Chapter 9
Organic/Inorganic and Sulfated Zirconia Nanocomposite Membranes for Proton-Exchange Membrane Fuel Cells

Sharf Ilahi Siddiqui and Saif Ali Chaudhry

Abstract Proton-exchange membrane fuel cells (PEMFCs) are one of the most promising commercial technologies used to produce clean energy with high efficiency, energy density, and low emission of harmful gases. Proton-exchange membrane (PEM) is a major part of fuel cell that plays an important role. However, these membranes are very expensive, thermally degradable at high temperature, and conduct protons only in aqueous condition that limits the performance of PEMFC. However, at lower operating temperature, the performance of fuel cell is affected, due to slow electrode kinetics. Recently, great attention has been paid to develop high temperature-tolerant PEM with high proton conductivity. The organic–inorganic composite PEM that can work at high temperature with high proton conductivity is being developed. These organic–inorganic membranes are created by incorporation of metal oxide nanoparticles in the polymer host such as Nafion with strong acid site. These membranes provide high proton conductivity, and chemical and thermal stability to PEMs. Sulfated zirconia (S–ZrO_2), a strongest super acid possessing protogenic groups, is being used as an inorganic filler for composite membranes which showed improved operation at elevated temperature. This chapter presents an overview of the commonly used polymer hosts and inorganic additives. The available literature on S–ZrO_2 nanohybrid membrane technology has been discussed in view of catalyzing the future research to develop more suitable PEM for fuel cell.

Keywords Fuel cells · Proton-exchange membrane · Perfluorinated sulfonic acid membrane · Organic/inorganic hybrid nanocomposite · Sulfated metal oxide · Sulfated metal oxide-doped membrane · Sulfated zirconia/polymer hybrid membrane

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S.I. Siddiqui · S.A. Chaudhry (✉)
Department of Chemistry, Faculty of Natural Science, Jamia Millia Islamia,
New Delhi 110025, India
e-mail: saifchaudhry09@gmail.com

S.I. Siddiqui
e-mail: sharf_9793@rediffmail.com

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Abbreviation

C-PAMPS	Cross-linked poly 2-acrylamido-2-methylpropane-sulfonic acid
NMPA	Nitrilotrimethyl triphosphonic acid
PBI	Polybenzimidazol
PDMS	Polydimethylsiloxane
PVA	Polyvinyl alcohol
PVPA	Polyvinylphosphonic acid
PWA	Phosphotungstic acid
S-CNT	Sulfated carbon nanotubes
SHNTs	Sulfonated halloysite nanotubes
SPAES	Sulfonated polyarylene ether sulfone
SPEEK	Sulfonated polyether ether ketone
SPES	Sulfonated polyether sulfone
SPSU	Sulfonated polysulfone
SSA	Sulfosuccinic acid
ZrP	Zirconium phosphate

1 Introduction

Proton-exchange membrane (PEM) is a major part of fuel cell system that plays an important role in the production of clean and efficient electricity [1, 2]. Fuel cells are electrochemical system in which, through electrochemical reaction with an oxidant, the chemical energy of fuel is converted into electrical energy without combustion (Fig. 1). Therefore, in the fuel cell system, production of electricity occurs [3]. Fuel cells are assembly of different parts; in which central part, where electrochemical processes take place, is most important and it contains the two sub parts namely electro catalyst and membrane. The central part is also known as separation part which acts as sandwich in between two electrodes, i.e., anode and cathode [4]. A schematic diagram of fuel cell is shown in Fig. 2. During electrochemical process, ions generated at anode move towards the cathode through the electrolyte membrane and produce water and heat with free electrons. Varieties of

