Russian Chemical Reviews **79** (2) 101 – 117 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n02ABEH004070

Polymer membranes for fuel cells: manufacture, structure, modification, properties

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Abstract. The state of the art in the field of synthesis, structural modification and practical use of polymer membranes for fuel cells is analyzed. Synthetic methods, physicochemical characteristics and specific features of their composition, microphase separation and the structure of water ionic channels are considered for different types of proton-conducting materials together with the approaches to enhancement of their operational characteristics. Attention is focused on Nafion and other fluorinated polymers as the materials that occupy the leading position as regards the design level and the broad use in small sized fuel cells. The newest developments in the field of alternative non-fluorinated membrane materials are also discussed, particularly, polycondensation polymer systems and hybrid organic-inorganic polymers. The bibliography includes 148 references.

I. Introduction

Nowadays, the industrially developed countries face the aggravated problems associated with production, distribution and environmental consequences of the use of various raw materials in the power and transport industries. These problems have become an object of international policy and an issue at the Group of Eight (G8) Summits.[1]

The release of vast amounts of toxic wastes as a result of conventional methods of consumption of energy resources has a negative effect on the environment, causes irreversible climatic changes, *etc*. The decisions taken within the framework of the agreement on cooperation between the European Community and the USA on the strategy of the development and the use of the concept of hydrogen energetics and fuel cells were directed at surmounting the aforementioned environmental problems.[2] This agreement has given a substantial impact on the studies aimed at energy saving and the development of hydrogen power engineering, which included studies on the use of solid polymer fuel cells (SPFC).

The activation and extension of studies in this field led to a sharp increase in the number of publications; reviews have appeared that give new insight into this problem.

Fuel cell (FC) is a chemical power supply, its long-term and permanent work is ensured by uninterrupted delivery of new portions of reagents to its electrodes and removal of the reaction products.

A possibility of direct production of electricity by a chemical reaction was first demonstrated by Sir W Grove in the 1830s. Throughout the next century, the development of the relevant theoretical concepts was carried on and different types of fuel cells were developed. In the USSR, the most substantial contribution to this field was made by Davtyan who published the world's first monograph on FC as early as 1947.

The manufacture of a fuel cell in 1962 with a polymer membrane based on sulfonated polystyrene was a significant event. This marked the onset of the first active stage in the research on the development of SPFC and, correspondingly, of polymer membranes required for their operation.[3]

Fuel cells and power units on their basis are advantageous over heat generators in

— the possibility of decreasing hazardous discharge by more than one order of magnitude;

— high efficiency (up to 90%) of fuel conversion into electric energy;

— silent operation;

— the possibility of using various fuel types.

Figure 1 compares graphically the levels of exhausts from different types of power generators.[4]

Hydrogen (from different sources) was used most often as the fuel for FC with oxygen or air as oxidants. Several classifications of FC are known of which one is based on the nature of the electrolyte used (Table 1).[5,6] All the units listed use oxygen or air as the oxidant; however, in alkaline FC, air should be thoroughly cleaned from CO_2 to prevent electrolyte carbonization. In systems based on polymer electrolytes, pure oxygen is used in order to enhance the FC efficiency.

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Received 24 April 2009
Uspekhi Khimii **79** (2) 117 – 134 (2010); translated by T Ya Safonova

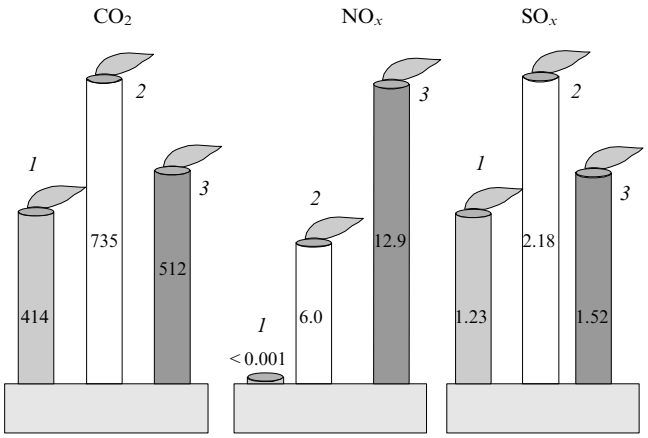


Figure 1. Comparison of the waste level [in g $(hp)^{-1}$ h^{-1}] from different types of power generators.[4]
(*1*) Ship FC, (*2*) battery of gas-turbine generators, (*3*) battery of diesel generators.

It is difficult to prevent degradation of catalyst layers on electrodes and disintegration of a porous matrix used for the H_3PO_4 immobilization, which is a drawback of phosphoric acid-based FC. The problem of retention of the carbonate melt within a porous matrix and insufficient stability of construction materials at the working temperatures in the range of 700 – 1000 °C limits the use of molten carbonate FC. By contrast, an increase in the service temperature is desirable for membrane FC, because this reduces sorption of CO contained in technological hydrogen on a platinum catalyst, which prevents poisoning of the latter. Membrane systems of the Nafion type are inefficient at high temperatures, which is apparently associated with the inability of the membrane to retain water under these conditions rather than with the thermal instability of the polymeric electrolyte as such.

The efficient operation of all types of FC is determined by the following common factors:

— specific design that can subject to perfection;
— catalyst efficiency;
— characteristic features of electrolyte operation.

The electrolyte is one of the principal components of a FC, it ensures ion transport between the electrodes and, at the same time, prevents fuel transfer from the anodic region to the cathodic one and diffusion of the oxidant in the opposite direction, which excludes their direct reaction. Oxide-based solid electrolytes and polymer electrolytes are preferred to liquid electrolytes, because they provide wider potential in the FC design and operation.

At present, the most impressive success was achieved in the development of FC based on polymer electrolytes in the form of thin membranes. The progress along this line is due to wide application of polymer membrane FC mainly as miniature power sources. The use of solid-oxide FC is apparently associated with the construction of high-power units in which the heat loss to the environment can be minimized.

In Russia, the agreement on hydrogen power engineering concluded between the Russian Academy of Sciences and the Mining and Metallurgical Company Norilsk Nickel

Table 1. Major types and some characteristics of fuel cells.[5,6]

FC type	Electrolyte	Working temperature /K	Fuel	Service life /h	Manufacturers, power	Problems
Alkaline	~30% KOH	353 – 370	pure H_2	up to 10 000	United Technology Co., Ural Electrochemical Plant in cooperation with S P Korolev RSC 'Energiya', 27 and 100 kW	sensitive to poisoning impurities in H_2; requires Pt
Phosphoric acid	98% H_3PO_4	463 – 490	technical-purity H_2	up to 50 000	United Technology Co., Toshiba, IFC, 12 kW – 11 MW	requires Pt; cathode corrosion; sensitive to poisoning impurities
Molten carbonate	Li_2CO_3 + K_2CO_3	893 – 923	H_2 + CO, CH_4, *etc*.	up to 20 000	USA, Japan, Germany, the Netherlands, Russia (Institute of High-temperature Chemistry UB RAS)	cathode corrosion; electrolyte migration; changes in electrode humidity
Solid oxide	ZrO_2 + Y_2O_3	1073 – 1273	H_2 + CO, CH_4, *etc*.	up to 60 000	USA, Japan, Germany, Italy, France, Russia [Institute of High-temperature UB RAS, RFNC,[a] The Special Boiler Design Plant 'Kotlostroenie' (St Petersburg)], ~100 kW	interaction between solid layers; technological problems
Solid polymer	Polymer membrane (Nafion, *etc*.)	343 – 363	H_2, MeOH	up to 20 000 – 30 000	Du Pont, Ballard Power Systems, up to 500 kW	requires Pt; highly sensitive to poisoning impurities and membrane wetting

[a] Russian Federal Nuclear Centre — E I Zababakhin All-Russian Research Institute of Technical Physics (Snezhinsk).

gave a substantial impact to the intensification of studies in the field of membrane FC.[7] In accordance with this agreement, the research programme includes a wide spectrum of studies on hydrogen power engineering and fuel cells including the development of proton-conducting polymer electrolyte membranes (PEM) for FC, the perfection of catalytic systems on electrodes and the advance in the FC design.

The authors of the present review are experts in the field of physical chemistry of polymers; thus, our main goal was to analyze the problem of the preparation of polymer membranes as the key scientific problem in the design of FC. Considerable attention is focused on the manufacture and perfection of polymer membranes of the Nafion type developed in the 1970s and produced in the USA on the industrial scale, because the process of production of this class of materials was not considered in open publications for a long time. Nonetheless, we also consider other polymeric systems that are being investigated and proposed as PEM in FC.

The review generalizes largely the scientific information published in the past 6–7 years; among the earlier studies, only the most important publications that have not lost their topicality and significance are mentioned.

II. Membranes for solid polymer fuel cells

The major requirements posed to materials for polymer electrolytes are as follows:

— high ionic (proton) conductivity;

— stability in redox media, at elevated temperatures in particular;

— inertness with respect to the catalyst that is supported on a material in question;

— low permeability with respect to the fuel or its components and to the oxidant (hydrogen, methanol, oxygen, *etc.*);

— mechanical stability, because the polymer electrolyte constituting the FC represents a thin membrane; the mechanical strength should be preserved on a sufficiently high level during long-term (up to 30 000 h) membrane operation in its hydrated state;

— ability to retain water under operational conditions, because the proton transfer occurs in a membrane in its hydrated state;

— stability of characteristics under conditions of long-term operation (several tens thousand hours);

— relatively low cost.

The compliance with the mentioned requirements is largely determined by the chemical structure of the elementary unit of the polymeric base of the membrane. Thus the proton conductivity is determined by the presence of ionogenic groups, mostly acidic. In practice, these can be sulfonic acid groups, phosphate or carboxyl groups. As regards the dissociation properties, sulfonic acid groups should be preferred (over phosphate and carboxyl groups). The structure of an organic fragment to which the sulfonic acid group is bound is also important: the proton conductivity decreases in the series fluorinated > aromatic > aliphatic residues. In addition, the proton-conducting properties depend on the ability of the corresponding group to undergo decomposition (*e.g.*, decarboxylation).

