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Proton-Exchange Membranes for Hydrogen–Air Fuel Cells

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Abstract—The review is devoted to recent advances in the development of polymer electrolytes for low-temperature (operating temperatures ~80°C) and medium-temperature (operating temperatures 160–180°C) fuel cells. At present the most used are perfluorinated polymer membranes, such as Nafion®, Aciplex®, Flemon®, and Dow®, owing to their high chemical stability and proton conductance, as well as good machinability. However, successful commercialization of fuel cells with such membranes is prevented by their high cost, as well as low proton conductance at low humidities and temperatures above 100°C. Much effort is underway to develop membranes alternative to perfluorinated ones, with emphasis on aromatic hydrocarbon polymers.

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The present work formulates principal requirements for membranes, compares physicochemical properties of various types, and summarizes results of testing various proton-conducting membranes in fuel cells.

In view of the growing thereat of global energy crisis, the problem of alternative energy sources, including fuel cells, has assumed particular significance. Over the past years stable tendency for substitution of classic liquid electrolyte fuel cells by those with polymer proton-exchange membranes (PEMFC) has been observed.

A hydrogen–air (hydrogen–oxygen) FC transforms the energy released by the oxidation of hydrogen with oxygen to water into electrical or heat energies. The principal advantage FCs offer compared with other hydrogen–oxygen energy generators is that they directly covert the most part of released energy into electricity. The performance of FCs can be above 80% [1]. It should be mentioned that the performance of already developed PEMFCs rarely exceeds 40% (which, however, is higher than the performance of heat engines). The electrochemical reaction between hydrogen and oxygen is separated in space and occurs on electrodes of the membrane electrode assembly.

Currently more and more attention has been focused on cells with alcohols (methanol, ethanol, glycerol, etc.) or carboxylic acids (most frequently, formic) as fuels. Most emphasis has been put on methanol–air FCs in view of their compact size and convenience of fuel storage. Specific characteristics of such FCs are still orders of magnitude worse that those of air–hydrogen, which is explained by the low activity of anode catalysts and high alcohol-permeability of proton-exchange membranes.

MEMBRANE ELECTRODE ASSEMBLIES OF FUEL CELLS

The principal unit of a FC is a membrane electrode assembly (MEA). In polymer FCs, it most commonly comprises a proton-exchange membrane with cathode catalyst applied on its one side and anode catalyst on the other. Collection of cathode and anode currents, feed of starting reagents, and removal of reaction products are performed via gas-diffusion layers (GDLs) that are generally made of carbon materials. Platinum black or platinum composites on a carbon (soot, carbon nanomaterials) support are used as catalysts. The latter can be applied both on the proton-exchange membrane and on GDL, or on both simultaneously.

In the course of FC operation hydrogen is ionized in the anode catalytic layer. The protonexchange membrane conducts protons to the cathode, whereas electrons come to an external electric circuit. On the cathode, protons which have traveled through the membrane, recombine with electrons and air oxygen. The rate of this reaction is proportional to the MEA active surface area, and , therefore, specific MEA characteristics (mA cm^{-2} or mW cm^{-2}) are commonly used.

$$\begin{array}{c} H_2 - 2\bar{e} = 2H^+ \text{ (anode)} \\ 4H^+ + O_2 + 4\bar{e} - 2H_2O \text{ (cathode)} \\ \hline 2H_2 + O_2 = 2H_2O \text{ (overall process)} \end{array}$$

The MEB proceeds to generate energy until hydrogen and air are fed. The theoretical emf od a hydrogen–oxygen FC at 25°C is 1.23 V and decreases according to Nernst's equation with decreasing reagent concentration (pressure) and increasing temperature. The open-circuit voltage of a real FC is rarely higher than 1 V or even lower if MEA operates under load conditions. Therefore, for high voltages a number of MEA are clamped together in a stack.

PROTON-EXCHANGE MEMBRANES

The "heart" of MEA is a proton-exchange membrane (PEM). Commonly, PEM is a polymer film with a hydrophobic main chain and acidic groups in the side chains. When contacting the polymer, water concentrates near acidic groups to form a nanosized hydrate cluster. Apart from water, different hydrated forms of mobile proton are also present in this region. Thus, the hydrophilic part of the polymer ensures effective proton transport, whereas the hydrophilic part stabilizes membrane morphology and mechanic strength.

The hydrophobic part of polymers normally contains aliphatic, aromatic, fluorinated, or nonfluorinated fragments. The most common acidic groups are sulfo groups; phosphoric acid residues are also used but rarer. Sulfonated polymers are considered to exhibit better performance in the presence of water vapors in their environment, whereas phospohrylated polymers are more stable thermally and their conductivity is less humidity-dependent.

For enhanced conductivity the hydrophilic regions of proton-exchange membranes are doped with water-soluble proton-generating substances (usually strong acids), nanosized oxides, or solid electrolytes. Sometimes proton-generating additives are introduced in the nonconducting polymer matrix. In the latter case, the hydrophilic region is formed by water coordination around the additive, after which phase separation occurs.

The principal function of PEM is to transport in the cathode region protons generated by hydrogen ionization on the anode. Therefore, the membrane conductivity should be as high as possible. Specific conductivities of about 10^{-1}–10^{-3} S cm^{-1} are considered sufficient for FC applications. Since FCs should ideally operate under conditions of wide variation of the temperature and humidity of both fuel and oxidant, in is desirable that effective proton transfer occurred just at such conditions. To avoid electric losses, the electronic conductivity should be a minimum (at least 2–3 orders of magnitude lower than ionic).

Furthermore, PEM functions as gas separator: It separates the anodic, hydrogen, side of MEB from cathodic, where air or oxygen is fed. Low gas permeability assumes particular importance when hydrogen is used under increased pressure. The gas permeability through the membrane lower than 10^{-1} ml min^{-1} cm^{-2} is considered sufficient for long-term FC functioning.