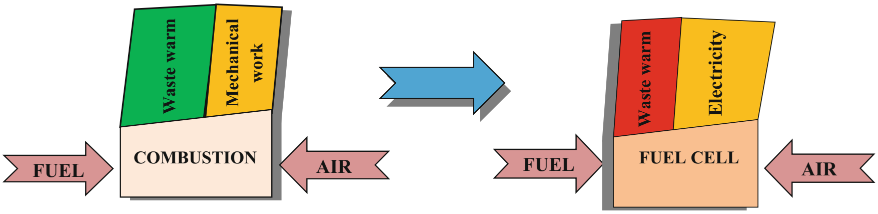

Fig. 1 Advantages of fuel cell reaction over combustion reaction

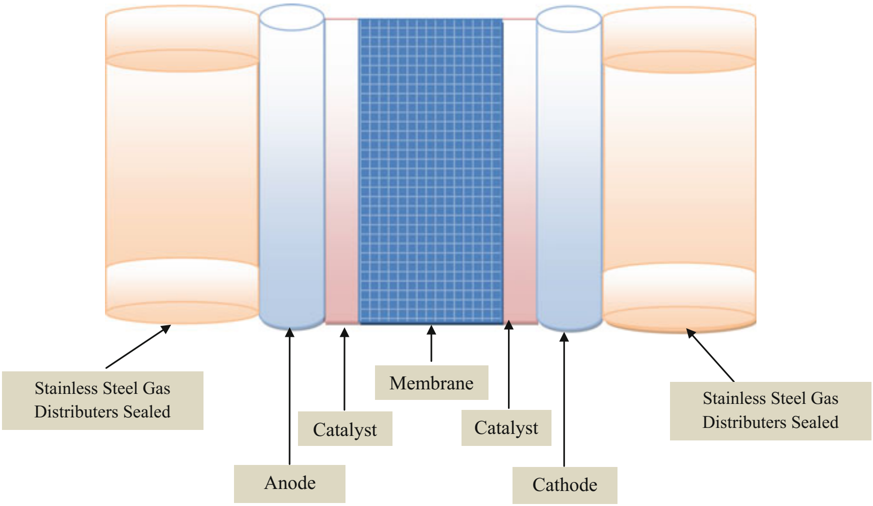

Fig. 2 Schematic representation of PEMFC

fuel cells are available in market, on the basis of different variables like type of fuel, exchange ion, oxidants and electrolytes, operating temperature, and pressure. However, the most important factor for various fuel cells is electrolyte used, which is responsible for the electrochemical process and separation between two electrodes in cell. On the basis of electrolytes, fuel cells are categorized as alkaline fuel cell, direct methanol fuel cell, phosphoric acid fuel cell, proton-exchange membrane fuel cell, solid oxide fuel cell, and molten carbonate fuel cell, in respect of electrolytes such as alkaline electrolyte solution, methanol electrolyte solution, phosphoric acid electrolyte solution, polymer electrolyte, solid oxide electrolyte, and molten carbonate electrolyte, respectively [5]. The short summary of most common types of electrolyte-based fuel cells is presented in Table 1. Among these, the proton-exchange membrane fuel cells (PEMFCs) are most useful for the production of clean electricity [1].

1.1 Proton-Exchange Membranes (PEMs)

Generally, hydrogen is used as fuel in proton-exchange membrane electrochemical cell (PEMFCs) [6]. PEMFCs contain both anode and cathode electrodes that are separated by proton-exchange membrane and on electrochemical reaction, with ejection of electron, H_2 changes into H^+ ion at anode and ejected electrons migrate towards the cathode through circuit to produce the electrical current. At the same time oxygen from air, passing through the cathode, combines with free electrons and hydrogen ions to produce water [3]. A schematic diagram of production of electricity in PEMFC is shown in Fig. 3.

Table 1 Characterization of different fuel cells

Fuel cell (FC)	Mobile ion	Operating temperature (°C)	Start up time	Power density (Kw/m^2)
Alkaline fuel cell (AFC)	OH^-	~50–200	Minute	0.7–1.8
Proton-exchange membrane (PEMFC)	H^+	~50–120	Second/minute	3.8–2.6
Direct methanol (DMFC)	H^+	~30–80	Second/minute	2.5–1.5
Phosphoric acid (PAFC)	H^+	~220	Hours	0.8–1.9
Solid oxide (SOFC)	O^{2-}	~600–100	Hours	1.5–2.6
Molten carbonate (MCFC)	CO_3^{2-}	~650	Hours	0.1–1.5

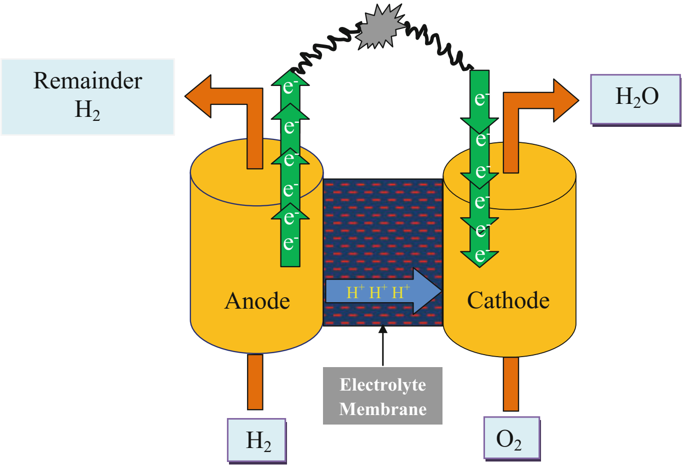

Fig. 3 A schematic diagram of production of electricity in PEMFC

Anode reaction : $2H_2 \rightarrow 4H^+ + 4e^-$
Cathode reaction : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Overall cell reaction : $2H_2 + O_2 \rightarrow 2H_2O$ + electrical energy + heat

Therefore, the fuel cell in which fuel is hydrogen, charge carrier is hydrogen ion (proton), and hydrogen ions permeate across the electrolyte towards cathode to produce heat, water, and electricity, is known as proton-exchange membrane fuel cell. Thus, PEMFCs are operated by proton-exchange membrane [7]. This proton-exchange membrane helps in carrying only the proton from anode to cathode and does not permit electron and thus separates electrons from hydrogen. Another feature of this membrane is that it is impermeable to the gases and serves as solid electrolytes for variety of electrochemical applications. Basically, solid polymeric electrolytes are used in PEMFC as PEMs, which have ability to transfer proton in moist condition instead of dry condition [8]. These solid polymeric electrolytes have gel-like structure and specific for cations or anions. Therefore, these polymeric electrolytes can be classified as cationic electrolytes, containing the negatively charged group, $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, $-PO_3H^-$, and $-C_6H_4O^-$, attached to the membrane backbone and anionic electrolytes containing the positively charged group, $-NH_3^+$, $-NRH_2^+$, NR_2H^+, NR_3^+, SR_2^+, and PR_3^+ [9]. These membranes have been proved as key feature for variety of fuel cell applications like automobile, back-up power, and portable power. Before polymeric electrolyte membrane or proton-exchange membrane electrolysis, alkaline electrolysis technology was being used for the same purpose. However, there were some drawbacks of alkaline electrolysis technology such as partial load, and low current density. To overcome these drawbacks polymeric electrolyte membranes or proton-exchange membranes (PEMs) were developed by General Electric (GE) company in 1960s. At that time, the performance of PEMFC obtained was 1.88 V at 1.0 A/cm^2, which was efficient as compared to alkaline electrolysis technology [10]. However, till the end of 1970s, the performance of alkaline electrolysis technology was improved and reported as 2.06 V at 0.215 A/cm^2 [11]. To operate PEMFC, first chemically stable polymeric membrane named as “Nafion” which is based on sulfonated polytetrafluoroethylene was developed by DuPont company in 1970s [12].

