Perspective Non-Fluorinated and Partially Fluorinated Polymers for Low-Temperature PEM FC

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Additional information is available at the end of the chapter

Abstract

The main requirement to the materials used to make membranes polymer electrolyte membrane fuel cells (PEM FC) is the combination of high proton conductivity and resistance to the FC operation conditions. Thus, the search for inexpensive and high-performance non-fluorinated or partially fluorinated materials for use as FC membranes is an actual task today, since the use of membranes based on perfluorosulfonate acid has a number of disadvantages limiting their application. The aim of this study is the investigation of sulfonated polyimide (SPI) and materials for use as FC membranes. The relevance of research stems from the fact that the use of the SPI will allow to increase the resistance of the membrane to the constantly changing environment in which PEM operates. The objects of research are sulfonated polyimides. SPIs, especially aromatic SPIs, are attractive to researchers, because of the possibility of obtaining a wide variety of chemical structures and also due to their excellent thermal, mechanical properties and high resistance to aggressive media. The results of this study will be methods of obtaining and evaluating the advantages and disadvantages of SPI-based materials. For the first time, special attention will be paid to advanced development based on SPI with the addition of crown-ether fragments.

Keywords: polyimides, poly(imide-siloxane), polyimidesters, polyimide matrix, fuel cell, proton-exchange membrane, proton exchange

1. Introduction

Fuel cells (FC) are chemical sources of current. They perform direct conversion of fuel energy into electricity, avoiding combustion processes and conversion of thermal energy

into electrical energy. In an ideal fuel cell, electrolyte and electrodes are not consumed and do not undergo any changes during the operation process – the chemical energy of fuel is converted directly into electricity.

The FC device is similar to the device of the galvanic cell. The main part of any fuel cell is the membrane-electrode assembly (MEA), which is a solid electrolyte layer with the applied electrodes. One side of the membrane (similar to liquid electrolyte in the galvanic element) is applied to the cathode and the other anode catalytic layers. Most often, the catalyst of the anode, molecular hydrogen dissociates and loses electrons. Cations of hydrogen are conducted through the membrane to the cathode, but the electrons are given to the external circuit because the membrane does not pass electrons. On the catalyst of the cathode, the oxygen molecule joins with an electron supplied from an external communications and with arrived proton to form water, which is the only product of the reaction. The current collecting at the cathode and anode sides, a supply source of reagents and withdrawal of the reaction products is carried through the porous gas diffusion layers (GDL), is usually made of carbon materials.

There are several different types of fuel cells classified according to the type of electrolyte. The type of the electrolyte depends on the most parameters of the FC, such as operating temperature, size, energy output, etc.

Fuel cells based on polymer electrolyte (proton-exchange) membrane (PEM) is designed to become compact sources of energy and replace petrol and diesel engines. These systems operate at relatively low temperatures up to 100°C. They quickly go on working power, and are compact, which is advantageous for use in transport. The main, and still not overcome the disadvantage of this type of FC is a weak resistance of the membrane to constantly changing environment in which operate PEM.

Membrane PEM FC works in conditions of constantly changing temperatures, high humidity, organic reagent and the formation of peroxides. The main requirement to the materials used to make membranes is the combination of high proton conductivity and resistance to the conditions of the FC. An important criterion is also the low cost of their production.

The first electrolytic membrane, which was developed by General Electric in the USA in the late 1960s to FC used in spacecraft of the Gemini, was sulfonated copolymer poly-(styrene-divinylbenzene). This polymer was not sufficiently resistant to oxidation under operating conditions of FC. A major breakthrough in technology proton-conducting membranes for fuel cells was the emergence of perfluorosulfonate acid (PFSA) Nafion – DuPont product obtained in the 1970s and Nafion counterparts from other firms, for example, Flemion® (Asahi Glass), DowMembrane® (Dow Chemical) and Aciplex® (Asahi Chemical).

However, the own proton conductivity of such membranes is extremely small, and effectivity proton transfer is determined by the presence of adsorbed atmospheric moisture. Moreover, the market value of the Nafion membranes is 700–800\$/m^2.

Despite the fact that PFSA are still excellent materials for membrane fuel cells, yet they have several significant shortcomings that limit their widespread application. These factors stimulate

the interest of researchers to finding cheap and high-performance alternative materials for use as membranes, fuel cells. Such polymers, as polyetherketone, polyetheretherketone, polysulfone, polyether sulfones and polyimides are particularly attractive for researchers. Due to the large diversity of possible chemical structures, including partially fluorinated, they have a high mechanical strength, chemical and thermal stability.

One of the most promising materials for the fabrication of membranes FC are the aromatic polyimides. Polyimides have high heat resistance, the most heat-resistant polyimides based on dianhydride pyromellitic and 1,4,5,8-naphthalenemethanol acids.

These polyimide films are hydrophilic and do not have proton conductivity. Therefore, to ensure high proton conductivity in polyimide chain introduce acidic groups (most often sulfonic – SO_3H, sometimes phosphoric). The membranes based on sulfonated polyimides (SPIs) (containing the main chain and/or branches of the group SO_3H), gas permeability for hydrogen is about three times lower than that of Nafion.

2. Perspective non-fluorinated and partially fluorinated polymers for low-temperature PEM FC

One of the advantages of fuel cells with polymer electrolyte membrane (PEM FC) indicate a high efficiency of conversion of fuel energy into useful energy, compared with current alternative systems, based on heat engines, whose efficiency is limited by Carnot cycle. It is believed that efficiencies can be over 80%. In practice, however, the efficiency of fuel cells with a polymer membrane is about 50%.

The main difference between fuel cells from other chemical current sources is the possibility of continuous fuel injection and continuous weaning current for potentially unlimited period of time. In practice, however, there is a severe degradation of all components of the MEA, which leads to a monotonous decrease of the voltage on the plates of FC (hence reduced efficiency) when fixing the subtracted current [1].

The "heart" of the MEA is a polymer electrolyte (proton-exchange) membrane (PEM). Typically, the proton-exchange membrane is a film of polymer with a hydrophobic main chain and the acid groups in the side chains. Water in contact with polymer is clustered close to the acid groups, forming nano-sized hydrated cluster. In this area, in addition to water contain various hydrated forms of the movable proton. Thus, the hydrophilic part of the polymer provides efficient proton transport, while the hydrophobic part stabilizes the morphology of the membranes and ensures their mechanical strength [2].

The hydrophobic part of the polymer usually contains aliphatic, aromatic, fluorinated or non-fluorinated fragments. As acid groups generating protons, sulfonates are most often used, more rarely acid residues of phosphoric acid. It is believed that the sulfonated polymers are more efficient in the presence of water vapor, while the more phosphorylated heat-resistant polymers and their conductivity is less dependent on humidity.

