Progress in ionic organic-inorganic composite membranes for fuel cell applications

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Over the past decade, organic-inorganic composite ionic membranes have gained tremendous attention for use in medium temperature fuel cells. The addition of a functional or nonfunctional inorganic into the organic material is usual practice in proton exchange membranes to improve their thermal stability and performance. In the development process, perfluorosulfonated membranes and their composites with inorganic materials dominate and show better thermal, mechanical and chemical stability, and proton conductivities at intermediate temperatures with low fuel drag. Concurrently, composites of hydrocarbon polymers, such as poly(arylene ether ketone)s, poly(benzimidazole)s, poly(arylene sulfone)s, poly(vinyl alcohol) *etc.*, have been developed as alternatives to perflurinated membranes. The present review addresses the basic route used to synthesize these composite membrane materials. The main emphasis has been given on the preparation procedures of inorganic materials, their modifications and composites with perfluorinated and hydrocarbon polymers. The properties are addressed with respect to fuel cell applications.

1. Introduction

The production of composite membrane materials by bridging organic and inorganic chemistry at a molecular level is an extensive and fascinating field of investigation. A major benefit of such hybrid research activities is linked to synergetic effects of organic and inorganic matrix with desired and improved properties in comparison to own unique properties of each components (organic or inorganic).[1] They expanded considerable

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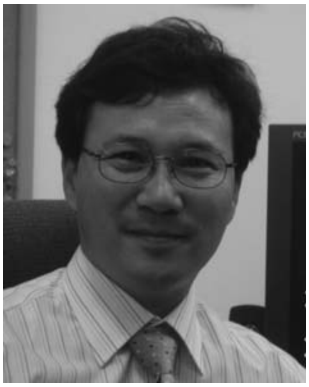

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Woonsup Shin has been at Sogang University as a Professor of Chemistry from 1995 after receiving a PhD at Texas A&M University and postdoctoral work at Stanford University. He is currently Chair of Interdisciplinary Program of Integrated Biotechnology and Head of Inorganic and Bio-Material Center. He is a member of the Korean Chemical Society, Korean Electrochemical Society, International Society of Electrochemistry, The Electrochemical Society, American Chemical Society and serves as Vice-Chair of the Bioelectrochemistry Division of the International Society of Electrochemistry.

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applications in optoelectronic,[2] ion-conduction,[3] biology,[4] catalysis[5] and membranes.[6]

Principally, ionic membrane materials have been developed for the medium temperature proton exchange membrane (PEM) fuel cell applications. Which have been identified as a nearly ideal solution to power the requirements for motor vehicle manufacturers, utility and nonutility generators, and portable electronic devices although efficiency is not up to the mark?[7] Most commonly used PEMs are perfluorosulfonated membrane for example 'Nafion' developed by Dow Chemicals and is a bench mark for most of researchers. But these membranes have limitations such as high cost, use at low temperatures (lower than 100 °C because of low thermal stability) and the need for high humidity to achieve high proton conductivity and high methanol flux.[8,9] But operation of proton exchange membrane fuel cells (PEMFCs) at intermediate temperatures (100–200 °C) enhances performance by accelerating electrode reactions without CO poisoning of the Pt catalyst. Alternatively, hydrocarbon based PEMs, which operates at intermediate temperatures have been well studied.[3,10,11] They suffer from the disadvantage of dehydration at higher temperature and interaction of absorbed water with the acid group present in the membrane for generating proton conductivity. The ability of PEMs to absorb a large fraction of water increases the proton conductivity, fuel permeability and reduces the mechanical properties. Also, the nature of acid groups, *i.e.* sulfonic, phosphonic and carboxylic acid, and their distribution affects the fraction of water content in the membranes. Thus design of new membranes that can conduct protons with little or no water is perhaps the greatest challenge in the science community.

One promising strategy for improvement in performance of PEMs by water management is incorporation of nanometre sized particles of hygroscopic metal oxides (silica, titania, and zirconia) which act as a water reservoir.[2,12] Furthermore, the methodology of introducing functional groups onto inorganic moieties has been successfully used to improve proton conductivity at higher temperature with low fuel flux and high mechanical and oxidation stability. This review gives an insight of literature available on possible approaches to develop organic-inorganic composite proton exchange membranes and their perspectives.

2. General consideration

2.1 Critical requirements from composite membrane materials

The critical requirement for the successful development of new ionic membrane materials are detailed in the following.

(1) Ionic conductivity: high ionic conductivity is the critical requirement and main deciding factor for ionic membranes. Basically, it depends on the type of functional groups present *i.e.* strongly ionic groups such as sulfonics,[13] phosphonic acids,[14] and quaternary ammonium salts *etc.*; and/or weakly ionic groups, for example, carboxylic acids,[15] hydroxyls, and primary,[16] secondary and tertiary amine groups *etc.* on the polymer backbone. The porosity of the membrane also affects the ionic conductivity. A highly porous membrane will have high ionic conductivity and *vice versa*. Thus in cases of organic-inorganic composite materials we can easily tune the pore structure of the membrane by appropriate organic or inorganic materials or synthetic methodology or even with ion-exchange groups. These are the big advantages for design of new generation ideal ionic polymers. Water content of the polymeric material has considerable effect on ionic conductivity. The higher the water content, higher is the ionic conductivity. But for wide number of applications, like fuel cell and electromechanical transducers low water content with high ionic conductivity is the primary requirement. Thus, in designing new types of ionic polymers one should keep in mind how one can lower down the water content by retaining good ionic conductivities.

(2) High permselectivity: the ionic polymer should have good permeability to counter ion but be impermeable to the co-ion. It basically depends on the type of ion-exchange groups present on the polymer backbone and its surface morphology, *i.e.* porosity of the membranes.

(3) Low electronic conductivity: the normal use of ionic membrane materials are in electro-membrane processes like electro-driven separation of ionic compounds, biologically important molecules, protein separation and fuel cell *etc.* In such cases, high electronic conductivity will decreases the open circuit potential of the system. But, exceptionally, in the case of electromechanical transducers, the presence of high surface electronic conductivity is essential for better actuation behavior of the polymers. Composites of metal nanoparticles and carbon nanotubes commonly have such requirements. Thus depending on the type of application, the requirements of electronic conductivity of the ionic polymers need to be tailored.

(4) Good chemical stability: this is another important deciding factor in the usefulness of the ionic polymers. For the wide range of applications the polymer should have good chemical stability, *i.e.* it should be resistant to a wide range of acids and alkalis over the complete pH range as well as stable in strong oxidizing, reducing and hydrolytic environments.

(5) Thermal stability: to render the applications in high temperature, the ionic polymers should have good thermal stability. Such requirement is challenging, but a demand of the future for high temperature fuel cell applications.

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(6) Good mechanical and dimensional stability. Good mechanical and dimensional stability is required in all membrane based processes. The ionic membrane should not lose its mechanical strength both in dry and hydrated states. It should not change its dimensions when the process medium changes. For example when the membrane process is carried out in low and high ionic strength media, or the pH of the medium changes during the process. In fuel cell applications the detachment of the electrode from membrane due to dimensional changes (non uniform expansion/contraction) must not occur. Thus, the polymer must be compatible with the environmental fluctuations and show least variations in its dimensions.

(7) Low cost: for the successful commercialization and sustainable growth, the cost of the synthesized ionic membrane materials should be as low as possible and the materials used in the synthesis process should be readily available.

The parameters, as discussed above, determining the membrane properties often have opposing effects. For example, high ionic conductivity results from the high water content and low cross-linking but decreases the mechanical and dimensional stability of the membranes. Thus there is a compromise between these properties to develop good ionic membrane materials. Hence the progress towards the development of optimum quality ionic polymer has wide challenges and needs to be designed carefully.

2.2 Basic synthesis approach

Generally, two types of approaches have been used to synthesize ionic organic-inorganic composite membrane materials as shown in Fig. 1. The first one deals with the formation of macro-composite or nano-composites in which domain size of the inorganic phase is of about micrometre or nanometre range, leading to enormous interfacial areas. A simple way of synthesizing these types of membrane is the physical blending of two components in an appropriate solvent. During the synthesis process care should be taken to avoid the unwanted precipitation of the components. Furthermore, each component should be well dispersed and compatible to each other. In the second case, the hybrid structure is obtained at the molecular level with entirely different properties by co-polymerization of one monomer usually inorganic, in the presence of other, usually organic polymeric solution in the proper solvent and catalyst. The general methodology used to prepare these membranes is a sol–gel process. This process occurs at room temperature in liquid state with organometallic precursors (TMOS, TEOS, Zr(IV)-propoxide, Ti(IV)-butoxide, *etc.*) by hydrolysis-condensation in presence of suitable catalysts, acid or base. The process makes it possible at low temperature a relatively easy molecular level incorporation of pure inorganic phase into an organic matrix,[17] which leads to vast applications. Nowadays, it is the fashion to use sol–gel to describe any low temperature preparation of organic-inorganic composite materials in which condensation polymerization of metal alkoxides takes place.

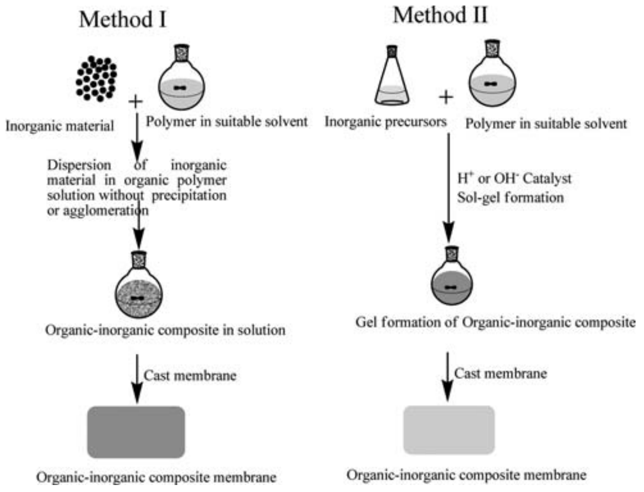


Fig. 1 A schematic presentation of the basic preparation methodology for ionic organic-inorganic composite membranes.

A sol is basically a dispersion of colloidal particles (size 1–100 nm) in a liquid, and a gel is an interconnected, rigid network with pores of sub micrometre dimensions and polymeric chains whose average length is greater than a micron. In the sol–gel process, the reaction of metal alkoxides and water in the presence of acid or base forms a one phase solution that goes through a solution-to-gel transition to form a rigid, two-phase system comprised of solid metal oxides and solvent filled pores. The physical and electrochemical properties of the resultant materials largely depend on the reaction conditions, *i.e.* the catalyst used. In the case of silica alkoxides,[18–20] it was observed that the acid catalyst reactions results in linear polymers, which are weakly cross-linked. These polymers entangle and form additional branches, resulting in gelation. Whereas base-catalyzed reactions form highly branched clusters due to rapid hydrolysis condensation of alkoxide silanes.[21] Gelation occurs by linking of these clusters[18–20] (Fig. 2). This difference in cluster formation is due to solubility of resultant metal oxides in reaction medium. The solubility of the silicon oxide is more in alkaline medium which favors the inter-linking of silica clusters than acidic medium. The hydrolysis condensation of Zr(IV)-propoxide, Ti(IV)-butoxide usually occurs very fast with white precipitation in the reaction mixture and uneven distribution in the organic matrix. In such cases the sol–gel reaction should be carried out in organic solvent with little water content and in the presence of ethylacetoacetate.

Both acid and base catalyzed reactions which occur in the sol–gel process are bimolecular nucleophilic substitution reactions. The fundamental steps involved are:

Hydrolysis of $M(OR)_4$ (where M is Si, Ti, Zr)

Fig. 2 A cartoon showing linear weakly cross-linked and highly branched clusters, A: acid catalyzed B: base catalyzed hydrolysis.

$$M(OR)_4 + H_2O \rightarrow M(OR)_3(OH) + ROH$$

Intermediates due to the partial hydrolysis include molecules with M–OH groups. Complete hydrolysis to form $M(OH)_4$ is very difficult to achieve. Instead, condensation may occur between either two –OH or M–OH groups and an alkoxy group to form bridging oxygen and a water or alcohol molecule. An example of a condensation reaction between two –OH with the elimination of water is shown below.