Bearing in mind the above requirements, it can be concluded that, in their properties, the perfluorinated polymeric systems or the aromatic polymeric systems, such as polybenzimidazoles (PBI), poly(ether ether ketone)s, *etc.*, functionalized with the corresponding acidic groups fit the polyelectrolyte membranes the best.

1. Fluorinated proton-conducting polymer membranes. Nafion

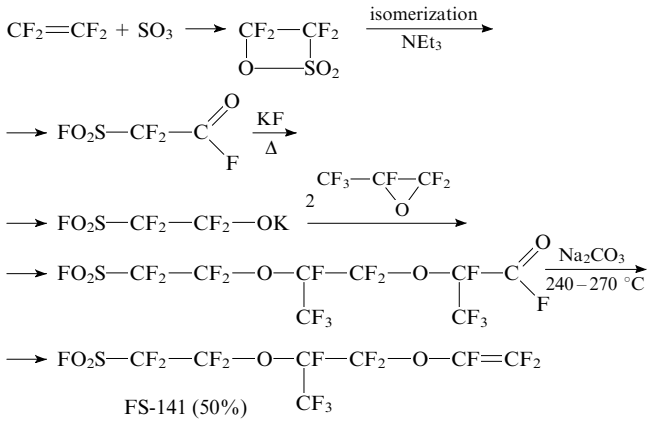
The first PEM that proved to be stable in many aspects was a membrane patented in 1966 by Du Pont. This is based on a co-polymer of tetrafluoroethylene (TFE) and perfluorinated vinyl ether with a terminal sulfonic acid derivative of the general structure

$$CF_2{=}CF(OCF_2CFY)_nOCF_2CFRSO_2Z$$

Y = F or CF_3; R = F or C_mF_{2m+1} (m = 1–10);
Z = F, OH, OMe, NH_2; n = 1–3.

The co-polymer was given a commercial name Nafion.[8,9]

A five-step synthesis of the functionalized monomer appeared in the literature later[10] by an example of perfluoro(3,6-dioxa-4-methyloct-7-ene)sulfonyl fluoride (*i.e.*, Y = CF_3, R = F, n = 1). The purity of the final product after distillation was 99.9%. In Russia, this product was referred to as FS-141.



A monomer with a similar chemical structure containing a sulfonic acid function was used in the preparation of the Aciplex membrane (a Nafion analogue) and patented later by the Asahi Chemical Co. (Japan):[11]

$$CF_2{=}CFO(CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_n(CF_2)_mXR$$

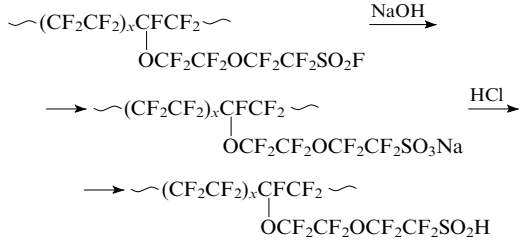
R = C_kH_{2k+1} or C_kF_{2k+1} (k = 1–10); n = 0, 1; m = 3–5; X = S, SO_2.

The Asahi Glass Technology company developed[12] a polyfluorinated sulfo-monomer perfluoro(3-oxahex-5-ene-1-sulfonyl fluoride) and the corresponding membrane polymer thereof. The Dow Chemical Company designed and patented[13] a monomer with a sulfonyl fluoride group nearer to the double bond, namely, $CF_2{=}CFOCF_2CF_2SO_2F$. A co-polymer thereof was named Dowlex; however, due to the low efficiency of co-polymerization of this monomer, the corresponding membrane did not find wide application.

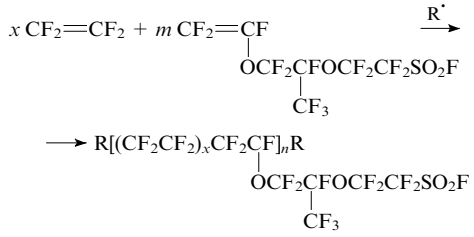
Schemes of syntheses of the aforementioned sulfo-monomers (including those containing carboxyl or ester groups) are presented in a review.[14]

Note that the above-mentioned perfluorinated monomers contained sulfonyl fluoride groups instead of sulfonic acid groups (they can be called precursor monomers). This allowed avoidance of side reactions during co-polymeriza-

tion and storage. The preparation of a polymer to be used in the manufacture of a membrane involved alkaline hydrolysis following co-polymerization to produce a sulfonic acid salt, which was later transformed into sulfonic acid upon treatment of the co-polymer with an inorganic acid:



As a rule, the co-polymerization of perfluoronated sulfonyl fluoride-containing precursor monomers (*e.g.*, FS-141) with tetrafluoroethylene is carried out in a fluorocarbon solvent (Khladone 318, 350 or 113) by using radical initiators of different structure (alkyl peroxides, perfluorinated alkyl peroxides, *etc.*).[3, 6, 8–14]



$x = 6–12$; $n, m = 1–2$.

A serious problem in co-polymerization of TFE and FS-141 was big difference in the reactivities of these monomers. For a long time, no data on the TFE reactivity have been available. Hence, when choosing the co-polymerization conditions, scientists used the data on the co-polymerization activity of fluorinated vinyl ethers of a similar structure.[10] In a recently published study,[15] the polymerization constants (r) of TFE and FS-141 at 35 °C were determined, $r_{TFE} = 9.0$ and $r_{FS\text{-}141} = 0.04$; the Alfey–Price parameters ($l = 2.23$, $Q = 0.019$) were calculated for FS-141. Thus, the difference in the monomer reactivities reached two orders of magnitude. The co-polymerization was performed by feeding TFE to the reactor with the less reactive sulfonyl fluoride-containing monomer to maintain constant pressure. Due to considerable changes in the viscosity of the polymerization system and problems with stirring of the system, the co-polymerization was stopped at the degree of conversion ~20%–25%, which enabled the preparation of a co-polymer of the required composition after which the co-polymer was washed from the unreacted monomer. One cannot avoid losses of the expensive sulfomonomer, which affects the cost of synthesized Nafion.

To assess quantitatively the co-polymer composition when studying the properties of Nafion, the notion of an 'equivalent weight' (EW) is employed, *i.e.*, the molecular weight of a polymer chain fragment per sulfonic acid group. The experimental EW of a co-polymer lies in the interval between two limiting values. The upper one was associated with the percolation threshold, *i.e.*, the minimum content of the ionogenic groups sufficient for ionic (proton) conductivity of a membrane as a result of formation of ionic clusters. The lower limit denotes the deterioration of physicomechanical properties of a polymer due to its substantial swelling and absorption of water, which can ultimately result in dissolution of Nafion in water. The EW of commercial Nafion is specified as 1100.[16] According to the data from reviews,[17–22] the optimal properties of Nafion are manifested for specimens with EW of 950–1100.

It has recently been shown [23–25] that the structure of the peroxide initiator the fragments of which are incorporated into the co-polymer as the terminal groups can substantially affect the thermal stability and durability of co-polymers and, correspondingly, the operational properties of the obtained PEM. It was confirmed experimentally that the use of perfluorinated peroxides as co-polymerization initiators allowed fabrication of membranes with enhanced thermal stability.

Water-emulsion co-polymerization of TFE with perfluorinated monomers containing sulfonyl fluoride groups has been patented.[26–30] Most often, this involved the use of water-soluble initiators (*e.g.*, persulfates) or persulfate-based redox initiating systems. Perfluorinated emulsifiers (*e.g.*, salts of perfluoropelargonic acid) were used as the emulsion stabilizers. The co-polymers were obtained as aqueous dispersions. The polymerization can be carried out up to ~ 50% conversion (and even higher, according to the patent data [29]) with respect to the sulfo-monomer. Although the method of emulsion polymerization seems promising, it has not yet found industrial application in the production of polyelectrolytes of the Nafion type.

Recently, a method of co-polymerization of TFE with FS-141 in an aqueous emulsion with radical initiators and a salt of a perfluorocarboxylic acid as the emulsion stabilizer has been patented.[31, 32] This made it possible to obtain a co-polymer of the Nafion type with the optimal EW and satisfactory melt indices. Prior to polymerization, the system was emulsified in a homogenizer of the rotor–stator type with the rotor speed of 8000–12 000 rpm. The degree of conversion could be raised to 70% with respect to the sulfo-monomer with the EW remaining constant. Such a version of co-polymerization was characterized by higher safety, since no Khladones are used and the reactions were conducted in aqueous media. Moreover, the increase in the degree of conversion made the process more economic due to the more complete consumption of the expensive monomer FS-141.

Co-polymerization in Khladone as the solvent was usually carried out at 30–80 °C depending on the type of the initiator used. The pressure of TFE in the system was most often maintained in the range of 0.3–0.8 MPa, which is not a critical parameter.[8–14] This ensured the TFE concentration in the liquid phase of the reaction system and, hence, the monomer ratio necessary for the synthesis of the co-polymer with the desired composition.

The considered principles underlie the processes used to produce perfuorinated membranes such as Nafion (Du Pont), Flemion (Asahi Glass Technology), Aciplex (Asahi Chemical), Dowlex (Dow Chemical). The application areas of these materials were discussed in reviews.[6, 10, 16–22] The advantages of this class of membranes include their high chemical stability, mechanical strength and high proton conductivity in the temperature range of 40–90 °C.