Most of the PEMs were developed as pure polymer membranes or polymer composite membranes [13, 14]. However, fluoropolymer Nafion-based PEMs were most common and commercially available [15]. Higher ion-exchange capacity (IEC), proton conductivity (σ), gas permeability, durability, water uptake, and thermal stability were the major requirements for significant performance of PEMFCs [16–20]. The advantages of Nafion-based PEMFCs were good thermal, chemical and mechanical stability, relatively high proton conductivity, high efficiency, and clean production of electricity without emission of polluting gases like CO_2, NO_2, SO_2, and CO. But the drawbacks of Nafion-based polymeric membranes were high production cost, and low operational temperature, which hindered the wide spread commercialization of fuel cell [3, 21, 22]. However, one more drawback found in currently used PEMFC technology, based on expensive perfluorinated membrane, is that it could operate effectively only under fully hydrated environment. For researchers, the problems to resolve include the lowering of cost of polymer membrane, increasing the operational temperature of PEMFC, operating the polymer membrane fuel cell in warm condition, and opening the new windows for PEMs. To solve all these problems, researchers are finding new technology for mass production of fuel cell with low cost. They are focusing on developing PEMs with high proton conductivity, low electronic conductivity, low permeability of fuel, low electro-osmotic drag coefficient, good chemical/thermal stability, good mechanical properties, and low green house gases emission. Performance, durability, and cost are major issues for the production of proton-exchange membranes. To overcome these issues, great efforts have been devoted for the development of new materials or modified polymeric membranes. The modified polymer

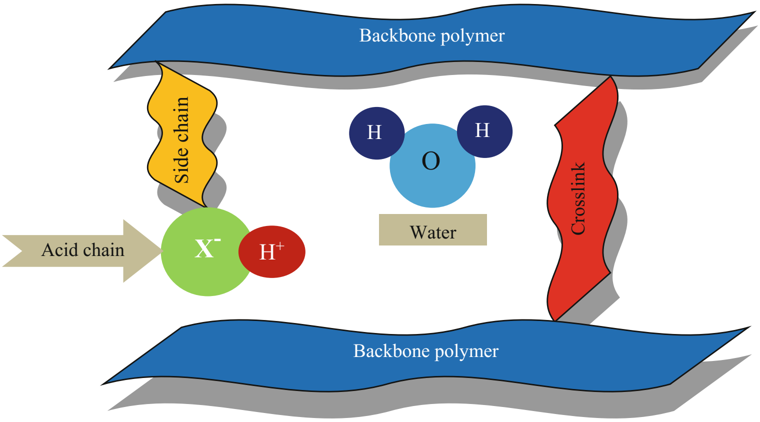

Fig. 4 Major components of polymer membrane

membranes as an alternative of PEMs are valid for performance of PEMFCs at low or medium temperature [21]. Therefore, it is necessary to develop high temperature membrane which can help to perform PEMFCs at high temperature. This so-called "high temperature membranes" could be developed either by the modification of polymer by acids, hygroscopic oxides (SiO_2 and TiO_2), and inorganic solid acid (ZrO_2 or TiO_2/SO_4^{2-}) or by developing completely new system of membrane [23, 24]. However, the lifetime stability of high temperature membrane is still major problem. Recently, attempts to resolve this problem, by right combination of elements of major components of PEMs, are underway. Polymer backbone, chemical cross-links, side chains, and pendant acid groups are four major components of membrane [25]. Figure 4 shows these components of membranes. The fluorine-containing polymer, hydrocarbon-based polymer, inorganic polymer, or a partially fluorinated polymer containing both C–H and C–F bonds in the polymer chain comprising a sulfonic, a carboxyl, a phosphoric acid, or a phosphonate groups may be the backbone. The carboxylic acid (–COOH), phosphonic acid ($-PO_3H_2$), sulfonic acid ($-SO_3H$), and sulfonylimide ($-SO_3NHSO_2CF_3$) are acidic groups bounded covalently to the fluorinated hydrocarbon such as polytetrafluoroethylene (PTFE). PTFE (Teflon) backbone provides stability to membranes in both oxidative and reductive environments. The thermomechanical properties, and inertness, of the membrane could be resolved by cross-linking of polymer backbone, and the number and strength of acid groups attached to backbone determine the electrolytic properties of membrane [26]. Researchers are working for the development of better alternative of PEMFC. Perfluorosulfonic acid membrane such as Nafion, sulfonated aromatic polymer membrane such as sulfonated poly(ether ether ketone), SPEEK, and sulfonated poly(ether ketone), SPEK, are commonly used modified membranes. These membranes contain the extremely hydrophobic backbone and hydrophilic functional groups. Extremely hydrophobic backbone provides the morphological stability to the membrane and hydrophilic functional groups act as

