Nafion and modified-Nafion membranes for polymer electrolyte fuel cells: An overview

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Abstract. Polymer electrolyte fuel cells (PEFCs) employ membrane electrolytes for proton transport during the cell reaction. The membrane forms a key component of the PEFC and its performance is controlled by several physical parameters, viz. water up-take, ion-exchange capacity, proton conductivity and humidity. The article presents an overview on Nafion membranes highlighting their merits and demerits with efforts on modified-Nafion membranes.

Keywords. Composite membrane; relative humidity; surface area; PEFC.

1. Introduction

Energy security[†] is one of the key challenges facing the mankind. A substantial proportion of our energy is met through fossil fuels derived from ultimately finite reserves and thus cannot be sustained indefinitely in the long-term. The deleterious effects of excessive consumption of carbonaceous fuels on the economy and ecology of a large part of the world is already apparent and well known to be recounted here. There is also a lurking fear that, at present and projected discovery, production and consumption rates, world oil-supply will fail to meet the demand in the near future. In response to these problems, green energy and sustainable living movements are gaining popularity. In recent years, while solar energy, geothermal energy, wind energy and fusion power technology have attracted attention, there is also increasing interest in hydrogen and its most efficient utilization in generating electrical energy. The latter is most appropriately achieved through fuel cells.
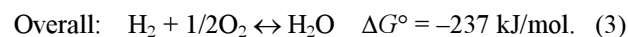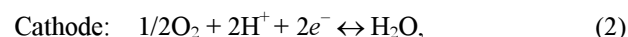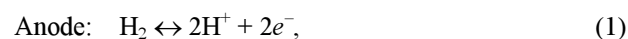
A fuel cell is an electrochemical power source with advantages of both the combustion engine and the battery. The difference between a battery and a fuel cell can be related to the definitions of a thermodynamic system and thermodynamic control volume (Mench *et al* 2008). In a thermodynamic system, no mass flux is permitted to cross the system boundaries like in a battery, while in a thermodynamic control volume, mass flux is permitted across the boundaries like in a fuel cell. Like a combustion engine, a fuel cell runs as long as it is provided fuel; and like a battery, fuel cells convert chemical energy directly to electrical energy. As an electrochemical power source, fuel cells are not subject to the Carnot limitations of heat engines. As early as in 1839, Sir William Grove discovered fuel cells by reversing water electrolysis to generate electricity from hydrogen and oxygen using an acid-electrolyte fuel cell. Since then fuel cell technology has evolved substantially.

Among the competing fuel cell technologies, polymer electrolyte fuel cells (PEFCs) are commercially most attractive owing to their quick start-up and ambient-temperature operations (Springer *et al* 1991; Gottesfeld and Zawodzinski 1997). PEFCs exhibit high-operational efficiencies with both specific and volumetric energy-densities comparable to internal-combustion engines while emitting no pollutants (Grant 2003). The operating principle of a PEFC is depicted in figure 1.

At the interface between anode and the electrolyte, the fuel is converted into protons (H^+) and electrons (e^-), a process which is made possible by a catalyst that is typically Pt-based. Polymer electrolyte membrane allows protons to flow through, but prevents electrons from passing through it. Electrons travel to the cathode through an external circuit producing electrical current and H^+-ions (protons) pass through the membrane from anode to cathode, where they combine with oxygen molecules and electrons to form water.

The half-cell reactions taking place in a PEFC are

$$\text{Anode:} \quad H_2 \leftrightarrow 2H^+ + 2e^-, \tag{1}$$

$$\text{Cathode:} \quad 1/2O_2 + 2H^+ + 2e^- \leftrightarrow H_2O, \tag{2}$$

$$\text{Overall:} \quad H_2 + 1/2O_2 \leftrightarrow H_2O \quad \Delta G° = -237 \text{ kJ/mol}. \tag{3}$$

The Gibbs free energy change ($\Delta G°$) of reaction (3) is related to the cell voltage by

$$\Delta G^\circ = -nFV_0, \tag{4}$$

where n is the number of electrons involved in the overall reaction, F the Faraday constant, and V_0 the cell voltage at thermodynamic equilibrium in absence of the current flow, i.e. under open-circuit condition. V_0 is the difference of the equilibrium electrode potentials at the cathode and the anode of the cell, and is calculated from

$$V_0 = -\Delta G/nF = 1\cdot 23 \text{ V.} \tag{5}$$

Although substantial improvements have been made in PEFCs, it has been difficult to realize them commercially owing to their cost. The estimated production cost per kW for a PEFC stack is presented as a Pi-chart in figure 2. It is obvious that the major cost of a PEFC stack is from membrane electrolytes, electrodes and bipolar plates (Tsuchiya and Kobayashi 2004). The following sub-sections describe Nafion and modified-Nafion membranes as electrolytes for PEFCs.
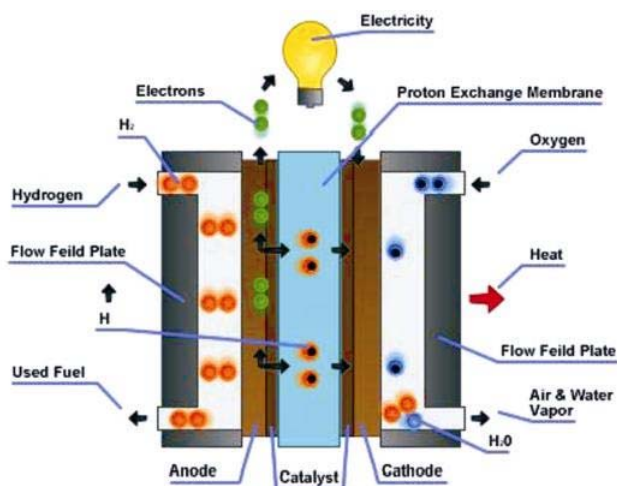

