

# Solid polymer electrolyte membranes for fuel cell applications—a review

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## Abstract

Fuel cells represent a clean alternative to current technologies for utilizing hydrocarbon fuel resources. Polymer electrolyte membrane fuel cells (PEMFCs) have acquired due importance as they are best suited for applications where a quick start up is required such as in automobiles. The prime requirements of fuel cell membranes are high proton conductivity, low methanol/water permeability, good mechanical and thermal stability and moderate price. Membranes and the operating parameters together have a profound influence on performance of PEMFCs. Perfluorinated ionomers, hydrocarbon and aromatic polymers and acid–base complexes have been described in the review. The performance of this special class of polymers, considering their structure–property relationship and the current research involving their applicability in fuel cell systems are presented. Modifications made to Nafion® membranes, the conceptual design of substitutes for perfluorosulfonic acid materials and modifications made to aromatic membranes to render them suitable for this application have been summarized. Promising avenues for further research in this area have been identified.

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**Keywords:** PEM fuel cell; Proton conductivity; Ion exchange membranes; Membrane preparation and structure

## 1. Introduction

Throughout the world, the need of the hour is power generation with environmental protection. This has prompted research in various aspects of fuel cells. Savings in fossil fuels, due to high efficiency of energy conversion, low pollution level, low noise and low maintenance costs render fuel cells preferable over other energy conversion devices. Fig. 1 shows a comparison of fuel cell performance with other energy conversion systems. Although fuel cells are not a recent development, the use of polymeric membranes as electrolytes has received a tremendous impetus in the recent past. It is because of this development that fuel cells are the premier candidates as portable source of power for light duty vehicles and buildings and as replacement for rechargeable batteries [1]. In addition to the development of materials for the fuel cell stack, PEMFC systems development has seen quite

revolutionary advances. Modeling activities have enhanced both the efficiency as well as the reliability of the systems. Recently, some exciting modeling work has been published [2,3] that should find use in facilitating the design of advanced unit fuel cell components. For example, an impressive growth in worldwide patent activity indicates a significant growth in technological advancement. Fig. 2 illustrates the increase in patent applications for PEMFC-related inventions that has occurred in recent years.

The PEM fuel cell gained prominence after an ion-exchange resin was incorporated as an electrolyte for space application by General Electric (GE), in 1959. This enabled the PEMFC over a period to surpass the solar cells and other alternatives. Based upon its perceived simplicity of design and weight advantages, combined with optimum compatibility [4], PEMFC currently finds a wide range of applications. In this context, a membrane that complies with the basic requirements of fuel cells and is inexpensive at the same time has been the principal goal of research. Before a review of current polymer membranes applied to fuel cells, a brief overview of fuel cells is appropriate.

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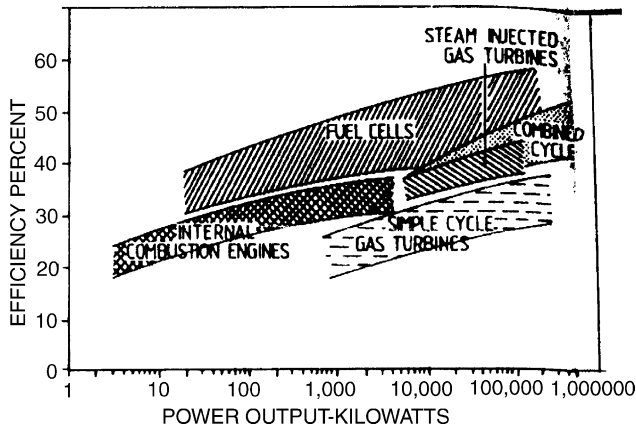


Fig. 1. Comparison of fuel cell performance with other energy conversion systems.

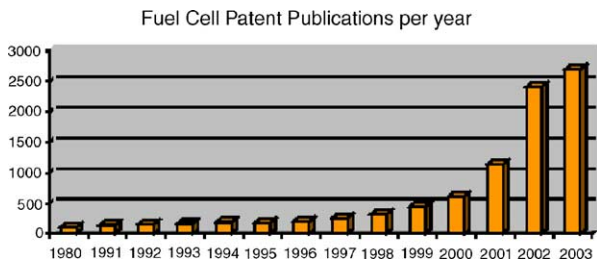


Fig. 2. Growth in research activity of PEM fuel cell represented as a plot of number of patents per year.

A schematic view of a polymer electrolyte membrane fuel cell is shown in Fig. 3. The H<sub>2</sub>/O<sub>2</sub> fuel cell, commonly referred to as polymer electrolyte fuel cell (PEFC), and the direct methanol fuel cell (DMFC) are the two types of fuel cells which use polymer electrolytes [5]. DMFCs have higher

energy density but exhibit shortcomings such as (a) slower oxidation kinetics than PEFC below 100 °C and (b) significant permeation of the fuel from the anode to the cathode resulting in a drop in efficiency of fuel utilization upto 50% [6].

The performance of PEM fuel cells is known to be influenced by many parameters including operating temperature, pressure and relative humidity of the gas streams etc. In order to improve fuel cell performance, it is essential to understand the effect of operating parameters on fuel cell performance. Fuel cell manufacturers and research institutes working in these areas have studied the effect of operating conditions on fuel cell performance but data, being proprietary in nature, is not available in the open literature [7–10]. Many simulation models have also been proposed to study PEM fuel cell performance [11–18].

Wang et al. [19] experimentally studied the effects of different operating parameters on the PEM fuel cell performance using pure hydrogen and air as fuel and oxidant, respectively. Experiments were conducted at different operating and humidification temperatures, operating pressures, and with different cathodes and anodes. Various combinations of these options were also evaluated. Wang et al. concluded that the performance of the PEM fuel cell improves with an increase in operating temperature and pressure when adequate humidification of gas stream is ensured. However, an inefficient performance was recorded, especially in the low current density region, when the operating temperature was higher than the gas stream humidification temperature.

Hydrogen permeation data and diffusion parameters at elevated temperatures are important for the selection and development of new materials for fuel cells operating at low temperature. A radiotracer method has been used to collect and analyze hydrogen permeation data across polymer mem-

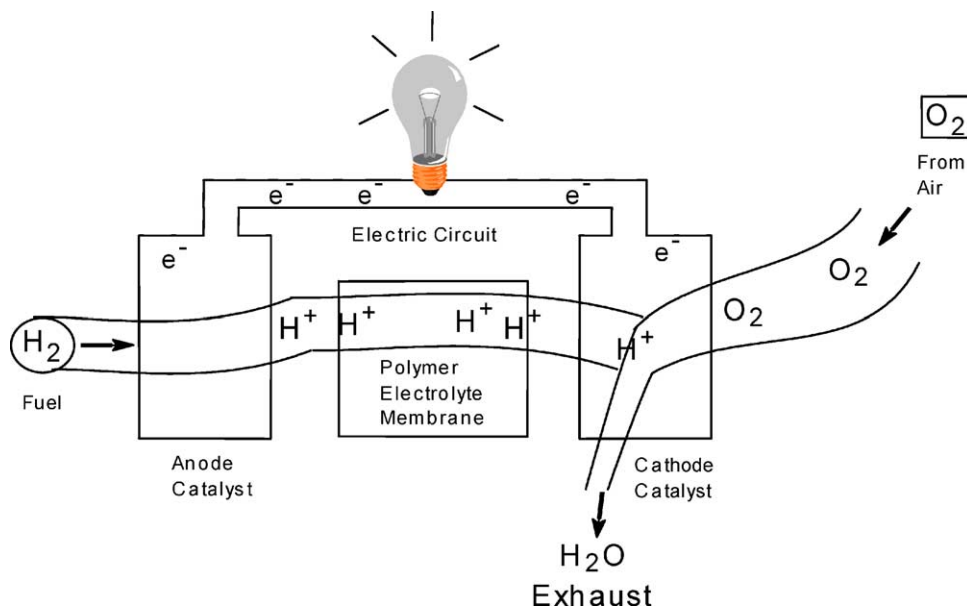


Fig. 3. Schematic view of a PEM fuel cell.

branes [20]. Stodilka et al. [21] used tritium as a radiotracer to determine the Arrhenius type of temperature dependence for permeation and diffusion of hydrogen in polymers. Hydrated tritium, HT, in an H<sub>2</sub>/HT gas stream was measured by ionization chamber tritium detector and a water trap. Permeation and diffusion coefficients and the respective activation energies were determined for Viton, Teflon, EPDM, Santoprene and Noryl using the time lag method. The measurements were consistent with theoretical investigations but indicated lower permeation and diffusion coefficients. This study provides a technique for selecting fuel cell materials for cell operating temperatures between 25 and 150 °C.