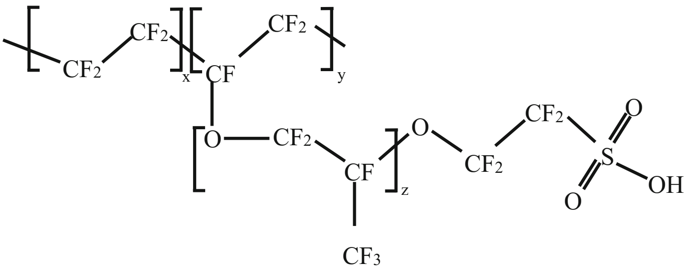

Fig. 5 Chemical structure of Nafion membrane

water reservoirs on aggregation. The perflourinated PEMs have been proved most chemically inert membranes [27, 28]. Hence, perfluorosulfonic acid membranes (Nafion PEMs) are the most commonly and significantly used PEMs that demonstrated fuel cell lifetimes over 2500 days below 100 °C [27]. Structure of Nafion membrane is shown in Fig. 5. The replacement of sulfonic acid group ($–SO_3H$) of Nafion with sulfonyl imide group (SO_2 $NHSO_2$ CF_3) increased the water uptake [29]. Similarly, Nafion with phosphonic acid group has improved thermal stability [30]. These results revealed that with the modification of acid groups, desire PEMs could be developed [31]. Higher proton conductivity, electrochemical stability, and mechanical strength of perflourinated PEMs (Nafion) could be achieved by polytetrafluoroethylene (PTFE) backbones [32]. The development of hydrocarbon backbone-based polymer demonstrated the high temperature performance of fuel cell at low relative humidity [33]. However, due to short lifetime, hydrocarbon backbone-based polymer membranes are not used these days. To overcome this disadvantage, polymer membranes such as polyether sulfones (PES), polyether ether ketone (PEEK), sulfonated polyether ether ketone (SPEEK), polyphosphazene (PP), sulfonated poly (phenylene sulfide) (SPPS), poly (4-benzoyl-1, 4-phenylene) (PPBP), polyphenylene oxide (PPO), poly (phenyl quinoaniline) (PPQ), polyimide, alkylsulfonated polybenzimidazol (AS-PBI), sulfoarylated polybenzimidazol (SA-PBI), and sulfonated poly (oxy-1, 4-phenyleneoxy-1, 4-phenylenecarbonyl-1, 4-phenylene) have been designed. Stable and cost-effective sulfonated trifluorostyrene, α, β, β-trifluorostyrene monomer substituted and a series of substituted-α, β, β-trifluorostyrene co-monomers membranes have also been developed [34, 35]. The solvent in PEMs fuel cell could be responsible for deciding the operating temperature. The operating temperature of fuel cell could be increased by replacing solvent like water (Bronsted base) with lower volatile solvent like H_3PO_4. Furthermore, H_3PO_4 and ionic liquid such as molten salt 1-butyl, 3-methyl imidazolium triflate (BMITF)-doped Nafion provided good conductivity at elevated temperature under relatively low humidity [36, 37]. However, there are some shortcomings such as H_3PO_4 being used is corrosive and ionic liquid is partly mobilized. To fulfill the requirement of PEMs, an alternate membrane was developed by Malhotra and Datta [38]. In order to improve water retention and simultaneously increasing acidic nature, they incorporated the inorganic acidic materials within the polymer (Nafion). The resultant membrane worked above 120 °C under low relative humidity. This alternate membrane was known as “high temperature membrane” and became very attractive approach for research. “High temperature membranes” are generally organic/inorganic hybrid nanocomposite membranes. The detailed study of polymer nanocomposite fuel cells with respect to the requirements of polymer electrolyte membranes, criteria for the selection of inorganic nanomaterials, preparation techniques of polymer nanocomposites, the requirements of electrolyte membrane applicable for fuel cell, and types of polymer membranes have been reviewed by Lade et al. [39].

2 Organic/Inorganic Hybrid Membranes

One of the unique functional properties of nature is to create the sophisticated materials that could carry out multiple functions within small volume. Organic/inorganic materials are one of these. On behalf of the nature, researchers are also producing the multifunctional synthetic organic/inorganic materials. This could be achieved by different methods; however, the sol–gel method has been used frequently. These synthetic materials, known as hybrid nanocomposites, are prepared by the nanoscale mixing of two phases, organic part such as polymer that provides flexibility and inorganic part such as inorganic acids and metal oxides that provides thermal and mechanical stability [40]. The features of organic and inorganic parts of a composite are illustrated in Fig. 6. Incorporation of inorganic phase into the organic phase brings changes in transparency, refractive index, adhesion, viscosity, flame resistance, solvent resistance, and decorative properties of the polymer [41–47]. Due to these advantages, of introducing inorganic material into the organic materials, hybrid nanocomposites are being used in different fields such as solid electrolytes, modified electrodes, electrochromic devices, functional biomolecules, bioreactor, biosensor, diagnostic devices, contact lenses, in bone