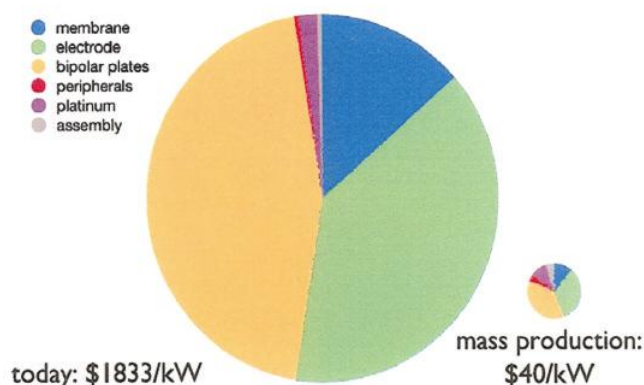**Figure 1.** Schematic diagram of a PEFC.

Figure 2. Estimated cost per kW for PEFC stack.

2. Nafion membranes as electrolytes for PEFCs

An effective membrane electrolyte for PEFCs, besides acting as a physical separator for the fuel and oxidant, must possess high ionic conductivity with little electronic component. It should be possible to cast them as thin and large surface-area membranes. The membranes should be stable in oxidizing and reducing environments prevailing during the operation of the PEFCs. The membrane must be easy to manufacture and be able to withstand the stress during electrode processing and attachment, and should be both mechanically and electrically robust to endure the start-up and shutdown schedules of the PEFCs.

As early as in 1940s, researchers were engaged in developing organic ion-exchange membranes for fuel cell applications (Grot 1985; Roziere and Jones 2003). These ion-containing polymers were termed as ionomers. It was believed that these ionomeric polymers would possess better properties, as they involve the interaction between polymer and ions. The earliest PEFC systems served as the power plants for Gemini space missions in the early 1960s. But the cells were short-lived due to the oxidative degradation of the membranes comprising a copolymer of sulfonated polystyrene and divinylbenzene. In the late 1960s, DuPont developed membranes from Nafion, a co-polymer of perfluoro-sulfonic acid with hydrophobic fluorocarbon backbone and hydrophilic sulfonic acid pendent side chains. This membrane was primarily used as a perm-selective separator in chlor-alkali electrolysers. In 1980s, the use of Nafion membrane helped realizing the concept of 'zero-gap' cell design. With the induction of zero-gap cell concept, the internal resistance of the PEFCs decreased and, as a result, the overall efficiency of the system increased substantially (Shukla and Raman 2003). The chemical structure of Nafion is depicted in figure 3.

Nafion is produced by co-polymerization of variable amounts of unsaturated perfluoroalkyl sulfonyl fluoride with tetrafluoroethylene. Nafion is commercially available in varying equivalent weights, viz. 900, 1100, 1200, etc. Equivalent weight (EW) represents grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form. Nafion membranes employing polymer with EW = 1100 are listed in table 1. These membranes
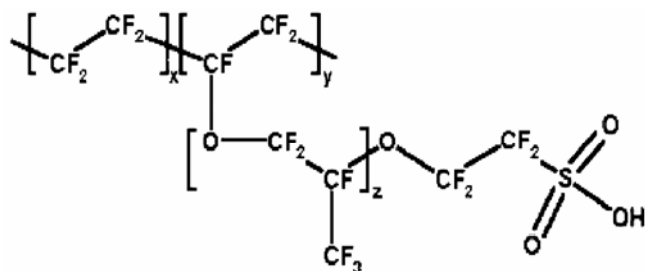

Figure 3. Chemical structure of Nafion.

are widely used in PEFCs due to their high proton conductivity and moderate swelling in water (Hickner *et al* 2004; Mauritz and Moore 2004). Nafion-117 membrane employs the polymer with equivalent weight of 1100 and has a thickness of 7 mils (1 mil = 1/1000 of an inch = 25·4 μm). Other cation exchange membranes with differing EWs of polymer and thicknesses designed for various applications are presented in table 2. Perfluorosulfonate cation exchange membranes with structures akin to Nafion have been developed by Asahi Chemical Company (Aciplex) and Asahi Glass Company (Flemion).

