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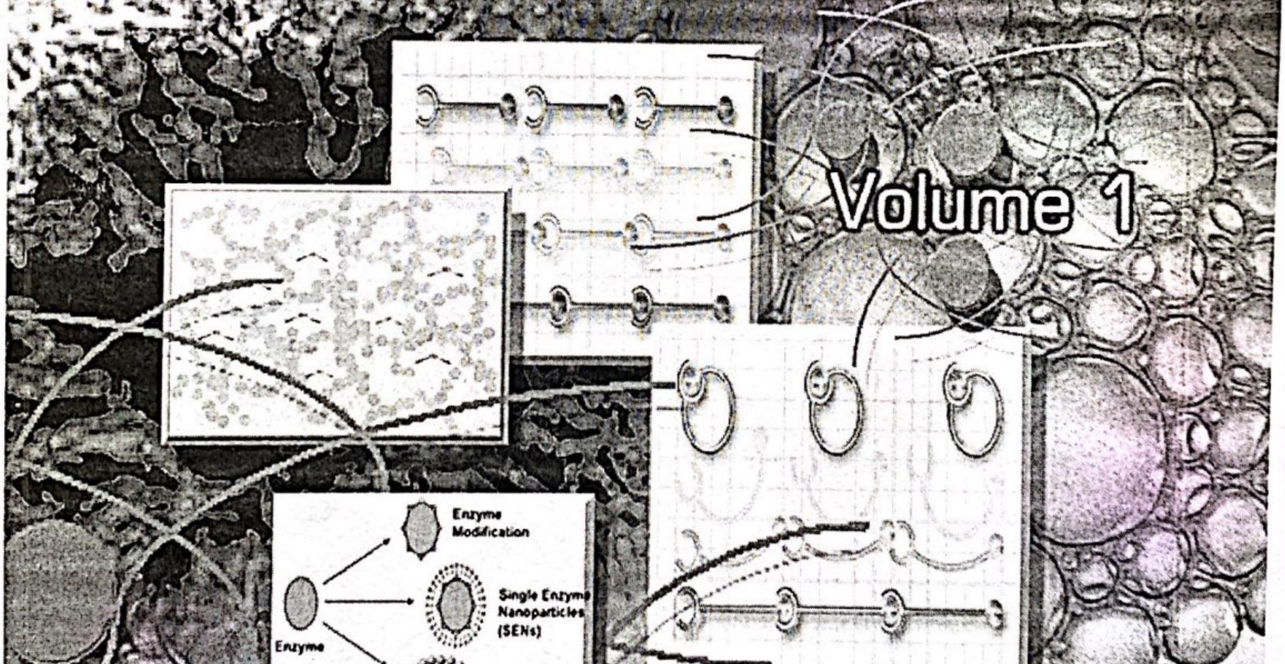

Volume 1

Inamuddin
Editor

Polymer Science and Technology

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24

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MATERIALS, DEVICES AND ALLIED APPLICATIONS

VOLUME 1

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DEDICATION

To my parents,
my wife Mrs. Khushbu Inam and
my loving son Mohammad Uzair Khan

CONTENTS

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Chapter 1

ADVANCES IN MEMBRANES FOR HIGH TEMPERATURE POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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ABSTRACT

The interest in the development of highly conductive and stable proton exchange membranes (PEMs) for high temperature polymer electrolyte membrane fuel cells (HT-PEMFC) is fast growing despite being a challenging research task. Various approaches have been used to design membranes with appropriate structures that can withstand the operation in HT-PEMFC in the temperature range of 100-200°C. In this chapter, the recent developments in the PEMs for HT-PEMFC are reviewed with attention paid to fast growing and promising PEM materials obtained by acid doping. PEM materials involving various modifications of commercial perfluorosulfonic acid (PFSA) membranes are also discussed. The future directions in research towards obtaining membranes with improved stability and cost effectiveness were also highlighted.

ABBREVIATIONS

ABPBI	Poly (2, 5-benzimidazole)
AHOR	Anodic hydrogen oxidation reaction
tBIPA	5-tert-Butyl isophthalic acid
BIS-B-AF	4, 4'-(hexafluoroisopropylidene) bis (benzoic acid)
BIzD	Benzimidazole derivatives
BnIm	Benzimidazole
$[Bmim]PF_6$	1-*n*-Butyl-3-methylimidazolium hexafluorophosphate

4-

[Bmim] BF_4	1-*n*-Butyl-3-methylimidazolium tetrafluoroborate
CO	Carbon monoxide
CORR	Cathodic oxygen reduction reaction
DAB	3, 3'-Diaminobenzidine
DBSA	4-Dodecylbenzene sulfonic acid
DC	Direct current
[Dema]Tfo	Diethylmethylammonium trifluoromethanesulfonate
[Dmoim]Tf	2, 3-Dimethyl-1-octylimidazolium triflate
DEPETEOS	Diethylphosphatoethyltriethoxy silane
DMFC	Direct methanol fuel cell
DBSA	4-Dodecylbenzene sulfonic acid
EIS	Electrochemical impedance spectroscopy
[Emim]H_2PO_4	1-Ethyl-3-methylimidazolium hydrogen sulphate
ETFE	Poly (ethylene-co-tetrafluoroethylene)
FEP	Poly (tetrafluoroethylene-*co*-hexafluoropropylene)
HPA	Heteropolyacid
HPEOS	Hyperbranched polyethoxysiloxane
HT-PEMFC	High temperature proton exchange membrane fuel cell
Im	Imidazole
MBAA	N,N'-methylenebisacrylamide
MDP	Mono-dodecylphosphate
MEA	Membrane electrode assembly
Na-TPA	Disodium salt of tungstophosphoric acid
NMR	Nuclear magnetic resonance
OCV	Open circuit voltage
PA	Phosphoric acid
PAA	Polyacrylic acid
PAAM	Poly(acrylamide)
PAES	Poly(arylene ether sulfone)
PAFC	Phosphoric acid fuel cell
PAMA	Polydiallyldimethylammonium dihydrogen-phosphate
PAMPSA	Poly (2-acrylamido-2-methyl-1-propanesulfonic acid)
PBI	Poly(benzimidazole)
PBI-imi	Poly (2, 2′-imidazole-5, 5′-bibenzimidazole)
PBI-OO	Poly-[(1-(4, 4'-diphenylether)-5-oxybenzimidazole)-benzimidazole]
PBI-ph	Poly [2, 2′-(*m*-phenylene)-5, 5′-bibenzimidazole]
PEEK	Poly(ether ether ketone)
SPEEK	Sulfonated poly(ether ether ketone)
PEG	Polyethylene glycol
PEGMAP	Poly(ethyleneglycol methacrylate phosphate)
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
PEI	Poly (ethylene imine)
bPEI	Branched poly (ethylene imine)
PEO	Poly(ethylene oxide)

PESf	Polyether sulfone
PFSA	Perfluorosulfonic acid
PI	Polyimides
PMA	Phosphomolybdic acid
PMMA	Polymethyl methacrylate
PPA	Polyphosphoric acid
P-PHM	Poly (vinylacrylate phosphoric acid monomers)
PPO	Polyphenylene oxide
PPOBI	Poly [2, (4'-oxyphenylene)-5-benzimidazole]
PS	Polystyrene
PSA	Poly (silamine)
PSf	Polysulfone
P(St-*co*-AN)	Poly(styrene-*co*-acrylonitrile)
PSSA	Poly(4-styrene sulfonic acid)
PSU $(NH_2)_2$	Ortho-sulfone aminated polysulfone
PTSA	p-Toluenesulfonic acid
PTA	Phosphotungstic acid
PVA	Poly(vinyl alcohol)
PVDF-*co*-HFP	Poly(vinylidenefluoride-co-hexafluoropropylene)
PVPA	Poly(vinylphosphonic acid)
PVP	Poly (vinyl pyrrolidone)
PVT	Poly (5-vinyltetrazole)
PVTr	Poly (1, 2, 4- vinyltriazole)
P(VTr-AN)	Poly (1,2,4- vinyltriazole- co- acrylonitrile
(P (VTr-VT-AN))	Poly (1, 2, 4- vinyltriazole-co-5-vinyltetrazole-co-acrylonitrile)
P (VT-AN)	Poly (5-vinyltetrazole-co-acrylonitrile)
PVTri	Poly (1-vinyl-1, 2, 4-triazole)
P4VIm	Poly (4-vinylimdazole)
P2VP	Poly (2-vinylpyridine)
P4VP	Poly (4-vinylpyridine)
PNVA	Poly(N-vinylamine)
PWA	Phosphotungstic acid
Py	Pyrazole
RH	Relative humidity
SiWA	Silicotungstic acid
sPEK	Sulfonated polyether ketone
S-PP	Polyphosphazene
SPSU	Sulfonated poly(arylene ether sulfone)
TAA	Tungstoarsenate acid
Tet	Tetrazole
Tri	Triazole
TPA	Tungstophosphoric acid
1-VIm	1-Vinylimidazole
4-VP	4-Vinyl pyridine
ZrP	Zirconium phosphate

1. INTRODUCTION

Fuel cells are one of the most interesting alternative environmental friendly power sources for meeting the fast growing energy demands in various sectors. Particularly, fuel cells utilizing proton exchange membranes (PEMs) as electrolytes are highly attractive for portable, mobile and stationary low temperature (60-80°C) applications. The replacement of liquid electrolyte, which is commonly used in electrochemical cells with solid PEM inherited them modular, simpler, emission free, efficient and corrosion free operation [1-25]. Today, significant advancements in polymer electrolyte membrane fuel cell (PEMFC) material and their engineering and technological aspects have been achieved leading to a wide range of portable and mobile applications, partly ready for commercialization.

The operation of PEMFC is relying on PEM in transferring protons resulting from due to oxidation of H_2 at the anode to the cathode. PEM also acts as a barrier between the fuel and oxidant gases, thus prevents their undesired mixing [26]. Perfluorosulfonic acid (PFSA) membranes such as Nafion$^{(TM)}$ (DuPont) and its analogous versions such as XUS® (Dow Chemicals), Aciplex® (Asahi Chemicals Co.), Flemion® (Asahi Glass Co.), BAM 3G® (Ballard) and CRA and CRS (Solvay), are widely used in PEMFC [27,28]. This is due to their high ionic conductivity coupled with chemical stability. Other alternative membranes such as Dais® membranes (Dais Co.), Gore-Tex® (Gore and Associate) and sulfonated poly(ether ether ketone) membranes (SPEEK) were also prepared to reduce the cost of PFSA membranes [29]. However, all membranes contain sulfonic acid groups which function properly only when they are saturated with water and this limits the PEMFC operating temperature to ≥80°C [3, 4, 30]. This requires an adoption of stringent requirements involving external humidification of the reactant gases making fuel cell balance of a plant more complicated [31].

To increase the efficiency and overcome some of the inherent problem associated with the use of hydrogen obtained from the reformed hydrocarbon fuels and water management system, high temperature operation (above 100°C) is desired for PEMFC. Particularly, better electrode kinetics, elimination of humidification, high tolerance to fuel impurities e.g. carbon monoxide (CO), higher efficiency and higher values of excess heat by cogeneration can be achieved [32]. However, commonly used PFSA membranes cannot sustain operation above 100°C as they undergo low water content, fast oxidative degradation and reduction in the mechanical stability, all of which lead to a decay in their performance [4,10,25,30,33,34,35]. Thus, development of PEMs for high temperature (HT) PEMFC has become the focal point of material research to obtain membranes suitable for operation above 100°C.

Various approaches have been used to develop alternative membranes for High temperature proton exchange membrane fuel cell(HT-PEMFC). This includes modification of Nafion$^{(TM)}$ membranes using inorganic fillers, acid/base composite membranes, acid doping of partially fluorinated membranes and hydrocarbon membranes. Phosphoric acid (PA) and derivatives loaded on polymeric substrates were recently proposed as alternative PEM. For example, excellent alternative acid-base composite membranes such as PA doped poly(benzimidazole) (PBI) [1,5,36-40], poly [2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (PBI-ph) [40], poly(2,2′-imidazole-5,5′-bibenzimidazole) (PBI-imi) [40] and radiation grafted poly(ethylene-co-tetrafluoroethylene)-*graft*-poly(vinylimidazole)(ETFE-g-poly(1VIm) membranes [36-38] were extensively investigated.

