Polymers application in proton exchange membranes for fuel cells (PEMFCs)

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Abstract:
This review presents the most important research on alternative polymer membranes with ionic groups attached, provides examples of materials with a well-defined chemical structure that are described in the literature. Furthermore, it elaborates on the synthetic methods used for preparing PEMs, the current status of fuel cell technology and its application. It also briefly discusses the development of the PEMFC market.

Keywords: proton exchange membrane, proton exchange membrane fuel cells, polymer electrolyte membrane, direct methanol fuel cell, fuel cells, Nafion

DOI: 10.1515/psr-2017-0018

1 Introduction

Energy development, including energy production, distribution and consumption, is vital to any country that aims at constant progress. Given the steadily growing demand for energy and constantly dwindling resources of such fossil fuels as coal, oil and gas, more and more attention is earned by modern solutions that lead to stabilization of the energy market and reduce emissions, such as is the case with fuel cells (FCs).

Fuel cell technologies have been rapidly growing lately because many scientists find it a promising and efficient power generation alternative. Recently, proton exchange membrane fuel cells or polymer electrolyte membrane fuel cells (jointly abbreviated as PEMFCs) have progressed particularly dynamically. Many research groups seek to develop proton exchange membranes that will give high proton conductivity, low electronic conductivity, low fuel permeability, a low electro-osmotic drag coefficient, good chemical and thermal stability, favourable mechanical properties, sufficient durability, and a competitive cost of manufacture. Polymer membranes are the “heart” of PEM fuel cells, and therefore, chemists investigate new strategies for synthesizing materials that would be suitable for their production. There is no reason to believe that the polymeric membrane revolution will end any time soon. In this review, we elaborate on the synthesis of membranes and describe the different types of polymer systems for PEMFC technology.

2 Historical background

Despite their modern character, fuel cells have actually been known for more than 150 years [1] (Figure 1). The history of fuel cells goes back to the early nineteenth century, when Humphry Davy, a British chemist and physicist, first described in 1801 the concept of a fuel cell. Then, in 1838, “The Philosophical Magazine” published a pioneering paper by Christian Friedrich Schönbein, a German-Swiss chemist, describing the electrochemical reaction between hydrogen and oxygen. In 1842, these previous achievements encouraged William Grove, a British lawyer and amateur scientist, to design the first fuel cell that used hydrogen and oxygen to produce electricity [2]. The device was called a “gas voltaic battery” – now often termed as the “Grove battery”. It consisted of several cells containing platinum electrodes placed in two small upturned vessels, one filled with hydrogen, the other with oxygen, both immersed in a bath with diluted sulphuric acid as the electrolyte. Problems with the corroding electrodes and instability of the materials, however, rendered Grove’s fuel cell an impractical solution. The term “fuel cell” itself was first used in 1889 by Charles Langer and Ludwig Mond who attempted to build a fuel cell by using air and industrial coal gas. Development of the internal combustion engine pushed the fuel cell technology out of focus for over half a century. Extensive research was resumed in the 1930s, when Francis Bacon, a British chemical engineer, successfully revisited the concept of the fuel cell.
Already in 1932, Bacon developed a prototype alkaline fuel cell (AFC). He introduced nickel gauze electrodes and used molten potassium hydroxide as the electrolyte, replacing the sulphuric acid \([3]\). Over almost thirty years Bacon improved the design and presented in 1959 a first practical and operational alkaline fuel cell that could generate 5 kW of energy. The same year another team, working for Allis-Chalmers, built a tractor powered by alkaline fuel cells (AFCs). The machine was widely exhibited across the United States. Meanwhile, Willard Thomas Grubb and Lee Niedrach, working for General Electric, developed an alternative fuel cell technology: proton exchange membrane fuel cells (PEMFCs). The evolution of PEMs for fuel cell applications began in 1955, when GE developed a new fuel cell type based on partially sulphonated polystyrene sulphonic acid membranes. PEMFCs were even employed in the Gemini V space mission. Nonetheless, the Apollo Programme and subsequent space missions of Apollo-Soyuz, Skylab and Space Shuttle used Bacon-designed alkaline fuel cells.