Some properties of this kind of membranes are presented by the example of Nafion-117 (EW = 1100, thickness 178 μm).[16, 19]

Property	Mean values
Ion exchange capacity	~0.91 (up to 1.0) mg-equiv
Surface resistance	~0.09–0.12 Ω cm^{-2}
Service life	thousands (tens of thousands) h
Proton conductivity	~10^{-1}–10^{-2} S cm^{-1} (~0.1 S cm^{-1} at 80 °C)
Current density at a voltage of 0.45 V	~250–640 mA cm^{-2}
Methanol diffusion coefficient	2×10^{-6} cm^2 s^{-1}
Water uptake	~15%
Power density	600–800 mW cm^{-2}
Cost	~$ 700 per m^2

Studies of the morphological structure are important for perfecting the structure and operational characteristics of Nafion and analogous proton-conducting membranes. The history of the development of these studies was surveyed in a review.[20] A significant contribution to the concepts on the Nafion morphology was made by Gierke who was the first to put forward the cluster model that described the structure of this material.[33] Using information from modern methods of small-angle X-ray and neutron scattering, it was possible to analyze the structural anisotropy of the Nafion and determine the sizes and distribution of clusters, channels and hydrated sulfonic acid groups in these channels.

Figure 2 shows a sandwich-like structure element of the Nafion morphological organization.[34]

Figure 3 portrays the structure of ion channels in Nafion.[35]

At present, it is generally accepted that the channels in Nafion are formed due to the phase separation between the

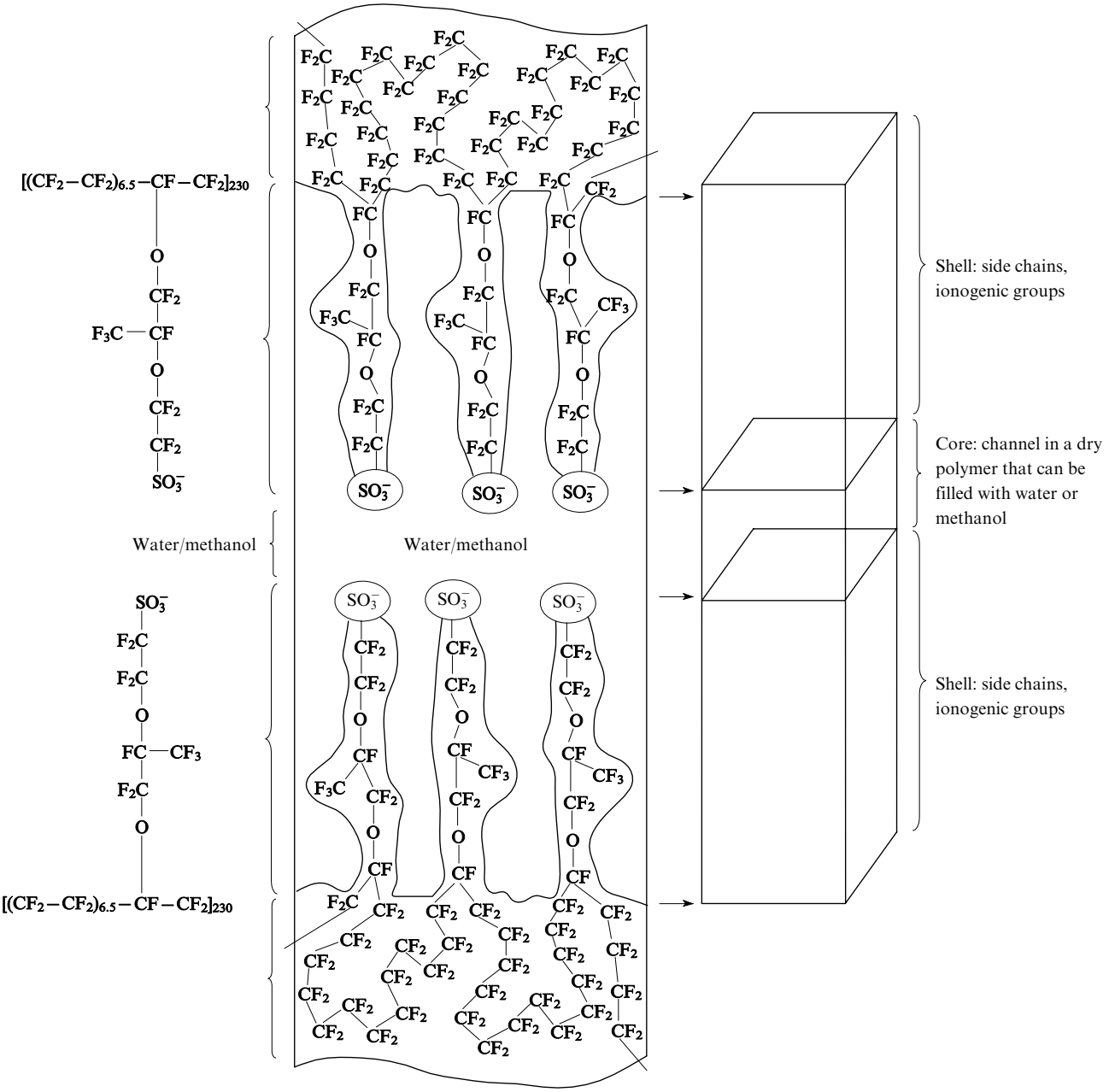
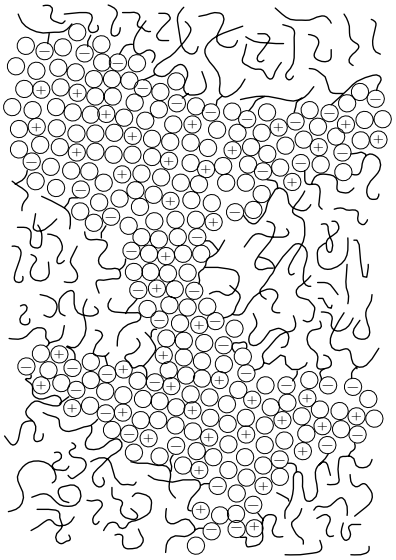


Figure 2. A sandwich-like structure element of Nafion morphological organization.[34]



⊖ SO_3, ⊕ proton-containing charge carrier, ○ H_2O.

Figure 3. Nafion microstructure.[35]

originally hydrophobic polymer chain and the hydrophilic sulfonic acid groups bound to the chain. The proton transport proceeds through the water-containing channels; the molecules of water are either bound to the acidic groups or fill the channel space.[20–22, 33–38]

The level of proton conductivity depends on such factors as the density of distribution of acidic groups in the membrane, the structure and morphology of the membrane polymeric framework and the water content. Attempts at better understanding of the relationship between the structure and the proton conductivity of a membrane were undertaken.[39–51]

The microstructure of Nafion and analogous PEM was studied by small-angle X-ray and neutron scattering in a sufficiently wide range of polymer–solvent ratios.[20, 35–37] It was noted[19] that for the nanophase distribution of PEM, the formation of interpenetrating domains is possible. In the same studies, it was pointed out that the variations of transport characteristics of the Nafion channels can be controlled by changing the solvent during membrane washings or by affecting the orientation of the channels formed (for example, by the electric field).

In a recent neutron small-angle scattering study, the fine structure of Nafion (Du Pont) was compared with its Russian analogue MF-4SK.[36] The differences in the structures of these materials were compared for the following membrane samples: 1) the initial sample, 2) the sample dried at 100 °C, and 3) the dried sample saturated with D_2O. The scattering intensity distributions as a function of the momentum transfer (q) has shown that for momentum transfers > 0.2 nm^{-1}, the intensities of scattering in Nafion and MF-4SK were similar. For small momentum transfers ($q < 0.2$ nm^{-1}), the scattering intensity for MF-4SK was increased considerably, whereas in Nafion this effect was insignificant. These results suggested that small scatterers (pores) dominate in Nafion, whereas in MF-4SK the contribution of larger pores was more pronounced. Calculations based on experimental data have shown that the number of small pores in the Nafion membrane was seven times larger than in MF-4SK.

The difference in the numbers of larger pores was also substantial. For pores of comparable sizes (~ 20 nm), their concentration was substantially higher in the MF-4SK copolymer. However, the saturation of the MF-4SK polymeric matrix with D_2O proceeded much more slowly than for Nafion: the Nafion membrane absorbed 17.2 wt.% D_2O in 2.5 h and the MF-4SK membrane absorbed only 12.3 wt.% D_2O. This suggests that in MF-4SK large pores are more poorly connected by channels, a part of pores remained unfilled and thus did not contribute to the conduction. Hence, due to peculiarities of their manufacture (or storage), the MF-SK membranes possess somewhat lower conductivity.

The conductivity of Nafion membranes was studied[45] by impedance spectroscopy as a function of temperature and sample pretreatment, in particular, hot-pressing. Depending on the water content and the pore size, two modes of membrane conductivity were observed with a change in the activation energy in a temperature interval from -50 to -15 °C. Later,[46] it was shown that at higher temperatures the activation energy changed insignificantly and was ~ 130 meV at 25–75 °C. The effect of the pore size distribution on the membrane characteristics was also discussed.[47]

A detailed investigation into the submicroheterogenic distribution of sulfonic acid groups and the interconnecting channels is also very important for explaining the mechanism of the proton conductivity of Nafion.

