# Polymer Electrolyte Membranes for the Direct Methanol Fuel Cell: A Review

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**ABSTRACT:** The direct methanol fuel cell (DMFC) has the potential to replace lithium-ion rechargeable batteries in portable electronic devices, but currently experiences significant power density and efficiency losses due to high methanol crossover through polymer electrolyte membranes (PEMs). Numerous publications document the synthesis and characterization of new PEMs for the DMFC. This article reviews this research, transport phenomena in PEMs, and experimental techniques used to evaluate new PEMs for the DMFC. Although many PEMs do not show significant improvements over Nafion®, the benchmark PEM in DMFCs, experimental results show that several new PEMs exhibit lower methanol crossover at similar proton conductivities and/or higher DMFC power densities. These results and recommendations for future research are discussed. © 2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 2201–2225, 2006
**Keywords:** electrochemistry; fuel cell; ionomer; membrane; polyelectrolyte

## INTRODUCTION

Over the past 15 years, research activity in direct methanol fuel cells (DMFCs) has grown exponentially (shown in Fig. 1). Fuel cells, in general, are attractive because they provide an innovative alternative to current power sources with higher efficiencies, renewable fuels, and a lower environmental cost. The DMFC, in particular, has generated interest in regards to portable electronic devices, with a potential to offer 10 times higher power densities than current lithium-ion rechargeable batteries.[1] Although there are several different types of fuel cells, the DMFC offers the most promising alternative for portable power applications, because it is a low temperature device, environmentally benign, and its fuel is portable and inexpensive. Therefore, considerable research effort is focused on miniaturizing and improving the efficiency of the DMFC.[2–4] Recently, a number of companies including Toshiba, Hitachi, Fujitsu, and Sanyo have all developed prototype laptops, cellular phones, and personal digital assistants that are powered by a DMFC.[5]

In general, a fuel cell works by converting chemical fuel into electrical energy. In the DMFC (Fig. 2), energy is converted when liquid methanol is directly catalytically oxidized at the anode and produces protons and electrons. Protons diffuse through a polymer electrolyte membrane (PEM) to the cathode, where they combine with electrons to produce electrical energy with water and carbon dioxide as byproducts. The anode, cathode, and overall cell reactions, respectively, are

$$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \qquad (1)$$

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \qquad (2)$$

$$CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2 \qquad (3)$$

In Figure 2, the anode catalyst/PEM/cathode catalyst composite is referred to as a membrane electrode assembly (MEA). Catalyst is usually adhered to the membrane and carbon fiber cloth, or gas dif-

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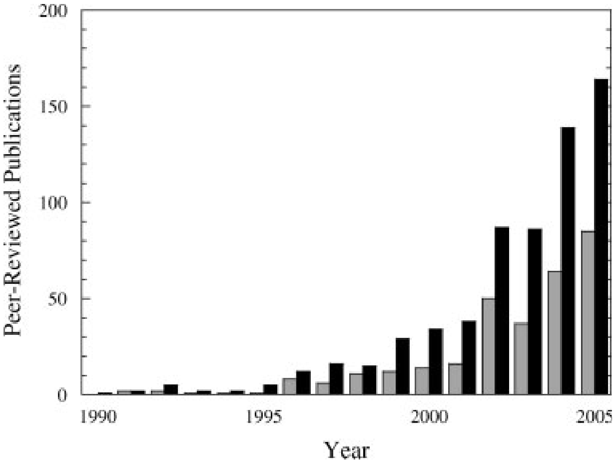


**Figure 1.** Peer-reviewed publications per year for 'methanol fuel cells' (solid bars) and 'membrane' and 'methanol fuel cells' (shaded bars). Data collected from ISI Web of Science® (http://isiknowledge.com).

fusion layer (GDL), is placed on each side of the MEA during PEM fuel cell tests.

Although current DMFCs report power densities double that of current lithium-ion rechargeable batteries with an overall efficiency $\sim$20–25%, there are critical factors that hinder the ability of the DMFC to reach its maximum efficiency ($\sim$100%): slow reaction kinetics at the anode and methanol crossover.[6] The oxidation of methanol is composed of a series of successive reactions creating formaldehyde and formic acid as intermediates that contribute to slow reaction rates and decreased cell voltage.[7] The switch from platinum to a bimetallic platinum/ruthenium for the anode catalyst provided some initial improvement in methanol oxidation rates.[6] Currently, the investigation of new anode catalysts to improve oxidation reaction rates is an active area of research as it applies to the DMFC.[8]

In addition, methanol crossover (high methanol permeability in the PEM) contributes to decreased overall cell efficiency and lifetime.[9–11] The reaction of methanol at the cathode results in a loss of fuel and cathode voltage and is referred to as a mixed potential. Typically, low methanol concentrations ($\sim$1–2 M; 4–8 vol %) are used in the DMFC to combat this problem, which limits the overall cell potential. If methanol crossover in PEMs was not an issue, a higher methanol concentration could be used, which would result in a significantly higher cell voltage. Note that $\sim$17 M or 69 vol % corresponds to the equimolar concentration coinciding with the anode half cell reaction (eq 1). Current DMFCs have an open circuit voltage ($\sim$0.7 V) approximately half of the electromotive force or reversible 'no-loss' cell voltage ($\sim$1.2 V) determined from the change in molar Gibbs free energy of the DMFC overall reaction. Figure 3 shows an ideal and typical DMFC performance (ambient conditions), where the differences (efficiency loss) can be observed over an operating current range.[6] Cell operating temperature, anode and cathode flow rates can all impact DMFC performance. However, methanol concentration, in particular, has a significant effect, where a 66% reduction in voltage at an optimal operating current density and a decrease in open circuit voltage are observed when the methanol concentration in the anode feed is increased from 2 to 6 M.[11]

Today, Nafion® (DuPont) is the most frequently used PEM in DMFCs (chemical structure shown in Fig. 4). It contains a hydrophobic fluorocarbon backbone and perfluoroether side chains containing a strong hydrophilic ionic pendant group, sulfonic acid. In Figure 4, the sulfonic acid group is shown in its anhydrous form, $SO_3H$. When exposed to water, its hydrolyzed form ($SO_3^-H_3O^+$) allows for effective proton transport across the membrane. In addition to high proton conductivity at optimal water contents, Nafion® membranes are also thermally, chemically, and oxidatively stable. These are several reasons why Nafion® is used not only in the DMFC, but also in PEM fuel cells that use hydrogen and other chemicals (e.g. ethanol) as their fuel. Despite all of these positive attributes, Nafion® suffers from high methanol crossover

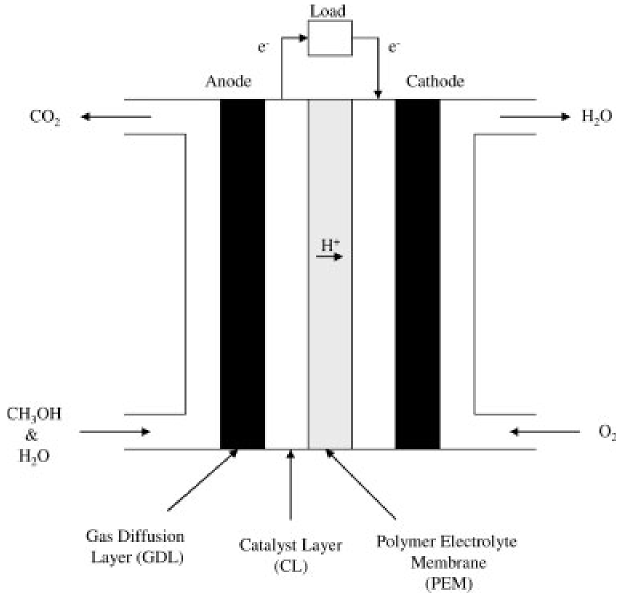


**Figure 2.** Schematic representation of the direct methanol fuel cell (DMFC).

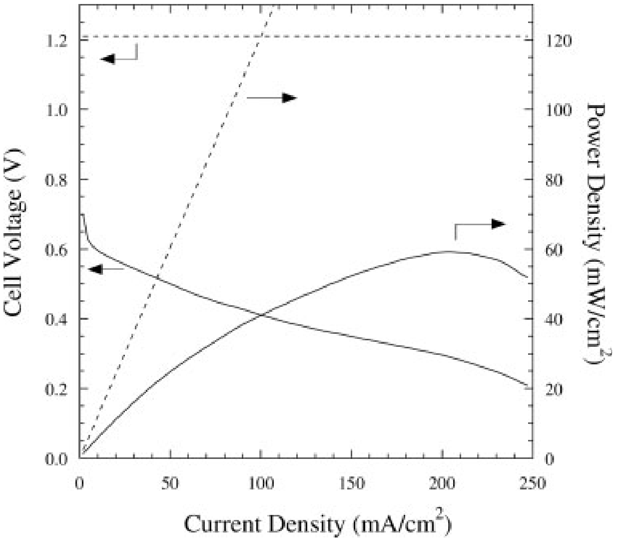


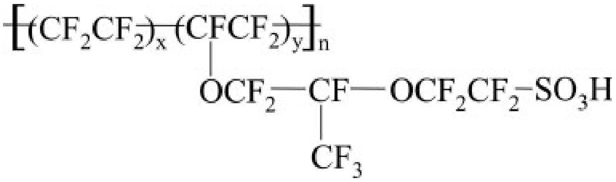
**Figure 3.** Fuel cell performance (voltage and power density *vs.* current density) for a typical DMFC operating under ambient conditions (represented by the solid lines). The ideal ('no loss' voltage) performance is represented by the dashed lines. Data adapted from Larminie and Dicks.[6]

rates. Therefore, another active area of research is focused on the development and evaluation of new PEMs (Nafion® replacements) that are methanol resistant. Figure 1 shows that approximately half of the research in the area of DMFCs is focused on membrane development. This article will highlight this research and review transport phenomena in PEMs as it pertains to the DMFC.

## LITERATURE REVIEW

### Overview

Although performing DMFC tests (voltage *vs.* current density and long term voltage response) on a newly developed PEM is the optimal experiment to gauge whether Nafion® can be outperformed, this test is only conducted on ~40% of the PEM development studies targeted for the DMFC application. DMFC tests require appropriate equipment and adequate MEA fabrication. Poor adhesion between the catalyst layer and the PEM has been cited as a reason for poor DMFC test results in a number of studies.[12–17] Therefore, a number of prescreening experiments are conducted on new PEMs to determine whether the investment in conducting DMFC tests is worthwhile. These tests include measuring proton conductivity, methanol permeability (crossover), water and methanol sorption, and thermal, mechanical, and chemical stability. The key prescreening measurements as it relates to minimizing crossover and improving DMFC efficiency are proton conductivity and methanol permeability. High proton conductivity gives an indication as to whether the new PEM will provide a significant voltage response, while low methanol permeability will alleviate the crossover problem discussed above. This will allow for a higher methanol feed concentration, which should also lead to a higher overall cell voltage and power density. Therefore, a high selectivity (*i.e.* proton conductivity/methanol permeability) and proton conductivity are desired.



$$\left[(\mathrm{CF_2CF_2})_x(\mathrm{CFCF_2})_y\right]_n \quad \mathrm{OCF_2{-}CF(CF_3){-}OCF_2CF_2{-}SO_3H}$$

**Figure 4.** Chemical structure of Nafion®.

Figure 5 shows the measured proton conductivity and methanol permeability for a number of investigations (listed in Table 1).[13,14,18–58] Each

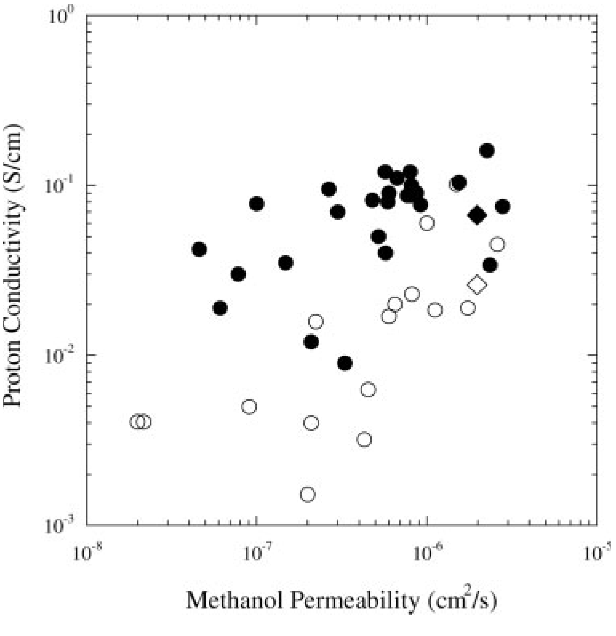


**Figure 5.** Proton conductivity *vs.* methanol permeability for a number of different PEMs (●, ○) and Nafion® 117 (◆, ◇). Solid and open symbols refer to proton conductivity measured in the plane (four-electrode technique) and normal to the plane of the membrane (two-electrode technique), respectively. Each data point corresponds to a different PEM (different study). Data and references are listed in Table 1.

