

## Is Nafion<sup>®</sup>, the only Choice?

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**Abstract:** It is a kind of an insight article and the motivation for this presentation is to examine

- (i) Whether at all is it possible to generate new membranes as alternatives to Nafion<sup>®</sup> at least for fuel cell applications?
- (ii) Why Nafion<sup>®</sup> is so overwhelmingly used as the chosen membrane for fuel cells (Nafion<sup>®</sup> panacea!)
- (iii) If there were to be some alternate membranes to Nafion<sup>®</sup> what parameters and properties become relevant in relation to those of Nafion<sup>®</sup>.

It is realized that the statement of questions may be easier than finding exact solutions to these posers, but however to set the thought process, this article comes up with some postulates which can form the basis for future discussion on this topic. It has been realized that no conclusive solutions can be provided but it is necessary to keep the track known so that one can at least hope to find the route if not the exact solutions right away.

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### Introduction

As a result of intensive research efforts around the globe, direct methanol fuel cell (DMFC) technology is in a decisive phase and it is attractive due to its simple system configuration and its high energy density next to hydrogen-oxygen fuel cell. The main impediment for commercialization in spite of the realization of acceptable performance levels is due to prohibitively high cost of the major component of the fuel cells namely catalysts that are employed in either of the electrodes and membrane. For the past three decades or so, no new alternate materials either in case of catalyst (noble metal based systems) or in the case of membranes (fluorine based systems) has been formulated, designed or employed. In terms of membrane materials, especially literature on proton conducting membranes is mostly revolving around Nafion<sup>®</sup> in spite of its well known limitations like high cost (~ 1000 \$/m), low performance under low humidity

and at high temperature conditions and high fuel crossover [1-3]. Above all, its preparation involves environmentally non-friendly fluorine based technology. In addition, chemical degradation in a fuel cell environment is also an issue of great concern for its reliability in long term operations. As the membranes become thinner, fluoride ions are detected in product water [4]. Hence, there is a clear need for opting to alternative membrane materials which can overcome the major drawbacks of Nafion<sup>®</sup>. This development alone can make the DMFC technology a commercially viable one. With this objective in mind a variety of alternate approaches have been developed and some of them can be listed as follows:

- (i) Modifying perfluorosulfonic acid (PFSA) membranes to improve their water retention capacity at temperatures above 373 K by crosslinking, or by forming composites with hygroscopic

- oxides, like  $\text{MO}_2$  ( where  $\text{M} = \text{Zr}, \text{Si}, \text{Ti}$ ) or with inorganic proton conductors [5,6],
- (ii) By opting for other non fluorinated polymer electrolytes [7-11] and
  - (iii) By designing inorganic organic composite membranes [12-17].

### Composite Membranes Vs Nafion<sup>®</sup> – A Closer Look

The following section will address on points of relevance such as why we look for composite materials, what are the components that were used in the formulation of composite membranes, and a comparative as well as parallel understanding of perfluorosulfonic acid membrane materials which commercially known as Nafion<sup>®</sup> by Dupont with the composite membranes in terms of *bondings, chemical and structural compositions and mechanisms* involved in proton conduction. This one frame analysis would serve as a valuable tool for DMFC investigators.

Composite membranes have attracted attention, because they exhibit controllable physical properties, such as thermal and mechanical behavior, by combining the properties of both organic polymers and inorganic compounds (hygroscopic oxides, solid inorganic proton conductors). In composite membranes, inorganic fillers of micrometer to nanometer size are uniformly distributed in the polymer matrix either by dispersing the preformed inorganic particles or by forming inorganic particles *in situ* into the polymer matrix. A number of impermeable fillers (e.g. oxides, clay) or proton conductive fillers (e.g. heteropolyacids, ZrP, metal hydrogen sulfates) have been exploited. The driving force in these developments appear to be to formulate a geometrical shape (in the form of

a formable film architecture) with proton conductivity induced in them by appropriate proton conducting materials. In this sense this is a multi-component system unlike the Nafion<sup>®</sup> membrane where in the proton conducting moiety is stitched to the film forming polymer architecture. Though multi-component systems can give rise to cumulative effects, there are other disadvantages associated with them. Since the bonding characteristics are not well defined, they are susceptible for easy removal (dissolution, leaching and other degradation processes in the presence of other constituents and possibly chemical reaction with them) and hence they have not been successful for the fuel cell application. Conceptual developments are required if one were to exploit composite membranes as substitutes for Nafion<sup>®</sup>, especially in terms of the bonding of the proton conducting substances with the film forming polymers. This is one aspect wherein some new concepts have to emerge to make composite membranes viable. The simple dispersion of the proton conducting species like heteropoly acids, ZrP and other substances though can give rise to proton conduction, since they are not stitched to the polymer and hence susceptible for degradation with respect to time. Secondly, since the proton conducting species are present as individual entity, it is not possible to enhance the conductivity like the Nafion<sup>®</sup> wherein the highly electronegative backbone environment makes the proton (very similar to bare proton) and hence give rise to exclusive Grotthus type conduction. This aspect is discussed in more detail below.