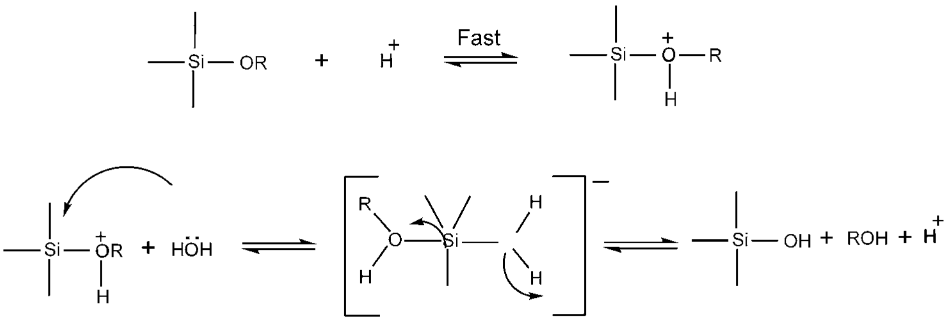
$$M(OR)_4 + M(OR)_3\,(OH) \rightarrow (RO)_3MOM\,(OR)_3(OH) + H_2O$$

Hydrolysis of $(RO)_3MOM(OR_3)_3$ resulted in $(RO)_2M(OH)OM(OR)_3$, which can undergo further polymerization reactions. The hydrolysis and polycondensation reactions are initiated at numerous sites and the kinetics of the reactions are therefore complex. When a sufficient number of interconnected M–O–M bonds are formed in a region, they interact cooperatively to form colloidal particles or a sol. With time the colloidal particles link together to form a three-dimensional network. At gelation, the viscosity of the solution increases dramatically and a solid object termed an alcogel results, a real sol–gel processes. A technologically important point is that alcogels can be formed in any shape or desired configuration. The possible mechanisms for both acid and base catalyzed reactions in case of silicon alkoxides is as shown in Fig. 3.

3. Inorganic materials

3.1 Functionalized and non functionalized silica materials

The name silica comprises a large family of products with general formula SiO_2 or $SiO_2 \cdot xH_2O$. It is a naturally occurring material found in minerals, such as quartz and flints, and in plants such as bamboo, rice and barley. But silica used in chemical applications has a synthetic origin.[22] There are two form of silica, crystalline and amorphous. The crystalline form involves a high degree of ordering. The active surface, which may participate in any chemical or physical interaction, is limited to the external surface of the crystalline particles. Amorphous silica occurs in various forms likes fibers, sheets, sols, gels and powders. It can be



Acid catalyzed mechanism

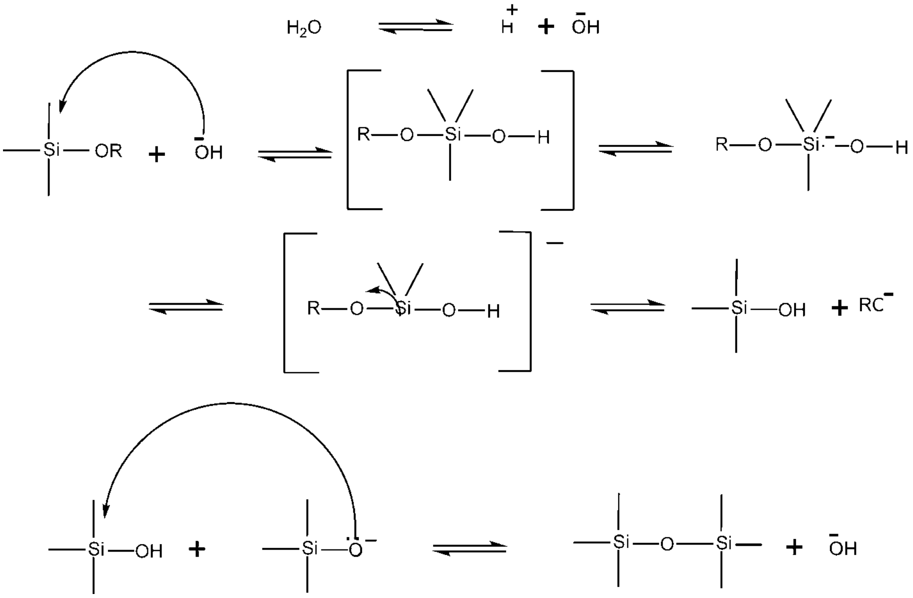


Fig. 3 The reaction mechanisms for acid and base catalyzed hydrolysis condensation of alkoxy silane.

fabricated according to the application. A main feature of interest is the porosity of the amorphous silica forms. Porosity introduces a large surface area inside the silica particles. As interphase processes require a large surface/mass ratio. So, amorphous silica is far more interesting for chemical and physical applications than their crystalline counterparts. It is commonly used in modifying the properties of the ionic polymers.

There are two techniques reported to synthesize silica particles used in modifying ionic polymers: the sol–gel method and the microemulsion method. The simple synthesis of monodisperse spherical silica particles is by means of hydrolysis of a dilute solution of TEOS in ethanol at high pH. Uniform amorphous silica spheres whose sizes ranged from 10 nm to 2 μm were obtained[22] simply by changing the concentrations of the reactants. This method appears to be simplest and most effective route for synthesizing monodispersed silica spheres. The commercially available silica nanoparticles *i.e.* nanosilica powder is mainly produced by the fuming and precipitation method in industry. Fumed silica is a fine, white, odorless, and tasteless amorphous powder. It is manufactured by a high-temperature vapor process in which $SiCl_4$ is hydrolyzed in a flame of oxygen–hydrogen. The silica has an extremely large surface area and smooth nonporous surface, which could promote strong physical contact between the filler and the polymer matrix. Precipitated silica is manufactured by a wet procedure by treating silicates with mineral acids to obtain fine hydrated silica particles in the course of precipitation. For the preparation of silica nanocomposites, fumed silica is commonly used and precipitated silica is rarely used since the precipitated one has more silanol (Si–OH) groups on the surface and consequently it is much easier to agglomerate than fumed one. The presence of hydroxyl groups on the surface holds individual silica particles together and aggregates remain intact even under the best mixing conditions if stronger filler-polymer interaction is not present. The dispersion of nanometre-sized particles in the polymer matrix has a significant impact on the properties of composites. A good dispersion may be achieved by surface chemical modification of the nanoparticles or physical methods such as a high-energy ball-milling process and ultrasonic treatment. The molecular level dispersion of silica can be achieved by *in situ* hydrolysis condensation of silica alkooxide monomers in the polymeric solution. In the sol–gel processes choice of silica precursors, catalysis and solvent system is very important.[13–16,23,24] Table 1 shows the potential functional and non functional silica precursors. Using these precursors one can prepare weakly or strongly positive and negatively charged organic-inorganic composite membrane materials as per the desire applications.

3.2 Zirconium phosphate

Zirconium phosphate is the most extensively studied inorganic material for proton exchange membranes fuel cells. Normal zirconium phosphate ($PO_4 : Zr = 2$) is obtained as a gelatinous amorphous precipitate when an excess of phosphoric acid or soluble phosphate is added to a soluble zirconium salt. The insoluble precipitate is considered as zirconyl salt[25] and the compound is represented as $ZrO(H_2PO)_2$.

Amphlett and his co-workers[26] postulated that it consists of a network of zirconium atoms linked together by bridging oxygen atoms. The phosphate groups were thought to be bonded to the zirconium atoms and to contain replaceable hydrogen atoms. Washing normal zirconium phosphate with water removes phosphate groups by hydrolysis. Larsen and Donald[27] exhaustively washed the normal phosphate with water and obtained a product in which $PO_4 : Zr = 1.72$. Baetslé and Pelsmaekers[28] precipitated zirconium phosphates from solutions containing $PO_4 : Zr$ ratios of 3, 2, and 1.75. The precipitates had different compositions but on washing, products of constant composition in which a $PO_4 : Zr$ ratio of 1.66–1.68 was obtained. The washed zirconium phosphates exhibited weak X-ray diffraction patterns from which it was determined that the unit cell is cubic with $a = 9.04$ Å. From these observed X-ray and density data, they proposed structure for zirconium phosphate as shown in Fig. 4.

Crystalline zirconium phosphate was synthesized by Clearfield and Stynes[29] for the first time in 1964. They initially prepared zirconium phosphate gels from hydrochloric acid solutions of zirconyl chloride using an excess of phosphoric acid as precipitant. Further, gelatinous precipitate was refluxed with phosphoric acid to give truly crystalline zirconium phosphate. They found that higher the concentration of refluxing phosphoric acid, faster the conversion rate into crystalline zirconium phosphate of formula $Zr(HPO_4)_2 \cdot H_2O$. The ion-exchange capacity of the resulting material was found to be ~2 meq. Na/g of the dried sample.

In a modified procedure, Alberti and Torracca[30] found the best result by dissolving a suitable zirconium salt (oxychloride or nitrate) in hydrofluoric acid followed by adding concentrated phosphoric acid and allowing the solution to evaporate. In a typical procedure, 5.5 g of $ZrOCI_2 \cdot 8H_2O$ was dissolved in 80 ml of water; 4 ml of 40% hydrofluoric acid and 46 ml of 85% phosphoric acid was added ito the stirring solution. It is well known that hydrofluoric acid is a good complexing agent for zirconium; when the concentration of hydrofluoric acid is sufficiently high, precipitation by phosphoric acid is then inhibited. However, when the fluoride ion concentration is lowered (*e.g.* by evaporation of hydrofluoric acid) the fluozirconate complex gradually dissociates and zirconium phosphate begins to precipitate. The X-ray data and ion-exchange capacity were matched with that of Clearfield's data.

There are two types of predominate zirconium hydrogen phosphate $Zr(HPO_4)_2 \cdot H_2O$[31] (henceforth ZrP) structures, α and γ (Fig. 5). Recent investigation has led to the discovery of two new structures synthesized *via* hydrothermal routes, designated as τ-ZrP and ψ-ZrP.[31] In α-ZrP, the layers consist of ZrO_6 octahedra in which zirconium atoms are located in same plane and bonded with one another by tetrahedral phosphate groups (HPO_4^{2-}) lying above and below the plane composed of zirconium atoms. On the other hand, in γ-ZrP, ZrO_6 is coordinated with two kinds of tetrahedron, $H_2PO_4^-$ and PO_4^{3-}.[32] The crystalline α-ZrP has composition $Zr(HPO_4)_2 \cdot H_2O$ with strictly stoichiometry and laminar structure.[32] The selective sorption properties of ZrP gels are affected by the crystallinity and degree of dehydration. Also, the latter characteristic strongly affects the exchange kinetics. But for both structures the α and γ forms are best for proton transporting due to their pendent –OH groups. Generally α-ZrP has higher reactivity, ion-exchangeability and intercalation property, than the γ form due to its abundant

Table 1 Functional and nonfunctional silica monomers useful in synthesis of ionic composite membrane materials

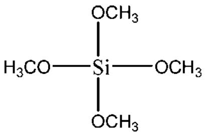
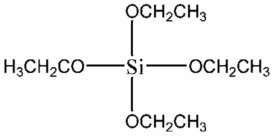
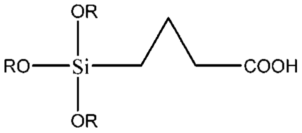
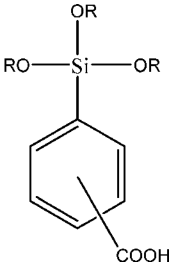
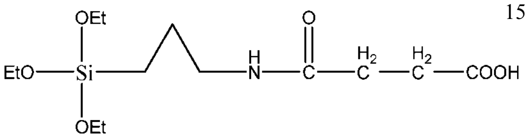
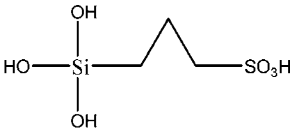
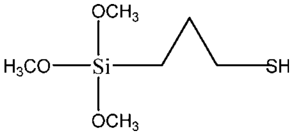
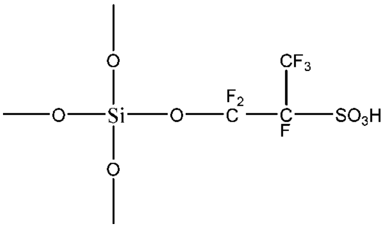
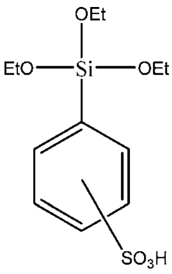
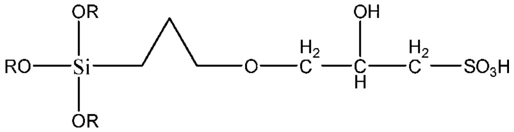
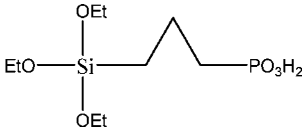
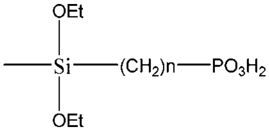
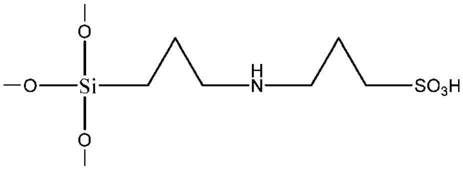
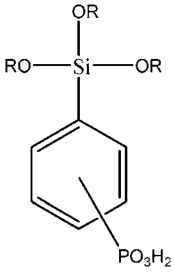
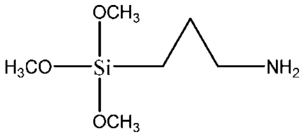
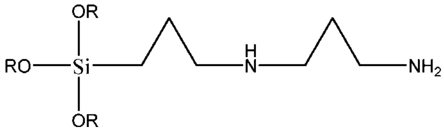
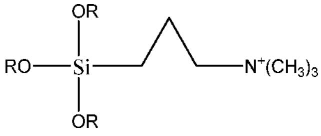
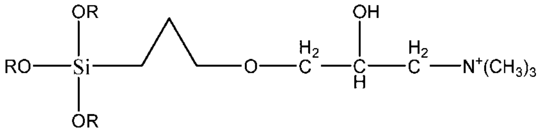
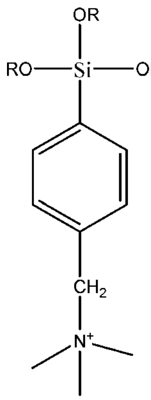
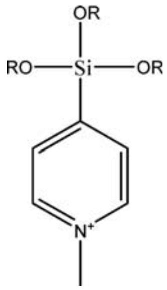
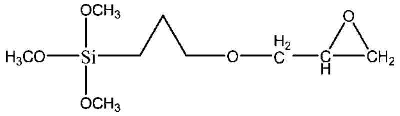
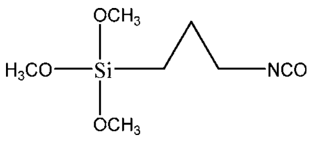
No.	Functional silica monomers	References
1		20
2		20
3		
4		
5		15
6		13,23
7		123
8		24
9		20,23
10		
11		118
12		14
13		
14		
15		16
16		
17		
18		