**Table 1.** PEMs Developed for the DMFC

| PEM | Proton Conductivity (S/cm) | Methanol Permeability (cm$^2$/s) (× $10^6$) | Reference |
|---|---|---|---|
| Blends of sulfonated poly[bis(phenoxy)phosphazene] and polybenzimidazole | 0.060[a] | 1.300 | 13 |
| Nafion®/montmorillonite nanocomposite | 0.087[b] | 0.770 | 14 |
| Crosslinked poly(vinyl alcohol)/poly(acrylic acid)/silica hybrid | 0.012[b] | 0.210 | 18 |
| poly(vinylidene fluoride-hexafluoropropylene) copolymer/Nafion® blend | 0.002[a] | 0.200 | 20 |
| Nitrile-functional, disulfonated poly(arylene ether sulfone) | 0.090[b] | 0.870 | 21 |
| Nafion®/ORMOSILS composite | 0.019[a] | 1.750 | 22 |
| Sulfonated poly(ether ether ketone ketone) | 0.040[b] | 0.575 | 23 |
| Sulfonated poly(styrene-*b*-ethylene-*r*-butadiene-*b*-styrene) block copolymer | 0.023[a] | 0.820 | 24 |
| Sulfonated poly(styrene)/poly(tetrafluoroethylene) composite | 0.110[b] | 0.670 | 25 |
| Sulfonated co-polyimide | 0.082[b] | 0.480 | 26 |
| 4-Dodecylbenzene sulfonic acid-doped polyethylene glycol/silica hybrid | 0.004[a] | 0.020 | 27 |
| Sulfonated poly(ethersulfone)-Cardo | 0.004[a] | 0.210 | 28 |
| Sulfonated poly[(aryloxy)phosphazene] | 0.035[b] | 0.148 | 30 |
| Sulfonated poly(styrene) | 0.050[b] | 0.520 | 31 |
| Sputter coated palladium on Nafion® | 0.016[a] | 2.23 | 32 |
| Phosphotungstic acid/poly(vinyl alcohol) composite | 0.006[a] | 0.454 | 33 |
| IonClad® R-1010 | 0.080[b] | 0.590 | 34 |
| Nano-silica layered Nafion® composite | 0.077[b] | 0.920 | 35 |
| Sulfonated poly(ether ether ketone)/zirconium oxide composite | 0.005[a] | 0.091 | 36 |
| Palladium deposited on Nafion® | 0.003[a] | 0.430 | 37 |
| 4-Dodecylbenzene sulfonic acid-doped poly(ethylene glycol)/silica hybrid | 0.004[a] | 0.022 | 38 |
| Nafion®/H-substituted montmorillonite composite | 0.087[b] | 0.800 | 39 |
| Polypropylene-*g*-poly(styrene sulfonic acid)/Nafion® laminate | 0.075[b] | 2.800 | 40 |
| Sulfonated poly(phthalazinone ether sulfone ketone)/silica hybrid | 0.034[b] | 0.415 | 41 |
| IPN of crosslinked poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and Nafion® | 0.019[a] | 1.120 | 42 |
| Sulfonated naphthalene dianhydride based polyimide copolymer | 0.120[b] | 0.800 | 43 |
| Sulfonated poly(arylene ether) copolymer | 0.100[b] | 0.810 | 44 |
| Sulfonated poly(styrene-*b*-ethylene-*r*-butadiene-*b*-styrene) block copolymer | 0.045[a] | 2.600 | 45 |
| Sulfonated polyimide | 0.120[b] | 0.570 | 46 |
| Nafion®/montmorillonite nanocomposite | 0.078[b] | 0.100 | 47 |
| Sulfonated poly(ether ether ketone) | 0.070[b] | 0.300 | 48 |
| Chemically crosslinked poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid)/poly(vinylpyrrolidone) blend | 0.090[b] | 0.600 | 49 |
| IPN of Nafion® and polypyrrole | 0.017[a] | 0.600 | 50 |
| Sulfonated polystyrene and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) blend | 0.034[b] | 2.350 | 51 |
| Poly(styrene sulfonic acid) grafted onto poly(vinylidene fluoride) | 0.102[a] | 1.500 | 52 |
| Crosslinked poly(vinyl alcohol) using sulfosuccinic acid | 0.015[b] | 0.330 | 53 |

**Table 1.** Continued

| PEM | Proton Conductivity (S/cm) | Methanol Permeability (cm$^2$/s) ($\times 10^6$) | Reference |
|---|---|---|---|
| Poly(vinyl alcohol)/poly(styrene sulfonic acid) blend | 0.004[a] | 1.00 | 54 |
| Nafion® 117 | 0.026[a] | 1.980 | 55 |
| Nafion® 117 | 0.067[b] | 1.980 | 56 |
| Sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) block copolymer | 0.004[a] | 0.090 | 55 |
| Sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) block copolymer | 0.019[b] | 0.150 | 56 |
| Nafion®/poly(vinyl alcohol) blend | 0.020[a] | 0.650 | 57 |
| Poly(vinyl alcohol)/poly(styrene sulfonic acid-*co*-maleic acid) blend | 0.095[b] | 0.266 | 58 |

[a] Two-electrode technique (through the plane of the membrane).
[b] Four-electrode technique (along the plane of the membrane).

data point corresponds to a separate study (different PEM), where solid symbols refer to proton conductivity measured along the plane of the membrane (four-electrode technique) and open symbols refer to proton conductivity measured through the plane of the membrane (two-electrode technique). The diamond symbols refer to Nafion® 117 (standard in the DMFC), where 117 refers to 1100 equivalent weight (EW) and 0.007 in. in thickness.[59,60] EW is proportional to the inverse of ion exchange capacity (IEC) – 1000/EW = milliequivalents of sulfonic acid per gram of dry polymer (Nafion® 117 has an IEC = 0.9 meq/g). The differences between the four- and two-electrode techniques will be explained in more detail later in the article.

It is clear from Figure 5 that there are a number of PEMs that possess lower methanol permeabilities at similar or even higher proton conductivities when compared with Nafion®. Other companies, such as Dow Chemical, Aciplex, Pall RAI, Asahi Chemical, and Solvay Solexis, have developed similar perfluorinated polymer membranes to Nafion®.[61,62] However, most of these PEMs possess similar transport properties to Nafion®.[61] Other PEMs developed in the literature for the DMFC constitute a variety of design approaches, such as the synthesis of new ionic (sulfonic acid) random and block copolymers,[21,23,24,26,28,30,31,36,43–46,48,51,57,63–72] graft copolymerization of ionic polymers unto hydrophobic membranes,[15,16,34,52,73] blending ionic and nonionic polymers,[13,20,17,49,53,54,57,58,74–88] the synthesis of interpenetrating networks of ionic and nonionic polymers,[42,50,89–99] incorporating a variety of fillers (e.g., silica, montmorillonite) into ionic polymer membranes,[12,14,18,19,22,25,27,29,33,37–39,41,47,92,100–118] and coating ionic polymer membranes with thin barrier coatings.[12,32,35,40,80,119–126] The subsections below highlight findings from these investigations.

## Random Copolymers

A number of sulfonic acid containing random copolymers have been synthesized for the DMFC.[21,23,26,30,31,36,44,46,48,51,63,65–67] Sulfonated poly(styrene) (SPS), a random copolymer of poly (styrene) and poly(styrene sulfonic acid) (PSSA) has been investigated for its use in the DMFC.[31,51] Interestingly, crosslinked PSSA membranes were one of the first PEMs used in fuel cells for the Gemini space program.[127] Additionally, sulfonated crosslinked polystyrene has been used in ion exchange columns and as water purification membranes.[128] SPS can be synthesized either by copolymerizing styrene and styrene sulfonic acid monomers or by postsulfonation[129] of poly(styrene) with a variety of sulfonating agents (e.g., acetyl sulfate, sulfur trioxide). Postsulfonation results in an electrophilic substitution of sulfonic acid to the aromatic group along the backbone of poly(styrene), and is a commonly used procedure to sulfonate polymers containing aromatic groups. This results in random copolymers, where the IEC or sulfonic acid content can be controlled by reaction conditions. Results from Carretta et al.[31] show a simultaneous increase of both proton conductivity and methanol permeability with increasing sulfonic acid content in SPS membranes. A sharp increase in both aforementioned transport properties was observed at 14 mol % sulfonation. Selectivities were higher than Nafion®; however, the authors question the chemical stability and durability of SPS membranes as it pertains to fuel cell applications.

Sulfonated poly(ether ether ketone) (SPEEK) and sulfonated poly(ether ether ketone ketone) (SPEEKK) have been synthesized through either polymerization[23,48] or postsulfonation[36,67] techniques producing random copolymers with sulfonic acid substituted directly to the aromatic backbone. These copolymers possess a number of beneficial attributes for the DMFC: good thermal stability, mechanical strength, and adequate conductivity.[23,36,48,67] Random copolymers synthesized by polymerization reveal that proton conductivity and methanol crossover both increase with increasing IEC of the membrane. However, selectivities ~7 times higher than Nafion® were observed at the highest IEC synthesized. Postsulfonated copolymers were less selective than these membranes, but an improved DMFC performance was demonstrated compared to the copolymers synthesized by polymerization.