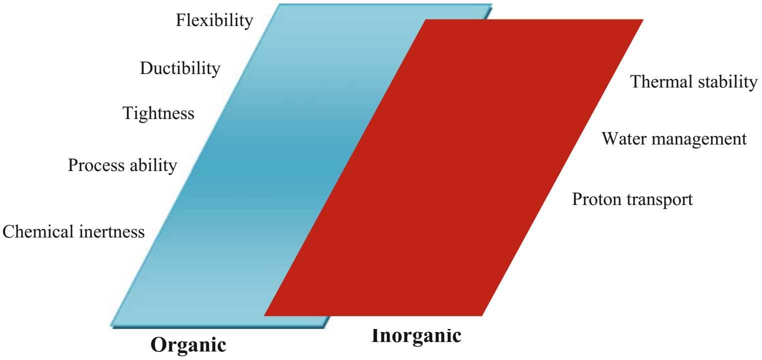

Fig. 6 Features of organic and inorganic parts in hybrid composite

replacement application, filling for dental restoration, and in the polymer electrolyte membrane and proton-exchange membrane fuel cells. The use of hybrid materials in the production of PEMs, is the advance technique and, fulfills the requirement of PEMs. PEMs with hybrid material have shown improved proton conductivity, high durability, better chemical and thermal stability, good mechanical properties, reduced electronic conductivity, decreased permeability of fuel, low production cost, and optimum performance at high temperature. Organic and inorganic hybrid membranes could be prepared by the incorporation of many types of inorganic fillers including inorganic acid and nano-sized metal oxides into the polymer matrix [24]. Liquid super acids may enhance the proton conductivity of membrane but they could not be applicable for the fuel cells because of their mobilization characteristics within PEMs [25]. Thus the solid acids became first choice as fillers. First hybrid membrane was developed by doping of inorganic solid acid (heteropoly acid), phosphotungstic acid (PTA), in ion-exchange polymer membrane (Nafion), which showed high proton conductivity and water retention at high temperature (120 °C) and low relative humidity (RH) [38]. However, PTA showed high solubility in water due to which it leached out from PEMs [48]. Recently, Nafion–PTA membranes were stabilized by heat and leaching out of PTA was reduced [49]. Because of high acidic and hydrophilic nature, different heteropoly acids (HPA), and heteropoly acid-derived salt-doped polymer membranes have been used in fuel cell. These membranes performed well at low humidity and high operating temperature with high water retention [50, 51]. However, the biggest drawback was the exploitation of acidity and hydrophilicity properties of HPA within polymer matrix. To overcome this drawback and to improve the performance of PEMs fuel cell at higher operating temperature and lower relative humidity; various nano-sized metal oxides have been added to the polymer matrix. Among these, MO_2 (M = Ti, Si or Zr) have frequently been used as inorganic filler [52]. The morphology of metal oxides plays an important role in the performance of polymer–metal oxide nanohybrid membrane at high temperature. However, the agglomeration of filler particles restricts the uniform dispersion of filler on the entire membrane, and thus resultant proton cannot transport effectively through the entire membrane. Therefore, uniform dispersion of inorganic fillers in polymer matrix for effective performance of PEMs is necessary. Different methods have been adopted for the fabrication of hybrid nanocomposite membranes with several advantages such as lower processing temperature, high homogeneity, favourable thermal or mechanical, and chemical stabilities, high durability, and reasonable purity of resulting material. As compared to conventional pathways, sol–gel method is more suitable for preventing the agglomeration of inorganic fillers which tend to reduce the size of inorganic parts and thereby the organic–inorganic phase separation. Sol–gel methods involve the hydrolysis of metal alkoxide [M(OR)n, M = Al, Si, Ti, Zr] in organic solvent followed by polycondensation. Hybrid nanocomposite membranes could be achieved by one of the approaches given below [53]:

1. The simultaneous hydrolysis and condensation of inorganic filler in the presence of desired polymer.
2. Performing the sol–gel process in the presence of desired polymer with functionalities.
3. The simultaneous polymerization of organic component with the formation of inorganic phase.

To achieve temperature-tolerant membrane, different nano-sized oxides such as SiO_2, TiO_2, Pt, Pt–SiO_2, and Pt–TiO_2 were doped in Nafion polymer [54–56]. These modified membranes showed much higher water uptake than Nafion. Under relatively low humidity, at 80 °C, these modified membranes showed lower resistance than Nafion. This was due to the suppression of H_2 crossover by Pt and subsequent sorption of water produced on the doped oxide. Jalani et al. [52] synthesized metal oxide (Zr, Ti, and Si)-doped hybrid membrane by sol–gel method. These synthesized nanohybrid membrane was completely transparent, homogeneous, and showed comparatively higher water retention than virgin Nafion at higher temperature (120 °C) and lower relative humidity (40%). However, only Nafion–ZrO_2 composites exhibited enhanced conductivity than virgin Nafion at 90 and 120 °C under low relative humidity [52]. This could be possible by enhanced acidity of Zr-based membrane, which was attributed to the decrease of equivalent weight in comparison to Ti- and Si-based nanocomposites. Miyake et al. [57] studied water content and conductivity of the Nafion–silica hybrid membrane and observed that modified membrane has higher water content than unmodified Nafion. The increase in water uptake at higher temperature was due to reorganization of the structure of the Nafion around the particles. The water uptake of Nafion–silica nanocomposite membrane changed with temperature, particle distribution in the membrane, porosity, and size of silica particle. The proton conductivity of Nafion and Nafion–silica nanocomposite membranes decreased with decreasing relative humidity, but was independent of silica particle size [58]. The improved thermal stability was observed for hollow silica sphere (HSS)-modified Nafion [59]. This composite showed higher water uptake and lower swelling degree within temperature range 40–100 °C. Higher water uptake efficiency was observed with smaller diameter of hallow silica sphere in Nafion. The improved proton conductivity was observed at 60–100 °C with 3–5% wt of HSS in composite membrane. Nano-sized SiO_2-embedded Nafion membrane fuel cell could operate at 130 °C, whereas, unmodified PEMs showed thermal degradation [60]. This was due to the high rigidity of modified Nafion. Similarly, inorganic additives such as TiO_2- and ZrO_2-filled PEMs performed well at higher temperature [61–66]. Presently, TiO_2 is considered most promising material because of high thermal, mechanical, photostability, powerful oxidation strength, and non-toxicity. Polymer/TiO_2 exhibits high conductivity, and the morphology of TiO_2 filler plays an important role in fuel cell performance at higher temperature. Recently, SnO_2 nanopowder-embedded polymer membrane fuel cell has been found suitable to operate at 120 °C under low humidity [67–69]. However, continuous ionic channels are another very important issue for water transport and high proton conductivity but still most of the membranes have short channel. Short channels restrict the content of absorbed water that creates discontinuation of hopping routs of proton. However, in the organic/inorganic hybrid membranes, protogenic groups of both inorganic fillers and polymer matrix were distributed on the interfaces and produced long-range ionic channels which were responsible for high proton conductivity of PEMs. One more important thing to consider for good PEMs is that the inorganic content in polymer should be balanced, as increase of inorganic filler in the polymer matrix results in decrease of proton conductivity (due to low proton conductivity of inorganic content) which may block the diffusion of the H^+ ions. It can be resolved by the incorporation of the acid functionalized inorganic fillers into polymer that can improve or preserve the proton conductivity of PEMs. Nawn et al. [70] developed polybenzimidazole–ZrO_2 nanocomposite membrane with varying oxide content (0–22 wt%) and studied the structure–property relationship of acid-modified and acid-unmodified membranes. Improved acid uptake and thermal and mechanical stabilities were observed from 0 to 8 wt%, while reverse effect was observed from 8 to 22 wt%. Acid-doped ZrO_2-modified polybenzimidazole (PBI) membrane fuel cell worked at high temperature, and low relative humidity, and showed ionic conductivity (0.104 S/cm) at very high temperature (185 °C). Similarly, phosphate–ZrO_2-doped Nafion membrane was developed which showed good results [71]. Nafion/ZrO_2–phosphate composite membranes showed enhanced thermal stability at 130 °C [72] and doping of 10% wt of zirconia–phosphate in polymer improved the thermal stability up to 140 °C at 90% relative humidity [73]. To improve the membrane proton conductivity at different temperatures and relative humilities, phosphated zirconia-sulfonated polyether sulfone nanohybrid membrane (ZrP–SPES) was synthesized by embedding zirconia in sulfonated polyether sulfone followed by treatment with H_3PO_4 [74]. Under 50% relative humidity, ZrP–SPES showed 0.01 S/cm proton conductivity at 90 °C, and at 90% relative humidity conductivity increased to 0.19 S/cm [74]. Recently, Ozdemir et al. [75] compared the proton conductivity of acid-modified polybenzimidazol (PBI) nanocomposite with the same percentage content of TiO_2, SiO_2, and ZrP inorganic fillers. To develop high temperature membranes, these inorganic fillers were dispersed in PBI and doped with H_3PO_4. Resultant, hybrid nanocomposites were thermally stable and showed improved acid retention capability. However, only SiO_2- and ZrP-dispersed nanocomposites showed improved proton conductivity. The highest proton conductivity (0.200 S/cm) was observed with PBI/ZrP having highest doped level of H_3PO_4. The composite membranes with TiO_2 showed low proton conductivity due to nonuniform membrane structure. Therefore, the various types of acid-modified inorganic filler-doped hybrid membranes are being produced to improve the membrane quality. Out of these, sulfated inorganic filler-embedded membranes showed excellent results. The comparative study of proton conductivity of different nanofiller-doped membranes is summarized in Table 2.