Nafion has ~40 Å clusters of sulfonate-ended perfluoroalkyl ether groups organized as inverted micelles arranged on a lattice (Hsu and Gierke 1983) as shown in figure 4(a). These micelles are connected by pores or channels of ~10 Å in size. These channels with $-SO_3^-$ groups invoke inter cluster ion-hopping of positively charged species. A model for proton conduction in Nafion based on three different regions within the polymer membrane has been proposed in the literature (Yeo and Eisenberg 1997). These regions are fluorocarbon phase (FC), interfacial region (IF) and ionic clusters (IC). Figure 4(b) shows cluster-network model for the interactions between polymer and water in Nafion membrane (Hsu and Gierke 1983). In Nafion membrane, FC region consists of polymer backbone, viz. the PTFE backbone of Nafion, IF region contains side chains comprising water and sulphonate groups and IC region contains absorbed water.

A simple structural conceptualization of cross-linked polyelectrolyte and clustered ionomeric system with anionic side-chain (Yeo and Eisenberg 1997) is shown in figure 5; they have also studied the diffusion of water in Nafion by sorption from the contacting liquid into dry samples and measuring water uptake as a function of time in the temperature range between 0°C and 100°C. The diffusion coefficient (D) of water in the membrane was found to increase from about 10^{-6} to 10^{-5} cm²/s with increasing temperature, and the activation energy was estimated to be 4·5 kcal/mol. The structural organization of Nafion membrane under different physiochemical conditions by invoking the balance between the elastic deformation of polymer matrix and various molecular interactions existing in the polymer has been discussed in the literature (Mauritz *et al* 1978).

Proton transport in Nafion has also been studied widely in the literature (Miyake *et al* 1983; Gebel *et al* 1993; Cappadonia *et al* 1995; Zadowzinski *et al* 1995; Wainright *et al* 1998; Choi *et al* 2005). Proton transport in Nafion depends on water content of the membrane. Although the precise mechanism for proton transfer in solvated form of Nafion is not completely understood, a qualitative picture is provided (Zawodzinski *et al* 1995) in figure 6. Generally, it is assumed that the state of water in Nafion membrane is not fixed. Some of the water is tightly bound to $-SO_3^-$ groups and is called chemically-bound water, which has lesser degree of hydrogen bonding than the bulk water; the latter is described as physically-bound water present in the central-pore region of Nafion membrane. The transfer of protons near pore sur-

Table 1. (a) Physical parameters of Nafion membranes.

Membrane type	*Typical thickness (μm)	Basis weight (g/m²)
Nafion – 112	51	100
Nafion – 1135	89	190
Nafion – 115	127	250
Nafion – 117	178	360

Table 1. (b) Physical properties of Nafion membranes.

Properties	Typical value
Water uptake (% water[a])	35
Tensile modulus (MPa)	
50% RH (25°C)	249
Water soaked (100°C)	64
Tensile strength (max. MPa)	
50% RH (25°C)	43[b], 32[c]
Water soaked (100°C)	25[b], 24[c]
Density (g/cm³)	2·0
¹H diffusion coefficients (cm²/s)	0.6×10^{-6}
Ion exchange capacity (mequiv./g)	0·9

[a]Water uptake from dry membrane soaked in water at 100°C for 1 h; [b]measured in machine direction; [c]measured in transverse direction, *at 25°C, 50% R.H.
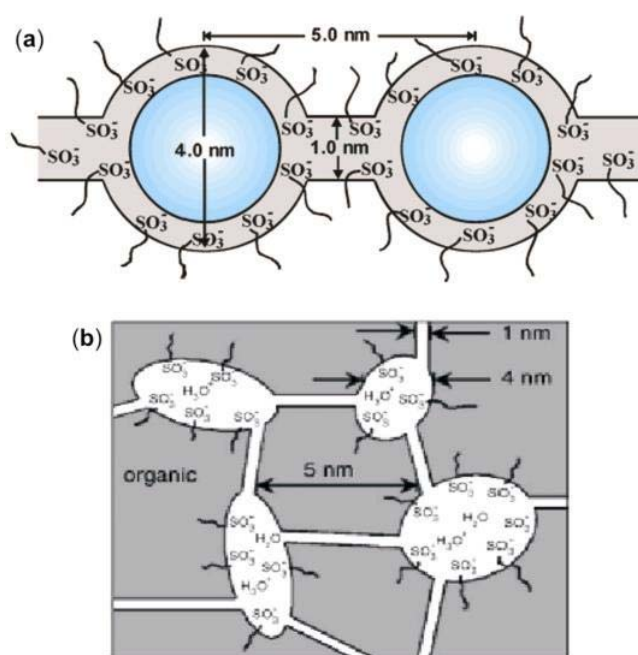

Figure 4. Cluster-network model for the interactions between polymer and water in Nafion membrane.

Table 2.   Physical properties of various commercially available cation-exchange membranes.