There are a number of requirements posed on PEM. For high FC performance ohmic losses across the membrane should be as low as possible, whereas the proton conductivity should be high. The mechanic strength of the membrane should be high enough to allow for pressing electrodes onto it and for operation at increased reagent pressures.

Along with water, a highly chemically active hydrogen peroxide is formed on the cathode. Therefore, the membrane should be highly resistant to oxidation and hydrolysis. Since the membrane partially absorbs water generated on the cathode, it tends to swell. Swelling is especially significant in cases where humid air is used. Excessive membrane swelling and its subsequent drying on multiple FC startup/shutdown cycles is quite an undesirable process resulting in destruction and flaking of the thin active layer deteriorative of FC characteristics. To prevent direct chemical (not electrochemical) reaction between reagents on the same electrode, the membrane should be gas-impermeable. The penetration of hydrogen into the cathode side is equivalent to leakage current, and it should be minimized to improve FC performance.

COMMERCIAL PROTON-EXCHANGE MEMBRANES

At present the most widespread is the perfluorinated ion-exchange membrane Nafion developed by DuPont in 1966. Accessible FC membranes almost all are versions of Nafion. Materials on the basis of such polymers are readily manufactured and exhibit fairly good characteristics at operating temperatures below 90°C. However, the intrinsic proton conductivity of Nafion membranes is extremely low, and the effectiveness of proton transfer in them depends on the quantity of water they have absorbed from air.

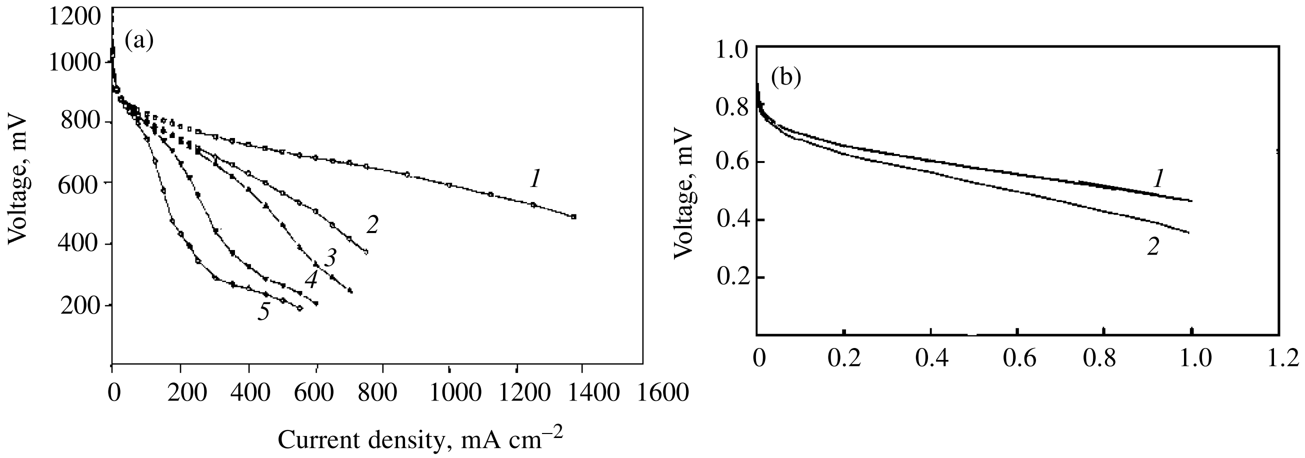


Fig. 1. Effect of CO admixtures in hydrogen on the voltage–current characteristics of fuel cells: (a) Nafion membrane, 80°C, P_{H_2} 0.22 MPa, P_{O_2} 0.24 MPa [2]. Content of CO, ppm: (*1*) 0 and (*2*–*5*) 50; (b) PBI/phosphoric acid membrane; 160°C; atmospheric pressure; reformate composition: 70% H_2, 29% CO_2, and 1% CO [3]; (*1*) hydrogen/air, and (*2*) reformate, 1% CO/air.

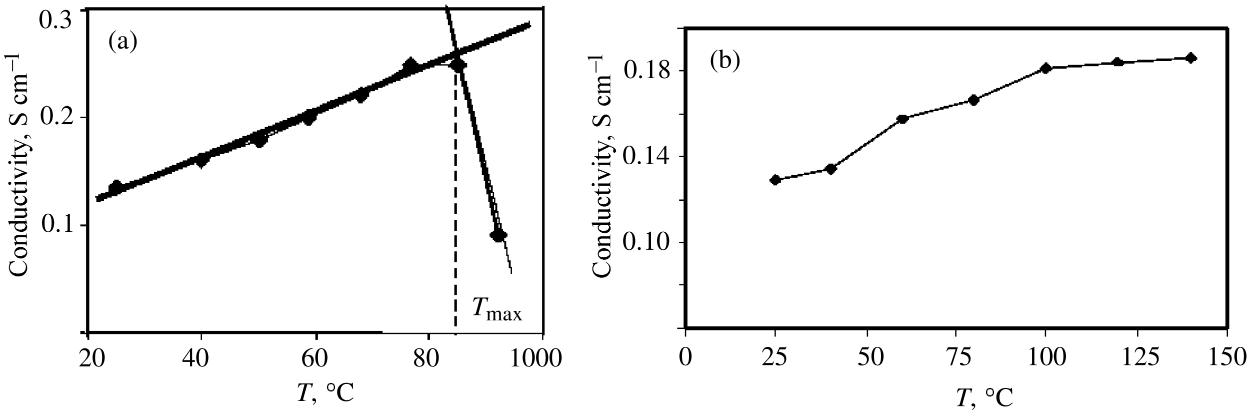
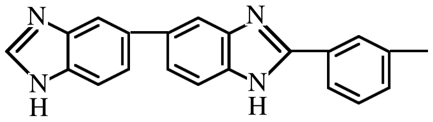


Fig. 2. Temperature dependences of the proton conductivity of (a) Nafion-117 and (b) PBI/phosphoric acid membranes [3].