Other type of membranes in forms of complexes of basic polymers e.g., poly (ethylene oxide) (PEO), poly (ethylene imine) (PEI), poly (acrylamide) (PAAM) and poly (vinyl alcohol) (PVA) with strong acids such as PA or protic ionic liquids (ILs) such as PMI/H_2PO_4 [41] were studied [42]. These membranes were found to be independent of humidification up to 200°C and showed excellent physico-chemical properties that made them applicable for HT-PEMFC. The researches related to some membranes operated in PEMFC above 100°C and PBI based membranes have been reviewed [4,10,17,25,30,34,35,42].

The objective of this chapter is to report the progress taking place in various approaches used to prepare PEM membranes for HT-PEMFC application. Particularly, attention is paid to membranes obtained by four main approaches including introducing nano-sized hygroscopic inorganic fillers, modification with solid proton conductors, use of non-volatile proton conducting solvents and modification of commercially available PFSA membranes.

2. PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCS)

PEMFCs are potentially high efficient environmental friendly devices for generating electricity. They have the ability to electro-catalytically convert the free energy of gaseous fuel in the presence of an oxidant to direct current (DC) electrical power without intermediate generation of thermal energy [7, 8]. Typically, the fuel is hydrogen and the oxidant is oxygen, however, the oxygen is replaced with air and the hydrogen may be derived from reformed organics such as methanol, natural gas or other hydrocarbons for practical reasons. Unlike batteries which have an output limited to the stored chemical energy, PEMFCs continue to generate electricity as long as the hydrogen is supplied to the anode and oxygen to the cathode. Furthermore, PEMFCs have very high current density and high energy per weight as well as per volume compared to other conventional power sources. Such advantages have made them very promising candidates for low temperature operations such as mobile (electric vehicles); portable and stationary applications i.e., power plants [7]. The latest developments in PEMFCs and their applications have been recently reviewed [4, 10, 17, 25, 30, 33-35, 43-46].

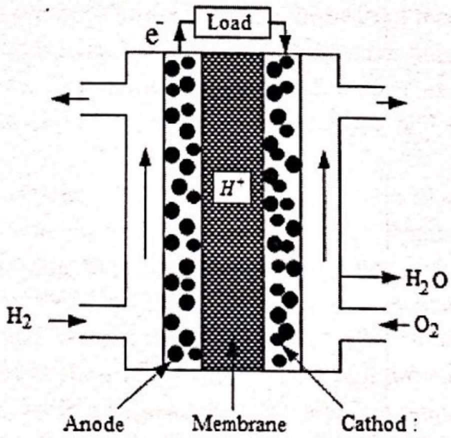


Figure 1. A schematic diagram of basic unit of proton exchange membrane fuel cell.

Like other electrochemical cells, PEMFC fundamental operational unit consists of two porous gas diffusion electrodes separated by an electrolyte (proton conducting membrane). A schematic diagram of PEMFC basic unit is shown in Figure 1. The two electrodes are conventionally made of polymer-bonded carbon-cloth/-paper having porous-structure and loaded with a small amount of a noble metal (catalyst) such as platinum. More details of the structure of gas diffusion electrodes and their application in PEMFC can be found elsewhere [7,47].

Hydrogen is oxidized at the anode to liberate electrons and protons and this is called anodic hydrogen oxidation reaction (AHOR) while protons and electrons react with oxygen at the cathode to form water and heat as by-products which is known as cathodic oxygen reduction reaction (CORR) as shown in the chemical equations 1-3 below:

$$\text{Anodic reaction: } 2H_2 \rightarrow 4H^+ + 4e^- \quad (1)$$

$$\text{Cathodic reaction: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

$$\text{General reaction: } 2H_2 + O_2 \rightarrow 2H_2O + \text{electric} + \text{power} + \text{heat} \quad (3)$$

Protons are conveyed from anode to cathode via PEM, whereas electrons flow through the electrical circuit. Since molecules cannot maintain ionic state for a very long time, they immediately recombine with other molecules in order to return to their neutral state. Similarly, protons in PEM stay in the ionic state by hopping from one molecule to other using the functional groups in the membrane [16, 25, 48-50]. The electrochemical reactions, which occur in PEMFC leads to formation of water and generation of waste heat which affect the performance and therefore it should be remove continuously [50].

2.1. Role of Proton Conducting Membrane in Proton Exchange Membrane Fuel Cells

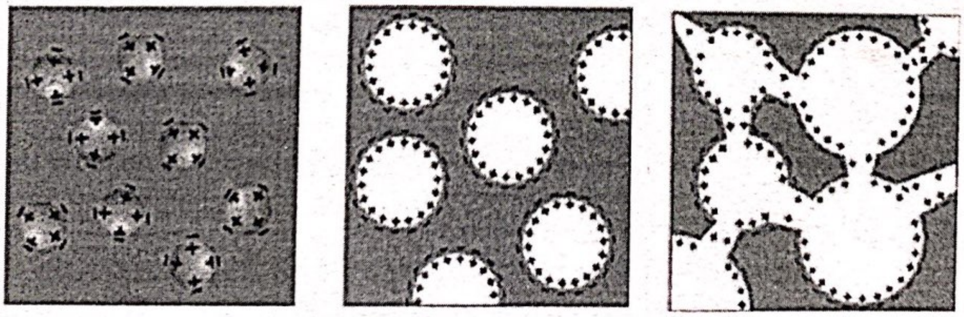
The proton conducting membrane is a polymeric network containing terminal, hydrophilic, sulfonic acid groups. The membrane is the heart of the PEMFC where it provides the following chemical and mechanical functions: 1) selective transport of the hydrogen ions from anode to the cathode, 2) prevention of the bulk mixing of hydrogen and oxygen, 3) protection of the catalyst layers on the electrode surface and 4) prevention of electron transfer.

Since, the membranes contain ionic sites, which are scattered across their structures; they remain in shrunken form in the dry state. As water is absorbed in the membrane, the hydrophilicity increases leading to the swelling of ionic sites forming ionic clusters. Further, water absorbance leads to phenomenon called percolation in which there is an increase in cluster size to the extent that they get connected to each other through tiny channels allowing water and proton passages as shown in Figure 2. Thus, the presence of sulfonic acid groups enables the membrane to absorb a large amount of water in a preliminary step before or after assembling the cell and this leads to the dissociation of the $-SO_3H$ group into aqueous H^+ and fixed $-SO_3^-$. The aqueous H^+ ions or the charge carrier in the hydrated membrane migrate across the membrane from anode to the cathode by passing form one $-SO_3^-$ group to another. The degree of hydration is a critical factor in the performance of the PEMFC. This is because it determines not only the mobility of H^+ but also the electro-osmotic drag, diffusion of water in the membrane and the permeability of the reactant gases. Dryness of the membrane causes a reduction in the cell performance, whereas excess water leads to cathode flooding problem and similar low performance [2]. Thereby, the membrane has to be kept under constant hydration by humidification of the reacting gases. Modelling and optimisation of the internal hydration of PEMFC have been addressed in various studies [2, 51-55].

2.2. Requirement for Proton Conducting Membrane for Proton Exchange Membrane Fuel Cells

The essential requirements for PEMs to be suitable for PEMFC application are:

1. Chemical stability (high resistance to oxidation, reduction, hydrolysis and dehydration),
2. Mechanical strength and stability under cell operating environment in addition to processability,
3. Compatible physical properties with the hot pressing of the membrane with the electrode (flat, non-reinforced, minimum thickness dense without pores, homogeneous, dimensional stability and not brittle in dry state),
4. Compatible electrochemical properties (strong acidic group, high proton conductivity in the range of $10^{-2}\ \Omega^{-1}cm^{-1}$, zero electronic conductivity, low resistance in the range of 1 to 3Ω),
5. Minimal transport properties to minimise columbic inefficiency (minimal water drag and low permeability of the reactant gases),
6. Thermal stability,
7. Low cost and high availability.


Membrane in dry state

Membrane incorporating water

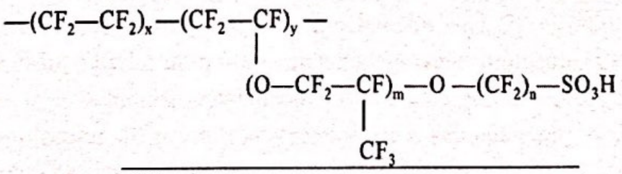
Fully water swollen membrane

Figure 2. Simplified perfluorosulfonic acid membrane structure according to water content [56]. Reproduced with permission from Gebel, G. *Polymer 2000, 4, 5829–5838*. Copyright © 2000, Elsevier B.V.

2.3. Current Status of Perfluorinated Sulfonic Acid and Alternative Proton Conducting Membranes

Several proton conducting membranes including Nafion(TM) (DuPont), Aciplex® (Asahi Chemicals Co.), Flemion® (Asahi Glass Co.), Gore-Tex (Gore and Associate), Ballard Advanced Materials, BAM, (Ballard) and Dais membranes, (Dais Co.), CRA and CRS (Solvay) and sulfonated poly(ether ether ketone) membranes (SPEEK) [27,28] are commercially available. Figure 3 represents general structure of commercial PFSA membranes. Of all, Nafion membrane is the most established product that has been intensively investigated and the majority of the available fuel cell systems rely on it. Nafion is also available in various versions of different equivalent weights and thicknesses as shown in Table 1. Several alternative commercial PEMs based on fluroinated and hydrocarbon structures are also availabe (Table 2). However, Nafion and analogous perfluorinated membranes are expensive because of fluorine chemistry involved in their production and require full hydration upon operation giving a complexity to the PEMFC system by including water management system. In addition, Nafion membrane is prone to viscoelastic relaxation at high temperatures (low hydrated T_g), which decreases both its mechanical properties and proton conductivity [42].

Various preparation routes have been applied to develop new alternative low cost membranes to overcome the high cost associated with PFSA membranes. Such approaches are briefly reviewed to set a ground for their counterparts used to develop similar PEMs for HT-PEMFC. The first approach includes modification of Nafion membranes with inorganic fillers [3,25,37,58-62] and surface coatings (formation of composite membranes) [8,25,32,43,62-102]. The second approach involves direct sulfonation of non-fluorinated polymer backbones such as polystyrene (PS) [69], polyphosphazene (PPA) [103], polyphenylene oxide (PPO) [104], polysulfone (PSf) [105] polyether sulfone (PESf) [80], polyether ether ketone (PEEK) [106], polybenzimidazole (PBI) [107] and polyimides (PI) [108]. However, this approach was challenged by the need for achieving sufficient sulfonation to obtain high proton conductivity in the membranes without compromising the mechanical integrity. The third approach involves sulfonation of pendent aromatic rings attached to a variety of copolymer (grafted) films obtained by chemical [109], plasma [110], thermal [111] or radiochemical graft copolymerization of styrenic monomers [48,112-120]. Reviews of previous efforts on sulfonic acid based proton containing membranes can be found elsewhere [3,121-123].



$$-(CF_2-CF_2)_x-(CF_2-\underset{|}{CF})_y-$$
$$(O-CF_2-\underset{\underset{CF_3}{|}}{CF})_m-O-(CF_2)_n-SO_3H$$

Membrane	m	n
Nafion 117	>1	2
Aciplex	0-3	2-5
Flemion	0-1	1-5
Dow	0	2

Figure 3. General molecular structure of commercial perfluorinated sulfonic acid.