Nafion<sup>®</sup> is highly conductive due to its structural property. The material, Nafion<sup>®</sup> consists of three regions: (i) a polytetrafluoroethylene (PTFE, DuPont's Teflon<sup>™</sup>)-like backbone, (ii) side chains of -- $\text{O---CF}_2\text{---CF---O---CF}_2\text{---CF}_2\text{---}$  which

connect the molecular backbone to the third region, and (iii) ion clusters consisting of sulfonic acid ions. When the membrane becomes hydrated, the hydrogen ions in the third region become mobile by bonding to the water molecules and moving between successive sulfonic acid groups. There are two advantages to the use of PFSA membranes in PEM fuel cells. First, because the structure is based on PTFE backbone, perfluorosulfonic acid (PFSA) membranes are relatively strong and stable in both oxidative and reductive environments. Second, the protonic conductivities achieved in a well-humidified PFSA membrane can be as high as  $0.2 \text{ Scm}^{-1}$  at PEM fuel cell operating temperatures. The high electronegativity (i.e. electron affinity) of the fluorine atom, bonded to the same carbon atom as the  $\text{SO}_3\text{H}$  group makes the sulfonic acid a superacid (similar to trifluoromethane sulfonic acid). Nafion<sup>®</sup> has the maximum electronegative environment possible, hence competing Nafion<sup>®</sup> with its conductivity may not be a good starting point. When one is looking for an alternative membrane other aspects like water retention ability, selectivity for the cross over of the fuel, mechanical strength and durability may have to be considered, and of course with appreciable proton conductivity which may be required to accomplish acceptable performance limits. A membrane with low methanol crossover and better performance at low humidity and at high temperatures is a good choice for DMFC application, even if it exhibits low conductivity compared to Nafion<sup>®</sup>.

In Nafion<sup>®</sup>, the proton transport is due to the classical ion exchange mechanism (Grotthus hopping mechanism [18]) and hence conductivity will be approximately four times higher compared to other mechanism (vehicle mechanism [19]). Fully hydrated membrane contains a water phase similar to bulk water (as assessed by its dielectric properties). The

phase separation is caused due to the extreme hydrophobicity of the perfluorinated polymer with the extreme hydrophilicity of the terminal sulfonic acid group of the Nafion<sup>®</sup> [20]. In the presence of water the hydrophilic part is hydrated and helps in further phase separation. The hydrophobic part provides good mechanical stability even in presence of water while the hydrated hydrophilic domains provide the high proton conductivity. Proton transport in water is generally a result of protonic defects and occurs through the breaking and reformation of hydrogen bonds. This is caused because the protonic defect weakens the intermolecular interaction which causes large variations in bond length combined with rapid breaking and forming of bonds. Like Nafion<sup>®</sup>, separation of hydrophobic and hydrophilic domain may not be possible in other system (e.g. SPEEK [20]). In composite membranes, one meets with hybrid transport mechanism because the inorganic component can also exhibit vehicular proton transport mechanism. Hence, conduction may not reach the magnitude that one observes in Nafion<sup>®</sup> (Grotthus mechanism). In essence, it appears that one may not be able to formulate at present a material that can have equivalent conductivity as that of Nafion<sup>®</sup>. This is particularly true that one can not create an electronegative environment more than that already available in Nafion<sup>®</sup>. Secondly the proton that is available in the sulphonic acid group is equivalent to the bare proton that is normally available in mineral acids.

Grounded on these logistics, one can see that turning away from Nafion<sup>®</sup> for a membrane material choice, it requires in particular hydration stability at high temperatures, low fuel crossover, mechanical, thermal, and oxidative stability as well as appreciable proton conductivity. And, of course, all of these objectives must be achieved while

maintaining low cost. In this direction, an extensive literature search has been carried out and a list of several composite materials with their potential attributes and characteristics relevant for low temperature fuel cell applications are made as given in **Table 1**. An effective way to achieve low-humidity and high-temperature operation is to recast polymers with fillers like silica [21-39], alumina [40-42], zirconia [43-45], titania[46-48], tungsten trioxide[49,50] which are hygroscopic in nature. They were incorporated into various polymers like, Nafion<sup>®</sup> [21,22,34-36,43,45,46,48,49], polytetrafluoroethylene (PTFE) [25,26], Nafion<sup>®</sup> NRE-212 membrane [39], Nafion<sup>®</sup>/polyaniline [27], sulfonated polysulfone [23], sulfonated poly(ether sulfone) [37], poly(vinylidene) fluoride (PVDF) [38,42], Nafion<sup>®</sup>/PTFE [28], Nafion<sup>®</sup>/Krytox [33], Poly(vinylidene) fluoride-chloro tetrafluoro ethylene, (PVDF-CTFE) copolymer [29], poly(ethylene glycol)/(4-dodecylbenzene sulfonic acid (PEG)/(DBSA) [30], Sulfonated styrene-(ethylene-butylene)-sulfonated styrene (SEBSS) [31], poly-(ethylene oxide)s (PEO) [24,50], Polyvinyl alcohol (PVA) [32,47], poly-vinylidene fluoride/poly-acrylonitrile (PVDF/PAN) [42], PVDF-g-PSSA (poly(styrene sulfonic acid) [40] and Sulfonated poly(ether ether ketone) (SPEEK) [44].