Therefore, such membranes should be operated under conditions of continuous wetting and hydrostating, which necessitates additional facilities and raises cost of electrochemical generators. It should also be noted that with hydrogen generated, say, by reforming (it is this hydrogen that is proposed to be employed in vehicles) a serious problem of catalyst poisoning with CO admixtures arises [1]. Figure 1a shows the effect of CO admixtures on the voltage–current characteristics of a FC with a Nafion membrane. It is seen that CO admixtures adversely affect the FC characteristics. Increased temperature can generally improve the performance of platinum catalysis (Fig. 1b). However, the proton conductivity of Nafion membranes above 90°C decreases dramatically (Fig. 2a), which makes such membranes impossible to use at elevated temperatures. The membranes themselves are very difficult to manufacture and quality membranes are expensive.

Another commercially available membranes that can be used at temperatures of up to 200°C are those made of polybenzimidazole (PBI) doped with phosphoric acid:



Phosphoric acid forms an acid–base complex with the polymeric matrix (PEMEAS, Celtec Division). The advantages of such membranes over Nafion membranes are their high proton conductivity in the absence of wetting (Fig. 2b) and high thermostability (up to 600°C). The operating temperature range of such MEA is 160–180°C. In this temperature range, hydrogen with a fairly high CO content can be used. Figure 1b shows the voltage–current characteristic of a FC made of Celtec-P 1000 PBI/orthophosphoric

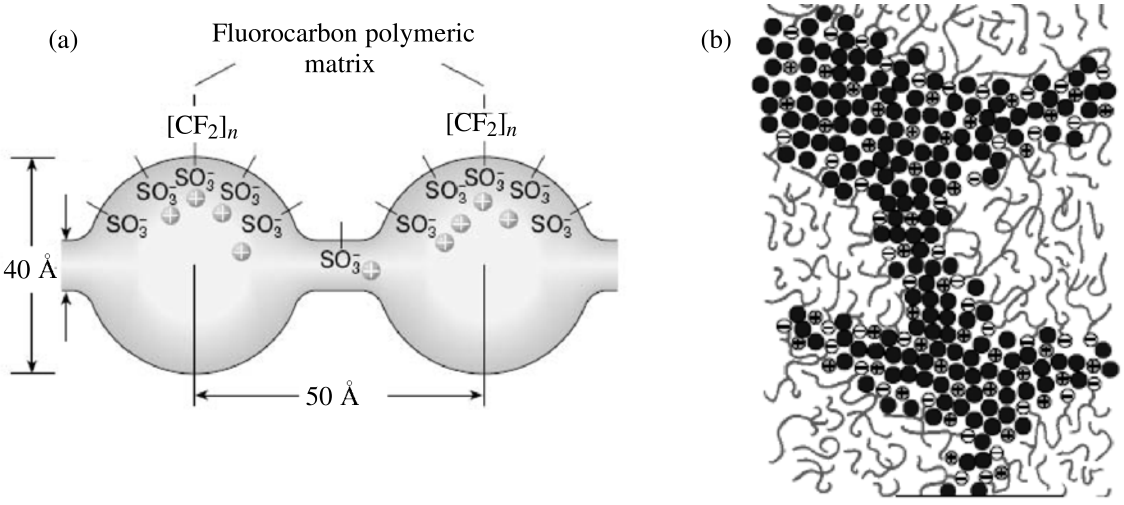


Fig. 3. Structural models of a Nafion membrane: (a) cluster–channel and (b) channel [4].

membrane electrode assemblies. As seen from the figure, even if hydrogen contains 1% of CO, the characteristics at such operating temperatures and low current densities deteriorate only slightly.

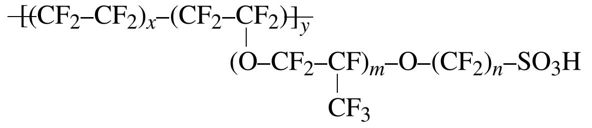
The principal problem is that membranes “are afraid” of liquid water that destroys the acid–base complex and washes out phosphoric acid to the catalytic and gas diffusion layers, which results in partial block of gas pore, this destroying bipolar plates and gas inlet system.

Removal of phosphoric acid from the polymeric matrix decreases the proton conductivity of the membrane. To avoid condensation of water vapor in the cathode area, the fairly laborious FC shutdown procedure is employed, which involves unloading, purging with dry argon to remove water vapor, sealing, and cooling. Clearly, such a laborious procedure requires additional equipment, which strongly increases the cost of electrochemical generators on the basis of electrode assemblies with a PBI/phosphoric acid membrane.

SULFONATED POLYMER MEMBRANES

Perfluorinated Unsaturated Copolymers

Nafion is a copolymer of tetrafluoroethylene and a monomer comprising perfluorinated vinyl ether side chains with terminal sulfo groups:



$$\left[(CF_2{-}CF_2)_x{-}(CF_2{-}\underset{\displaystyle (O{-}CF_2{-}\underset{\displaystyle CF_3}{\underset{|}{C}F})_m{-}O{-}(CF_2)_n{-}SO_3H}{\underset{|}{C}F_2})\right]_y$$

The ratio between the two comonomers can vary, thus varying the bulk capacity of the membrane. Industrially produced are membranes with equivalent weights (EW) ranging from 900 to 1300 g mol^{-1}, but the most widespread are those with EW 1000 and 1100 g mol^{-1}. Such equivalent weights ensure simultaneously high conductivity and reasonable mechanic properties. The thickness of the membranes may vary from 50 to 250 μm. The maximum proton conductivity of such membranes at 30°C is 0.2–0.05 S cm^{-1}, depending on equivalent weight (for example, the conductivity of Nafion with EW 1100 is 0,1 S cm^{-1}).