Table 1. Properties of various versions of Nafion membranes [57]. Reproduced with permission from Slade, S., Campbell, S. A., Ralph, T. R., Walsh, F. C. *J. Electrochem. Soc.* 2002, *149*, 1556-1564. Copyright © 2000, Electrochemical Society

Membrane	Dry thickness (μm)	Equivalent weight (gmol^{-1}/SO$_3$)	Area resistance (Ωcm^2)	Conductivity (Scm^{-1})	Water content at 25°C
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. Alternative commercial PEMs and their properties

Membranes	Manufacturer	Equivalent weight (gmol^{-1}/ SO$_3^{2-}$)	Thickness/ dry (μm)	Conductivity (mScm^{-1})	Water content (wt%)
Dow	Dow Chemicals	800	125	114	54
Flemion-T	Asahi glass	1000	120	N/A	N/A
Flemion-S		1000	80	N/A	N/A
Flemion-R		1000	50	140	38
Aciplex	Asahi chemicals	1000	120	110	43
Gore Select	Gore & associate	900-1100	5-20	28-96	32-43
BAM 3G	Ballard	375-920	140/wet	N/A	87
CRA	Solvay	460-720	160	45	N/A
CRS		460-590	160	50	N/A
R1010	Pall Gelman Sciences	835	40	70	N/A
R4010	IonClad	835	20	80	N/A

2.4. Proton Transport in Sulfonic Acid Membranes

There are two main mechanisms by which proton transport occurs through the water solvated membranes. These are: 1) migration of hydrated protons (hydronium ions) known as vehicular diffusion or water-assisted shuttle mechanism and 2) Grotthus mechanism or hopping of a proton from a hydronium ion to an adjacent water molecule (structural diffusion) through membrane. In a vehicular mechanism proton conduction occurs in a process that resembles normal molecular diffusion and depends on a vehicular physical transport where the molecular diffusion process takes place as a result of the movement of the hydrated proton aggregates i.e., H_3O^+ (hydronium ion), H_5O_2 (Zundel ion) and $H_9O_4^+$ (Eigen ion) through the aqueous environment as a single entity under the effect of electro-osmotic drag. Such diffusion is prompted by the presence of free volumes within the hydrophobic polymeric chains of the polymer backbone in PEM, which tend to repel the water molecules. The proton transfer by structural diffusion mechanism is assumed to occur by participation of bound water. It occurs by proton hopping from one hydrated ionic site to another across the membrane through a network of hydrogen bond formations and breakages among a series of dynamic hydrated proton aggregates such as H_3O^+, H_5O_2 and $H_9O_4^+$ [2,10,13,48,124-126]. Structural diffusion can be demonstrated by measuring proton self-diffusion rates [2,3]. Combination of these two diffusion mechanisms can exist leading to excellent conductivity.

2.5. Challenges Facing Sulfonic Acid Membranes in Proton Exchange Membrane Fuel Cells

There are number of challenges facing the PFSA membranes and their alternative materials. These challenges are the major driving force propelling vibrant and dynamic research efforts to develop HT-PEMs [8,10,18,19,42,127]. This includes high cost (500-700$/m^2) associated with the use of fluorine chemistry in their production; durability and material reliability of the hydrocarbon membranes under fuel cell operation conditions. Proton transport medium is water-dependent where water existing in free state dehydrates at temperature above 80°C and relative humidity below 100% bringing about reduction in the proton conductivity leading to a poor performance in PEMFC. A full hydration is required for keeping high proton conductivity. However, this limits the operating temperature of such membranes to values below 90°C (10,16,17,23,25,128). The optimum operating temperature of PEMFC with PFSA membranes is between 50-80°C and the pressure is between 1-5 bar with low CO and sulfur intolerance. The CO existing in the reformed H_2 fuel leads to the poisoning of catalysts which reduces proton conductivity, efficiency, durability and reliability. Therefore, purified H_2 is preferred for PEMFC operation making on-board production of H_2 in transportation application highly challenging. In addition, these membranes have low thermal, mechanical, chemical, electrochemical, oxidative and dimensional stability; degradation at temperatures above 100°C [4, 10, 13, 16, 17, 30, 33, 46, 76,129, 130]. To encounter such problems, operating PEMFC at temperatures above 100°C is highly desirable.

3. HIGH TEMPERATURE POLYMER ELECTROLYTE MEMBRANE FUEL CELL

Operating PEMFC above 100°C provides a wide range of advantages including the enhancement of its efficiency and economic viability. Particularly, the high temperature operation enhances the rate of reactions with respect to the electrochemical kinetics and catalytic activity for both electrodes. It also simplifies the water management system because only a single phase of water (vapour phase) exists. Thus, the risk of cell flooding is eliminated since the operation involves bound/freezing/vapourized water. The cooling system is also simplified due to the increase in the temperature gradient between fuel cell stack and the coolant. Importantly, high temperature PEMFC operation allows reformed H_2 obtained from hydrocarbons such as natural gas, gasified coal and methanol with impurities of 1-3% CO and 10 ppm SO_2 to be used without poisoning the catalyst layer of the electrodes. For example, at temperatures above 150°C, CO easily desorbs from Pt catalyst of the electrodes unlike at lower temperature (50-80°C) where traces of CO present in reformed H_2 causes an electrode poisoning. The high temperature operation also allows acceleration of the reaction kinetics leading to a reduction in the amount of Pt catalyst loading. This allows for simplification of the fuel cell processing system and possible integration of fuel cell stack with fuel processing units [4, 10, 13, 16, 17, 30, 33, 46, 127].

3.1. Proton Exchange Membranes for High Temperature Proton Exchange Membrane Fuel Cells

PEMFC efficiency and power density depend strongly on the mass transport properties in PEMs. In particular, the performance of a PEMFC depends largely on the physico-chemical nature of the membrane and its stability in the highly oxidative environment of atomic hydrogen and oxygen at elevated temperatures. Various studies have reported the development of a wide spectrum of PEMs suitable for HT-PEMFCs using different approaches and techniques. Particularly, three main approaches have been taken into account for the development of such membranes which are in composite forms: 1) introducing hygroscopic inorganic fillers (mostly nano-size) such as silica and titania to the polymer structure to enhance water retention capacity at elevated temperatures, 2) modification with solid proton conductors that have reduced or independent hydration (solid acid proton conductors) such as phosphate salts of zirconium (ZrP), titanium and caesium [13], and 3) replacement of water with less volatile solvent as proton transporting medium in the membrane i.e. replacement of water with a proton transport-assisting solvent that possess a higher boiling point (less volatile) such as PA, heteropolyacids, N-heterocycles or ionic liquids [62,131,132].

3.2. Membranes Obtained by Modification with Hygroscopic Inorganic Fillers

Modifications of membranes by introducing inorganic fillers have been reported in many occasions with intensive efforts dedicated to modify Nafion membranes. The use of fillers such as silica which is hygroscopic and has an extremely large surface area with smooth nonporous surface enhances a strong physical contact between the filler and the polymer matrix leading to an improvement of membrane water retention. Based on the size of fillers, two basic inorganically filled composite membranes have been explored: (i) macrocomposite membranes, which are a combination of polymer with an organic or inorganic structure of micrometer scale. These could be developed by simple physical mixing of inorganic into organic matrix with appropriate solvent and (ii) nano-composite membranes, which are a combination of the polymer with an organic or inorganic matrix of nanometer scale. [33].

Mauritz et al. reported a pioneering work on preparation of ionic nanocomposite membrane by dispersing silica (which is hygroscopic filler) into Nafion matrix using sol–gel technique. The obtained composites showed a 20% higher water uptake at room temperature compared to unfilled Nafion (15%) despite the low homogeneous distribution of silica particles. The incorporation of silica presumably provides large number of hydroxyl groups that tie up water leading to a reduction in the hydrophobicity of the fluorocarbon backbone of the membrane [65,133].

Similar Nafion/SiO_2 composite membranes based on self-assembled Nafion/SiO_2 nanoparticles were also prepared by reformative sol–gel process [134]. The self-assembled SiO_2 nanoparticles (average particle size of 2.8 ± 0.5 nm) were uniformly distributed in the Nafion/SiO_2 composite membrane. The incorporation of SiO_2 nanoparticles with 5 wt % led to a significant improvement in the performance in terms of stability/durability upon drawing current density of 600 mA/cm^2 with a degradation rate of 0.12 mV/min under cell and humidification temperatures of 100 and 60°C, respectively. The degradation rate of this membrane is almost 20 times smaller than that of pristine Nafion 212 membrane which was 2.33 mV/min measured under the same conditions.

Also, composite membranes based on Nafion filled with TiO2 mesoporous anatase TiO2 powders showed a significant improvement in PEMFC performance under low Relative humidity (RH) and elevated temperature. The composite membrane with 3 wt % of mesoporous anatase TiO_2 showed a highest power density of 669 mW cm^{-2} at a voltage of 0.4 V, a temperature of 120°C, and a RH>50%. This is 5.7 times higher than the power density value obtained under the same conditions with the recast Nafion membrane [135]. Table 3 presents a list of HT-PEMFC membranes obtained by modification of polymer matrix with various inorganic fillers. The various strategies and materials explored for developing organic-inorganic composite PEMs and their perspectives have been recently reviewed [33,152].

3.3. Membranes Obtained by Modification with Solid Proton Conductors

Modification of PEMs with solid proton conductor fillers having reduced or independent hydration has been investigated in many studies. Various solid acid proton conductors have been incorporated in PEMs. Among all, zirconium phosphate (ZrP) is the most extensively studied inorganic material in the membranes for PEMFC. There are two types of predominate zirconium hydrogen phosphate Zr $(HPO_4)_2.H_2O$ (henceforth ZrP) compared to predominated structures of (α-ZrP and γ-ZrP). [13]. However, α-ZrP is most common proton conductor that has been used in modification of Nafion into composite membranes [124,161-167].

The incorporation of α-ZrP particles with its acid nature in PSFA membranes such as Nafion, leads to an increase in the water retention with the ability to donate protons at elevated temperatures and eventually improves the membrane conductivity. Particularly, composite Nafion membranes having α-ZrP-based were investigated in HT-PEMFC due to their enhanced proton conductivities under high temperature. The composite Nafion115/ZrP membranes obtained by an exchange reaction involving Zr^{+4} ions followed by precipitation of ZrP after immersion of membrane in a PA solution exhibited a PEMFC performance of 1.0 A/cm^2 at 0.45 V compared to original membrane, which exhibited a performance of 0.25 A/cm^2 at 130°C and a pressure of 3 bars [168].

Similar composite membrane obtained by the recasting method showed a PEMFC performance of 1.5 A/cm^2 at 0.45 V under the same operating conditions [43]. The composite recast membranes also showed better stability at 130°C compared to the parent Nafion membrane, which was subjected to irreversible degradation. It was concluded that the proton conductivity of the composite Nafion membranes was not affected by the incorporation of ZrP. In another study, Nafion composite membrane with homogeneously dispersed α-ZrP particles obtained by an *in situ* precipitation of α-ZrP. The incorporation of α-ZrP loading resulted in an enhancement in the elastic modulus but decreased the membrane conductivity, particularly at low humidity. The improved elastic modulus exhibited an enlarged stability region at higher temperature (up to 140°C) and low RH values in comparison with the parent Nafion membrane [169].

Table 3. Summary of HTPEMFC membranes obtained by modification of polymer matrix with various inorganic fillers

Membranes	Conductivity (S cm^{-1})	Conditions	References
Nafion			
Nafion/SiO_2	6.0×10^{-2}	378 K, 100% RH	[136]
	1.07×10^{-2}	383 K, 70% RH	[93]
	9.0×10^{-2}	333K, 100% RH	[134]
Nafion/SiO_2/PWA	2.67×10^{-2}	383 K, 70 % RH	[93]
Nafion/ZrO_2	2.4×10^{-2}	408K, 100% RH	[137]
	$1.4 \times 10^{-3} - 1.82 \times 10^{-2}$	363K and 393 K, 10% RH and 40 % RH	[138]
Nafion/sulfated ZrO_2	1.05×10^{-1}	363 K, 80% RH	[139]
Nafion/TiO_2	2.3×10^{-2}	408K , 100% RH	[137]
	2.11×10^{-3}	298 K, 20 % RH	[140]
	8.93×10^{-3}	383 K, 70 % RH	[93]
	1.5×10^{-1}- 1.8×10^{-1}	353K-403K, 85% RH and 100% RH	[141]
Nafion/Al_2O_3	8.3×10^{-2}	418 K, 30% RH	[142]
Nafion/WO_3	2.5×10^{-2}	408 K, 100% RH	[137]
	1.01×10^{-2}	383 K, 70 % RH	[93]
Nafion/silica	2.27×10^{-1}	353 K, 100%RH	[143]
	2.6×10^{-2}	358 K, 50 % RH	[144]
Nafion/HfO_2	2.8×10^{-2}	408 K, 100% RH	[137]
Nafion/Ta_2O_5	1.6×10^{-2}	408 K, 100 % RH	[137]
SPES			
SPES/silica	2×10^{-3}	393 K, 50 % RH	[145]
SPEK			
SPEK/ZrO_2	3.4×10^{-2}	298 K, 0% RH	[79]
SPEK/(ZrO_2/PTA)	8.6×10^{-2} - 1.1×10^{-1}	363K and 383 K, 100% RH	[146]
PBI			
PBI/SiO_2	7.8×10^{-2}	453 K, 0% RH	[147]
	3×10^{-2}	393 K, 50% RH	[148]
PBI/(SiWA+ SiO_2)	1.2×10^{-3}	433K, 100%RH	[149]
PBI/ZrO_2	1.62×10^{-1}	453 K,0 % RH	[147]
PBI/TiO2	4.3×10^{-2}	423 K, 0% RH	[150]
	1.3×10^{-1}	398 K, 0% RH	[151]

Alternative composite membranes with better mechanical properties were prepared from SPEEK and ZrP using electro-driven migration of Zr^{4+} and simultaneous *in situ* precipitation of ZrP using PA under different electrical gradient. The incorporation of ZrP was found to have no impact on the thermal and mechanical stability of membranes. The presence of inorganic particles led to an improvement in high temperature conductivity despite its lower value compared to SPEEK at room temperature [170]. The use of SPEEK, an alternative to Nafion is motivated by its good performance and commercial availability of PEEK and its attractive properties [171,172]. This was accompanied by several investigations that led to an improvement in the membrane durability through applying techniques such as double crosslinking [173] and radiation induced grafting [174]. More details on various versions of improved SPEEK can be found in the review by Zhang and Shen [35]. Table 4 shows a summary of HT-PEMFC membranes obtained by modification of polymer matrix with solid proton conductors.