It has been shown that the water uptake by the oxide containing membrane is higher than that of the pristine polymer. Composite membranes with hygroscopic oxide exhibits improved thermal and mechanical stability than the parent polymer. They all in common exhibit reduced methanol permeability. Reduction in fuel crossover can be achieved either by physical or chemical means. The addition of hygroscopic oxide results in a change in

structure of the membrane, where the particles block part of the hydrophilic polymer channels through which protons migrate. At the same time narrowing of water channels allow low solvent permeation and electroosmotic drag coefficient. Other problems such as reduction in mechanical stability (becomes brittle) when the inorganic component loading reached a critical level, and decreased fuel cell performances were encountered.

In order to improve conductivity at low-humidity and high-temperature operating condition, *fast proton conductors* like heteropolyacids [13,15,51-67], zirconium phosphates [14,68-80] having dual role of being both hydrophilic and proton conducting have been incorporated into various polymer matrix. Fast proton conductors are the ones which exhibit conductivity greater than  $10^{-5}$  S  $\text{cm}^{-1}$  at 300 K with activation energy  $E_a < 0.4$  eV [81]. Polymer matrices like Nafion<sup>®</sup> [51,58,60,64,68,73], sulfonated polyether ether ketone (SPEEK) [54,59,65,67,76,80], polyethylene glycol (PEG) [57,63], Sulfonated polyethersulfone Cardo [77], sulfonated poly(arylene ether sulfone) [52], disulfonated poly(arylene ether sulfone) [69], Nafion<sup>®</sup>/Teflon<sup>®</sup> [70,71], Nafion<sup>®</sup>/polyphenylene oxide (PPO) [56],sulfonated polyether ether ketone (SPEEK)/Polybenzimidazole [79] Polybenzimidazole (PBI) [61,74], Poly(vinyl alcohol) (PVA) [13-15,53,62], Polyethyleneimine (PEI) [87], polystyrene grafted poly(ethylene-alt-tetrafluoroethylene) [72], poly-vinylidene fluoride (PVDF) [75] and poly (fluorinated arylene ether)s [78] have been exploited.

Among the active components employed the heteropolyacids (HPA) exhibit exceptionally high conductivities at room temperature, approximately  $0.17$  S  $\text{cm}^{-1}$ , when 29 water molecules are present as hydrated water in

the molecule. ( $n=29$ ) [82]. Owing to these characteristics, a series of composite membranes have been prepared by incorporating HPA into polymer matrices (refer to Table 1). Even though these solid acids can be providing high proton conductivity like mineral acids, their conductivity drops drastically once they are heated and dehydrated. The hydration sphere is connected to their conducting behaviour and it is essential that somehow the hydrated state of HPA has to be maintained in the polymer matrices. This is one of the necessary condition for these materials to be exploited in the transport through the membrane in Fuel cell applications. Moreover, HPAs are in general are soluble in water. As such, use of these materials in fuel cells implies the impossible requirements of retaining hydration to ensure high conductivity and removing by-product water to prevent dissolution. Solubility of HPA can be overcome by employing water insoluble salts of HPA at the same time retaining the required proton conductivity [14]. However it should be emphasized again that the proton conductivity is not linked to the polymer backbone and is not stitched to the polymer matrices and hence it is always possible that the stability and durability have to be ensured by proper protection within the polymer matrices but still maintaining the conductivity chain. The fabrication of membranes in this model can be difficult and hence repeatability of the membrane manufacture can become one of the issues in this case.

Zirconium phosphates are water-insoluble, and it is known that layered compounds containing intercalated hydronium ions exhibit reasonable conductivity at room temperature. ( $10^{-3}$  at 90 % RH [83]) However, the proton transport properties are highly dependent on the humidity level and thus for fuel cell applications water

management remains still a challenge. Attempts were made to improve the conductivity of layered compounds by intercalating Brønsted bases or functionalised organic radicals to replace the hydroxyl moieties of the phosphate group [84]. When the organic moieties contain a proton-generating function such as  $-\text{COOH}$ ,  $-\text{PO}_3\text{H}$ ,  $-\text{SO}_3\text{H}$ , or  $\text{NH}_3^+$ , these compounds can be used as proton conductors. For example, Zirconium alkyl sulfophenylphosphonates have been investigated for their conductivity under different temperature and relative humidity regimes for possible use in fuel cell applications [85].

As can be seen from Table 1, some of these composite membranes exhibit promising conductivities at temperatures above 373 K. However, most of these composite membranes have not yet been tested in fuel cells.

Although many other stable inorganic systems like layered silicates (e.g., montmorillonite [89], modified montmorillonite [86-88,90] and laponite [87], zeolites [98-102], calcium phosphate [103,104] and boron phosphate [105,106], have been dispersed in a variety of polymeric matrices and have been considered for membrane applications, the structure, degree of crystallinity, shape and dimensions of the particles, as well as their distribution in the various domains of the hydrated polymers, are not thoroughly investigated. Hence it is not possible to explicitly predict their possible behaviour in membranes useful for fuel cells. An overall observation when reviewing research in this field is that a tremendous effort has been invested in polymer electrolyte membrane development, but little effort has been expended in developing a clear understanding of the mechanisms that lead to polymer electrolyte membranes with improved proton transport properties. The goal of preparing

economical membranes, the attention should be directed to low-cost polymers filled with optimum amount of particles exhibiting desired properties. Both inorganic and organic components must be chosen depending on the swelling index and water of hydration of the components.