To improve the conductivity, the hydrophilic portion of the proton-exchange membrane is often injected with a water-soluble proton-generating additives (usually strong acid), nanoscale oxides or solid electrolytes. Sometimes the proton-generating additive is injected into a non-conductive polymer matrix. In this case, the hydrophilic part is formed by the coordination of water around the introduced additives with subsequent separation of phases.

The main function of proton-exchange membrane is to transfer the cathode area of a proton, resulting in ionization of hydrogen at the anode. Therefore, the membrane should have a maximum conductivity. The conductivity at the level of 10^{-1}–10^{-3} s/cm is considered adequate for use in FC. Because ideally, the work of FC need to carry in conditions of significant fluctuations of temperature and humidity as fuel and oxidizer, it is desirable that an efficient proton transfer occurred under these conditions. In order to avoid electrical losses, the electronic component of conductivity should be minimal (at least 2–3 orders of magnitude lower than the ionic component) [3].

In addition, the proton-exchange membrane plays a role of gas separation: it cuts off the anode side of the MEA, which contains hydrogen, from the cathode, where air or oxygen is blown. The low gas permeability when using hydrogen under high pressure is especially important. The permeability of the membranes of less than 10^{-2} ml/(min cm^2) is considered sufficient for long-term operation of the fuel cell.

The proton-exchange membrane is subject to a number of requirements. For the efficient operation of the fuel cell, ohmic losses in the membrane should be minimal, and the proton conductivity of the membrane is high. The membrane must have mechanical strength sufficient to pressing on the electrodes to the membrane and operation at elevated pressures of the reactants.

Since the formation of extremely reactive hydrogen peroxide on the cathode is possible, in addition to water, the membrane should possess high chemical stability to oxidation and hydrolysis. The water released at the cathode during the fuel cell works is partially absorbed by the membrane, leading to its swelling. This process is most noticeable when using the humidified air. Excessive swelling of the membrane with subsequent drying, after repeated enabling/disabling of the fuel cell, is extremely undesirable process that leads to destruction and exfoliation of the thin active layer and deterioration of the characteristics of the fuel cell. To prevent direct chemical (not electrochemical) reaction of the reactants on one of the electrodes is necessary that the membrane was gas-tight. Penetration of hydrogen on the cathode side equivalent leakage current and should be minimized in order to increase the efficiency of the fuel cell [4].

2.1. Main requirements for PEM

In order for the materials to be used in PEM fuel cells, they must have a number of conflicting requirements such as in Ref. [5]:

1. Low cost.

2. Good film forming ability.

3. Sufficient proton conductivity (≥100 MS/cm), weakly dependent on relative humidity.

4. The ability to retain moisture at high temperature.

5. Thermal, oxidative and hydrolytic stability.

6. Low permeability to fuel, for example, methanol $<10^{-6}$ mol (min cm)$^{-1}$.

7. Preservation of the strength properties at operation temperatures of FC (80–200°C) within the required time.

8. The possibility of disposal of spent membranes by standard methods.

It should be noted that the functional characteristics of membranes need to be optimized in the complex, because they are fundamentally interrelated. Indeed, it would not be quite correct to improve, for example, the proton conductivity of the membrane material, without regard to the mechanical properties and the stability of the membrane as a whole. A simple way to increase proton conductivity of the polymer sulfonic acid is, for example, to increase the number of sulfonate groups per unit volume (i.e., decreasing equivalent weight), but this path inevitably leads to obtaining material with poor mechanical properties, excessive swelling or even dissolving in water, which is the product of the reaction. Similarly, the phosphorylation or the increase of doping of polybenzimidazole by phosphoric acid leads to soft gel consistence, incapable of effective separation of reactants between cathode and anode.

On the other hand, losses in the membrane are determined by not specific but general resistance. This means that the transition to more durable membranes that could efficiently separate the reagents, being more delicate, with a mild deterioration in its conductivity could be an advantageous. In practice, however, the general principle is that an increase in mechanical stability of the membrane and reducing its permeability toward reactants, for example, by chemical linkage, always leads to the inevitable drop in conductivity.

2.2. Polymers used as proton-exchange membranes

The first electrolytic membrane, which was developed by General Electric in the USA in the late 1960s to FC used in spacecraft of the Gemini, was sulfonated copolymer poly-(styrene-divinylbenzene). This polymer was not sufficiently resistant to oxidation under operating conditions of fuel cells [6]. A major breakthrough in technology proton-conducting membranes for fuel cells was the emergence of perfluorosulfonate acid (PFSA) Nafion – DuPont product [7, 8].

2.2.1. Commercial proton-exchange membrane

Currently the most common membrane is a perfluorinated ion-exchange membrane Nafion developed by DuPont in the 1970s, there were also a number of analogous Nafion – products companies Asahi Glass (Flemion), Asahi Chemical (Aciplex), Dow Chemical, 3 M, FuMA-Tech (Fumapem), etc., wherein minor variations in the structure of side chain polymer molecules (**Figure 1**).
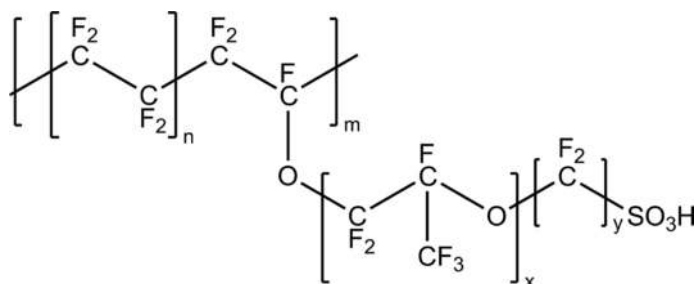
Figure 1. Structure of the Nafion membranes [2].

Membrane Nafion is a copolymer of tetrafluoroethylene and a possible co-monomer having a side chain of perfluorinated vinyl ether with end sulforaphanes.

Materials based on such polymers are high-tech, and able to get a pretty high-performance at operating temperatures up to 90°C. However, the own proton conductivity of the membranes is extremely small, and effective the proton transfer in them is determined by the presence of adsorbed atmospheric moisture, Therefore, these membranes are FC only work under conditions of constant wetting and hydrostatic, which requires the introduction of additional devices and increase rates of electrochemical generators [2, 9].

It is known that platinum catalysts are very sensitive to the purity of fuel. Negative impact on the catalyst may be present in such hydrogen as impurities hydrogen sulfide. Therefore, the preparation of fuel for low-temperature FC must include expensive phase removal of sulfur compounds and CO [9]. Increasing the operating temperature can in principle improve the efficiency of platinum catalysts. So, the permissible content of CO increases from 10 to 20 ppm at 80°C to 1000 ppm at 130°C. This significantly reduces the cost of the fuel. In addition, increasing the operating temperature allows for more effective heat dissipation and disposal of heat (the latter increases the total fuel efficiency).