Newer data that characterize the transport properties of channels in Nafion were reported by Roduner *et al.*[52] at the Europolymer Conference 2008. They studied the distribution of the proton conductivity across the membrane by electrochemical atomic force microscopy (EC-AFM) with nanosized probes switched to different channels in the membrane cross-section at a certain scanning rate. The obtained data were analyzed together with the results of determination of the Nafion microstructure by X-ray diffraction and small-angle neutron scattering. Measurements at different relative humidity have shown that the Nafion membrane surface was non-uniform and wide inactive ('dormant') surface areas exist between the active proton-conducting channels. The profiles of active site distribution over the cross-section, their variations with time and the changes in the activity of a given channel with time (activation and decay) were studied. It was shown that individual pores predominated as the proton conducting channels at low humidity, whereas associated channels of the 'bottleneck' type prevailed at high humidity. The results obtained made it possible to conclude that Nafion consists of a network of interconnected clusters measuring ~ 3 nm that represent inverse micelles and their activity in proton conduction processes may be non-uniform.[52]

The water content and the water transfer processes are very important in the determination of the efficiency of Nafion membranes. Water sorption, desorption and permeation in and through Nafion 112, 115, 1110 and 1123 membranes were measured[53] as functions of temperature in the range of 30–90 °C. The important role of water sorption and its transport in the operation of polymer electrolyte membrane fuel cell was pointed out. This determines the distribution of water throughout the fuel cell that affects the local proton conductivity. Water permeation increased with temperature. The water sorption by, and

diffusion through, a membrane are determined by the interfacial mass transfer, diffusion and swelling of the polymer. The rate of water transport in the Nafion membranes depends not only on the temperature and the actual state of water (liquid or gas); it is also weakly dependent on membrane thickness. For thin membranes at low temperatures, water permeability was limited by the interfacial mass transport at the membrane–gas interface. At higher temperatures and thicker membranes, the diffusion resistance across the membrane was higher. For reduced water contents, the membrane permeability decreased; this accounts for the higher water permeability of Nafion membranes in contact with the liquid phase as compared with the same sample in a flow of humid gas.

Desorption of water from saturated membranes was limited by the resistance to the mass transport between phases at the membrane–gas interface. Sorption from a humid gas was limited by the membrane swelling with the accumulation of water.

The published experimental results on the rates of different processes at the water transport are characterized by big difference in diffusion coefficients. Water sorption was determined by a combination of rates of Nafion membrane swelling and water diffusion, the desorption was determined by the rates of mass transport across the Nafion–gas interface and water diffusion, while the water permeation was determined by a combination of the interface mass transport and diffusion. Determination of rates of individual processes at the mass transport is only possible by a thorough analysis of data on the permeability and sorption for membranes of different thicknesses and at different temperatures.

Thus, the proton conductivity of Nafion membranes and similar materials was directly related to the water content in ion channels of PEM[51] and accompanied by the water transport from the anode to the cathode. To compensate the water loss, water vapour was delivered with hydrogen. The water loss also determined the optimum temperature range of fuel-cell operation when common unmodified Nafion was used (up to 90 °C).

Limiting the working temperature interval revealed yet another drawback in the Nafion operation within a FC associated with poisoning of the platinum catalyst on the electrode with impurities contained in hydrogen. The trace amounts of CO (>10 ppm) in the hydrogen fuel are adsorbed on the catalyst surface thus reducing its efficiency. At temperatures above 130 °C, the equilibrium of the CO and H_2 sorption on the platinum catalyst is shifted towards H_2 for thermodynamic reasons, which prevents the catalyst poisoning. However, at higher temperatures (~120–140 °C), the proton conductivity of membranes decreases substantially due to Nafion dehydration.

Thus, notwithstanding several important advantages of proton-conducting membranes of the Nafion type (chemical resistance, mechanical stability, high proton conductivity), the search for optimal temperature modes of their operation with allowance of the retention of water content, the porosity and the structure of proton-conducting channels and the effect of impurities in fuel, requires modification of Nafion membrane structure and properties. The additional stimuli to further development of research in this direction were the high cost of this material and the demand for replacement of hydrogen by other kinds of fuel, particularly, alcohols.

2. Modification of the Nafion structure

a. Modification with inorganic additives

A common approach to improve operational characteristics of the Nafion type membranes aimed at enhancing their water uptake ability and preventing their dehydration is their modification with hydrophilic inorganic components with high water retention capabilities. Such a modification of Nafion reduces water losses during membrane operation at elevated temperatures.

Nafion can be modified by impregnation with silica by treating the membrane in its H^+-form with a solution of tetraalkoxysilane followed by hydrolysis.[54–58] It was shown that modified membranes efficiently operate at temperatures above 100 °C (up to 140 °C). The proton conductivity of a membrane increased with the increase in the SiO_2 content up to its maximum at 10%–12% and decreased with the further increase in its concentration.

In parallel with studies on the effect of SiO_2 additives on the properties of Nafion, the effect of heteropolyacids with high intrinsic proton conductivity, namely, phosphotungstic acid $H_3PW_{12}O_{40}$ (PWA), silicotungstic acid, *etc*., was considered.[3, 57–63] It was shown that the heteropolyacids possess high proton permeability and can be immobilized in Nafion to form composites with the proton conductivity heteropolyacids exhibit high proton permeability at room temperature and can be immobilized into Nafion to form compositions of good proton conductivity $>10^{-2}$ S cm^{-1} at room temperature. However, due to the high solubility of heteropolyacids in water, they are usually immobilized in silica gel.[57] Phosphotungstic acid immobilized in silica gel in combination with poly(ethylene oxide) formed a hybrid proton-conducting system with conductivity of 10^{-3}–10^{-2} S cm^{-1} in the temperature range from room temperature to 140 °C. In a study along this line,[62] Nafion was employed instead of poly(ethylene oxide) to afford a Nafion–SiO_2–PWA composite membrane. The recast composite membranes were manufactured from a Nafion solution mixed with SiO_2 and PWA in an ultrasonic bath. Characteristics of the synthesized material were compared with the properties of a Nafion–SiO_2 composite prepared using a similar mixing procedure. Studies by scanning electron microscopy, X-ray diffraction analysis, thermographic analysis, thermal differential analysis and Fourier transform IR spectroscopy revealed substantial advantages of the described recast composite membrane due to the increase in the degree of crystallinity and water uptake. The crystalline phase content of the membranes was 20% for Nafion, 25% for Nafion–SiO_2, and 20% for the Nafion–SiO_2–PWA system. The water uptake was 26% for the original Nafion membrane, 32% for recast Nafion, 34% for the Nafion–SiO_2 composition and 38% for the Nafion–SiO_2–PWA system.

The observed effect can be explained by such factors as the hydrophilic nature of SiO_2 and PWA, the changes in the membrane crystallinity and the stronger interaction between absorbed water and the modified matrix.

As has been shown earlier,[3] the proton conductivity of membranes of the Nafion type is characterized by a nearly linear increase with the increase in the membrane water uptake. A membrane recast from Nafion absorbed larger amounts of water than the original industrial material. Some properties of the thus modified membranes are given in Table 2.[62] It is seen that sonication of membrane compositions modified with the SiO_2–PWA system resulted in a threefold increase in their proton conductivity.

Table 2. Proton conductivity of Nafion-type recast membranes and membranes modified by sonication.[62]

Membrane type	Thickness / μm	Surface resistance / Ω cm^{-2}	Proton conductivity /S cm^{-1} (see [a])
Nafion-115	100	1.23	8.13×10^{-3}
Nafion-115 – SiO_2	100	0.92	1.07×10^{-2}
Nafion-115 – SiO_2 – PWA	120	0.45	2.67×10^{-2}

[a] At 110 °C and 70% relative humidity.

Recasting of a membrane not only favoured higher water uptake, but also improved other properties as compared with the original material. Thus the use of composite membranes Nafion – SiO_2 and Nafion – SiO_2 – PWA resulted in higher current densities, *i.e.*, 320 and 540 mA cm^{-2}, respectively, as compared with 95 mA cm^{-2} for the original Nafion-115 membrane at the same external load.

A comparative study of the effect of different inorganic modifiers (SiO_2, SiO_2 – PWA, Al_2O_3 and ZrO_2) on the proton conductivity of the Nafion-type membranes was studied depending on the water-retaining ability of modifiers and the acid – base properties of their surface. The highest efficiency of the SiO_2 – PWA system was confirmed to be associated with the intrinsic acidity and the larger number of molecules of water of crystallization in PWA ($H_3PW_{12}O_{40} \cdot 36\,H_2O$). The extreme nature of the temperature dependence of the membrane resistance with the minimum at ~140 – 150 °C for the majority of mentioned fillers can be associated with the desorption of water located in pores and physically sorbed on the surface of fillers.

The effect of introduction of ultrafine TiO_2 powders on the properties of the composite Nafion membranes was analyzed.[64 – 66] The membrane material could also be modified by introducing fluorinated montmorillonite into the Nafion structure. The fabricated composite membranes were characterized by improved barrier properties towards methanol without any loss in proton conductivity.

It was assumed [67] that the increase in proton conductivity could occur by a mechanism that is highly improbable for energy reasons, which consists of dissociation of water molecules under the action of inorganic materials immobilized on the membrane surface and containing groups capable of efficient interaction with OH^- and H^+ (particularly, iron hydroxide-oxide and SiO_2 sol).

Attempts were undertaken [68] at modifying membranes of the Nafion type with different phosphorus-containing compounds. The following composite membranes were prepared: Nafion – ($7\,SiO_2 - 2\,P_2O_5 - ZrO_2$), Nafion – ($SiO_2 + H_3PO_4$), Nafion – ($SiO_2$ + PWA) and Nafion – ZrP (ZrP is zirconium hydrogen phosphate). All composite materials excluding Nafion – ZrP exhibited only slightly better high-temperature conductivity as compared with original Nafion. Modified Nafion – ZrP was characterized by the reduced proton mobility at higher activation energy. The results obtained showed that the improved characteristics of fuel cells observed earlier for composite membranes Nafion – ($7\,SiO_2 - 2\,P_2O_5 - ZrO_2$) and Nafion – ZrP cannot be solely attributed to the improved hydrophilic properties; the material structure and its effect of the proton mobility also played a significant role. Zirconium phosphate and caesium hydrogen sulfate served also as inorganic phase components of composite membranes.[69, 70]

Of special interest is the incorporation of ultrafine SiO_2 surface-functionalized by covalent binding of organosilicon compounds bearing terminal SO_3H groups [71, 72] (*e.g.,* by treatment of original silica nanoparticles with perfluoropropane-2,3-sultone). A membrane from Nafion filled with silica-SO_3H possessed enhanced proton conductivity dependent on the concentration of the added modifier (the maximum value was reached at the content of the modifier of 3% and was equal to 0.12 S cm^{-1}). The modified membrane was also characterized by improved barrier properties.

