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NON-FLUORINATED POLYMER MATERIALS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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■ **Abstract** The past 10 years have witnessed a tremendous acceleration in research devoted to non-fluorinated polymer membranes, both as competitive alternatives to commercial perfluorosulfonic acid membranes operating in the same temperature range and with the objective of extending the range of operation of polymer fuel cells toward those more generally occupied by phosphoric acid fuel cells. Important requirements are adequate membrane mechanical strength at levels of functionalization (generally sulfonation) and hydration allowing high proton conductivity, and stability in the aggressive environment of a working fuel cell, in particular thermohydrolytic and chemical stability. This review provides an overview of progress made in the development of proton-conducting hydrocarbon and heterocyclic-based polymers for proton exchange and direct methanol fuel cells and describes the various approaches made to polymer modification/synthesis and salient properties of the materials formed, including those relating to proton transport and proton conductivity, e.g., water diffusion and electro-osmotic drag. The microstructure, deduced from small angle X-ray and neutron diffraction measurements of representative non-fluorinated polymers is compared with that of perfluorosulfonic acid membranes. Different degradation mechanisms and aging processes that can result in chemical and morphological alteration are considered, and recent characterization of membrane-electrode assemblies (MEAs) in direct methanol and hydrogen-air (oxygen) fuel cells completes this review of the state of the art. While several types of non-fluorinated polymer membrane have demonstrated lifetimes of 500–4000 h, only a limited number of systems exist that hold promise for long-term operation above 100°C.[1]

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[1] List of abbreviations and acronyms: PEM, proton exchange membrane; DMFC, direct methanol fuel cell; MEA, membrane electrode assembly; PSU, Polysulfone; PES, Poly(ether sulfone); PEK, Poly(ether ketone); PEEK, Poly(ether ether ketone); PPQ, Poly(phenyl quinoxaline); PBI, Polybenzimidazole; P_3O, Poly(2,6-diphenyl-4-phenylene oxide); PPS, Poly(phenylene sulfide); RH, Relative humidity; PPZ, Poly(phosphazene); PPBP, Poly(4-phenoxybenzoyl-1,4-phenylene); PI, Polyimide; IEC, Ion exchange capacity; SAXS, small angle X-ray scattering; SANS, small angle neutron scattering.

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INTRODUCTION

Solid polymer electrolyte membrane (PEM) fuel cells have reached a technological stage where they offer a real challenge to conventional power-generating technologies, in particular for transportation (1). Their efficiency is higher, and they offer the possibility of zero emission at the point of use. Fuel cell efficiency is not a single number, however, it is a function of the power density at which the fuel cell operates, and thus the optimum nominal efficiency depends on the fuel cell performance and its capital cost (2). The electrolyte is implicated in both of these aspects. The function of the membrane in PEM fuel cells is twofold: proton conduction from the anode to the cathode, and effective separation of the anode and cathode gases. Nafion® is by far the most studied proton electrolyte for PEM fuel cells. Because of its poly(tetrafluoroethylene) backbone, it is chemically inert in both oxidizing and reducing atmospheres. Nafion membranes are highly acidic, have excellent proton conductivity ($9 \cdot 10^{-3}$–$12 \cdot 10^{-2}$ S cm^{-1} at 80°C in the range 34–100% relative humidity) (3), and unsurpassed longevity (>60,000 h) in a fuel cell environment. Despite these attributes, much research has been carried out over the past decade on exploring the possibilities of hydrocarbon-based membranes as candidate proton electrolytes for PEM and direct methanol fuel cells (DMFC). Most importantly, Nafion membranes are limited in their temperature range of operation to around 80°C, they have poor barrier properties to methanol, allowing methanol crossover from the anode to the cathode in a DMFC, high osmotic drag, which makes water management at high current densities difficult and, from the standpoint of recycling of the components of membrane-electrode assemblies (MEAs), the perfluorinated composition might become a future issue. These features are common to other perfluorinated membranes, such as those produced by Dow, Asahi Glass, and Asahi Chemical.

Consequently, much effort has focused on the development of alternative proton exchange membranes for PEM fuel cells and DMFC, in particular with the aim of increasing the temperature of operation of the fuel cell. Increase in temperature is attractive for a number of reasons: (*a*) improved tolerance of the electrodes to carbon monoxide, which enables the use of hydrogen produced by reforming of natural gas, methanol or gasoline; (*b*) simplification of the cooling system; (*c*) possible use of cogenerated heat; (*d*) increased proton conductivity; and (*e*) in DMFC, improved kinetics of the methanol oxidation reaction at the anode. However, increase in temperature confers the restraints. Because in the majority of proton-conducting polymer materials proton conduction is water-assisted, they exhibit the highest proton conductivity when fully hydrated (see below). This requires humidification of gas feeds before entering the fuel cell and the application of pressure to maintain adequate relative humidity. Pressurizing a system above around 3 atm gives a working upper limit for a water-saturated environment of around 135°C. Working beyond this temperature requires the development of new approaches to enable proton transport in a water-free environment. Finally, the high cost of Nafion is currently incommensurate with potential mass markets such as personal transport for example.

There are few non-fluorinated membrane materials appropriate for fuel cell application at temperatures above 80°C, the primary requirement being the temperature stability of the polymer. This generally means that the polymers are made up of polyaromatic or polyheterocyclic repeat units, and examples include polysulfones (PSU), poly(ether sulfone) (PES), poly(ether ketone)s (PEK), poly(phenyl quinoxaline) (PPQ), and polybenzimidazole (PBI). Developed for high-temperature applications, the thermal stability of these types of polymers is well documented. However, they are electrically insulating until modified. A variety of approaches have been developed for the preparation of polymer materials by derivatization of thermostable polymers for application in medium- or high-temperature PEM fuel cells (see below). The characteristics of the membranes prepared from these polymers clearly depend, at a first level, upon the chemical nature of the polymer backbone, but secondary level parameters such as the polymer molecular weight and molecular weight distribution, the nature of the solvent used for casting, and the possible presence of residual solvent in the polymer film also influence properties such as conductivity and membrane mechanical strength. The effect of such factors, sometimes less-well analyzed, can impede comparison of properties of nominally similar polymer membranes. Subsequent sections consider microstructural differences between Nafion and hydrocarbon-based membranes and the stability of non-fluorinated polymer membranes under conditions likely to prevail in a fuel cell (including thermohydrolytic stability, stability in an oxidizing environment and with respect to radical degradation). Water diffusion and electroosmotic drag, and fuel cell performance and durability are discussed in the final sections.

The number of published fuel cell tests and MEA longevity data are not extensive, and in particular there is little published information on testing at temperatures above 80–90°C. The availability of such data is essential to validate the approach of using non-fluorinated polymers as a component of PEMFC and DMFC membranes.

Recent progress in the area of non-fluorinated proton conducting membranes includes a survey by Savadogo (4), which covers the literature up to the end of 1997. For recent review articles on membranes for PEM fuel cells the reader is referred to References (5–9), as well as those on solid state protonic conductors (3, 10).

FROM HIGH-TEMPERATURE POLYMERS TO PROTON ELECTROLYTE MEMBRANES: FUNCTIONALIZATION BY THE ADDITION OF PROTOGENIC GROUPS

Several methods for the preparation of thermally stable proton-conducting polymers have been developed that include acid or base doping of a thermostable polymer, direct sulfonation of a polymer backbone, grafting of a sulfonated or phosphonated functional group on to a polymer main chain, graft polymerization followed by sulfonation of the graft component, and total synthesis from monomer building blocks (Figure 1). In addition, the proton-conducting properties can be

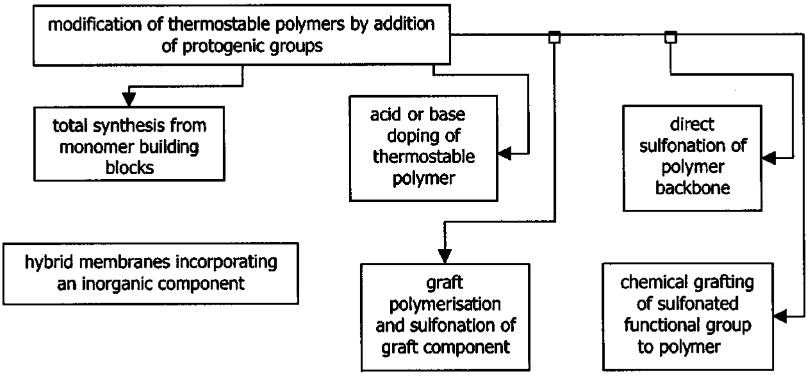


Figure 1 Development of proton-conducting membranes by the modification of thermostable polymers.

entirely conferred or enhanced by the addition of an inorganic proton conductor (11, 12); see the review by Casciola & Alberti in this volume (12a). The approach chosen depends on the particular properties and chemical reactivity of the polymer concerned.

Acid and Base Doping

Aromatic polybenzimidazoles are highly thermostable, with melting points $>600°C$ (13). The polybenzimidazole commercially available is poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole (PBI) (Figure 2). PBI shows some tendency to take up water, thus explaining the proton conductivity that is low ($\sim 10^{-7}$ S cm^{-1}) as shown even by the non-modified polymer (14, 15). PBI is basic (pK value of $\sim$5.5), and it readily forms complexes with organic and inorganic bases. Early mention of stabilized and plasticized PBI referred to PBI treated with sulfuric and phosphoric acid, respectively (13). Such treatment leads to a significant increase in the conductivity. The acid uptake reaches 5 mol H_3PO_4 per PBI repeat unit, far beyond the quantity usually understood by the term doped for other systems, and yet this is the term generally used to describe PBI-acid complexes. The properties of such doped membranes and their application in PEM fuel cells and in cells using hydrocarbons and methanol as fuels have been systematically studied by Wainright et al. (16, 17) and others (18–21) since 1994, culminating in the production by Celanese Ventures of MEAs based on phosphoric acid-doped PBI. This represented a landmark discovery; such membranes having low permeability to methanol and low electroosmotic drag opened new opportunities for DMFC and high-temperature operation (22). Doping with other acids (hydrochloric, perchloric, nitric acid) leads to membranes with similar conduction properties (23). Different methods are used for the formation of PBI–acid complexes, including the immersion of a PBI membrane in an acid solution of given concentration for

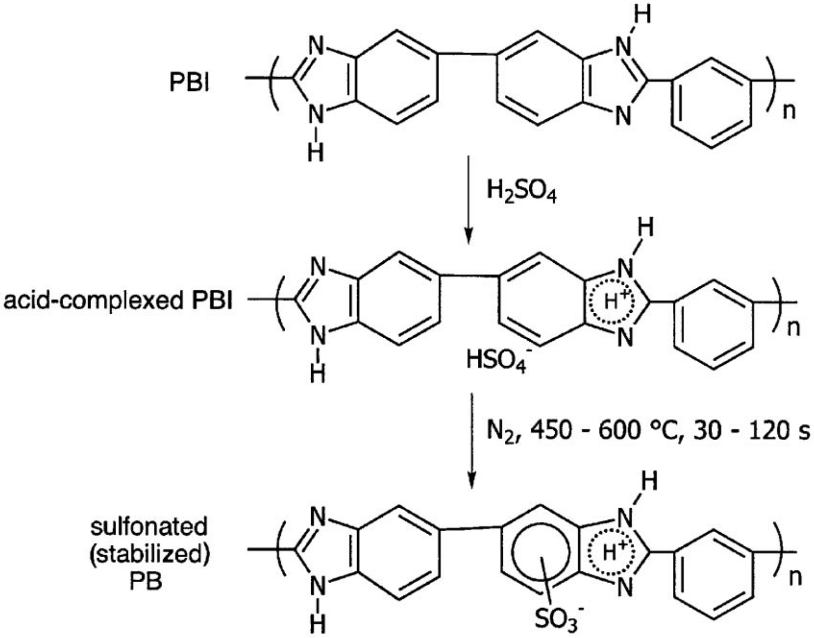


Figure 2 Synthesis route to sulfonated (stabilized) polybenzimidazole.

a given length of time, and direct casting from a solution of PBI and phosphoric acid in trifluoroacetic acid (24). A recent variant of this approach uses polyphosphoric acid as the condensing agent for the polymerization and as a membrane casting solvent. Absorption of water after casting leads to in situ hydrolysis of polyphosphoric to phosphoric acid in the membrane (22). The last route can be used to produce films with high acid content. In all cases, a homogeneous polymer electrolyte system is formed by dissolution of the acid in the PBI matrix, and doping levels $\geq$50 wt% are achieved. The conductivity depends on this doping level, which can also be expressed as the number of H_3PO_4 molecules per PBI repeat unit. For membranes with 0.07–0.7 H_3PO_4/PBI, the conductivity is 10^{-5}–10^{-4} S cm^{-1} at 25°C, whereas with composition 4–5 H_3PO_4/PBI, the conductivity is $>10^{-3}$ S cm^{-1} at 25°C (18) and $>3.10^{-2}$ S cm^{-1} at 190°C (17). This concept can be extended to other polymers (e.g., polybenzoxazole) and from acids to bases (25). Thus, inorganic hydroxides and organic bases such as imidazole also effectively increase the conductivity of PBI. These subjects are treated in depth in the chapter by Meyer & Schuster in this volume (25a).

Direct Modification of a Polymer Backbone

Polyarylene polymers, and polymers containing phenyl pendant groups such as styrene/ethylene-butylene/styrene, as well as heterocyclic systems, can be sulfonated by direct reaction with an appropriate reagent. The most attractive site for sulfonation depends both on the polymer structure and the directing effect of substituent groups, and advantages of simplicity and reproducibility of the sulfonation reaction under defined conditions are associated with this inherent reactivity. Sulfonating reagents used include sulfuric and chlorosulfonic acids, sulfur trioxide, and complex formation with trimethylsilylchlorosulfonic acid, etc. When the acid is both solvent and reagent, the sulfonation reaction takes place at the same time as dissolution, and the dissolution step is thus fully implicated in the homogeneity of sulfonation and reproducibility of the polymer microstructure and associated properties, in particular for polymers of low degrees of sulfonation (26). The functionalized polymer most readily formed is not necessarily that which is the most stable toward desulfonation under the high-temperature, high relative humidity conditions of the fuel cell, however, and alternative means enabling sulfonation at electron-poor sites have been developed in recent years. Ionomers prepared by direct sulfonation show statistical substitution along the polymer chain; other approaches (described below) allow the assembly of copolymers with a defined sulfonation pattern.

POLYBENZIMIDAZOLE In Celazole® PBI, the proximity of the imidazole ring to the fused benzene ring activates the latter toward electrophilic attack. However, PBI dissolved in sulfuric acid does not react appreciably (27), and thermal activation is required. This can be achieved by heat treatment of sulfuric acid–doped PBI membranes for short periods of time at 450–500°C leading to levels of substitution up to ~0.6 sulfonic acid groups/PBI (27–29) (Figure 2). However, such membranes are not amenable to further processing because the solubility of PBI in solvents such as dimethylacetamide is lost, and the sulfonated membranes can be recast only from sulfuric acid. In addition, the conductivity is barely higher than that of non-substituted PBI, even at highest degrees of sulfonation. These properties are in contrast to those observed for benzylsulfonate-grafted PBI (see below) and tend to suggest that crosslinking of sulfonated PBI chains has occurred, either by strong hydrogen bonding or through sulfone linkages, as might be expected given the high temperature needed to induce the sulfonation reaction.

POLY(PHENYLQUINOXALINES) Following the same approach, poly(phenyl quinoxaline) (PPQ) (Figure 3) can also be sulfonated as a cast film by briefly treating sulfuric acid–doped membranes at high temperature (30). Thus immersion of PPQ membranes in 50% H_2SO_4 for 2 h leads to a PPQ-sulfuric acid complex in which the hydrogen sulfate groups are converted to covalently bonded sulfonic acid at 300°C. The sulfonation level is poorly reproducible using this method, with non-homogeneous sulfonation occurring throughout the membrane (30). Unlike the sulfonated PBI membranes of low conductivity prepared using the immersion/thermal treatment approach, sPPQ displays proton conductivity values up to 0.1 S cm^{-1}, and further investigation of sPPQ membranes prepared using this method is justified on the basis of these results. However, the first modification of

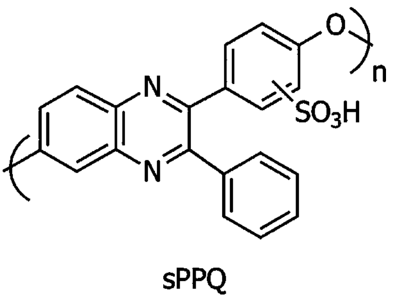


Figure 3 Sulfonated poly(phenyl quinoxaline).

PPQ by direct sulfonation for fuel cell membrane application was carried out by Ballard Advanced Materials (31) in its early efforts to develop low-cost polymers for use as proton exchange membranes. The outstanding question is whether sPPQ membranes prepared by immersion/thermal grafting show an advantage with respect to MEA lifetimes in a fuel cell over this first generation of Ballard Advanced Materials (BAM1G) membranes.