Characteristics of few commercial membranes which are or could be used in DMFCs are compared with composite membranes in **Table 2** for DMFC application. Water uptake for composite membranes is higher and it can be tuned by suitably varying the filler and its amount. IEC is competitively higher for composite membranes. These parameters have direct effect on increased proton conductivity at higher temperature in composite membranes compared to other commercial membranes. The increase in OCV in composite membranes compared to Nafion<sup>®</sup> 117 (0.65 V) indicated reduced methanol crossover to the cathode side. The results suggest that these membranes are suitable for application in DMFC. However, durability data and mechanical stability of composite membranes was not found. Although many composite membranes do not show significant improvements over Nafion<sup>®</sup>, these experimental results show them exhibiting lower methanol crossover at similar proton conductivities and/or higher DMFC power densities.

### **Futuristic Outlook: Where To Go?**

It is possible that the inorganic fillers or proton conducting species can also function as catalysts for the fuel thus decomposing methanol in the anode side of the fuel cell. This role of the components of membrane has not yet established or realized yet. However, it is possible salts of heteropoly anions can function as catalysts for the methanol decomposition and this could also result in

the reduced cross over of the fuel from the anode to the cathode side of the fuel cell. It is necessary that this role is identified and established so that new membrane development can have this additional criterion built in the search.

### **Perceptions**

In essence, in the purpose of this presentation is to emphasize that the search for alternate new membranes for fuel cell application should not start from the point of view of ionic conductivity since it may not be immediately possible to get a system which will have similar conductivities like that of Nafion<sup>®</sup>. On the other hand, even if one were to sacrifice a little at conductivity, it is possible to generate alternate membranes which can be superior to Nafion<sup>®</sup> in other properties like stability in less humid conditions, restricted or reduced swelling index as compared to Nafion<sup>®</sup>, and also showing improved activities against the limitations for fuel cross over from anode. These systems are at present based on composite or hybrid systems but it is desirable if the active component can be hooked on to the polymer matrices some how so as to improve the durability and also exploit the electronegative environment provided by the matrices. This is one direction in which future research endeavors will be focused.

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**Table 1. Summary of Inorganic-Organic Composite Membranes**

Membranes	(Water uptake %) [Swelling %] {IEC}	Conductivity $\sigma$ (S/cm) (Temp in °C) [RH %]	Diffusion coefficient/ permeability	Fuel cell performance	References
Silica as Filler					
Nafion-SiO <sub>2</sub>			$10^{-5} \text{ cm}^2 \text{ s}^{-1}$	DMFC-current density 0.6 A/cm <sup>2</sup> at 0.4 V (130 °C)	21
Nafion®/Aerosil (SiO <sub>2</sub> )	(30-40)	0.1 – 0.4 (90)	$0.1 \text{ mol m}^{-2} \text{ s}^{-1}$ Selectivity 4 - 6		22
sulfonated polysulfone/ SiO <sub>2</sub>		$5 \times 10^{-2}$ (25-90)		DMFC-Power density 0.18 W/cm <sup>2</sup> (120 °C, 2 M)	23
PEO/SiO <sub>2</sub>		$10^{-3}$ (80)			24
PTFE /amorphous fumed SiO <sub>2</sub>		0.22		DMFC-(OCV= 0.56 & 0.65 V) 50 and 130 mW cm <sup>-2</sup> at 80 and 130 °C, respectively	25
PTFE/SiO <sub>2</sub> (commercial SiO <sub>2</sub> sol)		0.1 (RT)			26
Nafion/polyaniline/SiO <sub>2</sub>	(20)	$9.1 \times 10^{-3}$ (50) [100]	methanol crossover is reduced by over two orders of magnitude	DMFC- 8 mW cm <sup>-2</sup> (40 °C, 2 M) two-fold lower than Nafion	27
Nafion/PTFE/ SiO <sub>2</sub>		$3.25 \times 10^{-3}$		DMFC-(OCV= 0.564 V) max. power density of 70 mA cm <sup>-2</sup> ( 70 °C, 2 M)	28
Poly(vinylidene) fluoride-chloro tetrafluoro ethylene, (PVdF-CTFE), copolymer/SiO <sub>2</sub>		$10^{-2}$ (RT)		DMFC- power density 1.4 mW cm <sup>-2</sup> & current density 10–20 mA cm <sup>-2</sup>	29
PEG / DBSA(4-dodecylbenzene sulfonic acid) /SiO <sub>2</sub>	(30-60) {0.5 - 1 m mol g <sup>-1</sup> }	$4 - 7 \times 10^{-3}$ (RT) [100]	$(0.78 - 2.1) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ Selectivity = $5.09 \times 10^3 - 1.87 \times 10^5$		30
Sulfonated styrene-(ethylene-butylene)-sulfonated styrene (SEBSS)/ SiO <sub>2</sub>			$8-14 \mu \text{ mol cm}^2 \text{ s}^{-1}$	DMFC- max. current densities are 74, 229, and 442 mA/cm <sup>2</sup> at (30, 60, and 90°C) at 0.3 V	31
PVA/functionalized SiO <sub>2</sub> / Glutaraldehyde		$10^{-1}$			32
Krytox- SiO <sub>2</sub> -Nafion®	(42)	$10^{-4}$ (130)			33
Nafion®/Diphenylsilicate		$2.39 \times 10^{-2}$		DMFC-OCV= 0.65 V (1.0 M)	34
Nafion / diphenyldimethoxysilicate	[30]	$10^{-2}$ (RT)		DMFC-comparable to Nafion	35
Nafion/Organic SiO <sub>2</sub> with thiol group		$1.57 \times 10^{-2}$ (RT) [100]		DMFC – Nafion 117> Nafion/Organic silica with thiol group> Nafion/ silica(unmodified) (75°C, 0.2 MPa O <sub>2</sub> & 1M)	36