Concluding this section, it deserves mentioning that the proton conductivity of Nafion can be improved by physical impact during the membrane casting, particularly, under the effect of an electric field, which favoured the alignment of ionic aggregations along the membrane thickness direction.[73]

Thus, it is evident that the past decade was marked by substantial advances in the improvement of operational characteristics of proton-conducting membranes of the Nafion type by modifying their structure with inorganic components. The temperature interval of membrane operation can be extended to the high-temperature range with enhancement of its proton conductivity, water retention and, partly, its barrier properties.

b. Modification of Nafion and related materials with polymeric systems

As has been noted earlier, a decrease in the EW of the base co-polymer in the manufacture of membranes from Nafion was accompanied by an increase in not only the proton conductivity, but also water uptake, swelling of the polymeric membrane and a decrease in its stability. Structural modification of Nafion can mitigate or eliminate these drawbacks.

Moreover, the necessity of using hydrogen purified from traces of CO made scientists consider the possibility of using other kinds of fuel (*e.g.*, methanol). This brought about a problem of membrane permeability in respect of such substances. This became yet another reason for the modification of the Nafion structure aimed at improving its structural characteristics and changing the Nafion membrane permeability with respect to other fuel types more accessible than hydrogen.

The physical and mechanical properties of membranes can be improved by grafting polystyrene to the Nafion membrane surface, either radiation-induced [74] or in supercritical CO_2, followed by sulfation with concentrated sulfuric acid.[75] The obtained graft systems manifest higher glass transition temperature of the membrane material, an increase in the ionic conductivity as compared with the original unmodified Nafion [75] and a certain decrease in its crystallinity (due to incorporation of amorphous polystyrene fragments).

Modification of Nafion membranes with water-proof polymers, namely, polyethylene, poly(hexafluoropropylene), co-polymers of hexafluoropropylene with propylene and ethylene, co-polymers of vinylidene fluoride with tetrafluoroethylene, *etc.*, was studied.[76] Grafting was induced by irradiation with an accelerated electron beam. The resulting water-proof membranes were promising candidates to be used in direct methanol FC.

The Nafion membrane surface was modified by impregnation with polypyrrole[77] the conducting properties of which favoured the efficient removal of electrons from the platinum layer of the electrode. It was proposed[78] to electrochemically introduce polypyrrole *in situ* into the membrane pores to prevent methanol crossover when the membrane is to be used in methanol systems.

The physical and mechanical properties of Nafion membranes were improved by introducing cross-linking monomers containing hydroxyl or amino groups into the system with two or more epoxy or isocyanate functional groups.[79]

A method of modifying proton-conducting Nafion-based membranes by the *in situ* polymerization of cationic monomers of types **A** or **B** introduced into the membrane was described.[80]

$$R^1_2C=CR^2C(=O)O(CR^1_2)_nCR^1_2N^+R^3_3A^- \quad \mathbf{A}$$

$$R^1C\equiv CC(=O)O(CR^1_2)_nCR^1_2N^+R^3_3A^- \quad \mathbf{B}$$

R^1 = F or H; R^2 = H, Me or Hal; R^3 = Me, Et; A^- = SO_3^-, Cl^-.

The chemical or radiation-induced polymerization of such monomers led to the formation of a protective layer that prevented partial dissolution of silicon tips upon interaction with perfluorosulfonic acid contained in the membrane and also to a substantial increase in the membrane resistance.

A patent was granted[81] for a method of manufacturing ultra-thin membranes with enhanced mechanical strength and high ionic conductivity (thickness less than 0.025 mm) combining inert highly porous polytetrafluoroethylene with proton-conducting Nafion that served as the filler. Bilayer or trilayer composite proton-conducting membranes[82] comprise a core with high EW (~800–1500) and one (facing the cathode of the FC) or two surface layers with reduced EW (~600–900). The optimal structures of these membranes somewhat exceed their single-layer analogues in the current density.

Different versions were described[76,83] for the synthesis of composite two-component membranes in which inert polymers [perfluorinated polymers and co-polymers, poly(vinyl chloride), poly(α,β,β-trifluorostyrene), poly(ether ketone), poly(ether sulfone), *etc.*] or porous inorganic materials (glass fibres, oxides, silicates) were impregnated with solutions (dispersions) of polymer electrolytes (Nafion, *etc.*). What is essential is the compatibility of the inert polymer and the polymer electrolyte (or its precursor). If a precursor was used, it is transformed into the ion-conducting form. Manufacturing of polymeric membranes by this method allows controlling the physicochemical properties by varying the component ratios or the degree of conversion of the precursor into the active form.

A possibility of modifying Nafion-115 with *in situ* polymerized phenol–formaldehyde resin and its subsequent sulfonation was described aimed at improving the properties of membranes for direct methanol FC.[84] The phenol–formaldehyde resin is well dispersed throughout the Nafion membrane. The proton conductivity of the composite membranes was close to that of Nafion, but methanol crossover was markedly reduced. Thus, these membranes proved to be more suitable for FC running on this fuel. The composite membrane substantially surpassed Nafion-115 in the maximum power density (114 and 78 mW cm^{-2}, respectively).

At the Uppsala University (Sweden), composite membranes were prepared[85] by diffusing poly(benzimidazole) from solution into Nafion membranes at different solution concentrations followed by drying at different temperatures. It was shown that the ratio between conductivity and methanol permeability could be increased by nearly 50% as compared with Nafion together with the improvement of the barrier properties with respect to methanol.

It was demonstrated[86] that ion-exchange membranes can be obtained by the preirradiation-induced graft polymerization of styrene or a mixture of styrene with divinylbenzene (cross-linking agent) onto cross-linked polytetrafluoroethylene films (RX-PTFE) followed by sulfonation of the graft polymers. The ion-exchange capacity values of the membranes were in the range of 1.5–2.8 mequiv g^{-1}.

A possibility of fabricating membranes by UV-induced grafting of styrene or similar monomers onto polytetrafluoroethylene followed by sulfonation was studied.[87] Such an approach made it possible to retain the fluorinated backbone of macromolecules and fabricate membrane systems with high thermal stability.

Somewhat later, this research group applied the same approach to grafting vinyl monomers into polytetrafluoroethylene or co-polymer films.[88] Thus a vinyl monomer, trimethoxy-*p*-styrylsilane, was grafted on (ethylene–tetrafluoroethylene) co-polymer films preirradiated with γ-rays. Then the trimethoxy-*p*-styrylsilane-grafted films underwent sulfonation, hydrolysis and condensation to form silane cross-links between the grafted chains. Thus a cross-linked proton-conducting polymer electrolyte hybrid membrane was obtained that combined the high proton conductivity with the high thermal stability. The optimal conditions for the synthesis (grafting and sulfonation) and properties of polymer electrolyte membranes (ion-exchange capacity, proton conductivity, water uptake and thermal stability) and the prospects for their use in fuel cells were determined. It was shown that in its properties a new hybrid membrane is comparable and even surpasses the styrene-grafted polymer electrolyte membranes.

Proton-conducting membranes for direct methanol fuel cells were synthesized based on the Nafion–poly(*p*-phenylene vinylene) composite polymer electrolyte.[89] The structure of this composite was characterized by UV-vis spectroscopy and scanning electron microscopy; in addition, ion exchange capacity, water contact angle and water uptake were determined.

Modification of Nafion-117 with organic silanes containing thiol groups was considered.[90] About 50% decrease in methanol crossover was noted; however, the proton conductivity of the membrane somewhat decreased.

Based on Nafion-117, a sulfonated polystyrene–Nafion composite system was manufactured according to a concept of semi-interpenetrating polymer networks (semi-IPN).[91] Such composite membranes exhibited enhanced proton conductivity at temperatures above 110 °C.

A multilayer proton-conducting composite membrane based on Nafion and sulfonated poly(benzimidazole) was fabricated[92] by impregnating the films of the latter with Nafion solutions.

The preparation of proton-conducting membrane for direct methanol FC on the basis of Nafion with multiwalled carbon nanotubes dispersed by melt-extrusion was described.[93] It was shown that the methanol permeability

of the obtained material decreased without any loss in ionic conductivity.

Concluding the survey of publications on Nafion and fluorinated PEM, certain data generalized from the 2003–2005 reports on the USA Programme on hydrogen energetics that involved national laboratories of leading universities should be mentioned.[94,95] Within the framework of this programme, the main advances were reached in the following directions.

1. Determination of the mechanism of the peroxide attack during the membrane operation that shortens its service life.

2. Substantiation of the merits of fluorinated initiating systems that afford fluorinated sulfonic acid-containing membrane co-polymers with fluorinated terminal groups upon co-polymerization.

3. Improvement of physical and mechanical properties of membranes by using the following modification methods:

— introduction of a finely dispersed nanosized silica modified with sulfo groups,

— modification of the Nafion matrix by introducing dendritic structures.

4. Development of water-insoluble organic-inorganic Nafion hybrid systems with thermal stability of up to 300 °C, proton conductivity of 0.35 S cm^{-1} at 80 °C and relative humidity of 5%.

5. The development of multi-block polymer systems with high proton conductivity, the use of ionic liquids as the proton-conducting media.

These results apparently represent an incomplete list of achievements from this programme; however, they demonstrate that polymer membranes of the Nafion type remain highly competitive in the series of proton-conducting materials developed so far and hold the leading position with respect to the level of their development, their proton conductivity and service life.