Temperature rise of FC is also significantly accelerates the electrode reaction, therefore, can be expected to reduce necessary for the efficient operation, of the quantities of the noble metal in the electrodes. However, the proton conductivity of Nafion-type membranes at temperatures above 90°C is drastically reduced (**Figure 2a**), making their use impossible at elevated temperatures. Obtaining membranes themselves are extremely time-consuming and the cost of quality of membranes of this type are large.

Another commercially available system that may be used at temperatures up to 200°C, are membrane based on PBI, doped with phosphoric acid (**Figure 3**).

Phosphoric acid forms an acid-base complex with a polymer matrix (membrane brand the company PEMEAS Celtec Division) [10]. The significant superiority of such membranes in comparison with the Nafion membranes is their high proton conductivity in the absence of moisture (**Figure 2b**) and high thermal stability (up to 600°C). The working temperature range for the MEA on the basis of such membranes is 160–180°C. The fuel cell in this temperature region enables the use of hydrogen with high co content.
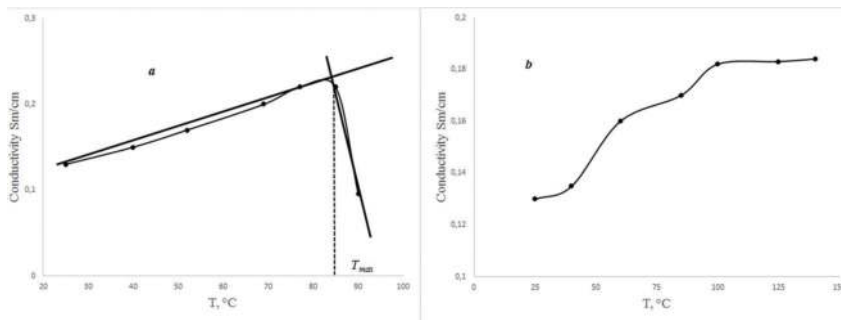
Figure 2. Dependence of proton conductivity for the membranes Nafion-117 (a) and on the basis of polybenzimidazole (PBI), doped with phosphoric acid (b), the temperature [4].
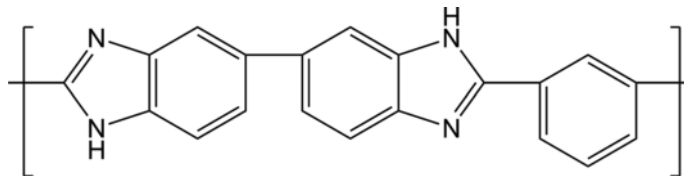

Figure 3. The structure of polybenzimidazole.

The main problem with membranes is that they are "afraid" of liquid water, in contact with which is destroyed in an acid-base complex and the phosphoric acid is washed out in the area of catalytic and diffusion layers, leading to partial blockage of the gas pores, degradation of bipolar plates and the gas-feed system. The removal of phosphoric acid from the polymer matrix reduces the proton conductivity of the membrane. To avoid condensation of water vapor in the cathode area using relatively time-consuming procedure for stopping the fuel cell, which consists of the removal of loading, purging dry argon to remove water vapor, sealing and cooling. Of course, such a laborious procedure requires additional equipment, which significantly increases the cost of electrochemical generators of the MEA on the basis of the membranes of PBI/phosphoric acid.

2.2.2. Non-fluorinated polymers

Due to the high cost of perfluorinated polymer sulfonic acids and also because of their high permeability toward methanol, great attention to various hydrocarbon polymer sulfonic acid was given in recent years. At a lower cost of production, those acids could be a substitute Nafion [5].

Typical examples of hydrocarbon polymers used as membranes, fuel cells are sulfonated polyetheretherketone, polyarylene, polysulfone and polyimides.

In general, in comparison with National, hydrocarbon polymers are characterized by both advantages and disadvantages. Typically, the synthesis of carbohydrate polymers of the least

costly than the synthesis of fluorine-containing polymers. The permeability of the hydrocarbon polymers on oxygen and methanol is lower than polyfluorinated polymers. Because of lower hydrophobicity of the macromolecules of hydrocarbon polymers in General, the sensitivity of their proton conductivity to the degree of hydration of the reactants supplied to the fuel cells is not as pronounced as perfluorinated sulfonic acids. This simplifies the control of water balance in the MEA during the work. The less pronounced hydrophobic properties of hydrocarbon polymers molecules are also allowing to retain water at high temperatures, which increases the possible working temperature range of the FC – in comparison with FC-based membranes Nafion and its analogs. However, the balance of conductivity and mechanical properties of hydrocarbon polymers is worse, in general, than for the perfluorinated polymeric sulfonic acid.

2.2.2.1. Sulfonated polystyrene and its analogs

The first real working generator on fuel elements, was the generator of General Electric power of 1 KW, which was used as a source of electricity and drinking water for astronauts participating in the Gemini project in the mid-1960s. However, the working life of this installation was limited due to the chemical degradation of the membranes based on sulfonated polystyrene under the action of peroxides, formed at the cathode. For such membranes the company Ballard Power Systems has developed a new series of sulfonated copolymers of α,β,β-trifluorostyrene and substituted α,β,β-trifluorostyrene.

Such polymers are known under the brand name Ballard Advanced third generation Membrane (BAM3G) and have a chemical structure shown in **Figure 4**.

Alternative and relatively cheap way of obtaining proton-exchange membranes is the method of grafting of ionogenic groups in the fluorinated polymer matrix. The method of radiation grafting is well known as a method of modification of polymers to modify their physical-chemical properties [11–16]. Radiation-grafted membranes get based on existing commercially
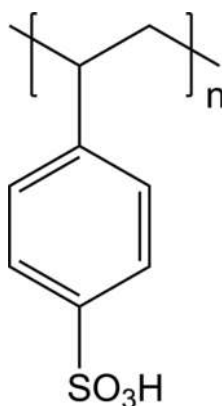

Figure 4. Structural unit of sulfonated polystyrene.

available films in three stages. In the first stage, a polymer film is irradiated with an electron beam or gamma radiation for the formation of free radicals in the polymer material. Next, to the polymer backbone sutured to the lateral pendants, which are then sulfonated. It is argued that the process of obtaining such membranes more economical than the manufacture of Nafion. Using this method you can modify the fluorine-containing materials in [17–20], but comparison of these materials with each other is difficult due to different sample conditions and different degree of grafting.

Most radiation-grafted membranes contain polystyrenesulfonic acid in side chains (**Figure 5**).

As a polymer backbone, a variety of fluoro-substituted polymers include polyvinylidene fluoride, a vinylidene fluoride copolymer with hexafluoropropylene with a different molar ratio of comonomers, a copolymer of tetrafluoroethylene with hexafluoropropylene, etc. [20–22].