Previous work summarizing PEM fuel cells *design alternatives* is described by Larminie and Dicks and EG&G Services [22]. It includes general description of materials and fuel cell configurations, the advantages and disadvantages of each design vis-a-vis the stack performance related to thermodynamics, water management, operating temperatures and pressures, and fuel and oxidant composition. Gottesfeld and Zawodzinski [23] provided a more research-oriented electrochemistry based discussion of fuel cell design. Glipa and Hogarth [24] from Johnson Matthey Technology Center, UK, and Rikukawa and Sanui [25] from Sophia University, Japan, identified membrane materials applicable for PEM fuel cells. Analysis of some bipolar plate materials is presented by Borup and Vanderborgh [26]. Mehta [27a,b] reviewed and provided analysis of fabrication options for cell designs within the context of vehicle applications. They also presented manufacturing alternatives described in the literature for membrane electrode assemblies and bipolar plates. Kerres [28] provided a comprehensive review on the state-of-the-art of the membrane development for the PEM fuel cell applications. Stone and Morrison [29] have contributed a detailed review of the key events that culminated in the exponential growth of PEMFC in relation to the development of businesses dedicated to the commercialization of this technology. Jannasch [30] reviewed the developments of different types of high-temperature proton conducting polymer electrolyte membranes. Meier-Haack et al. [31] reviewed the recent progress in the development of alternative membrane materials to perfluorinated ionomer material for fuel cell applications focusing on DMFC. The review of Roziere and Jones [32] emphasizes the need for developing new membranes to overcome the barriers in rapid commercialization of fuel cell.

This review covers the basic categories of membranes that have been the focus of attention, viz. perfluorinated ionomer (PFI) or perfluorosulfonated compounds (PFSA), non-fluorinated hydrocarbons, sulfonated poly(arylenes), and acid–base complexes. It provides a concise update on the current status of PEM fuel cell technology along with an overview of the membranes used in fuel cells and the factors affecting their performance. Other relevant information in terms of fuel cell history, pertinent to the discussion, is also provided.

## 2. Background

The evolution of membranes for fuel cell applications started as early as 1959 by GE with the testing of phenolic membranes, prepared by polymerization of phenol–sulfonic acid with formaldehyde. These membranes had low mechanical strength and a short lifetime of 300–1000 h and showed a power density of 0.05–0.1 kW m<sup>-2</sup> [33]. During 1962–1965, GE attempted to improve the power density by developing partially sulfonated polystyrene sulfonic acid membranes (prepared by dissolving polystyrene sulfonic acid in ethanol-stabilized chloroform followed by sulfonation at room temperature). This membrane exhibited a better water uptake and an improved power density of 0.4–0.6 kW m<sup>-2</sup> that enabled its application in NASA's Gemini flights [34]. Although initial attempts were unfruitful, GE subsequently redesigned their PEM cell and the new model P3, despite malfunctions and poor performance on Gemini 5, served adequately for the subsequent Gemini flights. However, this membrane exhibited brittleness in the dry state. Another approach to improve the mechanical strength and the life of the membrane was again undertaken by GE in the late sixties by preparing cross-linked polystyrene-divinylbenzene sulfonic acid membrane/polymer in an inert matrix. The life of the membrane ranged from 1000 to 10,000 h and the power density attained was 0.75–0.8 kW m<sup>-2</sup> [35]. The main problem encountered with all the above mentioned types of membranes was that the proton conductivities were not sufficiently high to reach a power density even as low as 100 mW cm<sup>-2</sup> [36].

In 1970s, Du Pont developed a perfluorosulfonic acid called “Nafion<sup>®</sup>” that not only showed a two-fold increase in the specific conductivity of the membrane but also extended the lifetime by four orders of magnitude (10<sup>4</sup>–10<sup>5</sup> h). This soon became a standard for PEMFC and remains so till today. The Dow Chemical Company and Asahi Chemical Company synthesized advanced perfluorosulfonic acid membranes with shorter side chains and a higher ratio of SO<sub>3</sub>H to CF<sub>2</sub> groups [37]. Table 1 provides a comparison of some commercial cation-exchange membranes.

## 3. Fuel cell membrane materials

### 3.1. Desired properties

Membrane is the core component of the PEM fuel cell. To achieve high efficiency the membrane must possess the following desirable properties

- high proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity;
- adequate mechanical strength and stability;
- chemical and electrochemical stability under operating conditions;
- moisture control in stack;

Table 1  
Properties of commercial cation-exchange membranes

Membrane	Membrane type	IEC (mequiv./g)	Thickness (mm)	Gel water (%)	Conductivity (S/cm) at 30 °C and 100% RH
Asahi Chemical Industry Company Ltd., Chiyoda-ku, Tokyo, Japan					
K 101	Sulfonated polyarylene	1.4	0.24	24	0.0114
Asahi Glass Company Ltd., Chiyoda-ku, Tokyo, Japan					
CMV	Sulfonated polyarylene	2.4	0.15	25	0.0051
DMV	Sulfonated polyarylene	–	0.15	–	0.0071
Flemion	Perfluorinated	–	0.15	–	–
Ionac Chemical Company, Sybron Corporation, USA					
MC 3470	–	1.5	0.6	35	0.0075
MC 3142	–	1.1	0.8	–	0.0114
Ionics Inc., Watertown, MA 02172, USA					
61AZL386	–	2.3	0.5	46	0.0081
61AZL389	–	2.6	1.2	48	–
61CZL386	–	2.7	0.6	40	0.0067
Du Pont Company, Wilmington, DE 19898, USA					
N 117	Perfluorinated	0.9	0.2	16	0.0133
N 901	Perfluorinated	1.1	0.4	5	0.01053
Pall RAI Inc., Hauppauge, NY 11788, USA					
R-1010	Perfluorinated	1.2	0.1	20	0.0333

- extremely low fuel or oxygen by-pass to maximize coulombic efficiency;
- production costs compatible with intended application.

Although interest in synthesizing polymers for different applications has been observed for about a century, major developments in this field were made only in the recent past [38]. Advances in the synthesis and characterization of polymers eventually resulted in improvements in thermal and mechanical properties of the polymers. A *scientific* approach, based on (a) structure–property relationship prevailing in the polymers, (b) the application of thermodynamics, mass transfer kinetics and (c) surface science (that controls complex morphologies) must be considered in order to ensure satisfactory performance of the membrane [39]. However, the factors affecting the performance of these alternatives, viz., level of hydration and thickness of the membrane, play an important role in deciding their suitability for application in fuel cell.

### 3.1.1. Factors affecting performance of membranes

**3.1.1.1. Hydration.** The performance of a membrane is dependent on proton conductivity, which in turn depends on prevailing levels of hydration. Higher conductivity is supported by higher levels of hydration. However, for operations with wet membranes, there is a possibility of the cathode being flooded which slows down the oxidation reaction. This is in particular a problem with Nafion<sup>®</sup>, because of a phenomenon known as electro-osmotic drag that has been studied by Zadowzinski et al. [40]. The electro-osmotic drag coefficient [EODC], which is a quantitative measure of hydration, is defined as the number of water molecules transported per proton. Their studies indicate that for Nafion 117 (175 μm) equilibrated with water vapor the EODC is about 1, while for that immersed in water is about 2.5. Zadowzinski et al. also

showed that the drag is mainly a function of water content and is independent of the type of Nafion<sup>®</sup> membrane used.