In several countries (USA, Germany, Japan, France), the compact power sources with Nafion-based polymer membrane FC with the power from 50 to 500 kW is technologically and technically supported and are commercially available. Their promising applications include combining FC into power sources with the power on the level of 1000 kW for submarines.[96] Thus as early as 2003, new submarines of 1700 tons displacement were launched. They were equipped with fuel cell batteries providing their autonomous navigation for approximately two weeks at a depth of about 400 m without any noise or increase in the engine temperature. Such submarines used a combination of diesel and electric power units and also reserve accumulators. The fuel cells ran on pure hydrogen synthesized directly on the submarine from metal hydrides capable of evolving hydrogen in the controlled mode when heated. After the hydrogen evolution, hydrogen absorption at low temperatures ensured recovery of the original metal hydride in the system.

3. Non-fluorinated polymeric systems for proton-conducting membranes

Recently, attempts were resumed to develop new PEM types by replacing the usual perfluorinated sulfonic acid-containing polymeric systems by other commercial polymers with aromatic backbones (polystyrenes, polycarbonates, polysulfones, *etc.*) with subsequent sulfonation.[97] The manufactured membranes were studied by various physicochemical methods aimed at identification of the proton transport channels, determination of the thermal stability of the developed systems and water sorption and desorption. The ion-exchange capacity was found to be comparable with that of commercial Nafion membranes. The best characteristics were demonstrated by sulfonated polycarbonate, namely, its exchange capacity was 0.57 mequiv g^{-1}, the tensile strength was 157 N mm^{-2} and the glass transition temperature was 120 °C; it manifested low affinity towards methanol (sorption 2.97%). The obtained results suggest the possibility of developing inexpensive proton-conducting membranes.

A comparative analysis of the level of R&D and the potential of using different PEM classes, namely, Nafion, sulfonated poly(α,β,β-trifluorostyrene) (BAM-3G), sulfonated poly(ether ether ketone), PBI and polyphosphazene for classical hydrogen–oxygen FC as well as for direct methanol FC and high temperature FC (Fig. 4) was given in a review.[17] It follows that, considering the hydrogen–oxygen FC, Nafion occupies the first place in both the level of R&D and its potential. For direct methanol FC, the sulfonated polycondensation systems (poly(ether ether ketones) and polyphosphazenes) should be preferred, whereas for high-temperature systems, polybenzimidazoles proved to be the best.

The results of experimental studies of various polycondensation polymeric membranes were considered in a review[18] where their characteristics were compared with

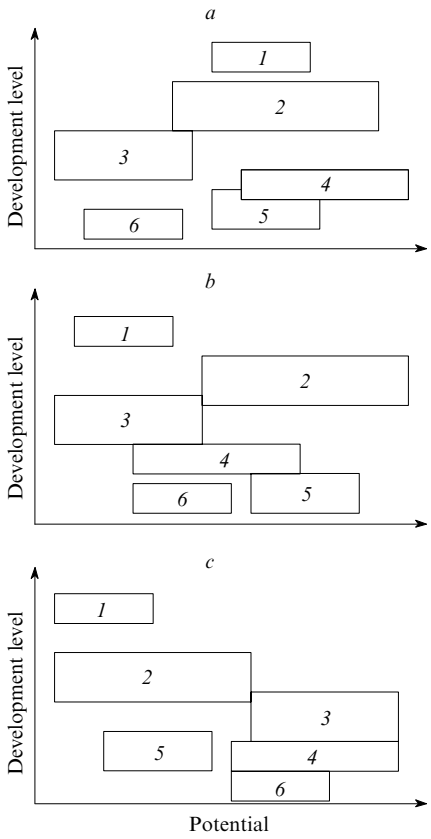


Figure 4. Ratio between the level of development and the potential of different materials to be used as membranes in hydrogen (*a*), methanol (*b*) and high-temperature fuel cells (*c*).[17]
(*1*) Nafion (*2*) sulfonated poly(ether ether ketones) and poly(ether ketones), (*3*) polybenzimidazoles (*4*) solid acids, (*5*) polyphosphazenes, (*6*) polyimidazoles.

those of Nafion for the first time. On the whole, it was shown that as regards the proton conductivity, the majority of polycondensation polymers are inferior only to Nafion and it is only at high temperatures that the PBI-based membranes become superior.

In recent years, quite a number of reviews were published that touched upon the synthesis and properties of condensation polymeric systems as the proton-conducting materials. In a series of reviews by Rusanov *et al.*,[98–104] approaches to the synthesis of many classes of condensation polymers [poly(benzimidazoles), poly(ether ether ketones), poly(ether sulfides), polyarylphosphazenes, polynaphthylimides] were described in detail as well as the polymer-analogous reactions of condensation systems. However, the analysis of the relationship between the proton conductivity and the chemical structure of polymeric systems under consideration and the prospects of optimizing their operational characteristics were given too briefly and insufficiently to draw any significant conclusions.

Another review [14] demonstrated the prospects for practical use and the properties of different sulfonated polyimides,[103–110] sulfonated poly(benzimidazoles),[18,111–115] sulfonated poly(aryl ether ketones),[116–119] sulfonated polyphosphazenes [120] and even sulfonated silicates.[121] As a whole, it should be emphasized that condensation polymer membrane systems are characterized by high thermal stability (up to 500 °C), tolerance with respect to admixtures of CO and CO_2 and low permeability towards different fuel types including methanol; they also surpass Nafion in mechanical strength. Thus, membranes based on the PBI–H_3PO_4 system remained stable at temperatures up to 500 °C; their fairly high proton conductivity increases with an increase in temperature and phosphoric acid content. The conductivity of PBI containing 500 mol % of H_3PO_4 (*i.e.*, 5 molecules of H_3PO_4 per PBI structural unit) at 190 °C was 3.5×10^{-2} S cm^{-1}. In addition, the membrane permeability of these materials towards fuel components was one order of magnitude lower as compared with that of perfluorinated polymer electrolytes, and they surpassed Nafion-based membranes threefold in mechanical strength.

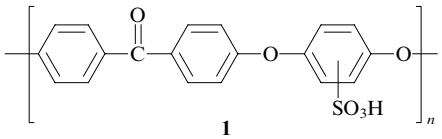
The first patents were granted to Pemeas Fuel Cell Technologies, which produced polybenzimidazole membranes for direct ethanol fuel cells. This company built a pilot plant for manufacturing membranes that was launched in 2004.[122] A membrane developed by this company on the basis of poly(2,2′-*m*-phenylene-5,5′-dibenzimidazole) under the name of Celtex-MEA was tested in a FC operating on a fuel system that contained 35% H_2, 64.8% N_2, 2000 ppm CO and traces of CO_2 and H_2O. It exhibited efficiency in a temperature range of 120–200 °C, tolerance to CO at concentrations above 50 000 ppm and had service life longer than 8000 h. Yet another membrane version named Celtex-V was destined for direct methanol FC.

Studies on the design of novel refined membrane systems based on condensation polymers are being carried on. Thus sulfonated poly(phthalazinone ether ketones) filled with silica-SO_3H nanoparticles were proposed.[72] In another study,[123] sulfonated poly(aryl ether ketones) containing benzophenone units and methyl groups linked with aromatic rings were synthesized; the Me groups enabled UV-induced cross-linking of the block-polymer. The cross-linkable sulfonated poly(arylene ethers) soluble in organic solvents and capable of forming flexible and transparent membranes by casting from solutions were fabricated.[124]

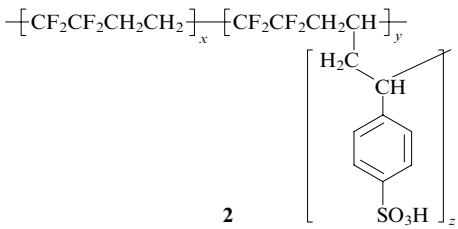
Recently, the synthesis of a novel sulfonated polyimide membrane containing triazole groups has been reported.[125]

Its efficiency and high durability were demonstrated in single fuel cell operation at 80 °C for 5000 h after which only insignificant decrease in the ion-exchange capacity was observed. At the same time, the molecular mass decreased by 10%, which resulted in a loss of mechanical strength. These changes were associated with the hydrolysis of polyimides and the membrane degradation was due to reaction with free radicals formed.

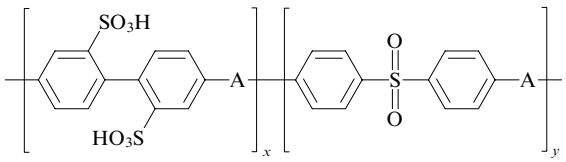
An in-depth analysis of the relationship between proton conductivity and the density of acid groups, effective proton mobility, the nature and rigidity of the polymer chain and the water content was carried out for a series of different randomly sulfonated polymer membranes.[126] This study aimed at the elucidation of fundamental relationships between the structure, morphology and properties of these materials in order to design new membranes with improved levels of proton conduction. The following polymer systems were studied: sulfonated poly(ether ether ketone) (SPEEK, **1**), poly(ethylenetetrafluoroethylene-*graft*-styrene sulfonic acid) (**2**), linear sulfonated polyimide (**3**), BAM membrane (**4**), sulfonated poly(α,β,β-trifluoro)styrene manufactured by Ballard Power Systems. Nafion (**5**) served as the reference material with the optimum combination of operational characteristics (reliability and service life), being also the best studied.



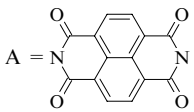
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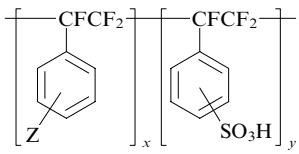


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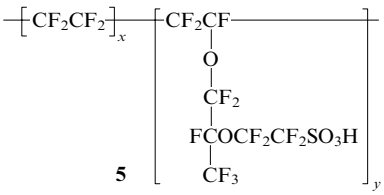
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4

Z = CN, NO_2, OH, OAlk, CO_2H, *etc.*



5

As regards their chemical structure, system **1** is an aromatic polymer, polyimide **3** can be assigned to polyaromatic rigid rod polymers and vinylic polymers **2** and **4** contain sulfonic acid groups in the lateral residues.

