures. It is also anticipated that in near future, membranes in this category may be made suitable alternatives to Nafion® for DMFC applications as they are known to have lower methanol permeability than Nafion®. Various polymers besides PBI have been evaluated for use in these types of membranes [175–178]. Bozkurt and Meyer have, for example, investigated poly(4-vinylimidazole)-H_3PO_4 complexes and found its stability through thermogravimetric studies to be about 423 K [175]. Lassegues et al. found complexes of amorphous polyamide with H_3PO_4 to have high conductivity but poor mechanical strength and chemical stability at temperatures above 563 K [176]. Hasiotis et al. have prepared blends of sulfonated polysulfones and PBI which were doped with H_3PO_4 [179,180]. These membranes showed improved mechanical properties and conductivities above 10^{-2} S cm^{-1} at 433 K at 80% RH, which was higher than for acid-doped PBI membranes under the same conditions.

6.3. Proton conductivity and electroosmotic drag

Another remarkable characteristic of acid doped PBI is its electro-osmotic drag co-efficient. For acid doped PBI, the electro-osmotic drag co-efficient was zero, while Nafion 117 showed an electro-osmotic drag co-efficient of 3.2. From the data on electroosmotic drag data and the dependence of ionic conductivity on extent of doping, Grotthus mechanism was suggested to be responsible for proton transport in doped PBI. As the doping increases, the distance between the clusters of acid sites decreases and the anion moieties support the proton hopping between imidazole sites. Data reported by Bouchet et al. also support a Grotthus mechanism [181]. Conductivity data of doped PBI at temperatures below the glass transition temperature, and the relatively high change in entropy (which could be due to the molecular rearrangements necessary for the Grotthus mechanism) show that such a mechanism is possible.

6.4. Fuel cell performance

Comparison of the performance at 473 K of a direct methanol fuel cell using acid complexed PBI prepared by doping of pre-formed membranes and by casting from a solution containing PBI and phosphoric acid has been made [182]. Membranes of the former type contain $5H_3PO_4$/PBI repeat unit and, of the latter type, $6H_3PO_4$/PBI. With 4mg cm^{-2} Pt–Ru alloy electrode as anode and 4mg cm^{-2} Pt black electrode as cathode, this DMFC produced power densities of 0.21 and 0.16Wcm^{-2}, respectively, at 500mAcm^{-2} (atmospheric pressure feed of methanol/water mixture in 2/1 mole ratio, and oxygen) [182]. Increased performance in the temperature range 423–473 K is attributed to lower methanol crossover due to the lower solubility of methanol in the membrane at higher temperatures, and to higher electrolyte conductivity.

Despite these advantages, PBI composites exhibit some disadvantages, like the long-term stability of doped PBI membranes is yet to be proven despite their excellent attributes for fuel cell applications [183,184]. The diffusion of unassociated H_3PO_4 on basic imidazole-*N* and the diffusion of methyl esters out of the PBI limit membrane performances; and the formation of phosphoric acid methyl esters cause the degradation of the composite membrane.

PBI–phosphoric acid has been studied for almost a decade for high temperature PEFC applications. Other PBI–acid systems are emerging in the literature for fuel-cell applications, however many aspects related to the development of PBI–acid systems for this application remain unclear: like the proton conduction mechanism at high temperatures with acid doping levels and relative humidity and comparison of these studies to those of the PBI–sulphuric acid system. More attention must be paid to the PBI–alkaline system because it opens the way to a new area of PBI modification and the development of solid polymer alkaline fuel cell (SPAFC).

Epilogue

The uses of membranes have increased in recent times due to various reasons especially from the points of view of energy conversion and also from the environmental concerns**.** Even though for each of the applications the required functionalities and characteristics are known to some degree of precision, designing and fabricating membranes of the required stability, functionality and also keeping the cost within reasonable affordable limits appear to be a un-surmountable proposition at this time due to various difficulties and limitations imposed with the synthetic strategies as well as the available methodologies. It appears one has to adopt some unconventional design strategies and also employ exotic synthetic strategies to formulate and design membranes of required and desirable quality. This challenge has been successfully faced by the scientific community and a number of alternate and viable technologies and methodologies have been proposed and experimented with. It is clear from this presentation that a successful formulation and fabrication of the required membrane is not far off, though one may visualize considerable barriers to be surmounted with.

The primary objective of this presentation is to bring out an analytical aspect of the state of art position of this technology so as to enable the practitioners to have an overall assessment of the situation in technology so that their march to the goal may be facilitated. If this presentation accomplishes this goal, the article would have served the purpose.

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