**3.1.1.2. Thickness.** One of the ways to avoid water drag or water crossover is to reduce the membrane thickness thereby enabling an improvement in the fuel cell performance. Other advantages of reduced thickness include lower membrane resistance (and therefore an enhancement in membrane conductivity), lower cost and rapid hydration. However, there is a limit to the extent to which membrane thickness can be reduced because of difficulties with durability and fuel by-pass. An ideal way to balance this would be to spatially control the acidic regions or increase the charge density in the chemical microstructure of the proton exchange membrane to obtain highly conductive materials. Charge density can be enhanced by synthesizing the membranes in asymmetric or thin film composite form. For example, asymmetric films of partially sulfonated polystyrene or poly(phenylene oxide) can be cast using chloroform as solvent and methanol as non-solvent [41]. Spatial control of the acidic regions can be brought about by surface modification of the membranes. For example, Chitosan can be surface modified by soaking it in an aqueous bath of sulfuric acid of suitable concentration to obtain the desired number of acidic regions [42]. The above mentioned techniques viz., spatial control of the acidic regions and increasing the charge density in the polymer film not only reduces the membrane thickness but also enables a suitable enhancement in the proton conductivity. Fig. 4 shows the electron micrograph of a PEM prepared by Holdcraft [43], which illustrates the control of microstructure. Susai et al. concluded from their studies of PEFC optimization that a thinner membrane might promote back diffusion and produce a greater concentration gradient of water, on account of enhanced rate of dehydration at higher temperatures. They

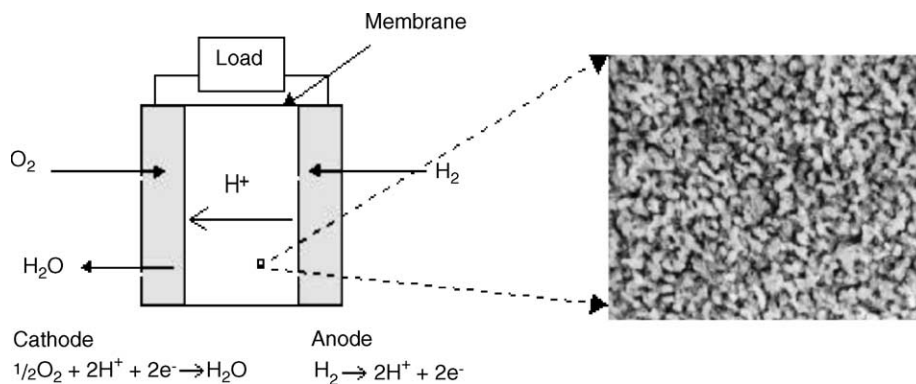


Fig. 4. A transmission electron micrograph of a proton exchange membrane (reproduced from ref. [43]).

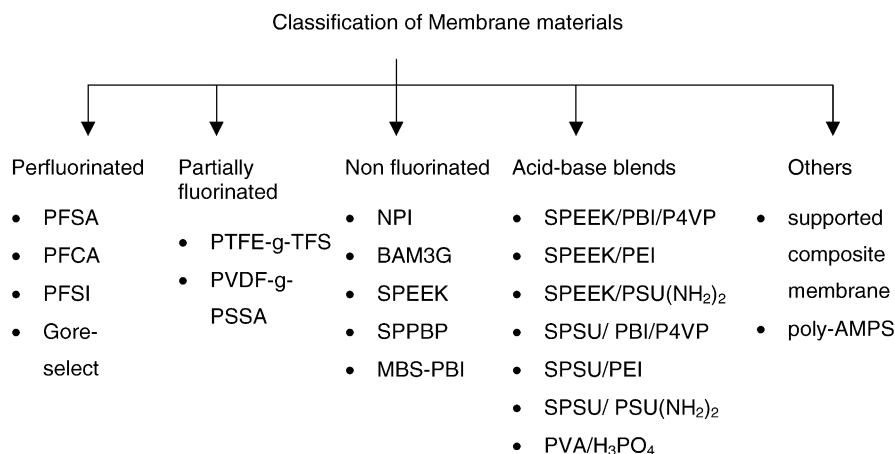


Fig. 5. Classification of membrane materials.

also reasoned that using a thinner membrane would allow the fuel cell to be run at lower humidity [44].

### 3.2. Types of membrane materials

Fig. 5 gives the classification of the membrane materials used for fuel cells. Membrane materials used till date for PEM fuel cells generally fall into different membrane systems, which can be classified as

- perfluorinated ionomers,
- partially fluorinated polymers,
- non-fluorinated membranes with aromatic backbone,
- non-fluorinated hydrocarbons,
- acid–base blends.

Table 2 [45,46] compares the structure, and physical properties of the different membrane systems to their in situ performance. From the table it can be noticed that the perfluorinated ionomers possess most of the desired properties and hence appear to be promising for fuel cell applications.

## 4. Perfluorinated membranes

The perfluorinated sulfonic acid membranes have been the subject of intense research. The key polymers used

currently in portable fuel cell applications have perfluorinated structures with attached sulfonic acid groups [47]. The perfluorinated polymer used most extensively and produced by DuPont goes by the trade name of Nafion<sup>®</sup>. Similar polymers are Flemion<sup>®</sup> produced by Asahi Glass and Aciplex-S<sup>®</sup> produced by Asahi Chemical. Among the three major types, the DuPont product is considered to be superior because of its high proton conductivity, good chemical stability and mechanical strength [48]. Its structure is shown in Fig. 6.

Two research areas currently of interest on Nafion<sup>®</sup> are the transport phenomena within the membrane and modifications made to the membrane to increase its performance as well as water retention capacity. Proton transport in Nafion<sup>®</sup> in the presence of variations in operating parameters such as temperature, membrane thickness, and water content have been analyzed.

### 4.1. Transport phenomena

Level of hydration is a critical parameter in Nafion<sup>®</sup> membrane that has to be maintained in order to retain its performance at temperatures above 100 °C (Section 2). In the presence of water, protons as well as the sulfonic acid groups

Table 2  
Structure–property relationships and in situ performance of polymers dealt in this study

Category	Structure	Physical properties	In situ performance
Perfluorinated membranes (pf)	<ul style="list-style-type: none"> <li>Fluorinated backbone like PTFE</li> <li>Fluorocarbon side chain</li> <li>Ionic clusters consisting of sulfonic acid ions attached to the side chains</li> </ul>	<ul style="list-style-type: none"> <li>Membranes are strong and stable in both oxidative and reductive environments</li> </ul>	<ul style="list-style-type: none"> <li>Membrane is durable upto 60,000 h [45]</li> <li>Proton conductivities in well humidified membranes are 0.2 S/cm at PEMFC operating temperatures</li> <li>Cell resistance of 0.05 <math>\Omega</math> cm<sup>2</sup> for 100 <math>\mu</math>m thick membrane with voltage loss of only 50 mV at 1 A/cm<sup>2</sup> is achievable</li> </ul>
Partially fluorinated membrane	<ul style="list-style-type: none"> <li>Fluorocarbon base</li> <li>Hydrocarbon or aromatic side chain grafted onto the backbone, which can be modified</li> </ul>	<ul style="list-style-type: none"> <li>Membranes are relatively strong in comparison to pf, but degrade fast</li> </ul>	<ul style="list-style-type: none"> <li>Less durable than perfluorinated ones</li> <li>Low performance</li> <li>On suitable modification, yield membranes with comparable proton conductivities</li> </ul>
Non-fluorinated hydrocarbon membranes	<ul style="list-style-type: none"> <li>Hydrocarbon base, typically modified with polar groups</li> </ul>	<ul style="list-style-type: none"> <li>Membranes possess good mechanical strength</li> <li>Poor chemical and thermal stability</li> </ul>	<ul style="list-style-type: none"> <li>Poor conductors of protons</li> <li>Exhibit low durability on account of swelling obtained by incorporation of polar groups into the polymer matrix</li> </ul>
Non-fluorinated aromatic membranes	<ul style="list-style-type: none"> <li>Aromatic base, typically modified with polar/sulfonic acid groups</li> </ul>	<ul style="list-style-type: none"> <li>Good mechanical strength</li> <li>Chemically and thermally stable even at elevated temperatures</li> </ul>	<ul style="list-style-type: none"> <li>Good water absorption</li> <li>Relatively high proton conductivity is attainable</li> <li>Conductance of SPPBP at 65 mol% of sulfonation is 10<sup>-2</sup> S/cm that is retained at temperatures above 100 °C [46]</li> </ul>
Acid–base blend membranes	<ul style="list-style-type: none"> <li>Incorporation of acid component, into an alkaline polymer base</li> </ul>	<ul style="list-style-type: none"> <li>Stable in oxidizing, reducing and acidic environments</li> <li>High thermal stability</li> </ul>	<ul style="list-style-type: none"> <li>Good dimensional stability</li> <li>Exhibit proton conductivity comparable to Nafion®</li> <li>Durability of the membranes is still to be proven</li> </ul>

are in the solvated form, and this greatly facilitates the “hopping mechanism of protons”.