In 1966, General Motors applied the fuel cell technology in ground transportation: the company manufactured the Electrovban, a concept car powered by hydrogen fuel cells. In the late 1960s, DuPont developed the first membrane based on polytetrafluoroethylene and perfluorovinyl ether, known under the tradename Nafion®. More and more companies initiated extensive research programmes aimed at eliminating the obstacles to commercial use of the fuel cell technology. The 1970s were the decade of growing environmental awareness of governments, companies and individuals. The oil crisis combined with the oil embargoes imposed by the Organization of the Petroleum Exporting Countries (OPEC) that began in 1973 refocused all the industrialized countries’ research efforts on the development of alternative methods of energy production. The world sought ways to reduce dependence on petroleum imports. In the 1980s, the United States Navy commissioned studies into the use of FCs in submarines, where their highly efficient, zero-emission, near-silent running offered considerable operational advantages. After some years, in the 1990s, the attention turned to fuel cell technology being used in small stationary applications. The governments of Germany, Japan and the UK offered dedicated funding for the development of new technologies suitable for residential micro-combined heat and power (micro-CHP) purposes. Fuel cells underwent meaningful developments and enhancements, leading to the modernization of various cell types such as a solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC) or direct methanol fuel cell (DMFC). The previous decade was characterized by increasing concerns over energy efficiency, energy security and carbon dioxide emissions. In the 2000s, funding for fuel cell research increased remarkably and

**Figure 1:** History of fuel cells [5–7, 7–18].
scientists focused on cost reduction and improving the operational performance to make fuel cells competitive with regard to conventional energy technology. State funding from the European Union, Canada, Japan, South Korea, and the United States had been targeted at fuel cell demonstration and deployment projects, primarily for stationary and transport fuel cells, and the related fuelling infrastructure. In the mid-2000s, buses became a promising application for fuel cells due to the combination of high efficiency, zero-emissions and ease of refuelling. In 2005, Intelligent Energy produced the first ENV (Emissions Neutral Vehicle): a motorcycle prototype completely designed for power fuel cells. The company successfully overcame the miniaturization barriers by employing direct methanol fuel cells (DMFCs) as a power source in portable electronic equipment, for example, portable computers, laptops, or mobile phones. From 2006 to 2009, dozens of fuel cell buses were distributed in the regular public transport service in Europe, China and Australia as a part of the HyFLEET/CUTE project. Finally, the fuel cell technology found an application in a number of vehicle types—cars, vans, buses, forklifts, bikes, scooters, submarines, ferries, electric boats and aircraft. Since 2014, the Toyota Mirai, the first fuel cell car, has been introduced for commercial lease and sale in limited quantities. Mirai in Japanese means “the future”. The car has started a new chapter in the automotive history. In addition, Mercedes, Ford, Mitsubishi, Honda, GM and many other companies have organized exhibitions with concept cars [4].

3 Fuel cells

A fuel cell is an energy conversion device that transforms the chemical energy of the reaction that takes place within it directly into electrical energy with the by-products of heat and water [19]. The fuel cell consists of two electrodes: an anode and a cathode that sandwich an electrolyte. Generally, all fuel cell technologies consume hydrogen and oxygen. The hydrogen gas from a fossil fuel and oxygen gas from the air are fed continuously to the anode and cathode, respectively. At the anode, the hydrogen fuel reacts with a catalyst, creating positively charged protons (H\(^+\)) and negatively charged electrons (e\(^-\)). The electrolyte membrane allows only the positive ions to flow from the anode to the cathode side and acts as an insulator for electrons [3]. These electrons want to recombine on the other side of the membrane to obtain a stable system, so the freed electrons pass through an external electrical circuit and travel to the cathode, while the protons are delivered via the electrolyte. This exchange releases electrical energy. Simultaneously, on the cathode side, as a result of the reaction between the oxygen, electrons from the electrode and protons from the electrolyte, water forms [20]. The structure of a simplified fuel cell is shown in Figure 2.

![Figure 2: Fuel cell operation diagram.](image)

Individual fuel cells can be collected into a unit and connected to each other in series, resulting in a “stack” of cells. The output of the stack can be adjusted by changing the number of individual cells.