There are two models of the proton transport in a Nafion membrane. According to Girke’s cluster–channel model (Fig. 3a), the membrane polymer matrix is self-organized so that water-filled clusters are formed, with sulfonated side chains turned to them. The clusters are separated by narrow channels which serve for proton transport. If the water content is low, the channels break, thus preventing proton transport.

The other model is channel, according to which membrane transport channels filled with water and sulfo groups are separated by hydrophobic polymeric chains (Fig. 3b). As the water content of the membrane decreases, the channel get narrower, and the proton conductivity decreases.

The above models imply that membranes accomplish proton transport only in the presence of a sufficient amount of absorbed water (Fig. 4). At temperatures above 90°C, the membrane loses water, and its conductivity sharply decreases (Fig. 2a).

Along with Nafion membranes, a number of structurally related proton-exchange membranes are produced, such as Acipex (Asahi Chemical Company)

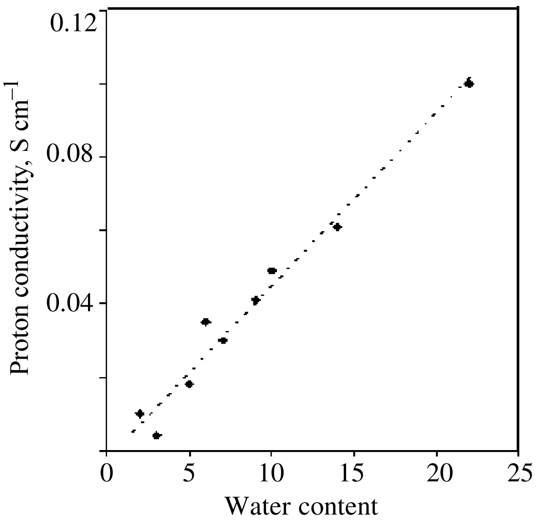


Fig. 4. Dependence of the proton conductivity of Nafion-115 membrane on water content (number of water molecules per one sulfo group) [5].

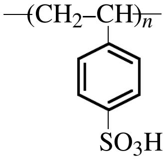
and Flemon (Asahi Glass Company). Dow Chemicals has developed a membrane that differs from Nafion in that its side chains are shorter and bound to the main polymer chain by ether groups. This polymer has a lower equivalent weight but preserves good mechanic properties.

Fuel cells with the above-mentioned membranes show close voltage–current characteristics (Fig. 5).

Sulfonated Polystyrene and Its Analogs

The first really operating FC generator was a General Electric 1-kW generator which was used as a source of electric power and drinking water for astronauts participating in the Gemini Project in mid-1960s. However, the endurance of this device proved to be limited because of the chemical degradation of sulfonated polystyrene membranes under the action of peroxides formed on the cathode. For such membranes, the Ballard Power Systems Company developed a new series of sulfonated copolymers of α,β,β-trifluorostyrene and substituted α,β,β-trifluorostyrene.

Such polymers are known as BAM3G (Ballard Advanced Membrane Third Generation) polymers and have the following chemical formula:



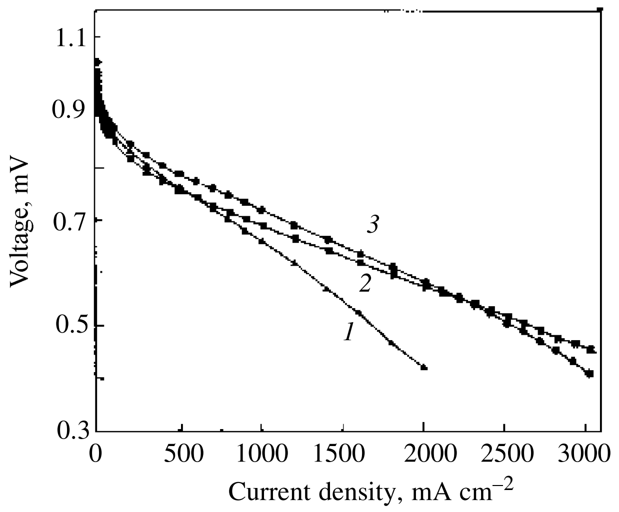


Fig. 5. Voltage–current characteristics of fuel cells with (*1*) Nafion-115, (*2*) Dow, and (*3*) Aciplex-S® 1004 membranes.

These membranes have a low equivalent weight (375–920 g mol^{-1}) and much higher swelling degrees compared to Nafion and Dow ones. When tested in fuel cells, BAM3G membranes show characteristics close to those of Nafion and Dow membranes at low current densities and better characteristics at current densities higher than 0,6 A cm^{-2} (Fig. 6) [6].