Sulfonation of various PPQs, prepared either by condensation of tetraamines and tetraketones, or by self-condensation polymerization of a bifunctional monomer of equivalent weight (EW) 400–800 g mol^{-1} can be carried out by reaction of dissolved PPQ in chlorosulfonic acid (31). The sulfonated polymer has a glass transition temperature of 220°C and is stable at up to 300°C in air. The site of sulfonation is *ortho* to the electron donating ether linkage, as when sulfonation is carried out by thermal grafting. The performance of MEAs prepared using sPPQs in a hydrogen/air fuel cell at a current density of 0.538 A cm^{-2} (500 A ft^{-2}) at 70°C is in the range 0.50 V (EW, 796 g mol^{-1}, thickness 110 μm) to 0.66 V (EW 427 g mol^{-1}, 47 μm). However, in long-term tests, the average MEA lifetime was only 350 h, with failure being attributed to transfer of reactant gases owing to increased permeability caused by progressive membrane embrittlement.

POLY(PHENYLENE OXIDES) The second generation of BAM membranes was concerned with more than one type of polymer and included poly(substituted-phenylene oxide). Oxidative coupling of 2,6-diphenylphenol gives poly(2,6-diphenyl-4-phenylene oxide) (P_3O), which is sulfonated in chlorosulfonic acid solutions at the more reactive backbone aryl group (Figure 4*c*). Polymers with EW 450 mol g^{-1} [ion exchange capacity (IEC) 2.22 meq g^{-1}] provide higher cell voltage at 0.538 A cm^{-2} (500 A ft^{2}, 0.68 V) than the BAM1G sPPQ of similar equivalent weight. However, lifetime was limited to 500 h by internal transfer of reactant gases across the MEA, with a contribution of both physical and chemical degradation processes to ultimate membrane failure; sP_3O membranes of such level of sulfonation show high swelling and poor mechanical resistance to tearing and poor tensile strength.

The central aryl group can be deactivated by substitution of bromide or cyanide functionalities on this ring. Harsher conditions of sulfonation are then required,

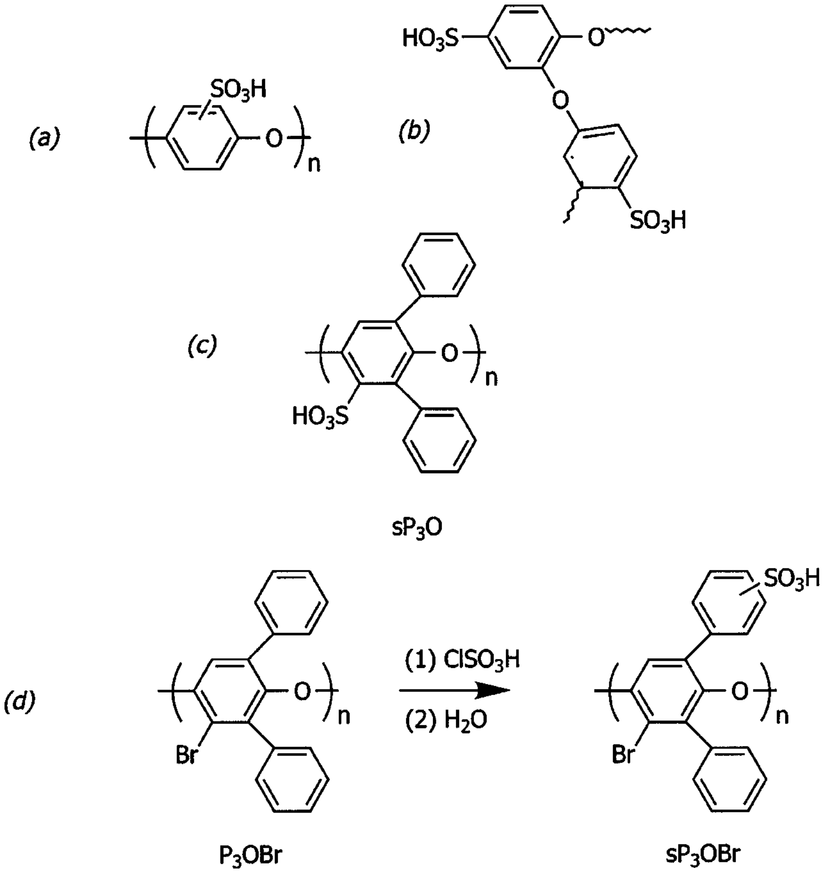


Figure 4 (*a*) Sulfonated poly(phenylene oxide); (*b*) crosslinked sulfonated poly(phenylene oxide); (*c*) sulfonated poly(2,6-diphenyl-4-phenylene oxide); (*d*) reaction scheme for the sulfonation of poly(3–bromo-2,6-diphenyl-4-phenylene oxide). Redrawn from (31).

and sulfonation takes place on one of the peripheral phenyl substituents (Figure 4*d*). Despite a predicted increase in oxidative stability, the fuel cell lifetime of these BAM2G variants was also 450–500 h, although the sP_3OBr ionomers gave the highest initial performance at the start-up of any of the Ballard Advanced Materials (31). Sulfonated poly(phenylene oxide) (Figure 4*a*) thermally crosslinked via allylphenol functional groups (Figure 4*b*) can be prepared by electropolymerization (32).

POLY(PHENYLENE SULFIDE) Poly(phenylene sulfide) (PPS) can be sulfonated in concentrated sulfuric acid (33). Higher levels of sulfonation are achieved using a polysulfonium cation in 10% SO_3/H_2SO_4 (34). Here, the strong electron

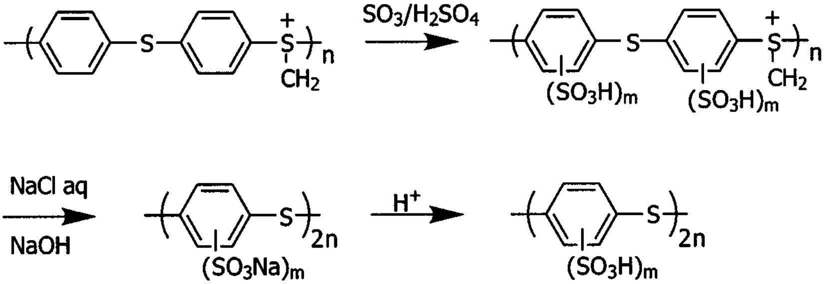


Figure 5 Synthesis of poly(phenylenesulfide sulfonic acid) via a poly(sulfonium) cation. Redrawn from (34).

withdrawing property of the sulfonium group in the main chain suppresses the crosslinking reaction and promotes sulfonation at 120°C. Demethylation and acidification steps lead to formation of a poly(phenylene sulfide sulfonic acid) (Figure 5). Although the high carrier concentration ensures high proton conductivity ($>10^{-2}$ S cm^{-1} at 20°C, 94% RH), the system is water soluble at a degree of sulfonation >30%. However, there may be application for PPS in a non-aqueous environment; blends of highly sulfonated (85%) poly(phenylene sulfide sulfonic acid) with poly(oxoethylene) display a conductivity under dry argon atmosphere of $1.3 \cdot 10^{-3}$ S cm^{-1} at 130°C (35).

POLY(ARYL ETHER SULFONES) Poly(arylene ether sulfone)s (PES) are thermoplastics having excellent thermal and mechanical properties. The basic repeat units in this family of polymers consist of phenyl rings separated by alternate ether and sulfone ($-SO_2-$) linkages, such as in the PES polymers that are commercially available from Victrex (Figure 6*a*). Polysulfones (PSU Udel®, BP Amoco) contain 2-propylidene spacers in addition to the ether and sulfone groups (Figure 6*b,d*). These spacers were hexafluorinated in the final member of the BAM2G polymers (31), as shown in Figure 6*c*. The aromatic ether (bisphenol) part, common to poly(etherketone)s and some polyimides, confers flexibility (as does to a certain degree the 2-propylidene link), whereas the sulfone group is stable with respect to oxidation and reduction.

Modification of poly(arylene ether sulfones) by addition of sulfonic acid using various reagents has been investigated extensively. Direct sulfonation using sulfuric or chlorosulfonic acid as both solvent and sulfonating agent can lead to some polymer chain degradation (36) that result in polymers with poor membrane-forming properties (27). sPES of ion exchange capacity (IEC) 1.8–3.0 (~100% sulfonation) has been prepared using SO_3 in dichloromethane (37). Polymers of IEC between 2.5 and 3.0 meq g^{-1} have conductivity close to that of Nafion, although they swell significantly at 80°C. An alternative method for sulfonation, reported to minimize side reactions, is based on reaction with an

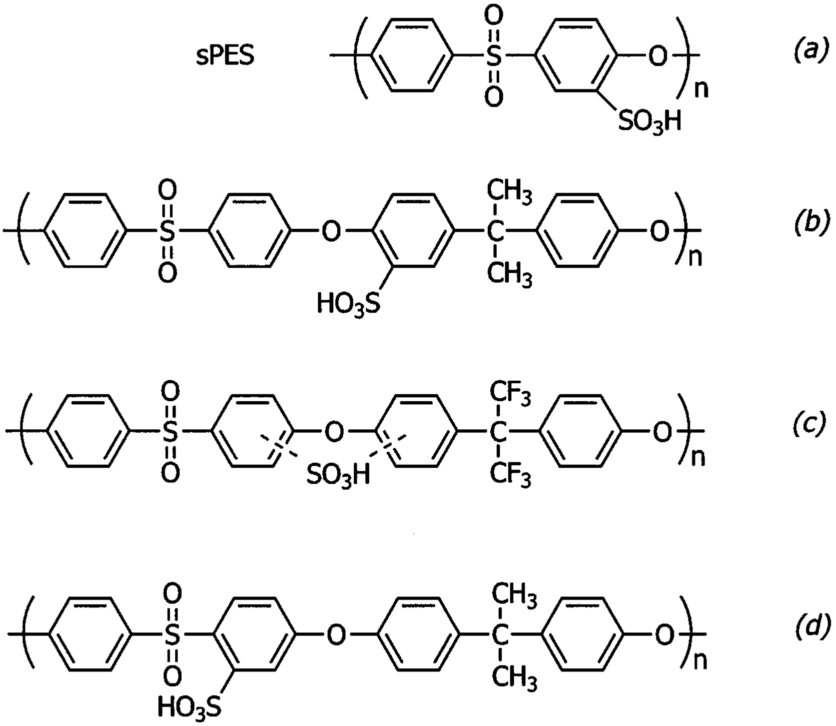


Figure 6 Sulfonated poly(ethersulfone) (*a*) and polysulfones sulfonated *ortho* to the ether group (*b*), and to the sulfone group (*d*). Structure of hexafluorinated sulfonated polysulfone [Ballard Advanced Materials second generation (BAM2G) sPSUF6] (*c*).

SO_3-triethylphosphate complex in dichloroethane solution. Complexed chlorosulfonic acid also allows milder direct sulfonation. Reaction of trimethylsilylchlorosulfonate with PSU gives a silylsulfonate polysulfone from which the trimethylsilyl moities can be cleaved to give the acid form of the alkaline sulfonate (37–39). As shown by the data of Figure 7*a*, the effective degree of sulfonation using this route is always lower than that theoretically possible based on reagent stoichiometry, but the efficiency of sulfonation is greater at longer reaction times. Sulfonation is rapid over the first 5 h of reaction and reaches a maximum of 1.35 mol SO_3H group per polymer repeat unit after 48 h (Figure 7*b*), suggesting a progressive deactivation of the aromatic rings electrophilic substitution as the reaction proceeds.

All the above electrophilic substitution reactions locate the sulfonic acid group at the most activated site *ortho* to the aromatic ether bond in the bisphenol A part of the molecule (Figure 6*b*). Such sulfonated polysulfones are expected to be less stable to desulfonation than those where sulfonation is directed to the electron deficient ring of the repeat unit. Kerres et al. have developed a direct sulfonation

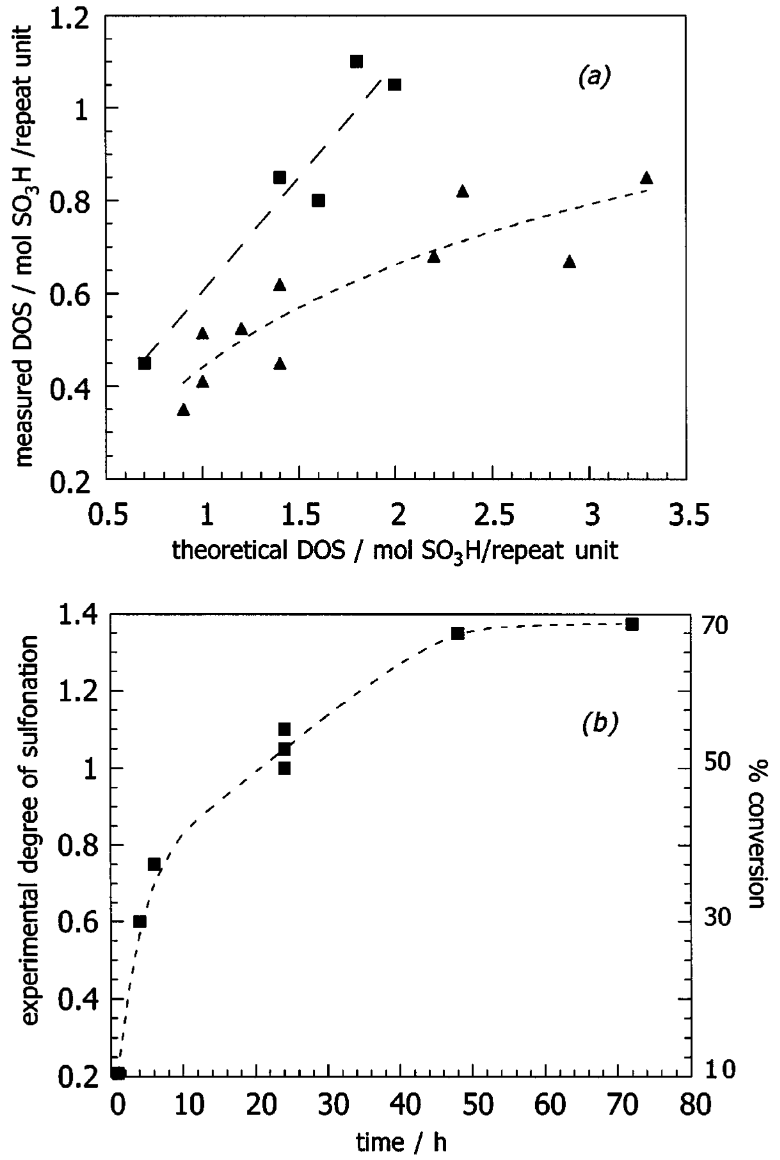


Figure 7 (*a*) Sulfonation of polysulfone (PSU) using $(CH_3)_3SiSO_3Cl$. Reaction conditions are 24 h at 35°C (*upper curve*) 4 h at 40°C (*lower curve*). All other conditions are identical. (*b*) Conversion with time of PSU to sPSU expressed as experimental degree of sulfonation at 35°C. Redrawn from (36) with permission of the authors.

method that proceeds via a lithiated intermediate formed by deprotonation with *n*-butyl lithium of the diphenylene sulfone segment (40). Reaction of the lithiated PSU with SO_2 and oxidation of the sulfinate thus formed leads to sPSU. Alternatively, lithiated PSU can be reacted with SO_2Cl_2 to yield PSU sulfochloride and thence PSU sulfonate. Such polysulfone sulfonated at a position *ortho* to the sulfone group is shown in Figure 6*d*.

The great tendency of sPES and sPSU to swell in hot water has led to the development of methods for crosslinking with the aim of improving mechanical stability. sPES membranes have been partially crosslinked through activation of the sulfonic acid groups via conversion to the sulfonic acid chloride/bromide or to the sulfonic acid imidazolide with subsequent reaction with aromatic/aliphatic diamines (Figure 8*a*) (37). This sulfonamide crosslinking is not sufficiently stable to hydrolysis for fuel cell applications, and use of the sulfonic acid group to crosslink polymer chains reduces the ion exchange capacity and hence the proton conductivity. Indeed, to preserve adequate electrical properties after crosslinking, polymers of higher degree of sulfonation that have possibly suffered some degradation through the harsher reaction conditions needed must be used, and such a possible effect on membrane lifetime may offset, to some extent, the advantages for mechanical strength conferred by reticulation.

Ortho sulfone sulfonated polysulfone has been crosslinked in two different approaches: via sulfinate alkylation, Figure 8*b* (41) and via disproportionation of sulfinic acid groups (42). The water uptake of *ortho* ether sulfonated PSU and crosslinked *ortho* sulfone sulfonated PSU is shown in Figure 9 as a function of the measured ion exchange capacity. These results suggest that crosslinking extends the IEC range over which the hydration number (λ) of sPSU remains <25, extensive hydration and swelling occurring above an IEC of 1.3 and 1.6 meq g^{-1} for non-crosslinked and crosslinked membranes, respectively. Membrane swelling also depends on the length of the crosslinking species.

POLY(ARYL ETHER KETONE) The poly(ether ketone)s are a family of polyarylenes linked through varying sequences of ether (E) and ketone (K) units to give ether-rich: PEEK (Victrex® PEEK, Gatone™ PEEK, Gharda Chemicals) and PEEKK (Hostatec®), or ketone-rich semicrystalline thermoplastic polymers: PEK (Amoco Kadel®, FuMA-Tech) and PEKEKK, Ultrapek®, BASF) (Figure 10). Oxidative and hydrolytic stability is expected to increase with increasing proportion of ketone segments, and experimentally, PEKK (Declar®, Du Pont) undergoes lower weight loss at 400°C under water/oxygen than either PEKEKK or PEEK. Some of these (Hostatec, Ultrapek) are no longer commercially available. The sulfonated poly(ether ketone) family of polymers has probably been more broadly and extensively studied in recent years than any other non-fluorinated system, with contributions from Kreuer, Kerres, Bauer, Rozière, and their co-workers and others, to studies ranging from modeling of the microstructure, proton transport properties, application in low- and medium-temperature PEMFC and DMFC, and as a component of polymer blend and hybrid inorganic-organic membranes.