Sulfonation of poly(ether sulfone)/ SiO <sub>2</sub> with phosphonic acid functionality	(28.73) {0.961 meq. g <sup>-1</sup> }	6.36 x 10 <sup>-2</sup>	4.89 x 10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup>	DMFC- 30W/cm <sup>2</sup> (70 °C, air at 10 psi )	37
PVDF/ SiO <sub>2</sub> with surface-anchored sulfonic acid		3.6 x 10 <sup>-3</sup> (75)		DMFC- (OCV =0.66 V) power density 32 mW cm <sup>-2</sup> (70 °C)	38
Cs <sub>2.5</sub> H <sub>0.5</sub> PWO <sub>40</sub> /SiO <sub>2</sub> /Nafion <sup>®</sup> NRE-212 membrane				H <sub>2</sub> /O <sub>2</sub> - better performance than Nafion <sup>®</sup> NRE-212 membranes (60 °C & 80 °C).	39
Alumina as filler					
Nafion/Al <sub>2</sub> O <sub>3</sub>				DMFC - current density of 0.4 A/cm <sup>2</sup> 0.4 V (130 °C)	21
PVDF-g-PSSA/Al <sub>2</sub> O <sub>3</sub>	(68)	4.5 x 10 <sup>-2</sup>	6.6 x 10 <sup>-8</sup> cm <sup>2</sup> s <sup>-1</sup> Selectivity 6.8 x 10 <sup>5</sup> S s cm <sup>-3</sup>	DMFC-max. power density 12 mW cm <sup>-2</sup> (2.5 M)	40
poly-vinylidene fluoride/poly-acrylonitrile (PVdF/PAN)/ Al <sub>2</sub> O <sub>3</sub>		0.10			41
poly(vinylidene) fluoride /alumina/ dodeca-tungstophosphoric acid		10 <sup>-3</sup> (< 50)			42
Zirconia as filler					
Nafion/ ZrO <sub>2</sub>	(24) {0.85 meq g <sup>-1</sup> }			H <sub>2</sub> /air - Power density 604 mW cm <sup>-2</sup> & 387 mW cm <sup>-2</sup> at 0.6 V ( T = 110 °C,100% RH & T = 130 °C,85% RH)	43
Sulfonated poly(ether ether ketone) (SPEEK)/ ZrO <sub>2</sub>		34 x 10 <sup>-3</sup> (25)	60-fold reduction of the methanol flux.		44
Nafion / sulfated zirconia	(27) {0.9-1.1 meq g <sup>-1</sup> }			H <sub>2</sub> /O <sub>2</sub> - 1.35 W/cm <sup>2</sup> (80 °C) and 0.99 W/cm <sup>2</sup> (120 °C) better than Nafion under same condition (1.28 W/cm <sup>2</sup> at 80 °C, 0.75 W/cm <sup>2</sup> at 120 °C)	45
Titania as filler					
Nafion/TiO <sub>2</sub>	(29) {0.93 meq g <sup>-1</sup> }	0.15–0.18 (85) [100]		PEMFC- Power density 0.514 & 0.256 W cm <sup>-2</sup> at 0.56 V ( 110 and 130 °C)	46
PVA/TiO <sub>2</sub>	(89)	10 <sup>-2</sup> (30)		Alkaline DMFC-maxi.power density 7.54 mW cm <sup>-2</sup> (60 °C)	47
Nafion <sup>®</sup> /sulfonated titanate		0.16 (75)	Reduced by 38 %, relative to Nafion	DMFC-57% higher power density (73.0 mW cm <sup>-2</sup> ) than Nafion	48
Tungsten trioxide as filler					
Nafion/ WO <sub>3</sub>	(37)	10 <sup>-2</sup> (100)		PEMFC- current densities of 300 and 540 mA/cm <sup>2</sup> at 0.4 V(110 °C)	49
PEO/WO <sub>3</sub> ·2H <sub>2</sub> O		10 <sup>-2</sup> -10 <sup>-3</sup> (R.T. to 120)			50
Heteropolyacid as filler					
Nafion/PTA, PMA, STA, SMA	(8)	0.06-0.08 (70) [100]		H <sub>2</sub> /air- current density of 0.1-0.9 A/cm <sup>2</sup> at 0.6 V (80 °C, 75 %RH)	51
Sulfonated poly(arylene ether sulfone)/PTA	(15-40) {1.4 meq g <sup>-1</sup> }	0.09 - 0.15 (30-100) [100]			52
Poly(vinyl alcohol)/ PTA	(157)	10 <sup>-4</sup>	6.16 x 10 <sup>-7</sup> to	H <sub>2</sub> /O <sub>2</sub> -current density of 46 mA cm <sup>-2</sup>	53