Regretfully, there is scarce information on these membranes in the literature. In particular, no data on their thickness, chemical composition, and mechanic strength are available. Whether BAM3G membranes

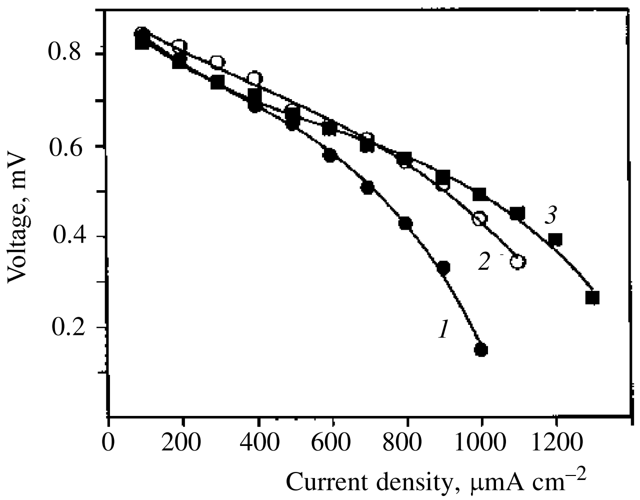


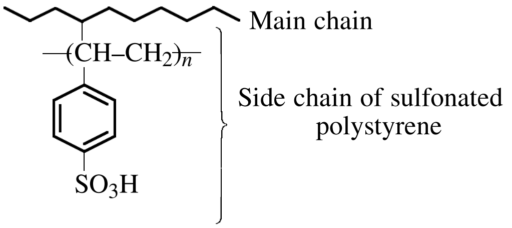
Fig. 6. Voltage–current plots for fuel cells with (*1*) Nafion-117, (*2*) Dow, and (*3*) BAM3G01 membranes [6].

can be used without moistening or at temperatures above 120–300°C is also unknown.

Radiation Grafting of Sulfonated Polystyrene

An alternative and a relatively low-cost mode of production of proton-exchange membranes involves grafting of ionogenic groups to a fluorinated polymer matrix. The radiation grafting technique is widely applied for modifying polymers with the aim to alter their physicochemical properties [7–12]. Radiation-grafted membranes are produced from commercial films by a threestage procedure. The first stage involves irradiation of a polymer film with electrons or γ rays to generate free radicals in the polymer material. Further on side chains are linked to the polymer backbone, and then they are sulfonated. It is stated that the production of such membranes is economically more feasible than that of Nafion. This technique allows modification of fluorinated materials [13–16], but the resulting materials are difficult to compare because of various conditions of their production and various grafting degrees.

Most radiation-grafted membranes contain poly(styrenesulfonic acid) in the side chains:



Most commonly, the polymer backbones are various fluorinated polymers, including poly(vinylidene fluoride), copolymer of vinylidene fluoride and hexafluoropropylene with varied comonomer molar ratios, copolymer of tetrafluoroethylene and hexafluoropropylene, etc. [17–19].

The proton conductivities of the membranes with a high degree of grafting compare with those of Nafion membranes (up to 0.11 S cm^{-1} at 100% humidity and room temperature [17, 18]). The same is true of the hydrogen permeability [19]. The proton conductivity is directly related with the ability of the membrane to absorb water, which, in its turn, is much dependent on the properties of the polymer matrix [17]. A considerable drawback of such membranes is their tendency for swelling: Their swell much stronger than Nafion membranes [18].

It should be noted that radiation-grafted membranes of this type are not free of the main drawback of poly(styrenesulfonic acid): They degrade during operation because of the attack of side chains with peroxides formed on the FC cathode. This makes such radiation-grafted membranes of limited usefulness in fuel cells.

Other Sulfonated Polymers

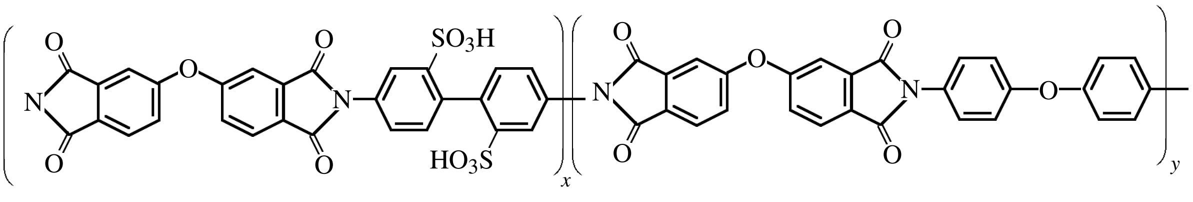
Such polymers as poly(ether ketones) (PEK), poly(ether ether ketones) (PEEK), polysulfones (PS), poly(ether sulfones) (PES), and polyimides (PI), are especially candidates for FC applications in view of their high chemical and thermal stability. mechanical strength, and wide variety of possible chemical structures, including partially fluorinated. Sulfo groups can be introduced in polymers in two ways: sulfonation of a ready polymer or polymerization of sulfonated monomers. Aromatic polymers are readily sulfonated with sulfuric acid, chlorosulfonic acids, and sulfur trioxide and its complexes.

Irrespective of the sulfonation procedure, the content of sulfo groups in the polymer should always be controlled, since, on the one hand, increased content of sulfo groups in the polymer increases the proton conductivity of the membrane, but, on the other, enhances the solubility of the polymer in water and the capacity of the membrane for swelling, thus deteriorating its mechanic characteristics.

Sulfonated Polyimides

Sulfonated polyimides (SPI) are produced by polycondensation of aromatic diamines with dianhydrides [20] of phthalic (**A**) and naphthalic (**B**) acids to form phthalic and naphthalic polyimides, respectively [21].