To understand the transport of water in perfluorosulfonic acid membranes, quantitative and qualitative modeling studies have been conducted for supporting the optimization of not only the composition of the membrane but operating conditions, thereby yielding higher efficiencies and power den-

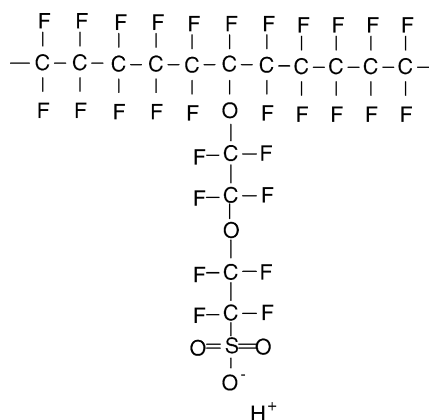


Fig. 6. Chemical structure of Nafion®.

sities. In terms of microscopic models, there have been many models based on statistical mechanics, molecular dynamics and macroscopic phenomena applied to the microscopic structure of the membrane. These models provide a fundamental understanding of processes like diffusion and conduction in the membrane on a microscopic scale including the effect of small perturbations, such as non-homogeneity of pores and electric fields on transport as well as the introduction of small-scale structural effects. The basis for all these models is the description of the microscopic structure of the polymer that was proposed in the early 1980s by Gierke and Hsu [49]. In their work, the authors correlated the experimental data through geometric and phenomenological relationships for the swelling of the polymer due to the uptake of water and its effect on the diffusion coefficient of water in the membrane pores. The correlation evolved by analyzing the data taken under different operating conditions led to the formulation of a widely accepted description of the polymeric membrane in terms of an inverted micellar structure in which the ion-exchange sites are separated from the fluorocarbon backbone thus forming spherical clusters (pores), which are connected by short narrow channels. The model was hence termed as ‘cluster network’ model. When the membrane is

dry, an average cluster has a radius of about 1.8 nm and it contains about 26  $\text{SO}_3^-$  groups distributed on the inner pore surface. In the swollen state the diameter increases to about 4 nm and the number of fixed  $\text{SO}_3^-$  groups goes upto  $\sim 70$ . Under these conditions, each pore is filled with about 1000 water molecules and the connecting channels have a diameter and a length of about 1 nm. Gierke and Hsu also proposed the use of percolation theory for the correlation of electrical conductivity with the water content of the membrane. According to this theory, there is a critical amount of water available in the membrane, below which ion transport is extremely difficult due to the absence of extended pathways. Above and near the threshold, the conductivity,  $\sigma$  follows the law:

$$\sigma = \sigma_0(c - c_0)^n$$

where  $c$  is the volume fraction of the aqueous phase,  $c_0$  the percolation threshold for the water content in the membrane,  $n$  a universal constant which depends on the dimensions of the system (usually about 1.5 in 3-D systems) and  $\sigma_0$  a pre-factor related to the molecular interactions that can only be computed from specific microscopic models. A comparison between experimental results and percolation theory showed an extremely good agreement. After the seminal work by Gierke and Hsu, other investigators have focused their attention on modeling of the microstructure and of the percolative features of ionic conductivity in perfluorosulfonic acid membranes. Interesting results on the modeling of microstructure have been reported by Okada et al. [50], who, by interpolation of experimental data, demonstrated that around 50% of the water molecules in the membrane were associated with the  $\text{SO}_3^-$  sites (primary hydration layer) or the protons, and the remaining 50% are “semi-free” in the pores (secondary, tertiary, etc., hydration layers).

Recent studies propose an interpretation of the percolation properties of proton conductivity as a function of water content using a “random network model” [51], which is a modification of the “cluster network model”. This model includes an intermediate region wherein the side chains ending with pendant sulfonic acid groups, that are ionically bonded to the perfluorinated backbone, tend to cluster within the overall structure of the material resulting in the formation of hydrated regions. Unlike the “cluster network model”, the hydrated regions in this model are distributed randomly in the polymer matrix, which facilitates quicker transport of protons upon the rotation of these side chains. In this case although the hydrated regions drift apart, the traverse motion of protons through the membrane is possible. A schematic of the cluster network and random network models is depicted in Fig. 7. Haubold et al. verified through small angle X-ray scattering experiments (SAXS) that the “random network model” could be applied to Nafion® [52]. James et al. deployed the atomic force microscopy (AFM) technique and found the “random network model” to be generally acceptable, especially in the region of 9–34% relative humidity. This study was carried out on the commonly available Nafion 117 [53].

In addition to proton transport, considerable interest has been shown by investigators to the transport of other species in Nafion® membranes. Transport of ionic species through Nafion® was investigated by Gardner and Anantaraman [54]. It was noticed that the conductance of Nafion® is anisotropic and the tangential component of conductivity of Nafion 117 membrane was  $8.56 \times 10^{-2}$  S/cm. at 100% relative humidity whereas the normal component depended linearly on pressure. This has important consequences for Nafion® use in that this phenomenon can lead to energy losses in the tangential direction because of lower resistance. Gardner and Anantaraman also suggested that the anisotropy could be due to the clustering of ionic species near the interface away from the hydrophobic phase or could be a result of orientation of polymer chains during extrusion.

#### 4.2. Modifications made to Nafion®

Several efforts have been made to improve performance of Nafion® and to ascertain water retention at higher temperatures. The influence of addition of silica to Nafion®, as studied by Antonucci et al. [6], was to improve the retention of water in the membrane and to enable the operation of the fuel cell above 130 °C. Such a membrane could be used in a DMFC at 145 °C with power density of 240 mW/cm<sup>2</sup>. A similar method for retaining water in Nafion® at higher temperatures by incorporating silica as well as titanium dioxide into a Nafion® composite to enable its use in DMFC was studied by Baradie et al. [55]. This membrane exhibited a significant improvement in proton conductivity but did not retard methanol crossover.

Wasmus et al. [56] sought to improve the performance of a DMFC by equilibrating Nafion 117 membrane with phosphoric acid. An improvement in the reaction kinetics accompanied by high conductivity up to 200 °C and lower methanol crossover were observed. A reduction in methanol crossover by coating a thin layer of plasma polymerized tetrafluoroethylene (with vinyl phosphoric acid) on Nafion® membrane was attempted by Mex and Muller [57]. Finsterwalder and Hambitzer investigated a similar method of depositing a PTFE source with chlorosulfonic acid on Nafion® in order to obtain a low methanol crossover [58]. A significant reduction in methanol crossover at the cost of a drop in conductivity was achieved.