Insofar as the trial-and-error method had not led to any substantial progress in the membrane development, the authors of the above study [126] attempted to find a structure–property relationship for the considered polymer membrane systems and to propose on its basis the scientific principles of selecting PEM with optimal characteristics. This analysis relied on the results of studying the formation of ionic channels for proton transport, which was manifested by the phase separation of the hydrophobic polymer backbone from the hydrophilic part of the polymer with sulfonic acid groups.[127–129] A significant role is played by not only the number of sulfonic acid groups, but also the features of their distribution within the polymer matrix and the water content in the channels.

Let us consider several important results mentioned in another study.[20, 35]

A comparison of the Nafion (**5**) and SPEEK (**1**) microstructures (Fig. 5) showed that in Nafion the water channels are wider and characterized by the higher connectivity. In the narrower SPEEK channels, protons have to be located closer to the SO_3 groups bound with the polymeric matrix and are subjected to stronger attractive forces enhanced by the basicity of polymer **1**. This explains the weaker mobility of protons in SPEEK as compared with Nafion.

The results of several published studies confirmed the aforementioned operation characteristics of these types of membranes. Thus the microphase separation was observed [130] in sulfonated polyimide membranes where the polyimide backbone bears sulfonic acid-terminated side alkoxy chains. The possibility of enhancing the proton conductivity of polyimides with sulfonic acid groups in the side chains was demonstrated.[131]

A comparison of the microstructural characteristics of materials **2**, **4** and **5** has shown that whereas the latter (Nafion) showed clear indications of microphase separation in the form of ion aggregates, the majority of ion channels in polymer **2** were distributed uniformly, while the BAM membrane (**4**) demonstrated ion aggregation with uniform distribution and less developed localization of ionic domains.[43, 45] On the whole, system **2** was characterized by more pronounced microphase separation and higher conductivity as compared with system **4**.[126]

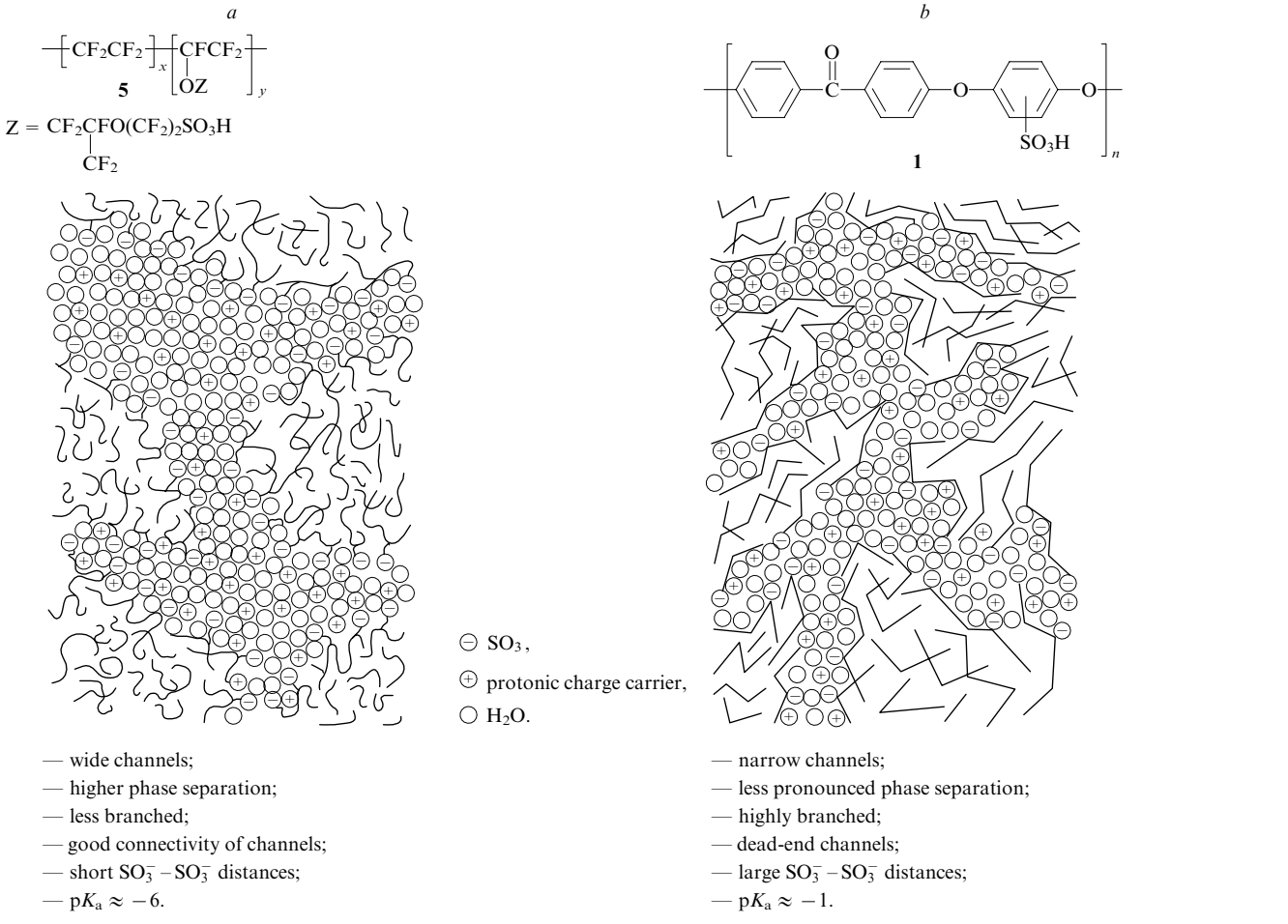


Figure 5. Structure of proton-conducting channels in Nafion (*a*) and sulfonated poly(ether ether ketone) (*b*).[20]

The complex nature of the dependence of proton conductivity on the structural features of PEM, namely, on the domain structure, the sulfonic acid group concentration in the membrane, water content, proton effective mobility, was revealed.[20, 52, 126] The relationship between these parameters turned out to be more complicated than that assumed in the earlier studies. Figure 6 depicts schematically membranes that differ in the degree of tortuosity of conducting channels and the distance between the neighbouring SO_3H groups. The different sizes of channels and the presence of dead ends determined the deviations of the proton conductivity from its theoretical values.

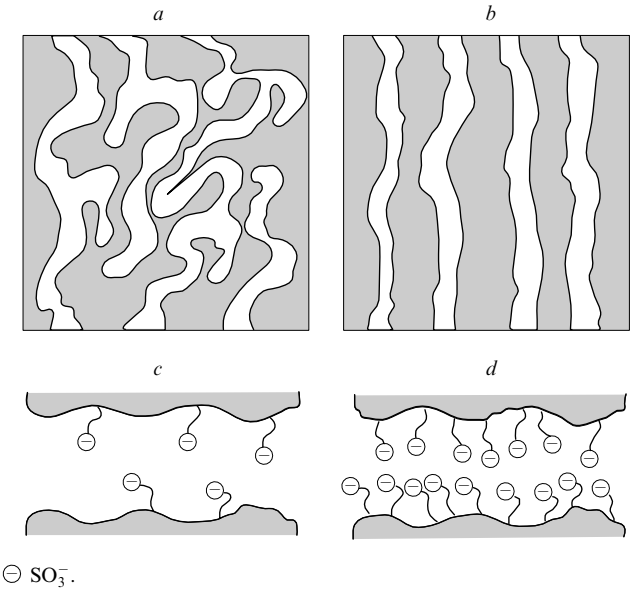
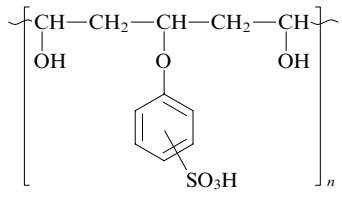


Figure 6. Schematic presentation of aqueous domains in proton-exchange membranes (white) with more (*a*) and less (*b*) tortuous channels. The spatial arrangement of acid groups within aqueous channels of the membranes with larger (*c*) or smaller (*d*) distances between the neighbouring sulfonic acid groups.[126]

Yet another non-fluorinated system for PEM was proposed by Dobrovol'skii *et al.*[132] The polymer systems based on poly(vinyl alcohol) (PVA) etherified with phenolsulfonic acids (PSA) were employed for manufacture of highly efficient proton-conducting membranes.



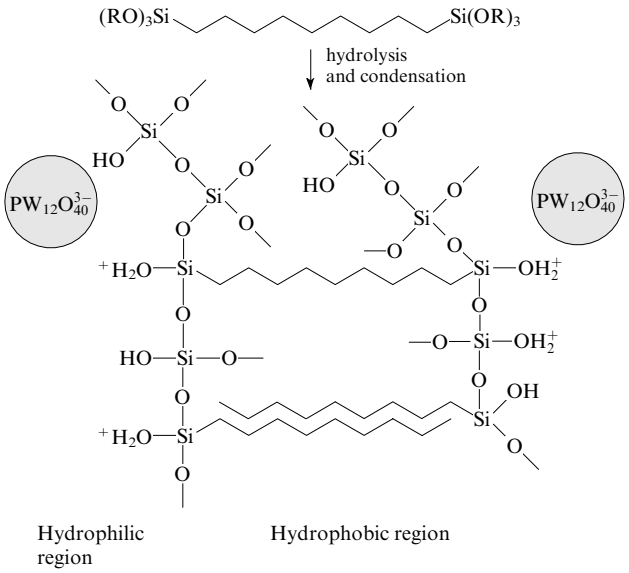
The conductivity of such a system depended on the PVA : PSA ratio and increased with the increase in the PSA content, affected little by humidity and remained sufficiently high up to 80 °C.