The hydrogen permeability of membranes of this type is three times as low as that of Nafion-117 membranes [22]. It was shown that sulfonated naphthalic polyimides compare well with Nafion in fuel cells at least within 3000 h operation. At the same time, the characteristics of membranes on the basis of sulfonated phthalic polyimides deteriorate dramatically after 70 h of operation. It is suggested that hydrolysis of phthalimide structure leads to cleavage of polymer chains and embrittlement of membranes. Since six-membered naphthalic polyimide cycles are much more resistant to hydrolysis, their chemical structure better fits the requirements to FC membranes. The use of such polymers is hindered by their extremely poor solubility. Thus, they are only soluble in chlorophenol. To go around this problem, one should slightly modify the chemical structure of the polymer; for example, with 2,2'-diamino-3,4'-diphenyl



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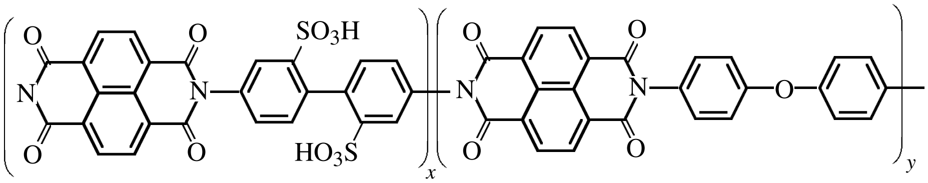

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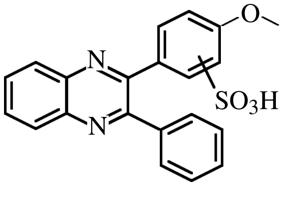
ether as nonsulfonated ether, a polymer soluble in *m*-cresol was obtained [23].

Sulfonated Polyphenylquinoxalines

Ballard Advanced Materials has investigated this polymer family over the past decade. The first series of polymers on the basis of polyphenylquinoxalines (PPQ), designated as BAM1G, was produced by direct sulfonation of PPQ:



BAM1G membranes of various thickness (40–120 μm), both dry and wet, exhibit good mechanic properties. BAM1G membranes with EW 390–420 compare well with those of Nafion117 but degrade in FC within a fairly short time (about 350 h) [24]. Obviously, these membranes cannot compete with perfluorinated ones.

Sulfonated Poly(Aryl Ether Sulfones)

Poly(aryl ether sulfones) involve phenyl rings intervened alternating ether and $-SO_2-$ bridges. Most study has been given to commercially available Udel poly(aryl ether sulfones) (PAES) (Fig. 7a) and Victrex poly(ether sulfones) (PES). Poly(aryl ether sulfones) can be partially fluorinated, like BAM2G membranes produced by Ballard Advanced Materials.

Sulfonation of PAES was thoroughly studied [25, 26] to show that a polymer containing more than one sulfo group per one monomeric unit is impossible to obtain [26]. Using a milder sulfonating agent (trimethylsilyl chlorosulfonate) instead of hard (chlorosulfonic acid) allows one to avoid polymer destruction or cross-linking. However, under mild conditions a limited degree of sulfonation can only be attained [27].

Direct sulfonation of PAES results, depending on conditions, in two different arrangements of sulfo groups: ortho to the ether bridge of bisphenol **A** (Fig. 7a) [28] or in the diaryl sulfone part (Fig. 7b) [29] which is the most resistant to hydrolysis. In the first case, membranes on the basis of sulfonated PAES at sulfonation degrees of higher than 30% are water-soluble and thus are unsuitable for FC applications. Upon sulfonation into the diaryl sulfone part, water-soluble membranes are formed at sulfonation degrees of higher than 65% [29]. Attempted cross-linking of such membranes to make them less water-soluble was reported [30]. However, cross-linked membranes get brittle at low humidities and show unsatisfactory results on testing in fuel cells.

Sulfonated PES membranes (Fig. 7d) are water-insoluble. With PES, the proton conductivity close to that of Nafion membranes is attained at sulfonation degrees of about 90%. However, such membranes exhibit strong tendency for swelling (swell 3 times as strong as Nafion at room temperature); the swelling degree increases sharply at 80°C, which impairs the mechanic properties [28]. To solve this problem, cross-linking with diamines was applied, which decreased not only the swelling degree, but also conductivity [28].

When tested in FC, water-insoluble membranes on the basis of sulfonated fluorinated PAES first exhibit better characteristics than Nafion-117 and Dow membranes [24], but their endurance is limited to nearly 500 h.

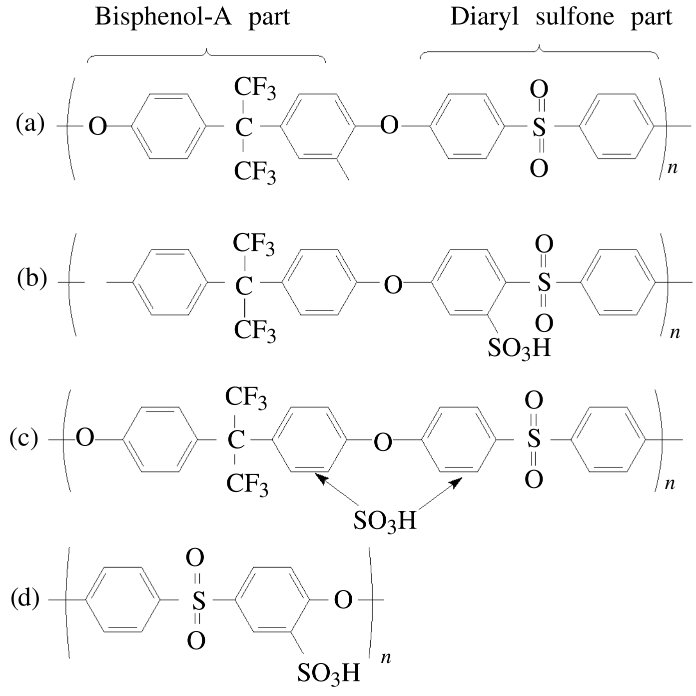
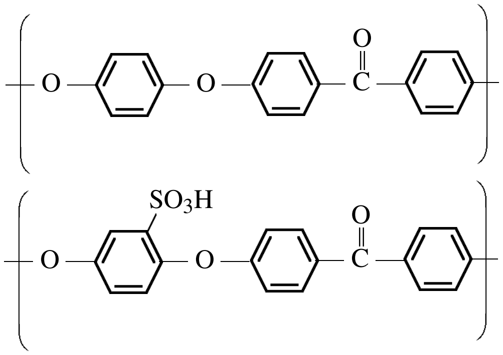


Fig. 7. Various poly(aryl ether sulfones): (a) PAES sulflonated in the *ortho* position with respect to the bisphenol A bridge [28]; (b) PAES sulfonated in the diaryl sulfone moiety [29]; (c) BAM2G polymer; and (d) sulfonated PES.