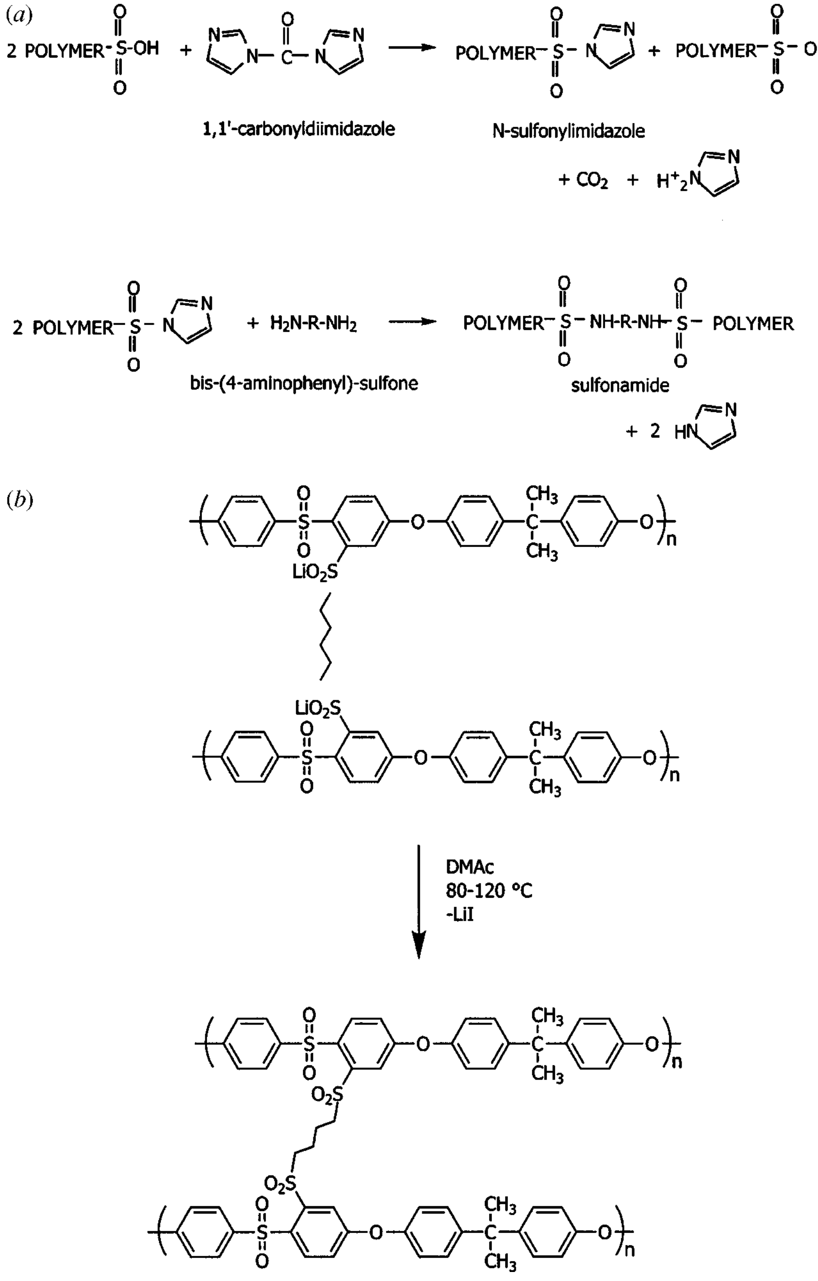


Figure 8 Crosslinking of sulfonated polyethersulfone and polysulfone. (*a*) Sulfonamide crosslinking via reaction of sulfonic acid imidazolide with aromatic or aliphatic diamines. Redrawn from (37). (*b*) Crosslinking by *S*-alkylation of the sulfinate group of partially oxidized sulfinated PSU with diiodobutane. Redrawn from (41).

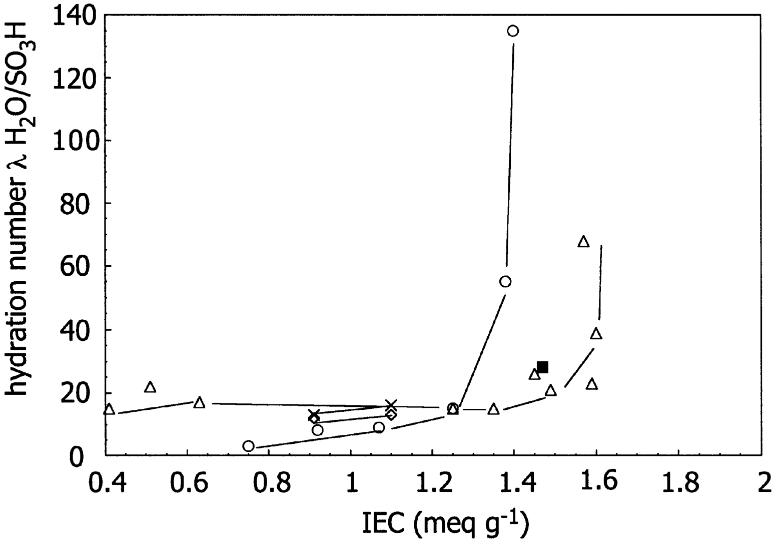


Figure 9 Dependence of hydration number of non-crosslinked and crosslinked sulfonated polysulfones on ion exchange capacity. Membranes immersed in water at 80°C. (◇), non-crosslinked, cycle 1 (39); ×, non-crosslinked, cycle 2 (39); ○, non-crosslinked (36); △, crosslinked by sulfonate/sulfinate disproportionation (42); ■, butane crosslinked (92). Redrawn with permission of the authors.

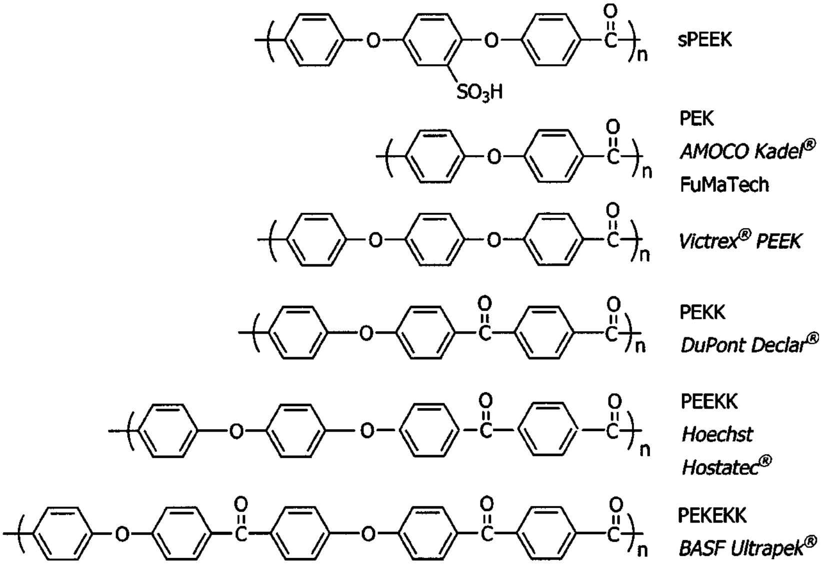


Figure 10 Sulfonated poly(ether ether ketone) and structures of representative membranes of the poly(ether ketone) family.

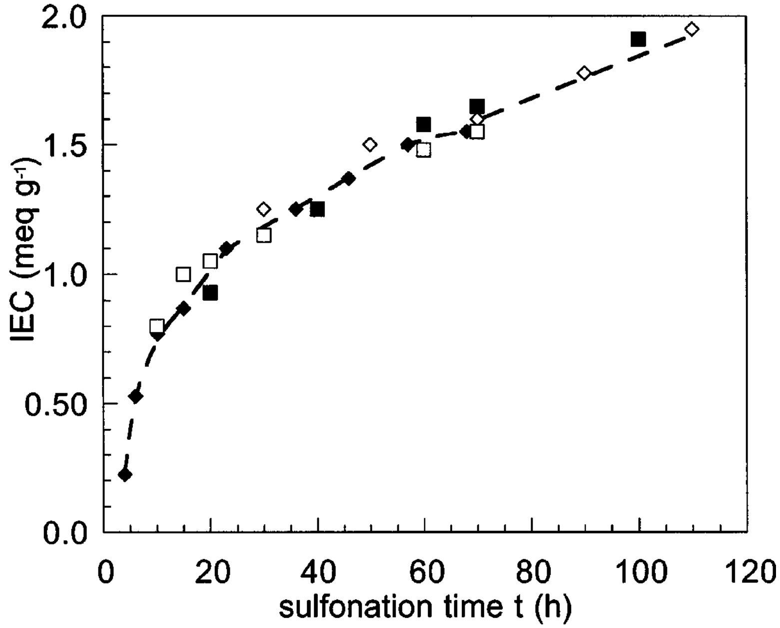


Figure 11 Reaction of Victrex® poly(ether ether ketone) (PEEK) with concentrated H_2SO_4 at room temperature. Comparison of the increase of IEC of sPEEK with reaction time reported by (44) ◆; (45) ◇; (26) ■; J. Rozière, D.J. Jones & M. Marrony, unpublished results, □.

The poly(ether ketone) currently most readily available commercially is Victrex PEEK, and the data reported below refer to a polymer from this source. The presence of adjacent *ortho*-directing ether groups confers highest reactivity to the four equivalent sites on the hydroquinone unit situated between the ether segments. *Ortho*-ether substitution by sulfonic acid groups can be carried out in concentrated sulfuric acid or oleum, the extent of sulfonation being a function of the reaction time and temperature and SO_3 concentration (26, 43–45). Data on the IEC of sulfonated PEEK as a function of reaction conditions (Figure 11) show excellent agreement between authors and underline the reproducibility of the degree of sulfonation under defined conditions. The initial PEEK concentration in sulfuric acid does not influence the progress of the reaction (46). The solubility of sPEEK in various media as a function of IEC is shown in Table 1. These data indicate that dissolution in *N*-methylpyrrolidone (needed for membrane casting) becomes possible above an ion exchange capacity around 0.9 meq g^{-1}, whereas solubility in hot water occurs above an IEC of around 1.8 meq g^{-1}. This range defines the appropriate degree of sulfonation for fuel cell membranes based on sPEEK unless the polymer is crosslinked, blended, or otherwise modified. ^1H NMR spectroscopy is one means of estimating the degree of sulfonation, since protons α to a sulfonic acid group are

TABLE 1 Swelling of sulfonated PEEK membranes

IEC Meq g^{-1}	*N*-methylpyrrolidone	Ethanol	Water
0	−	−	−
0.5	−	−	−
0.8	+	−	−
1.0	++	−	sw
1.1	++	−	sw
1.55	+++	sw	sw
1.8	+++	++	+
2.0	+++	+++	++
2.1	+++	+++	++
3.0	+++	+++	++

− stable in boiling solvent; sw swollen.

+ incomplete dissolution; ++ solution after heating; +++ solution at 25°C.

shifted downfield compared with the position of the other two protons in the hydroquinone ring. The degree of sulfonation so approximated can be lower than the ion exchange capacity determined by titration through accessibility or crosslinking, for example.

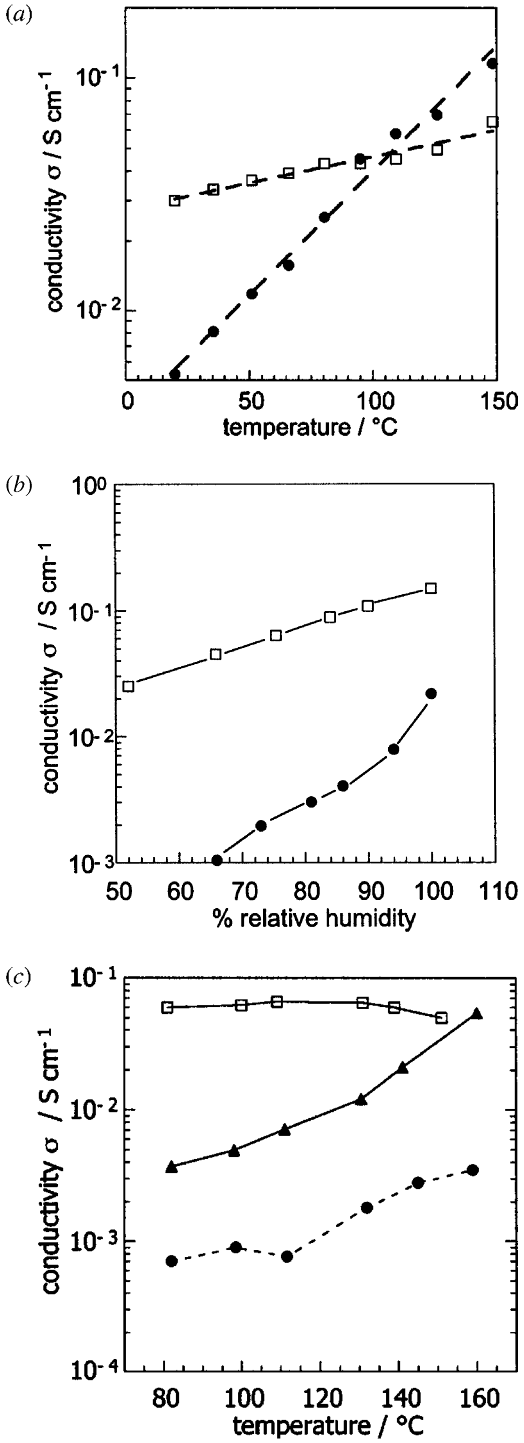
Properties of sPEEK are generally a function of the degree of sulfonation. Under dynamic conditions, sPEEK starts to lose weight between 240 and 300°C (44, 45) depending on the rate of heating and, to a lesser extent, the degree of sulfonation. The sulfur content of the residue recovered after heating sPEEK at 400°C decreased by ∼90%, indicating that thermal decomposition begins by desulfonation (47). Combustion of the polymer occurs above 450°C. The T_g increases from 150°C (PEEK) to around 230°C in sPEEK of 60% sulfonation.

As for other polyaromatic polymers, the proton conductivity of sPEEK depends not only on the degree of sulfonation and ambient relative humidity and temperature, but also on the thermal history of a given membrane and the possible presence of residual solvent from the casting stage. A short summary of various studies is presented here. Whereas the numerical data are those for sPEEK, the general conclusions also apply to other sulfonated non-fluorinated polyaromatics. The increase of conductivity with temperature at 100% relative humidity depends on the pre-treatment imposed on the membrane (Figure 12*a*). For example, for a sPEEK membrane of IEC 1.6 meq g^{-1} and thickness 60 μm pre-treated in boiling water for 4 h prior to measurement, the conductivity showed weak temperature dependence from 0.03–0.07 S cm^{-1} over the temperature range 25–150°C, whereas that of a non-treated membrane maintained at 100% relative humidity increased by more than a factor 10 over the same range (44). The degree of hydration attained by the membrane after prolonged immersion in boiling water is maintained when the membrane is removed, and it is greater than that of a membrane conditioned in an environment of 100% relative humidity. This is further discussed below. As shown by the data of Figure 12*b*, the conductivity of non-treated sPEEK membranes shows greater dependence on the relative humidity than does that of Nafion; the former increases by an order of magnitude between 66 and 100% relative humidity at 100°C to reach 0.02 S cm^{-1}, whereas the conductivity of Nafion increases by a factor of 4 (44). Proton conductivity thus relies more heavily on the amount of water beyond that in the first and second hydration spheres in sPEEK than in Nafion (6, 48). Measurements made as a function of temperature at a relative humidity of 75% (Figure 12*c*) show that highly sulfonated PEEK (IEC 2.48 meq g^{-1}, degree of sulfonation ~90%) displays the same conductivity as Nafion at 160°C, whereas that of sPEEK at lower degree of sulfonation ~60% (IEC 1.6 meq g^{-1}) is an order of magnitude lower under these conditions (49). Interaction between polymer chains decreases with increasing temperature, favoring greater hydration of the polymer at a given value of the relative humidity. The diffusion coefficients and electroosmotic drag in sulfonated poly(ether ketone) is discussed further below.

Although determination of conductivity of membranes represents key ex situ characterization, a difference in values between reports in the literature can be attributed, rightly or wrongly, to a different method of measurement. For membranes destined for fuel cell application, in situ measurement in a working fuel cell (50) is the most relevant and can also serve to validate ex situ evaluation. For example, using the linear region of the polarization curve of sPEEK (IEC 1.6 meq g^{-1}) at 100°C, or using the current interrupt method, leads to a conductivity of $5 \cdot 10^{-2}$ S cm^{-1}, in agreement with that derived from impedance spectroscopy at 100°C and 100% relative humidity (44). Appraisal of the literature shows that sPEEK membranes drawn from *N*-methylpyrrolidone solution (6, 44, 49) have higher conductivity ($\geq 10^{-2}$ S cm^{-1}) than those cast from dimethylformamide ($\sim 10^{-5}$ S cm^{-1}) or dimethylacetamide (45, 47). Such amide-based solvents commonly used for solution casting of sPEEK membranes can interact with the sulfonic acid groups and have detrimental influence on proton conduction properties if not completely eliminated from the formed membrane. This provides a plausible explanation for the significant discrepancy in conductivity data between authors for sPEEK of similar degrees of sulfonation.