Poly(imide)s have received considerable interest because they are both thermally and oxidatively stable.[26,43,65,66] Specifically, six-member ring poly (imide)s are favored compared with five-member ring poly(imide)s because of lower ring strain and better hydrolytic stability.[43,66] McGrath and coworkers[43,66] polymerized disulfonated polyimide random copolymers, which allowed for a disulfonation (two sulfonic acid groups per monomeric unit) as high as 86 mol %. A proton conductivity and methanol permeability of 0.12 S/cm and $8.00 \times 10^{-7}$ cm$^2$/s, respectively, were reported, where both increased with increasing IEC. Ultimately, these membranes were found to be unstable under fuel cell conditions. Other researchers report sulfonated poly(imide)s consisting of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and a sulfonated aromatic diamine, which comes from one of two groups. One group includes polymers in which the sulfonic acid groups are directly bound to the polymer backbone, such as 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS), and the other group consists of polymers where sulfonic acid groups are attached to the side chains, such as 2,2′-bis(3-sulfo-propoxy)benzidine (2,2′-BSPB). These polymers had five times higher selectivity compared with Nafion®.[26] Sulfonated polyimide, produced by synthesizing sulfonated diamine monomers, 3-(2′,4′-diaminophenoxy)propane sulfonic acid followed by polymerizing the monomer with 1,4,5,8-naphthalenetetracarboxylic dianhydride had methanol permeabilities two times lower than Nafion® with similar proton conductivities.[44] Another study synthesized a polyimide containing trifluoromethyl groups. A 70% decrease in methanol crossover compared to Nafion® was observed.[65]

Another polymer of interest is poly(phosphazene), because of its thermal and chemical stability and the ease at which side chains can be attached to the —P=N— backbone.[63] These polymers can also be easily sulfonated to control IEC and therefore proton conductivity. Allcock and coworkers[30] sulfonated and crosslinked (using gamma radiation) poly[(aryloxy)phosphazene] and obtained proton conductivities approximately half of Nafion®, but selectivities ~7 times higher. Another study sulfonated and crosslinked (with UV light) poly [bis(3-methylphenoxy)phosphazene] and demonstrated conductivities and crossover rates that were comparable with Nafion® in a temperature range of 21–72 °C. These membranes exhibit good thermomechanical strength up to 173 °C.[63] Pintauro and coworkers[13] sulfonated poly[bis(phenoxy)phosphazene] (SPOP) and subsequently blended with polybenzimidazole (PBI) to induce the formation of crosslinks. Data from this study shows that increasing PBI content results in decreased conductivity. This was attributed to increased crosslinking, which resulted in reduced water sorption and the immobilization of protons by interaction with the basic sites of PBI limiting charge transport. Overall, selectivities of SPOP-PBI membranes were approximately twice that of Nafion® with methanol permeabilities 3–20 times lower than Nafion®. Slightly lower DMFC voltages compared to Nafion® were reported. Stability tests showed a cell voltage loss of ~0.8 mV/h, which was attributed to growing contact resistance between the SPOP–PBI membrane and the Nafion® binder in the catalyst layer.

A membrane of sulfonated poly(ether sulfone) [a polymer with six-membered aromatic rings linked with sulfide bonds] and 9,9-bis(4-aminophenyl fluorene) (CARDO) exhibited high mechanical, thermal, and chemical stability.[28] These membranes have proton conductivities and methanol permeabilities approximately one order of magnitude lower than Nafion® at room temperature. Another study on sulfonated poly(ether sulfone) demonstrated 10 times lower methanol permeabilities than Nafion®.[126]

Sulfonated poly(arylene ether sulfone) and sulfonated poly(arylene ether benzonitrile) random copolymers have been synthesized by McGrath and coworkers.[21,44] Both copolymers have similar aromatic backbones, which are attractive due to their thermal, mechanical, and oxidative stabilities. Synthesizing these copolymers consisted of a direct copolymerization method of disulfonated and unsulfonated monomers where 30–35 mol % of the repeat units were typically disulfonated. Transport properties of the sulfonated poly(arylene ether sulfone) membranes yielded selectivities ~3 times higher than Nafion®, while the selectivities of the poly(arylene ether benzonitrile) membranes were ~4 times higher than Nafion®. Polarization curves from DMFC tests for the poly (arylene ether benzonitrile) membranes showed higher cell voltages at corresponding current densities compared to Nafion®.

## Graft Copolymers

Several investigators have grafted SPS or PSSA on a variety of hydrophobic polymers, such as poly(ethylene-tetrafluoroethylene) (ETFE), poly(vinylidene fluoride) (PVDF), and low-density poly(ethylene) (LDPE).[15,16,34,52,73] In these studies, graft copolymerization usually consisted of exposing the hydrophobic polymer membrane to a radiation source, which promotes the formation of radicals and functional groups on the membrane. This was followed by an *in situ* graft copolymerization of styrene or styrene sulfonic acid monomers. In the case of grafting styrene, copolymerization is followed by postsulfonation of the membrane.

Hatanaka and coworkers[16] investigated the relationship between the degree of grafting and proton conductivity for membranes consisting of PSSA grafted on ETFE. At low degrees of grafting (< 30 wt %), conductivity was significantly lower than Nafion®. At 30 wt % grafting, the conductivity showed an abrupt increase to values approximately double that of Nafion®, and the conductivity continued to increase linearly up to 50 wt % grafting. Methanol and water uptakes increased linearly with the degree of grafting, and the selectivity for water to methanol was higher compared with Nafion®. Methanol permeability experiments showed a 30% decrease compared with Nafion®, however, the fuel cell performance of these graft copolymer membranes was lower than Nafion®. The investigators attribute this to poor bonding between the catalyst layer and the membrane.

In a study by Scott and coworkers,[15] a methanol permeability 15 times less than Nafion® was observed for graft copolymer membranes of SPS and PVDF. Generally, these membranes exhibited higher fuel cell voltages at higher current densities. However, the stability of the MEA, specifically, adhesion of the catalyst layer to the membrane was an issue (delamination was observed when removing the MEA from the fuel cell). Further work by Scott and coworkers[52] on PSSA grafted on ETFE, PVDF, and LDPE demonstrated approximately three times higher selectivities compared to Nafion® with lower methanol crossover and higher proton conductivity than Nafion®. DMFC performance tests showed decreased performance with grafted ETFE and PVDF over time, but grafted LDPE membranes improved with time. Grafted ETFE membranes developed by Saarinen and coworkers[73] exhibited good long term DMFC performance at lower efficiencies than Nafion® 115 (with 90% lower methanol crossover when compared with Nafion®). Their study highlights the economic advantage of using graft copolymer membranes, where they cite ~20 times cost reduction per area of membrane compared with Nafion®.

Tricoli et al.[34] investigated commercial graft copolymer membranes, IonClad® *R*-1010, a membrane composed of PSSA side chains grafted to a perfluorinated polymeric backbone, and IonClad® *R*-4010, a membrane composed of PSSA grafted to a tetrafluoroethylene/perfluoropropylene copolymer. Proton conductivities were similar to Nafion®, while methanol permeabilities were almost four times lower.

## Block Copolymers

A number of sulfonic acid containing block copolymers (i.e. ionic block copolymers) have been synthesized for the DMFC.[24,45,49,56,57,64,68–72] Ionic block copolymers are attractive because they chemically conjoin both ionic and nonionic monomers on the same polymer backbone in an ordered sequence. Block copolymers provide a unique template, where microphase separation occurs on a nanometer scale because of the thermodynamic incompatibility between unlike blocks forming a variety of self-assembled morphologies including spheres arranged on a cubic lattice, hexagonally packed cylinders, interpenetrating gyroids, and alternating lamellae.[130] This provides the potential for unique ordered morphologies, where transport properties can be tailored.[72]

Initial studies on sulfonated block copolymers focused only on the sulfonation and the structural and thermal characterization of styrene-based block copolymers at low ion exchange capacities (IECs).[130–136] These reports did not address transport properties. Recently, a number of investigators have examined the transport properties of sulfonated block copolymers at higher IECs (~1–2 meq/g), and have shown comparable conductivities to Nafion® (0.9 meq/g).[137–140]

Various research groups have examined sulfonated poly(styrene-*b*-ethylene-*r*-butylene-*b*-styrene) (*S*-SEBS).[24,45,69–70] The styrene block of SEBS was sulfonated with a standard postsulfonation process in all of these studies. Similar to studies with SPS, both proton conductivity and methanol permeability increased simultaneously with increasing sulfonation levels.[24,45] Proton conductivities and selectivities similar to Nafion® were reported.[45] Another study investigated the effect of casting solvent choice on morphology and transport properties in *S*-SEBS membranes.[24,70] Both proton conductivity and methanol permeability increased by an order of magnitude when the casting solvent was changed from tetrahydrofuran (THF) to a THF/methanol mixture. Small-angle X-ray scattering (SAXS) results revealed a morphological transition from a preferentially ordered lamellar structure to a nonperiodic structure coinciding with the increased transport rates.[70] However, these morphological transitions did not significantly change the selectivity of the membrane.

A similar block copolymer, sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) (*S*-SIBS), has been investigated.[56,68,71] Similar to *S*-SEBS, both proton conductivity and methanol permeability increased as IEC increased. Elabd and coworkers[68,71] synthesized membranes with IECs up to 2 meq/g and observed proton conductivities three times higher than Nafion®. However, the selectivities were similar to Nafion® at all IECs. SAXS revealed a morphological transition from a preferentially lamellar morphology oriented in the plane of the membrane (anisotropic) at IECs ranging from 0.5–1 meq/g to a nonperiodic cocontinuous morphology (isotropic) at IECs ranging from 1.1 to 2 meq/g. This structural transition coincided with a discontinuity in the transport property trend. Additionally, proton conductivity increased by three orders of magnitude in *S*-SIBS membranes with a change in casting solvent from toluene to a toluene/ethanol mixture. SAXS revealed structural changes as a function of different casting solvents.

Other block copolymers such as sulfonated poly(styrene-*b*-ethylene) (*S*-SE)[71] and sulfonated hydrogenated poly(styrene-*b*-butadiene) rubber (HSBR)[72] have been investigated as alternative PEMs. *S*-SE has proton conductivities as high as 0.11 S/cm (four-electrode), and a bi-continuous structure was observed with small-angle neutron scattering (SANS). For sulfonated HSBR, the SBR was hydrogenated to eliminate the double bonds in the butadiene block and then the styrene blocks were sulfonated. After sulfonation, the membranes exhibited lower proton conductivities and methanol permeabilities compared with Nafion®.

Poly(arylene ether sulfone-*b*-polybutadiene) block copolymers were synthesized by a polycondensation reaction of poly(arylene ether sulfone) and poly(butadiene) and then postsulfonated.[64] Relatively high conductivities were achieved at low IECs: 0.0302 S/cm at 0.624 meq/g (two-electrode). This result suggests that sulfonic acid groups on the flexible segments of the block copolymer can arrange into a more favorable morphology for transport.

## Blends

Research on polymer blends includes polyvinyl (alcohol) (PVA) and Nafion®[57] PVA and PSSA,[54] PVA and poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA),[58,74] PVA crosslinked with sulfosuccinic acid,[53] PVA and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS),[58,75] PAMPS and poly(2-hydroxyethyl methacrylate) (PHEMA),[76] sulfonated poly(sulfone) and acid-doped PBI,[77] sulfonated poly(ether ketone) and PBI,[17] and sulfonated poly(sulfone)/poly(ether sulfone) and SPEEK/poly(ether sulfone).[78] It is interesting to note that PVA is present in a number of these studies. Pivovar et al.[79] first suggested the use of PVA for DMFCs along with other polymers, such as polyacrylonitrile (PAN), PVDF, and PBI. These polymers have previously been investigated as it applies to pervaporation (liquid/vapor separation of binary mixtures) of ethanol/water mixtures (ethanol dehydration). The chemical selectivity of water over ethanol suggests that these polymers may increase proton/methanol selectivity. Their study focused on comparing acid conductivities to methanol permeability. Since these polymer membranes alone are not proton conductors, it is difficult to project clear conclusions from their data. However, this article has motivated a number of studies that blend PVA with proton conducting polymers with the goal of increasing conductivity/crossover selectivity.