Table 1 (*Contd.*)

No.	Functional silica monomers	References
19		
20		
21		115
22		116

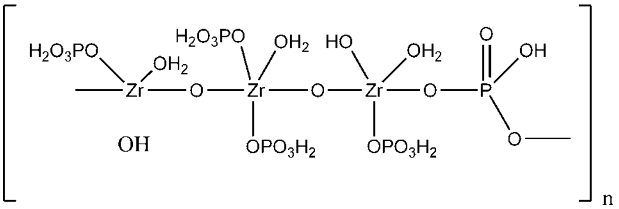


Fig. 4 Larsen and Vissers' proposed structural formula for zirconium phosphate.

hydroxyl group,[32] which extends into interlayer region and forms hydrogen bonded network with water. The hydroxyl proton can react with sodium hydroxide or any alkyl amine. Upon reaction, the structure of α-ZrP remains unchanged, while interlayer distances increases to accommodate the guest ion or molecule. The transport mechanism in α-ZrP at room temperature is dominated by surface transport and it is four orders of magnitude higher than the bulk transport. Isoconductance measurements also indicate that the conductivity varies linearly with the number of surface phosphate groups. Additionally conductivity is highly dependent on degree of hydration, by varying two orders of magnitude of relative humidity; conductivity increases from 5 to 90%.[31] Further, recent research has confirmed the dominance of surface transport by modifying P–OH groups.[31–35]

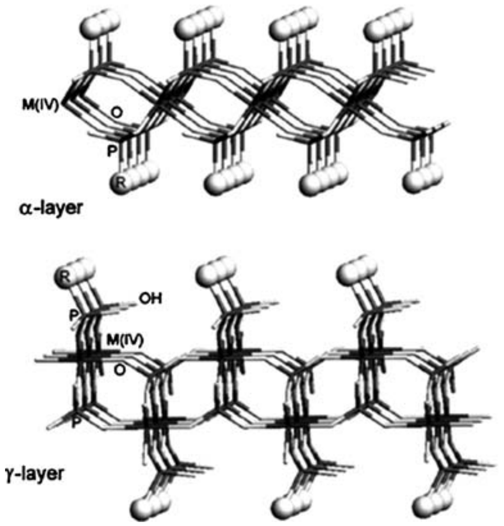


Fig. 5 A schematic presentation of the α- and γ-layered structures of ZrP.[35,36]

Modification has been done with functionalized organic moieties or Brønsted bases.[33] Significant improvement in conductivity was achieved with intercalation of strong acidic functional groups, $-SO_3H$ into the interlayer region (there was little improvement with the weak –COOH groups). Zirconium alkyl sulfophenylphosphonates or the variety of $[Zr(O_3PC_6H_4SO_3H)0.85(O_3PC_2H_5)1.15\cdot nH_2O;\ (Zr(O_3PC_6H_4SO_3H)x(O_3PCH_2OH)_{2-x}\cdot nH_2O)]$ have been investigated for their conductivity under different temperature and relative humidity regimes.[36–38] The best conductivity reached in the anhydrous state with ethylsulfophenyl phosphonate: 1.2×10^{-5} S cm^{-1} at 180 °C (as compared to 10^{-6} S cm^{-1} for microcrystalline α-ZrP). This value puts it amongst the best fully anhydrous proton conductors.[36,38] In hydrated conditions at 20 °C the conductivity increased from 10^{-4} at 22% RH (relative humidity) to 1.6×10^{-2} S cm^{-1} at 90% RH while at 100 °C conductivities as high as 0.05 S cm^{-1} with 90% RH were reported. Unfortunately at less than 50% humidity, the conductivity of sulfophenylphosphonates showed increased dependence as compared to standard α-ZrP. However at 65% RH and 100 °C still they are capable of conducting at 0.01 S cm^{-1}.[39] The significant advantage of sulfophenylphosphonates is that; as temperature is increased from ambient conditions to 100 °C there is no drop in conductivity indicating hygroscopic nature has not been affected. More recent work[34] has shown that the zirconium sulfoarylphosphonates also display high conductivity values, although it is strongly affected by humidity. The different zirconium compounds were synthesized with sulfonic acid attached to a phenyl, benzyl or to a fluorinated benzyl group. The highest conductivity reported for sulfophenylphosphonates is up to 5×10^{-2} S cm^{-1} at 100 °C to 2×10^{-2} S cm^{-1} at 150 °C with 100% RH.

Honma and co-workers[35] developed a proton exchange membrane based on organically modified zirconia by a self-assemble sol–gel process. The monomers were covalently bonded at the zirconia interface to form macromolecular inorganic–organic networks. By altering the inorganic–organic molar ratios, a range of flexible and rigid films showed good chemical tolerance, mechanical property and thermal stability up to 325 °C. The proton conductance was obtained after treating membranes with 85% H_3PO_4 at 150 °C. The proton conductivities of phosphoric acids-incorporated inorganic–organic hybrids were found about 7×10^{-4} S cm^{-1} at 180 °C.

3.3 Heteropoly acids

Heteropoly acids have a very long history in basic and applied science. They are part of a large class of polyoxometalates (POMs) and are composed of a metal such as tungsten, molybdenum or vanadium; oxygen; an element from the p-block of the periodic table, such as silicon, phosphorous or arsenic and acidic hydrogen atoms. The conjugate anions of the heteropoly acids (HPAs) are known as polyoxometalates, having metal-oxygen octahedra as the basic structural unit.[40] The first characterized and the best known of these is the Keggin heteropolyanion typically represented by the formula $XM_{12}O_{40}^{x-8}$ where X is the central atom (Si^{4+}, P^{5+}, *etc.*), x is its oxidation state, and M is the metal ion (Mo^{6+} or W^{6+}). The Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 (Fig. 6).[40]

The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4. Among a wide variety of HPAs, Keggin's are the most stable and more easily available. Generally, solid HPAs form ionic crystals composed of heteropolyanions, counter-cations (H^+, H_3O^+, H_5O^{2+}, *etc.*) and hydration water. The crystal structure depends on the amount of hydration water.[40] This water can be easily removed on heating, whereby the acid strength is increased due to the dehydration of protons. This is a reversible process accompanied by changing the volume of crystal cell. Unlike the rigid network structure of zeolites, in HPA crystal the Keggin anions are quite mobile. Not only water but also a variety of polar organic molecules can enter and leave HPA crystal. HPAs ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$) based on the Keggin structure have some of the highest reported acidity and solid state proton conductivities at room temperature. Their proton transport has been extensively studied and thus becoming an increasingly popular proton conducting additive in proton exchange composite membranes for use under dry and/or elevated temperature conditions of fuel cell.[41–43]

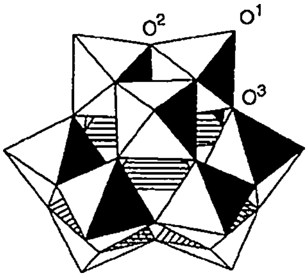


Fig. 6 The Keggin structure of the $XM_{12}O_{40}^{x-8}$ anion (R-isomer): 24 terminal (O^1), edge-bridging (O^2), and cornerbridging (O^3) oxygen atoms.

4. Organic materials

The first ever organic material used in a fuel cell was a styrene-divinyl benzene copolymer followed by perfluorinated membranes in the 60s.[10] To date perfluorinated membranes are dominant and subject of research to many groups worldwide due to their excellent chemical stability and proton conductivity. These are the bench mark for many researchers to find alternative membranes even though they have the disadvantage of thermal instability, high reactant flux and high cost. A large amount of literature is available[8–10,12,44] on alternative membranes to perfluorinated materials which includes: (a) acid functionalized or doped poly(benzimidazole) (b) poly(arylene ketone) (c) poly(arylene sulfone) (d) poly(sulfides) (e) poly(phynelene oxides) (f) poly(phosphazenes) *etc.* Within this wide range of alternative membrane materials, no membranes are available for real-world applications. Now world research is progressing in the direction of organic-inorganic composite ionic membranes which are the only hope of meeting the requirements of fuel cells and other applications.

5. Organic-inorganic composite materials

The use of composite membranes in fuel cell is very attractive because they exhibit high ionic conductivity and mechanical strength. Also they resist dehydration and exhibit fuel non-permeation. Table 2 gives brief information about the organic and inorganic components of the composite ionic membranes with highlighted properties. Basically two types of organic-inorganic composite membranes are being developed: (i) macro-composite 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. These could be developed by *in situ* polymerization of inorganic monomer in the presence of an organic matrix with suitable solvent and catalyst.

5.1. Inorganic composites of perfluorinated ionic membranes

The perfluorinated proton exchange membranes were developed by polymerization of monomers which can be converted into cations. These perfluorinated PEMs were commercialized in the trade name Nafion by DuPont, Flemion by Asahi glass and Aciplex by Dow Chemicals. The general structure is shown in Fig. 7. The properties of these long-side-chain perfluorinated PEMs (*e.g.* Nafion/Flemion/Aciplex) and the short-side-chain perfluorinated PEMs (*e.g.* Dow) are as follows: (a) EW range = 800–1500; (b) conductivity = 0.20–0.05 S cm^{-2} (for example, conductivity 1100 EW = 0.1 S cm^{-2} and conductivity 850 EW = 0.15 S cm^{-2}).[20] Morphologically they consist of clusters of long sulfonate-terminated side chains in a perfluorocarbon matrix that has a degree of ubiquitous crystallinity. These Quasi-order crystallinity gives *d* spacing around 35–50 Å, as evidenced by presence of single broad peak in small angle X-ray scattering (SAXS).[45,46] This spacing forms the clusters of solvent molecules water and exhibit good conductivity at room temp. But as the temperature increases, the quasi-order crystallinity gets disturbed and dehydration

Table 2 Ionic organic-inorganic composite membranes with important physical and electrochemical properties