Sulfonated PEEK can also be chemically crosslinked, either by reaction with a suitable aromatic or aliphatic amine, or by thermal treatment under vacuum to induce intra-/inter-chain polymerization of the sulfonic acid groups (51).

POLY(PHOSPHAZENE)S In principle, two general approaches can be used for the preparation of sulfonated polyphosphazenes (sPPZ). In the first, an aryl oxide, alkoxide or arylamine that already bears a terminal sufonic acid or sulfonate group, replaces the chlorine atoms in poly(dichlorophosphazene). The second approach involves the synthesis of phosphazenes with unsubstituted aryloxy side groups, followed by sulfonation of these side groups. Polyphosphazenes offer a variety of different polymer compositions through the nature of the side chains on the $P = N$-backbone, and some of the most thermally and chemically stable polyphosphazenes


(a)
conductivity σ / S cm-1
10-1
10-2
0
50
100
150
temperature / °C
(b)
conductivity σ / S cm-1
10^0
10-1
10-2
10-3
50
60
70
80
90
100
110
% relative humidity
(c)
conductivity σ / S cm-1
10-1
10-2
10-3
10-4
80
100
120
140
160
temperature / °C

bear aryloxy side groups that can be functionalized to introduce acidic units, including carboxylic, sulfonic, and phosphonic acid groups. Sulfonating agents have included SO_3, and concentrated and fuming sulfuric and chlorosulfonic acids. Using a range of aryloxy- and arylamino-phosphazenes (monomers and the corresponding polymers), Allcock & Fitzpatrick (52) showed that $ClSO_3H$/dichlorethane gave crosslinked insoluble products, while use of sulfuric acid led to polyphosphazenes sulfonated primarily at the para-position. A decrease in molecular weight by a factor of 4 to 70 indicates that some skeletal cleavage occurred, predominantly in fuming sulfuric acid, enhanced at higher temperature, and essentially during the first 10 mins of reaction. These polymers are soluble in water above 30% sulfonation. Films of ethane-crosslinked polyphosphazene can be sulfonated from the surface inward. Crosslinking prevents the surface of the film from dissolving in water, thus allowing sulfonation to proceed through the material; however, the outer surface absorbs water to form hydrogel regions.

Poly[bis(phenoxy)phosphazene]s have also been sulfonated in dichloroethane with SO_3 (53, 54). The ion exchange capacity increases gradually with SO_3/PPZ mol ratio for poly[(3-methylphenoxy)(phenoxy)phosphazene] and poly [(4-methylphenoxy)(phenoxy)phosphazene], whereas the corresponding ethyl-substituted polymers are unstable under the reaction conditions employed (53). The first stage of sulfonation involves complexation of SO_3 to nitrogen of the $P = N$-backbone, with subsequent arenesulfonation taking place on the methylphenoxy, rather than the phenoxy, side group. Non-crosslinked sulfonated poly[bis(3-methylphenoxy)phosphazene] (Figure 13) softens and deforms above 76°C and is soluble in liquid methanol. Figure 14 represents the dependence of the proton conductivity on membrane swelling for three sulfonated non-crosslinked samples of different ion exchange capacity (55). The data show that conductivity above 10^{-2} S cm^{-1} is attained only by samples that undergo a volume change in water at 25°C of $>50\%$, i.e., those with IEC >1.2 meq g^{-1}. The high proton conductivity under these conditions is attributed to clustering of sulfonated polymer domains and the close proximity of sulfonic acid groups, estimated as 4.7–4.9 Å (55). Photocrosslinking can be initiated by benzophenone via a hydrogen abstraction mechanism with the methylphenoxy side chain (56–58), giving crosslinked membranes that are thermomechanically stable to 173°C. Although crosslinking through such sites is clearly without consequence on the number of sulfonic acid groups (ion

Figure 12 Conductivity of Victrex® sulfonated poly(ether ether ketone). (*a*) Temperature variation at 100% RH. sPEEK of IEC 1.6 meq g^{-1}. (●) no pre-treatment of the membrane. (□) membrane water-swollen by boiling in water for 4 h before mounting in the conductivity cell (44). (*b*) Variation with relative humidity at 100°C. □ Nafion®-117; ● sPEEK of IEC 1.6 meq g^{-1}. No pre-treatment of the membrane (44). (*c*) Temperature variation of Nafion-117 (□) and sPEEK of IEC 2.48 (▲) and 1.6 (●) meq g^{-1} at 75% relative humidity. Redrawn from (49) with permission of the authors.

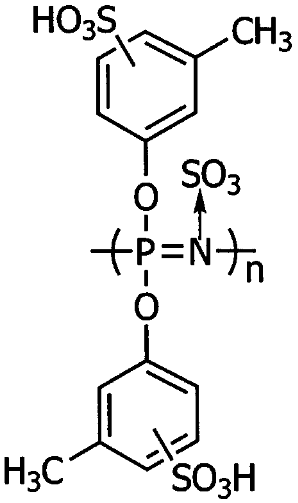


Figure 13 Sulfonated poly[bis(3-methylphenoxy)-phosphazene].

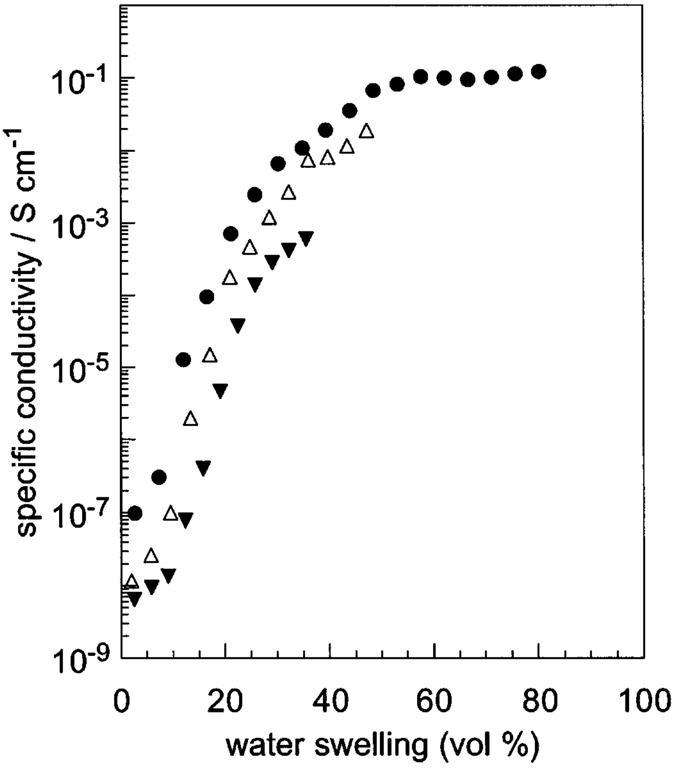


Figure 14 Non-crosslinked sulfonated poly[bis(3-methylphenoxy)phosphazene]: proton conductivity as a function of membrane water uptake at 25°C (55) for three membranes of ion exchange capacity: ●, 1.6; △, 1.2: ▼, 0.8 meq g^{-1}. Redrawn with permission of the authors.

exchange capacity 1.4 meq g^{-1}), the water uptake from liquid water is lower, with the hydration number decreasing from 19 to 13 H_2O/SO_3H in non-crosslinked and crosslinked poly[bis(3-methylphenoxy)phosphazene], respectively. Nevertheless, the proton conductivity of both types of membrane is identical, 0.04–0.08 S cm^{-1} over the range 30 to 65°C (58) at 100% relative humidity. Membrane-electrode assemblies prepared from the above sPPZ blended with polyacrylonitrile have been tested in DMFC at 60°C (59). Conduction properties at higher temperatures have not been reported, and, indeed, the temperature range of application of modified polyphosphazenes is not well-defined at present.

Phosphonic acid–substituted PPZ has been prepared from a precursor polymer bearing a bromophenoxy side group by treating first with butyllithium and then with diphenyl chlorophosphonate. The resulting phosphonate ester is converted to phenyl phosphonic acid groups through basic hydrolysis and subsequent acidification (60, 61). As depicted in Figure 15, the number of phosphonic acid groups incorporated is controlled by the length of the (bromophenoxy)(methylphenoxy)

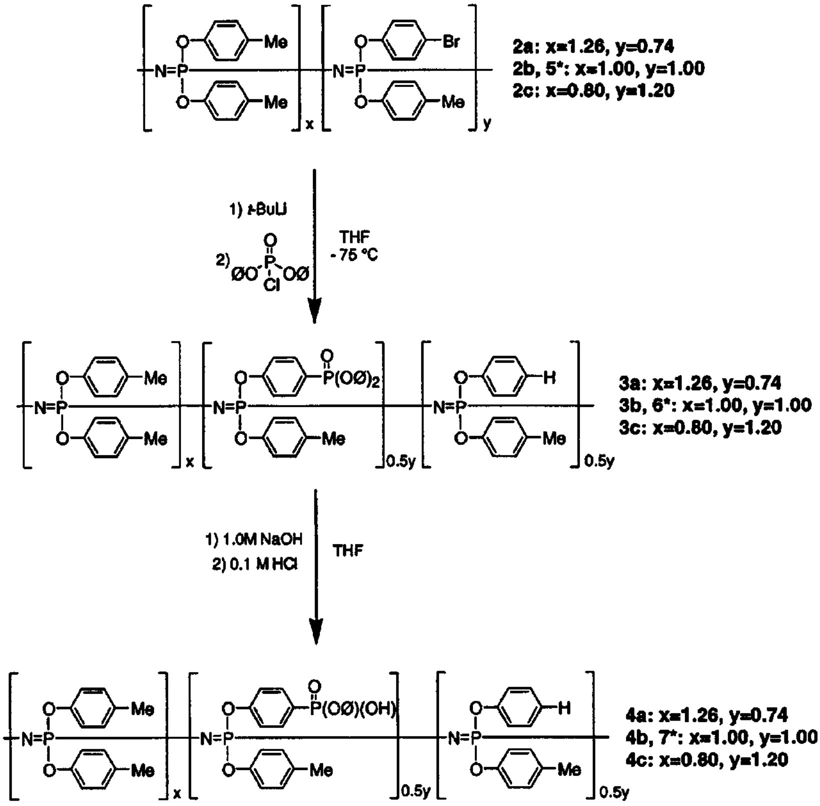


Figure 15 Synthesis of phosphonic acid substituted polyphosphazenes. Reprinted from Reference (61). *J. Membr. Sci.* Copyright 2002 with permission from Elsevier.

segment of the copolymer, relative to that of the bis(methylphenoxy) segment, and polymers with IECs of 1.17, 1.34, and 1.43 meq g^{-1} have been prepared, corresponding to P-OH contents of 37, 45, and 50% per polymer repeat unit, respectively. Water swelling at room temperature of dried phenylphosphonic polyphosphazene membranes is in the range 11–32 wt%, lower than that of sPPZ of lower IEC (1.07 meq g^{-1}) and of Nafion measured under the same conditions (38 and 30%, respectively) (61). The room temperature proton conductivity ($\sim$0.05 S cm^{-1}) and the low methanol diffusion coefficients (12 times lower than that of Nafion-117) also point to possible application of these membranes in DMFC, although conduction properties at higher temperature and variable relative humidity have not yet been reported. Polyphosphazenes with sulfonimide side groups (62) have recently been reported to give a power density of 0.47 W cm^{-2} at 80°C in a hydrogen/oxygen fuel cell (63).

Grafting of a Functional Group

Grafting an acidic functional group onto a polymer main chain provides the opportunity of controlling the ion exchange capacity and the site of sulfonation, which, however, remains random over the designated sites. Polybenzimidazole (PBI) can be derivatized by replacing the imidazole hydrogen with aryl or alkyl substituents (14, 64). This method was developed for further improving the chemical stability of PBI by introduction into the imidazole ring of groups less reactive than the imidazole hydrogen, and it provides the opportunity of tuning the properties of the polymer by the choice of the substituent. In this synthesis (Figure 16), hydrogen abstraction with LiH is followed by reaction of the PBI polyanion with a functionalized grafting species, which includes both sulfonated and carboxymethyl (65) groups. The synthesis (14, 66, 67) and electrochemical characterization of benzylsulfonate (14) and sulfopropyl *N*-substituted (67) PBI have recently been

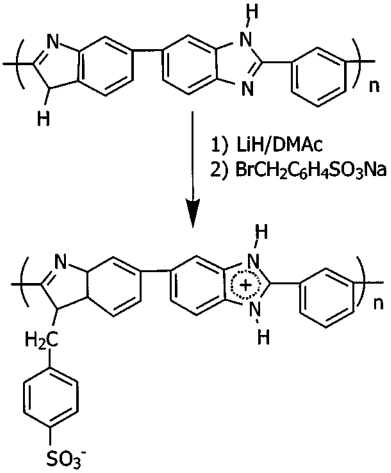


Figure 16 Synthesis route to benzylsulfonated polybenzimidazole via polyanion formation (14, 66).

described. Control over the extent of functionalization can be exerted at one or both of the reaction steps, i.e., by limiting the number of –NH sites ionized and/or by limiting the ratio of the sulfonated side chain group to PBI. Thermogravimetric analysis shows onset of weight loss at around 360°C, higher than in polyarylene polymers in which the sulfonic acid is directly substituted onto the polymer main chain. Solubility and textural properties of PBI are increasingly significantly modified as the degree of sulfonation increases. The water uptake and conductivity of sulfonated PBI of different degrees of sulfonation are represented in Figure 17 (68). The shape of the two curves is similar, water uptake corresponding to a hydration number of ~7 water molecules per sulfonic group, almost independently of the degree of sulfonation. This is only about half the water uptake of Nafion or sulfonated poly(ether ketone) membranes. The hydration number (under 90% relative humidity) is slightly higher, ~11, in sulfopropylated PBI (67). Figure 18 shows the conductivity of benzylsulfonate-grafted PBI, non-modified PBI, and Nafion-117 derived from resistance measurements at 25°C in aqueous phosphoric acid. Membranes were allowed to equilibrate for 8 h prior to measurement. Under these conditions of measurement, the conductivity of benzylsulfonate grafted PBI is in the range $3 \cdot 10^{-3}$ to $2 \cdot 10^{-2}$ S cm^{-1} (concentration range of H_3PO_4: 0–10 mol dm^{-3}), much higher than that of non-grafted PBI (~10^{-5} S cm^{-1}). At 140°C, the conductivity of sulfopropylated PBI is 10^{-3} S cm^{-1}; the presence of the alkyl side chain raises the question of the stability of this system under conditions of fuel cell operation.

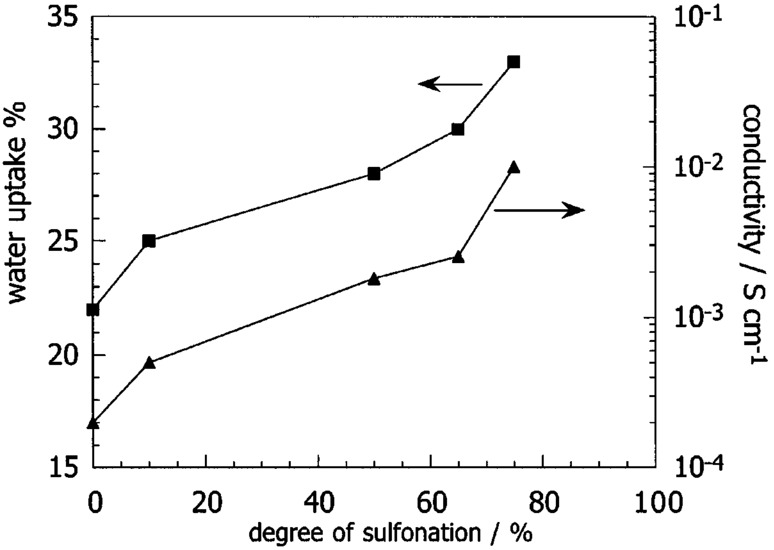


Figure 17 Conductivity and water uptake of benzylsulfonate grafted polybenzimidazole (68).

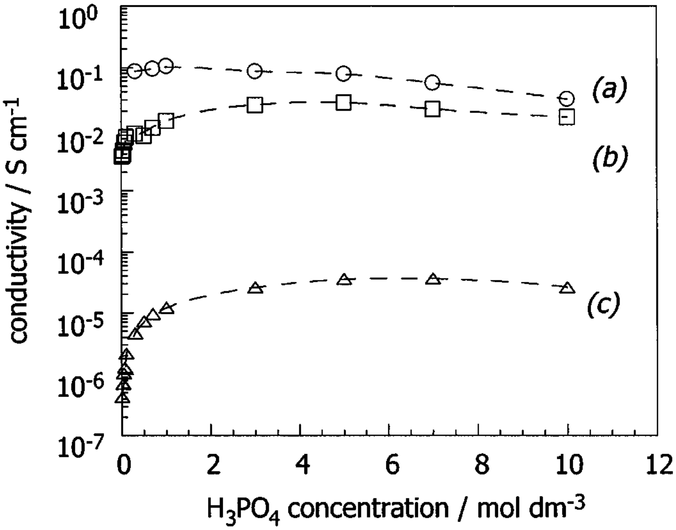


Figure 18 Conductivity at 25°C of (*a*) Nafion-117, (*b*) benzylsulfonate-grafted polybenzimidazole, and (*c*) polybenzimidazole. Conductivity derived from resistance measurements at 25°C in aqueous phosphoric acid as a function of the H_3PO_4 concentration. Membranes equilibrated for 8 h prior to measurement (5).