DeLuca and Elabd[57] investigated the transport properties of Nafion®/PVA blends as a function of composition and annealing temperature. One key observation was the trends in proton and methanol transport in the Nafion®/PVA blend membrane at 50 wt % PVA. As annealing temperature increased, proton conductivity remained relatively constant, while methanol permeability decreased by almost an order of magnitude. These trends differ from most investigations, where proton and methanol transport usually increase or decrease simultaneously in sulfonic acid containing polymers with changes in polymer properties. Infrared spectroscopy supports these results in which the hydroxyl infrared band increased in wavenumber with increasing annealing temperature, suggesting more interaction between the hydroxyl groups in PVA and the sulfonic acid groups in Nafion®. Also, the Nafion®/PVA blend membrane at 5 wt % PVA and 230 °C annealing temperature had a similar proton conductivity, but three times lower methanol permeability when compared with Nafion®. This increased selectivity was not observed in Nafion®/PVA blend membranes (5 wt % PVA) at other annealing temperatures.

Blends of PVA with other sulfonic acid containing polymers have also been studied. PVA/PSSA blend membranes were investigated at various PSSA contents and annealing temperatures.[54] At 17 wt % PSSA and an annealing temperature of 110 °C, methanol crossover was half of Nafion®, but proton conductivity was an order of magnitude lower. Wu et al.[54] suggests that annealing the blends induces crosslinking between the hydroxyl groups in PVA and the sulfonic acid groups in PSSA, which is supported by reduced swelling and infrared spectroscopy data. Similarly, polymer blends of PVA and PSSA-MA were investigated, where introducing maleic acid reduced membrane swelling when compared with pure PSSA.[58,74] In addition, the hydroxyl groups in PVA were crosslinked in this study with glutaraldehyde to further reduce swelling. Blending PVA with PSSA-MA (3:1 mol ratio) in a 1:1 weight ratio yielded proton conductivities as high as 0.095 S/cm and methanol permeabilities an order of magnitude lower than Nafion®.[58] In comparison to PVA/PSSA membranes, PVA/PSSA-MA membranes exhibited a 46% increase in proton conductivity and almost a 5-fold decrease in methanol permeability. SAXS results suggest that crosslinked PVA/PSSA-MA membranes possess narrower ionic channels when compared with Nafion®, which the authors attribute to the decrease in methanol permeability.

PVA crosslinked with sulfosuccinic acid revealed similar transport property trends when compared with PVA/PSSA blends. A maximum in selectivity was observed at 17 wt % sulfosuccinic acid and an annealing temperature of 130 °C (0.015 S/cm; $3.3 \times 10^{-7}$ cm$^2$/s).[53] Although this is technically not a polymer blend, this polymer is similar in concept to crosslinked blends that have both a sulfonic acid containing polymer and PVA.

Qiao and coworkers[49] investigated PVA/PAMPS blends, where PVA was crosslinked with glutaraldehyde and poly(vinylpyrrolidone) (PVP) was added as a stabilizer. They report a proton conductivity of 0.088 S/cm (four electrode) and a methanol permeability of $6.0 \times 10^{-7}$ cm$^2$/s. In another study by the same investigators,[75] different aldehydes (*n*-butylaldehyde/terephthalaldehyde, *n*-hexylaldehyde/terephthalaldehyde, and *n*-octylaldehyde/terphthalaldehyde) were used to crosslink the PVA/PAMPS blends without PVP. By using different auxiliary aldehydes, the crosslinking spacer length can be controlled, where an increased crosslinker spacer length (while maintaining constant terephthalaldehyde concentration) resulted in an increase in water sorption. Although methanol permeability was not measured in this study, a proton conductivity of 0.12 S/cm (four-electrode) was reported.

Walker investigated polymer blends containing PAMPS and PHEMA.[76] Nafion® (5 wt %) was added to this blend to increase flexibility in the dry state. At small PAMPS content (4 wt %), conductivities similar to Nafion® were reported, but the membranes were still too brittle in the dry state. Methanol crossover experiments were not measured in this study. Polymer blends of sulfonated poly(sulfone) and acid-doped PBI were investigated.[77] These membranes did not show any significant improvements for use in a DMFC, but proton conductivities were comparable to Nafion® at 80 °C. Kerres et al.[17] developed blends consisting of different poly(ethersulfone)s and poly(etherketone)s, which exhibited lower methanol crossover in DMFC tests, but problems with adhesion between the membrane and electrodes were reported. Additionally, blends of sulfonated poly(sulfone)/poly(ether sulfone) and SPEEK/poly(ether sulfone) were developed.[78] Methanol permeability coefficients approximately two orders of magnitude lower than Nafion® were reported, but clear conclusions could not be drawn as proton conductivity was not measured.

A number of investigators have explored PBI in PEMs for the DMFC.[80–88,141–147] PBI is interesting because it possesses both donor and acceptor hydrogen bonding sites, high thermal stabilities, chemical resistance, and mechanical strength. It has been used in acid-base blend membranes with PEEK and polysulfone,[80] and it has been *N*-substituted with methyl and ethyl groups and doped with phosphoric acid.[81] The former study shows a 10-fold decrease in methanol permeability, but does not include conductivity experiments. In the latter study, methanol crossover was less than Nafion®, but proton conductivities were not comparable (3 orders of magnitude lower).

## Impregnated Membranes

A number of researchers have impregnated polymers within membranes using several strategies, including *in situ* polymerization and sorption within both swollen dense membranes and porous membranes. Smit et al.[89] demonstrated *in situ* polymerization of poly(pyrrole) within a Nafion® membrane. This procedure entailed immersing Nafion® in an acid electrolyte containing the monomer and then polymerizing within the membrane galvanostatically in an electrochemical cell. Results show a decrease in methanol permeability when compared with Nafion® (no conductivity data was reported here). Another study incorporates poly(pyrrole) within a Nafion® membrane with *in situ* polymerization, where peroxide was used as the free-radical initiator.[90] A decrease in methanol and water sorption compared to Nafion® was reported (permeability and conductivity data were not reported here). Park and coworkers[50] impregnated Nafion® membranes with poly(pyrrole) using *in situ* polymerization and observed ~5 times increase in selectivity compared to Nafion®. A sulfonic acid containing polymer, poly(2-acrylamido-2-methyl-1-propanesulfonic acid-*co*-1,6-hexanediol propylate diacrylate-*co*-ethyl methacrylate), (*i.e.* crosslinked PAMPS), was polymerized within a Nafion® membrane and then subsequently crosslinked.[95] A reduction in methanol permeability compared to Nafion® was observed, while a high proton conductivity was maintained. Bae et al.[91] also used a similar method to impregnate poly(1-vinylimidazole) (PVI) within a Nafion® membrane. Results showed a 25% increase in both methanol permeability and proton conductivity when compared with Nafion®. Poly(furfuryl alcohol) was impregnated within Nafion® membranes and revealed improved DMFC performance (at 7 wt % poly(furfuryl alcohol) in Nafion®) with a maximum power density ~180% higher than Nafion® and higher cell voltages at all current densities.[92]

Hobson and coworkers[93] used a variety of methods to incorporate acid-doped PBI into a Nafion® membrane, such as spin coating, dipping, and screen printing. Spin coated membranes reduced methanol permeability by 58% when compared with Nafion®. Dipped membranes produced varied results over a range of PBI contents, but the best data reported a 50% reduction in methanol permeability compared to Nafion®. Both of these methods, however, resulted in low proton conductivities. Screen printed membranes had similar proton conductivity to Nafion® with a 50% reduction in methanol permeation. These membranes also had improved DMFC performance when compared with Nafion®. The working current density range was increased by 42%, and the maximum power density was increased by 46%.

Another study polymerized and crosslinked styrene monomers within a PVDF matrix followed by sulfonation of the impregnated polystyrene.[94] The authors refer to this membrane as a "semi" interpenetrating network (IPN) and suggest that these membranes do not follow the same transport mechanisms as Nafion® and grafted PSSA systems; this is prescribed to differences in water flux properties and distribution of sulfonic acid moieties. These membranes resulted in lower methanol permeabilities (95% less) and higher DMFC power densities when compared with Nafion® 117.

IPN membranes of crosslinked P(AMPS-*co*-HEMA) and PVA were developed by Walker.[95] Free-radical copolymerization and crosslinking of AMPS and HEMA were performed in a PVA matrix. PVA was crosslinked in a subsequent step with glutaraldehyde. Since the two crosslinking reactions were independent of one another, Walker suggests that conductivity and crossover could be altered independently. This infers that the crosslinking of AMPS and HEMA can be tailored to achieve high proton conductivities, and the crosslinking reaction of PVA can be optimized to induce the lowest methanol permeability. This concept was initially confirmed with water and methanol sorption experiments. These IPNs were thermally stable up to 150 °C, and further investigations are being conducted into the use of these membranes in DMFCs over 100 °C.

Yamaguchi and coworkers[96] have clearly shown the benefits of polymer-filled microporous membranes in comparison to crosslinked polymers in both experiment and theory. Their results demonstrate that polymer-filled microporous membranes can effectively suppress the same amount of swelling compared to a highly crosslinked polymer, while increasing selectivity. Recently, their work[97,98] was applied to the DMFC application, where polymer-filled microporous membranes demonstrated an increase in proton conductivity without a significant increase in methanol crossover. Polymer swelling was controlled with a microporous host membrane, where different host membranes were more effective than others. More recently, Yamaguchi and coworkers[99] filled a microporous crosslinked high density poly(ethylene) substrate with poly(acrylamide *tert*-butyl sulfonate). In their study, DMFC performance was relatively constant over a wide range of methanol feed concentrations. Their work shows that confining a polymer electrolyte within a porous support suppresses polymer swelling (methanol uptake) without compromising proton conductivity significantly.

## Composite Membranes

Polymer membranes containing micrometer to nanometer size fillers (composite membranes) have been explored intensely for the DMFC.[12,14,18,19,22,25,27,29,33,37–39,41,47,100–118] A variety of fillers, including silica,[18,19,38,41,50,105,115] zirconium phosphate,[109] phosphotungstic acid,[100] molybdophosphoric acid,[112] Aerosil (silicon dioxide powder),[112] ORMOSILS (organically modified silicates),[22] silane-based fillers,[22] titanium oxide,[109] hydroxyapatite,[104] laponite,[117] montmorillonite,[14,47,110] zeolites,[114] and palladium,[116] have been incorporated in a number of different polymer membranes including Nafion®.

Silica has been frequently used as a filler, and these composite membranes demonstrate improved thermal[100] and mechanical stability,[27] and maintain adequate water uptakes at elevated temperatures.[27] Silica has been incorporated within PVA/phosphotungstic acid (PWA),[100] polyethylene glycol (PEG) membranes doped with 4-dodecylbenzene sulfonic acid (DBSA) (via sol–gel process),[27,38] crosslinked PVA/poly(acrylic acid) (PAA) blends,[18] Nafion®/PWA (via sol–gel process),[19] sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK),[41] macroporous silica matrix,[105] and *S*-SEBS.[115] In all studies, introducing silica leads to decreased methanol permeability when compared with the parent polymer. Several problems were encountered, such as decreased water transport (resulting in lower proton conductivities), membranes becoming too brittle when the inorganic phase loading reached a critical level, and decreased fuel cell performance. These silica composite membranes generally shared similar trends and ranges with respect to proton conductivity ($\sim$0.01–0.03 S/cm) and methanol permeability ($\sim 1–5 \times 10^{-7}$ cm$^2$/s).[18–19,27,38,41,100,105,115] The membranes containing PEG and DBSA exhibited permeabilities an order of magnitude lower than Nafion®, while its conductivity was only half the value (selectivity ~double compared with other silica composite membranes).