Fuel cells are classified, generally, by the choice of electrolyte and fuel. So far, there have been six major groups of fuel cells, summarized in Table X [20]. There are also other groups of fuel cells which are less popular but which may find specific application in the future such as air-depolarized cells, sodium amalgam cells, biochemical fuel cells, inorganic redox cells, regenerative cells and alkaline metal-halogen cells [2]. Based on the literature surveys, the main advantages, disadvantages and suitability for specific applications are briefly presented in forthcoming sections of the review [19, 21–27].
3.1 Alkaline fuel cells (AFCs)

Alkaline fuel cells are the oldest fuel cell system. AFCs generate electricity by using an aqueous solution of potassium or sodium hydroxide as the electrolyte [3]. At the anode, hydrogen gas combines with negative charged hydroxyl ions to release water molecules and electrons. These electrons reach the cathode through an external electrical circuit and combine with oxygen and water to form negatively charged OH$^{-}$ ions that may transfer to the anode through the electrolyte. AFCs generally perform in temperatures between 60 and 200 °C. Two main advantages of AFCs include their quick start and high power density – about 1 kW m$^{-3}$. The major disadvantage is their sensitivity to carbon dioxide that converts KOH into potassium carbonate. The resultant salt may precipitate on the pores of the electrodes and eventually block them. Moreover, carbonate formation depletes hydroxyl ions from the electrolyte, which reduces the electrolyte conductivity and consequently the cell’s performance [3]. Therefore, AFCs typically require the use of pure oxygen or at least purified air, which considerably increases the cell operating costs. Thus, the alkaline fuel cells are rarely used for commercial purposes, though they are employed in other transportation services.

3.2 Phosphoric acid fuel cells (PAFCs)

Phosphoric acid fuel cells are a type of cells that use relatively stable, concentrated liquid phosphoric acid as their electrolyte. Since the ionic conductivity of H$_3$PO$_4$ is low at low temperatures, PAFCs operating range is about 150–250 °C. The hydrogen oxidized at the anode splits into protons and electrons. The electrons pass through the external electrical circuit, whereas the protons are transferred through the electrolyte. On the cathode side, the redox reaction between positive hydrogen ions, electrons and oxygen gas results in water formation [3]. Unlike AFCs, PAFCs are able to work on hydrogen contaminated with CO$_2$. However, the presence of CO significantly affects the performance of the cells due to poisoning of the platinum electrode catalyst. Carbon monoxide absorption is reported to arise from the dual site replacement of one H$_2$ molecule by two CO molecules on the platinum’s surface [28]. The sulphur containing compounds can also reduce the effectiveness of PAFCs in result of sulphur adsorption on the electrode’s surface [29]. The main advantage of phosphoric fuel cells is their capacity to generate and separate electricity and useful heat at the same time. The process of combined heat and power (CHP) production is termed as cogeneration. The waste heat captured from the cells can be easily used in most commercial and industrial applications. The drawback of PAFC is its high cost of manufacture due to the need for properly dispersed platinum catalyst coating electrodes [30].

3.3 Solid oxide fuel cells (SOFCs)

Solid oxide fuel cells (also called ceramic fuel cells) are characterized by a solid ceramic electrolyte, which is metallic oxide. Dense yttria stabilized zirconia (YSZ), a crystal structure of zirconium dioxide (ZrO$_2$) with the addition of yttrium oxide (Y$_2$O$_3$), is the most commonly used electrolyte for SOFCs due to its high chemical and thermal stability and good ionic conductivity. The ceramic fuel cells can produce electricity in the range of 600–1000 °C. At the cathode, the oxygen is reduced to oxygen ions O$_2^-$$. The oxygen ions diffuse into the electrolyte material and migrate to the anode, where they react with the fuel, generally hydrogen and carbon monoxide, producing water and carbon dioxide, as well as heat and electricity [19]. The main advantage of SOFCs is their high operating efficiency of 50–60%. Furthermore, the waste heat can be recycled to make additional electricity by cogeneration, and hence, CHP operation increases the fuel efficiency by up to 80%. The SOFC systems have demonstrated minimal air pollutant emissions and low greenhouse gas emissions, but some drawbacks, such as their high cost, very long start-up and cooling-down times, as well as sensitivity to sulphur and other contaminants, significantly limit their use. SOFCs are mainly used for medium and large stationary power applications (ranging to 250 kW capacity) [30].

3.4 Molten carbonate fuel cells (MCFCs)

Molten carbonate fuel cells are high temperature cells operating at approximately 600–700 °C. MCFCs use a combination of molten alkali carbonates (lithium or sodium), suspended in a porous, chemically inert ceramic matrix of beta-alumina solid electrolyte (BASE), which is an isomorphic form of aluminium oxide complexed with a mobile ion such as Na$^+$, K$^+$ or Li$^+$ [31]. At the anode, hydrogen gas reacts with the oxidizing agent, namely CO$_3^{2-}$ from the electrolyte. The anode reaction products are water and carbon dioxide, while electrons...
released to the external circuit are transferred to the cathode, where a reduction reaction of the oxygen and carbon dioxide occurs. As the result of the cathode reaction, carbonate ions are formed and released to the electrolyte.