A significant improvement in the conductivity of Nafion®, at elevated temperatures, by incorporating perfluorinated ionomers in Nafion® matrix and by doping it with heteropolyacids such as phosphotungstic acid, phosphomolybdic acid, phosphotinic acid in Nafion® was targeted and achieved by Bahar et al. [59]. A similar attempt to attain improved ionic conductivity and high power density with the incorporation of silicotungstic acid (SA) and thiophene (TH) in Nafion 117 membrane was made by Tazi and Savadogo [60]. Water uptake in the Nafion® incorporated with SA was 60% and with both SA and TH it was 40% compared to the normal value of 27% for Nafion 117. Thus a substan-

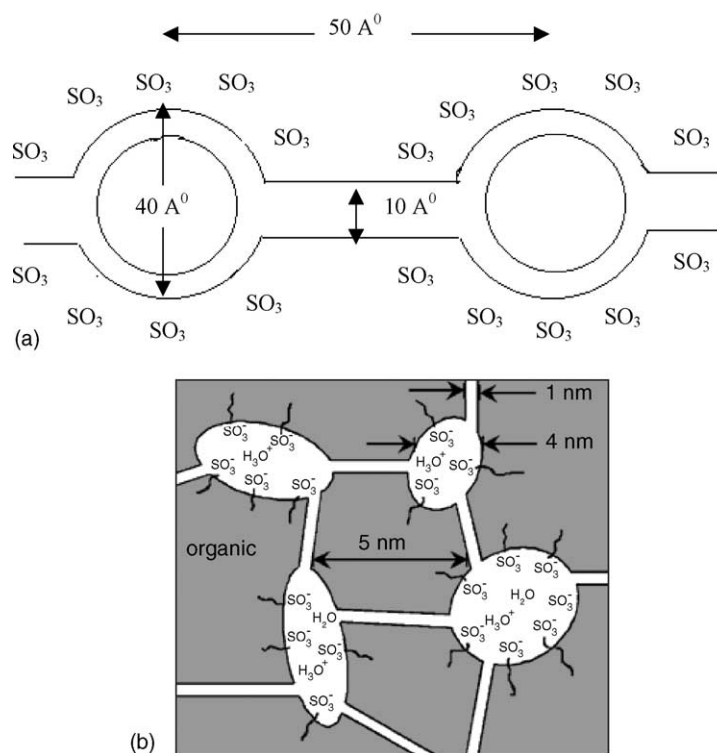


Fig. 7. (a) Transport phenomena of species in Nafion® membranes; (b) schematic view of modified cluster network model.

tial improvement in ionic conductivity was observed. Nafion 117 combined with TH showed highest current density with a maximum of 810 mA/cm<sup>2</sup> at 600 mV compared with a value of 640 mA/cm<sup>2</sup> for Nafion 117.

#### 4.3. Limitations of Nafion® membrane

From the preceding discussion, it is clear that Nafion® and related polymers are still being intensely examined in view of the complex cell requirements of high proton conductivity and outstanding chemical stability combined with longevity of 60,000 h at 80 °C. The major disadvantages of these PFSA materials are

- the high cost of membrane amounting to US\$ 700 per square meter [61],
- lack of safety during its manufacture and use [62],
- requirement of supporting equipment [63],
- temperature related limitations [25].

Safety concerns arise from evolution of toxic intermediates and corrosive gases liberated at temperatures above 150 °C. Decomposition products could be a concern during the manufacturing process or vehicle accidents and could limit fuel cell recycling options.

Supporting equipment requirements for uses with PFSA membranes are extensive as described by Gilpa and Hogarth [24] and Crawford [64]. Among the equipment needed, the hydration system adds considerable cost and complexity to the vehicle power train.

Degradation of PFSA membrane properties at elevated temperatures is another serious drawback. Conductivity at 80 °C is reduced by more than 10 folds relative to that at 60 °C [25]. Also, the phenomena related to membrane dehydration, reduction of ionic conductivity, decreased affinity for water, loss of mechanical strength due to softening of polymer backbone and increased parasitic losses through high fuel permeation are observed at temperatures above 80 °C.

With regard to the application in direct methanol fuel cells (DMFC), Nafion® exhibits a high methanol permeability greater 80,000 Barrers at 80 °C, which drastically reduces the DMFC performance and renders it unsuitable for DMFCs [65]. Efforts are directed to eliminate the disadvantages such as crossover problems and loss of hydration above 100 °C.

Despite its shortcomings, Nafion® is still the polymer of choice for most PEFC and DMFC applications. However, it is likely that Nafion® will be replaced by an alternative membrane in the future [66]. In order to overcome few of the disadvantages of the PFSA membranes enumerated above, the authors are also carrying out research work to identify promising alternatives [67,68]. Rikukawa and Sanui [25] suggest that in order to produce materials that are less expensive than Nafion, some sacrifice in material lifetime and mechanical properties may be acceptable, provided the cost factors are commercially realistic. Hence the use of hydrocarbon polymers, even though they had been previously abandoned due to low thermal and chemical stability, has attracted renewed interest.



Table 3

Design information of membranes considered as alternatives to PFS (reproduced from ref. [27b])

S. no.	Membrane type (category)	Design methodology
1	Gore-Select™ membrane (f)	Ultra-thin integral composite consisting of a base material preferably made of expanded PTFE that supports an ion exchange material such as perfluorinated sulfonic acid resin, perfluorinated carboxylic acid resin, PVA, divinyl benzene (DVB), etc. A surfactant is usually employed to ensure impregnation [59]
2	Perfluorocarboxylic acid (f)	Copolymer of tetrafluoroethylene (TFE) and perfluorovinyl ether (PFVE). The molar ratio of PFVE to TFE gives a measure of ion exchange capacity [71]
3	Bis(perfluoroalkylsulfonyl) Imide (f)	Copolymerization of sodium 3,6-dioxo-4-trifluoro methyl perfluorooctyl trifluoromethyl with TFE [72]
4	$\alpha,\beta,\beta$ -Trifluorostyrene grafted membrane (pf)	Grafting of $\alpha,\beta,\beta$ -trifluorostyrene and PTFE/ethylene copolymers [23]
5	Styrene grafted and sulfonated poly(vinylidene fluoride) membranes [PVDF-G-PSSA] (pf)	Pre-irradiation grafting of styrene onto a matrix of PVDF after electron beam irradiation. The proton conductivity can be increased by crosslinking with DVB [73]
6	BAM3G membrane (Ballard advance material of third generation membrane) (nf)	Polymerization of $\alpha,\beta,\beta$ -trifluorostyrene, includes monomers selected from a group of substituted $\alpha,\beta,\beta$ -trifluorostyrene [74]
7	Membrane of base-doped with S-polybenzimidazoles (PBI) (nf composites)	Introduction of organic and inorganic bronsted bases to sulfonated PBI [75]
8	Crosslinked/non-crosslinked (SPEEK) (nf)	Direct sulfonation of PEEK in conc. sulfuric acid medium yields high proton conductivity along with thermal stability [76]
9	Imidazole doped sulfonated polyetherketone (SPEK) (nf)	Complexation with imidazoles to obtain high proton conductivities [77]
10 & 11	Methylbenzenesulfonated PBI/methylbenzenesulfonate poly( <i>p</i> -phenylene terephthal amide) membranes (nf)	These alkylsulfonated aromatic polymer electrolyte posses very good thermal stability and proton conductivity when compared to PFSA membranes, even above 80 °C [25]
12	Sulfonated naphthalenic polyimide membrane (nf)	Based on sulfonated aromatic diamines and dihydrides. Its performance is similar to PFSA [78]
13	Sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP) (nf)	Derived from poly( <i>p</i> -phenylene) and structurally similar to PEEK. Direct sulfonation results in a proton conductive polymer [79]
14	Supported composite membrane (other)	Made of ion conducting polymer and poly- <i>p</i> -phenylene benzobisoxazole (PBO) substrate [80]
15	Poly(2-acrylamido-2-methylpropanesulfonic acid) (other)	Made from polymerization of AMPS monomer. AMPS monomer is made from acrylonitrile, isobutylene and sulfuric acid [81]

f, Fluorinated; nf, non-fluorinated; pf, partially fluorinated.

## 5. Hydrocarbon membranes

Hydrocarbon membranes provide some definite advantages over PFSA membranes. They are less expensive, commercially available and their structure permits the introduction of polar sites as pendant groups in order to increase the water uptake. In association with Rikukawa and Sanui, Gilpa and Hogarth identified 60 alternatives to PFSA membranes. Among these 15 membranes showed potential for replacing Nafion® membranes [69,70]. Table 3 summarizes information on synthesis of these 15 candidate materials [71–81]. The structures of prominent ones under this category are given in Figs. 8 and 9.