A number of investigators have also explored heteropolyacids as fillers in polymer membranes.[102,106,107,111,113] Heteropolyacids are strong acids composed of heteropolyanions and protons as the counterions and are good proton conductors in their crystalline form.[111,137] A heteropolyanion is a self-assembled structure that consists of one or more heteroatoms (e.g., phosphorus) surrounded by several additional metal-oxygen polyhedrons (metals include zirconium, tungsten, molybdenum). Composite membranes with heteropolyacids include zirconium oxide in SPEEK,[102,107,111] boron phosphate within a perfluorosulfonic acid ionomer, organosilyl derivatives of divacant tungstosilicates in SPEEK,[106] and zirconium phosphate sulfophenylenphosphonate in sulfonated polyetherketone (SPEK).[113] Several researchers suggest that this strategy will reduce methanol crossover because of increased tortuosity (impermeable fillers), while increasing proton conductivity (heteropolyacid enhances proton mobility). Conductivity tests on these membranes were often measured at high temperatures (70–110 °C). Conductivities up to 0.035 S/cm (two-electrode) were observed at 110 °C.[106] An important issue regarding these composites is the potential for the heteropolyacids to leach out of the membrane in methanol/water solutions, which can result in lower conductivities. To maintain reasonably high conductivities, a technique must be developed to trap the acids inside the membranes.

Incorporating layered silicate nanoparticles (e.g., montmorillonite, Laponite, and modified montmorillonite) into polymers, such as Nafion® and SPEEK, is another strategy researchers have explored to make nanocomposite membranes for the DMFC.[14,47,110,117] Montmorillonite and its derivatives were chosen as fillers because they enhance the mechanical properties of the membrane,[47,117] improve barrier properties,[14] prevent excessive swelling,[117] and can conduct ions.[110] Interestingly, three different research groups prepared nanocomposite membranes of montmorillonite in Nafion® using different techniques. Song et al.[47] mixed (with ultrasonication) montmorillonite with Nafion® and solvent cast the mixture into membranes. Jung et al.[110] used pulverization, mixing, and heat pressing to produce Nafion®-montmorillonite nanocomposite membranes. Thomassin et al.[14] melt-mixed the two components and extruded the membranes. The most promising results were obtained from the solvent cast membranes in which proton conductivity was ~20% higher than Nafion® and methanol permeability was ~20 times less than Nafion®.[47] In this study, X-ray diffraction reveals that the montmorillonite filler was uniformly dispersed and exfoliated. Also, glass-transition temperatures shifted to higher temperatures in the composites, suggesting a stronger interaction between the filler and polymer. The heat pressed membranes exhibited surprisingly low conductivities compared to results obtained by Song and coworkers. Permeability experiments were inconclusive as their methods were incomparable to other standard experimental techniques. Significant differences between composites of Nafion® and montmorillonite *vs.* Nafion® and modified montmorillonite were not observed. The extruded samples containing montmorillonite were found to have increased methanol permeability when loading increased.[14] The authors suggest that the lack of interactions between the filler and the polymer created a crude dispersion observed by transmission electron microscopy (TEM) causing this transport trend. When Cloisite 30B was dispersed in Nafion®, methanol permeability decreased ~33% with only a 0.5 wt % filler content. When DMFC tests were performed on the Cloisite 30B nanocomposites, performance dropped ~50% when compared with Nafion®.[14] Data from the SPEEK nanocomposites showed decreased proton conductivities (~300%), methanol permeabilities (~75%), and fuel cell performance (~25%) compared to Nafion®.[117]

Other researchers developed composite membranes of PVDF filled with nanoparticles, such as silica, zirconia, and aqueous mixtures of acids.[118] These membranes exhibited lower methanol crossover compared to Nafion®, but due to the use of aqueous acids, corrosion-resistant materials for the fuel cell would be required in the fuel cell assembly. Palladium nanoscale agglomerates were impregnated into Nafion® membranes to decrease methanol diffusion by increasing toruosity.[37] These membranes were an order of magnitude lower in methanol permeability compared to Nafion®, but conductivity also decreased significantly.

## Coated membranes

Coating PEMs with thin barrier layers is a technique that a number of investigators have pursued through a variety of deposition techniques.[12,32,35,40,119–126] One study coated a Nafion® membrane with charged palladium particles via self-assembly, where a layer-by-layer technique was employed to achieve 1–5 double layers of palladium.[120] A methanol crossover two orders of magnitude lower than uncoated Nafion® was observed at three self-assembling double layers, while the conductivity continually decreased as more double layers were formed on the surface. In addition to this study, other researchers have deposited thin palladium layers on Nafion® membranes.[32,121,124] Ma et al.[124] sputter coated palladium onto Nafion® membranes; however, a crack-free barrier layer could not be produced with this procedure. Yoon et al.[32] developed homogeneous films (crack-free) with palladium particles <30 nm via sputter coating, where methanol permeability decreased by an order of magnitude with only a slight decrease in proton conductivity. Other researchers used an electroless plating technique, in which Nafion® was submerged in a palladium sulfate solution, followed by submersion in a hydrazine solution to coat Nafion® membranes with palladium. Only a slight decrease in methanol crossover was observed.[121]

Other studies have utilized radiation techniques to coat PEMs.[35,80,119,125] A nano-silica coated Nafion® membrane has been fabricated with plasma enhanced chemical vapor deposition.[35] Methanol permeability decreased 67%, while proton conductivity only decreased 21% compared to Nafion®. However, DMFC tests reveal a lower performance compared to Nafion®. Another study used hexane/hydrogen plasma irradiation to deposit a thin barrier layer on the surface of a Nafion® membrane.[80] This resulted in a lower methanol crossover with only ~0.3 $\mu$m barrier layer. Low-dose electron beam (e-beam) exposure has also been used to modify the surface of Nafion® membrane resulting in a thin barrier layer (~1.5 $\mu$m).[119] Infrared spectroscopy reveals that e-beam exposure mainly affects the hydrophilic side chains and not the fluorine rich backbone. DMFC tests confirm higher power densities after e-beam exposure.

Shao and coworkers[119] developed a multilayer composite with a Nafion® membrane coated on both sides with PVA using an immersion technique. These membranes were exposed to post treatments, sulfonation followed by crosslinking with glutaraldehyde. Three immersions resulted in a 61% increase in selectivity. For MEA preparation, a PVA-coated Nafion® 112 membrane (1:1 wt ratio) was sandwiched between two Nafion® 112 membranes. The Nafion® 112 layers were placed on the outside of the multilayer composite in an effort to enhance catalyst adhesion to the membrane and increase conductivity. A 5–10% increase in cell voltage at all current densities was observed for the multilayer composite of Nafion® and PVA. Other polymers, such as poly(1-methyl pyrrole), have also been coated on Nafion® membranes.[126] Methanol permeability showed a ~1000 times decrease compared to uncoated Nafion® but proton conductivity showed a similar decrease. Ren et al.[101] dipped a SPEEK membrane in a Nafion® solution to coat both sides of the membrane. This resulted in a 4-fold decrease in methanol permeability, but conductivity decreased to half the value of Nafion®.[101] In addition, several other studies have used lamination techniques to coat Nafion®.[40,122,123] A 37% reduction in methanol crossover was exhibited in multilayer membranes consisting of 44 $\mu$m thickness SPEEK membrane sandwiched between two Nafion® membranes.[123] Laminated membranes consisting of poly(propylene)-*g*-PSSA and Nafion® showed a consistent decrease in methanol permeability with increased crosslinking density. Also, DMFC tests showed a 22% increase in voltage compared to Nafion®.[40]

## TRANSPORT PHENOMENA IN PEMS

To understand the performance of the PEMs developed by various research groups (results shown in Fig. 5 and Table 1), transport phenomena in PEMs must be considered. A detailed account of various aspects of transport phenomena in PEMs can be found elsewhere.[148] In this section, transport phenomena in PEMs as it relates to the DMFC (transport of protons, water, and methanol) is highlighted.

Typically, the transport of small molecules across a dense (nonporous) polymer membrane follows a solution-diffusion mechanism.[149] Transport can be described as sorption of solutes into the membrane (upstream or high concentration side), diffusion across the membrane (concentration gradient is the driving force), and desorption of solutes out of the membrane (downstream or low concentration side). Overall, the transport rate is determined by a permeability coefficient (P), which is a product of the solubility (S) and the diffusion coefficient (D).

$$\mathrm{P} = \mathrm{SD} \tag{4}$$

Solubility is the equilibrium parameter based on solute-polymer thermodynamics, while the diffusion coefficient is a kinetic parameter based on the free-volume or structure of the polymer. The ratio of desired (1) to undesired (2) solute permeabilities is referred to as selectivity ($\alpha$).

$$\alpha_{1/2} = \frac{P_1}{P_2} = \frac{S_1 D_1}{S_2 D_2} \tag{5}$$

Overall, this generally describes selectivity for solute-polymer systems (e.g., gases or organic vapor/liquid diffusion in nonionic dense polymer membranes). However, for transport phenomena in PEMs (ionic polymers), there are a number of additional parameters to consider, such as ion transport, the ionic structure of the polymer, and a potential difference (for fuel cell tests).

Experimentally for the separate proton conductivity and methanol permeability measurements, the transport of protons (desired) and methanol (undesired) are the two primary diffusing solutes of interest. The steady-state flux of protons in a membrane can be described by the Nernst-Planck equation[150]:

$$-j_1 = D_1 C_1 \left( \frac{\nabla C_1}{C_1} + z_1 \frac{F \nabla \psi}{RT} \right) \tag{6}$$

where $D_1$, $C_1$, and $z_1$ are the diffusion coefficient, concentration, and charge, respectively, for protons. Also, in eq 6, $F$ is Faraday's constant, $R$ is the gas constant, $T$ is the temperature, and $\psi$ is the electrostatic potential. With the aid of the Nernst-Einstein relation, proton conductivity ($z_1 = +1$) can be related to its diffusion coefficient[150]:

$$\sigma_1 = \frac{D_1 C_1 F^2}{RT} \tag{7}$$

For methanol, the steady-state flux can be described by Fick's law as

$$-j_2 = D_2 \bigtriangledown C_2 \tag{8}$$

where $D_2$ and $C_2$ are the diffusion coefficient and concentration, respectively, for methanol. When the concentration of methanol on the upstream side of the membrane, $C_{2o}$, is constant and there is a zero-sink boundary condition for concentration on the downstream side, then eq 8 can be represented as

$$j_2 = \frac{D_2 K_2 C_2}{L} \tag{9}$$

where $K_2$ is the partition coefficient (the ratio of methanol concentration inside the membrane to