Table 4. Summary of HT-PEMFC membranes obtained by modification of polymer matrix with solid proton conductors

Membrane combination	**Conductivity (S cm^{-1})**	**Conditions**	**E (kJ mol^{-1})**	**References**
Nafion/α-ZrP	0.1	373 K, 100%RH		[18]
SPEEK/α-ZrP	0.01	298 K, 100%RH		[22]
STA/α-ZrP polymer compound	1.9×10^{-2}	373 K, 100%RH		[153]
Imidazole/Nafion (transverse)	0.1	433 K, 100%RH		[19]
Zirconium				
α-Zr $(O_3POH)_2.H_2O$	10^{-5} to 10^{-6}	293 K, 90%RH	25	[69]
α-Zr $(O_3POH)_2$	1×10^{-7}	453 K, 00%RH		[154]
Pellicular α-Zr $(O_3POH)_2. nH_2O$	1×10^{-4}	293 K, 90%RH	28	[104]
α-Zr $(O_3POH)_{1.27}(O_3PC_6H_4SO_3H)_{0.73}.nH_2O$	1.6×10^{-2}	293 K, 90%RH	18	[155]
	8×10^{-3}	373 K, 60%RH		[155]
α-Zr $(O_3POH)_{1.15}(O_3PC_6H_4SO_3H)_{0.85}$	1.2×10^{-4}	453 K, 00%RH	63	[155]
α-Zr $(O_3POH)_{1.27}(O_3PC_6H_4SO_3H)_2.3.6H_2O$	2.1×10^{-5}	378 K, 85%RH		[119]
γ-Zr $(PO_4)(H_2PO_4).2H_2O$	2×10^{-5}	293 K, 90%RH		[156]
γ-Zr $(PO_4)(H_2PO_4)_{0.54}(HO_3PC_6SO_3H)_{0.46}.nH_2O$	1×10^{-2}	293 K, 90%RH	21	[113]
Zirconium phosphate (sol-gel)	3×10^{-2}	293 K, 50%RH	40	[157]
Zirconium phosphate pyrophosphate	1.3×10^{-3}	293 K, 90%RH	19	[158]
	2×10^{-6}	373 K, 02%RH		[158]
Titanium				
Ti $(HPO_4)_{0.25}(O_3PC_6H_5)_{0.12}(O_3PC_6H_4SO_3H)_{1.63}$	1.3×10^{-1}	278 K, 85%RH	60	[119]
Caesium				
β-Cs $(HSO_4)_2(H_x(PS)_4)$	3×10^{-5}	363 K, 0%RH		[18]
	1.6×10^{-2}	473 K, 0%RH		[18]
α-Cs $(HSO_4)_2(H_2(PO)_4)$	2.5×10^{-3}	313 K, 0%RH		[18]
Other				
Fullerene	7×10^{-7}	293K, 0%RH		[159]
Poly(styrene-co-methacrylate) silica hybrid composite doped with Tungsto-phosphoric acid	1.0×10^{0}	393 K, 0% RH		[96]
Poly (2,5-benzimidazole) (ABPBI) with PMo_{12}	3×10^{-2}	458K, 0% RH		[160]

3.4. Membranes Obtained by Modification with Less Volatile Proton Assisting Solvent

3.4.1. Doping with Heterocyclic Solvents

The replacement of water with a less volatile proton transport-assisting solvent of higher boiling point has been explored for developing PEMs for operating PEMFC at high temperature. Heterocycles, nitrogen-containing species, such as imidazoles and pyrazoles are potential proton carriers to be incorporated in PEMs for HT-PEMFC. This is because the high electron density on nitrogen is partially reduced by the conjugated aromatic system leading to an improvement in the oxidative stability of nitrogen. It was reported that because imidazoles' melting temperature is 90°C, which at ambient pressure is higher than that of water, imidazole can be used to replace liquid water phase in PEMs operated above 100°C. Doping imidazole, which is chemically a strong Bronstedt base is useful to improve acid doping level of the membrane and can increase the basic group number in the membrane. The dissociation of the proton from the -NH group makes imidazole to act as a proton donating agent. The conductivity of liquid imidazole was reported as high as 10^{-3} Scm^{-1} at 90°C [175].

The use of heterocyclic compounds such as imidazole and pyrazole as the proton conducting groups was first proposed by Kreuer et al. [175]. The ability of imidazole to conduct protons was determined for complex membranes composed of sulfonated PEEK doped with imidazole and pyrazole at elevated temperature. Subsequent, the imidazole doping was extended to PFSA membranes such as Nafion [176]. The imidazole modified membranes polymer showed remarkable proton conductivity at high temperature without external humidification.

The challenges facing imidazole modified membranes include the slow leaching of small imidazole molecules despite having a boiling point of as high as 256°C leading to lower conductivity and lack of sufficient mechanical strength. For example, imidazole membranes with copolymers of 4-vinylimidazole with vinylphosphonic acid and 2-acrylamido-2-methylpropanesulfonic acid provide very low proton conductivity (10^{-8}-10^{-10} Scm^{-1}) at 120°C without external humidification [177]. Such membranes are also subjected to thermo-oxidative degradation of imidazole making such heterocyclic modified membranes challenging for long-term HT-PEMFC applications. Thus, no successful fuel cell tests have been reported based on acidic polymers with imidazole doping or imidazole grafted polymers and this is possibly due to the poisoning effect of imidazole to the platinum catalysts [74]. Recently, an acceptable PEMFC performance for Nafion doped with a combination PA and imidazole in a cell using new Pt-Co-Mo catalyst for electrodes has been reported [178]. The replacement of imidazole with 1,2,3-triazole provides an alternative dopant that proved to possess sufficient electrochemical stability and high proton conductivity for fuel cell applications [5].

3.4.2. Doping with Phosphoric Acid

PA is another proton transport-assisting solvent with higher boiling point that has been frequently explored for preparation of membranes for HT-PEMFC. PA is a highly viscous liquid, which can be used in operating temperature in the range of 150-220°C. Due to reasonably high K_a and K_b in terms of equilibrium constants, PA shows a very high degree of self-dissociation of ~ 7.4%. So, PA acts as the proton conducting species and proton donating species in PA based membranes. The extremely high proton mobility of PA was estimated at the melting point (T= 42°C) to be 2 x 10^{-5} cm^2s^{-1} with a total conductivity of 7.7 x 10^{-2} Scm^{-1} [5]. Hence, the incorporation of PA into the membrane structure through doping with a basic polymer backbone yield a complex membrane capable of conducting protons at elevated temperature in PEMFC [5].

Table 5. Membranes modified with heterocyclic solvents

Membranes	Maximum proton conductivity (S cm^{-1})	Conditions	Molar ratio	References
Polyacrylic acid, PAA/Im	1×10^{-3}	393 K	1	[179]
Aliginic acid/ Im	2×10^{-3}	403 K	2	[180]
Poly(vinylphosphonic acid), PVPA/Im	5×10^{-3}	403 K	2	[181]
	7×10^{-3}	423 K	~1	[182]
Poly(ethyleneglycol methacrylate phosphate), PVPA/MeIm	7×10^{-3}	423 K	~1	[182]
PEGMAP/Im	2×10^{-4}	433 K	1	[183]
Poly(4-styrene sulfonic acid), PSSA/Im terminated triethyleneglycol (imi3)	5×10^{-4}	298 K	0.5	[184]
PAMPSA/Im	1.45×10^{-3}	373 K	2	[185]
Nafion/Im	1×10^{-1}	353 K	10%w/w	[74]
P4-VIm/H_3PO_4	2×10^{-4}	298 K	2	[186]
Benzimidazole (BnIm)				
Adipic acid/BnIm	4×10^{-3}	403 K	2.0	[187]
PVPA/BnIm	1×10^{-3}	423 K	2	[188]
MDP/BnIm	1×10^{-3}	423 K	2	[189]
PEGMAP/BnIMm	3.5×10^{-5}	423 K	1	[183]
PSSA/BnIm	5×10^{-4}	423 K	1.5	[190]
Nafion/BnIm	8.64×10^{-3}	473 K	8.5	[191]
Pyrazole (Py)				
PVPA/Py	8×10^{-4}	423 K	~1	[182]
Triazole (Tri)				
PVPA/Tri	2.3×10^{-3}	393 K	~2	[192]
PAMPSA/Tri	9.3×10^{-4}	413 K	2	[192]
PSSA/Tri	1.6×10^{-2}	423 K	1	[184]
SPSU/1H-1,2,3-triazole	1×10^{-2}	383 K	8.3	[193]
SPSU/1H-1,2,4-triazole	5×10^{-3}	413 K	8	[194]
Nafion/1,2,4-triazole	2.3×10^{-2}	433 K	14.5	[191]
Nafion/PVTri	5.3×10^{-4}	493 K	1	[195]
PVTri/H_3PO_4	4×10^{-3}	413 K	2	[196]
PVTri/ p-Toulenesulfonic acid (PTSA)	1.2×10^{-2}	383 K	2	[197]
PVTri/trifilic acid	1.2×10^{-2}	353 K	1.5	[198]
Tetrazole (Tet)				
PVT/H_3PO_4	3.05×10^{-3}	383 K	1	[199]

The PA doping can be performed through: i) direct casting of a basic polymer such as PBI polymer and doping acid from a solution of PBI using PA in trifluoroacetic acid solution, ii) immersing of the cast polymer membranes into concentrated PA and iii) preparation of PBI in polyphosphoric acid (PPA) and forming membranes by direct casting (sol-gel process) [5]. The physico-chemical properties of the membranes prepared by different methods are quite different despite the similarity in the doping levels.