Sulfonated poly(ether ether ketones) (S-PEEK)

Poly(ether ether ketones) form a class of aromatic semicrystalline polymers whose backbone is formed by phenyl rings intervened by ether and carbonyl (–CO–) groups:



Such polymers are highly thermally and chemically stable and sparingly soluble in organic solvents. Sulfonation decreases their crystallinity but increases solubility [31, 32]. Nonsulfonated polymers are stable up to 500°C and sulfonated, up to 240°C. There are various procedures for PEEK sulfonation [33–35]. Since the sulfonation reaction is electrophilic, in PEEK the sulfo group is successfully inserted into the aromatic nucleus between two ether bonds because of the high electronic density on this nucleus. One monomeric unit can take up only one sulfo group. Chlorosulfonic acid is an unsuitable sulfonating agent, since it destroys PEEK [36]. Therefore, concentrated sulfuric acid is most commonly used for these purposes [37, 38]. In the latter case, the sulfonation degrees reach 30–100%, and no polymer cross-linking and degradation are observed [39]. However, in the heterogeneous sulfonation of PEEK with sulfuric acid, one cannot ensure random alternation of sulfonated and nonsulfonated polymeric units at sulfonation degrees of lower than 30% [38]. The arrangement of sulfo groups on sulfonation can be successfully controlled using as starting material a random polymer obtained by copolymerization of monomers susceptible and insusceptible to sulfonation [40]. The use of such directed molecular design techniques make it possible to avoid additional and sometimes unpredictable macromolecular reactions in the course of sulfonation.

The solubility of sulfonated poly(ether ether ketones) depends on their sulfonation degree. Thus, at the sulfonation degree of 30%, the polymers are soluble in DMSO, DMF, and *N*-methylpyrrolidone. At the sulfonation degree of 70% the polymer is soluble in methanol, and at sulfonation degrees of higher than 70%, in water. The water absorptivity of S-PEEK at the sulfonation degree of 65% and humidity of 100% is 8%. At the same sulfonation degree and humidity, the conductivity of S-PEEK is low, about 10^{-5} S cm^{-1} [41]. At high sulfonation degrees, S-PEEK membranes have high swelling degrees; to decrease them, chemical cross-linking or agents forming strong hydrogen bonds are applied [42]. For example, Cui et al. [43] obtained membranes on the basis of mixtures of S-PEEK with amino derivatives of poly(aryl ether sulfone), polyamides, and poly(ether imines). The swelling degree of such membranes can be decreased due to formation of strong hydrogen bonds between polymer molecules or of polysalts, which, however, partially blocks sulfo groups and adversely affects the proton conductivity of the membranes. Sulfonated polyphosphazenes.

Polyphosphazenes are a new class of polymers which hold much promise for FC applications due to their thermal and chemical stability and feasibility for structural modification via introduction of various side chains in the main –P=N– chain. Proton-exchange membranes on the basis of sulfonated polyphosphazenes may well serve as an alternative for perfluorinated membranes. However, there has been little work on synthesis and properties of such membranes. The problem consists not in the preparation of water-soluble polymers or their hydrophilicity/hydrophobicity ratio [44]. One of the main synthetic routes to such polymers involves reaction of poly(dichlorophosphazene) with a various nucleophilic agents to form highmolecular organic polymers whose properties are much dependent on the nature of side substituents.

Allcock et al. [45] sulfonated aryloxy- and arylaminophosphazenes with concentrated sulfuric acid. 1,3-Propane sulfone can also been used as sulfonating agent, but the resulting sulfonation degree is fairly low [46]. Aryloxypolyphosphazenes can also be sulfonated with sulfur trioxide in dichloromethane. As shown by Monotonery et al. [47], when the SO_3/monomeric unit molar ratio is lower than one, C-sulfonation occurs exclusively with subsequent attack on the polymeric chains to form an $\equiv N \rightarrow SO_3$ complex, whereas at increased SO_3 amounts, other processes occur along with C-sulfonation.

Sulfonation of polyphosphazenes generally forms water-soluble polymers [44]. At the same time, water-insoluble membranes can be prepared by means of cross-linking followed by heterogeneous sulfonation [48]. Water-insoluble membranes can also be obtained both via controlled alkylation or sulfonation of the polymer.

ORGANIC–INORGANIC COMPOSITE MATERIALS FOR POLYMER ELECTROLYTES

One of the ways to improving mechanic and thermal properties and decreasing dependence of electrotransport characteristic on humidity is to prepare composite PEM materials with nanosized inorganic additives dispersed in the polymer matrix. Such known proton-exchange polymers as Nafion, sulfonated polystyrenes and polysulfones, polybenzimidazoles, and others are used as matrices. All inorganic additives cab be divided into two big groups: nanosized oxides or salts that do not generate protons and keep strongly structurally bound water (silicon, titanium, zirconium, aluminum oxides, zeolites, etc.) and inorganic solid proton-exchange electrolytes (most frequently, heteropolyacids, zirconium phosphates, and cesium hydrosulfate). Whereas additives of the first type work mostly to improve transport of protons generated on the polymer electrolyte surface, the role of second-type additives is more intricate: They strongly keep the structural water, and proton transfer and generation of additional protons involved in ionic transport in the composite material occur in their crystallite bulk.