Polymer	Inorganic material	Descriptions	References
Nafion	Tetraethylorthosilicate	$\sim$20% increase in water uptake compare to Nafion	45,48
	Cross-linked network of 4,4′-methylenedianiline and 3-glycidoxypropyltrimethoxysilane	$\sim\sigma = 3.4 \times 10^{-2}$ S cm^{-1}, $\sim P = 1.1 \times 10^{-8}$ cm^2 s^{-1}	50
	Diphenyldichlorosilane and mercaptopropyltrimethoxysilane	$\sim\sigma = 2.2$–1.0×10^{-1} S cm^{-1}, water content 16–21%, $\sim P = 2$–1×10^{-6} cm^2 s^{-1}	51–55
	ZrO_2	20–25% higher water uptake, $\sigma = 2 \times 10^{-2}$ S cm^{-1} *i.e.* 8–10% higher, 30–40 mA cm^{-2} higher current at 0.5 V compared to Nafion® at 90–120 °C	57,58
	Sulfated- ZrO_2	$\sim\sigma = 2.3 \times 10^{-1}$ S cm^{-1} 105–135 °C, single cell performance 1.35 W cm^{-2}	60,61
	$Zr(HPO_4)_2$	$\sim\sigma = 1.6$–2.7×10^{-1} S cm^{-1}; current density 0.25–1.5 A cm^{-2} at 0.45V	63
	Heteropolyacids	Water content 60–95%, $\sim\sigma = 1.5$–9.5×10^{-2} S cm^{-1}; current density 0.695–0.940 A cm^{-2}	12,68,69
	SO_3H-heteropolyacid-SiO_2	Single cell performance at 80–200 °C 33–44 mW cm^2	70
	Poly(oxypropylene) backboned quaternary ammonium salt modified Montmorillonite	Water content $\sim$28–32%, $\sigma = 4$–6×10^{-2} S cm^{-1}, current density 0.56 A cm^{-2} and power density 0.13 W cm^{-2} at 0.2 V	73
	SO_3H modified clay	Water content $\sim$70–87%, $\sigma = 0.2$–3.0×10^{-2} S cm^{-1}, current density 7.20 A cm^{-2} and power density 4.30 W cm^{-2} at 0.6V and 80 °C	74
PVDF	$ZrO_2{\cdot}SO_4$	$\sigma = 1.2$–5.2×10^{-2} S cm^{-1}, single cell power 32 mW cm^{-2}.	56
PVDF-HFP copolymer	Heteropolyacids	Current density 1.6 A cm^{-2}	42
SPEEK	SiO_2	$\sigma \geq 1.0 \times 10^{-2}$ S cm^{-1}	80,81
	SiO_2–N-(-3-triethoxysilyl propyl)-4,5-dihydroimidazole	40% reduction in water content and P = 13% reduction	82
	Montmorillonite	$\sim$50% water content, $\sim\sigma = 1.2 \times 10^{-2}$ S cm^{-1}, $\sim P = 10^{-8}$ cm^2 s^{-1}	86
	Laponite	$\sim$50% water content, $\sim\sigma = 0.3 \times 10^{-2}$ S cm^{-1}, current density = 3.70 Acm^{-2} at 0.6 V	85
	Heteropolyacid	$\sigma = \sim1 \times 10^{-1}$ S cm^{-1} at 100 °C	88–91
	TiO_2	$\sim$5% water content, $\sigma = \sim0.2 \times 10^{-2}$ S cm^{-1}, $\sim P = 0.5$–2.0×10^{-6} cm^2 s^{-1}	97
	BPO_4	$\sim$35% water content, $\sigma = \sim2 \times 10^{-2}$ S cm^{-1}, $\sim P = 0.5$–2.0×10^{-6} cm^2 s^{-1}	98
SPAEEKK	SiO_2	$\sigma = 2.0$–9.7×10^{-2} S cm^{-1}, $\sim P = 1.4$–6.9×10^{-7} cm^2 s^{-1}	79
PPEK	SO_3H–SiO_2	Water uptake 35%, 3.6 fold increase in σ	83
SPEK	SiO_2–N-(-3-triethoxysilyl propyl)-4,5-dihydroimidazole	40% reduction in water content and P = 13% reduction	82
Poly(ether sulfone)	SO_3H–SiO_2	Water uptake $\sim$20% and $\sigma = \sim1 \times 10^{-2}$ S cm^{-1} at 90% humidity	23
Poly(ether sulfone)	PO_3H_2–SiO_2	Water uptake $\sim$28%, $\sigma = \sim6.3 \times 10^{-2}$ S cm^{-1}, $P = 5 \times 10^{-7}$ cm^2 s^{-1}.	105
	$Zr(HPO_4)_2$	$\sigma = \sim1.9 \times 10^{-1}$ S cm^{-1} at 90 °C and 90% humidity	106
Poly(biphenyl ether sulfone)	Ag–SiO_2	Better oxidative stability and long term cell performance with low limiting current density 10 mA.	103
Poly(ether imide)	SO_3H–SiO_2	Water uptake $\sim$20% and $\sigma = \sim1 \times 10^{-2}$ S cm^{-1} at 90% humidity, good hydrolytic and oxidative stability	23
Poly(vinyl alcohol)	SiO_2	$\sigma = \sim1 \times 10^{-3}$ to 10^{-1} S cm^{-1}, $P = 1 \times 10^{-7}$ to 10^{-8} cm^2 s^{-1}	107,108
	SO_3H–SiO_2	Water uptake $\sim$32%, $\sigma = \sim0.1$–1.2×10^{-3} S cm^{-1}.	19
	PO_3H_2–SiO_2	Water uptake $\sim$123%, $\sigma = \sim5.5 \times 10^{-2}$ S cm^{-1}, $P = \sim1.9 \times 10^{-6}$ cm^2 s^{-1}.	109
PEG	SiO_2	$\sigma = \sim1 \times 10^{-4}$ S cm^{-1}	116,117
	Heteropolyacid	$\sigma \geq 1 \times 10^{-2}$ S cm^{-1}	118
	$Zr(HPO_4)_2$	$\sigma = \sim1 \times 10^{-4}$ S cm^{-1} at 80 °C	35
—	Heteropolyacid, PDMS	$\sigma = \sim7.7 \times 10^{-2}$ S cm^{-1} high temperature stability.	119

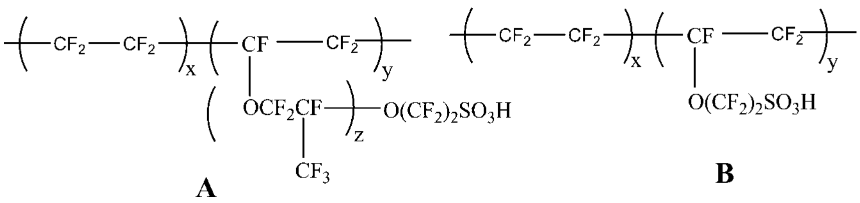


Fig. 7 General structures of A: Nafion membrane B: Dow membrane; x, y and z vary with the membrane.

results into lower conductivity. However, it is possible to retain quasi-order cryastallinity and hence conductivity by incorporation of crystalline materials such as silica, zirconia, titania *etc.* into the polymer matrix. This will act as a water storage medium enabling good proton conductivities even at 145 °C.[47]

5.1.1. Perfluorinated/SiO_2 composite ionic membranes.

Mauritz has done pioneering work in preparing ionic "nanocomposites" *via* sol–gel techniques, where the inorganic matrix was molecularly dispersed into the Nafion matrix.[45,48,49] He exploited the fact that pendant $SO_3^-H^+$ group clusters catalyse the sol–gel reaction. In this procedure, as shown graphically in Fig. 8, the Nafion membrane was swollen in an alcohol/water solution. A mixture of tetraethylorthosilicate (TEOS) and alcohol was added to the swelling solution containing the Nafion membrane, where TEOS molecules presumably migrate to $SO_3^-H^+$ group clusters. After the sol–gel reactions, the *in situ* inorganic phase was cured. This was accomplished by placing the membrane in a vacuum oven at 100 °C, where the solvents, alcohol and water evaporate and the condensation of SiOH groups proceeds.[45,48] He also observed with Nafion 117 (1100 equivalent wt) composite membrane that weight uptake of dried samples increases linearly with immersion time in sol. This suggests that as immersion time increases the SiO_2 percolates the Nafion. However, there were a significant number of SiO_2 deposits on the surface, making it necessary to clean the surfaces of the membranes with alcohol after the immersion process to avoid surface layer formation.[49] The SiO_2 distribution profile across the membrane was mentioned. It is higher near the surface and decreasing to a minimum in the middle creating SiO_2 concentration gradient. This unevenly distributed SiO_2 concentration gradient was reduced using an acid catalyzed, pre-hydrolyzed silicon alkoxide solution in alcohol, so that partially hydrolyzed species, such as $(RO)_{4-x}$ $Si(OH)_x$ molecules migrate to the $SO_3^-H^+$ clusters of Nafion at the same time membrane becomes swollen. However, a slight concentration gradient is hard to avoid because of the difficulty of diffusion in the narrow channels of Nafion membrane. Nafion/SiO_2 composites showed a higher water uptake at room temperature (~20%) compared with unfilled Nafion (~15%). Presumably, the sol–gel silica provides a large number of hydroxyl groups that tie up water molecules. The hydrophobicity of the fluorocarbon backbone and pendant side chains appears to be reduced by the incorporation of SiO_2.[48,49]

The proton exchange membranes with low methanol permeability were constructed by incorporating Nafion into a covalently cross-linked network composed of 4,4′-methylenedianiline (MDA) and 3-glycidoxypropyltrimethoxysilane (GPTMS).[50] The hybrid membrane was prepared by acid hydrolysis of GPTMS in appropriate amount of ethanol. The robust framework with full of covalently bonded silica showed both good proton conductivity (*i.e.*, $\sigma = 3.4 \times 10^{-2}$ S cm^{-1}) and ultralow methanol permeability (*i.e.* $P = 1.1 \times 10^{-8}$ cm^2 s^{-1}) compare to bare Nafion-117 ($\sigma = 4.5 \times 10^{-2}$ S cm^{-1} and $P = 2.2 \times 10^{-6}$ cm^2 s^{-1}) under the same experimental conditions.

The hygroscopic silica nanoparticles used in most of references are single functional *i.e.* hydrophilic even though nanoparticles that are both hydrophilic and proton conductive (*i.e.*

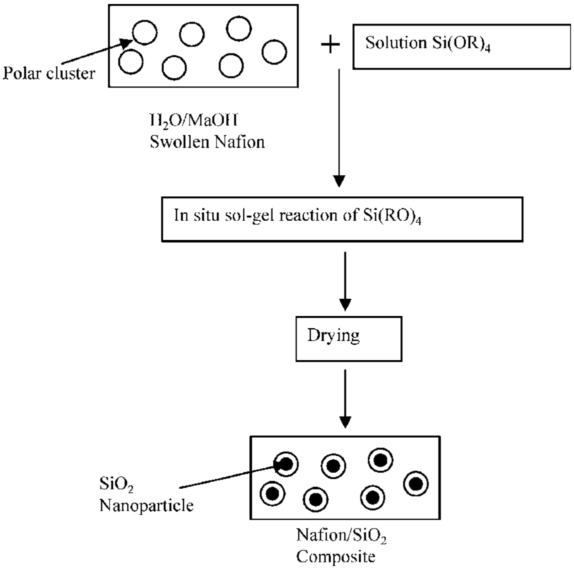


Fig. 8 A schematic presentation of the preparation of a Nafion/SiO_2 composite.[41]

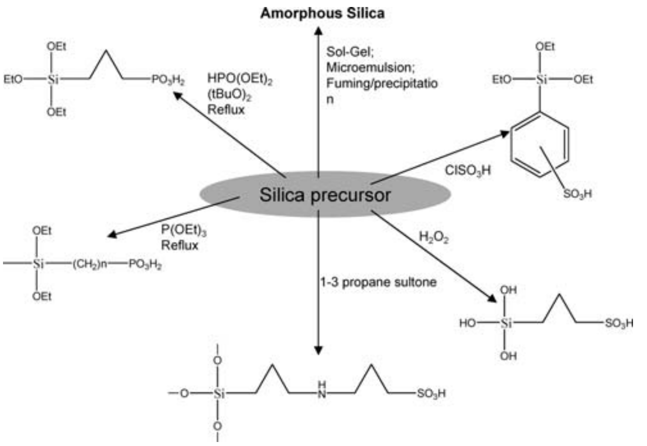


Fig. 9 Common non functional and functional silica materials used in organic-inorganic composite proton exchange membrane preparation.

bifunctional) as shown in Fig. 9 would have been preferred. Wang *et al.* and Li *et al.*[51–53] made an attempt to developed functional silica nanoparticles followed by its composite with Nafion (E.W. = 1100 g mol^{-1} SO_3H). In the synthetic protocol, sulfonation of silica precursor, phenethyltrimethoxysilane (PETMS) was carried out with chlorosulfonic acid. A stoichiometric amount of chlorosulfonic acid was drop wise added into PETMS under rigorous stirring and kept at room temperature for 2 to 3 h to ensure complete sulfonation of phenethyl groups. After sulfonation, measured amounts of absolute ethanol and deionized (D.I.) water were added for the hydrolysis condensation of sulfonated PETMS. Hydrolysis of sulfonated PETMS was carried out under self-acid-catalysis of the sulfonic groups under stirring for 1 day. Then finally obtained sol was mixed to appropriate amount of Nafion solution in ethanol to give composite membranes with specific composition. The resulting membranes shows about 2.7–5.8 times higher conductivity than bare Nafion membrane with good dimensional stability. Also these composite membranes shows better single cell performance and low methanol permeability in fuel cell at temperature rang 25–75 °C. The bifunctional silica nanoparticles developed into pre-swelled Nafion membrane by hydrolysis co-condensation of TEOS and γ-propyl mercaptotriethoxysilane (MPTMS) followed by oxidation of mercapto group enhances water sorption and proton conductivity than unmodified Nafion.[54,55] A key parameter governing the performance of these Nafion/SiO_2 hybrid membranes is the MPTMS/TEOS ratio used for the formation of the functionalized silica domains. The hybrid membrane obtained by a higher ratio MPTMS/TEOS exhibit intrinsically higher activation energy for the proton transport at high water activity and an enhanced proton conductivity in the range of temperature 40–70 °C at lower water activity (0.4–0.5).

A new approach for synthesizing low-cost perfluorinated organic-inorganic composite PEMs based on PVDF and silica with surface-anchored sulfonic acid groups has been reported by Duvdevani *et al.*[56] The membrane was thermally stable up to 250 °C. Preliminary tests on fuel cell showed cell resistance with a non-optimized membrane in the range of 3 Ω cm^{-2} and maximum power density of 32 mW cm^{-2} at 70 °C. The crossover-current density for a 100 μm thick membrane was measured in 1M methanol at 80 °C and found to be 110 mA cm^{-2}.