Pivovar et al. studied the applicability of pervaporation membranes in DMFC [82]. Poly(vinyl alcohol) (PVA) mem-

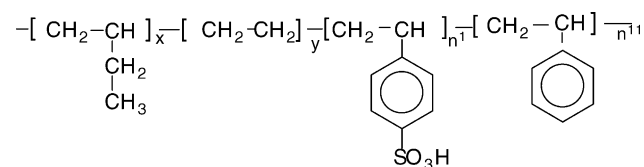


Fig. 8. Structure of poly(butadiene styrene) block copolymer.

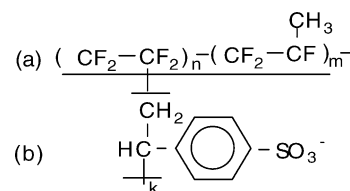


Fig. 9. Structure of grafted membranes: (a) FEP main; (b) sulfonated polystyrene side chain.

branes are known to be good methanol barriers. Based on this observation, a method of crosslinking PVA was suggested so that the extent of swelling in water could be controlled. It was also felt that the high water permeability should signal high proton conductivity atleast when the membranes are equilibrated with phosphoric acid.

## 6. Aromatic polymers

In order to enhance stability at elevated temperatures, aromatic hydrocarbons can be (a) incorporated directly into the backbone of a hydrocarbon polymer or (b) polymers modified with bulky groups in the backbone to render them

Table 4  
Modification of aromatic polymers

S. no.	Membrane type	Modification information	Ref.
1	Sulfonated polystyrene	Sulfonating polystyrene using acetyl sulfate as sulfonating agent. On increasing sulfonation, the ionic conductivity were comparable to Nafion <sup>®</sup> ( $10^{-3}$ to $10^{-2}$ S/cm). However, discontinuity in the properties at 15% sulfonation was noted	Carretta et al. [86]
2	Hydrogenated poly(butadiene-styrene) (HPBS)	Synthesized by heterogeneous sulfonation of poly(butadiene-styrene). On blending with polypropylene an enhancement in both the thermal properties and proton conductivity resulted	Bashir et al. [87]
3	Styrenic system of styrene divinyl benzene (SDVB)	Grafting SDVB to poly(fluoroethylene-co-hexafluoropropylene) (FEP), followed by sulfonation thereby obtaining membranes very similar to PFSA	Buchi et al. [88]
4	Polystyrene graft polymer	Crosslinking styrene/acrylonitrile ore obtained from <i>N</i> -vinylpyrrolidone/2-acrylamide-2-methyl-1-propane sulfonic acid graft polymer using divinylbenzene in order to obtain better stability in an oxidative environment	Becker and Schmidt-Naake [89]
5	Sulfonated polysulfone	Synthesized using sulfur trioxide-triethyl phosphate complex as the sulfonating agent. Relatively high IEC and good mechanical properties were attained	Noshay and Robenson [90]
6	Sulfonated poly ethersulfone (SPES)	SPES was synthesized and covalently crosslinked using substituted diamine-sulfone to provide additional mechanical strength and high proton conductivity for operations above 100 °C	Kice and Puls [91]
7	Sulfonated polyaryls	Polyetherketones were modified by blending with polymers containing immobilized heterocycles such as imidazole, pyrazole or benzimidazole as proton solvating species for obtaining high proton conductivity. The water cross-over drastically reduced while maintaining high proton conductivity	Kreuer [92]
8	Impregnating fleeces on polytetrafluoro ethylene (PTFE) matrix	Impregnating polysulfone, microglass fibre as well as a composite matrix constituting of both the fleeces on a PTFE matrix. Unlike the two impregnated fleeces, the composite membranes did not exhibit a comparable or lower resistance than Nafion 117	Stefan Haufe and Ulrich Stimming [93]
9	Sulfonated polyetherether ketone(SPEEK)and sulfonated poly(4-phenoxy benzoyl-1,4-phenylene)	Sulfonating PEEK and PPBP using concentrated sulfuric acid. Thermal stability upto atleast 200 °C was obtained and a conductance of about $10^{-2}$ S/cm at 65 mol% Sulfonation in case of SPPBP observed while SPEEK showed conductance two orders of magnitude lower for the same mol% of sulfonation	Kobayashi et al. [94]
10	Sulfonated poly [bis(3-methyl phenoxy) Phoszene]	Sulfonating the base polymer with sulfur trioxide followed by crosslinking, yielding higher proton conductivity, lower water and methanol diffusion co-efficient besides excellent chemical and thermo mechanical stability when compared to Nafion <sup>®</sup>	Guo et al. [95]
11	Sulfonated polyimide (PI)	Sulfonating PI using sulfur trioxide to obtain properties comparable to Nafion 117	Vallejo et al. [96]
12	Poly(arylene)	Synthesis of sulfonated naphthalene type polyimide to obtain high proton conductivity and low water/methanol diffusion coefficients unlike PFSA	Gebel et al. [97]
13	Sulfonimide compound	Crosslinking sulfonimide synthesized using a macromolecular substitution approach to produce phosphazene bearing pendant sulfonimide groups to obtain high proton conductivities	Hofman et al. [98]
14	Poly[aryloxyphosphazene] polymers	Treatment of the aryloxyphosphazenes bearing bromo-phenoxy side groups with <i>t</i> -butyllithium followed by diphenylchlorophosphonate followed by conversion to phenyl phosphonic acid groups	Allcock et al. [99]

suitable for conduction of protons. Polyarylenes are high temperature rigid polymers with  $T_g > 200$  °C owing to the presence of inflexible and bulky aromatic groups [83]. The aromatic rings offer the possibility of electrophilic as well as nucleophilic substitution. Polyethersulfones (PESF), polyether ketones (PEK) with varying number of ether and ketone functionalities (such as PEEK, PEKK, PEKEKK, etc.), poly(arylene ethers), polyesters and polyimides (PI) are

some of the relevant examples of main chain polyarylenes [84].

Studies reveal that polyesters must be avoided, as the ester group imparts instability in aqueous acids while polyaromatics are often preferred for fuel cell application due to their thermal stability. The specialty polymers on suitable modification are not only thermally stable but exhibit stability in oxidizing, reducing and acidic environments

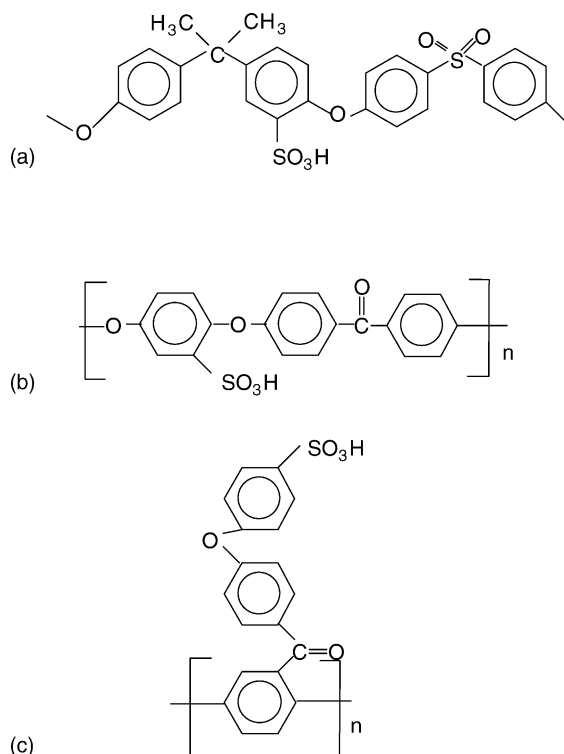


Fig. 10. Structures of (a) SPSU, (b) SPEEK and (c) SPPBP.