Benzylsulfonate-grafted PBI displays a high conductivity as long as the membranes are kept fully hydrated. Once highly sulfonated systems are exposed to a dry environment, they dry out and become brittle. The original flexibility can be recovered completely only by immersing the sulfonated membranes in a dilute aqueous solution of organic or inorganic bases for a short time (15–60 min); such treatment disrupts the hydrogen bond network between donor and acceptor sites on the grafted PBI chains. This can be clearly identified by infrared spectroscopy (Figure 19) (69), where the strong and broad absorption in the wavenumber region between 2200 and 3700 cm^{-1} in the spectrum of benzylsulfonate-grafted PBI is characteristic of a strongly hydrogen bonded system. This absorption is much reduced in breadth and intensity after immersion in a solution of alkali metal hydroxide, tetramethyl hydroxide, imidazole, etc.

Benzylsulfonate-grafted PBI is remarkably stable in solutions of 3% H_2O_2/Fe(II), showing neither degradation of physical integrity nor loss of conductivity, refuting the possible scission at the benzyl link through free radical attack. Unfortunately, in situ fuel cell experimental data are not yet available. These systems merit further study as electrolytes in both hydrogen and direct methanol fuel cells, in particular in applications where low-electroosmotic drag is required (7).

The same hydrogen abstraction/grafting route has been used to prepare phosphothylated PBI, but the resulting polymer was insoluble in organic solvents, and the

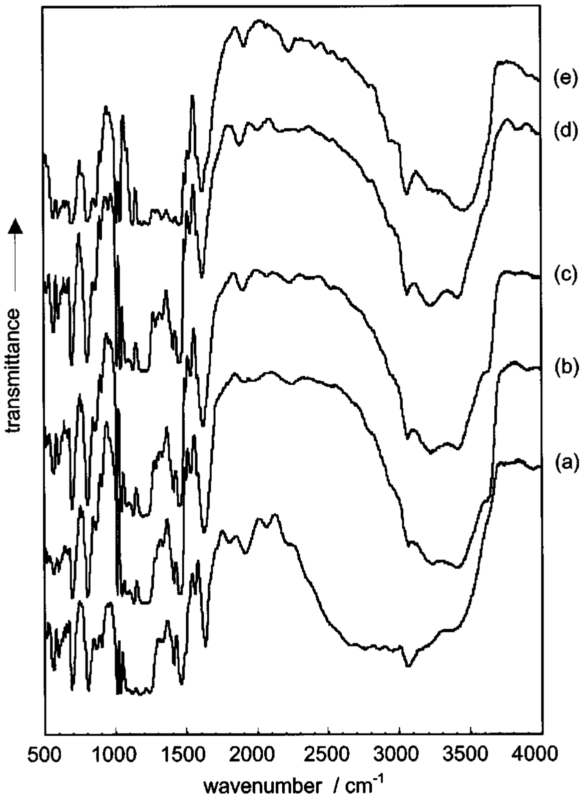


Figure 19 IR spectra of proton form benzylsulfonate grafted polybenzimidazole before (*a*) and after (*b*–*e*) immersion in inorganic hydroxides (1 mol dm^{-3}, 1 h, 25°C); (*b*) LiOH, (*c*) NaOH, (*d*) KOH, and (*e*) CsOH. Note the loss of intensity between 3700 and 2200 cm^{-1} in (*b*–*e*).

material could not be recast as a membrane. The conductivity of a pressed pellet is ~10^{-3} S cm^{-1} (8).

Other polymers have also been developed in which the sulfonic acid group is borne by a pendant group distant from the main chain. Although strictly not a grafted system, an interesting recent example is sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (sPPBP), produced from 2,5-dichloro-4′-phenoxybenzophenone (70) as Parmax$^{\text{TM}}$-2000 membranes by Maxdem Inc., where the polyphenylene backbone bears pendant ketone and ether-linked units in a structure similar to a PEK (Figure 20). These pendant groups are sulfonated by sulfuric acid at the *para* position of the terminal phenoxy unit. sPPBP is soluble in DMF, DMSO, and NMP above 30% sulfonation, and, as shown in Figure 21, its proton conductivity

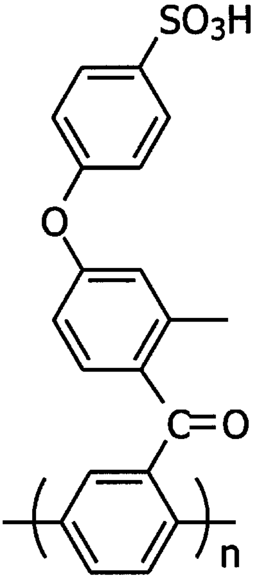


Figure 20 Sulfonated poly(4-phenoxybenzoyl-1,4-phenylene).

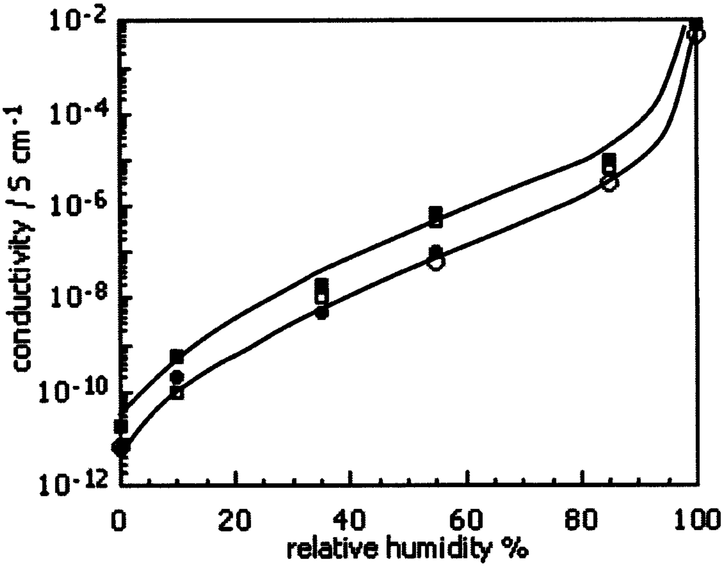


Figure 21 Conductivity of sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (sPPBP) as a function of relative humidity at room temperature. Redrawn from (47) with permission of the authors.

is strongly dependent on the relative humidity, increasing by 8 to 9 orders of magnitude between 0–100% relative humidity at room temperature. sPPBP of 65% sulfonation cast from DMF has a proton conductivity of $\sim10^{-2}$ S cm^{-1} at 100% relative humidity, suggesting that the casting solvent has less influence on proton conduction properties of sPPBP than sPEEK. The pendant groups likely influence polymer microstructure, with greater separation between hydrophobic regions and clustered sulfonic acid groups.

Direct Polymerization from Monomer Units

POLY(ETHER SULFONE)S AND POLY(ETHER KETONE)S Greater tailoring of polymer composition is possible by the direct synthesis of a new polymer from monomer building blocks functionalized with sulfonic acid or sulfonate groups than can be attained by simple polymer modification. Control of the position, number, and distribution of protogenic functions along the polymer backbone could provide access in the future to more thermohydrolytically stable sulfonated polymers and allow tuning of the microstructure and concomitant salient properties such as conductivity and degree of swelling. In reality, the range of polymers that can be produced is limited by the commercial availability or, at least, the ease of preparation of the corresponding monomers, and eventual multistage syntheses that would tend to increase costs could render the polymer less attractive for industrial use than one prepared by direct sulfonation. Nevertheless, for certain classes of polymer (polyimides, polybenzimidazole), the total synthesis route is more appropriate than direct sulfonation, and it has been largely used for the development of sulfonated polyimides. More recently, and with the aim of placing the sulfonated moiety at the more stable *ortho*-ketone or *ortho*-sulfone sites, respectively, sulfonated poly (etheretherketone) and poly(ether sulfone) have also been synthesized ab initio.

For example, nucleophilic substitution condensation polymerization of 4,4′-dichlorodiphenylsulfone, 4,4′-biphenol, and 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone leads to a random sulfonated poly(arylene ether sulfone) with two sulfonic acid groups per repeat unit, and in which the sulfonic acid groups are sited on the deactivated sulfone-linked rings (Figure 22) (71). Location of the ionomer group on the deactivated phenyl ring should improve stability toward desulfonation because the intermediate carbocation required for desulfonation is more difficult to stabilize on such a sulfone-deactivated ring. There is a change in the polymer microstructure as the content of disulfonated monomer component increases: The size of the hydrophilic ionic domains increases from 10 to 25 nm and becomes interconnected to form a cocontinuous morphology above 50 mol%. At this percolation limit, two glass transition temperatures develop and water uptake increases drastically, tending to solubility. Polymer membranes with ion exchange capacity of 0.41 to 2.2 meq g^{-1} prepared by varying the monomer molar ratio have a conductivity of 0.01–0.16 S cm^{-1} at 30°C. Materials with a degree of sulfonation of 40 to 50% could be adapted for fuel cell application when the question is not only the performance, but in particular the hydrolytic stability and lifetime of this direct

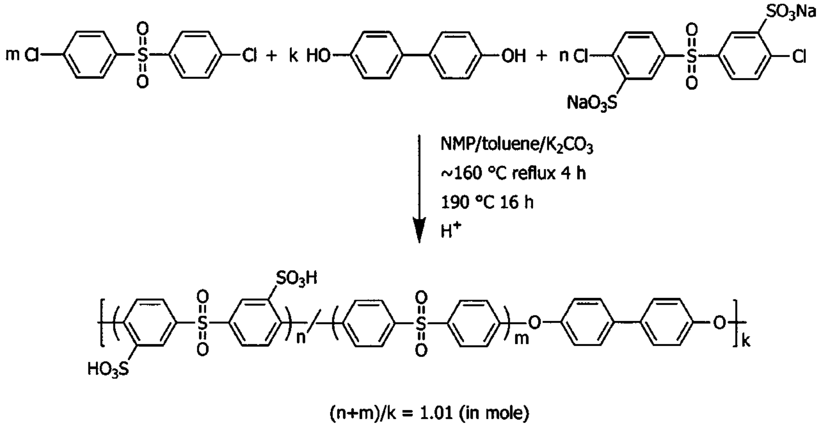


Figure 22 Direct polymerization synthesis of random sulfonated poly(arylene ether sulfone)s. Redrawn from (71) with permission of the authors.

polymerization sulfonated poly(ether sulfone) compared with that of congeners prepared by direct sulfonation.

Sulfonated poly(ether sulfone)s having the sulfonic acid group at the less stable site *ortho* to the ether link can be prepared from 4,4′-difluoro-diphenylsulfone and hydroquinone 2-potassium sulfonate/hydroquinone (72). Using the same approach, sulfonated poly(ether ketone) homo- and copolymers have been prepared from 5,5′-carbonylbis(2-fluorobenzene sulfonate) using the reaction shown in Figure 23 (72). The best mechanical properties are exhibited for a polymer with one sulfonic acid group per three aromatic units [i.e., corresponding to a sulfonated poly(ether ether ketone) with 100% sulfonation], when the experimentally determined IEC of a polymer membranes with molecular weight 53000 g mol^{-1} was 2.29 meq g^{-1}. No conduction properties on these *ortho* ether—sulfonated, direct polymerization poly(ether ketone)s and sulfones—are reported.

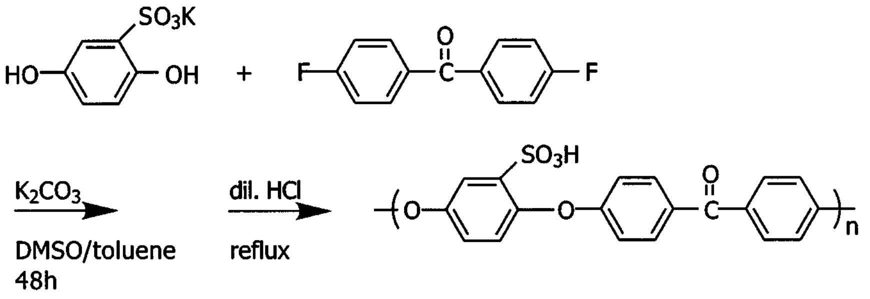
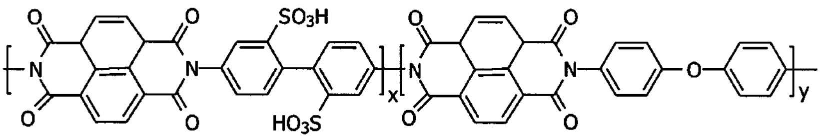


Figure 23 Direct polymerization synthesis of sulfonated poly(ether ether ketone). Redrawn from (72).

POLYBENZIMIDAZOLE AND POLYIMIDES Sulfonated polybenzimidazole can be prepared, for example, by the polycondensation of 2-sulfoterephthalic acid with 1,2,4,5-tetraaminobenzene tetrahydrochloride at 190°C (73, 74). Further derivatization by grafting of sulfopropyl groups leads to a water-soluble polymer (75); in principle, however, the number of pendant sulfonic acid groups grafted in the second stage could be limited in order to avoid solubility. No conclusions can yet be made concerning electrical properties on the basis of the partial conductivity measurements reported to date, but the number of charge carriers available by such double sulfonation is expected to lead to high proton conductivity.

Sulfonated polyimides have recently been successfully developed in several laboratories. Mercier and co-workers [Besse et al. (76), Cornet et al. (77), Faure et al. (78), and Genies et al. (79)] first synthesized various random and sequenced sulfonated copolyimides from naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCD) or 4,4-oxydiphthalic anhydride (OPDA), 4,4′-diaminobiphenyl-2,2′-disulfonic acid (BDSA), and common non-sulfonated diamine monomers such as oxydianiline (ODA). The incorporation of diamine comonomers adjusts properties such as flexibility and water uptake by pushing apart the rigid rod backbone of the polymer, thereby creating free volume for water. Two-stage polycondensation of BDSA-OPDA-ODA and BDSA-NTCD-ODA gives phthalic and naphthalenic sulfonated polyimide (sPI) copolymers, respectively, that have been extensively studied (76–79). Sulfonated phthalic polyimides degrade hydrolytically and chain scission occurs rapidly in water at 80°C (79, 80). The molar ratio of BDSA-NTCD or BDSA-OPDA in the first stage of polycondensation gives the length of the ionic sequence, while the subsequent introduction of ODA and the remaining dianhydride spaces the ionic blocks with hydrophobic sequences. These latter sequences have some residual flexibility, whereas the phenylene bonds in the sulfonated moiety confer a glassy character. Polymers of various equivalent weight and different ratios (x/y) of sulfonated (x) to neutral (y) diamine (Figure 24) have been prepared that can be cast into membranes from *m*-cresol. The length of the block sequence for a constant equivalent weight has greater impact on water uptake and conduction properties than does a variation of the equivalent weight for polymers with the same block length. For membranes swollen in liquid water, the hydration number increases with the length of the ionic block sequence, but the conductivity



x/y = 30/70, x = 1 - 9

x = 5, x/y = 30/70, 40/60, 50/50

Figure 24 Naphthalenic sulfonated polyimides (77, 78).

decreases (from $1.8 \cdot 10^{-2}$ to $4 \cdot 10^{-3}$ S cm^{-1} for sPI of equivalent weight 793 g mol^{-1} when the length of the ionic block increases from 3 to 9 units) (81). This observation seems in contrast with the general idea that conductivity increases with the hydration number and suggests that the conductivity also depends on microstructural changes accompanying the increase in block length. However, for a given sPI composition, the conductivity follows the generally observed trend of increasing with the degree of hydration (Figure 25). For the same block length (5)

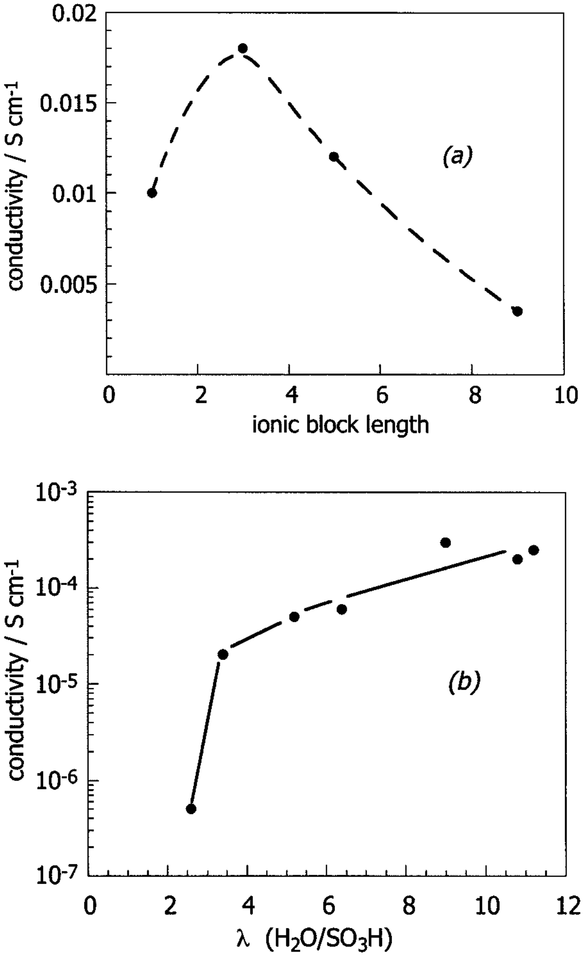


Figure 25 Proton conductivity of naphthalenic sulfonated polyimides with $x/y = 30/70$ (ion exchange capacity = 1.26 meq g^{-1}, see Figure 24 for structure). (*a*) Variation of conductivity with ionic block length; (*b*) variation of conductivity with hydration number for a polymer of ionic block length (x) = 5. Redrawn from (77) with permission of the authors.

and different EW, the hydration number for membranes immersed in water is constant ($\lambda = 19$ H_2O/SO_3H). As already noted for other sulfonated polymers such as sPEEK, the water uptake by sPI is significantly higher for membranes soaked in water (λ ~17–30 H_2O/SO_3H for sPI with $x/y = 30/70$) than for membranes exposed to a saturated water vapor environment (λ ~10–11 H_2O/SO_3H) where the hydrophilic/hydrophobic block ratio to some extent influences the hydration number. In a fuel cell, naphthalenic sPI membranes of IEC 1.26 meq g^{-1} (60 μm thickness) provide 0.5 V at 0.5 A cm^{-2} (H_2-O_2, 4 bar abs., 70°C) (76). However membrane durability in an H_2-O_2 fuel cell is directly related to the hydrolytic stability determined ex situ (82, 83), which closely depends on the number of sulfonic acid groups in the 4,4′-diaminobiphenyl-2,2′-disulfonic acid/naphthalene-1,4,5,8-tetracarboxylic dianhydride/oxydianiline (BDSA/NTCD/ODA) copolymer. Thus sulfonated polyimides with ion exchange capacities of 0.86, 1.26, and 1.98 meq g^{-1} have fuel cell lifetimes under steady state conditions at 0.3 A cm^{-2}/80°C of 600, 300, and 20 h, respectively (83).