Membrane	Membrane type	IEC (mequiv./g)	Thickness (mm)	Gel water (%)	*Conductivity (S/cm)
Asahi Chemical Industry Company Ltd., Chiyoda-ku, Tokyo, Japan					
K 101	Sulfonated polyarylene	1·4	0·24	24	0·0114
Asahi Glass Company Ltd., Chiyoda-ku, Tokyo, Japan					
CMV	Sulfonated polyarylene	2·4	0·15	25	0·0051
DMV	Sulfonated polyarylene	–	0·15	–	0·0071
Flemion	Perfluorinated	–	0·15	–	–
Ionac Chemical Company, Sybron Corporation, USA					
MC 3470	–	1·5	0·6	35	0·0075
MC 3142	–	1·1	0·8	–	0·0114
Ionics Inc., Watertown, MA 02172, USA					
61AZL386	–	2·3	0·5	46	0·0081
61AZL389	–	2·6	1·2	48	–
61CZL386	–	2·7	0·6	40	0·0067
Du Pont Company, Wilmington, DE 19898, USA					
N 117	Perfluorinated	0·9	0·2	16	0·0133
N 901	Perfluorinated	1·1	0·4	5	0·01053
Pall RAl Inc., Hauppauge, NY 11788, USA					
R-1010	Perfluorinated	1·2	0·1	20	0·0333

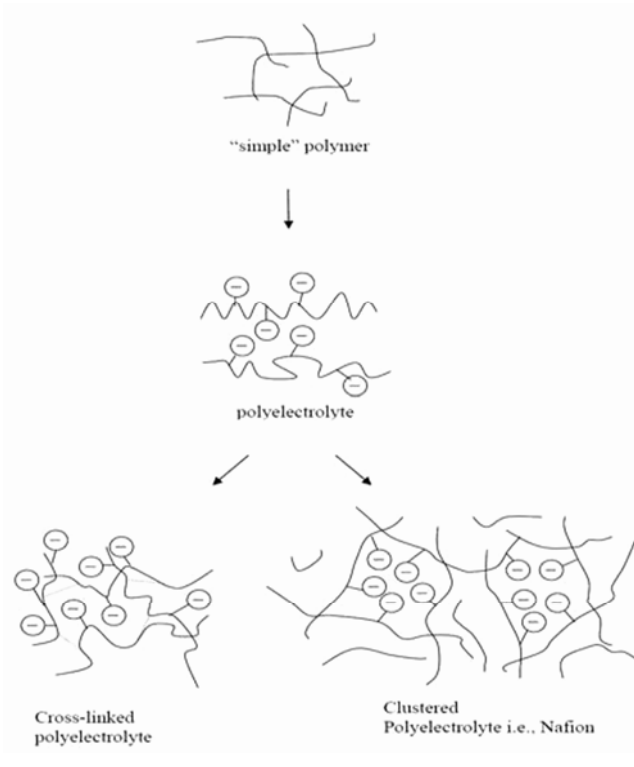*at 30°C and 100% relative humidity.

Figure 5.   Simple structural conceptualization of cross-linked polyelectrolyte and clustered ionomeric system with anionic side chain.

face within 3–4 Å, which is roughly the thickness of water molecule, takes place through tightly-bound water molecules along the $-SO_3^-$ groups due to the electrostatic attraction.
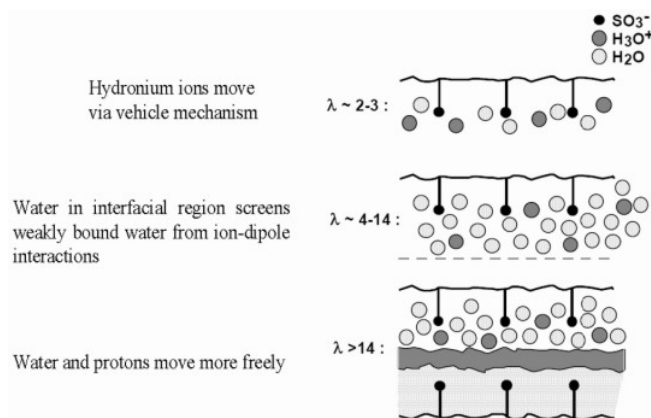

Figure 6.   Qualitative picture of proton transport in Nafion.

As the membrane becomes saturated, the size of pores increases, increasing the bulk-like portion of water, which facilitates high rate of proton transfer in the middle of pores. Thus, the overall rate of proton transfer increases with pore radius until it reaches saturation where the average diameters of pores are 4–6 nm. Proton conduction in Nafion occurs through the ionic channels formed by micro or nano phase separation between the hydrophilic proton exchange sites and the hydrophobic domains (Kreuer 2001). The present development of PEFCs is strongly linked to advantages and disadvantages of Nafion membrane under different operating conditions. Proton transfer in Nafion membrane relies on dissociation of protons from the constituent $-SO_3H$ groups in presence of water, which limits its application in PEFCs above 80°C (Chalkova *et al* 2005).

Table 3. Conductivity values for solid-acid conductors.

Membrane system	Comments on ionic conductivity
Nafion/silica	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion–titania	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion–zirconia	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/ZrP	Conductivity similar to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/CNT	Improved conductivity and mechanical strength leading to better PEFC performance
Nafion/Cesium phosphate	Conductivity similar to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/mordenite	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/HPA (HPA: PWA, SWA, PMA)	Improved conductivity over Nafion. But suffers leaching of HPA.
Nafion/imidazole	Good conductivity. However, imidazole poisons the Pt catalyst during PEFC operation

HPA (hetero polyacid); PWA (phospho tungstic acid); SWA (silico tungstic acid); PMA (phospho molybdic acid).