The oriented nanodomain structures synthesized by plasma-induced surface graft polymerization of 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPSA) to track-etched polycarbonate as a matrix was studied.[133] The morphology of the nanodomain structure was determined by scanning electron microscopy and attenuated total reflection Fourier transform IR spectroscopy. With a decrease in the domain size, the proton conductivity of the synthesized polyelectrolyte increased sixfold at the most as compared with isotropic bulk poly-AMPSA gel membrane.

Thus, studies of different PEM randomly sulfonated in the backbone, including condensation polymers show that the domain structure, the contents of sulfonic acid groups and water in ion channels of PEM are among the most important factors affecting the proton conductivity.

4. Hybrid polymer membrane systems

This new rapidly developing research direction is associated with the synthesis of hybrid polymer membranes. A new class of amphiphilic organic-inorganic hybrid membranes have been produced by the sol–gel processing of bridge polysilsesquioxanes and doped with acidic fragments of phosphotungstic acid.[134]



Hybrid polymer membranes synthesized by the sol–gel method for different ratios of 3-glycidyloxypropyl(trimethoxy)silane and phosphonoacetic acid[135] retained thermal stability up to 200 °C, mechanical strength and transparency and exhibited conductivity up to 8.7×10^{-2} S cm^{-1}. An organic-inorganic hybrid PEM was prepared by radical co-polymerization of trimethoxysilylmethylstyrene and (1-phenyl)vinylphosphonic acid.[136] The manufactured membranes retained stability up to 180 °C and their proton conductivity reached 3.7×10^{-2} S cm^{-1}.

An interesting approach has recently been proposed[137–141] by ITM Power Ltd. and ITM Fuel Cells Ltd. as is reflected in a series of patents and publications.

They concern, in particular, fabrication of membrane electrode assemblies (MEA) that include electrodes and an ion-exchange polymer membrane comprising hydrophobic and hydrophilic segments containing a 'strong' ionic group. Such a polymer is prepared by the γ-radiation-induced *in situ* co-polymerization of a mixture of hydrophobic and hydrophilic co-monomers including a monomer containing the 'strong' ionic group. The polymer is preferably cross-linked by applying post-polymerization radiation or by using a cross-linking agent. These PEM are claimed to exhibit high proton conductivity and controllable hydrophilicity; moreover, it is possible to recycle platinum when utilizing spent MEA. A possibility of reducing costs of the

membrane and the MEA operation by one order of magnitude as compared with Nafion membranes was reported.

The preparation of a series of hybrid organic–inorganic polyelectrolyte membranes to be used in direct methanol FC with semi-interpenetrating polymer networks (semi-IPN) based in a poly(vinyl chloride) (PVC) matrix and silica covalently bound to the co-polymer was described.[142] The synthesis involved the following stages: 1) co-polymerization of styrene, *p*-vinylbenzyl chloride and divinylbenzene impregnated into a VC film, 2) reaction of the chloromethyl-containing polymer with (3-methylaminopropyl)trimethoxysilane, 3) sol–gel process in an acidic medium and 4) sulfonation. The structure of interpenetrating co-polymers within the PVC matrix with chemically linked silica imparts high mechanical strength to the membranes. With the increase in the silica content, proton conductivity and water content decreased, whereas the resistance to oxidation increased. For the hybrid membranes, the proton conductivity-to-methanol permeability ratio was higher than for Nafion-117. Thus, the hybrid membranes are the promising candidates for the use in direct methanol FC.

Recently, fabrication of improved proton-conducting membranes based on interpenetrating polymeric networks (IPN) has been documented.[143–148] The polymer materials described in both a patent[143] and a paper[144] were proposed for the design of extended wear soft contact lenses. An analogous solution that employed other polymeric systems was described.[145, 146] One of the developed hybrid membranes was granted with a RF patent[147] and its properties and the method of synthesis were described in detail in a publication.[148]

In the fabrication of IPN, one of the networks built of 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPSA) as the sulfonic acid-containing component in combination with acrylonitrile (AN) and *N*-vinylpyrrolidone (N-VP) was hydrophilic and its main function was to provide the proton conduction; the other network built of AN and N-VP in a different ratio was more hydrophobic and provided the membrane with satisfactory mechanical strength and the barrier properties with respect to components of the FC working medium (oxygen, hydrogen). Varying the AN : N-VP co-monomer ratio in the preparation of the second network and the mass ratio of networks (the optimal content of the second network is 10% – 15% of the first network mass) enabled control over the proton-conducting, water-retaining and mechanical properties of the IPN produced and mahufacture of membranes with high proton conductivity and improved mechanical strength in the hydrated state up to elevated (90 °C) temperatures. Such IPN exhibited proton conductivity (σ_H) of 0.12 – 0.31 S cm^{-1} at 20 °C and 0.019 – 0.095 S cm^{-1} at 90 °C. In addition, the physical and mechanical properties of hydrated IPN-based membranes could be substantially improved, namely, the ultimate tensile strength (σ_p) was 2.04 – 2.54 MPa and the elastic moduli of materials (E) increased up to 3.52 – 4.85 MPa, which allowed these membranes to be used in the temperature range up to 90 °C.

Moreover, a possibility was demonstrated for improving the physical and mechanical properties of membranes by preparing additional cross-linked structures by the sol–gel method through the introduction of modifying hydrolyzable co-polymers of the alkoxysilane type (trimethoxy(vinyl)silane, triethoxy(vinyl)silane, 3-(trimethoxysilyl)propyl methacrylate) in the first stage of synthesis of co-polymers with ionogenic groups.

Hydrolytic treatment of such co-polymers resulted in hydrolysis of the alkoxysilane groups to the silanol groups, which was followed by their partial condensation at elevated temperatures.

The increase in the alkoxysilane concentration at a constant AMPSA concentration in the monomer mixtures increased the proton conductivity (at moderate temperatures) of the polymer membranes of all structures studied. This can be explained by both the appearance of additional randomly distributed links, which changed the distribution of the ionogenic sulfonic acid groups in the co-polymer, and the increase in the number of the non-condensed silanol groups, which improved the water-retaining properties of the co-polymer and optimized the transfer of hydrated protons through the membrane. The introduction of modifiers also made it possible to manufacture membranes that are mechanically strong at elevated (90 °C) temperatures albeit with slightly lower proton conductivity.

Modifying IPN membranes with organosilicon monomers proved to be the most effective. Organosilicon modifiers introduced into the network 1 of a membrane made it possible to obtain IPN with enhanced physical and mechanical properties (σ_p = 2.24 – 2.59 MPa, E = 4.50 – 9.58 MPa) with retention of high proton conductivity (σ_H = 0.087 – 0.21 S cm^{-1} at 20 °C and 0.025 – 0.078 S cm^{-1} at 90 °C).

Table 3 shows some characteristics of proton-conducting hydrogel membranes synthesized in our studies.

As can be seen, proton-conducting membrane systems characterized by satisfactory strength parameters, water-content and proton conductivity were mahufactured based on accessible monomers.

Table 3. Characteristics of proton-exchange polymer membranes based on interpenetrating networks.[148]

Polymer network 1 composition (mass %)				Polymer network 2 composition (mass %)			Mass ratio network 2 : network 1	EW	Proton conductivity / S cm^{-1}		Mechanical properties at 20 °C		
AN	N-VP	AMPSA	EGDM [a]	AN	N-VP	EGDM [a]			20 °C	90 °C	σ_p/MPa	E/MPa	ε (%)[b]
41.2	41.2	16.5	1.1	49.5	49.5	1.0	0.77	2221	0.122	0.052	2.04	–	180
41.2	41.2	16.5	1.1	49.0	49.0	2.0	0.19	1495	0.273	0.095	2.05	3.52	183
50.0	31.6	16.5	1.9	59.1	38.9	2.0	0.29	1619	0.124	0.025	–	–	–
50.0	31.6	16.5	1.9	20.0	77.9	2.1	0.35	1694	0.314	0.019	–	–	–

[a] EGDM is ethylene glycol dimethacrylate; [b] ε is relative elongation at rupture.

III. Conclusion

The analysis of studies on the development of proton-conducting polymer membranes made it possible to distinguish three periods of their evolution. The first period (the 1960s – 1970s) was marked with bright achievements in the development of first fuel cells and fabrication of membranes of the Nafion type and FC thereof. After a period of certain decay, a new rise in the activity of studies in the field of fuel cells and, correspondingly, in the development of polymeric membrane systems was observed in the 1990s.

Three groups of polymer systems suitable for the application in PEM for FC are clearly distinguished. The first group contained perfluorinated sulfonic acid-containing polymers, namely, Nafion and its analogues, and also different versions of these systems structurally modified according to various principles and approaches. Studies in this direction substantially advanced as regards their practical implementation, namely, at present, membranes of the mentioned type are already manufactured on the industrial scale and used in FC of different types.

The second group of polymer systems suitable for the manufacture of PEM comprised condensation polymers. This type of membranes are widely employed at present and considered to be very promising taking into account their thermal stability and the possibility of usage in a wide temperature range. Membranes based on polybenzimidazoles are produced on a pilot scale so that one can expect considerable extension of their application field in the nearest future.

The third group of polymer systems for membranes is represented by hybrid systems including hydrogels. The scientific basis substantiating the prospects of their application is only in the stage of development; however, the features of their structure, the accessibility and simplicity of their fabrication make expedient their further studies.

This review was prepared with the financial support by the Presidium of the Siberian Branch of the Russian Academy of Sciences and the Department of Chemistry and Materials Science of the Russian Academy of Sciences (Project 'Development of principles of control over the structure and properties of proton-conducting ion-exchange membranes based on hybrid systems' within the programme 5.3 OKhNM RAN 'Development and investigation of macromolecules and macromolecular structures of new generations').

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