Other groups have reported that some copolyimide membranes containing bulky and/or angled comonomers (84, 85) have produced higher proton conductivities than Nafion, possibly by increasing the free volume available to water. Polymer interchain spacings derived from X-ray diffraction are higher by ~0.1–0.4 Å for sulfonated polyimides [incorporating an angled (e.g., oxydianiline, ODA) or a linear but bulky comonomer, e.g., bis(aminophenyl)polyphenylbenzenes] than those for the corresponding BDSA-NTCD homopolymer (84, 85). These studies concentrate on varying the non-sulfonated diamine moieties. Polyimides have also been prepared using other commercial (86, 87) and non-commercially available sulfonated diamines (80, 88–90). Some of the resulting sulfonated polyimides are soluble in DMSO (88), and their conductivities can exceed 0.1 S cm^{-1} at room temperature/100% relative humidity (84, 88, 90). However, the most relevant additional question in the context of application as fuel cell membranes is their thermohydrolytic stability. Limited data are available: A membrane of BDSA/NTCD/1,4-bis(4-aminophenyl)-2,3,5,6-tetraphenylbenzene softened after 500 h in water at ≥90°C (85), whereas a sulfonated polyimide synthesized from BDSA/NTCD/bis[3-(aminophenoxy)-4-phenyl]isopropylidene became brittle after ~200 h in water at 80°C (80). Other data indicate higher hydrolytic and oxidative stability for random polyimides than for the corresponding sequenced polyimide membranes (88). The relationship between these ex situ tests and in situ fuel cell characterization has not been reported.

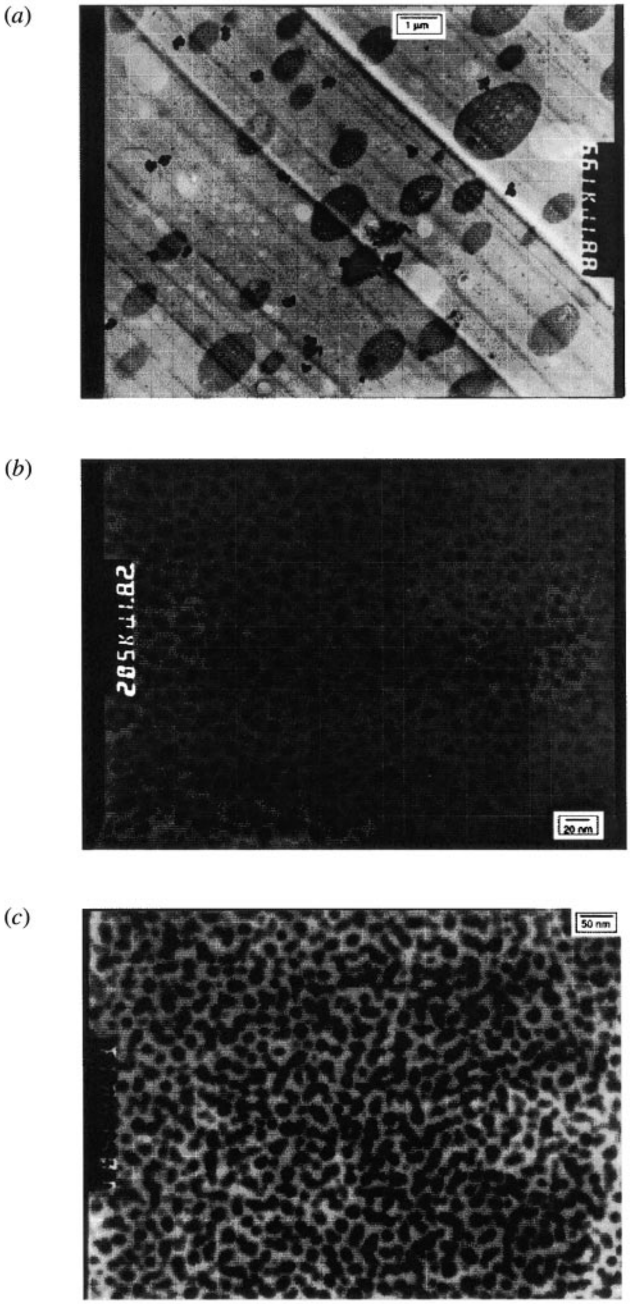
Polymer Blends

Polymer blending is a potentially versatile way of tuning the properties to those desirable for fuel cell application. The miscibility between two polymers can be effectively improved by favoring specific interactions between the polymer chains, such as ionic interaction, hydrogen bonding, or ion-dipole interactions, which also act to crosslink the blend and modify mechanical and swelling properties. Ionically crosslinked polymer blends are prepared by associating a sulfonated polymer (for example in its triethylammonium form) with a basic polymer, followed by acid washing to regenerate the protonic material. The degree of formation of ionic crosslinks depends upon the relative acid and base strengths of the components. Weakly basic polymers act as hydrogen bond acceptors for the protons on the acidic polymer; for more basic polymers, proton transfer from the acidic component produce an ionically crosslinked membrane. Kerres et al. (91–95) have explored this approach extensively by associating a range of commercial and specifically synthesized polymer blend components and has identified, in particular, the suitability of acid-base membranes for application in DMFC.

For example, sulfonated PEEK and PSU have been used in blends with PBI, as well as with more weakly basic components such as polyetherimine, poly(4-vinylpyridine), diaminated PSU (91, 92), and other modified PSUs containing pendant basic aromatic groups (93). The effective ion exchange capacity is a good measure of the extent of proton transfer to the basic polymer. Even in sPSU-PBI and sPEEK-PBI blends, the experimentally determined IEC is higher than the value calculated on the basis of complete proton transfer (91). The ionic interaction increases the glass transition temperature, T_g, of the blend membranes compared with that of either of the components by 15 to $>50°C$ in sPSU-PBI. Such effects depend upon the relative proportion of sulfonated and basic polymer and the base strength of the latter. Blends with a low ionic crosslinking density (weakly basic components, few sulfonic acid sites) are microphase separated. This may be seen in Figure 26 (92), where the images (*a*) and (*b*) of a microphase-separated membrane have been prepared using sPSU of ion exchange capacity 1.7 meq g^{-1}; image (*c*) is of an ionically associated membrane prepared with sPEEK of IEC 2.95 meq g^{-1}. Swelling in water and brittleness in the dry state are both lower than for the corresponding nonblended sulfonated polymer membrane to the extent that a water-soluble sPEEK becomes virtually insoluble on blending with PBI. These advantages are lost at higher temperature as the degree of ionic crosslinking is severely reduced above 70°C for sulfonated polymer-aminated PSU and above 110°C for sulfonated polymer-PBI; above these temperatures, reverse proton transfer occurs with an associated increase in solubility of the sulfonated component. Therefore, a challenge remains to associate both covalent and ionic crosslinking in order to combine the reduced swelling of the former with the flexibility and mechanical stability of the latter. The specific proton resistance is plotted in Figure 27 as a

⟶

Figure 26 TEM micrographs of polymer blend membranes (*a*, *b*) 95 wt% sulfonated polysulfone (ion exchange capacity 1.7 meq g^{-1}) and 5 wt% polybenzimidazole at magnification (*a*) 6000× and (*b*) 250,000× . (*c*) Polymer blend membrane of 79 wt% sulfonated poly(ether ether ketone) (IEC 2.93 meq g^{-1}) and 21 wt% polybenzimidazole. The measured effective ion exchange capacities of membranes (*a*, *b*) and (*c*) are 1.19 and 0.96 meq g^{-1}, respectively. Reprinted from Reference (92). *J. Membr. Sci.* Copyright 2001 with permission from Elsevier.


(a)
1 μm
(b)
20 nm
(c)
50 nm

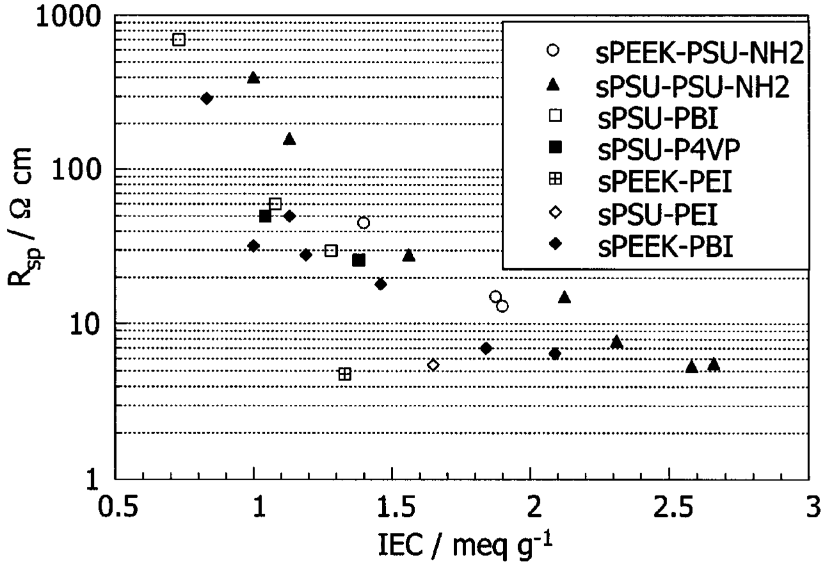


Figure 27 Specific proton resistances of representative polymer blend membranes at 25°C. Redrawn from (91). sPEEK: sulfonated poly(ether ether ketone); PSU-NH_2, *ortho* sulfone aminated polysulfone; sPSU, sulfonated polysulfone; P4VP, poly(4-vinylpyridine); PEI, polyethyleneimine; PBI, polybenzimidazole.

function of the ion exchange capacity for a range of acid-base blend membranes. The lowest resistance at moderate IEC values is shown by sPEEK-aminated PSU, sPEEK-PBI, and sPSU-aminated PSU blends (91). These compositions are of particular interest for direct methanol fuel cell application because the permeability of methanol is a factor of 10–20 (at 40°C) lower than that of Nafion (94). This is most relevant to fuel cell operation at low-current densities, where electroosmotic drag plays a lesser role. At a current density of 300 mA cm^{-2}, a MEA of sPEEK-PBI gave 500 mV at 110°C, with low methanol crossover (95). Higher power densities (~0.25 W cm^{-2}) are provided by other blends (sPEK-PBI-aminated PSU, sPEK-PBI), but methanol crossover is also higher.

The PBI component of blend membranes can also be acid doped. Acid doping increases the concentration of proton charge carriers, but the benefits with regard to mechanical properties conferred by the ionic interaction are lost at low temperature. In fact, the conductivity of phosphoric acid–doped PBI and sPSU-PBI membranes (doping level 500 mol%) is essentially identical in a dry atmosphere at 175°C (0.02 S cm^{-1}) (96). Indeed, the current density versus cell voltage curve at 190°C on hydrogen/air (1 bar absolute pressure) shows similar behavior to that given by a H_3PO_4-doped PBI alone. The long-term advantage of improved high-temperature tensile strength conferred by the presence of the sulfonated component still requires demonstration under these high-temperature/low-relative humidity conditions.

MICROSTRUCTURE OF NON-FLUORINATED POLYMERS

Description of the microstructure of sulfonated hydrocarbon–based and perfluorinated systems is made in same general terms, although there are important differences of detail. Sulfonated polyimides show some particular microstructural features that are discussed below. In all types of polyelectrolytes, the sulfonic acid groups tend to cluster to a greater or lesser extent into hydrophilic regions that are hydrated or solvated in the presence of water, or water/methanol, and the polymer backbone segregates to a greater or lesser extent into hydrophobic regions. The hydrophilic domains interconnect and are responsible for the transport of water and protons; the hydrophobic regions provide morphological stability and prevent dissolution in water. As for Nafion, a three-region model has been proposed in which the ionic clusters coexist with amorphous and crystalline hydrophobic domains. In Nafion, the characteristic separation length is 5 nm (solvent volume fraction 0.4). In hydrocarbon-based polymers, the lower acidity of the sulfonic acid groups, the absence of fluorinated groups, and the greater rigidity of the polymer backbone conferred by the presence of aromatic groups all contribute to reducing the nanoseparation of hydrophobic and hydrophilic domains, which influences the proton transport properties, in particular by a strong dependence of proton conductivity on water content. In the block copolymer approach for the synthesis of a sulfonated polymer, the ionic groups are gathered in blocks along the polymer chain and are separated by long hydrophobic sequences. Such molecular structural phase separation allows the formation of larger ionic domains than those in which sulfonic acid groups are distributed randomly.

A model based on a cubic system of hydrophilic channels in a hydrophobic matrix parameterized using data from small angle X-ray scattering (SAXS) and water self-diffusion coefficients (obtained by pulsed field gradient NMR) led to a description of the microstructure of sulfonated polyetherketones (sPEEKK). sPEEKK is made up of highly branched, narrow channels that have more dead-end components than the wider, less-branched channels of Nafion. The more extensive hydrophobic–hydrophilic interface region in sPEEKK results in greater separation between sulfonic acid functional groups (6, 7). For both types of polymer, both the characteristic separation length and the channel diameter increase with solvent volume fraction, whereas the dimension of the internal interface region passes through a maximum value whether in water, methanol, or water/methanol (M. Schuster, M. Ise, K.D. Kreuer, G. Gebel & J Maier, in preparation). Such observations are highly relevant to the variation of proton conduction properties of sulfonated poly(ether ketone)s with hydration, as well as other factors related to water and methanol permeation such as electroosmotic drag. There is similarity between observed conduction and swelling properties of sulfonated polyphosphazenes and poly(ether ketone)s that is reflected at the microstructural level, with nanoseparation increasing with the degree of hydration. However, in addition, diffraction intensity in sulfonated polyphosphazenes in the wide-angle range points to some two-dimensional short-range order in that is not completely disrupted by swelling (55).

Sulfonated polyimides (sPI) prepared by block copolymerization using naphthalenic dianhydride, present no well-defined ionomer peak in small-angle neutron scattering (SANS), only a broad shoulder on an intense small-angle upturn in intensity (77). This indicates that the distribution or shape of the ionic domains is different from that of sPI prepared from a phthalic dianhydride (78) and from that of Nafion and suggests that the polymer chain rigidity strongly influences the microstructure. This ionomer peak in naphthalenic sPI is situated at very low angles, corresponding to a separation length of 25 nm, such that the microstructure corresponds to hydrophobic domains embedded in a hydrophilic continuous phase (77). The evolution of scattered intensity at higher angle is not typically Porod-type, possibly due to the existence of an internal structure in the ionic domains or resulting from interdomain connections. SAXS spectra of sulfonated polyimides recorded across the thickness of the membrane and parallel to the plane of the membrane provide evidence for structural anisotropy (lamellar or disc-like), which increases as the block character increases (77). Such morphology may arise from a preference of the solvent for one of the blocks. Polymer blends and growth of inorganic particles or networks in situ in a polymer solution provide a means of modifying the polymer microstructure because the membrane structure reforms at the same time as the precipitation of the inorganic and/or organic components (12).

STABILITY CONSIDERATIONS AND SWELLING

Sulfonation of thermostable polymers is generally accompanied by an increase in glass transition temperature, T_g. The presence of pendant SO_3H groups produces steric hindrance to intersegmental motion and reduces mobility and flexibility, and the sulfonic acid groups interact and form strong hydrogen bonds that increase chain rigidity. For example, the T_g of polybenzimidazole increases from 417 to 447°C on addition of one benzylsulfonic acid group per PBI repeat unit; that of sulfonated poly(ether sulfone) increases as a function of the sulfonation level from 227°C for non-modified PES to 333°C for a material in which essentially all repeat units are sulfonated (37).

The particularly aggressive environment in a PEMFC or DMFC can initiate different types of degradation mechanisms and aging processes that result in either chemical or morphological/textural alteration. Such modification might arise from desulfonation, chain scission caused thermohydrolytically, or by free radicals generated at the electrodes or loss of mechanical properties owing to excessive swelling.