	{0.794 m mol g <sup>-1</sup> }		$8.31 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$	DMFC- current density of 80 mA cm <sup>-2</sup> (80 °C)	
s-Polyether ether ketone (PEEK)/Heteropolyacids(tungstophosphoric acid, (TPA), molybdophosphoric acid, (MPA) & disodium salt of tungstophosphoric acid, (Na-TPA)	sPEEK -TPA (600) sPEEK – MPA (320) sPEEK - Na-TPA (400)	sPEEK -TPA $9.5 \times 10^{-3}$ sPEEK - MPA $3.0 \times 10^{-3}$ sPEEK - Na-TPA $5.8 \times 10^{-3}$ (100)			54
Sulfonated polyethersulfone Cardo/PTA	(52)	$6.7 \times 10^{-2}$ (110)			55
Nafion/polyphenylene oxide (PPO)/phosphomolybdic acid (PMA)		0.03	$2.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	DMFC –(OCV=0.75 V) current density 160 mA/cm <sup>2</sup> 0.35 V.	56
polyethylene glycol/silica/lacunary heteropolyacid (H <sub>8</sub> SiW <sub>11</sub> O <sub>39</sub> )	{2–2.5 meq g <sup>-1</sup> }		$1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	Poor performance compared to Nafion <sup>®</sup> 117	57
Nafion <sup>®</sup> / Sulfonic-functionalized heteropolyacid/silica nanoparticles				DMFC- Power density 33 mW cm <sup>-2</sup> (80 °C) 39 mW cm <sup>-2</sup> (160 °C) and 44 mW cm <sup>-2</sup> ( 200 °C)	58
SPEEK/silica/divacant tungstosilicate [ $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ] <sup>8-</sup>		$13 \times 10^{-3}$ (110) [100]	$0.8 \times 10^{-16} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$		59
Nafion /SiO <sub>2</sub> / PWA	(38)	0.01 (100) [40]		PEMFC-current densities of 540 mA/cm <sup>2</sup> at 0.4 V (110 °C)	60
PBI /PWA/SiO <sub>2</sub>		$3.0 \times 10^{-3}$ (100) [100]			61
PVA/PWA/SiO <sub>2</sub>	[10-30]	0.017 (RT)	$10^{-7}$ to $10^{-8} \text{ cm}^2/\text{s}$ . Selectivity 0.02 x 10 <sup>7</sup>		62
PVA/silica/silicotungstic acid		$(4.13\text{--}8.31) \times 10^{-3}$ (80 to 100) [100]			15
PEG/SiO <sub>2</sub> /PWA	(44.7)	10 <sup>-3</sup>	$1.05 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$	H <sub>2</sub> /O <sub>2</sub> –(OCV=900 mV) DMFC-(OCV=650 mV)	63
Nafion <sup>®</sup> /PTA supported on SiO <sub>2</sub> , ZrO <sub>2</sub> and TiO <sub>2</sub>		15% superior conductivity compared to Nafion <sup>®</sup> (120) [ 35]	low crossover compared to Nafion <sup>®</sup>		64
SPEEK/heteropolyacids loaded MCM-41	(74-83)	$6.7\text{--}8.1 \times 10^{-3}$ (140)			65
Polyethyleneimine (PEI)/Tungstosilicate mesoporous materials(Si-MCM-41)		$6.1 \times 10^{-2}$ (100) [100]		(OCV= 0.93 V) current density= 42.9 mA/cm <sup>2</sup> power density=18.3mW/cm <sup>2</sup> (100 °C, 100% RH)	66
Sulfonated polyether ether ketone (SPEEK) /heteropolyacid-loaded Y-zeolite	(70-98)	$7.8 \times 10^{-3}$ (140)			67
PVA/zirconium	[90] {0.9 meq	10 <sup>-2</sup> (100) [60]	$5 \times 10^{-7} (\text{cm}^2 \text{ s}^{-1})$		13