5.1.2. Perfluorinated/ZrO_2 composite ionic membranes.

Compared with silicon alkoxides, hydrolysis and condensation reactions of Zr alkoxides occur rapidly because Zr has a lower electro-negativity and an ability to form several coordination states upon reaction with water.[57] Fig. 10 show the acid functionalized and non functionalized ZrO_2 commonly used in the modification of proton exchange membranes. Datta and co-workers[58] predicted the conductivity of *in situ* sol–gel method prepared ZrO_2-Nafion nanocomposite membranes as a function of relative humidity. The nanocomposite membrane showed higher proton conductivity compared to Nafion at the same temperature and humidity conditions due to the improved water uptake, provision of strong acid sites and higher bulk to surface water ratio, which is critical for higher proton conductivity and better fuel cell performance. He has showed improvement in fuel cell performance at 80 °C as compared to other membranes. However, Nafion-SiO_2 exhibited subsequently lower performance than bare Nafion as contrary to results reported in literature. The reason for poor performance may be attributed by high EW perfluorinated backbone. At 110 °C and 0.5 V, ZrO_2 composite membranes have about 30–40 mA cm^{-2} higher current density compared to bare Nafion membranes, while SiO_2 membranes had similar performance to Nafion and constantly increased when temperature raised to 135 °C. They obtained best performance at same temperature with low molecular weight Nafion-ZrO_2 composite membrane.[58] The reason for the higher fuel cell performance was the formation of acid sites with sulfated zirconia. This approach opened an window for acid modification of zirconia to improvement fuel cell performance.

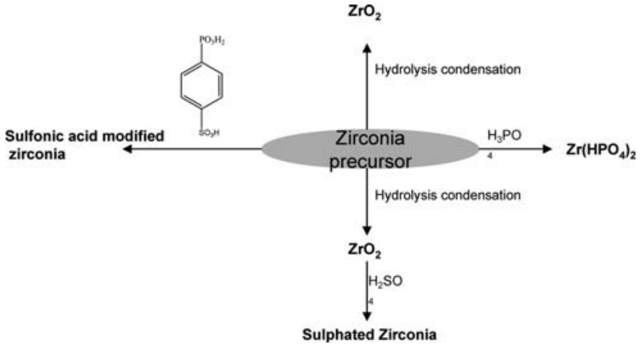


Fig. 10 A schematic presentation of the modification of zirconia.

Sulfated zirconia (S–ZrO_2), a solid state super-acid, exhibits a Hammett acid strength H_0 of −16.03, and was recognized as the strongest solid acid.[59] Hara and Miyayama studied the proton conductivity of S–ZrO_2 prepared by three different methods and found that it had a high conductivity of 2.3×10^{-1} S cm^{-1} at 105–135 °C.[60] Datta and co-workers[61] had synthesized *ex situ* and *in situ* S–ZrO_2–Nafion PEMs and evaluated their performance for higher temperature/lower RH operation. The promising potential of the S–ZrO_2–Nafion composite showed improved hydration as well as conductivity at higher temperature and lower RH conditions. The polarization and power density curves of the single cells with Nafion 112, recast Nafion membrane and 15 wt% S–ZrO_2–Nafion composite membrane on H_2/O_2 at 80 °C (gases saturated at 80 °C, RH ≈ 1) and 120 °C (gases saturated at 110 °C, RH ≈ 0.6) has been reported[62] with the inlet pressure of $PH_2 = PO_2 = 0.2$ MPa. The result suggested that when operated at normal operational temperature, the cell performance with 15 wt% S–ZrO_2/Nafion composite membrane reaches 1.35 W cm^{-2}, which is superior to the single cell performance of Nafion 112 (1.22 W cm^{-2}) and recast Nafion (1.28 W cm^{-2}). They have the best performance of about 0.99 W cm^{-2} at 120 °C for S–ZrO_2/Nafion composite membrane compare to bare Nafion-112 (0.75 W cm^{-2}) and bare recast Nafion membrane (0.72 W cm^{-2}).

Zirconium phosphate (ZrP) is an inorganic proton conductor and highly hygroscopic insoluble solid[63] and discussed in section 3.2. It has been shown, for example, that zirconium phosphate glasses prepared through a sol–gel route have a proton conductivity of 10^{-2} S cm^{-1} at room temperature under conditions of full humidification.[64] It has been electrochemically[65] and chemically[66] precipitated *in situ* in the pores of a per-fluorinated ionomer membrane for PEFC applications. The composite membranes can be prepared by incorporating the zirconium phosphate into the membrane using the procedure described by Grot and Rajendra[66] or by recasting from a Nafion solution with zirconium ions as described by Savadogo.[12] Zirconium phosphate was incorporated into Nafion *via* an exchange reaction involving Zr^{+4} ions followed by precipitation of zirconium phosphate after immersion of membrane in a phosphoric acid solution. The usual preparation sequence given by Savadogo[12] is as follows: (i) the membranes are swollen in a 1 : 1 vol methanol–water solution; (ii) dipped in zirconylchloride; (iii) rinsed and placed in a 1M phosphoric acid solution. This process leads to an insoluble zirconium phosphate in the nano-pores of the membrane. The properties of these membranes can be summarized as follows: (i) a composite membrane based on a commercial Nafion-115 membrane exhibited a performance of 1 A cm^{-2} at 0.45 V, whereas an unmodified membrane exhibited a performance of 0.25 A cm^{-2} for an H_2/O_2 PEMFC at 130 °C and a pressure of 3 bars. With the same operating conditions, the cell performance was 1.5 A cm^{-2} at 0.45 V for the composite recast membrane. The composite recast membranes showed a stable behavior over time when maintained at 130 °C, while non-composite membranes show irreversible degradation. The proton conductivity was found to be similar for pure Nafion and Nafion-ZrP. The activation energy associated with the proton conduction was found to be similar for pure Nafion (9.34 kJ mol^{-1}) and composite Nafion-ZrP (9.82 kJ mol^{-1}). This indicates that the presence of zirconium phosphate does not significantly change the proton conduction mechanism in a well-hydrated membrane. The slight improvement was attributable either to the hydroscopy of the zirconium phosphate or to the reduction in the number of free spaces in the nano-pores, promoting capillary condensation and thus water retention and proton conductivity.[63] Modified Nafion structures based on surface modification (surface cross-linking, *etc.*) and/or bulk modification (Nafion-inorganic hybrid structures or barrier layer laminated composite structures) are under development at DuPont[12] for DMFC applications. The recasting process of the DuPont composite membrane is not known, but the above results on Nafion-ZrP composite membrane may induce some comments for further developments: (i) determination of the stability of the composite membrane with time, and a study of whether or not the dopant is retained in the composite membrane over an extended period; (ii) the stability of cell performance based on the composite membrane, in particular at cell temperatures higher than those of the humidifiers; (iii) determination of the fuel-cell exhaust, and the anode and cathode catalyst compositions, and of whether or not they are contaminated by the dopant; and (iv) monitoring of the conductivity of the composite membrane with time. In the other efforts Nafion-ZrP modified with room temperature ionic liquids has been used for the conductivity improvement but they have lower conductivity and have been explained in the review in ref. 12.

Zirconium sulfophenyl (ZrSPP) and zirconium alkyl sulfophenyl phosphonates[36–38,67] showed increased conductivity dependent on relative humidity and discussed in section 3.2. They made efforts to make composites of these materials with the Nafion to increase the conductivity at high temperatures above 100 °C by dispersing the particles of ZrSPP synthesized from $ZrOCl_2$ and m-sulfophenyl phosphonic acid. The composite membranes showed 700 mA cm^{-2} current density in fuel cell which was four times better than recast Nafion at 100 °C.

5.1.3. Perfluorinated/heteropoly acids composite ionic membranes. The usual method for the preparation of composites of perflourinated membranes with heteropoly acid is *in situ* casting from the ionomer solution. The sequence proposed for composite membrane preparation by Ramani *et al.*[68,69] is as follows: by reducing the volume of commercial 5% Nafion solution to 50% followed by mixing with the appropriate concentration of HPA: silicotungstic acid (STA), phosphotungstic acid (PTA) or phosphomolybdic acid (PMA), to produce Nafion-STA, Nafion-PTA and Nafion-PMA composites respectively; membranes of various thicknesses (15–500 μm) have been made by a solvent evaporation method. After solvent evaporation at room temperature, the membranes were dried on a plate at 45–60 °C for 24 h and then in an oven at 130–170 °C for 4 h. The resulting films were peeled off and washed with deionized water and stored. The ionic conductivity, water uptake, tensile strength and thermal properties of Nafion-STA, Nafion-PTA and Nafion-PMA were compared with Nafion-117. The effect of membrane thickness and HPA concentration on their physico-chemical properties were studied. It was shown that water uptake of various membranes increases in order of: Nafion-117 (27%) < Nafion-STA (60%) < Nafion-PTA (70%) < Nafion-PMA (95%). The ionic conductivity increases in order of: Nafion-117 (1.3×10^{-2} S cm^{-1}) < Nafion-PMA (1.5×10^{-2} S cm^{-1}) < Nafion-PTA (2.5×10^{-2} S cm^{-1}) < Nafion-STA (9.5×10^{-2} S cm^{-1}). The tensile strength of the membranes decreases in the order of: Nafion-117 (15 000 Pa) < Nafion-STA (14 000 Pa) < Nafion-PMA (8000 Pa) < Nafion-PTA (3000 Pa), while their deformation (ε_{max}) changes in the order of: Nafion-STA (45%) < Nafion-PMA (70%) < Nafion-PTA (170%) < Nafion-117 (384%). The voltage–current characteristics of polymer electrolyte fuel cells (PEFC) were determined.[12] From the cell voltage–current plots, the current density at 0.600 V of PEMFCs based on various membranes varies in the order of: Nafion-117 (640 mA cm^{-2}) < Nafion-STA (695 mA cm^{-2}) < Nafion-PTA (810 mA cm^{-2}) < Nafion-PMA (940 mAcm^{-2}).

Sulfonic acid functionalized heteropolyacid-SiO_2 nanoparticles were synthesized by grafting and oxidizing of a thiosilane compound with a micro-emulsion technique.[70] Sodium bis(2-ethylhexyl)sulfosuccinate and heteropoly acid PTA was dissolved in water and mixed with cyclohexane to form a well-defined micro-emulsion phase. Tetraethoxysilane (TEOS) was dropped into the microemulsion phase and stirred at room temperature for 12 h. The resulted PTA-SiO_2 nanoparticles were collected by centrifugation and repeatedly rinsing with acetone. For the improvement of hydrophilic and proton conducting properties, sulfonic acid groups were introduced onto the surface of the silica. It was carried by grafting and oxidizing of thio-silane compound.[19,71] 3-Mercaptopropyltrimethoxysilane (MPTMS) was dissolved in toluene and refluxed with PTA-SiO_2 nanoparticles for 24 h at 120 °C. After reflux, the nanoparticles were washed with dry toluene and dried for several hours at 120 °C. The oxidation of thiol group to sulfonic acid was carried out by treating the dried thiol-modified nanoparticles with aqueous H_2O_2 (30 wt%). The suspension was stirred at room temperature for 12 h. After the oxidation treatment, the resulting solution was centrifuged and washed separately with water and ethanol. The wet nanoparticles were suspended in 1 M H_2SO_4 solution for 4 h. Finally washed several times with water and ethanol and dried at 80 °C under vacuum. The atomic ratio of S/Si which was calculated by XPS measurement was found 0.105.[70,71] The composite membranes were prepared by suspending functionalized PTA-SiO_2 in 5 wt% Nafion solution and dried at 120 °C. The function of the sulfonic acid-functionalized PTA-SiO_2 nanoparticles was to provide a proton carrier and act as a water reservoir in composite membrane at elevated temperature. The DMFC performance of the composite membrane was evaluated at temperatures from 80 to 200 °C. The power density was 33 mW cm^{-2} at 80 °C, 39 mW cm^{-2} at 160 °C and 44 mW cm^{-2} at 200 °C, respectively.

Malers *et al.*[42] prepared composite membranes from polyvinylidenedifluoride-hexafluoropropylene (PVDF-HFP) and different heteropoly acid with weight ratio 1 : 1. For the first time they have presented complete polarization curves for a number of heteropoly acids (HPAs), $H_3PW_{12}O_{40}$, $H_3P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$, and $H_6As_2W_{21}O_{69}$ as the only proton conducting component and hence showed promising candidates for solid acid fuel cell performance at >200 °C. The high proton conductivities reported at RT are demonstrated in fuel cells using HPA/PVDF-HFP composites with limiting current densities as high as 1.6 A cm^{-2} using dry O_2 and H_2. Moderate fuel cell activity was demonstrated for $H_3PW_{18}O_{62}$ at 120 °C and 25% RH. Unfortunately all of the materials studied were somewhat porous and the open circuit potentials observed were somewhat low. They were also able to show that a HPA fuel cell could be shorted by reduction of the HPA to a heteropoly blue under exceptional circumstances. They have demonstrated higher proton conductivities than those reported in the literature and can be translated in to impressive currents in PEM fuel cells at RT with no external humidification. However, HPAs on their own do not have sufficient mobility of their protons for fuel cell temperature operation at 100 °C. Interestingly these materials may have application in high temperature PEMs at 200 °C. Although a small subset of the many structures available has been investigated. One HPA, $H_3P_2W_{18}O_{62}$, did show moderate activity at 120 °C with the application of some humidity. All of the membranes studied were certainly not optimized and suffered from porosity issues.