The major advantages of MCFCs include their high efficiency of 50–60%, suitability of cheap nickel electrodes for providing sufficient activity, and more efficient than other fuel cells operability with CO containing bio-fuel derived gases [32]. Their main drawback is the corrosive and mobile electrolyte requiring the use of nickel and high-grade stainless steel for the cells’ hardware. Furthermore, the higher operating temperatures promote material problems, impacting the mechanical stability of the fuel cell. The MCFCs have found various stationary and marine applications, where their large size and weight, combined with their long start-up time, matter less.

### 3.5 Direct methanol fuel cells (DMFCs)

Direct methanol fuel cell technology is relatively new when compared to other fuel cell types. Like the PEM fuel cell, the DMFC uses a polymer electrolyte membrane. The system is fuelled with methanol. At the anode, the methanol undergoes an oxidation reaction with water, releasing carbon dioxide, protons and electrons. The protons are transported from the anode through the membrane to the cathode, where they react with oxygen and electrons to form clean water. Water consumed at the anode is reproduced at the cathode. Due to their low efficiency, DMFCs are targeted at portable electronic applications such as cameras or notebook computers, where energy and power density are more important than efficiency, mainly for the capacity range from 1W to 1kW. One of the major advantages is that the anode electrode, made of platinum and ruthenium particles, draws the hydrogen gas from the methanol, thereby reducing the overall cost due to the absence of the reformer [3, 33].

### 3.6 Proton exchange membrane fuel cells (PEMFCs)

The proton exchange membrane fuel cell (also termed the “polymer electrolyte membrane fuel cell”) utilizes a solid polymer membrane as the electrolyte. The PEMFCs have received increasing worldwide attention due to their potential of reducing our energy use, pollutant emission, and dependence on fossil fuels [34]. In PEMFCs, the hydrogen gas is oxidized to form proton ions and eject electrons at the anode. The positive ions pass through the electrolyte membrane, while electrons are forced to flow to the electrical circuit and generate the electricity. In the next step, they flow to the cathode and react with oxygen and $\text{H}^+$ to form clean water.

The “heart” of a single electrolyte fuel cell is the membrane electrode assembly (MEA). It consists of a proton exchange membrane (PEM) and two gas diffusion electrodes (GDE), formed by two catalyst layers (CL) and two porous gas diffusion layers (GDL) [35].

For a properly operating fuel cell, an effective membrane electrode assembly is needed. The MEA plays a crucial role in three transport processes: (i) the transport of protons from the PEM to the CL, (ii) the transport of electrons from the current collector to the CL through the GDL and (iii) the transport of the reactant and product gases to and from the CL and the gas channels [36].

The proton exchange membranes (PEM) are the main subject of this review, as described in the next section. In the gas diffusion electrode (GDE), the important component is the catalyst layer. CT is in direct contact with the membrane and the gas diffusion layer. It is also termed the “active layer”, because it impacts the efficient oxidation of the hydrogen gas. In both the anode and the cathode, the CL is the place of the half-cell reaction in the PEMFC. The layer with the catalyst is where the protons, electrons and gases, so-called three phases, are found (Figure 3) [37]. Platinum or platinum alloys are common materials used to produce the catalyst layer. Nowadays, due to the rapid development of the novel sputtering methods, it is possible to reduce the consumption of the noble metal [38–40].
The second component of the gas diffusion electrode is the gas diffusion layer [41]. The porous layer ensures: (i) an effective diffusion pathway of gases to the catalyst, (ii) the removal of the by-produced water outside of the catalyst layer and the prevention of flood, (iii) the storage of water on the surface for conductivity through the membrane, (iv) transfer of the heat during the cell’s operation, (v) sufficient mechanical strength to prevent the membrane electrode assembly expansion in result of water absorption [42]. Typically, the gas diffusion layers are made of porous carbon paper, or carbon cloth, with a thickness in the range of 100–300 µm [36].

The MEA is typically sandwiched with two bipolar plates (BPs) with a current collector and gas channels [36]. The diagram of a single typical proton exchange fuel cell is shown in Figure 4.

Figure 3: Transport of gases, protons and electrons in PEMFCs.