The values of proton conductivity of the obtained membranes at high degrees of grafting are compared with Nafion up to 0.11 s/Cm under 100% humidity and room temperature. The same can be said about the permeability of hydrogen [22]. The value of proton conductivity is directly related to the ability of the membrane to absorb water, which in turn substantially depends on the properties of the polymer matrix. Usually, a significant disadvantage of these membranes is their high degree of swelling, greatly exceeding the values for Nafion [20, 21].

2.2.2.2. Sulfonated polyphenylquinoxalines

Ballard Advanced Materials has been researching this group of polymers over the past 10 years. The first series of polymers based on polyphenylquinoxalines (PPQ), named BAM1G, was obtained by direct sulfonation of the PPQ (**Figure 6**).

BAM1G membrane different thickness (40–120 μm) has good mechanical properties in dry and wet conditions. The characteristics of these membranes with equivalent weight of 390–420 is comparable to Nafion-117, however, the duration of work in the fuel cell before the
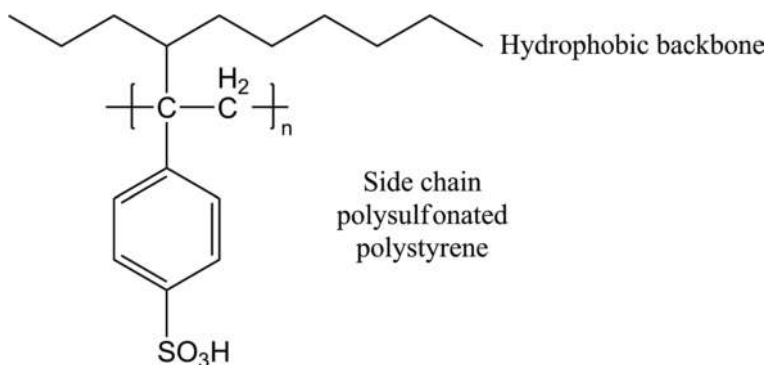

Figure 5. Structure of the polymer with sulfonated styrene in the side chain. The main chain is hydrophobic.
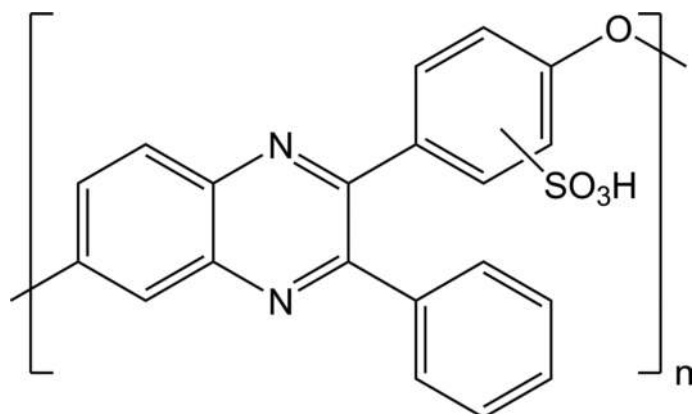
Figure 6. The structural unit of sulfonated polyphenylquinoxaline.

onset of degradation is low, averaging 350 h [23]. It is obvious that they are not able to make real competition perfluorinated membranes.

2.2.2.3. Sulfonated polyarylethersulfones

The basis of polyarylethersulfones is phenyl rings, separated alternately by ether and sulfonic groups. The most researched commercially available Udel polyarylethersulfones (PAES) (**Figure 7**) и and Victrex polyethersulfones (PES). PAES can be partially fluorinated, like Ballard Advanced Materials BAM2G membranes.

The processes of sulfonation of PAES have been studied in detail in [24, 25] and it is shown that for the case of PAES it is impossible to obtain a polymer containing more than one sulfogroup per monomer unit. The use of a softer sulfonating agent (methylsilylchlorosulfonate), in contrast to a rigid sulfurating agent (chlorosulfonic acid), avoids the destruction or cross-linking of the polymer. A disadvantage of sulfonation under mild conditions is the limited degree of sulfonation [26].

Direct sulfonation of PAES, depending on the conditions, leads to two different variants of the arrangement of the sulfogroups in the ortho position to the ether bridge of bisphenol-A (**Figure 7a**) see [27] or to the diarylsulfonic part (**Figure 7b**) see [28], which is most resistant to hydrolysis. In the first case, membranes based on sulfonated PAES are water-soluble at sulfonation degrees of more than 30%, which does not allow their use in fuel cells.

When sulfonated in the diarylsulfonic part, the membranes become water-soluble only at degrees of sulfonation greater than 65% [28]. Attempts have been made to cross-link such membranes in order to reduce solubility in water [29]. However, the cross-linked membranes become brittle at low humidity and show unsatisfactory results when tested in a fuel cell.

Membranes based on sulfonated PES (**Figure 7d**) are insoluble in water. In the case of PES, proton conductivity at the Nafion level is reached at degrees of sulfonation of the order of 90%, however,
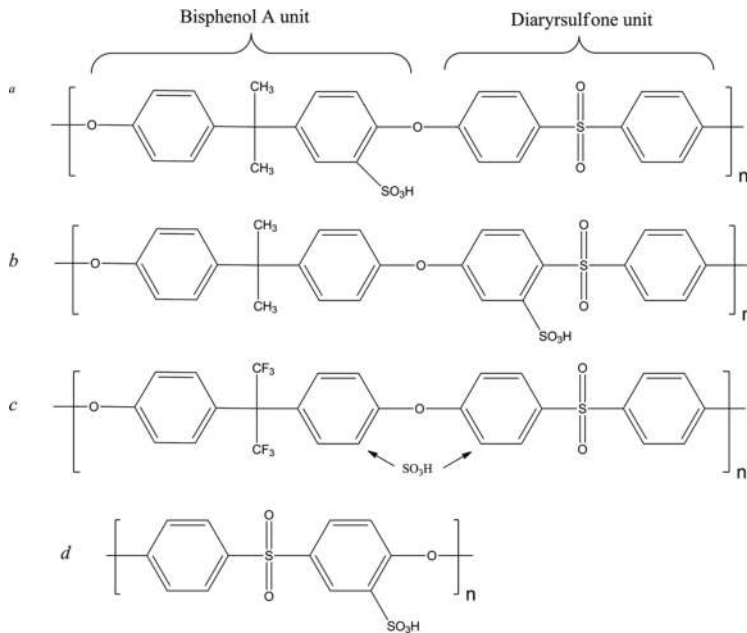
Figure 7. Various polyarylethersulfones: PAES, sulfonated to the ortho position to the ether bridge of bisphenol-A (a); PAES, sulfonated to the diarylsulfonic part (b); polymer BAM2G (c); sulfonated PES (d) [24, 25].

such membranes have a high degree of swelling (three times greater than Nafion at room temperature), which increases significantly with increasing temperature to 80°C and impairs the mechanical properties. To overcome this problem, the membranes were cross-linked with diamines, which reduced not only the degree of their swelling, but also the conductivity [27].