5.1.4. Perfluorinated/miscellaneous inorganic composite ionic membranes.

Various authors have tried different approaches to develop miscellaneous inorganic composites of perfluorinated PEMs. The composite membranes developed from Nafion-115 and zeolite by a supercritical CO_2 activation method show a decrease in methanol permeability as well as proton conductivity with an increase in zeolite content.[72] It was shown that overall performance increases as compare to bare Nafion-115 with appropriate composition, which was determined by the selectivity parameter (*i.e.* ratio of proton conductivity : methanol permeability).

Lin *et al.*[73] studied clay composite membranes developed from montmorillonite (MMT) and Nafion. The modification of the montmorillonite with poly(oxyproplene)-backboned quaternary ammonium salts was utilized to improve the compatibility with Nafion. They evaluated the membrane performance in terms of water uptake, ion exchange capacity (IEC), methanol permeability, proton conductivity, and cell performance. They observed slight decrease in the water content, ion-exchange capacity and proton conductivity; but about 40% decrease in methanol permeability for the 5% MMT-POP-400-Nafion composite membrane. The same composite membrane shows the current density of 56 mA cm^{-2} and power density of 13.3 mW cm^{-2} in single cell performance at a potential of 0.2 V. The composite membrane from sulfonic acid modified clay: laponite and Nafion was studied by Bebin *et al.*[74] The clay powder was modified by helium plasma under a pressure of 0.1 mbar using a 13.56 MHz frequency for 2 min. The activated clay was immediately immersed in a 3% (w/v) solution of p-styrene sulfonate in DMF and refluxed for 48 h. The grafted clay washed with DMF to remove unreacted monomers and oligomer moieties. The composite membranes were prepared by a recasting Nafion solution mixed with modified Laponite particles. The measured proton conductivity of the composite membrane was higher than that of the commercial Nafion in the temperature ranges 20–95 °C with a more significant difference at low relative humidity. At 80 °C and 0.6 V optimized composite membrane showed 720 mA cm^{-2} current density, which was corresponds to 20% improvement in power density (430 mW cm^{-2}). At higher temperature, 120 °C with dilute cathode gas, air at lower pressure 3 bars; induce a drastic dehydration effect in the cell. The sensitivity of the membrane to humidity was easily observed with these cell conditions. With these fuel cell conditions Nafion membrane could deliver 390 mA cm^{-2} of current at 0.6 V while the composite reach 500 mA cm^{-2}, a 30% improvement in power density.

5.2. Inorganic composites of poly(arylene ether)s

Poly(arylene ether)s are well known engineering materials and thought to be an alternative candidate to perfluorinated polymers in high performance PEMs because of their availability,

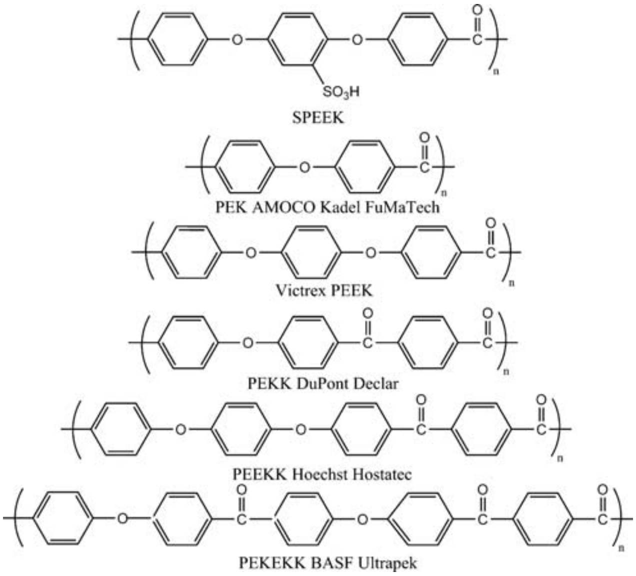


Fig. 11 Structure of sulfonated poly(ether ether ketone) and representative membranes of poly(arylene ether ketone) family.

processability, options for chemical modification, and anticipated stability in a fuel cell environment. Specifically, poly(arylene ether) materials such as poly(arylene ether ether ketone) (PEEK), poly(arylene ether sulfone), and their derivatives are the focus of investigations. The synthesis of these materials has been widely reported.[10,75] The poly(ether ketone) candidates from the polyarylene family differentiate through varying sequences of ether (E) and ketone (K) units to give ether rich: PEEK (Victrex® PEEK, GatoneTM PEEK, Gharda Chemicals) and PEEKK (Hostatec®), or ketone-rich semicrystalline thermoplastic polymers: PEK (Amoco Kadel®, FuMA-Tech) and PEKEKK, Ultrapek®, BASF)[44] (Fig. 11). Oxidative and hydrolytic stability increase with increasing proportion of ketone segments as in case of PEKK (Declar®, Du Pont), and undergoes lower weight loss at ~400 °C under water/oxygen than either PEKEKK or PEEK. In recent years, sulfonated poly(ether ketone) has been extensively studied than any other non-fluorinated system, with contributions from Jones, Kreuer, Kerres, Bauer, Rozière, and their co-workers and others,[3,10–12,47,76,78] to studies ranging from modeling of the microstructure, proton transport properties, application in low- and medium-temperature PEMFC and DMFC, and as a component of polymer blend and hybrid inorganic–organic membranes.

Direct methanol fuel cell performance has been reported using hydrogen as fuel for a sulfonated PEEK membrane with an ion exchange capacity of 1.6 meq g^{-1} and 18 μm thickness.[76] They have obtained 0.5 mA cm^{-2} current density with oxygen and air at voltages of 0.8 V and 0.72 V respectively, and temperature of 90 °C. With SPEEK membranes of 70 μm thickness they reported higher performance at 85 °C than Nafion-115 under the same test conditions. Patent reports claim 4000 h of functioning for SPEEK with an IEC of 1.47 meq g^{-1} at a modest cell temperature of 50 °C,[77] giving a maximum power density of 0.386 W cm^{-2} at 0.52 V, whereas at 90 °C at constant current density of 0.5 mA cm^{-2} SPEEK has attained 1000 h of functioning without failure.[44] At higher temperatures, poly(arylene ether ketones) suffers from dehydration. It exhibits less pronounced hydrophobic/hydrophilic separation and different morphological behavior.[78] This results in significant reduction in electro-osmotic drag and proton conductivity. Authors worldwide tried to over come these problems by making composites with charged and uncharged inorganic moieties.

Guiver and co-workers[79] developed a composite membrane from sulfonated poly(arylene ether ether ketone ketone) (SPAEEKK) with pendant sulfonic acid groups. A series of hybrid membranes made from SPAEEKK incorporating different amounts of silica nanoparticles were reported using the sol–gel reaction with tetraethyl orthosilicate (TEOS). The performances of hybrid membranes were investigated in doped and un-doped H_3PO_4 states. The H_3PO_4 doped SPAEEKK/silica hybrid membranes showed an improvement in membrane properties. The improvement is claimed on the basis of uniform distribution of nano-sized silica particles and H_3PO_4 into the membrane matrix. The silica has an effect on the state of water in the membranes. The $\equiv$SiOH groups of silica provide strong hydrogen bonding sites and increases contents of the bound to free water ratio into the membrane matrix. Further it retains water molecules at elevated temperatures and thus maintains proton conductivity. The proton conductivities of un-doped and doped H_3PO_4 hybrid membranes were in the range from 0.02 to 0.082 S cm^{-1} and from 0.024 to 0.097 S cm^{-1}, respectively. The methanol permeabilities ranged between 1.4 × 10^{-7} and 6.9 × 10^{-7} cm^2 s^{-1}. In comparison with Nafion-117 (proton conductivity 0.1 S cm^{-1} and methanol permeability 7.7 × 10^{-6} cm^2 s^{-1} at 80 °C), an H_3PO_4 doped SPAEEKK/silica hybrid membrane had 0.078 S cm^{-1} proton conductivity and 6.06 × 10^{-7} cm^2 s^{-1} methanol permeability at 80 °C. The methanol permeability is 92.1% lower than Nafion-117. At 30 °C, the conductivity and permeability values of Nafion-117 were 0.078 S cm^{-1} and 2.52 × 10^{-6} cm^2 s^{-1}, respectively; while H_3PO_4 doped SPAEEKK/silica hybrid membrane had values of 0.032 S cm^{-1} and 2.02 × 10^{-7} cm^2 s^{-1}, with permeability being 92% lower. It shows H_3PO_4 doped SPAEEKK/silica as potential candidates for polymer electrolytes for DMFC and PEMFC applications.

The nanocomposites prepared from aminophenyl functionalized silica and sulfonated poly(ether ether ketone) SPEEK showed conductivity higher than 0.01 S cm^{-1} at 25 °C and 100% RH. The improvement in proton transport was claimed to be caused by the presence of a membrane micro-structure and extensive silica-membrane interfacial regions.[80] The existence of the interpenetration of the SPEEK polymer and functionalized aminophenyl silica networks with a domain size of about 4 nm indicates possible confinement of the polymer within the composite membrane. It was also claimed that nano-phase composite membranes up to 50 wt% silica can be obtained with SPEEK cast in dimethylsulfoxide. Composite membranes cast in lower dielectric constants such as dimethylformamide are translucent and more brittle.

Moeller and co-workers[81] prepared composite polyelectrolyte membranes from solutions of sulfonated poly(ether ether ketone) (SPEEK) (DS 64%) and polyethoxysiloxane (PEOS) with *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole as the compatiblizer in dimethylacetamide, following the concept of a semi-interpenetrating network. The *in situ* transformation of PEOS into SiO_2 was done in a “water free” process. The morphology of the films obtained was controlled by a phase segregation process, determined by the rate of evaporation of the solvent and by the transformation of PEOS into SiO_2-particles in the presence of suitable catalyst. By addition of *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole they showed a dramatic reduction in the size of SiO_2 particles. Proton conductivity of resultant composite membranes was lower than the Nafion-115. Nunes *et al.*[82] showed a 13% reduction in methanol permeability and a 40% reduction in water flux with decrease in membrane conductance using composite membranes from SPEK (sulfonated poly(ether ketone)) and SPEEK. They prepared composites with *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole and TEOS. Part of the membranes were prepared by first reacting the polymer with 1,1′-carbonyl-diimidazole (CDI) and aminopropyl triethoxysilane. Some other part of CDI was reacted with part of the sulfonic groups of the polymer, followed by addition of aminopropylsilane (APS), leading to alkoxy silane groups covalently linked to the polymer.

It was claimed,[83] that a composite membrane prepared from the derivative of poly(arylene ketone) family, *i.e.* poly(phthalazinone ether ketone) (PPEK) and SO_3H-functionalized SiO_2 showed 3.6 fold increase in conductivity and low methanol permeability compared to bare sulfonated PPEK. The acid functionlized silica was prepared from commercial available silica particles of 10–20 nm size and glycidyl phenyl ether (GPE).[84]

Well ordered silica materials such as Montmorillonite, Laponite and MCM-41, are familiar polymer filling materials. When polymers are mixed with these natural or synthetic inorganic materials, their properties are considerably improved. These inorganic materials have characteristics properties of improving mechanical strength, impact resistance and reducing permeability of gases and moisture.[85] The PEMs composite membrane prepared from SPEEK and Montmorillonite by simple solution mixing and casting showed reduction in proton conductivity and methanol permeability. The organically modified montmorillonite showed a dramatic decrease in methanol permeability with retention of proton conductivity of 1.2×10^{-2} S cm^{-1} at 90 °C. This value is close to Nafion-115.[86] A 370 mAcm^{-2} current density at 0.6 V for 10% Laponite/SPEEK composite membrane was reported. They performed fuel cell test for 100 h at 70 °C with same current density.[85] Further increase in fuel cell performance was reported by modification of laponite with imidazole glycidoxypropyl triethoxysilane (IGPTES) and 3-2-imidazolin-1-yl-propyltrimethoxysilane (IPTMS) to decrease methanol permeability without losing membrane conductivity.[87] The same type of results were shown for an MCM-41/SPEEK composite membrane by same author.