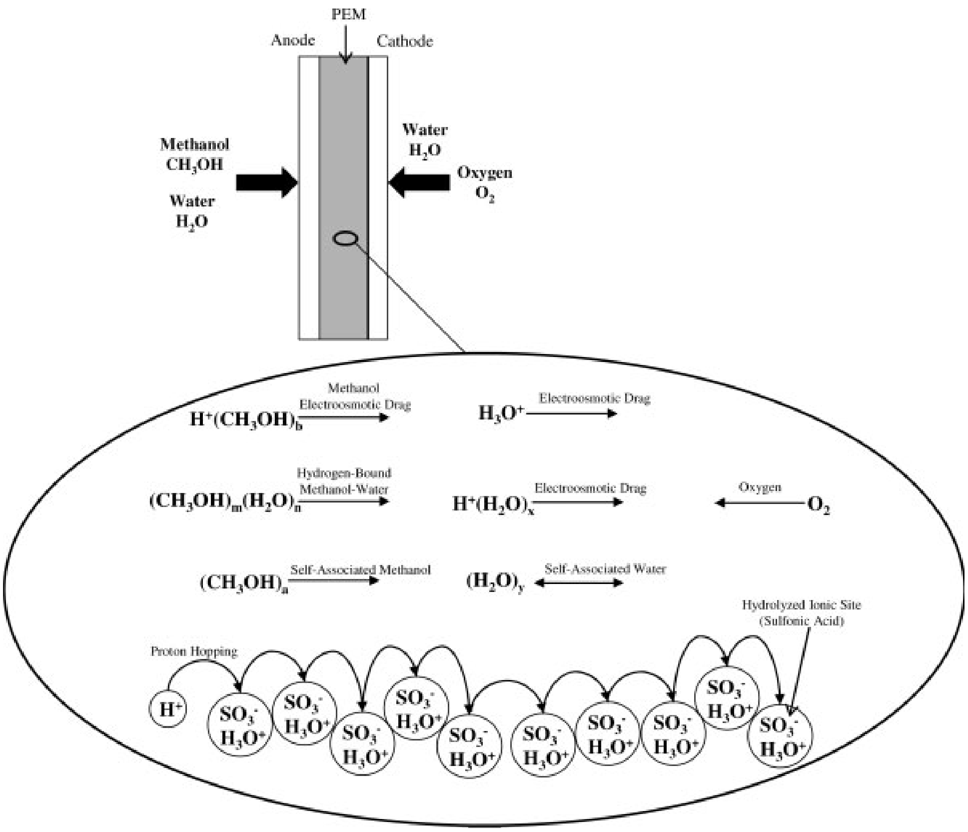


**Figure 6.** Multicomponent molecular transport mechanisms in PEMs for the DMFC.

that in the adjacent solution) and the product $D_2K_2$ is the methanol permeability, $P_2$. Selectivity for protons to methanol can be defined as the ratio of proton conductivity to methanol permeability:

$$\alpha_{1/2} = \frac{\sigma_1}{P_2} = \frac{D_1C_1F^2}{D_2C_2RT} \qquad (10)$$

Note that conductivity and permeability are both proportional to their respective diffusion coefficients, and are the two separate quantities that are experimentally measured in the PEM development studies reviewed in the previous section. For enhanced DMFC performance, a high proton conductivity and high selectivity is desired (*i.e.* a high value for $\alpha$ in eq 10). Aside from temperature effects, the driving factors that affect selectivity are the diffusion coefficient of protons, $D_1$, the concentration of protons in the membrane or concentration of fixed ion sites in the membrane, $C_1$, the diffusion coefficient of methanol, $D_2$, and the partition coefficient of methanol in the membrane, $K_2$. Increasing membrane selectivity is a difficult problem since several of these factors are interdependent and also a function of several other parameters. For instance, $D_2$ is a function of both water and methanol concentration in the membrane, but also a function of molecular size and polymer free volume, and $K_2$ is a function of $C_1$ and also a function of water/methanol uptake and the solute-polymer interaction parameter. Also, $D_1$ is a function of $C_1$ and also hydration (water uptake) and membrane structure.

The equations above are a simplified view of the problem; the transport of protons, water, and methanol in PEMs is multifaceted and is affected by phenomena on two different length scales: Ångstrom (molecular) and nanometer. Furthermore, during DMFC operation, the diffusion of protons, water, and methanol will occur simultaneously in the PEM, and all diffusants will be under the influence of an applied voltage. On a molecular length scale, researchers have suggested several molecular transport mechanisms for protons, water, and methanol in PEMs (illustrated in Fig. 6).[68,79,151,152] For proton transport, two different mechanisms have been suggested: proton "hopping" (Grotthus), where protons hop from one hydrolyzed ionic site ($SO_3^-H_3O^+$) to another across the membrane, and electroosmotic drag, where protons

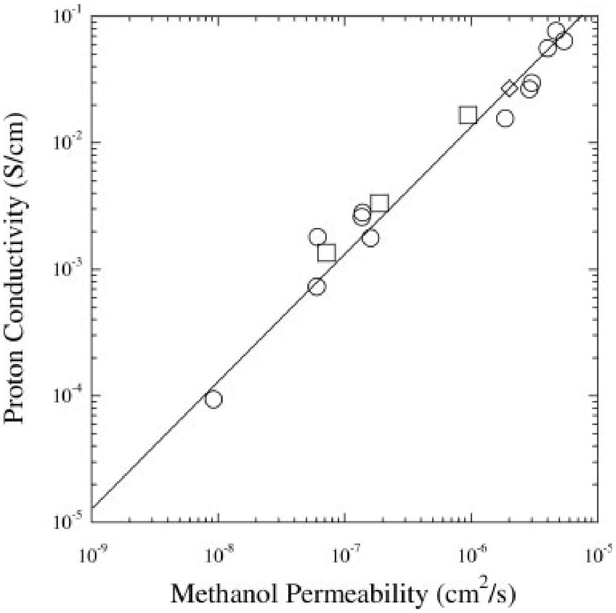


**Figure 7.** Proton conductivity (two-electrode technique) *vs.* methanol permeability for Nafion® 117 (◇), S-SIBS (○), and *S*-PS (□) membranes. The solid line represents a linear regression of the data, where the slope is the selectivity (proton conductivity/methanol permeability = 1.32 × $10^4$ S s/cm$^3$). Data from Elabd et al.[68]

bound to water ($H^+(H_2O)_x$) drag one or more water molecules across the membrane. Water also has two suggested transport mechanisms: electroosmotic drag and concentration gradient driven diffusion (this probably occurs as self-associated clusters: $(H_2O)_y$). The diffusion of methanol in water can diffuse in a variety of forms: a self-associated cluster, $(CH_3OH)_a$, a complex hydrogen-bound to water, $(CH_3OH)_m(H_2O)_n$, and also a complex bound to protons, $H^+(CH_3OH)_b$, where the latter is similar to the electroosmotic drag mechanism. The flux equations listed above (eqs 6 and 8) do not account for multicomponent diffusion (the effect of the concentration gradient of one component on the flux of another), the interactions between the solutes and between the solute and the polymer, and the electrostatic potential gradient for both water and methanol. Therefore, flux equations for protons, water, and methanol should incorporate both the Nernst-Planck (electrostatic potential gradient) and Stefan-Maxwell (multicomponent diffusion) framework.

Although a detailed picture of all the molecular transport mechanisms has not yet been unraveled, a number of studies have reported key trends observed in most sulfonic acid containing PEMs.[31,56,68,79,151,152] Standard experiments show that proton conductivity increases with increasing water content, ion content, and temperature. Increasing ion content leads to an increase in the hydrophilic and ionic nature of the polymer, which results in higher conductivities and higher water levels in PEMs.[68] However, if the water content reaches values that are too high, the membrane will experience lower mechanical strength and poor water management. Also, when the temperature reaches higher values (> 80 °C), the membrane will dehydrate, which leads to a reduction in proton conductivity and poor water management.[153] Higher water values also lead to higher swelling in polymers, which usually results in higher methanol crossover.[68] Therefore, most investigations observe that proton and methanol transport usually increase or decrease simultaneously in sulfonic acid containing PEMs with changes in polymer properties. Figure 7 shows the proton conductivity and methanol permeability for several different sulfonic acid containing PEMs (Nafion®, SPS, and *S*-SIBS).[68] All of the membranes have a similar selectivity regardless of ion content, water content, or polymer chemistry, architecture or morphology. This suggests that protons and methanol have similar molecular transport mechanisms in sulfonic acid containing PEMs, which makes it difficult to improve selectivity for the DMFC application.

On a nanometer scale, transport in PEMs is dependent on ionic structure, unlike the transport in homogeneous nonionic polymer films.[154,155] There are a number of publications that have examined the structure of PEMs, particularly Nafion®, using a variety of techniques (most often X-ray scattering).[156–161] A number of models for the structure of Nafion® have been suggested, and the details of these findings are beyond the scope of this article. Details on Nafion® have recently been reviewed by Mauritz and Moore.[162] Although there are diverse opinions regarding the detailed morphology, there is a consensus that microphase segregation occurs in many PEMs. Aggregates of ions form due to the electrostatic interactions between ion pairs, leading to the formation of two phases: ion-rich domains and ion-poor domains (shown in Fig. 8). The ion-rich domains (aggregates of ions) are referred to as ion clusters, while ion-poor domains are mostly the hydrophobic part or backbone of polymer.[154] In particular, X-ray analysis of Nafion® by Gierke and coworkers[156] suggests that ion clusters approximately ~5 nm in size are inter-

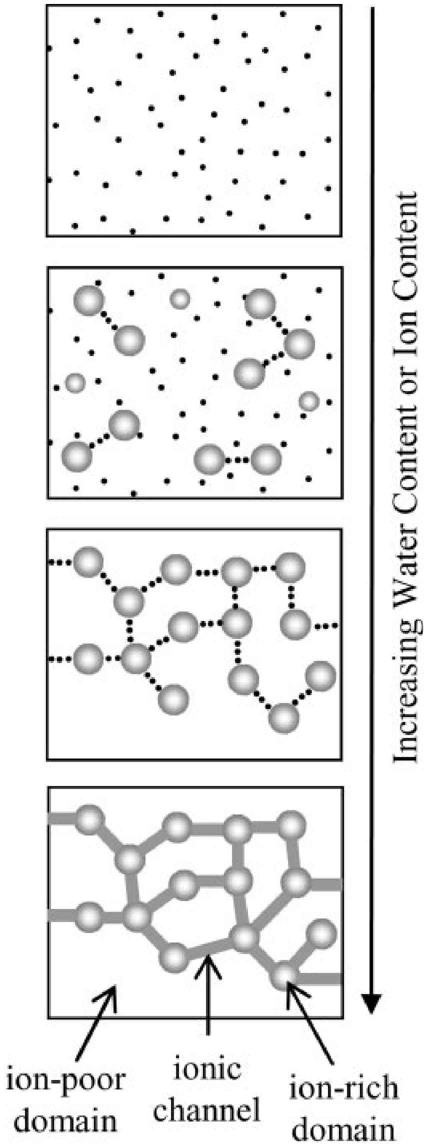


**Figure 8.** Illustration of the suggested evolution of ionic nanostructure in PEMs. Adapted from Weber and Newman.[148]

connected by small narrow ionic channels ~1 nm in diameter. A number of other morphological models for Nafion® have also been suggested.[162]

Figure 8 shows a suggested evolution of morphology that occurs in PEMs, where isolated ion clusters become interconnected with increasing water content or ion content. This is known as an insulator-to-conductor transition or percolation threshold, whereby the transport of molecules and ions are facilitated through this interconnected ionic network. It is evident based on several investigations that the diffusion of ions (protons) and water are affected by the ionic nanostructure and follow a percolation model.[56,155,163–166]

In percolation theory, conductivity or diffusivity follows a power-law dependent model:

$$\frac{\sigma}{\sigma_o} \propto \frac{D}{D_o} \propto (\phi - \phi_c)^{\gamma} \tag{11}$$

where $\gamma$ is the critical exponent and $\phi$ and $\phi_c$ are the volume fraction and critical volume fraction of the diffusion phase, respectively. The critical volume fraction is the critical concentration where the percolation threshold occurs (*i.e.* where isolated regions become interconnected and diffusion begins to occur). $\sigma$ and $D$ are the observed conductivity and diffusivity, respectively, and $\sigma_o$ and $D_o$ are the inherent conductivity and diffusivity, respectively, in the diffusing phase. Kirkpatrick[167] calculated values of 1.6–1.7 for $\gamma$ using a three-dimensional lattice model simulation with a random distribution of the minority phase. A more recent simulation gives a value of 2.0 for $\gamma$.[168] Values for $\gamma$ give an indication of the nonideality or randomness of the PEM structure; as this approaches lower values than the ones reported here for a random-order simulation, then the system becomes more ideal or ordered. Table 2 reports percolation values determined from a number of investigations on various PEMs.