Membranes based on sulfonated fluorinated PAES that are insoluble in water show better performance when tested in a fuel cell compared to Nafion-117 and Dow membranes see [28], but their service life is limited to about 500 h.

2.2.2.4. Sulfonated polyetheretherketones (S-PEEK)

PEEK is a class of aromatic semicrystalline polymers based on phenyl rings separated by ether and carbonyl (−CO-) groups (**Figure 8**).

These polymers have a high thermal stability, chemical resistance and have limited solubility in organic solvents. With the introduction of sulfogroups into the main chain of polymers, their crystallinity decreases and the solubility increases [30, 31].

These non-sulfonated polymers are stable up to 500°C, and sulfonated polymers are stable up to 240°C. There are various procedures for sulfonation of PEEK [32, 33]. Since the sulfonation reaction proceeds by the electrophilic mechanism, in the case of PEEK, the sulfogroup is successfully introduced only into the aromatic nucleus between the two ether bonds because of the high
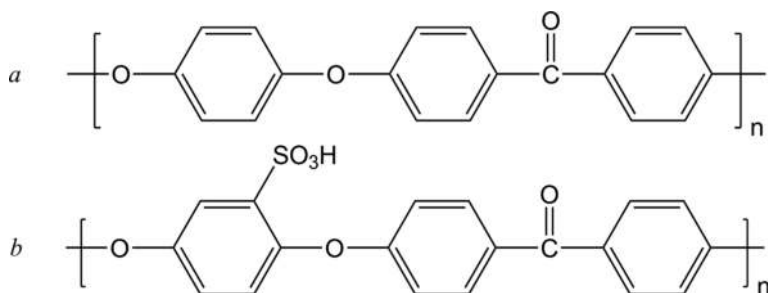
Figure 8. Structural units of PEEK: Basic PEEK (a) and sulfonated (S-PEEK) (b).

electron density in this nucleus. It is possible to add only one sulfogroup to the monomer unit. In the case of PEEK, the use of chlorosulfonic acid as a sulfurizing agent destroys the polymer see [34], therefore concentrated sulfuric acid is used for this purpose [35, 36]. It is possible to achieve a degree of sulfonation of 30–100% without cross-linking and polymer degradation. However, in the sulfonation of PEEK by sulfuric acid under heterogeneous conditions, it is impossible to achieve a random sequence of sulfonated and non-sulfonated polymer units with a sulfonation degree of less than 30% [37]. Successful control of the arrangement of the sulfogroups in the polymer chain can be achieved by using a precursor polymer obtained by copolymerization of amenable and non-sulfonated monomers, followed by sulfonation of the resulting random copolymer [38]. Similar methods of directed design of molecular structure prevent additional and sometimes unpredictable macromolecular reactions in the process of sulfonation.

The solubility of these polymers directly depends on the degree of sulfonation. Thus, with a degree of sulfonation of more than 30%, the polymers are soluble in DMSO, DMF, N-methylpyrrolidone. With an increase in the degree of sulfonation up to 70%, the polymer dissolves in methanol, and at a degree of sulfonation more than 70% – in water. The absorption of water by membranes based on S-PEEK at a degree of sulfonation of 65% and humidity of 100% is 8%. With the same degree of sulfonation and humidity, the conductivity of S-PEEK is small – about 10^{-5} S/cm [39]. At high degrees of sulfonation, membranes based on S-PEEK have high degrees of swelling. To reduce swelling, chemical cross-linking of macromolecules or the addition of agents forming strong hydrogen bonds are used [40]. For example, in Ref. [41] membranes based on mixtures of S-PEEK with amine derivatives of polyarylester sulfone, polyamides and poly-facets were obtained. The degree of swelling of such membranes can be reduced by strong hydrogen bonds between the polymer molecules or the formation of polysols, which, however, results in partial blocking of the sulfogroups and a decrease in the proton conductivity of the membranes.

2.2.2.5. Sulfonated polyphosphazenes

Polyphosphazenes (**Figure 9** in Ref. [42]) are a new class of polymers that are promising for use in FCs due to their thermal and chemical stability and the ability to easily vary the chemical structure of the polymer over a wide range by introducing various side chains into the main chain.
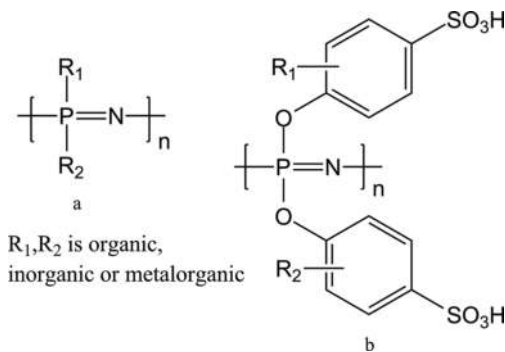
Figure 9. The structural link of polyphosphazene basic (a), sulfonated (b) [43].

Proton-exchange membranes based on sulfonated polyphosphazenes may well act as an alternative to perfluorinated membranes. However, there are only a limited number of papers devoted to obtaining and investigating the properties of such membranes. Difficulties are associated with obtaining water-insoluble polymers and matching their hydrophilic/hydrophobic properties [44]. One of the main methods for the synthesis of these polymers is the reaction of polydichlorophosphazene with various nucleophilic agents to form organic polymeric derivatives with a high molecular weight, the properties of which depend to a large extent on the nature of the side substituents. The sulfonation of aryloxy- and arylaminophosphazenes with concentrated sulfuric acid was carried out in Ref. [45]. It is also possible to use 1,3-propanesulfone as a sulfurizing agent, however, the degree of sulfonation is low enough. Aryloxypolyphosphazenes can also be sulfonated with sulfur trioxide in dichloromethane. It is also possible to use 1,3-propanesulfone as a sulfurizing agent, but the degree of sulfonation is low enough [46]. Aryloxypolyphosphazenes can also be sulfonated with sulfur trioxide in dichloromethane. It was shown in Ref. [47] that at the molar ratio of SO_3 to the amount of monomeric units, only C-sulfonation is observed and the polymer chains attack with the formation of the $\equiv N \rightarrow SO_3$ complex, while increasing the amount of SO_3 there is not only C-sulfonation.

2.3. Proton-conducting membranes based on polyimides

One of the promising materials for the manufacture of membranes TE are aromatic polyimides (PI). Polyimides are characterized by high heat resistance, and the most heat-resistant polyimides based on pyromellitic dianhydride and 1,4,5,8-naphthalenetetracarboxylic acids, which practically do not soften before the beginning of thermal decomposition, and their thermal decomposition temperature is more than 500°C (**Figure 10**).