A series of composite membranes has been reported for incorporation of HPA: tungstophosphoric acid, its disodium salt and molybdophosphoric acid into a partially sulfonated PEEK and its derivatives.[88–91] These membranes exhibited a rather high conductivity of 10^{-2} S cm^{-1} at ambient temperature, and up to a maximum of about 10^{-1} S cm^{-1} above 100 °C. It was also mentioned that there was an increase in thermal stability of composite membranes by DSC (differential scanning calorimeter) studies due to intermolecular interaction between SPEEK and HPA. The main disadvantage of these HPA-SPEEK composite membranes is the dissolution of HPA in the water formed by the electrochemical process of current generation with a consequent decay of cell performance.[92]

Many workers devoted research to overcoming the polyelectrolyte dissolution problem by entrapment of HPA into the host material, mostly silica oxide networks. Usually, the heteropolyacid was fixed through covalent or coulombic interactions. This involved the reaction between protons and SiO_2, resulting in a decrease in the acid strength. The decrease in acid strength was described during investigations of ^{31}P MAS NMR, which shows a chemical interaction between the protons of HPA and SiO_2.[92] There are two different approaches for covalent or coulombic entrapment of HPA into the polymeric matrix: the *in situ* generation of an oxide network by the sol–gel process from alkoxysilanes followed by covalent bonding of HPA with silica matrix and the modification of the anion structure of the heteropolyacid.[93] The covalent bonding between HPA and inorganic phase was carried out using organosilyl derivatives of the divacant tungstosilicate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and GPTS (3-glycidoxypropyltrimethoxysilane). The presence of nucleophilic surface oxygen atoms at vacant site on Lacunary heteropolyacids $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ forms an effective organic-inorganic material, which allows covalent grafting of electrophilic groups. The organic functionality was linked to the polyanion surface by E–O–W bridges (E: Si(IV), P(V), Sn(IV), Ge(IV), or Ti(IV)), resulting in saturation of heteropolyanion surface. In this way organic-inorganic composite materials have been synthesized by addition of reactive organic groups (vinyl, allyl, methacryl, and styryl) to the lacunary heteropolyacids, $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and $[\alpha\text{-SiW}_{11}\text{O}_{396}]^{8-}$.[94] Nunes and co-workers[92] introduced GPTS into the anion structure of lacunary heteropolyacid enabling its attachment to a host material, by an epoxy ring opening reaction with appropriate functional groups present in the surface of the host material, without involving the protons and therefore without affecting the acidity of the heteropolyacid. He got the membrane conductance to of the same order as the plane membrane with good bleeding stability in aqueous methanol solution. To avoid the problem of bleeding, a composite membrane of HPA loaded Y-zeolite and SPEEK has been reported[95] and found to be suitable for PEM applications.

The conductivity of the SPEEK increases with increase in degree of sulfonation; its mechanical properties show a parallel progressive deterioration leading to a downfall of conductivity. To overcome this problem, TiO_2 was used as filler in 90% degree of sulfonated PEEK. Because of rapid hydrolysis of $Ti(OBu)_4$ in aqueous condition, the composites were prepared under non hydrolytic condition using two routes. In one route $Ti(OBu)_4$ (1.11 mmol, 0.33 mL) and pyridine (12 mmol, 1 mL) were added. And in the second route, a sol was prepared by adding $Ti(OBu)_4$ (1.11 mmol, 0.33 mL) and 2,4-pentandione (acac, 2.4 mmol, 0.22 mL) in DMAc (3 mL) at 0 °C. The resulting solutions were added to the SPEEK solution (1.68 g, 4.58 meq) and stirred at room temperature for 1 h. The solvent was evaporated to 5 mL at 120 °C, and then cast onto a Teflon plate and heated until dry. After cooling to room temperature, the resulting membranes were peeled off and dried at 100 °C for 10 h, then further dried under vacuum at 80 °C for 2 d for complete solvent removal. Before use, the membranes were treated with 5 M H_2SO_4. The

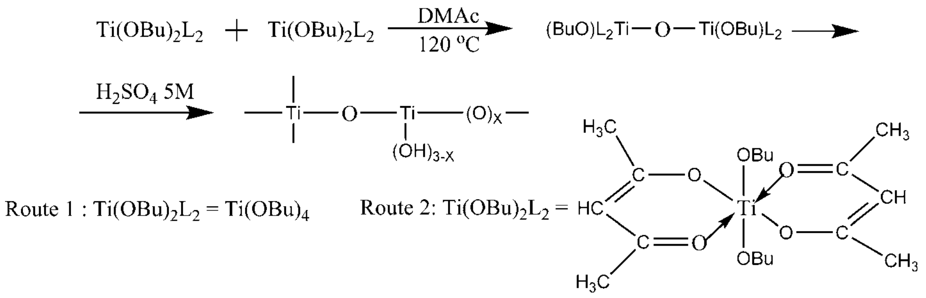


Fig. 12 The reaction scheme for the preparation of TiO_2.

reaction scheme is shown in Fig. 12. The prepared membranes showed a conductivity of about 5.8 × 10^{-2} S cm^{-1} at 120 °C in fully hydrated conditions.[96,97] The methanol permeability of Nafion-115 membrane is 2.32 × 10^{-6} cm^2 s^{-1} at room temperature while it was between 0.5 × 10^{-6} and 2 × 10^{-6} cm^2 s^{-1} for composite membrane with 65% sulfonated PEEK and TiO_2,[97] which is considerably smaller than that of Nafion-115 membrane. The same membranes having 5wt% TiO_2 have been reported the maximum fuel cell performance.

The SPEEK/BPO_4 composite membranes were prepared from tripropylborate $(C_3H_7O)_3B$ and phosphoric acid (H_3PO_4), in equal molar proportion by a sol–gel method.[98] The weight percentage of BPO_4 in the composite membranes was determined by assuming total conversion of precursors to BPO_4. Initially SPEEK was dissolved in *N*,*N*-dimethylacetamide (DMAc) at room temperature to prepare a 10 wt% solution and filtered. The requisite quantity of H_3PO_4 was added to the polymer solution and stirred with a magnetic stirrer for 10 min. Then, $(C_3H_7O)_3B$ was added and further stirred for 10 min. The resulting solution was degassed under vacuum and cast onto a flat-bottom Petri dish for membrane formation. The composite membranes showed six fold increases in conductivity with 30% loading of BPO_4.

5.3. Inorganic composites of poly(arylene ether sulfone)s

Poly(arylene ether sulfone)s are another engineering material used in proton exchange membranes fuel cell. Los Alamos National Laboratory and Virginia Polytechnic Institute created the biphenol based poly(arylene ether sulfone) (PES) and a poly(arylene ether benzonitrile) (PEBN) membranes. It was reported[99,100] that for these membranes water uptake correlated proportionally with ion exchange capacity (IEC) and it is decreasing in the order of PES, PEBN and Nafion®. Nevertheless, methanol permeability, which is typically proportional to water uptake and IEC, was two times higher for Nafion® than the other two membranes.

The MCO of PES and PEBN are nearly equal (81 × 10^{-8} and 87 × 10^{-8} cm^2 cm^{-1}) with 0.5 M methanol at T = 30 °C. At a slightly higher (10%) membrane resistance, the MCO is a factor of 2 lower than for Nafion® (167 × 10^{-8} cm^2 cm^{-1}). The combination of MCO and resistance properties results in a 50% improvement in selectivity, regardless of membrane thickness. The DMFC with this membrane has shown a performance of j = 200 mA cm^{-2} (compared to 150 mA cm^{-2} for Nafion®) at 0.5 V, T = 80 °C and ambient air pressure.[101] Another prospective DMFC membrane (originally developed for PEMFC) composed of modified poly(ether sulfone) (PES) is sulfonated poly(arylene thioether sulfone) (sPTES).[102] This membrane was synthesized at the Air Force Research Laboratory (AFRL) and had the following advantages: high chemical and thermal stability; higher proton conductivity (>100 mS cm^{-1}) than Nafion® 112 (80 mS cm^{-1}) at T = 65 °C and RH = 85%; comparable performance to Nafion® in DMFC applications; specific area resistance (ASR) of 0.13 cm^{-2} at 80 °C and H_2/air feed (compared to 0.18 S cm^2 for Nafion®) retains large amounts of water over a wide temperature range; cheaper than Nafion®

There are reports of better performances of poly(arylene ether sulfone)s membrane in fuel cell, however their chemical stability is always questionable because of oxidative degradation of nonfluorinated backbone.[103] The generation of hydroxyl and hydroperoxyl radicals in either anode or cathode after a 2-electron reduction reaction between H_2 and O_2 cross over the PEM to opposite electrode responsible for chemical stability of membranes.[104] In the perfluorinated backbone, C–F bond energy is high (485 kJ mol^{-1}). The fluorine atoms wrapped the C–C main chain closely to avoid attack from oxidative free radicals. This is the cause of that the film has good oxidation resistance. However, in the non-fluoride PEMs, the C–H bond dissociation enthalpy is lower and that oxidative degradation occurred easily. For the non-fluoride proton exchange membrane, oxidative degradation problem has become more prominent.

Xing *et al.*[103] developed composite membranes from a simple dispersion of Ag–SiO_2 particles in sulfonated poly (biphenyl ether sulfone) (SPSU-BP) to increase chemical stability against oxidative degradation by catalytic decomposition of generated H_2O_2. He observed that the initial limiting currents of the two membranes, with Ag–SiO_2 and without Ag–SiO_2, were very similar, about 5 mA. But after 22 h the former membrane showed high limiting current of about 70 mA. Whereas, the latter membrane, even after 40 h, showed a lower limiting current of about 10 mA.

The composites of the bifunctional silicas are always preferred in fuel call applications.[23] The composite membranes prepared by the methyl phosphorylation of aminopropyl silane and sulfonated poly(ether sulfone) showed an increase in proton conductivity and decrease in methanol permeability compared to Nafion-117.[105] It was also reported that the current–voltage polarization curves were in good agreement with Nafion-117.

The chemical and hydrolytic stability of amorphous silica during fuel cell operation is still questionable.[106] The incorporation of zirconia and zirconium phosphate into hydrocarbon membranes are, in practice, composite membranes prepared from zirconium phosphate and sulfonated poly(ether sulfone) which showed an increase in proton conductivity at higher temperatures. But there are no such reports available on the fuel cell performance of these composite membranes and hence it is the subject of intensive study.

5.4 Inorganic composites of polybenzimidazole

Polybenzimidazole (PBI) based proton exchange membranes are successful hydrocarbon membranes for fuel cell applications. PBI is an aromatic heterocyclic basic polymer (pK_a = 5.5) which can be complexed with strong acids or very strong bases. Bare PBI is an electronic and ionic insulator but becomes a very good ionic conductor after doped with acids in the proper conditions and remains an electronic insulator.[12,99] The composite of PBI–phosphoric acid has been extensively studied at Case Western University, USA for high temperature DMFC applications.[12,99] It was observed that the *in situ* casted PBI/phosphoric acid composite membrane exhibited better performance in DMFC than the composite membrane prepared by immersing preformed PBI film into the phosphoric acid solution. Depending on the preparation method of PBI, the properties of the composite membranes varies. But in general it has high proton conductivity, low electro-osmotic drag, capable of operating at high temperature (T = 200 °C) and low gas humidification, low MCO and low cost in comparison with Nafion/perfluorinated ionomers.

The major disadvantage is leaching of the low molecular weight acid in hot methanol solutions. These problems were solved by the addition of high molecular weight phosphotungstic acid as a replacement of the low molecular weight acid. At $T > 130$ °C the conductivity of the doped PBI membrane is similar to Nafion® (30 mS cm^{-1} at 130 °C and 80 mS cm^{-1} at 200 °C).

5.5 Inorganic composites of poly(vinyl alcohol)

Poly(vinyl alcohol) (PVA) is a synthetic polymer having excellent film forming, emulsifying and adhesive properties accompanied with good resistant to oil, grease and organic solvents. It has high tensile strength and flexibility. Its melting point, 180–230 °C depending on the degree of hydrolysis makes it a promising candidate in DMFC applications. The presence of reactive –OH group further adds options of chemical modification to tailor its properties.