[85]. Table 4 summarizes the efforts made in this direction and gives design information of membranes considered as alternatives to PFSA [86–99]. Several research groups are working with different sulfonated polymers containing diarylsulfone units [100–111]. Direct sulfonated polyimides have also been extensively investigated [112–115]. Asensio et al. have investigated sulfonated polybenzimidazoles and have found it to exhibit superior performance to Nafion at higher temperatures [116,117]. Poly(aryloxyphosphazene)s functionalized with phenyl phosphonic acid units and sulfonimide units [118] have found application as candidate materials for fuel cells. Blending and radiation crosslinking of polyphosphazenes have also been investigated as means to reduce water swelling and methanol permeation of these ionomers [119]. Schuster et al. showed that imidazole-terminated ethylene oxide oligomers can reach conductivities of up to  $10^{-5}$  S cm<sup>-1</sup> at 120 °C [120]. The structures of prominent polymers under this category are presented in Fig. 10.

## 7. Acid–base complexes

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.

### PBI/H<sub>3</sub>PO<sub>4</sub>

The poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole)/phosphoric acid (PBI/H<sub>3</sub>PO<sub>4</sub>) complex is both intriguing and promising at the same time. It has shown a great deal of potential for medium temperature fuel cell applications and hence many attempts were made to understand and optimize this particular system. Extensive studies have been conducted at Case Western Reserve University, on PBI complexes. The structure of the reactants and the PBI product are shown in Fig. 11 [122]. Qinfeng et al. have characterized the phosphoric acid doped PBI [122] with the doping level defined as the molar percentage of acid per repeat unit of the polymer. Since it is an acid–base complex, the conductivity of doped PBI does not depend on humidity in contrast to Nafion<sup>®</sup>. However, such complexes are sensitive to the doping level and temperature. At 450% doping and a temperature of 165 °C, the conductivity of PBI membrane was about  $4.6 \times 10^{-2}$  S/cm. It was also observed that at very high levels of doping (around 1600%), the conductivity could reach 0.13 S/cm. A fuel cell was operated with a doped PBI/H<sub>3</sub>PO<sub>4</sub> membrane at 190 °C and atmospheric pressure yielding a power density of 0.55 W/cm<sup>2</sup> and a current density of 1.2 A/cm<sup>2</sup> [121]. At such elevated temperatures, the poison tolerance of the electrode catalysts is significantly improved compared with that at lower temperatures.

Another remarkable characteristic of acid doped PBI, as reported by Qingfeng et al. is its electro-osmotic drag coefficient (EODC). For acid doped PBI, the EODC was zero, while Nafion 117 showed an EODC of 3.2. From the electro-osmotic 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 supports a Grotthus mechanism [123]. 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.

A PEFC operating with a 500% doped PBI produced a maximum power density of 25 W/cm<sup>2</sup> with a current density of 700 mA/cm<sup>2</sup> at 150 °C. The membrane reportedly had low gas permeability, excellent oxidative and thermal stability and good flexibility at 200 °C [124]. However, the system was stable for an experimental period of 200 h and the water produced by the reaction was sufficient to maintain the fuel cell performance. It is concluded that PEFC employing the doped PBI membranes, can operate efficiently at low humidity in contrast to a Nafion<sup>®</sup> membrane.

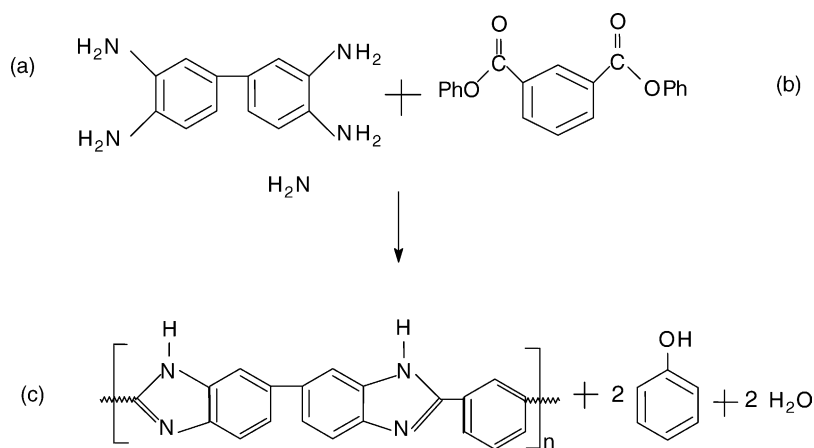


Fig. 11. Structure of (a) tetraaminobiphenyl, (b) diphenylisophthalate and (c) poly[2,2'-(*m*-phenylene)-5,5' bibenzimidazole].

Samms et al. complexed PBI with acids such as sulfuric acid, hydrochloric and phosphoric acid to achieve an improvement in conductivity. For  $\text{H}_2/\text{O}_2$  fuel cell, a proton conductivity of  $9 \times 10^{-3}$  S/cm for PBI acidified with  $\text{H}_3\text{PO}_4$  was recorded which is higher than  $8 \times 10^{-4}$  S/cm obtained for pure PBI membranes [125]. 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 [126–129]. Bozkurt and Meyer have, for example, investigated poly(4-vinylimidazole)- $\text{H}_3\text{PO}_4$  complexes and found its stability through thermogravimetric studies to be about  $150^\circ\text{C}$  [126]. Lassegues et al. found complexes of amorphous polyamide with  $\text{H}_3\text{PO}_4$  to have high conductivity but poor mechanical strength and chemical stability at temperatures above  $90^\circ\text{C}$  [127]. Hasiotis et al. have prepared blends of sulfonated polysulfones and PBI which were doped with  $\text{H}_3\text{PO}_4$  [130,131]. These membranes showed improved mechanical properties and conductivities above  $10^{-2}$  S  $\text{cm}^{-1}$  at  $160^\circ\text{C}$  at 80% relative humidity, which was higher than for acid-doped PBI membranes under the same conditions.

The long-term stability of doped PBI membranes is yet to be proven despite their excellent attributes for fuel cell applications [121–124]. Other acid base blends are described in Table 5 [132–137]. The structures of prominent acidic and basic polymers and their complexes are given in Fig. 12.

## 8. Future prospects

From the aforementioned discussions, it can be noted that despite the advancement in the PEMFC field, some restrictions are still encountered. The constraints can be primarily classified as identification of appropriate membrane mate-

rial, keeping in view the desired membrane properties, and accelerating the commercialization of the technology. The potential routes to overcome these drawbacks can be identified by considering the following aspects.

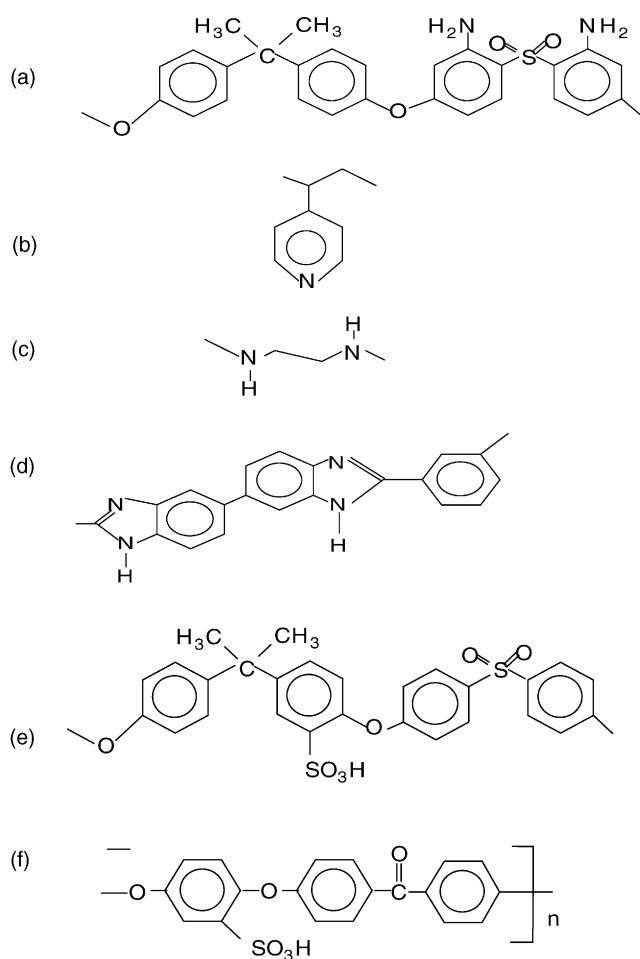


Fig. 12. Structure of basic polymers (a–d) and acidic polymers (e, f).