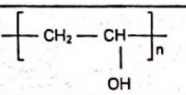
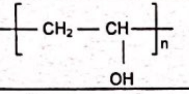
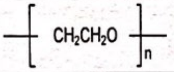
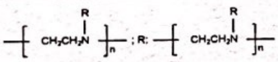
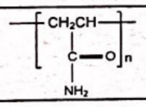
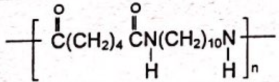
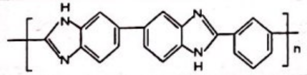
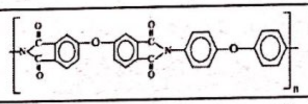
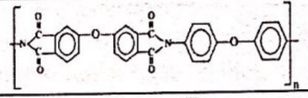
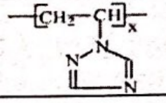
Among all membranes, PA doped PBI has been widely tested in PEMFCs operating at high temperatures (120-200°C) [4,115]. The membrane backbone (PBI) is a basic ((pKa $\approx$ 6)) aromatic and heterocyclic polymer having robust mechanical and chemical stability (does not ignite up to 600°C) within the operating temperature range. It also has a high glass transition temperature (T_g) which is in the range of 425-436°C. The basic nature of PBI enhances the solubility of the acid in polymer, allowing doping levels up to 50 without any adverse effect on the polymer properties [4,115]. PBIs are further stabilized by acid doping, which imparts greater flexibility to PBI films [4,115]. The higher thermal stability of PBI in the membranes after PA doping supports the higher temperature operation in PEMFC without interrupting the proton conductivity. On the other hand, PA (electrolyte) supports the conductivity in less-water situations by formation of hydrogen-bonded network structures. The unusual high conductivity of PA is due to its hydrogen bonded structure, which forms proton transferring chains. This is because acid rather than water is primarily responsible for the proton conductivity, although water can also contribute to the enhancement of proton conductivity. The presence of some molecules of water increases the amount of charge carriers and assist proton conductivity by enhancing acid dissociation, which is achievable independent of external humidification taking place by water diffusion generated at cathode. Hence, PA doped PBI membranes can be operated without humidification of the reactant gases [4, 16, 156, 200]. Table 6 lists molecular structures of some acid/base complex proton conductors and their properties.

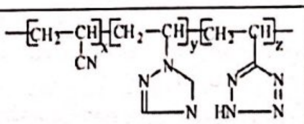
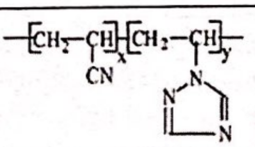
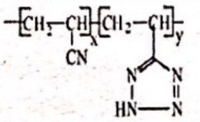
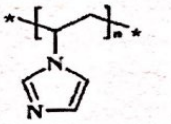
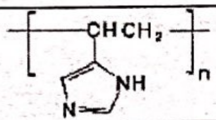
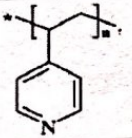
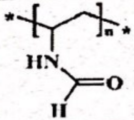
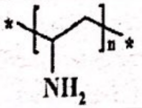
PA doped PBI membrane was first reported by Wainright et al. (1995) (commercial brand name Celtec®) [128]. This membrane showed several advantages over low temperature PEMs e.g., Nafion® as early discussed in this review. Savinell and co-workers were the first to propose PA doped PBI membrane for PEMFC operation at 100-200°C [128]. After being seen as potential alternative membrane material, PA doped PBI membranes were widely investigated by many research groups worldwide [4,128, 200-206].

The most widely studied PBI is the commercial available *m*-PBI; composite membranes with PBI are also reported for use in direct methanol fuel cell (DMFCs). Since PBI polymer is not a proton conductive in its native state, so it was sulfonated prior to blending with Nafion® polymer. Composite membrane thus prepared showed a higher protonic conductivity of 0.032 S/cm as compared to Nafion® which is 0.07 Scm^{-1}. PBI based HT-MEAs (Celtec®) operates at temperatures 120–180°C are especially suitable for reformed-hydrogen based PEMFCs. Membrane decomposition from peroxide can be avoided with HT-PEMs, e.g., Celtec® membranes owing to the higher stability of PBI compared with PFSA membranes and high operating temperature which results in the survival time of H_2O_2 being minimized [4,8,68,128,156].

According to reviews recently published in literature [115], a number of novel materials have been investigated for the purpose of achieving higher conductivities and working temperatures in the membranes for HT-PEMFC. Among all, polybenzimidazoles (PBIs) have been considered as promising host substrate due to their high thermal stability and excellent membrane forming properties. To produce proton-conducting membranes that can operate at temperatures *ca.* 200°C, PBI membranes can be impregnated with variable amounts of PA. Several research groups have studied the use of PBI to develop PA acid-loaded membranes. The obtained membranes have been successfully tested in PEMFC at temperatures up to 200°C using H_2, methanol and propane as fuels. PA doped benzimidazole polymers being better than PBI in term of synthesis have been successfully employed as solid electrolytes in electrochemical super capacitors and sensors [207].

Table 6. Anhydrous proton exchange membranes based on H_3PO_4 blends

Type of Membrane	Polymer Structure	Doping Ratio	Maximum RT Conductivity (S cm^{-1})	Application	References
PVA-H_3PO_4	 $\left[CH_2-\underset{OH}{CH} \right]_n$	-	~ 10^{-5}	Hydrogen sensor	[209]
PEI-H_3PO_4	 $\left[CH_2-\underset{OH}{CH} \right]_n$	0<x<1	~ 10^{-5}	-	[210]
PEO-H_3PO_4	 $\left[CH_2CH_2O \right]_n$	0<x<2	~ 10^{-5}	-	[211]
PVA-H_3PO_4-IPN	-		10^{-4}- 10^{-5}	Hydrogen sensor	[212]
PEO-PMMA-H_3PO_4	-		> 10^{-3}	Fuel cell	[213]
bPEI-H_3PO_4	 $\left[CH_2CH_2\overset{R}{N} \right]_n ; R: \left[CH_2CH_2\overset{R}{N} \right]_n$	0<x<3	10^{-4}	Electrochromic display	[210]
PAAM-H_3PO_4	 $\left[CH_2\underset{\underset{NH_2}{C=O}}{CH} \right]_n$	0.6<x<2	10^{-3}	Electrochromic display	[214]
PAAM-H_3PO_4-MBAA	-		~ 10^{-3}	-	[215]
Nylon 610-H_3PO_4	 $\left[\overset{O}{\overset{\Vert}{C}}(CH_2)_4\overset{O}{\overset{\Vert}{C}}\underset{H}{N}(CH_2)_{10}\underset{H}{N} \right]_n$	0<x<3	~ 10^{-3}	-	[216]
PBI-H_3PO_4		0<x<3	~ 10^{-6}	-	[217], [218]
PI-H_3PO_4		0.5<x<4	10^{-6}	Fuel cell	[219]
PI-H_3PO_4-Im		1<x<4	-	Fuel cell	[220]
PVTr-H_3PO_4		0<x<1	$10^{-5.1}$-$10^{-5.45}$	Fuel cell	[221]

Type of Membrane	Polymer Structure	Doping Ratio	Maximum RT Conductivity (S cm^{-1})	Application	References
(P(VTr-VT-AN))-H_3PO_4		0<x<1	10^{-5}-$10^{-5.75}$	Fuel cell	[221]
(P(VTr-AN))-H_3PO_4		0<x<1	$10^{-5.25}$-$10^{-5.75}$	Fuel cell	[221]
P (VT-AN)-H_3PO_4		0<x<1	8×10^{-2}	Fuel cell	[37,38, 222]
P(1-VIm)-H_3PO_4		0<x<7	10^{-1}-10^{-2}	Fuel cell	[205]
P(4-VIm)-H_3PO_4		0.5<x<2	10^{-1}-10^{-2}	Fuel cell	[38]
P(4-VP)-H_3PO_4		0<x<1	10^{-1}-10^{-2}	Fuel cell	[38]
PNVF-H_3PO_4		0<x<1	10^{-1}-10^{-2}	Fuel cell	[38]
PVAm-H_3PO_4		0<x<1	10^{-1}-10^{-2}	Fuel cell	[38]

PBI doped with PA has been tested and confirmed as an excellent proton conducting membrane for PEMFCs; power density of 250 mWcm^{-2} at 150°C was obtained from membrane electrode assemblies (MEAs) using PA doped PBI with platinum loading of 0.5 mg cm^{-2}, and humidification temperature as low as 48°C for hydrogen and 28°C for oxygen. H_2SO_4 and PA doped PBI MEAs were later prepared by Savadogo and co-workers. These authors reported high performance of of 650 mW cm^{-2} at 185°C at ambient pressure without any specific hydration before measuring the polarization curves. It was suggested that H_2SO_4 doped PBI membranes were better in performance than Nafion® membranes even at temperatures of 50-70°C. Li et al. also reported excellent results independent of gases humidification for PA doped PBI membranes at one atmosphere pressure. Cells were operated and tested using PBI.6.2H_3PO_4 as electrolyte membrane, H_2/O_2 as fuel and oxidant respectively, at temperature up to 190°C, power density of 550 mW cm^{-2} with a current density of 1200 mA cm^{-2} were achieved [208].

Because water produced when protons react with oxygen are enough to keep a good humidification, it has been clearly demonstrated that humidification of reactant gases is not necessary in these types of fuel cells. H_3PO_4 doped PBI membranes perform well and found to be independent of humidification even above 100°C. Conversely, since conductivity of the membrane increases, humidification of the reacting gases can also contribute to increase power. Comparing PBI and poly(2,5-benzimidazole) (BPBI) MEAs (both doped with a similar acid wt %) similar performances in H_2/O_2 were noted for both polymers [4].

Similar acid doping levels and running in test cells under the same conditions ABPBI and PBI achieved similar performances of about 165-175 mW cm^{-2}. Using water-methanol as fuel, and oxygen at ambient pressure in direct methanol fuel cells (DMFCs), acid-doped PBI MEAs yielded power density of ≈ 0.1 W cm^{-2} with current densities of 275-500 mA cm^{-2} at 200°C. PA doped PBI fuel cells have been fuelled mainly by hydrogen, but methanol, ethanol and propanol or even propane have also been found useful as fuel. Performance of PBI and related membranes under different experimental conditions were studied by Benicewicz's group, e.g., doped pyridine containing PBI membrane for hydrogen PEMFC at 120-160°C showed very good performance. Certain valuable long-term durability tests of PBI membranes were carried out using variety of test protocols designed to simulate fuel cell operation conditions, with variable outcome, e.g., PBI membranes in a single cell and a 500 W stack, operated in continuous mode at 0.4 A cm^{-2} and 160°C was studied under simulated reformed H_2 and air. The cell was progressively switched from a cathodic to an anodic mass transfer limited operation, while a single cell's ohmic resistivity in the stack was almost unaffected by 1100 h of ageing. Operating the stack for 658 h, the same behaviour and an additional increase in cell voltage distribution heterogeneity was exhibited. Since post-testing experiments revealed that the platinum content decreased, and also anode electrochemical active area decreased dramatically, this behaviour was thefore not due to the electrolyte membrane. Conversely, at the same operating temperature of 160°C, Benicewitz's group reported a long-term durability study on cells with *p*PBI membranes, finding a cell voltage degradation rate of 4.9 $\mu V\ h^{-1}$ for steady-state operation [4].

PA loss rates were generally low and indicated that long term operation (> 10 000 hours) was possible without significant performance degradation due to H_3PO_4 loss from the membrane. *In situ* electrochemical impedance spectroscopy (EIS) was used to show that PBI/PA membrane fuel cells exhibit very good performance in the temperature range of 160–180°C with an ohmic resistance similar to that of Nafion®. On the other hand, EIS indicates a significant loss of catalyst activity and increase in mass transport resistance due to relatively high potential at open circuit voltage (OCV). Moreover, electrochemical hydrogen pumping capability using a high-temperature (> 100°C) polybenzimidazole (PBI) membrane was demonstrated with and without humidification at ambient pressures with tests for nearly 4000 h. Continuous aging tests for 600 h at constant discharge current (640 mA cm^{-2}) were performed on PBI/PA high-temperature PEMFC in order to establish factors limiting long-term durability. At elevated temperature, even at 200°C, PA doped PBI membrane possess good performance. Also, lifetime of 3500 and 500 h at 120 and 150°C have been reported for PA doped PBI based PEMFCs under continuous operation [4, 5].

It was recently reported that similar to phosphoric acid fuel cell (PAFC), the performance degradation of PA-PBI based HT-PEMFCs mainly comes from the platinum catalyst aggregation which may be possibly due to the dissolution and re-deposition of platinum particles in PA at high temperature and migration of platinum crystallites on the carbon support. Also, cell performance may be gradually lowered due to leaching of PA from the electrodes and electrolyte layers; in the cathode side, liquid water may be produced at atmospheric pressure when the operating temperature is lower than 100°C. Thus, the PA-PBI based HT-PEMFCs are still problematic for automobile applications which require multiple thermal cycles with frequent restart and shutdown [5].