However, the heat resistance of polyimides is well regulated by varying the nature of the monomers and is usually 300–430°C [48]. Most aromatic polyimides are insoluble in most organic solvents, are inert to the action of oils, and also hardly change under the action of dilute acids.
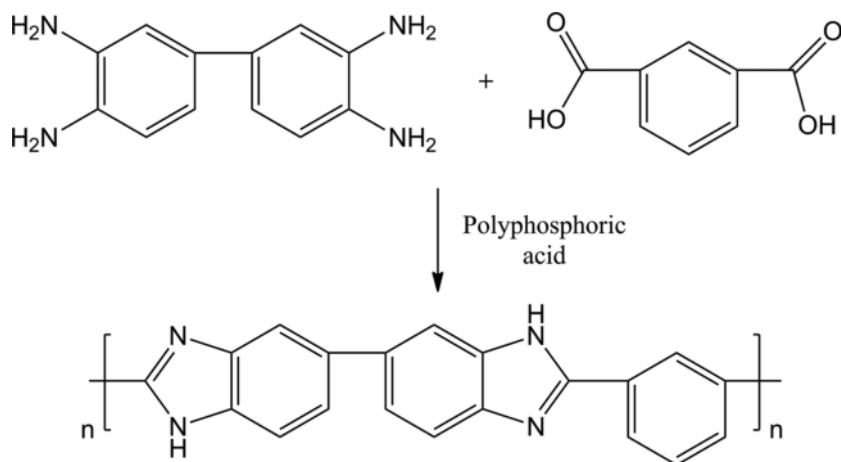
Figure 10. General scheme for the preparation of polyimides. For the preparation, one dianhydride and one or more diamines are used, therefore Q, most often aromatic, and X, Y, Z may be different or identical, both aromatic and aliphatic.

With the introduction into the side chain of various substituents, especially card groups (phthalide, phthalimidine, fluorene and anthrone), the solubility of polyimides is substantially improved. Thus, poly (pyromellitimide) of dianylinophthalein (I) dissolves in DMF, m-cresol, sim-tetrachloroethane, hexafluoro-2-propanol, polyimides 3,3′, 4,4′-benzophenone tetracarboxylic (II) or 3,3′, 4, 4′-diphenyloxydetracarboxylic acid (III) and dianilinfluorene are also dissolved in methylene chloride, chloroform [49].

By themselves, polyimide films have very low proton conductivity. Therefore, to ensure high proton conductivity, acid groups are introduced into the polyimide chain (most often sulfonic acid – SO_3H). In membranes based on sulfonated polyimides (containing in the main chain and/or in the branches of the group SO_3H), the gas permeability for hydrogen is approximately three times lower than for Nafion-117 [50].

The use of polyimides for the manufacture of membranes is hampered by their extremely poor solubility. Fortunately, this problem can be solved, as shown above, by the chemical structure of the polymer, for example, when a 2,2′-diamino-3,4′-diphenyl ether is used as the unsulfonated diamine, a polymer soluble in m-cresol can be obtained.

Polyimides exhibit different resistance to the action of water vapor in different ways. Since polyimide chains in membrane materials will be responsible for mechanical strength and resistance to fuel cell (FC) conditions, it is necessary to choose such structures of monomers (aromatic tetracarboxylic acid dianhydrides and aromatic diamines) that will yield polyimide matrices that are stable under the action of water vapor.

2.3.1. Stability of polyimides in an water environment

It is necessary to consider what determines the stability of polyimides in water environment. Pure water under normal conditions for polyimide films does not work, however, when

boiling in water, the films gradually lose their high mechanical properties [51]. In strongly alkaline (pH > 12) or strongly acidic (pH < 2) media, hydrolysis accelerates sharply, and the film is completely destroyed. This phenomenon is associated with the destruction of imidic bonds. Resistance to hydrolysis depends most strongly on the chemical structure of the dian-hydride component of the unit. In particular, polypyromellitimides are among the least resis-tant to hydrolysis of polyimides [52]. The authors suggest that the hydrolysis of polyimides in neutral environment proceeds through tetrahedral compounds according to the scheme (**Figure 11**).

Further, an amide bond is broken. The limiting stage is the first, namely, the breaking of the imide cycle. The mechanism of alkaline hydrolysis in the example of polypyromellitimides was considered in Ref. [53]. A polyimide film when immersed in a 4 M water solution of KOH at 20°C swells, turns pale, and after few hours becomes colorless while retaining strength and flexibility. After treatment with hydrochloric acid and heating for 30 min at 140°C, this film, according to the results of IR spectroscopy and its physical properties, becomes similar to the original one. In the described conditions, the polyimide regenerates.

To study hydrolytic stability, the authors in Ref. [54] synthesized and studied less stable phthalic (I) polyimides, compared to naphthalic (II) polyimides (**Figure 12**). The resistance of polyimides to hydrolysis was investigated by IR spectroscopy. Thermal stability, pro-ton conductivity, water absorption and ion-exchange capacity of polyimides were also measured.

Comparing the IR spectra of both series of polyimides after aging in water at 80°C for 4 h, the intensity of 1784 cm^{-1} peaks characteristic for the C = O bond in the case of a series of
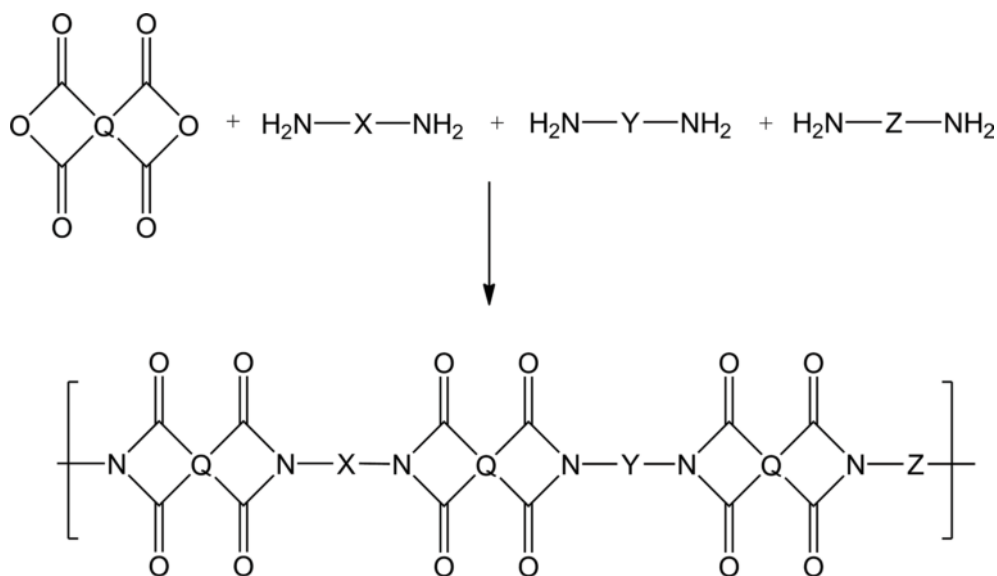