Thermal and Thermohydrolytic Stability

One of the first considerations is that of the thermal stability of high-temperature polyelectrolytes based on the PEK family, PSU, PI, PBI, etc. Thermogravimetric analyses of sulfonated non-fluorinated membranes generally show a weight loss above around 250°C (in air, using a ramp rate of 1°C/min), which results from condensation of $-SO_3H$ groups followed by loss of SO_2, whereas combustion of the polymer occurs at a significantly higher temperature (>500°C). In a dry oxidizing environment, the temperature range of application of such membranes is thus limited by the onset of alteration of the sulfonic acid functions.

However, as these polymers were originally developed for applications in environments different from those prevailing in a PEM fuel cell, i.e., extremes of temperature and corrosivity, but water-free, their stability under thermohydrolytic conditions, in particular of the sulfonated form, is of prime importance. Polyphenylenesulfide, poly(ether sulfone), poly(ether ketone), and polyimide families show reasonable stability at 300°C, while none of the polymers is stable under air/water at 400°C (97). Under inert and saturated water vapor conditions at various temperatures, the stability of sulfonated derivatives of poly(ether ether ketone), poly(ether sulfone), polybenzimidazole, and poly(phenylquinoxaline) can be represented by the temperature of 5% weight loss by the polymers (Figure 28)

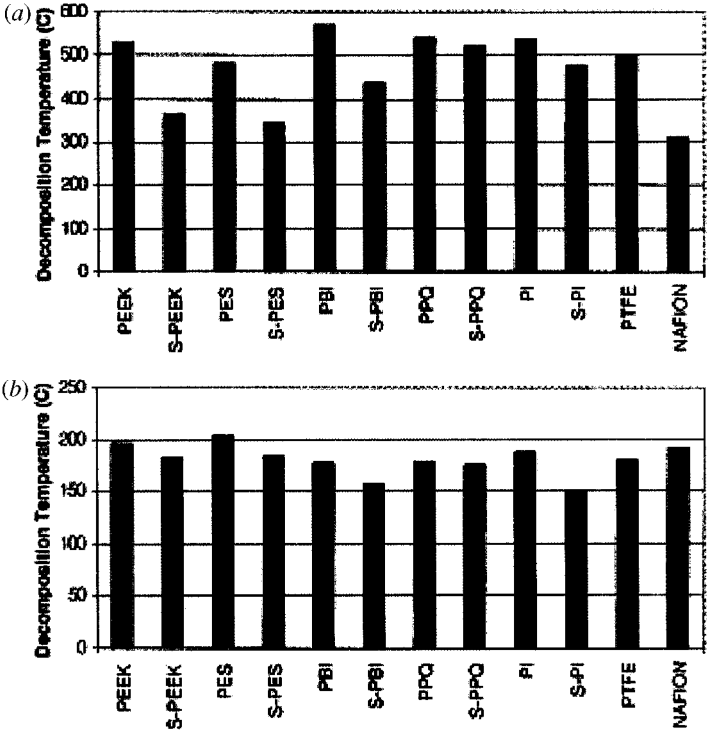


Figure 28 Temperature of 5% weight loss of non-sulfonated and sulfonated poly(ether ether ketone), PEEK; poly(ether sulfone), PES; polybenzimidazole, PBI; poly(phenylquinoxaline), PPQ; polyimide, PI; poly(tetrafluoroethylene), PTFE and Nafion in (*a*) helium and (*b*) saturated water vapor. Reprinted from Reference (98). *Polym. Degrad. Stab.* Copyright 2000 with permission from Elsevier.

(98). Whereas in a dry environment all of the polymers retain their integrity to at least 330°C, their stability is radically different under saturated water vapor. Under inert conditions, the decomposition temperature is higher for the sulfonated non-fluorinated polymers than for Nafion. Under saturated vapor conditions, all materials (both sulfonated and non-sulfonated) show some decomposition between 150 and 200°C, although the thermohydrolytic stability of the sulfonated polymers is always lower that that of the corresponding nonmodified material. As a general observation, sulfonated polyaromatic polymers are slightly more stable than sulfonated polyheterocyclic systems. Sulfonated samples submitted to thermohydrolytic treatment at 225°C all show loss of sulfonic acid groups to some extent. Not surprisingly, desulfonation occurs for sPES, sPPQ, and sPEEK under saturated vapor conditions, and evidence for hydrolysis of the diarylketone group is seen by infrared spectroscopy for highly sulfonated PEEK (98). The relative ease of the desulfonation reaction is a corollary of the ready direct sulfonation of PES, PEEK, and PPQ for example using sulfuric acid (see above).

Swelling

Whereas the generally water-assisted mechanism of proton transfer requires a degree of membrane swelling for adequate proton conductivity, uncontrolled water uptake can lead to mechanical degradation. The hydration number (λ, nH_2O/nSO_3H) of sulfonated polyelectrolyte membranes depends upon water activity and temperature, and it strongly influences their proton conductivity and dimensional stability. The water uptake of a sulfonated polymer membrane of a given type of polymer at a given temperature increases with the degree of sulfonation. Kreuer (6) has carried out a detailed study of the hydration behavior of sulfonated poly(ether ether ketone ketone) (sPEEKK) of ion exchange capacity in the range 0.78–1.78 meq g^{-1} and of Nafion (IEC 0.9 meq g^{-1}). All the membranes show three regimes: one in which the hydration number is invariant with temperature, one in which the hydration number increases very rapidly over a narrow temperature interval, and a transitional region between these two regimes. The water uptake in liquid water is generally significantly higher than that obtained by conditioning under high relative humidity. Nafion shows similar behavior (Schroeder's paradox) at high temperatures, interpreted as the difficulty in condensing vapor within the pores of the membrane. The onset of rapid swelling in liquid water occurs at lower temperatures for sPEEKK (at 65, 85, and ~120°C for sPEEKK of IEC 1.78, 1.4, and 0.78 meq g^{-1}, respectively) than for Nafion (145°C), and it is irreversible to some extent, thus allowing a certain control of the maximum water uptake at a lower temperature by appropriate preconditioning. The primary hydration sphere is made up of 3 water molecules in Nafion and 5 in sPEEKK, with more loosely bound water representing a further 11 and 5 molecules, respectively; thereafter water is present as a second phase (with $\lambda > 55$). At the onset of extended swelling, the membrane softens and becomes mechanically weak, and this occurrence is often a major contributor to membrane failure in a fuel cell. At high water uptake, profound deformation of the hydrophilic regions of the polymer leads to an irreversibly swollen state that is accompanied by marked decohesion and disentanglement of the polymer chains, exacerbated by the lack of crosslinking and the rigid nature of these families of polymer.

Swelling of sulfonated polymer membranes in dilute methanol solutions has also to be considered in the context of application in DMFC. Sulfonated poly(etherketone)s of high degree of sulfonation are soluble in concentrated aqueous solutions of methanol. Even at lower concentrations, the hydrophobic and hydrophilic moieties of methanol interact with the corresponding regions of sulfonated non-fluorinated polymers, tending to modify the microstructure by distending the channels and leading to increased swelling. The water/methanol content of sPEEK membranes is the same as that of the solution in which the membrane was immersed, showing the absence of any concentration or dilution effect and suggesting that both water and methanol are located in the same region of the polymer (7). Different approaches to limiting swelling have been developed that include crosslinking and blending and inclusion of inorganic components able to reinforce the polymer through ionic interaction (99, 11).

Possible Degradation by Radical Species

Species such as HO• and HO_2• could arise from oxygen diffusion through the membrane and incomplete reduction at the anode, and possible degradation mechanisms involving oxidizing species and hydroxy radicals must also be considered. Comparative assessment of membrane stability toward oxygen-containing radicals can be approached using the Fenton reaction medium [H_2O_2/Fe(II)] and characterizing membrane physical integrity, mechanical properties, ion exchange capacity and conductivity, etc. with time. The mechanical degradation and partial loss of IEC of sPEEK in such a medium depend strongly on the concentration of hydrogen peroxide and, to a lesser extent, on the degree of sulfonation of the polymer. Non-sulfonated PEEK membranes are unaffected by H_2O_2/Fe(II). The real problem of evaluating the stability of membranes to such radical attack lies in the difficulty in relating such ex situ "accelerated aging" tests to in situ aging in a fuel cell, insofar as the conditions under which such radical species are formed in the fuel cell, and their concentration are unknown (82). Thus whereas sPEEK membranes can function for hundreds to thousands of hours in a fuel cell (J. Rozière, D.J. Jones, B. Bonnet & B. Bauer, unpublished data; 51), it has been shown that similar membranes become brittle with partial loss of their IEC after 4 to 8 h in Fenton reaction solutions of 3% H_2O_2/1 ppm Fe(II) at 68°C (82). For sulfonated styrene(ethylene-butene)styrene (DAIS proton exchange membrane), ex situ tests were used to predict a lifetime at 60°C of 2500 h (100).

Electron paramagnetic resonance spectroscopy could be a promising tool for identifying degradation products resulting from HO• radical attack. It has been used with a variety of sulfonated aromatic molecules, models for sulfonated hydrocarbon polymers such as PEEK, polystyrene, or PES (101). The dominating

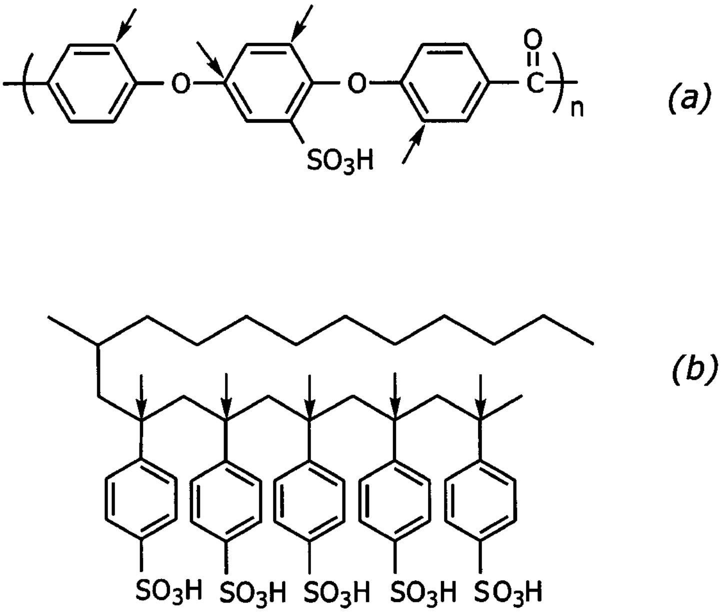


Figure 29 Possible sites for HO• radical attack on sulfonated polymers. Redrawn from (101).

reaction is the addition of HO• to the aromatic rings, preferentially in the *ortho* position to alkyl and RO-substituents (since the *para* position is substituted and thus blocked). For polymers with benzylic α-H atoms, acid-catalyzed elimination of water according to Figure 29 can lead to chain scission, in a mechanism relevant for any benzyl-grafted polymer. Methoxybenzenesulfonic acid underwent loss of OCH_3, believed to be initiated by *ipso* attack of HO•. Although this mechanism would be of relevance for polymers such as polysulfone or poly(ether ketone) having phenoxybenzene ether bridges where it could lead to bond breaking within the C-O-C linkages, phenoxy radicals were not observed in electron paramagnetic resonance experiments on media of pH values lower than 5. The application of such an approach to real proton electrolyte membranes is of obvious interest, as well as the development of techniques enabling the detection of radical species in situ in order to be able to assess the potential gravity of radical attack in a working fuel cell.

WATER DIFFUSION AND PROTON CONDUCTIVITY, ELECTROOSMOTIC DRAG

For sulfonated polyaromatic membranes such as poly(etherketones) (as well as the corresponding ionically and covalently crosslinked congeners), the water self-diffusion coefficient D_{H_2O} for a given water content is lower than that of Nafion,

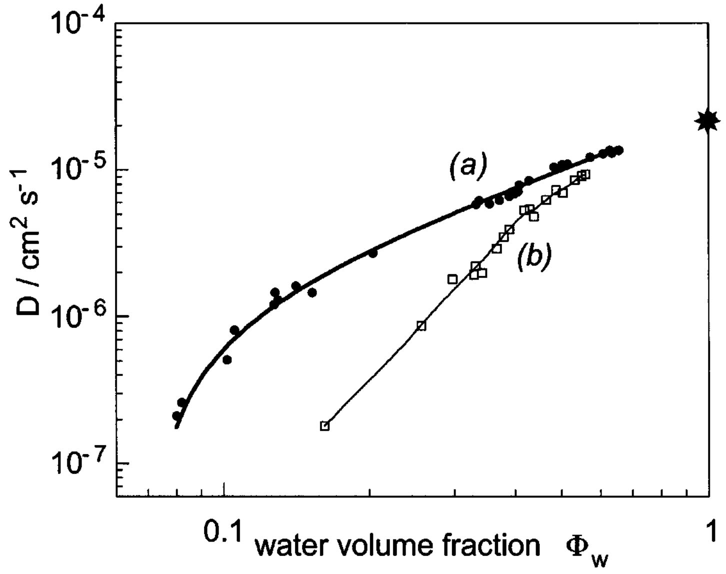


Figure 30 Water self-diffusion coefficients as a function of water volume fraction in (*a*) Nafion and (*b*) sulfonated poly(ether ketone) membranes (M. Schuster, M. Ise, K.D. Kreuer, G. Gebel & J. Maier, in preparation). (✱) indicates water self-diffusion coefficient of pure H_2O.

unlike at highest water volume fractions where the self-diffusion coefficients are similar (48, 102; M. Schuster, M. Ise, K.D. Kreuer, G. Gebel & J. Maier, in preparation) (Figure 30). In addition, at the short-range level, the protonic charge carriers are more strongly associated with the immobilized sulfonate groups in sulfonated PEK-type polymers than they are in Nafion. The stronger confinement of water in the narrow channels of polyaromatic polymers also leads to a lower dielectric constant for the water of hydration (about 20, compared with almost 64 in fully hydrated Nafion, as determined by dielectric spectroscopy) (6, 104). The proton mobility D_σ is roughly related to the water diffusion coefficient, and it shows a similar dependence on water volume fraction. The larger average separation of neighboring sulfonic acid functions in polyaromatic polymers, the lower degree of dissociation of less acidic functional groups in hydrocarbon based polymers than in superacidic Nafion, and the decreasing dielectric screening of the anionic counter charge all contribute to a lower proton conductivity at low water contents for sPEK-type polymers than for Nafion. At very high water contents, however, D_σ is higher than D_{H_2O}, indicating the contribution of some intermolecular proton transfer.

In a functioning fuel cell, proton transfer through the membrane to the cathode leads to drift of water in the same direction. The electroosmotic drag coefficient,

K_{drag}, is defined as the number of water molecules transferred through the membrane per proton and, for high-temperature operation of PEMFC and DMFC, K_{drag} should be small in order to avoid an increase in membrane resistance caused by depletion of water at the anode side. Its magnitude can be determined in different ways including electrophoretic NMR (105). The K_{drag} of acid-doped polybenzimidazole is close to zero, thus enabling a PBI fuel cell to operate at high temperature and low gas humidification without drying out of the membrane (106). However, the particular microstructure of polyaromatic hydrocarbon polymers confers a distinct advantage with regard to electroosmotic drag and water permeation, parameters that depend directly on the size of the hydrophilic channels. Even at low degrees of hydration, K_{drag} is no lower than 1, since this corresponds to the lowest proton hydrate, H_3O^+. Under these conditions, the proton transfer proceeds through displacement of the hydronium ion [vehicle mechanism (107)]. In general, the K_{drag} increases with increasing membrane water content (102). The narrow channels of sulfonated poly(ether ketone)s limit collective flow of water through the membrane, and as a result, the K_{drag} in sPEEKK is lower than in Nafion by a factor of 2 to 3 (Figure 31). This discrimination is lost at very high water content, when K_{drag} for Nafion and poly(etherketone)-based membranes are almost identical. Water permeation decreases more strongly with decreasing water volume fraction in sulfonated poly(etherketone)s than in Nafion, but at high water contents it is a

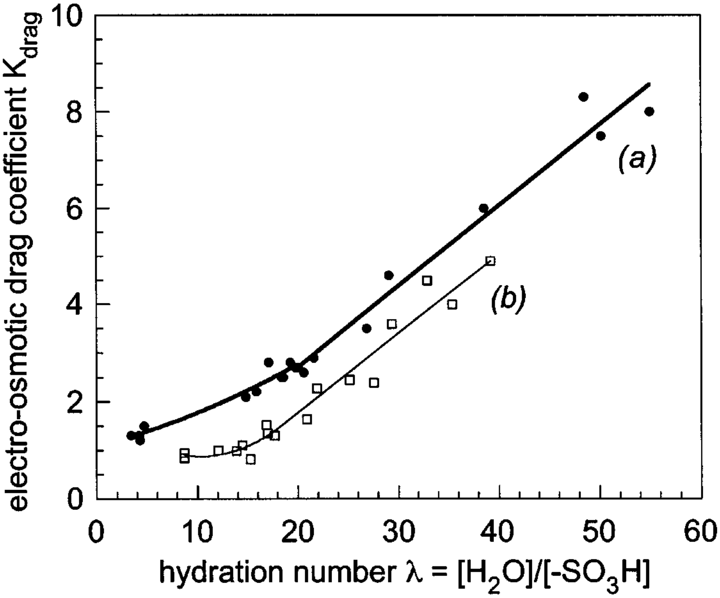


Figure 31 Electroosmotic drag coefficient of (*a*) Nafion and (*b*) sulfonated poly(ether ketone) membranes obtained from electrophoretic NMR as a function of the hydration number (M. Schuster, M. Ise, K.D. Kreuer, G. Gebel & J. Maier, in preparation).

factor 2 lower than that of Nafion. Water permeation is affected, among other factors, by channel diameter and the strength of the polymer-water interaction (7).