In a study by Hu et al. the performance of PA-doped polybenzimidazole with electrodes bound by PBI ionomer in a PEMFC operated for 500 h at 150°C, using H_2 and O_2 at a constant load of 640 $mAcm^{-2}$ and measurements taken every 24 hours was evaluated. The performance decreases linearly after the first 100 h at a rate of 150 mVh^{-1} [223] when cell voltage was 0.58 V. The degradation mechanism of this membrane was investigated by Zhai et al. through performing a test for 550 h. The first 500 h was made in a continuous operation at 640 $mAcm^{-2}$, whereas the last 50 h was discrete operation with shutoffs every 12 h [224].

3.4.3. Radiation Grafted and Acid Doped Membranes

Preparation of high temperature proton exchange membranes (HT-PEMs) using radiation-induced graft copolymerization method followed by acid doping is an alternative promising method for achieving stable membranes. Particularly, radiation induced grafting of heterocyclic monomers such as 1-vinylimidazole (1-VIm) and 4-vinyl pyridine (4-VP), vinylamine, and allylamine onto partially fluorinated (e.g., copolymer ethylene-tetrafluoroethylene, ETFE) or fully fluorinated (copolymer tetrafluoroethylene and hexafluoropropylene, FEP) base films provide weak basic ready-made precursors that can be doped with acids such as H_3PO_4. A mechanism for preparation of PEM by radiation induced grafting of poly (4-VP) onto ETFE films followed by phosphoric acid doping is shown in Figure 4.

Various radiation-grafted and acid doped membranes were reported in the literature. Schmidt et al. reported preparation of phosphoric acid doped membranes obtained by radiation induced grafting of poly (4-VP), poly (vinylamine) and poly (1-VIm) onto ETFE films followed by PA doping at 100°C for at least 2 h [38]. This led to composite material 80 wt % of acid, having reasonable thermal and mechanical stability (160°C in air). The membranes showed specific proton conductivities in the range of 20-100 $mScm^{-1}$ at 120°C without humidification. The membrane delivered power densities up to a 150 $mWcm^{-2}$ without humidification when testing in PEMFC at 120°C, which is comparable with H_3PO_4 doped PBI membranes [38].

Similar membranes prepared by radiation induced grafting of 1-vinylimidazole and 4-vinylpyridine onto ETFE film also showed comparable results. The membranes achieved proton conductivity with 10^{-2} Scm^{-1} magnitude at 34 and 49% grafting levels at room temperature without humidification [36]. This method proved to be simpler and has fewer problems than methods involve synthesis by polymerization reactions for obtaining similar membranes [2,36].

A summary of other acid doped radiation grafted membranes is given below:

1. Poly (2-VP) and poly(4-VP)-*graft*-poly(vinylidine fluoride) copolymers and their pH-sensitive microfiltration membranes. [225]
2. ETFE-*g*-poly(4-VP), ETFE-*g*-poly(1-VIm) and ETFE-*g*-poly(vinyl amine) obtained after hydrolysis of ETFE-g-poly(*N*-vinyl formamide) membranes. [37,38]

3. ETFE-*g*-poly(N-vinyl-2-pyrrolidone), ETFE-*g*-poly(2-VP) and ETFE-*g*-poly(4-VP).[226]

3.5. Disadvantages of Using Phosphoric Acid Composite Membranes for High Temperature Proton Exchange Membrane Fuel Cell Applications

A number of problems linked to development of reliable PA-doped PBI membranes were encountered. This includes leaching of acid from the membranes leading to phosphate anions migration to the cathode and their adsorption on the catalyst and amorphous carbon particles. Consequently, the corrosion rate increases and eventually the degradation of membrane/electrode assembly is accelerated leading to a drastic drop in the performance [156].

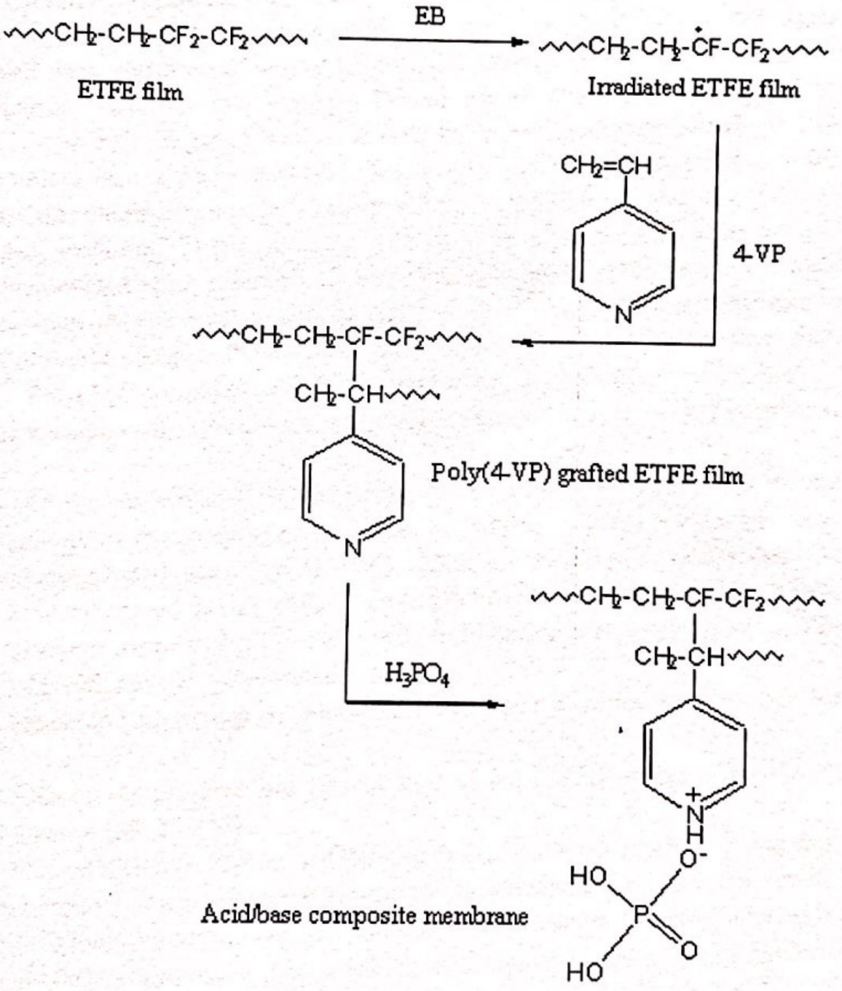


Figure 4. Plausible mechanism of preparation of phosphoric acid doped poly(4-vinylpyridine) grafted ETFE membrane.

Another disadvantage of PA-doped PBI membranes is that when PA is mixed with PBIs, the ionic conductivity decreases with the increase in the polymer content. The presence of water produced at the cathode assists and increases its proton conductivity despite the possible loss of water as a result of dehydration of PA at high temperatures [4,19,25,107,227]. To overcome the problems associated with PA-doped PBI membranes, novel acid-base complexes are being investigated, taking into consideration the use of other polymers apart from PBI or doping with non-volatile acid and liquids different from PA [25].

3.6. Alternative Membranes Based on Benzimidazole Derivatives

Apart from *m*-PBI, other PBI derivative polymers were found suitable for preparation of proton conducting membranes for PEMFCs after doping with acids. Polybenzimidazoles based on 3,3′-diaminobenzidine (DAB) and 5-tert-butyl isophthalic acid (tBIPA) or 4,4′-(hexafluoroisopropylidene)bis(benzoic acid) (BIS-B-AF) membrane possess better combination of physical and gas permeation properties compared to the PBI based on isophthalic acid. From synthesis of three different PBIs having same PA loading, conductivity of the different polymers was found similar. Doping two homologous polymers: sulfonated and non-sulfonated with the same amount of acid, the sulfonated membrane showed higher conductivity. Also, among many possible PBIs, a very promising material is ABPBI. PA doped ABPBI was studied by several workers and they all found out that ABPBI has some merits over PBI including: 1) ABPBI absorbs much more acid than PBI when treated with identical concentrations of PA solutions, 2) ABPBI membranes have the same performance as PBI under the same experimental conditions and 3) ABPBI can be produced easily and more safely from a single cheap monomer and apart from ABPBI, other A-B type PBIs are possible. Poly[2,(4′-oxyphenylene)-5-benzimidazole] (PPOBI) obtained by homopolycondensation of 3, 4-diamino-4′-carboxydiphenyl oxide was studied recently [4,228,229].

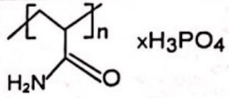
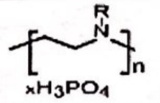
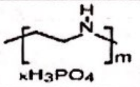
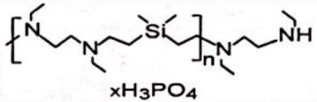
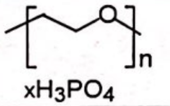
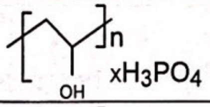
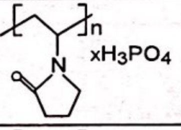
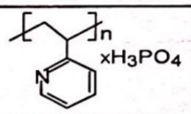
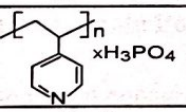
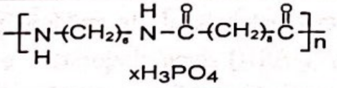
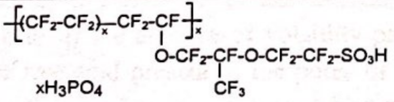
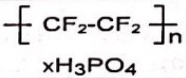
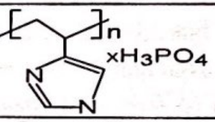
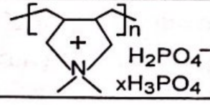
To improve the performance of membranes based PBI or its derivatives in terms of proton conductivity of the complex and mechanical stability, various approaches have been attempted including functionalization of mPBI, [230], use of inorganic additives [148, 231-233], polymer blending and doping with different electrolytes [18,234-238]. The synthesis of PBIs with different structures [239-244] and optimization of preparing and operating parameters [245-255] have also been attempted.

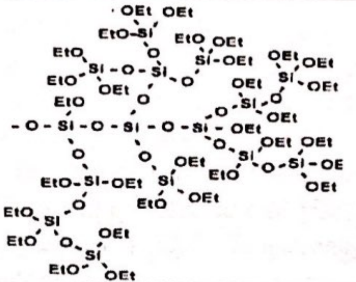
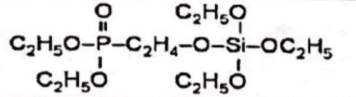
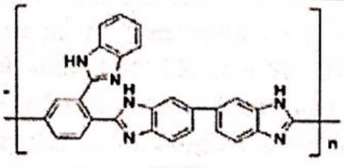
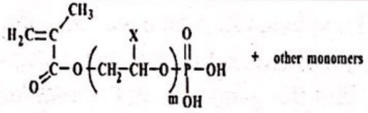
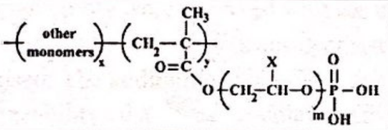
The structure and properties of alternative PA doped polymer matrices are listed in Table 7.

More details on the progress and present state of the PA/PBI complex for HT-PEMFC have been published [30, 35,256].

Among various methods, doping of PBI with hexafluoroisopropylidene group was found to remarkably improve the membrane performance. A membrane with high PA doping levels as high as 30–40 molecules/repeating unit showed tensile strength and elongation at break of >0.8 MPa and 100%, respectively. The membrane also demonstrated a proton conductivity of 0.09 S cm^{-1} at 180°C under anhydrous conditions. The power density of PEMFC with this membrane achieved 430 $mWcm^{-2}$ at 1 Acm^{-2} at 160°C and atmospheric pressure with CO tolerance up to 0.2% at 160°C [257].