In addition to these findings, several recent investigations have clearly demonstrated the effects of ordered and oriented ionic nanostructures on transport properties. Ding et al.[169] demonstrated increased proton conductivity in poly (styrene) grafted with PSSA side chains compared to SPS, a random copolymer. They concluded that the increase in proton conductivity was attributed to a more ordered ionic nanostructure. Cable et al.[170] stretched Nafion® to induce orientation of ionic nanostructure and demonstrated a 40% difference in conductivity when measured in and normal to the plane of the membrane (anisotropic conductivity). Maki-Ontto et al.[171] also demonstrated anisotropic conductivity (an order of magnitude difference) in proton conductive polymers that were sheared to induce an oriented lamellar nanostructure. Elabd et al.[55] demonstrated anisotropic conductivity in a proton conducting block copolymer (*S*-SIBS) with oriented lamellar nanostructures. The effect of ordering in ionic nanostructure was also demonstrated in a lower critical exponent compared to Nafion®, shown in Table 2. These studies reveal the significant impact that ordered and oriented ionic nanostructures can have on transport properties in PEMs. This relationship between transport properties and ionic nanostruc-

**Table 2.** Percolation Values in PEMs

| PEM | $\gamma$ | $\phi_c$ | Reference |
|---|---|---|---|
| Nafion® | 1.5 ± 0.02 | 0.10 | 180 |
| Poly(methyl methacrylate-*co*-methacrylic acid) | 1.35 | 0.26 | 161 |
| Poly(styrene-*co*-methacrylic acid) | 1.7 | 0.165 | 162 |
| Sulfonated poly(phenylene oxide) | 1.5 | 0.16 | 163 |
| Sulfonated poly[bis(3-methylphenoxy) phosphazene] | 1.26 | 0.175–0.25 | 164 |
| Sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) | 0.76 | 0.077 | 56 |

ture in PEMs raises a critical issue as it relates to experimental transport techniques. This is discussed in the following section.

## EXPERIMENTAL TECHNIQUES

The experiments described in the literature review primarily focused on transport properties (proton conductivity and methanol permeability) and DMFC performance tests. Proton conductivity is measured with electrochemical (or AC) impedance spectroscopy (EIS), while methanol permeability is usually measured with a liquid diffusion cell. EIS applies an alternating current over a broad frequency range, where the resistance of the membrane can be determined from the real impedance data (or the $x$-intercept of the regression of the imaginary *vs.* real impedance data over a high frequency range). Typically, a four-electrode technique (in the plane of the membrane) is preferred over the two-electrode (through the plane of the membrane), because of the significant frequency dependence on impedance at low frequencies due to interfacial impedance.[172] However, the two-electrode technique measures the membrane impedance in the same direction as methanol transport, which is the direction that is relevant for the DMFC. Generally, impedance measurements with the two-electrode technique are conducted at the upper limit of the frequency range, where there is only a minor dependency on frequency.[172] The proton conductivity for Nafion® 117 (diamond symbols in Fig. 5) shows a 2.5-fold difference in conductivity between the two techniques: 0.067 S/cm and 0.027 S/cm for the four and two-electrode techniques, respectively.[55,56] These values are similar to other values reported in literature for Nafion® 117 using these two techniques at similar temperatures: 0.067 S/cm,[173] 0.061 S/cm,[174] 0.054–0.082 S/cm,[34] for the four-electrode technique; and 0.024 S/cm,[173] 0.022 S/cm,[175] for the two-electrode technique. Some researchers suggest that the differences are primarily due to the differences in the two techniques; while others suggest that there may be a slight ionic microdomain orientation during the commercial extrusion process of Nafion® membranes causing this effect. Regardless, the values reported here give a magnitude of conductivity required to obtain a voltage response for a DMFC.

However, the differences between these techniques should be considered more thoroughly when investigating other PEMs. For example, a study by Elabd and coworkers[55] demonstrates an order of magnitude reduction in proton conductivity, when

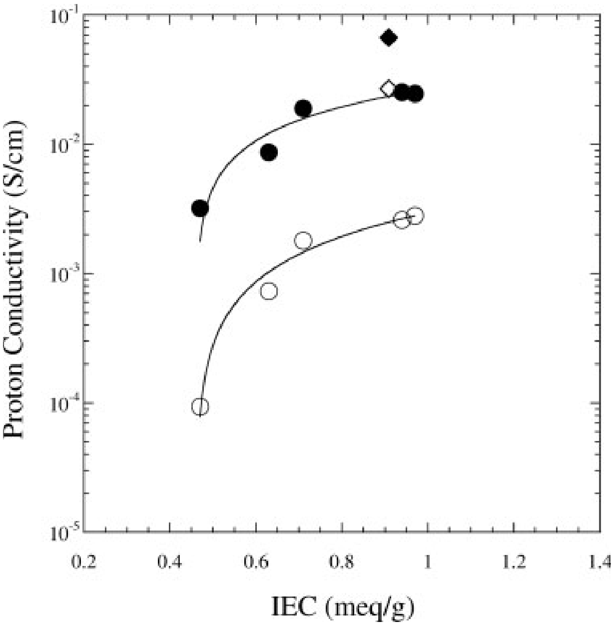


**Figure 9.** Proton conductivity measured in the plane and normal to the plane of the membrane *vs.* IEC for Nafion® 117 (◆, ◇, respectively) and *S*-SIBS membranes (●, ○, respectively). Data from Elabd et al.[56]

comparing the two-electrode technique to the four-electrode technique, for sulfonated block copolymer membranes (*S*-SIBS) with a lamellar morphology with a preferred orientation in the plane of the membrane (shown in Fig. 9). For this study, if the four-electrode technique is used, the membranes exhibit selectivities ~5–10 times higher than Nafion® 117 with slightly lower proton conductivities. With the two-electrode technique, selectivities are similar to Nafion® 117 with conductivities an order of magnitude lower. Other investigations have demonstrated similar relationships between conductivity and structure in self-assembled oriented polymer systems.[171,176]

These studies highlight the importance of cautiously interpreting conductivity results in this field. For example, one study on palladium coated-Nafion® membranes appears promising at first glance.[37] Proton conductivities of 0.11 S/cm are reported using the four-electrode technique. However, three other studies[32,37,120] on similar palladium coated-Nafion® membranes report proton conductivities ranging from 0.003 to 0.02 S/cm using the two-electrode technique. Similar to data in Figure 9, the difference between these two techniques is over an order of magnitude. Assuming methanol permeabilities are similar, selectivity values for the four-electrode study will appear 10–100 times higher in the former study compared to the latter studies. Another study on montmorillonite dispersed within Nafion® (filler are narrow flat sheets oriented in the plane of the membrane) reveals an order of magnitude decrease in methanol permeability, but only a slight decrease in proton conductivity with increased filler loading.[47] These conductivity measurements were conducted with the four-electrode technique, therefore these trends may be misleading. These examples stress the importance of critically examining transport data as it relates to polymer structure.

For methanol permeability experiments, most researchers use a side-by-side diffusion cell, where the PEM is sandwiched between donor (upstream side) and receptor (downstream side) compartments. The donor compartment is charged with methanol (~1–2 M) and the concentration of methanol is measured on the downstream side as a function of time. The permeability can be determined from the slope of the early time data,[56] where a variety of detection methods have been used, including gas chromatography,[14,29–31,39,41,46,48,53,175] refractometry,[33,35,36,42,47,50–52,54,58] and FTIR-ATR spectroscopy.[55–57] The latter technique is an in-line flow-through technique that provides reliable early time data, where numerous data points can be collected. The former detection techniques usually require extracting only a few aliquots from the receptor side at selected time intervals.

One of the drawbacks of the diffusion cell is that a potential difference is not applied, and therefore, the permeability of methanol determined may be different than the crossover experienced in the DMFC. Several researchers have developed techniques to determine the methanol permeability in electrochemical cells using a variety of techniques, such as measuring $CO_2$ formation at the anode[73] or crossover current.[9,16,100,37,177] The crossover current can be extracted from the DMFC potential, where the performance of a DMFC can be modeled as[10]:

$$V_{\text{cell}} = E_{\text{cell}} - \eta_{\text{an}} - \eta_{\text{cat}} - \eta_{\text{xover}} - \eta_{\text{ohmic}} \tag{12}$$

$V_{\text{cell}}$ is the cell voltage, $E_{\text{cell}}$ is the difference between the half-cell potentials of the anode and cathode at the reference current density $i_o$, $\eta_{\text{an}}$ and $\eta_{\text{cat}}$ are the anode and cathode overpotentials, respectively, $\eta_{\text{xover}}$ is the methanol crossover overpotential, and $\eta_{\text{ohmic}}$ is the ohmic overpotential. The crossover overpotential is proportional to the flux of methanol through the membrane, which is governed by methanol concentration, pressure gradient, and electroosmosis:

$$\eta_{\text{xover}} = \chi j_2 \tag{13}$$

where $\chi$ is a lumped term constant. From this relationship and the following expression, the methanol permeability can be determined experimentally[12,177]:

$$i_{\text{cross}} = i_d \frac{6\xi x_o}{\ln(1 + 6\xi x_o)} \tag{14}$$

where $i_d$ is the limiting methanol permeation current density measured voltammetrically, $\xi$ is the electroosmotic drag coefficient of protons in the membrane, and $x_o$ is the molar fraction of methanol in the feed stream. The experiment entails exposing the anode side of the MEA to a known concentration of methanol and the cathode side to a humidified nitrogen environment.[11] A dynamic potential (~0.1–1 V at 1–2 mV/s) is applied to the cathode side, and the limiting methanol permeation current density is obtained by measuring the limiting current of the methanol electro-oxidation process at the platinum/membrane interface.

**Table 3.** Highly Selective PEMs

| PEM | Proton Conductivity (S/cm) | Methanol Permeability (cm$^2$/s) ($\times 10^6$) | $\alpha_{1/2}/\alpha^*_{1/2}$ | Reference |
|---|---|---|---|---|
| Sulfonated co-polyimide | 0.082[a] | 0.480 | 5 | 26 |
| Sulfonated poly[(aryloxy)phosphazene] | 0.035[a] | 0.148 | 7 | 30 |
| Montmorillonite dispersed in Nafion® | 0.078[a] | 0.100 | 23 | 47 |
| Sulfonated poly(ether ether ketone) | 0.07[a] | 0.300 | 7 | 48 |
| Poly(vinyl alcohol)/poly(styrene sulfonic acid-*co*-maleic acid) blend | 0.095[a] | 0.266 | 11 | 58 |
| Nafion® 117 | 0.067[a] | 1.98 | 1 | 56 |

$\alpha_{1/2,}$ conductivity/permeability selectivity; $\alpha^*_{1/2}$; conductivity/permeability selectivity of Nafion® 117.

[a] Four-electrode technique (along the plane of the membrane).

Similar to DMFC testing, these types of electrochemical measurements require MEA fabrication. This entails the deposition of a catalyst ink consisting of catalyst, polymer, and solvent onto each side of the PEM (Pt/Ru on the anode side and Pt on the cathode side). There are a variety of deposition techniques that have been explored, such as spraying, screen printing, blade coating, sedimentation, and electrospraying. However, the most common technique to deposit the catalyst layer unto the PEM is a hot press/decal transfer technique. This technique consists of painting the catalyst onto a hydrophobic support (e.g. PTFE-coated fiberglass) allowing the solvent to evaporate and then repeating this procedure until the desired catalyst amount (~1–5 mg/cm$^2$) is loaded onto the support. A PEM is sandwiched between two catalyst loaded supports and heat pressed at a specified pressure, temperature, and time. The catalyst layer is then transferred onto each side of the PEM to fabricate the MEA.