Figure 11. Scheme of the first and second stage of hydrolysis of polyimides in a neutral environment.
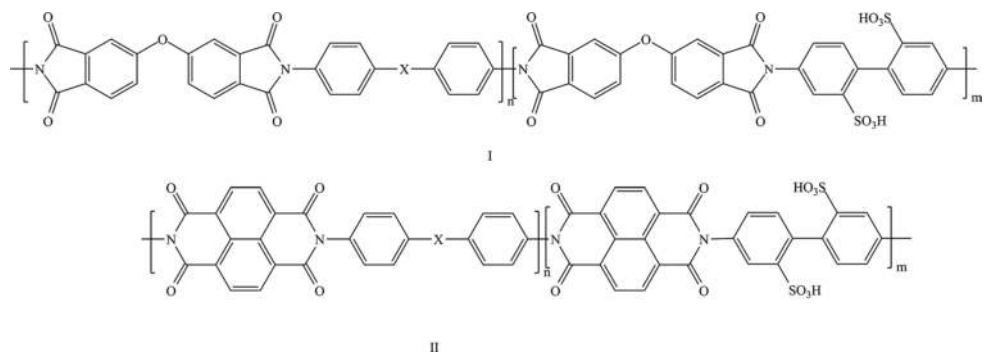
Figure 12. Phthalic (I) and naphthalic (II) series of sulfonated polyimides (where X: –O– or –CH$_2$–).

naphthalic polyimides was higher than in the case of phthalic polyimides. In addition, in the case of naphthalic polyimides, the peaks characteristic of the S = O bond did not decrease or disappear. Similarly, naphthalic polyimide films retained their mechanical integrity even after 3 days of soaking. Phthalic polyimides disintegrated after 52 h.

The presence in the polymer structure of a binaphthalic dianhydride fragment and benzophenone groups in the meta-position toward the imide ring should additionally increase the hydrolytic stability of the polyimide [55–58].

The best hydrolytic stability of naphthalic polyimides appears to be due to steric hindrance, which hinders the approach of water to attack the carbonyl carbon atom of the imide ring (see **Figure 11**).

The influence on the hydrolytic stability can also be exerted by diamine, by increasing (decreasing) the electron density (decrease (increase) in the electrophilicity) of the carbonyl carbon of the imide cycle, for example:

A. The introduction of a voluminous aliphatic fragment into the diamine structure both into the main chain and as side branches [59, 60].

B. The introduction of bridging electron-donor sulfur atoms or phenoxy groups into the main polyimide chain, in addition to substantially reducing the electrophilicity of carbonyl carbon, significantly increase the hydrolytic stability [61–64].

C. Membranes that are made from polyimides, with sulfonated side branches are more stable than similar membranes, where sulfogroups are in the main chain [65].

D. In contrast, the introduction of trifluoromethyl groups, which have a strong electron-withdrawing effect, would threaten the stability of the imide group [66].

E. The hydrolysis reaction of imide rings is reversible, this assumption was confirmed by the fact that cross-linked SPI, with a different chain length of cross-linker, is much more resistant to hydrolysis than non-cross-linked and resistance to hydrolysis increased in proportion to

the reduction of the length of the chain of the cross-linking agent [67]. Thus, the main chain of polyimide can be restored provided that the fragments are closely spaced [68].

F. It was recently discovered that membranes based on porous spongy, non-sulfonated polyimides (matrices), the pores of which were filled with different SPIs, showed higher hydrolytic stability than membranes obtained from the same SPI, but not in the PI matrix [69].

2.3.2. Solubility of polyimides

The solubility of polyimides strongly depends on the chemical structure of the polymer. Two key factors in the development of soluble polyimides are the decrease in the regularity (repeatability of the links) of the main chain and the minimization of the density of imide rings along the main chain. Progress in solving these problems was achieved using fluorine-containing dianhydrides, such as 4,4-(hexafluoroisopropylidene) diphthalic anhydride, or by including oxygen atoms in the diamine (e.g., oxydianiline). In addition, aliphatic side chains were included in diamines to reduce the interaction between polyimide chains and increase solubility. In the previous decades, a large number of structural changes were undertaken, including the inclusion of thermally stable, flexible or asymmetric bonds in the main chain and the introduction of bulky substitutes. Polyimides containing bulky triphenylamine units along the polymer backbone are amorphous and have good solubility in many solvents, excellent film formation and high thermal stability [49].

2.3.3. Sulfonated polyimides (SPI)

It is shown [50] that the sulfonated naphthalic (six-membered imide cycles in the circuit) polyimides when working in the fuel cell demonstrate results comparable to Nafion, at least when working up to 3000 h. At the same time, the characteristics of the membranes based on sulfonated phthalic (five-membered imide cycles in the circuit) of the polyimides is significantly deteriorated after 70 h of operation. It has been suggested that in the process of hydrolysis of phthalic imide structure, there is a rupture of the polymer chains and the membrane becomes brittle. Since six-membered cycles of naphthalic polyimide are much more stable to hydrolysis, their chemical structure meets the requirements for FC membranes. The permeability of methanol through the membrane SPI is much lower than for PFSA membranes [70].

The use of SPI as proton-conductive membranes was first demonstrated in Ref. [71]. The main driving force for the development of SPI research was the search of cheaper alternatives to commercially available Nafion developed by DuPont. Very soon it was discovered that, although SPI swell in high humidity conditions needed to operate fuel cells, however, they showed high values of proton conductivity comparable to Nafion. The water absorption and the coefficient of osmotic pressure are not significantly changed in a wide range of temperatures in contrast to Nafion. Such features make SPI preferred for use in fuel cells operating at medium-temperature range, also SPI less membranes degrade when enabling/disabling FC and also better retain water on the anode side of the MEA.

While the first generation of the SPI electrolytes showed values of conductivity of $2\cdot10^{-3}$ s/cm, up to $4\cdot10^{-2}$ Sm/cm in [72, 73] which were significantly lower than the conductivity of Nafion, the next generation SPI electrolytes gave satisfactory values of conductivity to 1.67 Cm/cm at 120°C in Ref. [74] and 1201 Cm/cm at 80°C for SPI/graphene composite material.

These materials are currently considered promising candidates for the use as FC with PEM, working in the temperature range from 40 to 100°C. In addition, SPI membranes exhibit a permeability to methanol is several times lower than in Nafion, particularly at elevated temperatures [75, 76].

Tests made on FC based on the membranes from variety of SPI showed that the operating time of FC is strongly dependent on the temperature regime of its work. FC on the basis of SPI with sulforaphane in the side chains, in general, worked longer than FC based on SPI with sulfonate groups in the main chain, but still inferior to Nafion. Although testing of SPI membranes was carried out in a real working environment, working time of FC is depended not only on the stability of the membrane, but also on the quality of the connection of electrodes to the membrane [77, 78].