Table 7. Different PA blended polymers (other than PBI and APBI)

Polymer	Structure	xH_3PO_4	σ (S cm^{-1})	T(°C)	References
PAAM		2.4	1.1 x 10^{-2}	20	[214]
PEI		0.7	3.4 x 10^{-5}	100	[258]
BPEI		3.0	10^{-4}	50	[210]
		1.5	1.3 x 10^{-2}	100	[258]
PSA		0.8	10^{-5}	160	[259]
PEO		0.42	3 x 10^{-5}	27	[258]
PVA		0-0.77	10^{-9}-5×10^{-3}	30	[260]
		0.26	10^{-5}	27	[258]
PVP		2	3 x 10^{-6}	27	[258]
P2VP		2	10^{-4}	27	[258]
P4VP		2	5.8 x10^{-3}	100	[258]
Nylon 6-10		2-2.5	10^{-4}-10^{-3}	25	[216]
Nafion® 117		5/SO_3^-	0.02	175	[261]
Teflon®		50 wt %	3-4 x 10^{-3}	100	[262]
P4VI		2	10^{-4}	RT	[186,205, 263]
PAMA		2	10^{-2}	100	[264]

Polymer	Structure	xH_3PO_4	σ (S cm^{-1})	T (°C)	References
HPEOS		0.35	0.033	160	[265]
DEPETEOS	 $C_2H_5O-\overset{O}{\underset{C_2H_5O}{P}}-C_2H_4-O-\overset{C_2H_5O}{\underset{C_2H_5O}{Si}}-OC_2H_5$	0.35	0.033	160	[265]
BI*p*PBI	 BI*p*PBI	0.81	0.16	180	[266]
P-PHMhom		3.1	5x10^{-3}	100	[129]
P-PHMcop		3.1	5x10^{-3}	100	[129]

3.7. Alternative Benzimidazole Polymers Doped with Heteropoly Acids

One way to increase proton conductivity and thermal stability of PEMs is to overcome the PA leaching problem at elevated temperatures through the addition of solid inorganic proton donors i.e., heteropoly acids (HPAs), which are subset of polyoxometalates that are widely studied as dopants. HPAs are interesting for preparation of proton conducting membrane due to: i) the absence of volatility problem, ii) proton conduction through self-dissociation of free acid present in the pores of composite membrane, iii) possibility for a reduction in the fuel crossover challenge and iv) aiding of water retention [43]. HPAs possess the highest proton conductivity among inorganic solids at temperatures near ambient, which is in the range of 0.1-0.2 Scm^{-1}. HPAs have Keggin structures, which are unique and demonstrate activity as in both acidic and redox forms [8,33,267]. HPAs also have hydrogen-bonded hydration water network and have been long characterized as solid acids [4,8,60,207]. For example, silicotungstic acid (SiWA) is very strong as sulfuric acid and can replace it as an acid catalyst. The Keggin structure of SiWA allows molecules to hydrate and dehydrate without much significant structural changes and the molecules is thermally stable in the solid state for use in vapour phase reactions at high temperatures 400-500°C [268]. In summary, the incorporation of inorganic proton donors into the polymer electrolyte matrix enhances the properties of the obtained PEMs such as proton conductivity and thermal stability.

Various studies reported the use of HPAs as dopants for sulfonated and chitosan based membranes on frequent occasions. Zaidi et al. used the casting method to prepare composite membranes from HPAs such as H_3 $[Pmo_{12}O_{40}].29H_2O$ (PMoA), H_3 $[PW_{12}O_{40}].nH_2O$ (PWA) and poly (ether ether ketone) (PEEK), achieving conductivities up to 10^{-2} S cm^{-1} at ambient temperature and 10^{-1} S cm^{-1} above 100°C [71]. Phosphotungstic (PWA) $[H_3PW_{12}O_{40}\,29H_2O]$ and silicotungstic/acids (H_3 $[PW_{12}O_{40}]$, SiTA) were studied as dopants in PBI/PWA–SiO_2 and PBI/SiTA–SiO_2 membranes [4, 25]. Other HPAs include phosphomolybdic acid (PMA) $[H_3Pmo_{12}O_{40}$ $29H_20]$; silicomolybdic acid $[SiMo_{12}O_{40}]$; disodium salt of tungstophosphoric acid (Na-TPA) $[Na_2\text{-}H_3PW_{12}O_{40}]$; Tungstoarsenate (iii) acids (TAA) are also available. However, the molecular nature of HPAs cluster species makes them soluble in many common solvents including water, which restrict their use as dopants in PEMs for fuel cells [5, 18, 25, 60,200, 207].

To overcome the soluble nature, HPAs are incorporated with other hygroscopic proton conducting fillers in the membranes using various combinations. Nunes et al. prepared composite membranes of SPEEK/Zr or SiO_2 NPCs doped with different HPAs such as TPA and MoPA. It was found that the bleeding-out of the HPAs markedly reduced by adsorption of the HPA particles to the inorganic nanoparticles, water and MeOH permeability of the membranes significantly reduced compared to the pure SPEEK membrane [79].

In organic matrices such as sulfonated poly(ether ketone) (SPEK) and SPEEK, different HPAs and inorganic networks of ZrO_2, SiO_2, TiO_2 and $RsiO_{3/2}$ can be used to produce composite membranes. For example, 60-fold reduction in methanol flux and 13-folds reduction in conductivity were observed with the incorporation of ZrO_2. A 40-fold decrease in water permeability without a significant decrease in the proton conductivity was observed when SiO_2 is used. The addition of SiO_2/ZrO_2 resulted in a decrease in the water content and methanol permeability that was coupled with a reduction in the leaching of HPA. Furthermore, membranes containing tungstophosphoric acid (TPA) exhibited high conductivity values [8,146].

Kerres et al. immobilized TPA and MoPA in acid-base blend membranes from (SPEEK) and PBI. Membranes with superior proton conductivities to Nafion® were obtained. It was found that the bleeding-out of MoPA from acid-base blend membranes was much higher than the bleeding-out of TPA by aqueous membrane post-treatment.

Composite polymer membranes based on sPSU containing BIzD and TPA was prepared and characterized by Tan et al. The washing-out of the TPA markedly reduced by addition of the BIzD compounds [200].

Sulfonated poly(arylene ether sulfone) (sPSU) composite membrane showed reasonable bleeding-out of HPAs, the membrane polymer matrix together with an excellent thermal stability and good proton conductivities especially at elevated temperatures (about 300°C). The membrane also showed a much higher water retention capacity at 100-280°C than the pure sulfonated copolymer [269].Similar composite membrane based on HPAs/sPSU was tested in DMFCs [269]. The membrane showed reasonable bleeding-out of HPAs from the polymer matrix, excellent thermal stability, good proton conductivities (especially at 300°C) and higher water retention within 100-280°C than the pure sulfonated copolymers [8]. Novel poly (vinyl alcohol) (PVA) embedded with PTA was also reported in the literature [202]. In another study, HPAs was immobilized in membranes based on cheap polycationic-biopolymer such as chitosan. This introduced strong electrostatic interactions between chitosan (polycations) and HPAs (polyanions) forming insoluble polyelectrolytes (anions and cations) complexes. This prevents HPAs from dissolving in water and leak out during cell operation, ultimately resulting in degradation in performance [60].

A series of composite membranes based on SPEEK with embedded HPAs were investigated for electrochemical and thermal properties. The introduction of these fillers resulted in increased *Tg* and brought about substantial gain in proton conductivity. The conductivity of the composite membranes exceeded 10–^{2} Scm^{-1} at room temperature and reached a value of about 10–^{1} Scm^{-1} above 100°C [71]. Nafion-silica composite membranes doped with phosphotungstic acid (PTA) and SiWA showed better performance at high temperatures for DMFC operations (about 145°C) together with improved kinetics for methanol oxidation reaction. The ionic conductivities of the composite membranes prepared from Nafion® and HPAs SiWA, PTA and PMA) were higher than those of pure Nafion® membranes [8]. Based on the aforementioned studies, combination of PMA/PTA is considered to be the best dopant for PEMs [60, 71,270,271].

3.8. Membrane Impregnated with Ionic Liquids

One promising approach to increase the operating temperature of PEMs is to use ionic liquids (ILs) as anhydrous proton conductor's carriers for proton transport [272-274]. ILs are molten salts at ambient temperature having unique properties that can be adjusted via chemical alteration of the cation or anion to produce application specific compounds. Cation and/or anion can be functionalized and this changes properties such as hydrophobicity/ hydrophilicity and specific chemical interactions.

ILs which consist of a combination of Brönsted acids and bases that form hydrogen bonds and act as proton carriers have been considered effective proton transfer carrier for HT-PEMFC. They have unique properties such as high proton conductivity (1 x 10^{-2} Scm^{-1} at 160°C), high thermal and chemical stability. They are also non-volatile, non-flammable and have high viscosity.

Protic ILs was experimentally proven to have high proton conductivity when loaded on a membrane in a PEMFC operated at dry conditions. It has excellent thermal and chemical stability, wide electrochemical stability windows, exceptionally high ability to form hydrogen bonds, negligible vapour pressure and wide operating temperature range. Thus, protic ILs can be used as new electrolytes by doping with ionomeric polymers such as Nafion for PEMFC operating above 100°C [10,18,25,62,82,274-282].

Membranes loaded with protic ILs may be (i) membranes with adsorbed ILs and (ii) membrane with covalently or electrostatically bounded ions. Imidazolium, which exists as a liquid at extremely low temperatures is used most frequently as ILs' cations,whereas tetrafluoroborate, hexafluorophosphate, and trifluoromethane sulfamide are used as ILs'anions. For example the combination of 1-ethyl-3-methyl imidazolium cation and N,N-bis(trifluoromethane) sulfamide anion provides a fluid with ionic conductivity despite presence of week interactions. Moreover, ILs such as 1-*n*-butyl-3-methylimidazolium hexafluorophosphate([Bmim]PF$_6$),1-*n*-butyl-3-methylimidazolium tetrafluoroborate([Bmim]BF$_4$),Diethylmethylammonium trifluoromethanesulfonate ([Dema]Tfo), 2,3-dimethyl-1-octylimidazolium triflate ([Dmoim]Tf), and 1-ethyl-3-methylimidazolium hydrogen sulfate ([Emim]H$_2$PO$_4$) were reported to be promising candidates for application in proton conducting membranes that can be used in PEMFC at high temperature without humidification [275, 277, 280-282].

Various studies were carried out on composite membranes loaded with ILs for HT-PEMFC, majority of such studies performed in the laboratories of Watanabe [283-285] and Angell [286-288]. Details of data on ILs based membranes were gathered and published in the review by Greaves et al. [289]. Particularly, Ye et al. proposed [Bmim] H_2PO_4 as an electrolyte for PEMFC [18], [Bmim]BF_4 and [Bmim]PF_6 for commercial alkaline fuel cell [290]. Membranes containing 2,3-dimethyl-1-octylimidazolium triflate ([Dmoim]Tf) was synthesized and tested in a single fuel cell at 100°C and a power density of 1 mW.cm^{-2} was obtained, but no fuel cell test at temperature higher than 140°C was conducted [291]. Lee et al. tested the potential of [Dema]Tfo as an electrolyte in PEMFC and a power density of 100 mw.cm^{-2} was obtained at 80°C [292]. However, majority of such studies either provided no or low temperature PEMFC test results. Other reports such as the study carried out by Gao et al. provided PEMFC test at 120°C and 168°C using [Emim] H_2PO_4 membrane as an electrolyte [293,294]. Nevertheless, no practical proton conducting membranes based on protic ILs for PEMFCs have been reported, despite the presence of reports on testing some of these membranes on laboratory scale directly as non-volatile electrolyte to replace water in Nafion® membrane for HT-PEMFC under anhydrous conditions. Moreover, majority of the research on ILs was limited to a relatively small group of salts, typically with cations containing saturated hydrocarbon substituent [18,295-297].