Table 5  
Acid–base blends

S. no.	Membrane materials	Blend ratio	Physical properties	Observations	In situ performance	Ref.
1	SPEEK/PBI	90/10	High temperature tolerance at 350 °C; thermally stable; good miscibility	Short-term tests (300 h) yield comparable performance to Nafion 112	Higher voltages of 650 mV obtainable at high current densities of 1000 mA/cm <sup>2</sup> for hydrogen fuel cell	Keres and coworkers [104,132–136] Figs. 9 and 10
2	PVA/H <sub>3</sub> PO <sub>4</sub>	Highly doped	Good mechanical strength  Thermally stable upto 70 °C	With decreasing acid concentration, grotthus transport mechanism decreases  Mechanism likely at low temperatures	Low open cell voltage (a max. of 436 mV with very low current density of 1 mA/cm <sup>2</sup> )  Maximum conductivity of 10 <sup>-1</sup> S/cm at 100 MV	Vargas et al. [137]
3	PBI/H <sub>2</sub> SO <sub>4</sub>	500% doping	Good mechanical strength; thermally stable	Doped PBI shows greater potential for fuel cell operating at moderate temperatures	Conductivity of 6 × 10 <sup>-2</sup> S/cm achievable	Samms et al. [125]

### 8.1. Identification of alternate membrane materials

In spite of the extensive research effort globally, the need for new polymers which could satisfactorily serve as suitable inexpensive alternatives to Nafion<sup>®</sup>, still exists. A review of the literature yields the following suggestions for the development of efficient proton conducting membranes.

- The acid–base blends (Table 5) of specialty polymers have not been explored as yet. The main advantage of using high temperature specialty polymers is related not only to the thermal stability, but more to the expected stability in oxidative, reducing and acidic environments. Hence, sulfonated bisphenol-A-polysulfone (SPSU) or sulfonated polyphenylene oxide (SPPO) and their derivatives could be the choice of membrane materials as candidates for acid–base blends for final use in proton exchange fuel cell. SPSF and SPPO could be ionically crosslinked with a polybase such as poly(ethyleneimine) (PEI) or poly(benzimidazole) (PBI), to produce useful acid–base blends. These blends are expected to offer good mechanical, chemical and thermal stability to the membrane in combination with high proton exchange capacity.
- Membranes based entirely on aromatic high performance polymers such as poly ether ketone (PEK) and poly(phenylene oxide) can offer an interesting substitute for Nafion<sup>®</sup>. These polymers demonstrate good chemical stability in association with other crucial requirements for a fuel cell membrane. Some of them allow direct electrophilic sulfonation and subsequent membrane casting from organic solutions, which may prove to be economical.
- Incorporation of submicron particles of metal(IV) phosphates such as zirconium phosphate (ZrP) and tin phosphate (SnP) in polymer matrices tend to increase the proton conductivity of the polymers. For this purpose, precipitation from a solution containing M(IV) ions, within an appropriate polymer matrix, can offer a number of advantages:

- i. elimination of the dissolution of the membrane material formed by the direct swelling of the polymers selected;
- ii. proper mixing of inorganic and organic components at molecular level offering good mechanical stability compared with purely organic membrane;
- iii. since proton conductivity is the result of transport of protons on the surface of the proton conductor particles, an increase in surface area (smaller particle size) will increase the conductivity obtained for a mixed matrix membrane;
- iv. these membranes may cost the same as the conventional polymers;
- v. with increasing proportion of metal particles, appreciable degree of improvements in proton conductivity specially at high temperature can be anticipated. However, the influence of metal particles on mechanical characteristics needs to be investigated.

Hence, submicron size inner transition metal phosphates could be prepared and doped in the matrices of specialty polymers such as bis-phenol-A-PSF or PPO.

### 8.2. Accelerating the commercialization of the technology

The fuel cell market is estimated to have risen to \$1.3 billion in 2003 [138] up from an estimated \$355 million in 1998. With commercialization of most of the fuel cell technologies rapidly falling in place, this market is expected to increase to an estimated \$3.3 billion by 2005 suggesting an AAGR (average annual growth rate) of 18.7%. It has also been anticipated that fuel cells for residential accommodations will be manufactured in the range 1–10 kW and portable fuel cells will be built in the sub-watt to 5 kW range [139]. Between 2000 and 2010, an estimated 130 GW of new generating capacity will be installed in the US. In world markets, within a much closer time frame, an estimated 550 GW of generating capacity will be added as per these projections.

For the fuel cell markets to be profitable a significant number of development activities, both academic and commercial are essential. Presently the academic organizations are targeting improved performance and reliability, dramatic cost reduction, ease of manufacture, optimization for use in specific applications, operation under reduced or zero external humidification and at higher temperatures. Academicians can also support the development of demonstration projects that showcase fuel cell technology, validate product reliability and output and provide data necessary for commercialization [136]. Industry on the other hand can engage in standardizing the specifications of the fuel cell components, increasing production volumes, which can result in reduction of production costs. The sooner this demand is generated, the faster the industry will be able to reduce costs and access new markets. Industries should also support research and development and product development thereby accelerating the process for commercializing the technology.

## 9. Conclusions

Based on literature survey, the various solid polymer electrolytes tested for fuel cell applications as proton conducting membranes are reviewed. From the work carried out so far world wide, fuel cell membranes could be divided into four broad categories viz. perfluorinated ionomers, non-fluorinated hydrocarbons, sulfonated polyarylenes and acid–base complexes. From the review, it is evident that Nafion<sup>®</sup> is the prominent polymer in the first category; while s-PPBP shows the best potential for the third category and phosphoric acid doped PBI membranes appear most promising in the fourth category. These polymers meet the requirements of fuel cell membranes such as ionic conductivity, chemical and thermal stability besides low fuel permeability. Studies on the transport phenomena and methods to improve the performance of these membranes are reviewed. The review reveals that Nafion<sup>®</sup> is a more “mature” membrane. Much research has been conducted on the details of the transport of protons through the polymer matrix and on novel methods of improving its properties but development of a sturdy inexpensive substitute to Nafion<sup>®</sup> is yet to materialize. Progress in the third (sulfonated polyarylenes) and fourth (acid–base blends) categories has been steady, and in each case work is still focused on investigating the mode of proton transport and on the practical applications of these membranes in a PEM fuel cell. However, with studies in these areas continuing extensively, the class of membranes based on acid–base complexes appears competitive to Nafion<sup>®</sup> in ease of preparation and cost-effectiveness. Suitable modifications might render these complexes a promising alternative, provided that the long-term endurance is proved.

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## Nomenclature

BAM3G	ballard advance material of third generation membrane
I-d-SPEK	imidazole doped sulfonated poly(ether ketone)
MBSPBI	methyl benzenesulfonated polybenzimidazoles
MBSPTA	methyl benzenesulfonated poly( <i>p</i> -phenyleneterephthalamide)
NPI	naphthalenic polyimide
PBI	polybenzimidazole
PEI	poly(ethyleneimine)
PFCA	perfluorocarboxylic acid
PFSA	perfluorosulfonic acid
PFSI	bis(perfluoroalkylsulfonyl)imide
Poly-AMPS	poly(2-acrylamido-2-methylpropanesulfonic acid)
PSU(NH <sub>2</sub> ) <sub>2</sub>	ortho-sulfone aminated polysulfone
PTFE-g-TFS	$\alpha,\beta$ -trifluorostyrene grafted onto poly(tetrafluoroethylene) with post sulfonation
PVDF-g-PSSA	styrene grafted on sulfonated poly(vinylidene fluoride)
P4VP	poly(4-vinyl pyrrolidone)
SPEEK	sulfonated poly(ether ether ketone)
SPPBP	sulfonated poly(4-phenoxy benzoyl-1,4-phenylene)
SPSU	sulfonated polysulfone

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