Table 2 Comparative proton conductivity of different hybrid nanocomposites

Polymer	Inorganic nanofiller	Ionic conductivity	Ref.
Nafion 115	–	41–61 mS/cm	[99]
	ZrP	24–60 mS/cm at 25 °C, 100% RH	
Nafion	S-CNT	0.01 S/cm	[100]
Nafion	S–SiO_2	59 mS/cm at 140 °C	[76]
SPEEK	–	0.0152 S/cm	[81]
	SHNTs	0.0245 S/cm	
SPEEK	Silane/silica	5 mS/cm at 90 °C, 100% RH	[101]
SPEEK	SiO_2/ZrP	0.09 S/cm	[102]
SPEEK	S–ZrO_2	3.88 mS/cm	[96]
PBI	S–ZrO_2	0.104 S/cm at 185 °C	[70]
PBI	ZrP + H_3PO_4	9×10^{-2} S/cm at 200 °C	[75]
		0.200 S/cm	
SPES	ZrP + H_3PO_4	10^{-2} S/cm at 50% RH, 90 °C	[74]
		0.19 S/cm at 90% RH, 90 °C	
PVPA	S–TiO_2	0.03 S/cm at 150 °C	[77]
C-PAMPS	S–ZrO_2	2.4×10^{-1} S/cm at 80% RH, 100 °C	[90]
PDMS	ZrO_2 + PWA	8×10^{-2} S/cm at 150 °C	[103]
SPSU	S–TiO_2 + NMPA	0.002 S cm^{-1} at 150 °C	[104]
PVA/SSA	SiO_2	10^{-3}–10^{-2} S/cm	[105]
PVA/glycerin	ZrP	10^{-4}–$^{-3}$ S/cm	[106]

3 Organic-Sulfated Metal Oxide Hybrid Membrane

Many types of acid-modified oxides such as sulfated silica (S–SiO_2) [76], titania (S–TiO_2) [77], and zirconia (S–ZrO_2) [78] are frequently used as super acid fillers to incorporate in polymers, and the sulfated nanoparticle-incorporated polymer membranes have shown higher proton conductivity. The acid-modified nanoparticles provide continuous ionic channel within polymer matrix and the resultant proton pathways allow the migration of protons with low resistance that improve proton conductivity. These acid-modified metal oxide-doped polymer membranes are thermally, and mechanically, stable than the other solid super acids. Sulfated silica (S–SiO_2)-modified nanocomposite membrane have shown much higher proton conductivity than the virgin polymer at various temperatures (40–140 °C) [76]. Higher proton conductivity for S–SiO_2-modified nanocomposite membrane was 0.059 S/cm at 140 °C [76]. Recently, S–SiO_2-modified Nafion nanohybrid membrane showed good proton conductivity at high temperature and low relative humidity. The silica and sulfonic groups responded for improvement in membrane hydration and proton conductivity, respectively. Moreover, proton conductivity was much affected by silica particle size as 20–30% improved conductivity was observed with less than 50 nm particle size under 100% humidity at 80 °C, while 22–42% improvement was observed with small size particles at 120 °C under same humidity.

However, at 120 °C under 50% humidity, the sulfonated particles were less efficient [79]. These S–SiO_2-modified nanocomposite membranes were fabricated by modification of Stöber silica particles with mercapto propyltriethoxysilane dispersed in pre-concentrated solution of Nafion followed by oxidation of mercapto groups to sulfonic acids by heating the membrane in 10 wt% hydrogen peroxide for 1 h. Several sulfated titania (S–TiO_2)-modified polymer membrane-based fuel cells have been developed for use at higher temperature. Poly(vinylphosphonic acid)-sulfated titania (PVPATS)-based nanocomposite membrane has shown more thermal and chemical stabilities at much higher temperature [77]. TGA and DSC characterization techniques confirmed the thermal stability of nanocomposite membranes up to 200 °C. The formation of phosphonic acid anhydride was verified by TGA study and on increasing the sulfated nanoparticles content in polymer, the shift in *Tg* of membrane towards higher temperature was observed by the DSC study. The proton conductivity of PVPATS was 0.03 S/cm at 150 °C. Recently, to improve thermal stability of polymer membrane, Aslan and Bozkurt mixed poly (vinylphosphonic acid)-sulfated titania (PVPATS) with poly (1-vinyl 1, 2, 4-triazole) (P (VTri))/sulfated nano-titania (TS) (PVTriTS) [80]. They observed that the temperature-tolerant power of newly modified binary membrane increased up to ~300 °C and *Tg* of binary membrane decreased with the increase of PVPATS content in PVTriTS–PVPATS binary membrane. However, at 150 °C, the proton conductivity was 0.003 S/cm. Moreover, ~60% enhanced proton conductivity was observed with thermally and mechanically stable sulfonated halloysite nanotubes (SHNTs) incorporated in sulfonated poly(ether ether ketone) (SPEEK) membrane [81]. Among all the solid acids, sulfated zirconia (SO_4^{2-}/ZrO_2) is considered strongest super acid, which exhibited highest acidity and proton conductivity [82, 83]. However, little information on sulfated zirconia (S–ZrO_2) and its composite materials is available. S–ZrO_2/Nafion and S–ZrO_2/SPEEK are examples of the modified membranes. Nafion/S–ZrO_2 membranes, prepared by several methods, having a structure with homogeneous surface were stable up to 120 °C. There is good ion-exchange membrane formation between S–ZrO_2 and Nafion as indicated by FTIR and SEM analyses. Its screening has demonstrated the highest conductivity and water uptake at high temperature.