3.9. Summary of Membranes Obtained by Modification of Sulfonic Acid Ionomers

Nafion membranes are the most widely investigated membranes (among perfluorosulfonic acid membranes) in PEMFC operating below 100°C. However, such membranes were found to be unsuitable and showed low conductivity mostly caused by the water loss in addition to high fuel crossover when PEMFC operating temperature is raised above 90°C. Thus, extensive efforts have been exerted to modify Nafion and its alternative PFSA membranes to sustain the high-temperature operation in PEMFC. To achieve such objective, various research approaches have been adopted including (a) replacement of water with non-aqueous and non- or low-volatile solvents, (b) improvement of water management, which simplifies the operation at high temperature, to understand this approach, one should bear in mind that the water balance in a PEMFC involves the following mechanisms: (1) water supply from the fuel and oxidant (humidification); (2) water produced at the cathode (current density); (3) water drag from the anode to the cathode (current density, humidity, temperature); and (4) back-diffusion of water from the cathode to the anode (concentration gradient and capillary forces) [298], and (c) modification of Nafion using different materials, processes and techniques. Particularly, modification of such membranes followed three approaches to achieve low humidification operation at high temperatures (above 100°C). This includes the use of : i) thinner membranes, which improves water management during PEMFC operation, reduces the cost of materials and lowers the internal resistance, (ii) pore filled (composite) perfluorosulfonic acid membranes with reinforcement micro PTFE fibrils or porous ETFE sheets to overcome the reduction of mechanical strength and the increase in swelling of very thin Nafion membranes at higher temperatures in addition to cost reduction

[115], for example, Nafion membranes of 5-30 μm thickness possessing excellent proton conductivity and mechanical properties have been produced using reinforcement. Such thin membranes have improved conductivity and water management through effective back-diffusion of water from cathode to anode [115], (iii) forming composites with solid organic proton conductors and vi) Forming composites with hygroscopic oxides. The latter class of membranes was discussed in details under the class of composite membranes. Nafion membranes modified by blending Nafion solution with organic polymer solutions are mostly subjected to phase separation problems caused by the difference in the nature of the two polymers. [299,300]. To overcome such problems, Nafion is blended with PBI and doped with PA leading to a 55% increase in the stability compared to PA doped PBI at 150°C without humidification [299].

A summary of studies on various modified PFSA membranes and their analogous alternative materials are given below:

1. Recasting of a blend of Nafion solution with sulfonated FEP powder [301].
2. Incorporating bi-functional particles such zirconium phosphate and HPA in the PFSA membranes both of which are hydrophilic and proton conductors. The decrease of the chemical potential of the water inside the membrane leads to an additional proton conduction pathway creation, hydrogen-bonding sites provision for water in the membrane in order that membrane hydration to be increased coupled with a reduction in proton transport and water evaporation resulted from the presence of hydrophilic inorganic additives. Low humidification and high temperature operation of both H_2/O_2 (air) and DMFC fuel cells were enabled by water retention enhancement [115].
3. Modification of PFSA (Nafion®) membranes with different organic and inorganic materials [115].
4. Modification of PFSA (Nafion®) membranes, by incorporating hygroscopic oxides and solid inorganic proton conductors [62,131,132].
5. Modification of Nafion® membranes with plasma etching and palladium sputtering processes leading to some merits including increased in the roughness of the membrane surface, decreased methanol permeation and improved open circuit voltages and current-voltage performance of the fuel cells [61].
6. Modification of Nafion membranes with inorganic conductors/fillers to enhance water retention within the membrane such as zirconium phosphate, zirconium oxide, silicon oxide [62,131,132].
7. Using a polymer matrix containing ILs) and Nafion [302,303], ILs and PBI-H_3PO_4 [18], protic IL and poly(styrene-*co*-acrylonitrile) [P(St-*co*-AN)] [273,278], ILs and polyethylene oxide (PEO) [276], protic IL and sulfonated polyimide [292], ILs and poly(vinylidenfluoride-co-hexafluoropropylene) (PVDF-*co*-HFP) [279].
8. Loading of Nafion with less water dependent proton conductors such as PA, N-heterocyclic monomers (HPAs) [18].
9. Combining ILs with Nafion® 117 membranes reinforced with sulfonated multifunctional polyhedral oligomeric silsesquioxanes [302].
10. Impregnation of ILs impregnated SPEEK membranes obtained casting process [62].
11. Sulfonation of poly-[(1-(4, 4'-diphenylether)-5-oxybenzimidazole)-benzimidazole] (PBI-OO) membrane [62].

12. Formation of organic/inorganic composite materials based on poly ethylene glycol (PEG)/SiO_2 [19].
13. Combination of 4-dodecylbenzene sulfonic acid (DBSA)/SiO_2 acidic moieties [304].
14. Formation SPEK/SPSU/ ortho-sulfone aminated polysulfone [PSU $(NH_2)_2$/P (4-VP)] and PBI composite membranes [304].
15. SPEEK modified silica and SPEEK modified zirconium phosphate [305,306].

4. PROTON CONDUCTION MECHANISM IN HIGH TEMPERATURE PROTON CONDUCTING MEMBRANE

Several membranes were developed for PEMFC at high temperatures. Membranes based on PA-acid-doped PBI, hybrid Nafion® and SPEEK with incorporated zirconium phosphate (ZrP) are among the widely investigated membranes. Particularly, in PA-doped PBI, the acid molecule is immobilized by protonating a benzimidazole ring and free acid is yielded from further addition of acid, which can be washed by water. The proton conductivity mechanism of PA-doped PBI occurs mainly by Grotthus mechanism especially at temperatures above 100°C. The proton transfer occurs by hopping following the order: acid–acid, acid–water, or acid–benzimidazole ring as also shown in equations 1-4 [4].

$$H_3PO_4\ (H_2PO_4^-)...H{-}O{-}H > H_3PO_4...H_2PO_4^- \tag{1}$$

$$> N{-}H^+ ...H_2PO_4^- \tag{2}$$

$$> N{-}H + ...H{-}O{-}H \tag{3}$$

$$> N{-}H + ...N{-}H \tag{4}$$

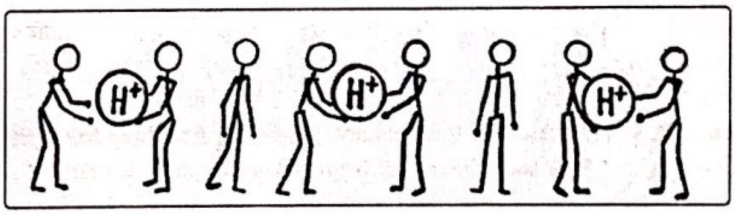
Such conductivity mechanism allows these membranes to operate at temperatures as high as 200°C without humidification. The membranes are only hydrated by water produced in the cathode of PEMFC. The nuclear magnetic resonance (NMR) studies showed that phosphate anion activities added to the wide-distance of proton movements, but polymeric movement is not a contributing factor. This indicates that the mobile or free acids between polymers chains are the major conductivity-contributing factor. PBI and its other derivatives can be doped with various inorganic acids (H_2SO_4, H_3PO_4, HCl, HBr, CH_3SO_3H, $CH_3CH_2SO_3H$, HPAs, PILs) due to the basic nature of PBI ring (pK_a = □5.5). Such acids are responsible for providing good proton conductivity to the membrane and the order of conductivity is given after immersion of PBI membranes in different concentrated acids for ten days in the sequence: $H_2SO_4 > H_3PO_4 > HNO_3 > HClO_4 > HCl$ [4].

Conductivity values achieved for each acid are detailed elsewhere in the literature [4]. Though the use of sulfuric acid leads to a maximum conductivity; PA remains the preferred choice. Generally, the conductivity depends on the quantity of the acid present in the membrane, as the acid content increases the conductivity increases until a maximum conductivity in dry PA doped PBI membrane comparable with pure acid itself is obtained. Activation energy (E_a) decrement with the amount of water present in pure PA, PA doped

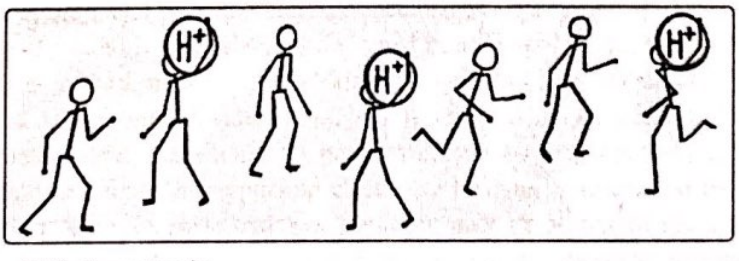
PBI or PA doped ABPBI is important; humidification increases conductivity of PA doped membrane. Variation of the temperature with conductivity is also a very relevant factor. The conductivity increases with temperature at low relative humidity up to 180-200°C for membranes based on PBI and ABPBI. Temperature, humidity, the nature of nano-impregnating acid, time of immersion in the acid bath and method used for the preparation of membrane all affect conductivity of the membrane, PBI prepared by doping in acid baths at room temperature does not produce dehydration [4,122,134].

On the other hand, proton transfer in composite perfluorinated sulfonic acid membranes can occur by two main mechanisms, the proton solvated by water molecules moves by (vehicle mechanism) and diffuses through the membrane dragged by a ''vehicle'' which is H_3O^+ when the membrane is hydrated. These carriers diffuse through the membrane due to its microstructure. The second mechanism based on the transfer of protons from a water molecule to another (Grotthus or hopping mechanism) is faster. Through deprotonation-protonation processes which strongly depend on the mobility, number and structure of these proton acceptor and donor sites in the membranes proton hopping is often realized in Grotthus mechanism. A sketch representing the two mechanisms of proton conduction in the membranes is given in Figure 5.

Under anhydrous conditions, PA doped PBI membranes exhibit proton conduction at temperatures up to 200°C, although water is not required, some level of humidity is beneficial. Water prevents condensation of PA at temperatures above 100°C and can further increase the proton conductivity. However, the proton transport mechanism is not yet fully understood, but it is thought to be similar to proton conduction in pure PA, since it has been shown that interactions with PBI have little effect on the proton conductivity; as the amount of imbibed PA increases, the conductivity approaches a mechanism similar to that of pure phosphoric acid [4].



Grotthus/hopping mechansim



Vehicular mechansim

Figure 5. Sketch representing mechanisms of proton conduction in high temperature proton conducting membranes.

CONCLUSION AND PROSPECTIVES

Operating PEMFC at temperatures above 100°C is highly desired to overcome the technical challenges associated with low temperature operation and increase the efficiency. This require proton conducting membranes that can be used at elevated temperatures up to 200°C. Various methods involving different membrane formulation routes have been investigated. Among alternative materials, composite membranes incorporating solid proton conductors are important class of materials that have widely tested for HT-PEMFC. The development of such composite membranes follows three approaches involving; 1) introducing inorganic filters to improve water retention capacity of PFSA membranes at elevated temperatures, 2) modification with water-independent solid proton conductors such as ZrP and 3) replacement of water with non-volatile solvents that possess higher boiling points such as PA, heteropolyacids, N-heterocycles or ionic liquids. The proton conductivity was further enhanced by introducing nano-sized proton conductor fillers which enhanced compatibility and reduced water dependency. However, majority of the composite HT-PEMFC membranes have relatively low conductivity and lose water at high temperatures with only few of them showed sufficient proton conductivity comparable to fully hydrated Nafion membranes.

Of all composite materials, membranes involving acid/base complex formation have been subjected to intensive investigations. Particularly, PA acid-doped PBI membranes are the most successful materials for high temperature PEMFC operating preferably under ambient pressure that reached commercialization. These membranes have been well-characterized and found to meet properties required for HT-PEMFC. The early generation of these membranes were challenged by PA leaching and polymer degradation at high temperatures. However, the later generation of PA doped membranes showed an improved performance by increasing ionic conductivity and stability using substituted PBI materials.

Other membranes that have received wide attention are modified PFSA membranes, which have been successfully operated at temperatures up to 120°C under ambient pressure and up to 150°C under pressures of 3-5 atm. Alternative sulfonated hydrocarbons and their inorganic composites exhibited promising conductivity and thermal stability at temperatures above 100°C. More evaluation is needed for these membranes to determine their life time in high temperature PEMFC.

Despite the immense efforts exerted to develop HT-PEMFC membrane materials, the performance of the majority of the obtained membranes is far from satisfaction. There are several necessary strategies that should be adopted to minimize the challenges and speed up the development of such membranes by taking many of them from laboratory scale to pilot production. These strategies include: 1) design polymers to control structure and morphology in order to manipulate interactions, 2) perform systematic investigation on all types of membranes and determine their optimum electrolyte loading 3) understand the interactions between loading fillers (proton conductors) and the polymer matrix of the membranes, 4) perform rigorous PEMFC test at elevated temperature under dynamic conditions without additional humidification, 5) conduct long term stability tests to establish suitability of the chemical, thermal and mechanical stability of the membranes, 6) compare the obtained results with the corresponding established membranes, develop protocols for making MEA suitable for different PEMFC applications (stationary, portable and automotive) and 7) adopt short and cost-effective procedures to keep membranes attractive. Finally, it worth mentioning that there is no single type of membrane that can meet the requirements of HT-PEMFC for all automotive and stationary applications and this is due to complexity of the operating conditions in each case.

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