The strongly increased swelling of sulfonated poly(etherketone)s in water/methanol mixtures modifies the K_{drag}, which increases with increasing methanol concentration, further justifying the approaches of polymer blending and crosslinking. The water and methanol diffusion coefficients of sulfonated poly[bis(3-methylphenoxy)phosphazene] membranes measured by desorption kinetics and tracer diffusion NMR are more than an order of magnitude lower than those of sulfonated poly(etherketone)s and almost two orders of magnitude lower than those of Nafion (58, 108). On the other hand, as the microstructure of sulfonated polyphosphazenes and poly(ether ketone)s show many similarities, further experimental work is still needed to clarify the origin of any differences in the transport behavior between sPPZ and other sulfonated non-fluorinated polymers.

FUEL CELL PERFORMANCE OF NON-FLUORINATED MEMBRANES

The evaluation of sulfonated hydrocarbon polymers in fuel cells is still in an early stage, but results published by various groups, in particular on sulfonated poly(ether ketone)s and sulfonated polysulfones and blends thereof, are starting to constitute a performance database that can be compared with the earlier published results on the Ballard Advanced Materials first and second generation (BAM1G and BAM2G) membranes, corresponding to sulfonated poly(phenylquinoxaline) and poly(2,6-diphenyl-4-phenylene oxide). Each type of sulfonated membrane will have an optimal operating window of fuel cell temperature and pressure within which the membrane lifetime is highest, and even a small deviation from these conditions can lead to drastic reduction of membrane durability. It should be borne in mind that cell assembly parameters such as gasket design and compression, for example, can be the cause of premature membrane failure. In this respect, much of fuel cell hardware was developed for Nafion membranes and requires adapting for optimal lifetime of non-fluorinated systems in order to take into account their particular properties.

Sulfonated sPEEK membranes have been tested in both hydrogen and oxygen (air) in direct methanol fuel cells. Using hydrogen, for a membrane of ion exchange capacity 1.6 meq g^{-1} and 18 μm thickness, the cell voltage at 0.5 mA cm^{-2} at 90°C is 0.8 V and 0.72 V with oxygen and air, respectively (44). Such thin membranes that are neither crosslinked nor reinforced will probably not have sufficient mechanical stability in the fuel cell. sPEEK membranes of 70 μm thickness gave higher performance at 85°C than Nafion-115 under the same test conditions, in particular at high current densities when the membrane can dehydrate (44). As described above, the electroosmotic drag of sulfonated poly(ether ketone)s is lower than that of Nafion at this temperature, which should reduce drying-out at the anode side. Patent reports claim 4000 h of functioning of sPEEK with IEC

1.47 meq g^{-1} at a modest cell temperature of 50°C (51), giving a maximum power density of 0.386 W cm^{-2} at 0.52 V, whereas at 90°C at constant current density of 0.5 mA cm^{-2}, sPEEK has attained 1000 h of functioning without failure (J. Rozière, D.J. Jones, B. Bonnet & B. Bauer, unpublished data). In single-cell testing, the Parmax^{TM}-2000 membrane gives 0.8 V at 0.8 mA cm^{-2} on hydrogen–air at 90°C, with a lifetime of 200 h (V.J. Lee, private communication).

Under similar operating conditions, a cell voltage $\leq$0.3 V is given by sulfonated polysulfone at 0.5 mA cm^{-2}, for which poor electrode/electrolyte interface may be at least partially responsible (39) by contributing a high ohmic resistance. Indeed, for sulfonated polyimide membranes, some improvement in fuel cell performance was observed when impregnating the electrodes with a mixture of Nafion and sulfonated polyimide solutions to improve compatibility. At 70°C in an H_2—O_2 fuel cell, naphthalenic sPI with IEC 1.26 and 1.98 meq g^{-1} provided 0.5 and 0.6 V, respectively, at 0.5 mA cm^{-2} (76), and a lifetime of 3000 h has been obtained at 60°C, 0.25 mA cm^{-2}, with an output of about 0.63 V (78). However, membranes of high IEC are hydrolytically unstable.

In DMFC, the most promising fuel cell performance is being obtained on membranes based on sulfonated poly(ether ketone)s and their blends, and recent results indicate power density as good as that given by Nafion, with the difference that polyaromatic membranes can be restarted over several weeks without degradation at temperature >100°C. Thus non-blended sPEEK (60 μm thickness) gives a power density of 150 mW cm^{-2} at 120°C, whereas an sPEEK-PBI-PSU-NH_2 blend has given 250 mW cm^{-2} at 110°C (95). The DMFC operating at 120°C with sPEEK membranes can be shut down and started up without a change in performance over a period of more than two months (M. Dupont, J. Rozière, D.J. Jones & B. Bauer, unpublished data).

CONCLUSIONS AND PERSPECTIVES

Many sulfonated non-fluorinated polymers have been reported, and much of the available data point to high proton conductivity for the majority of the systems when hydrated. For fuel cell application, however, and as pointed out above, the satisfactory proton conductivity conferred by an adequate level of sulfonation must not be to the disadvantage of membrane mechanical strength and swelling, since these properties are essential for long-term fuel cell operation. Comparison between systems is difficult because measurements are often not made under the same experimental conditions. This is particularly true for single-cell fuel cell testing because of the many variables influencing fuel cell performance. Tables 2 and 3 summarize recent data reported on a range of candidate fuel cell membranes, in terms of conductivity, hydration number and fuel test performance, and lifetime. Most systems are well-characterized for their proton conductivity under a range of temperature and relative humidity conditions, with most frequent experimentation on fully swollen membranes. Under these conditions, most

TABLE 2 Summary of conductivity properties and hydration number of non-fluorinated polymer membranes

Polymer	IEC (meq g^{-1})	Hydration number at 25°C (membranes swollen in water) mol H_2O/SO_3H	Hydration number at 100°C (membranes swollen in water) mol H_2O/SO_3H	Conductivity at 100°C, 100% RH (S cm^{-1})	Application type	Reference
Sulfonated poly(ether ether ketone)	1.6	20	52	0.04	H_2-O_2	(6, 44)
	1.3	15	37	0.01	DMFC	[a]
	0.6–2.2	N/A	N/A	0.02–0.04	N/A	(27, 42, 45)
	2.48			0.09[b]		(49)
Sulfonated poly(4-phenoxybenzoyl-1, 4-phenylene)	2.0	9[c]	N/A	0.01	H_2-air	(47)[d]
					DMFC	[d]
Sulfonated polysulfone	1.1	15	17	0.01 (80°C)	H_2-O_2	(39)
	0.41–2.2	5–40	N/A	0.08–0.17	H_2-O_2	(71)
	0.92–1.61	5–10	5–135	0.01–0.05	H_2-O_2	(38)
Sulfonated (styrene/ethylene-butylene/styrene)	1.78	5	N/A	0.04	H_2-air	(100, 109) (110)
Sulfonated (butadiene styrene)	1.85	69	N/A	N/A	H_2-O_2	(111)
Sulfonated (ethylene styrene)	33–51 mol% sulfonation			0.07–0.10		(112)
Sulfonated naphthalenic polyimides	1.26	18–30	N/A	0.004–0.02	H_2-O_2	(76–78)
	1.63	19	N/A	0.014		(77)
	1.98	19	N/A	0.037		(76)
	N/A	10[c]	N/A	0.8 (75°C)		(85)
	1.6–2.7	N/A	[e]	0.09–0.21 (80°C)		(88, 90)
Sulfonated poly [bis(3-methylphenoxy) phosphazene]	1.2	20[c]	[f]	0.09 (65°C)	DMFC	(55, 59)
		12[c,g]		0.06 (65°C)		

(*Continued*)

TABLE 2 (*Continued*)

Polymer	IEC (meq g^{-1})	Hydration number at 25°C (membranes swollen in water) mol H_2O/SO_3H	Hydration number at 100°C (membranes swollen in water) mol H_2O/SO_3H	Conductivity at 100°C, 100% RH (S cm^{-1})	Application type	Reference
Phenylphosphonic acid functionalized poly(aryloxy phosphazenes)	1.17–1.43		N/A	0.04–0.06 (25°C)	DMFC	(61)
Sulfonimide functionalized polyphosphazene	0.99	ca. 23	N/A	0.06 (25°C)	H_2-O_2	(63)
Sulfonated PEEK-aminated polysulfone blend	1.58	N/A	N/A	0.03	H_2-air	(92)
Sulfonated PEEK-polybenzimidazole blend	1.26	9	N/A	0.03	H_2-O_2	(92)
Sulfonated PEEK-polybenzimidazole-A95 blend[h]	0.7	18	N/A	0.015	DMFC	(92, 95)
Phosphoric acid doped sulfonated polysulfone (25–50%)-polybenzimidazole (75–50%) blend	0.81[i]	[j]	N/A	0.02–0.2[k] (80% RH)	H_2-O_2 QDMFC[l]	(96) (113)

[a] M Dupont, J Rozière, D.J. Jones & B. Bauer, unpublished data.

[b] after prior heating at 75% relative humidity to 140°C.

[c] at 100% RH.

[d] V.J. Lee, private communication.

[e] water uptake (% w/w) of 56–122% at 80°C.

[f] water uptake (% w/w) 11–32% at 25°C.

[g] crosslinked polyphosphazene.

[h] A95: PSU modified with one group $-C(OH)R_2$, $R = 1,4$-phenylene-$N(et)_2$.

[i] IEC of sulfonated polysulfone component.

[j] water uptake (% w/w) of 10–19% at 25°C depends on composition of blend.

[k] depends on level of H_3PO_4 doping.

[l] quasi-direct methanol fuel cell (reformed hydrogen directly from a methanol reformer).

N/A: not available.

TABLE 3 Summary of fuel cell performance properties of non-fluorinated polymer membranes

Polymer	IEC (meq g^{-1})	Application type	Membrane thickness (μm)	Temperature/ pressure at anode/cathode (°C/bar/bar)	Current density at 0.7 V (mA cm^{-2})	Maximum power density (W cm^{-2})	Lifetime (h)	Conditions of current density/ temperature/ pressure at anode/cathode for life test	Reference
Sulfonated poly(ether ether ketone)	1.6	H_2-O_2	70	85/2.6/2.6	600	0.6			(6, 44)
	1.6		40	45/1/1	410	N/A	4300	0.05V, 50/1/1	(51)
	1.3	DMFC	60	120/1/3	135 (at 0.5 V)	0.14 (120°C)	1440[a]	[a]	[b]
Sulfonated poly (4-phenoxybenzoyl-1,4-phenylene)	2.0	H_2-air	25–50	90	0.8 V (at 0.8 A cm^{-2})	N/A	200	1 A cm^{-2} at 80°C, H_2-O_2	(47)[c]
		DMFC	25–50	110	360 (at 0.5 V)	0.30 (110°C)	N/A	N/A	[c]
Sulfonated polysulfone	1.1	H_2-O_2	20–100	80	400	N/A	N/A	N/A	(39)
	0.41–2.2	H_2-O_2			N/A				(71)
	0.92–1.61	H_2-O_2	N/A	80/4/4[d]	200	N/A	500	0.25 A cm^{-2} at 80/4/4	(38)
Sulfonated (styrene/ ethylene-butylene/styrene)	1.78	H_2-air	60	45/1/1	135[e]	0.5	N/A	N/A	(100, 109) (110)
Sulfonated (butadiene styrene)	1.85	H_2-O_2	60	N/A	327 (at 0.5 V)	.164[f]	N/A	N/A	(111)
Sulfonated naphthalenic polyimides	1.26	H_2-O_2	70	70/4/4	500	N/A	3000	0.25 A cm^{-2} at 60/3/3	(78), (76, 77)
	1.63								(77)
	1.98			70/4/4	800	N/A			(76)
Sulfonated poly[bis(3-methylphenoxy) phosphazene]	1.2	DMFC[g]	148	60	40 (at 0.5 V)	0.05	N/A	N/A	(55, 59)
Phenylphosphonic acid functionalized poly(aryloxy phosphazenes)	1.17–1.43	DMFC	N/A	N/A	N/A	N/A	N/A	N/A	(61)

(*Continued*)

TABLE 3 (*Continued*)

Polymer	**IEC (meq g^{-1})**	**Application type**	**Membrane thickness (μm)**	**Temperature/ pressure at anode/cathode (°C/bar/bar)**	**Current density at 0.7 V (mA cm^{-2})**	**Maximum power density (W cm^{-2})**	**Lifetime (h)**	**Conditions of current density/ temperature/ pressure at anode/cathode for life test**	**Reference**
Sulfonimide functionalized polyphosphazene	0.99	H_2-O_2	100	80/3/5	220	0.47	N/A	N/A	(63)
Sulfonated PEEK-aminated polysulfone blend	1.58	H_2-air	29	65/1.5/1.5	600	N/A	N/A	N/A	(92)
Sulfonated PEEK-polybenzimidazole blend	1.26	H_2-O_2	37	70/2/2	400	N/A	N/A	N/A	(92)
Sulfonated PEEK-polybenzimidazole-A95 blend[h]	0.7	DMFC	60	110/4/2.5	475 (at 0.5 V)	0.25	N/A	N/A	(92, 95)
Phosphoric acid–doped sulfonated polysulfone (25–50%)-polybenzimidazole (75–50%) blend	0.81[i]	H_2-O_2	80–110	130–190/1/1	50–150	0.33	N/A	N/A	(96)
		QDMFC[j]	80–110	200/1/1	320	0.55	N/A	N/A	(113)

[a] discontinuous operation.

[b] M Dupont, J Rozière, D.J. Jones & B. Bauer, unpublished data.

[c] V.J. Lee, private communication.

[d] composite membrane containing 7 wt% phosphoantimonic acid.

[e] no humidification.

[f] temperature not specified.

[g] DMFC data on a sulfonated crosslinked poly[bis(3-methylphenoxy)phosphazene]–polyacrylonitrile blend with effective ion-exchange capacity 1.15 meq g^{-1}.

[h] A95: PSU modified with one group –C(OH)R_2, R = 1,4-phenylene-*N*(et)$_2$.

[i] IEC of sulfonated polysulfone component.

[j] quasi-direct methanol fuel cell (reformed hydrogen directly from a methanol reformer).

N/A: not available.

of the polymer systems of Table 2 display a conductivity $>10^{-2}$–10^{-1} S cm^{-1}. The conductivity is significantly more dependent on hydration number/relative humidity than on temperature. The decrease in conductivity with decreasing water content is a direct result of the inherently lower acidity and nanoseparation of polyaromatic polymers compared with perfluorosulfonic acid systems. Fragility in the dry state and increasing softness and deformability in the wet state can to some extent be circumvented by crosslinking or by other approaches such as lamination and blending with other polymers, or by incorporating a physical support. Advantage over perfluorosulfonic acid systems is provided in functionalized polybenzimidazole and in sulfonated poly(ether ketone)s by their lower electro-osmotic drag coefficient, which acts to diminish the problem of membrane dry-out in an operating fuel cell. Little data are available on conductivity measurements above 100°C, although those on acid-doped polybenzimidazole and on sulfonated poly(ether ether ketone) are important exceptions. Tables 2 and 3 also highlight the lack of published information on long-term fuel cell operation, in particular above 80°C. Such measurements are time-consuming, and the stability of other fuel cell components can become a dominant source of performance degradation. The development of a generalized and viable means of ex situ prescreening experiments would be beneficial in assessing the suitability of a membrane for fuel cell use. The data of Tables 2 and 3 identify those systems in which most complete characterization has been made. Apart from Nafion and similar perfluorosulfonated polymer membranes, long-term fuel cell functioning at 50–80°C has so far been published on a limited number of polyaromatic and polyheterocyclic systems: 3000 h at 70°C for a sulfonated polyimide, and >4000 h for sulfonated poly(ether ether ketone) at 50°C. For operation above 80°C, membrane systems based on sulfonated poly(ether ketone)s and functionalized polybenzimidazole are among the most promising. The lifetimes mentioned above refer to hydrogen–oxygen (air) operation; until recently the lack of membranes suitable for direct methanol fuel cell operation precluded any life testing. The encouraging performance tests recently obtained with acid-base blend membranes in DMFC should be completed by durability testing. Start-up/shut down over two months of discontinuous testing at 120°C, using a membrane electrode assembly based on sulfonated poly(ether ether ketone) of active area 400 cm^2, provided a set of encouraging data in the field of DMFC.

Reported life-test experiments are performed at different temperatures and pressures and different current densities (or cell voltages). Ultimately, one of the roles of the life-test is to identify the operation conditions giving optimal performance/lifetime for a given MEA; a specific polymer membrane will be best applied within a particular temperature range and associated with a particular type of application (residential, transport, portable) and fuel (hydrogen, methanol). Thus a form of accelerated aging is simply to use experimental conditions lying outside the defined optimal operation window, but unfortunately, none of the systems described in this review has been sufficiently comprehensively studied to enable legitimate use of this approach.

Polymers functionalized other than with sulfonic acid groups (phosphonic, sulfonamide), as well as sulfonated polymers built from monomer units with sulfonic acid group placed such as to limit hydrolytic attack, are all recent and significant developments. Finally, it is expected that the most durable, performing, and viable membranes will result from fine-tuning the chemical composition and the architecture of the polymer, and tailoring of the membrane microstructure. The development of a low-cost and reliable high-temperature membrane represents a technological breakthrough with important implication for stationary and, more critically, transport applications.

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