Figure 4: Schematic diagram of a proton exchange membrane fuel cell.
The BPs are responsible for the following functions (i) to distribute the fuel and oxidant within the cell, (ii) to facilitate water management within the cell, (iii) to separate individual cells in the fuel stack, (iv) to carry the current away from the cell and (v) to facilitate heat management. The most commonly used BP material is natural or synthetic graphite due to its excellent chemical stability [43].

Proton exchange fuel cells are lightweight compact systems, suitable for discontinuous operation at temperatures between 50 °C to 100 °C and above 100 °C to 200 °C for low temperature (LT-PEMFCs) [44] and high temperature (HT-PEMFCs) units [45], respectively. The LT-PEMFC performance is superior to the HT-PEMFC, but only under pure hydrogen conditions [46]. When using hydrogen gas directly from the fuel processor, that is, without any prior purification, poisoning of the catalyst through CO adsorption occurs [47]. Moreover, the low temperature PEMFCs pose serious water management challenges, whereas the high temperature of PEMFCs can operate at dry conditions, and no humidifiers are needed [48].

Comparison of PEMFCs with the other fuel cell technologies shows that the important advantages of the proton exchange fuel cells are their highest power density, longer lifetime, potentially faster start-up (measured in seconds) and cheaper manufacturing costs (Table 1). From the efficiency point of view, the higher working temperature ensures higher efficiency due to the higher reaction rate. What is equally important, the working temperature above 100 °C may cause a decrease in the conductivity of LT-PEMFC induced by vaporizing the water, which plays a vital role in proton transportation in low temperature PEM fuel cells. In this case, better temperature above 100 °C may cause a decrease in the conductivity of LT-PEMFC induced by vaporizing the water, which plays a vital role in proton transportation in low temperature PEM fuel cells. In this case, better temperature above 100 °C may cause a decrease in the conductivity of LT-PEMFC induced by vaporizing the water, which plays a vital role in proton transportation in low temperature PEM fuel cells.

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Table 1: Comparison of different fuel cell systems [3, 20, 58, 59].

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>AFC</th>
<th>PAFC</th>
<th>SOFC</th>
<th>MCFC</th>
<th>PEMFC</th>
<th>DMFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common electrolyte</td>
<td>Solution of potassium hydroxide</td>
<td>Phosphoric acid</td>
<td>Solid ceramic inorganic oxide</td>
<td>Molten potassium or lithium carbonate</td>
<td>Solid polymeric proton exchange membrane</td>
<td>Solid polymer membrane</td>
</tr>
<tr>
<td>Anode reaction</td>
<td>$2H_2 + 4OH^- \rightarrow 2H_2O + 4e^-$</td>
<td>$2H_2 \rightarrow 2H_2O + 4e^-$</td>
<td>$2H_2 + 4CO_2 \rightarrow 2H_2O + 4CO_2 + 4e^-$</td>
<td>$2H_2 + 4CO_2 \rightarrow 2H_2O + 4CO_2 + 4e^-$</td>
<td>$2H_2 \rightarrow 2H_2O + 4e^-$</td>
<td>$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$</td>
</tr>
<tr>
<td>Cathode reaction</td>
<td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td>
<td>$O_2 + 4e^- \rightarrow 2H_2O$</td>
<td>$O_2 + 2CO_2 \rightarrow 2H_2O + 4CO_2 + 4e^-$</td>
<td>$O_2 + 2CO_2 \rightarrow 2H_2O + 4CO_2 + 4e^-$</td>
<td>$O_2 + 2CO_2 \rightarrow 2H_2O + 4CO_2 + 4e^-$</td>
<td>$O_2 + 2CO_2 \rightarrow 2H_2O + 4CO_2 + 4e^-$</td>
</tr>
<tr>
<td>Fuel</td>
<td>Pure H₂</td>
<td>Pure H₂</td>
<td>H₂, CO, CH₄, other hydrocarbons</td>
<td>H₂, CO, CH₄, other hydrocarbons</td>
<td>Pure H₂</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Oxidant</td>
<td>O₂ in air</td>
<td>O₂ in air</td>
<td>O₂ in air</td>
<td>O₂ in air</td>
<td>O₂ in air</td>
<td>O₂ in air</td>
</tr>
<tr>
<td>Charge carrier</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>O₂⁻</td>
<td>CO₂⁻</td>
<td>H⁺</td>
<td>H⁺</td>
</tr>
<tr>
<td>Operating temperature (°C)</td>
<td>60–200</td>
<td>150–250</td>
<td>600–1000</td>
<td>600–700</td>
<td>50–200</td>
<td>60–200</td>
</tr>
<tr>
<td>Capacity (kW)</td>
<td>10–100</td>
<td>50–1000</td>
<td>&lt;1–3000</td>
<td>&lt;1–1000</td>
<td>&lt;1–250</td>
<td>0.001–100</td>
</tr>
<tr>
<td>Electrical Efficiency (%)</td>
<td>60</td>
<td>&gt;40</td>
<td>50–60</td>
<td>&gt;50–60</td>
<td>35–45</td>
<td>30–40</td>
</tr>
<tr>
<td>Power density (W m⁻²)</td>
<td>~1.0</td>
<td>0.8–1.9</td>
<td>0–1.5</td>
<td>1.5–2.6</td>
<td>3.8–6.5</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>Installation cost (US$ kW⁻¹)</td>
<td>1800–1900</td>
<td>2100</td>
<td>3000</td>
<td>2000–3000</td>
<td>&lt;1500</td>
<td>1500–1800</td>
</tr>
</tbody>
</table>