4 Sulfated Zirconia Nanocomposite Membranes

Sulfated zirconia (S–ZrO_2) is a strongest super acid as compared to ZrO_2 due to the protogenic groups available on S–ZrO_2 [84, 85]. Basically, S–ZrO_2 has Hammett acid strength of −16.03 which is much higher than H_2SO_4 (−11.9). Super acids are those which have stronger acidity than 100% perchloric or sulfuric acid [86]. Higher acidic strength is responsible for super acidity of S–ZrO_2 which is claimed by changing the color of Hammett indicator at $pKa < -12$ [87]. Moreover, it has been reported that strong acid site is responsible for the isomerization and long-range ionic channel [88]. Because of high acidity and water affinity, sulfated zirconia nanoparticles have been used as an alternative of Nafion [78]. Thus, S–ZrO_2-based cell performed as good ionic conductor but the maximum power density of sulfated zirconia-based cell was about 1/3 as compared to Nafion-based cell [78]. To improve the cell performance, researchers attempted for S–ZrO_2/Nafion hybrid membrane and observed that improved results could be achieved by two different approaches either by treating zirconia particles in sulfuric acid or by the thermal decomposition of $ZrOCl_2$ and $(NH_4)_2SO_4$. However, it is very difficult to dope sulfate groups on ZrO_2 surface. To attach significant sulfate groups onto the ZrO_2 surface, multistep approach has been attempted [89]. Yao et al. [90] prepared S–ZrO_2 nanoparticles by electrospinning of PVP/$Zr(OPr)_4$ composite nanofiber mats [91] followed by the compression [92], heat treatment, immersion of mats in H_2SO_4, and calcination. The successful formation and structure of S–ZrO_2 was confirmed by the XRD and FTIR studies. Because of need of high temperature-tolerant membrane, Yang et al. prepared [71] S–ZrO_2/Nafion PEMs and used as electrolyte in fuel cell. First, they prepared fine powder of S–ZrO_2 by the reaction of dry $Zr(OH)_2$ with boiled 0.5 M H_2SO_4 followed by filtration and calcination at 110 °C and 700 °C, respectively, and then crushed and added this prepared fine powder to Nafion solution to recast into a membrane (Fig. 7). The prepared S–ZrO_2/Nafion membrane showed good conductivity at high temperature. Zhai et al. [93] developed S–ZrO_2/Nafion hybrid membrane by the recasting of different S–ZrO_2 contents, and Nafion, and then used as electrolyte in the cell. The membrane physiochemical properties were examined by the ion-exchange capacity