phosphate/silicotungstic acid	$g^{-1}$				
Zirconium phosphate or Zirconium sulphophenyl phosphate (ZrSPP) as filler					
Nafion/ zirconium phosphates		0.025 [92]		Poor performance compared to Nafion	68
Disulfonated poly(arylene ether sulfone)/ Zirconium hydrogen phosphate	(40-60)	0.027 (80) [100]	$7.5 \times 10^{-7}$		69
Nafion <sup>®</sup> /Teflon <sup>®</sup> /Zr(HPO <sub>4</sub> ) <sub>2</sub>				H <sub>2</sub> /O <sub>2</sub> - current density 400 mA/cm <sup>2</sup> at 0.73 & 0.59V( 80 & 120 °C)	70
Nafion/PTFE/zirconium phosphate		$2.38 \times 10^{-3}$ (70-80)	$1.64 \times 10^{-4}$ (wt% cm hr <sup>-1</sup> )	Poor performance compared to Nafion	71
zirconium phosphate/ divinylbenzene (DVB) crosslinked, sulfonated, polystyrene grafted poly(ethylene-alt-tetrafluoroethylene)/poly(vinyl difluoride)	{1.8–2 meq g <sup>-1</sup> }	$40 \times 10^{-3}$ (130 ) [90]			72
Nafion/ZrSPP		$10^{-1}$ (110) [98]		H <sub>2</sub> /O <sub>2</sub> -current density 700 mA/cm <sup>2</sup> (100 °C)-four times higher than Nafion at 0.4 V	73
Polybenzimidazole/ zirconium tricarboxybutylphosphonate		$3.82 \times 10^{-3}$ (200 )			74
PVDF/Zirconium sulfophenylphosphonate, Zr(HPO <sub>4</sub> ) <sub>1.0</sub> (O <sub>3</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H) <sub>1.0</sub> )	(46)	$2 \times 10^{-3}$ (120) [90]			75
SPEEK/zirconium phosphate sulfophenylphosphonate		0.03 (60) [100]			76
Sulfonated poly(etheretherketone) cardo/ zirconium phosphate sulfophenylphosphonate	(10-40)	$10^{-2}$ (22) [100]	$45 \times 10^8$ (cm <sup>2</sup> s <sup>-1</sup> ) reduced by one order of magnitude compared to Nafion $\sigma/P$ ratio $7 \times 10^4$ ( 25 °C)		77
Poly (fluorinated arylene ether)s/ Zirconium phosphate sulfonated	(85.6)	$1.63 \times 10^{-2}$ (RT)		PEMFC- maximum power densities of 481 mW/cm <sup>2</sup> & 300 mW/cm <sup>2</sup> at 960 mA/cm <sup>2</sup> and 640 mA/cm <sup>2</sup> (120 °C & 130 °C), respectively. Higher voltage and maximum power density than Nafion	78
sPEEK/ZrPh/PBI	[0.6]	$11.5 \times 10^{-3}$ (25)	$4.0 \times 10^3$ barrer (1 barrer = $10^{-10}$ cm <sup>3</sup> [S TP]cm/(cm <sup>2</sup> s cmHg ))	DMFC - power density value 14.7 mW/cm <sup>2</sup> for 58.8 mA/cm <sup>2</sup> (110 °C, 138 % RH)	79
PVA/zirconium phosphate/ Cesium salt of silicotungstic acid	(100) [85] {3 meq g <sup>-1</sup> }	$10^{-2}$ (100) [50]	$2 \times 10^{-6}$ (cm <sup>2</sup> s <sup>-1</sup> )	DMFC-maximum power density 6mWcm <sup>-2</sup> (OCV=0.652 V) is higher compared to Nafion <sup>®</sup> 115 (0.610 V)	14