The sulfonic acid functionalized organic–inorganic hybrids based on (PVA)/SiO_2/sulfosuccinic (SSA) acid were reported.[107] In the hybrid membranes, sulfosuccinic acid served as both sulfonating as well as cross-linking agent. The proton conductivity and methanol permeability of the hybrid membranes were studied with changing SSA content from 5 to 25 wt% and found very much depends on SSA contain They found proton conductivities in the range of 10^{-3} to 10^{-2} S cm^{-1}, and the methanol permeability 10^{-8} and 10^{-7} cm^2 s^{-1} range. They claimed the decrease in methanol permeability in the presence of silica particles. Similarly, composite membranes of PVA/SiO_2 with copolymer of 2-acrylamido-2-methyl-propanesulfonic acid (AMPS) and 2-hydroxyethyl methacrylate (HEMA) crosslinked by poly(ethylene glycol) dimethacrylate (PEGDMA) has been reported.[108] They found proton conductivities of 0.02–0.11 S cm^{-1} with significantly lower fuel permeabilities than that of Nafion. Sulfonic acid functionalized silica/PVA composite membranes have been reported, created by a sol–gel method, where –SO_3H groups were introduced by oxidation of –SH group present in mercaptopropylmethyldimethoxysilane (MPDMS).[19] The resulting membrane had good thermal and electrochemical properties. The phosphonic acid functionalized silica/PVA composite proton exchange membrane has been reported. The phosphonic acid functionalisation was carried by phosphomethylation of aminopropyltriethoxysilane in aqueous medium.[109] The resulting composite membrane had an excellent methanol barrier capability with good hydrophilicity and proton conductivity at higher temperatures. From selectivity parameter, they found, 50% silica loaded PVA composite with 3 h of phosphorylation resulted best proton-exchange membrane. It was about 20% more suitability in comparison to Nafion 117 membrane for direct methanol fuel cell applications. Apart from the silica composites, heteropolyacid and zirconium phosphate composite membranes have been reported with good proton conductivity and lower methanol permeability.[110,111]

5.6 Miscellaneous organic-inorganic composite ionic materials

The classic approach for developing new types of organic-inorganic composite PEM materials is sol–gel chemistry. The commonly used precursors in sol–gel chemistry are tetramethoxysilane (TMOS) and Tetraethoxysilane (TEOS).[112–114] The introduction of organic functional groups into these inorganic precursors leads to organically modified sol–gel materials, called ormocers or ormosils or ceramers. The main advantages to have organic groups in sol–gel materials are: (i) during the preparation of purely inorganic materials, they can control the reaction rates of the reactants, the rheology of the sols, or the homogeneity and microstructure of the derived gels. (ii) The organic groups can be modified with different functional groups; acid functionalization is very common in fuel cell applications. The resulting final materials are composed of inorganic (oxidic) structures cross-linked or substituted by functionalized organic groups. For fuel cell applications, these hybrid materials can be prepared by two approaches. The first one is the physical mixing of acid functionalized molecules with an ormosil matrix and second one is the covalent linking of acid functionalized molecules with an ormosil matrix. The latter approach requires precursors in which the organic group is bonded to the oxide-forming element in a hydrolytically stable way.[115]

Honma *et al.*[116,117] did pioneering work in organic-inorganic composite proton exchange membrane development. In his initial approach the poly(ethylene oxide) (PEO) was end capped with triethoxysilane. PEOs of different molecular weights were mixed with silica precursors such as 3-isocyanatopropyltriethoxy silane in N_2 atmosphere at 70 °C for 5 days to give PEO with end capped urethane linked silica as shown in Fig. 13. By this method, they have produced a flexible, free standing membrane. The proton conductivity was obtained by dispersing monododecylphosphate into these ormosil matrixes. The obtained membrane showed good proton conductivity of about 10^{-4} S cm^{-1} at higher temperatures. In other efforts[117] he controlled the hydrophobic/hydrophilic characteristic of the membrane by organically bridged tri-alkoxysilane (bridged polysilsesquioxanes) precursors. They were used temperature tolerant polymers such as polyethers, alkylenes and aromatics to bridge alkoxysilane functional groups for organic-inorganic hybrid monomers. The proton conductivity was obtained by addition of heteropolyacids such as PWA into the sol. Fig. 14 shows the molecular structure of the organically bridged polysilsesquioxane monomers used in their work, where bifunctional polyalkylenes (ethane, hexane, octane, decane *etc.*, $(CH_2)n$: $n = 2$ to 14) were terminated by alkoxysilanes. The bridged polysilsesquioxanes were synthesized using the three most common methodologies, (1) metallization of aryl, alkyl, or alkynyl precursors, followed by reaction with a tetrafunctional silane, (2) hydrosilylation of dienes (or polyenes) or less commonly diynes, and (3) reaction of a bifunctional organic group with an organotrialkoxysilane bearing a reactive functional group. The bridged

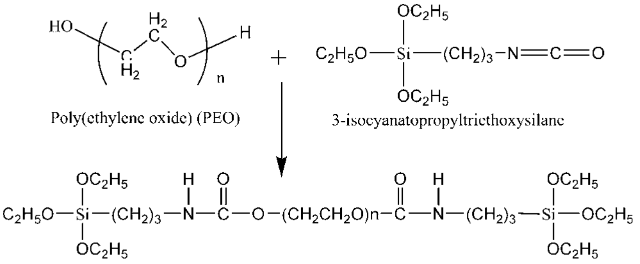


Fig. 13 A schematic presentation of the end capped silica.[116]

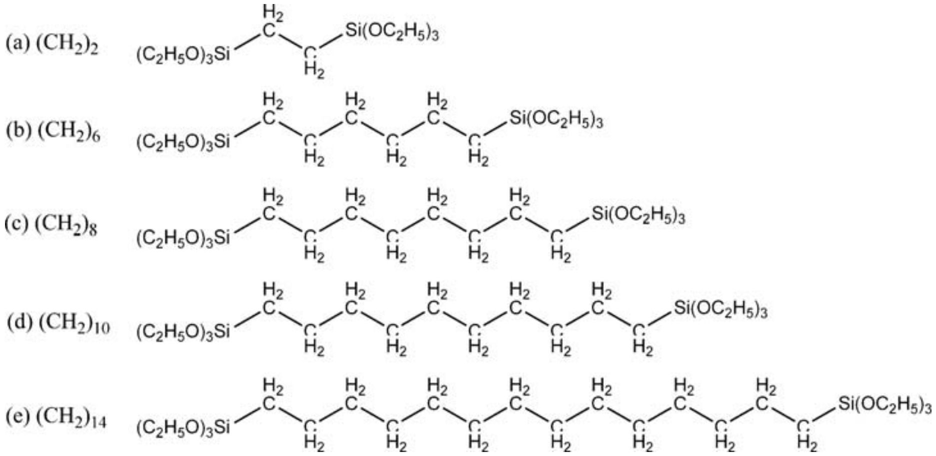


Fig. 14 Structures of different bridged polysilsesquioxanes.

polysilsesquioxanes they obtained either by synthesis using hydrosilylation reactions or from commercially (Gelest) available monomers.[118] The resulting membranes exhibited large proton conductivities (>10 $^{-2}$ S cm^{-1}) at high temperatures of up to 160 °C, where the conductivity of the hybrid membrane can be tailored by varying the processing conditions, such as the amount of water in the sol solution and the equivalent weight of PWA incorporated in the macromolecules. The fast ionic conduction in the resulting materials may be based on the synthetic mechanism of amphiphilic macromolecules in the solution. The bridged octane hybrid membrane showed the humidity dependence for the conductivity from 120 to 160 °C, while the conductivity decreases exponentially with the water vapor pressure. The conductivity exceeds 2×10^{-3} S cm^{-1} level even at 20% R.H. at 120 °C. Proton conductivity was stable above 100 °C with a small dependence on the R.H. The flexible polymer electrolyte membranes with zirconia, titania and polydimethylsiloxane (PDMS) of different molecular mass: 4500 and 600 have been reported.[119] The membranes showed thermal stability and flexibility up to 300 °C proton conductivity of about 7.7×10^{-2} S cm^{-1} by addition of 12-phosphotungstic acid (PWA).

These above discussed ionic inorganic material dispersed membranes have the drawback of leaching of the ionic conducting materials (heteropolyacids) with time. This could be prevented by forming covalent bonds between the ionic conducting material and the inorganic precursors. In the first effort, Honma and co-workers[35] developed zirconia membranes with trimethylene glycol, octamethylene glycol and hexadecanediol by the sol–gel method. The self-assembled hybrid organic-inorganic membranes showed high flexibility, chemical tolerance, and thermal stability, and good mechanical properties up to 325 °C. The maximum proton conductivity of about 7×10^{-4} S cm^{-1} at 180 °C was obtained after putting the hybrid membrane into 85% H_3PO_4 at room temperature or boiling at 150 °C. This is due to the formation of a zirconium phosphate type texture in the polymer matrix.

Proton conductive glasses are another type potential ionic materials used in DMFCs.[120] Protons are highly mobile when they are strongly hydrogen bonded in glasses, and their conductivity is primarily determined by the degree of hydrogen bonding and the concentration of mobile protons in the glass structure. In the case of silicate and phosphate glasses, protons are bound with oxygens to form hydroxyl groups attaching to network forming cations, such as Si^{4+} and P^{5+} ions. Comparing silicate glasses with phosphate glasses, the hydroxyl groups in phosphate glasses are strongly hydrogen bonded.[121–123] The existence of P_2O_5 in the glass composition plays a significant role in providing high protonic conduction. The content of protons in glasses decreases with an increase in the sintering temperature of the glasses. Therefore, it is desirable to prepare a glass with a large amount of protons at low temperature, like in a sol–gel process. By a sol–gel process, Wang and Nogami *et al.*[123–125] have independently prepared plates and films of hydrated phosphor–silicate glasses with proton conductivities of about 10^{-3} S cm^{-1}. However, the gelation time of the glass membrane in their sol–gel process is about 1–6 months. Tung and Hwang[120] reported a short time synthetic methodology for inorganic proton conductive electrolytes based on hydrated phosphor–silicate glass by an accelerated sol–gel process with water/vapor management. Due to the formation of the P_2O_5 and SiO_2 network structure, the hydrated phosphor–silicate glass membranes show good thermal stability. They observed two or three kinds of pore sizes in the synthesized glass membranes. Increasing the P_2O_5 content of the glass membrane leads to a decrease of its major pore size and an increase of its porosity. However, it was observed that the pore size of the glass membrane becomes larger when its P_2O_5 content was higher than 40%. They also observed conductivity and methanol permeability increase with increasing the content of the P_2O_5, and interestingly, a maximum selectivity (the ratio of the conductivity to permeability) observed at the 30% P_2O_5 and 70% SiO_2 in glass membrane. From the above discussion it is clear that the membranes with desired properties can be prepared by appropriate rationing of P_2O_5 and SiO_2. But, the main drawback of these proton conducting glasses is their fragile nature, which prevents them from use in a wide range of applications.

6. Concluding remarks and perspective

From the above discussion it is evident that the addition of inorganic materials improves the membrane's thermal, mechanical and chemical stability, ionic conductivity at intermediate temperature with low fuel drag. The improvement in these properties is due to the combined effect of organic and inorganic phases, which are usually bound together with hydrogen bonding and ionic interactions. The addition of acid functionalized and non-functionalized silica material is usual practice for improving fuel cell performance. But the literature is lacking in systematic and comparative research on the effects of degree of crystallinity, size, orientation, and distribution of added silica particles into the membranes. The effect of other metal oxides such as TiO_2, ZrO_2, *etc.* has not been extensively studied and needs to explore in details. In composite with metal phosphonates; only zirconium phosphate has been well studied by Alberti and Casciola[11] and other metals phosphonates need to be investigated.

In the investigation processes, inorganic material should be accommodated in the organic matrix in such a way that it should permit the utilization of maximum elementary functions in a small volume, and hence optimize complementary possibilities and properties of the inorganic and organic components. A very interesting and appealing approach has been proposed by Sanchez and co-workers.[126] They prepared transparent hierarchical hybrid functionalized membranes using *in situ* generation of mesostructured hybrid phases inside a non-porogenic hydrophobic polymeric host matrix by surfactant template method. The formation of hierarchically ordered domains was favored by the hydrophobic character of the non-porogenic polymer, allowing the surfactant molecules to organize in micelles together with the hydrolysis–condensation of inorganic ($M(OR)n, M =$ Si, Ti,…) or hybrid ($R–Si(OR)_3$) precursors. They proposed two different polymers, one highly hydrophobic containing perfluorinated chains, poly(vinylidene fluoride) (PVDF), and a second less hydrophobic, poly(vinyl butyral), as a host organic matrix associated with two different templates, an ionic surfactant, cetyltrimethylammonium bromide (CTAB), and a non-ionic surfactant, $C_{12}H_{25}(EO)_4$ (BRIJ 30). To avoid segregation and sedimentation of the inorganic network during the concentration step, the synthesis requires an adequate solvent to be selected with specific physico-chemical properties (solubility, hydrophilicity, volatility). Among organic solvents, tetrahydrofuran (THF) has the most suitable behavior for the synthesis of these mesostructured hybrid materials. In addition to the polymer–solvent choice, functionalization of the inorganic phase was possible by means of this one-pot synthesis using a selected precursor carrying an active organic group R. So, direct functionalization of the silica network was performed using organosilane precursors ($R–Si[OR]_3$) (R being any function such as mercaptopropyl, phenylethyl, methyl, and so on) co-condensed with $Si(OR)_4$ as the silica precursor (OR being OEt). They further extended this approach to ionic polymer composites, such as composites with Nafion and found considerable increase in their performance.

This synthetic pathway looks appealing with regards to the formation of hierarchically ordered ionic particles into the host organic matrix with a homogeneous distribution. But an important drawback is the orientation of hierarchically ordered particles. Usually, in the casting method, orientation of the inorganic particles favors parallel arrangement to the membrane surfaces. This parallel orientation increases the length of the transport pathway concomitant lowering of the conductivity in ionic polymers. So for the ideal ionic membrane, hierarchically ordered ionic channels/particles should orient vertical to the membrane surface. This concept was proved by Azzaroni *et al.*[127,128] He proposed a new approach to the facile large-scale fabrication of robust silicon membranes with artificial, ordered two dimensional ion-conducting channels from ordered two-dimensional macroporous silicon and poly(sulfo-propyl methacrylate) hybrid materials. Ordered two-dimensional macroporous silicon was rendered proton conducting by growing a thick uniform polyelectrolyte brush using surface-initiated atom transfer radical polymerization throughout the porous matrix. This method proves the concept of orientation of ion-conducting channels vertical to the membrane surface and may find good applications in some specific areas. But, lack of membrane flexibility renders wide utilization.

Thus ionic membranes with ordered two dimensional ion-conducting channels vertically aligned to the membrane surface with excellent mechanical, chemical and dimensional stability and flexibility is an urgent need of advanced energy and biotechnology applications.

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