2.4. Proton-conducting membranes with block structure based on polyimides

According to Ref. [5] there are not so much easily synthesized structures of dianhydride aromatic tetracarboxylic acids giving during polymerization of imide cycle naphthalic type. It should be noted that obtaining of the diamines is much easier than dianhydrides and almost all the variety of polyimide structures is achieved through various diamines. However, not all structures of aromatic diamines are easily synthesized and allow you to obtain a sulfonated polyimide with satisfactory hydrolytic stability [79, 80].

Copolymerization is one of the most common and successful ways of preparing new materials with the necessary properties arising from the presence of several structures with different chemical or physical properties in one polymer chain. In order to increase the efficiency of FC operation, it is necessary to develop polymeric electrolyte membranes of block structure (block copolymers) that each repeating polymer block will perform a certain function and to give the final materials unique properties that are inaccessible to conventional polymers.

The most common type and appropriate type of units for inclusion in the PI circuit are polysiloxane, see [81], its characteristics of linear organosilicon polysiloxane meet the requirements of the PEM FC. One of the most common polysiloxane – polydimethylsiloxane (PDMS) among all synthetic polymers has the very high flexibility of the polymer chain. Another important advantage of polysiloxanes is their heat resistance and oxidation resistance.

Figure 13 shows the process of obtaining such block polymers [82].

Polyimide chains of block copolymer are sufficiently rigid formations, sulfonate groups 3,3'-benzylisothiocyanate provide high proton conductivity. Experimental fuel cells, constructed with the use of such membranes showed output current, comparable to the FC based on Nafion [83]. Siloxane blocks are in them as a fragment, which increases the mobility and hydrophobicity of the chain, which ensured the formation of a large number of proton-conducting channels in the membrane [84]. Stitching also gives the membrane additional mechanical strength.
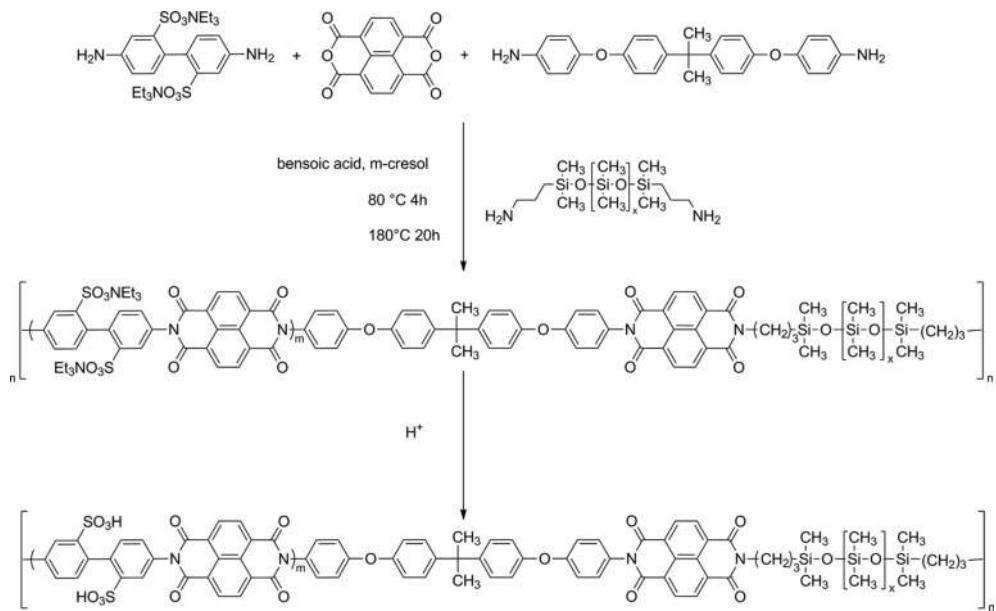
Figure 13. Synthesis of sulfonated poly(imide-siloxane).

Modification of polyimide chains of inclusions of crown ethers, may also improve mechanical properties and increase the solubility, reducing the rigidity and the regularity of polyimide chains. In addition, the size of the cavity of some crown ethers correspond to the diameters of the channels, these inclusions can provide additional ion conductivity, provided they are aligned properly for the formation of conducting channels [85].

3. Conclusion

Emerging market of FC is the main driving force pushing the scientific community for the development of inexpensive and high-performance membrane materials. That is, the cost of manufacturing proton-conducting membranes contributes most to the value of FC and, as a consequence, the cost of the produced energy. FC running on methanol are the most promising for transportation and portable electronic applications because of the serious problems associated with the storage and use of hydrogen.

Despite the fact that PFSA are still excellent materials for membrane fuel cells, their prices are still consistently high and they do not fully satisfy all of the requirements of PEM, in particular on the permeability of methanol. These factors stimulate the interest of researchers to finding cheap and high-performance alternative materials for use as membranes, fuel cells.

Polymers such as polyimides, despite their poor solubility and hydrolytic stability, are attractive to researchers due to the wide variety of possible chemical structures. Polyimides,

including partially fluorinated, have high mechanical strength, chemical and thermal stability. In addition, naphthalic polyimides, when operating in a fuel cell, exhibit results comparable to Nafion, at least when operating up to 3000 h.

One of the solutions to overcome the shortcomings of the PI, would be the development of PEM block structure (block copolymers), polyimide-based, where each repeating polymer unit performs a specific function, which together lead to the satisfaction of all conflicting requirements of PEM. However, development of such PEM is complicated by the fact that improving one characteristic (e.g., increasing the number of groups-proton acceptors in polymer chains), thereby deteriorating the other parameters (in this example, the deterioration of the mechanical stability, swelling and the formation of a non-conductive gel). On the other hand, improving the mechanical parameters of the PEM (e.g., cross-linking of the polymer) often leads to a deterioration of proton conductivity. Therefore, modeling of the PEM design must be complex. It is necessary to select the block structure of the copolymer a way to find the optimum implementation of the requirements of PEM FC. In view of the extremely high thermal stability of the polyimide base, the potential for the use of materials should not be limited to low-temperature FC only. Due to the possibility of introducing imidazole-containing blocks, and phosphoric acid groups, it is also possible to develop materials for medium-temperature phosphoric acid FC.

Our group has developed laboratory techniques for the preparation of monomers for the production of membranes based on SPI, as well as inclusion blocks, to improve their properties. According to the developed methods, experimental samples of monomers and inclusions were made. The properties of the experimental samples are investigated and characterized. A laboratory procedure for the production of SPI films and block copolymers based on them has been developed. According to the developed methods, experimental membrane samples were prepared. Research and adjustment of the properties of experimental samples are being carried out.

Acknowledgements

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