3. Modified-Nafion membranes as electrolytes for PEFCs

Conductivity of Nafion membranes often varies substantially depending on the system, membrane pre-treatment, and prevailing equilibrium parameters. At 100% RH, the conductivity of Nafion is generally about 0.1 S cm^{-1} at 60°C that drops by several orders of magnitude as the humidity is decreased. It is, therefore, mandatory to hydrate Nafion membranes to keep the ionic inclusions bridged. Transport of water is generally due to protonic defects and occurs through the breaking and forming of bonds. This is caused because the protonic defects weaken the intermolecular interaction affecting large variations in bond lengths combined with rapid breaking and forming of bonds.

Hydrophilic ceramic/inorganic fillers, such as SiO$_2$, TiO$_2$, ZrO$_2$, zeolites, are added to Nafion matrix to retain water in the composite membrane at higher temperatures and low humidity (Miyake *et al* 2001; Song *et al* 2004, 2006; Jalani *et al* 2005; Klein *et al* 2005; Panero *et al* 2005; Borup *et al* 2007). These hydrophilic inorganic materials, when incorporated with Nafion, increase the binding energy of water as well as the number and strength of acid sites. The addition of inorganic fillers narrows the hydrophilic channels in Nafion matrix from 7.9 to 6.5 nm, facilitating proton conduction. Besides, the filler particles have affinity to absorb and retain water in the Nafion matrix. Table 3 summarizes different inorganic additives/fillers that have been added to the Nafion matrix for operating PEFCs at high temperatures and low relative humidity values. Solid-acid proton conductors like zirconium phosphate, titanium phosphate, caesium phosphates and heteropolyacids have also been explored

as additives to Nafion to facilitate proton transport at reduced or zero hydration levels in the matrix. Although this concept seems promising, the success so far remains limited and the interaction between the inorganic phase and proton conductor stands vaguely understood. The best possible way to test the limitations of these membranes is to study them as prototype MEAs in PEFCs. There are many other significant issues that need to be resolved before solid-acid membranes are used in PEFCs. These include standard operating parameters such as mechanical strength, durability, cyclability, synthetic conditions, and design issues including catalyst compatibility and scale-up.

3.1 *Nafion membranes with inorganic filler as electrolytes for PEFCs*

In order to realize optimum PEFC performance and to make the system simple, it is highly desired to operate PEFCs at elevated temperature ($>80°C$) and reduced RH values at atmospheric pressure. To this end, Nafion-composite membranes suitably modified with ceramic/inorganic fillers, viz. SiO$_2$, TiO$_2$, ZrO$_2$, zeolite etc are widely used to facilitate proton conductivity in stringent environmental conditions (Watanabe *et al* 1998; Adjemian *et al* 2002; Jung *et al* 2002; Aricò *et al* 2003; Ramani *et al* 2005; Sacca *et al* 2005).

In the literature, membranes with inorganic fillers have been fabricated by a variety of techniques. One method includes impregnating inorganic oxide particles as fine powders into the Nafion ionomers and fabricating a composite membrane (Mauritz *et al* 1995; Baglio *et al* 2005). Another method includes addition of a precursor, gene-

rally as acidic metal alkoxides solution, into the Nafion ionomer for fabricating a composite membrane, and then converting the precursor material into the desired proton conducting oxide (Aparicio *et al* 2005; Lin *et al* 2005; Jiang *et al* 2006b). In most of the cases, solid polymer electrolyte, Nafion, is soaked in inorganic metal alkoxide precursor or alcoholic solution of one or more metal alkoxides till the desired amount of the inorganic filler permeates through the pores of Nafion (Miyake *et al* 2001; Adjemian *et al* 2002). After soaking the surface, the membrane is copiously rinsed to wash away surface metal alkoxide followed by hydrolyzing the metal alkoxide in the membrane with water. Incorporating the inorganic fillers into the polymeric matrix by above process may be inhomogeneous as, in such fillings, it is possible that some portions of the matrix may contain only a little oxide or no oxide at all. It is also possible to find enriched concentrations of filler particles in the bottom part of the membrane due to the sedimentation of heavier ceramic/inorganic fillers. As a result, the solid fillers in the composite membranes are devoid of imparting sufficient proton conductivity in the composite membrane under dry conditions.

In the literature, hydrophilic zirconia (ZrO_2) particles and its sulphate and phosphate forms have been considered as active filler materials with Nafion for the above stated purpose. The water uptake and proton conduction properties of the composite membrane depend on size and structure of the materials embedded with them. Sulfate-promoted super-acid zirconia (S-ZrO_2) has been reported as an active ceramic filler with Nafion membrane to increase the water uptake property of the membrane and provide additional acidic sites for proton diffusion (Hogarth *et al* 2005; Thampan *et al* 2005; Zhai *et al* 2006; Navarra *et al* 2007). Zirconium phosphate as hydrophilic and proton conducting material has been incorporated into various polymer matrices (Bauer and Porada 2005; Hill *et al* 2006; Jiang *et al* 2006a; Boutry *et al* 2007). It is also noteworthy that proton conduction in these materials predominantly takes place by surface transport through the interlayer regions in the presence of water.