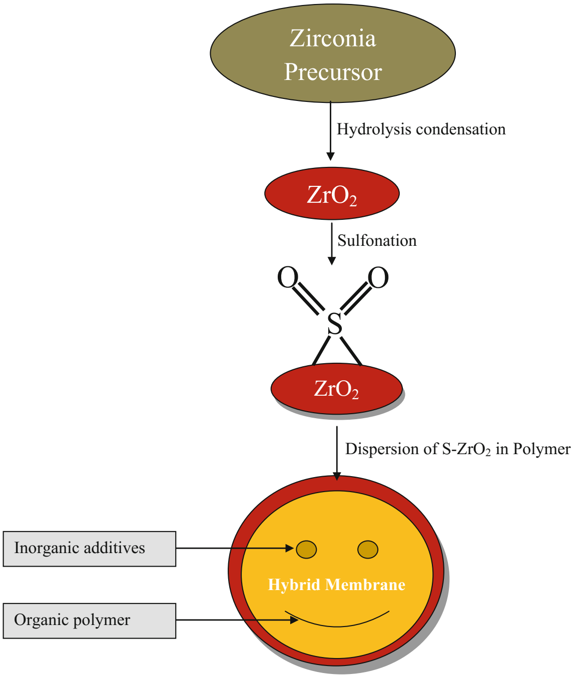

Fig. 7 Preparation steps of thermally stable organic–inorganic hybrid membrane

(IEC), and water uptake measurements. SEM, XRD, TGA, and FTIR studies revealed that S–ZrO_2 well dispersed in Nafion matrix and increased zirconia content in the matrix improved crystallinity, IEC, and initial degradation temperature of the hybrid membrane. The best performance of cell was observed with 15 wt% S-zirconia that showed lower resistance than Nafion membrane at high temperature and low relative humidity. At fewer than 2 atm pressures, IECs based on H_2/O_2 were 1.35 and 0.99 W/cm^2 at 80 °C and 120 °C, respectively. Navarra et al. [94] demonstrated the effect of super acid zirconia content in Nafion matrix that significantly enhanced the hydration level, and acidity, along with improvement in thermal, and transport properties, of composite membranes. High conductivity was realized with 5 wt% of super acid content in S-zirconia/Nafion membranes [94]. Proton conductivity of S-zirconia/Nafion composite membranes was attributed to the surface properties of S-zirconia. Hydrophilic nature of filler surface was confirmed by the higher water uptake capacity for composite membrane. The presence of SO_4^{2-} group on S-zirconia-embedded Nafion showed the highest water diffusion coefficient. Lin et al. [95] reviewed that on doping electrospun super acidic fiber (S–ZrO_2) in Nafion a large amount of protogenic groups aggregated in the interfacial region between acidic fiber and the Nafion matrix that formed regular channel for facile proton transport. Nafion is not only the polymer used in the fabrication of high temperature composite membrane but other polymers have also been used. However, S–ZrO_2-modified sulfonated poly(ether ether ketone) (SPEEK) has exhibited better performance. Results revealed that S–ZrO_2 content in SPEEK is responsible for the enhanced proton conductivity and oxidative stability of membrane. Moreover, SPEEK sulfonation time also showed attractive effect on the proton conductivity and oxidative stability of membrane. Recently, Mossayebi et al. [96] optimized the effects of SPEEK sulfonation time and S–ZrO_2 content. Optimum proton conductivity and oxidative stability were found to be 0.00388 S/cm and 102 min, respectively, after 6.9 h of sulfonation time and 5.94 wt% content of sulfated zirconia. Water uptake and acidity of S–ZrO_2/SPEEK-based membrane could be improved by doping Pt catalyst in S–ZrO_2 [97]. This modification in S–ZrO_2/SPEEK membrane provided the self-humidifying nature in membrane that showed highest proton conductivity. In comparison to virgin SPEEK membrane, the SPEEK/Pt–S–ZrO_2 showed improved power density from 0.54 to 0.95 Wcm^{-2} under the dry condition. S–ZrO_2 fiber-filled cross-linked poly 2-acrylamido-2-methylpropane-sulfonic acid (C-PAMPS) hybrid PEM was fabricated from poly 2-acrylamido-2-methylpropane-sulfonic acid (PAMPS) polymer matrix for high water uptake capacity [90]. C-PAMPS alone showed high proton conductivity [98] and on the incorporation of S–ZrO_2 in C-PAMPS, S–ZrO_2/C-PAMPS showed improved proton conductivity. An S–ZrO_2 fiber/C-PAMPS hybrid membrane was developed by immersing S–ZrO_2 fiber in 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) monomer, followed by the addition of azobisisobutyronitrile (ABIN), where ABIN was used as initiator and ethylene glycol diacrylate (EGD) as the cross-linker. Polymerization provided the long-range channels to the membrane due to significant distribution of protogenic groups of both S–ZrO_2 and C-PAMPS at the inorganic/organic interfaces.

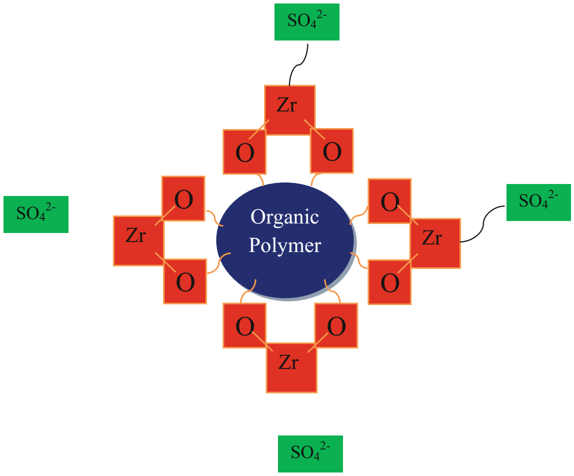

Fig. 8 S–ZrO_2/polymer hybrid nanocomposite membrane

These long-range channels helped to attract water molecules and provided the hopping pathway to protons which was responsible for the high proton conductivity. As compared to the C-PAMPS conductivity (0.087 S/cm), S–ZrO_2/C-PAMPS nanohybrid showed much higher conductivity (0.24 S/cm) with introduction of 20% S–ZrO_2 at 100 °C and under 80% of humidity and 20% of cross-linking degree. However, the existence of S–ZrO_2 and cross-linking degree of C-PAMPS decreased the ion-exchange capacity of membrane while, the fiber-induced interconnected ionic channels kept the proton conductivity and water content at a high level over the entire temperature range (Fig. 8).

The diameter of the fiber affected the ionic channel, with the decrease in diameter of fiber, and the number of ionic channel was increased that enhanced hopping pathway of proton which led to the proton conductivity. The highest proton conductivity (0.34 S/cm) was observed with thinner fiber (85 nm). The investigations suggested that the great improvements in PEMFC using sulfated zirconia polymer nanohybrid membranes are possible.

5 Conclusion and Future Prospects

Doping of sulfated metal oxides, especially sulfated zirconia (S–ZrO_2), into polymer matrix of Nafion or other polymers enhances the chemical and mechanical stability of polymer membranes and also increases the proton conductivity. These are required conditions for the working of fuel cell. The sulfated zirconia (S–ZrO_2)-modified membranes provide continuous ionic channels and thus enhance proton pathways to allow more protons to transport with low resistance that lead to improve proton conductivity. Moreover, polyaromatic structure membrane such as SPEEK with acidic metal oxides has been considered as preferred choice for high temperature membranes. The modification of S–ZrO_2/SPEEK with self-humidifying additive caused improvement in the self-humidifying nature of membranes which improved water uptake and acidity of S–ZrO_2/SPEEK. The chapter concludes that PEM with S–ZrO_2 provides high-performance fuel cell as compared to membranes with other additives.

However, increase in content of fillers in polymer or imbalanced dispersion of fillers causes lowering of performance of PEM fuel cell. Therefore, a future prospective based on this study is to develop more useful PEMs with high proton conductivity, and high thermal stability, and need to design polymer membrane with controlled structure and morphology.

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