For DMFC testing, the MEA is then sandwiched between two carbon cloth diffusion layers (GDL) and bolted into a fuel cell test fixture. DMFC test are then conducted by sweeping potential from the open circuit voltage to a lower voltage (~0.1–0.2 V) in small increments and time steps and recording the current. These tests can be conducted at a variety of operating conditions: anode and cathode feed flow rates and back pressures, cell temperatures, and methanol feed concentrations. However, as stated before, increasing the methanol feed concentration above 2 M has a significant effect on the cell voltage.[11] Furthermore, a number of studies report poor adhesion between the catalyst layer and the PEM resulting in poor DMFC test results.[12–17] Therefore, the majority of PEM development investigations for the DMFC application focus only on the key prescreening experiments (proton conductivity and methanol permeability) rather than conducting electrochemical measurements.

Aside from the techniques described above, other experimental techniques have been used to measure transport coefficients in PEMs. In particular, Zawodzinski and coworkers[151,152] designed a diffusion cell using capillary pressure to measure electroosmotic drag and also used pulsed field gradient spin-echo $^1$H nuclear magnetic resonance (NMR) to measure the diffusion coefficient of protons. Other researchers have used NMR and electrochemical cells[100] to measure the diffusion coefficient of methanol in PEMs.[178–180] These techniques along with others have provided valuable information regarding transport mechanisms.

## CONCLUSIONS AND RECOMMENDATIONS

In this article, the development of new PEMs for the DMFC has been reviewed. Currently, Nafion® is the standard PEM for the DMFC; however, its high methanol crossover leads to significant losses in fuel cell power density and efficiency. Numerous Nafion® replacements have been developed and several demonstrate higher selectivities at similar proton conductivities (listed in Table 3) and/or higher DMFC power densities compared to Nafion®. Various PEM development strategies have been explored. These include incorporating proton conducting polymers into a variety of frameworks, such as random copolymers, graft copolymers, block copolymers, blends, impregnated membranes, composites, and coated membranes.

There are strengths and weakness associated with each of these synthetic routes. Most of the random copolymers that were investigated (synthesized either by copolymerization or postsulfonation) consisted of aromatic backbones, which provide thermal and mechanical stability. Furthermore, several of these investigations report increased selectivity at conductivities similar to Nafion® (see Table 3). However, many of these investigations report that increases in sulfonic acid content resulted in a simultaneous increase in both proton conductivity and methanol permeability. The block copolymers developed were usually postsulfonated and produced sequentially ordered ionic and nonionic blocks that resulted in unique morphologies. Changes in morphology resulted in significant changes in proton conductivity, but this also resulted in similar changes in methanol permeability. Similar to most random copolymers, block copolymers possessed similar selectivities to Nafion® over a wide range of proton conductivities and methanol permeabilities (see Fig. 7). Synthesizing graft copolymers consisted of copolymerizing sulfonic acid containing polymers onto preexisting hydrophobic membranes. Several investigations report slightly higher selectivities when compared with Nafion®, but also report difficulties associated with catalyst layer/PEM adhesion during DFMC testing. A number of investigators blended both proton conductive and water/methanol selective polymers. Several studies report increased selectivity when compared with Nafion® at similar proton conductivities (e.g., PSSA-MA/PVA blend). However, the transport results among these studies vary considerably and these blends are dependent on a number of interdependent parameters, such as blend composition, miscibility, crosslinking, and morphology. Also, increased crosslinking and water/methanol selective polymer content usually result in a membrane that is brittle in its dry state, which is problematic for the DMFC application. Researchers have impregnated proton conductive polymers within solvent resistant polymer membranes and reported decreases in methanol crossover and improvements in DMFC performance. The membrane matrix can act to suppress swelling, but also leads to decreased proton conductivities depending on the conductive polymer content. A number of researchers have synthesized composite membranes by either loading PEMs with methanol impermeable fillers (e.g. clay flakes) or proton conductive fillers (e.g. heteropolyacids). Impermeable fillers can increase thermal and mechanical properties and reduce methanol permeability. However, increasing impermeable filler content usually results in a simultaneous reduction in proton conductivity and mechanical failure (at loadings $> 10$ wt %). The 'bleeding out' of heteropolyacid is also cited by many investigators as a problem with conductive filler/PEM composites. Coating thin barrier layers on PEMs has been demonstrated by various researchers. Slight increases in DMFC performance have been demonstrated in a few studies, but usually an increase in barrier coating thickness resulted in a simultaneous decrease in both proton conductivity (through the plane) and methanol permeability.

Among the articles reviewed, Table 3 lists the PEMs with the highest proton/methanol selectivities with similar proton conductivities to Nafion®. The montmorillonite/Nafion® composite membrane appears to have the highest selectivity; however, these conductivity measurements were conducted along the plane of the membrane, where the impermeable filler particles were narrow flat sheets oriented in the plane of the membrane. This suggests that had the conductivity been measured through the plane of the membrane, the selectivity would be much lower than the value reported here. The PSSA-MA/PVA blend has a selectivity over an order of magnitude higher than Nafion®. Most proton conductive polymers or PEMs contain sulfonic acid, which is a super acid that possesses high ionic conductivity due to strong attractive forces with cations (particularly hydrogen ions) and is hydrophilic, but also has a higher affinity for methanol than water. Therefore, incorporating another polymer with functional groups (e.g. hydroxyl groups) that have a higher affinity for water than methanol is intriguing. However, a number of other investigations that report transport properties on PVA blends do not report selectivities this high. Additionally, incorporating polymers within the blend that may not be oxidatively stable and are brittle in their dry state may not translate into improved DMFC performance. Despite these shortcomings, proton conductive polymer blends warrant further study to develop a more in depth understanding of the relationship between transport properties and blend parameters, such as blend composition, miscibility, crosslinking, and morphology. The other PEMs listed in Table 3 are all sulfonic acid containing random copolymers with selectivities ~5–7 times higher than Nafion®. These polymers contain aromatic backbones, which provide mechanical, thermal, and oxidative stability for DMFC operation. Further studies will be required to determine why several random copolymers are more selective compared to others.

In addition to the transport results listed in Table 3, several PEM development studies have reported significant increases in DMFC performance. Nafion® exposed to a low dose electron beam yielded a 32% increase in its maximum power density compared to Nafion® 117.[118] Acid-doped PBI coated Nafion® membranes had improved DMFC performance compared to Nafion® where the maximum power density was increased by 46%. Surprisingly, a PEM of poly(furfuryl alcohol) (7 wt %) impregnated within Nafion® resulted in a 180% increase in maximum power density compared to Nafion® 115, where higher cell voltages were maintained at all current densities.[92]

On the basis of the investigations above, it is not completely clear why these PEMs in particular result in higher selectivities and improved DMFC performance compared to Nafion®. An overall observation when reviewing research in this field is that a tremendous effort has been invested in PEM development, but little effort has been invested in developing a clear understanding into the mechanisms that lead to PEMs with improved transport properties. Future studies should emphasize developing a deeper understanding of the molecular transport mechanisms in new PEMs and new experimental techniques to measure multicomponent transport that captures the interactions between diffusants (protons, water, and methanol) and the polymer membrane.

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## NOMENCLATURE

*Abbreviations*

| | |
|---|---|
| 2,2′-BSPB | 2,2′-bis(3-sulfo-propoxy)benzidine |
| BAPBDS | 4,4′-bis(4-amino-phenoxy)biphenyl-3, 3′-disulfonic acid |
| CARDO | 9,9-bis(4-aminophenyl fluorene) |
| DBSA | 4-dodecyl benzene sulfonic acid |
| DMFC | direct methanol fuel cell |
| EIS | electrochemical impedance spectroscopy |
| ETFE | poly(ethylene tetrafluoroethylene) |
| FTIR-ATR | Fourier transform infrared, attenuated total reflectance |
| HSBR | sulfonated hydrogenated poly(styrene-*b*-butadiene) rubber |
| IEC | ion exchange capacity |
| IPN | interpenetrating network |
| LDPE | low density poly(ethylene) |
| MEA | membrane electrode assembly |
| NMR | nuclear magnetic resonance |
| NTDA | 1,4,5,8-naphthalenetetracarboxylic dianhydride |
| ORMOSILS | organically modified silicates |
| PAA | poly(acrylic acid) |
| PAMPS | poly(2-acrylamido-2-methyl-1-propane sulfonic acid) |
| PAN | polyacrylonitrile |
| PBI | polybenzimidazole |
| PEG | poly(ethylene glycol) |
| PEM | polymer electrolyte membrane |
| PHEMA | poly(2-hydroxyethyl methacrylate) |
| PSSA | poly(styrene sulfonic acid) |
| PSSA-MA | poly(styrene sulfonic acid-co-maleic acid) |
| PTFE | poly(tetrafluoroethylene) |
| PVA | poly(vinyl alcohol) |
| PVDF | poly(vinylidene fluoride) |
| PVI | poly(1-vinylimidazole) |
| PVP | poly(vinylpyrrolidone) |
| PWA | phosphotungstic acid |
| SAXS | small angle X-ray scattering |
| SANS | small angle neutron scattering |
| SPEK | sulfonated polyetherketone |
| SPEEK | sulfonated poly(ether ether ketone ketone) |
| SPEEKK | sulfonated poly(ether ether ketone ketone) |
| SPOP | sulfonated poly[bis(phenoxy) phosphazene] |
| SPPESK | sulfonated poly(phthalazinone ether sulfone ketone) |
| SPS | sulfonated polystyrene |
| S-SE | sulfonated poly(styrene-*b*-ethylene) |
| S-SEBS | sulfonated poly(styrene-*b*-ethylene-*r*-butadiene-*b*-styrene) |
| S-SIBS | sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) |
| TEM | transmission electron microscopy |
| THF | tetrahydrofuran |

*Equation Symbols*

| | |
|---|---|
| $C$ | concentration |
| $C_1$ | concentration of protons |
| $C_2$ | concentration of methanol |
| $C_{2_\mathrm{D}}$ | concentration of methanol on upstream side of membrane |
| $D$ | diffusion coefficient |
| $D_0$ | inherent diffusion coefficient |
| $D_1$ | proton diffusion coefficient |
| $D_2$ | methanol diffusion coefficient |

| | |
|---|---|
| $E_{\text{cell}}$ | half-cell potential difference between the cathode and anode |
| $F$ | Faraday's constant |
| $i_{\text{cross}}$ | crossover current density |
| $i_{\text{d}}$ | limiting methanol permeation current density |
| $j_1$ | steady-state flux of protons |
| $j_2$ | steady-state flux of methanol |
| $K_2$ | partition coefficient of methanol |
| $P$ | permeability coefficient |
| $P_2$ | methanol permeability coefficient |
| $R$ | gas constant |
| $S$ | solubility |
| $T$ | temperature |
| $x_{\text{o}}$ | molar fraction of methanol in the feed stream |
| $V_{\text{cell}}$ | cell voltage |
| $z$ | charge |
| $z_1$ | charge of a proton (+1) |

*Greek Letters*

| | |
|---|---|
| $\gamma$ | critical exponent |
| $\eta_{\text{an}}$ | anodic overpotential |
| $\eta_{\text{cat}}$ | cathodic overpotential |
| $\eta_{\text{ohmic}}$ | ohmic overpotential |
| $\eta_{\text{xover}}$ | methanol crossover overpotential |
| $\xi$ | electroosmotic drag of protons |
| $\sigma_0$ | inherent conductivity |
| $\sigma_1$ | proton conductivity |
| $\phi$ | volume fraction of diffusion phase |
| $\phi_{\text{c}}$ | critical volume fraction of diffusion phase |
| $\chi$ | lumped term constant |
| $\psi$ | electrostatic potential |

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