Nafion–zirconium phosphate composite membranes have been fabricated by a variety of techniques (Damay and Klein 2003; Alberti *et al* 2005). Conventionally, water absorbing pre-formed fine zirconia powder is dispersed in Nafion ionomer solution to form Nafion–zirconia composite membrane. The composite membrane is then treated in phosphoric acid followed by drying at suitable temperature for forming Nafion–zirconium phosphate composite membrane. Another method includes cation exchange between the ionomer and zirconium cationic species followed by membrane treatment with phosphoric acid to precipitate zirconium phosphate within the hydrophilic regions of the ionomer. In an *in situ* preparation of the zirconium phosphate, phosphoric acid is reacted with either zirconyl chloride or with zirco-

nium alkoxide at desired temperatures; zirconium phosphate, thus prepared, is embedded within Nafion ionomer to form a composite membrane.

Incorporating zirconium phosphate into the polymeric matrix by the aforesaid processes could result in a non-homogeneous matrix with such fillers. It is also likely that phosphoric acid may not be covalently bound within the membrane. It is also possible to end-up with enriched concentrations of the phosphoric acid on the surface of the composite membrane, which when operated in the PEFC may cause leaching of the phosphoric acid along with the product water. Among the various aforesaid techniques for preparing Nafion-mesoporous zirconium phosphate composite membranes, only the *in situ* preparation of zirconium phosphate for embedding with Nafion ionomer to form a composite membrane appears attractive for avoiding the presence of any surface bound acid. But, even in this preparation, both low porosity and low internal-surface-area of zirconia particles limit the hydrophilicity of the composite membrane. In order to increase the porous nature of zirconium phosphate, efforts have been expended to develop mesoporous zirconium phosphate (MZP) materials either by hard-template approach or by surfactant-assisted route (Davis *et al* 1988; Dessau *et al* 1990; Estermann *et al* 1991; Haushalter and Mundi 1992; Khan *et al* 1996; Sayari *et al* 1996; Jimenez *et al* 1998; Castellon *et al* 1999). MZP as a surface-functionalized solid-super-acid-proton-conducting medium as well as inorganic filler with high affinity to absorb water helps fast proton-transport across the membrane electrolyte suitable for PEFC operation especially at low RH values.

3.2 *Nafion–silica composite membranes as electrolytes for PEFCs*

To obviate the aforesaid limitations, preparation of Nafion–silica composite membranes by embedding silica particles as inorganic fillers in perfluorosulfonic acid ionomer by a novel water hydrolysis process (Sahu *et al* 2007) is reported. In this process, a homogeneous, transparent and less viscous inorganic sol is first prepared by controlled water hydrolysis to silicon alkoxide without any external acidic or basic environment. Subsequently, the required amount of the sol is incorporated into the polymer matrix. The less viscous sol enters the fine pores of perfluorosulfonic acid (PFSA) and due to acidic nature of the latter forms Si–OH network in the pores, which on heating at 90°C under vacuum form Si–O–Si linkages in the composite membrane. A transparent polymer film is thus obtained without any particle/phase segregation. The composite membranes have been tested in hydrogen/oxygen PEFCs at varying RH between 100% and 18% at elevated temperatures at atmospheric pressures.

Performance of H_2/O_2 PEFC employing Nafion–silica composite membranes is studied by obtaining the fuel

cell polarization data as a function of varying load current-density. Figure 7 compares the polarization curves for the Nafion–silica composite and commercial Nafion-1135 membranes under fully-wet condition ($\approx$ 100%RH) at 60°C under ambient pressure. In all the experiments, the flow rates for both the fuel and the oxidant are fixed so as to preclude any water retention in the cell. Nafion–silica composite membranes with varying silica content show better performance in relation to Nafion membranes. The peak power density of 720 mW/cm^2 for the PEFC is achieved with Nafion–silica (10 wt.%) composite membrane as compared to 550 mW/cm^2 for the PEFC with Nafion-1135 membrane under identical operational conditions. Proton conductivity in the Nafion–silica composite membrane is attributed to protons that are transferred through hydrogen bonding with water-filled ion pores. However, an excess of silica phase in Nafion matrix reduces the PEFC performance due to electrode flooding in the PEFC. Accordingly, the peak power density for the PEFC with Nafion–silica (15 wt.%) composite membrane is lower in relation to PEFC with Nafion–silica (10 wt.%) composite membrane.

Polarization data for PEFCs with Nafion-1135 and Nafion-silica composite membranes under near-dry conditions ($\leq$ 18% RH) are shown in figure 8. At these RH values, the humidification of hydrogen gas is inapt to operate PEFCs with pure Nafion membranes as the PEFCs yield a peak power-density of only about 30 mW/cm^2 at 100 mA/cm^2 primarily due to the poor conductivity of the Nafion membrane. By contrast, under identical conditions, PEFCs employing Nafion-silica composite membranes perform much better in relation to those with pristine-Nafion membranes. The performance of PEFCs with Nafion–silica composite membranes increases gradually with increasing silica content in the Nafion matrix. A peak power-density of 300 mW/cm^2 is achieved at

1200 mA/cm^2 for the PEFC employing a Nafion–silica composite membrane with 15 wt.% silica while operating at 60°C under atmospheric pressure. It is, therefore, quite obvious that PEFC performance is purely related to water-management. In commercial Nafion membranes, the limited availability of water at the anode, electroosmotic drag of water from anode to cathode and insufficient water back-diffusion from cathode to anode cause the membrane to dehydrate. The membrane dehydration is manifested with an increase in ohmic resistance of the cell leading to decreased cell performance. By contrast, in the case of composite Nafion membranes, due to water retention characteristics of the silica, such a problem is obviated.