Nanostructured Oxide Materials

The most studied nanosized oxide composites are Nafion–SiO_2 systems. The sol–gel procedure for introduction of perfluorined membranes in narrow hydrophilic channels, devised by Mauritz [49], was further developed in a number of works. Techniques for introduction of lowmolecular organosilicon compounds in a polymer film with subsequent hydrolysis in the hydrophilic channel or for preparation of films of composite materials by pouring a dispersion containing organosilicon compounds on Nafion [50–52].

Regardless of increased water content, the conductivity of hybrid membranes in moist media decreases with increasing SiO_2 content and is lower than the conductivity of unmodified membranes. However, in the absence of moisture in the environment and at elevated temperatures (above 80°C), modified membranes exhibit a higher conductivity than unmodified Nafion, reaching 10^{-4}–10^{-7} S cm^{-1} at 100°C. Moreover, some composite membranes become "self-moistening" due to back diffusion of water formed in the cathode region [53]. For improved conductivity of composite membranes, nanosized platinum was suggested to introduce, along with SiO_2, to the polymer matrix for oxidation of hydrogen with oxygen into water [54].

Composite membranes, due to their low alcohol permeability and higher working temperature, are candidates for methanol fuel cells. Thus, the specific power of the element at 145°C and 0.5 V can attain 350 mA cm^{-2}.

Introduction of other nanosized oxides in proton-exchange polymer matrices leads to the same results as with silicon dioxide. Thus, as shown in [55], titanium dioxide and tungsten trioxide additives decrease the degradation temperature of the membrane. All oxides in methanol fuel cells operated at 110°C and 70% RH enhance membrane conductivity at decreased humidity in the following order:

$$\text{Nafion/SiO}_2 > \text{Nafion/WO}_3 > \text{Nafion/TiO}_2 > \text{Nafion}.$$

Nanosize Carbon Materials

Over the past years nanosize materials came into use as additives to proton-exchange membranes. Thus, Nafion-117 membranes were doped with a mixture of fullerene and fullerenol [56]. Such membranes, compared to the starting materials, stronger kept water and exhibited enhanced conductivity at decreased humidity. In [57], carbon nanotubes were used to improve the mechanic properties of Nafion. The transport characteristics of 50-μm composite membranes containing 1% of nanotubes were close to those of Nafion NRE-212, and the mechanic characteristics were much better.

Crystalline Solid Electrolyte Materials

Among polymers doped with crystalline electrolytes, systems containing zirconyl phosphates (ZrP) and heteropolycompounds deserve mentioning. Crystalline zirconium hydrophosphate in the form $Zr(HPO_4)_2 \cdot H_2O$ [58] and its related layered structures exhibit a high proton conductivity at room temperature (more than 10^{-2} S cm^{-1}) and preserve it up to 300°C [59, 60]. Introduction of such compounds into a proton-exchange matrix enhances thermal stability of the latter. Thus, the conductivity of the Nafion–ZrP system at 100°C and 100% humidity is 0.1 S cm^{-1} [61] and that of the S-PEEK–ZrP system in the same conditions is 0.01 S cm^{-1} [62]. Properties of hybrid membranes on the basis of sulfonated poly(ether ketones) and amorphous SiO_2 and zirconium phosphate particles (zirconium sulfophenyl phosphate and zirconium phosphate) as a function of temperature and humidity were studied. The presence of particles always favored increased proton conductivity at 100°C. A detailed review of the preparation and properties of proton-exchange inorganic and organic–inorganic systems containing inorganic phosphates is given in [63].

Keggin-type heteropolyacids, like $H_3PW_{12}O_{40} \cdot nH_2O$ and $H_4SiW_{12}O_{40} \cdot nH_2O$, with a high water content exhibit the highest recorded room-temperature conductivity among solids. However, their conductivity is strongly dependent on ambient conditions, since it is associated with the presence in the structure of crystal water which is readily lost at decreased ambient humidity and increased temperature. Heteropolyacids are highly catalytically and electrocatalytically active in the solid phase and in solution. Testing of solutions of these acids in fuel cells showed that the electrode–electrolyte boundary in such systems is much less sensitive to CO admixtures in hydrogen [64]. Fuel cells on the basis of solid heteropolyacids were prepared [65], but they exhibited poor mechanic properties. Introduction of heteropolyacids into a polymer matrix was found to hold greater promise.

Composite membranes in the Nafion–heteropolyacid ($H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$) with particles of about several μm were synthesized and studied in [66]. The resulting membranes all possessed enhanced proton conductivity at temperatures of above 100°C at low humidity. Molybdenum-containing compounds proved to be susceptible to redox reactions in fuel cells. Some authors observed gradual washing out of heteropoly compounds due to its dissolution in water formed in the FC cathode region. To stabilize membranes, protons were partially replaced with Cs^+, NH_4^+, Rb^+, and Tl^+ ions. It was shown that such additives prevent washing-out of heteropolycompounds from membranes with water and that the membranes have a low hydrogen permeability even at a 28-μm thickness, and their conductivity at 120°C and 35% RH is 1.6×10^{-2} S cm^{-1}. The MEA of a hydrogen–air FC with a Cs^+-stabilized membrane showed good characteristics at 120°C and 35% RH [67].

In [68], the composition of Nafion–SiO_2–$H_3PW_{12} \cdot O_{40}$ composite membranes was optimized. The conductivity of the membranes was better compared with Nafion-117, and tests in direct methanol fuel cells showed that such membranes are much more effective than nondoped membranes (at 80°C, the open circuit voltage is 0.75 V against 0.68 V for Nafion, and the maximum power is 70 mW cm^{-2} against 62 mW cm^{-2} for Nafion). As shown in [65], Nafion–SiO_2 hybrid membranes doped with phosphotungstic and silicotungstic acids [65] can work at 145°C in methanol fuel cells.

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