SPEK/ZrP/ZrO <sub>2</sub>	(21.5) [100]	0.8 (25)	$9.75 \times 10^{-3}$ barrer $8247 \text{ g h}^{-1} \text{ m}^{-2}$	DMFC- exhibits lower performance compared to Nafion	80
Layered silicate nanoparticles (e.g., montmorillonite, Laponite, & modified montmorillonite) as filler					
Nafion 115/sulfonated montmorillonite	(93)	0.93	$1.14 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	DMFC - 30 mW cm <sup>-2</sup> for composite and for Nafion 115 membrane (25 mW cm <sup>-1</sup> ) at 0.35 V	86
SPEEK/MCM-41		$8-16 \times 10^{-3}$	$3 \times 10^{-17} (\text{m}^2 \text{ s}^{-1} \text{ Pa}^{-1})$		87
SPEEK/laponite		$3-10 \times 10^{-3}$ (90)	$3 \times 10^{-17} (\text{m}^2 \text{ s}^{-1} \text{ Pa}^{-1})$		
SPEEK/organic-montmorillonite (OMMT)	(150)	$1.2 \times 10^{-2}$ (90) [100]	$10^{-8} \text{ cm}^2 \text{ s}^{-1}$		88
Nafion®/poly(oxyproplene)/montmorillonite (MMT)	(32) {0.89 mmol g <sup>-1</sup> }	$60-90 \times 10^{-3}$	$0.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ Selectivity =5500	DMFC - maximum power density 13.3 mW cm <sup>-2</sup> , current densities of 56 mA cm <sup>-2</sup> at 0.2 V	89
Nafion/organic sultones and perfluorinated sultone grafted montmorillonite (MMT)	{0.8-1.1 mmol g <sup>-1</sup> }	0.13 (50) [98]	Reduced by 40% compared to Nafion	DMFC - current densities 140 mA cm <sup>-2</sup> , at 0.3 V	90
Polyimide (PI), polyamideimide (PAI), polyvinylidene fluoride PVDF/ styrene-ethylene-butylene-styrene elastomer (SEBS)/phosphosilicate (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> )		PI/ (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> ) - $1.6 \times 10^{-2}$ (150) [18]  PAI / (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> ) - $1.5 \times 10^{-3}$ (150) [18]  PVdF/(P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> ) - $8.1 \times 10^{-4}$ (130) [25]  SEBS/ (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> ) - $6.9 \times 10^{-3}$ (130) [25]		PI/ (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> )-(OCV=0.9 V)- power density of 20 mW cm <sup>-2</sup> (150 °C, 4 % RH)  PAI / (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> )-(OCV=0.95 V)-power density of 52 mW cm <sup>-2</sup> (30 °C, 60% RH)  PVdF/(P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> )-(OCV= 0.79 V) Power density of 29 mW cm <sup>-2</sup> (130 °C, 25% RH)  SEBS/ (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> )-(OCV=0.72 V)-Power density of 34 mW cm <sup>-2</sup> ( 110 °C, 30% RH)	91
Phosphatoantimonic acid as filler					
Sulfonated polysulfone/ Phosphatoantimonic acid		$10^{-2}$ (80) [92]			91
Noble metals (Pt, Ru) as filler					
(Pt-SiO <sub>2</sub> )nafion coated /SPEEK/PTFE				H <sub>2</sub> /O <sub>2</sub> -(OCV= 0.98 V) maximum power density of 0.8 W cm <sup>-2</sup>	93
Pt/SiO <sub>2</sub> / Nafion/PTFE	(54) [6.7]		$10^{-3} \text{ cm}^2/\text{s}$	PEMFC-1.65 W cm <sup>-2</sup> -(80 °C) performance with the Pt-SiO <sub>2</sub> /Nafion/PTFE- was better than that NRE-212	94
Pt/ZrP/Nafion		0.06 [RT]		PEMFC - 275 mA/cm <sup>2</sup> at 0.620 V	95
PtRu/Nafion		0.18 (90) [100]		DMFC- ~28% and 31% higher at 30 and 45 °C than the pure Nafion	96
Ag/SiO <sub>2</sub> /sulfonated poly(biphenyl ether sulfone	(60-100)			H <sub>2</sub> /O <sub>2</sub> -exhibits better performance compared to parent polymer	97
Zeolite as filler					
Nafion/Zeolite(ZSM-5)	(30)	0.14 (RT)	$1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$		98
Nafion/chabazite & clinoptilolite				DMFC- Maximum power densities 350–370 mW cm <sup>-2</sup> and 200–210 mW cm <sup>-2</sup> at 140 °C	99

Poly(tetrafluoroethylene) (PTFE)/zeolite	(60-80)	0.01 (RT)		DMFC-Highest current and power densities were 50 mA/cm <sup>2</sup> and 4mW/cm <sup>2</sup> (70°C)	100
Pt/zeolite–Nafion (PZN)	(38.6)			H <sub>2</sub> /O <sub>2</sub> (50 °C,dry) 75% of the performance obtained at 0.6 V with humidified reactants at 75 °C	101
Nafion/mordenite		0.01 (70) [100]		H <sub>2</sub> /O <sub>2</sub> - current densities 400 mA cm <sup>-2</sup> , at 0.5 V (100°C)	102
Phosphates as filler					
Nafion/calcium phosphate			$1.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$		103
Nafion/CHP (calcium hydroxyphosphate)	(34)		$0.6 \times 10^{-7} \text{ cm}^2/\text{s}$		104
Sulfonated poly(ether ether ketone)/boron phosphate	(50-130)	0.065 (70) [100]			105
SPEEK/PBI/boron phosphate	(25)	$5.9 \times 10^{-3}$			106



**Table 2. Characteristic of commercial and composite membranes for DMFCs**

Membrane	Water uptake (%)	IEC (meq g <sup>-1</sup> )	Methanol diffusion coefficient (cm <sup>2</sup> s <sup>-1</sup> )	DMFC performance	Proton conductivity (S cm <sup>-1</sup> )	Reference
Nafion 117	21	0.9	1.72x10 <sup>-6</sup>	OCV= 0.65 V 100 mAcm <sup>-2</sup> (0.5 V, 70°C, 2 bar air, 2 M)	0.095 (25°C)	30,107, 110
CRA-08 <sup>a</sup>	33.7	1.4 -2.2	0.58x10 <sup>-6</sup>		0.045 (60°C)	108,109
IonClad <sup>®</sup> R1010 <sup>b</sup>		1.2	0.6x10 <sup>-6</sup>		0.146 (60°C)	110,111
SPEEK	30	1.7	17.5x10 <sup>-7</sup>	25 mAcm <sup>-2</sup> (0.5 V, 80°C, 2M)	0.013 (60°C)	112,113,114
Composite membrane	40-80	2-3	10 <sup>-8</sup>	OCV=0.75 V 160 mA/cm <sup>2</sup> (0.35 V)	0.1-0.93 (90°C)	14,22,30,47,56,57,62,86

a-Polyethylene-Tetra-fluoroethylene grafted sulphonyls-supliers Solvay

b-Tetra-fluoroethylene grafted poly(styrene sulfonic acid)-supliers Pall