3.3 *Nafion–mesoporous zirconium phosphate composite membranes as electrolytes for PEFCs*

Synthesis of mesoporous zirconium phosphate (MZP) by co-assembly of a tri-block copolymer, viz. pluronic-F127, as a structure directing agent and a mixture of zirconium butoxide and phosphorous trichloride as inorganic precursors has been recently reported (Sahu *et al* 2009). Nafion–MZP composite membrane is obtained by employing MZP as surface-functionalized solid-super-acid-proton-conducting medium as well as inorganic filler with high affinity to absorb water and fast proton-transport across the electrolyte membrane even under low relative humidity conditions. The presence of large pores and high internal-surface-area ameliorates the hydrophilic character of the internal pore-surfaces and results in a solid super-acid exhibiting fast proton-conduction. MZP, thus synthesized, is impregnated with the Nafion ionomer to realize a proton-conducting composite membrane.

Figure 9 shows the FTIR spectra for the calcined zirconium phosphate with a strong sharp band centred at
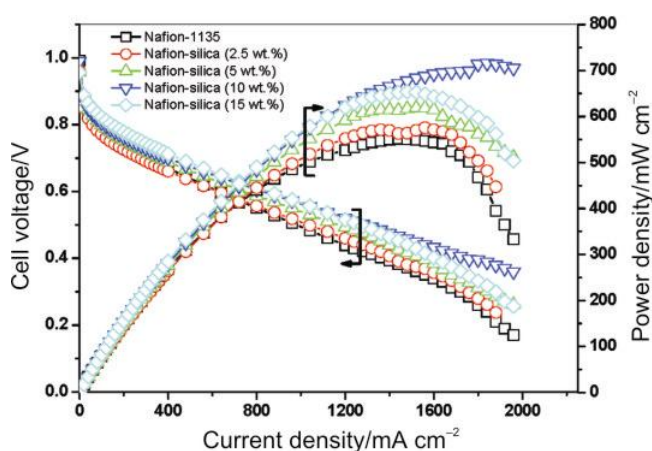

Figure 7. Performance of H$_2$/O$_2$ PEFC with Nafion-1135 and Nafion–silica composite membranes at 100% RH under atmospheric pressure operating at 60°C.
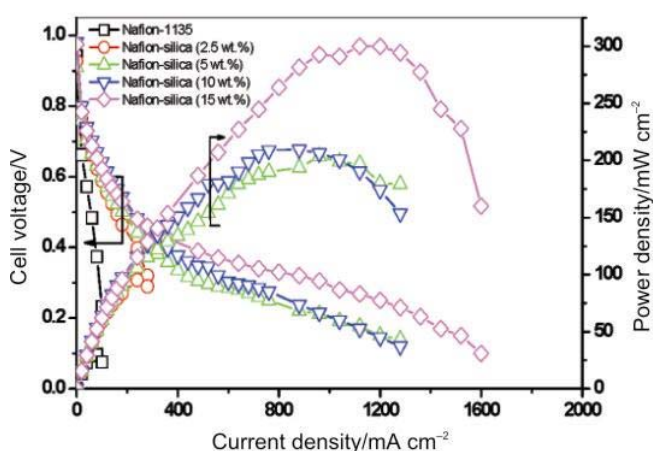

Figure 8. Performance of H$_2$/O$_2$ PEFC with Nafion-1135 and Nafion–silica composite membranes at 18% RH under atmospheric pressure operating at 60°C.

1070 cm^{-1} corresponding to P–O stretching vibration. The broad peak at 2373 cm^{-1} corresponds to the P–O–H stretching vibration and the other broad band at around 3435 cm^{-1} is attributed to asymmetric OH-stretching of water molecule while the weak peak at 1640 cm^{-1} indicates the bending of water molecule. The peak at 749 cm^{-1} indicates P–O–P symmetric stretching.

Figure 10 depicts the polarization curves for the PEFCs with Nafion-MZP composite membranes and commercial Nafion-1135 membrane under ~100% RH at 70°C. PEFCs containing Nafion-MZP composite membranes with varying MZP content show better performance than the PEFC with pristine-Nafion membrane. Maximum proton conductivity with the composite membrane is attained at an intermediate loading of MZP. Peak power density of 725 mW cm^{-2} is achieved for the PEFC with Nafion-MZP (5 wt.%) composite membrane in relation to 655 mW cm^{-2}
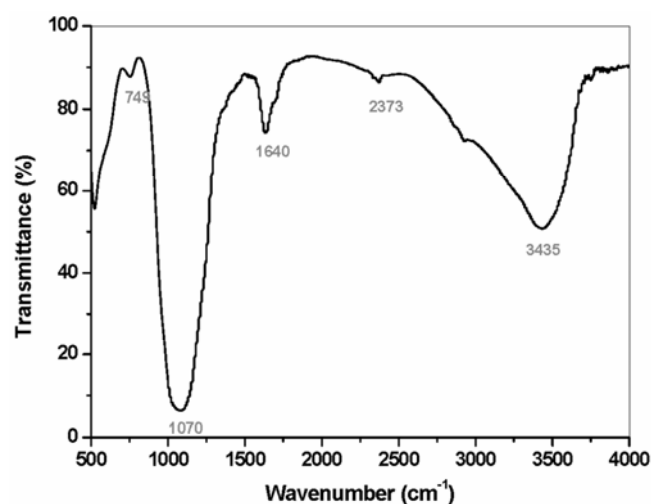

Figure 9. FTIR spectrum for MZP powder.

for the PEFC with Nafion-1135 membrane operating under identical conditions. Accordingly, it appears that the presence of MZP as a surface functionalized solid super-acid proton conducting medium in the Nafion matrix assists the Nafion-MZP composite membrane to achieve higher proton conductivity in relation to pristine-Nafion membrane.

Polarization data for PEFCs with Nafion-1135 and Nafion–MZP composite membranes under near-dry condition (~18% RH) are shown in figure 11. At these RH values, PEFCs with pristine Nafion-1135 membranes yield a peak power-density of only about 224 mW cm^{-2} at 500 mA cm^{-2}, primarily due to the poor conductivity of the Nafion membrane. By contrast, under identical conditions, PEFCs employing Nafion–MZP composite membranes perform much better. The performance of PEFCs with Nafion–MZP composite membranes increases gradually with increasing MZP content in the Nafion matrix. A peak power-density of 353 mW cm^{-2} is achieved at 1100 mA cm^{-2} for the PEFC employing a Nafion–MZP composite membrane with 5 wt.% MZP while operating at 70°C under atmospheric pressure.

Nafion–inorganic composite membranes exhibit lower resistance and hence PEFCs with such membranes sustain higher load current-densities particularly under low relative humidity conditions in relation to the pristine-Nafion membranes. This provides an alternative route to fabricate composite membranes with filler particles that absorb water and act as a water reservoir to keep the membrane wet even at low relative humidity values. These membranes help PEFCs to sustain periods of inlet-stream draught without excessive loss in membrane conductivity. Consequently, the humidification exigencies for PEFCs in an operating system are mitigated, which helps cutting system complexity and hence its cost.
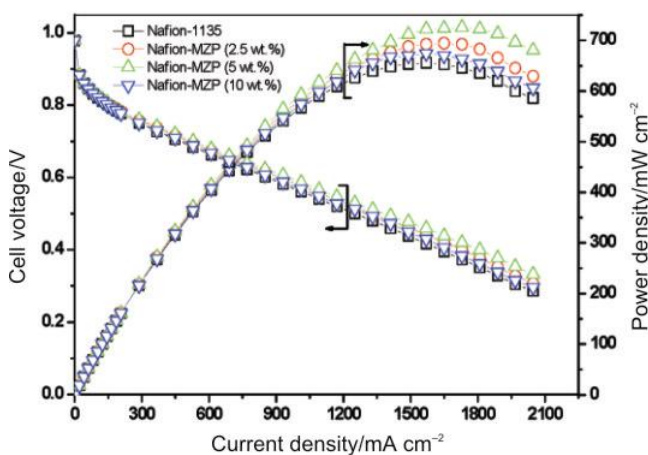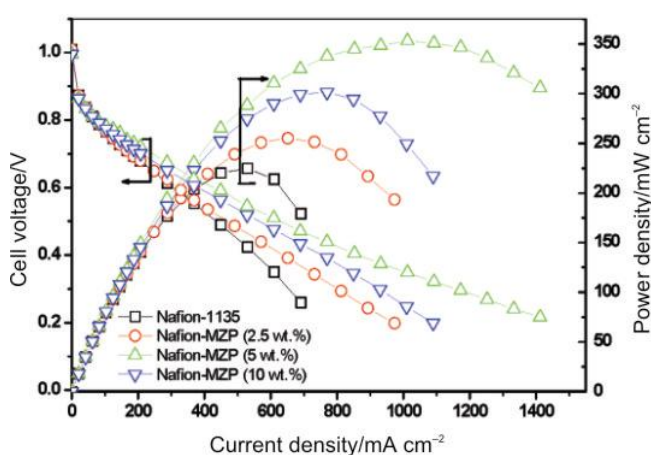

Figure 10. Performance of a H$_2$/O$_2$ PEFC employing Nafion-1135 and Nafion–MZP composite membranes at 100% RH at 70°C under atmospheric pressure.

Figure 11. Performance of a H$_2$/O$_2$ PEFC employing Nafion-1135 and Nafion–MZP composite membranes at 18% RH at 70°C under atmospheric pressure.

4. Conclusions

Polymer electrolyte fuel cells have reached a high level of development with applications ranging from cars to aerospace. But a stigma in their commercialization is their cost. To this end, it is most desirable to develop thermally stable and cost-effective polymer electrolyte membranes as substitute to Nafion. This article reviews various Nafion and Nafion-modified membranes for application in polymer electrolyte fuel cells. Modified-Nafion membranes perform better than pristine-Nafion membranes as electrolytes for PEFCs. Among the various modified-Nafion membranes, Nafion–inorganic composite membranes appear to be the most promising electrolytes for PEFCs.

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