Various features make the PEMFCs one of the most promising and attractive technologies for a wide variety of power applications ranging from automotive, through stationary to portable power systems. There are hundreds of companies involved in various aspects of the fuel cell industry, for example, Ballard Power System, United Technologies Corporation, Nuvera, General Electric FCS, Plug Power, Intelligent Energy, Novars, Smart Fuel Cell, Toshiba, Sanyo, and Hydrogenics. Moreover, a vast range of electronics companies (e.g. Nippon Telegraph, Telephone, Sanyo, Samsung and IBM) and automobile manufactures (e.g. Chrysler, Ford, Renault, Toyota, Nissan, General Motors, BMW, MAN, Hyundai) have presented various applications and prototype
vehicles that use PEMFCs [51–57]. Although PEMFCs have been demonstrated in buses, cars, motorcycles and portable power units, there are still many unresolved commercialization issues, especially the manufacturing cost. Nevertheless, PEMFCs are expected to be fully commercialized in the next ten or fifteen years [51].

4 Proton exchange membranes for fuel cells

Proton exchange membranes (PEMs) are essential components of membrane electrode assemblies (MEA). A PEM is, generally, a semipermeable membrane made from an ionomeric polymer. Fundamental functions of such proton exchange membranes are as follows: (i) the transport of protons, (ii) the separation of reactants and (iii) electric insulation between the anode and cathode [22]. Common themes critical to all high-performance proton exchange membranes include (i) high ionic conductivity, (ii) low permeability to fuel and oxidants, (iii) a low electro-osmotic drag coefficient, (iv) oxidative, hydrolytic and thermal stability, (v) adequate mechanical properties, allowing to obtain as thin as possible membrane (thickness approximately 10–250 μm), (vi) long lifetime, (vii) low cost and (viii) the capability of fabrication into membrane electrode assemblies (MEAs) [60, 61]. The publication list as shown in Figure 5 undoubtedly proves that the polymer electrolyte membranes for fuel cells are objects of intent interest. Recently, the number of publications about PEMs has clearly risen, indicating that the development of polymer membranes is a very active and popular field.

![Figure 5: The number of publications found in three scientific databases (Scopus, Science Direct, and Web of Science). The search keywords were “proton exchange membrane” and “proton exchange membranes” in all fields.](image)

In this section, we will focus on the presentation of the seven main types of materials used in preparing proton exchange membranes. The division is based on the differences in the polymer chain structure and the presence of various functional groups. These are: poly(perfluorosulphonic acid) membranes, partially fluorinated and non-fluorinated polystyrene-based membranes, polybenzimidazole/H$_3$PO$_4$ membranes, polyphosphazene membranes, sulphonated polyimide membranes, sulphonated poly(arylene ether ketone)-based membranes and natural polymer- and bio-inspired-based membranes. Details of their properties and possible approaches to the synthesis are described in the following sections.

4.1 Poly(perfluorosulphonic acid) membranes

Currently, the most commercially applied proton exchange membranes are based on the poly(perfluorosulphonic acids) (PFSAs), also termed as perfluorosulphonic acid ionomers (PFSIs). In the late 1960s, DuPont developed and patented one of the most popular materials, the first from the PFSIs group [62]. The company registered it under the trade name Nafion$^\text{®}$. Up to now, Nafion$^\text{®}$ and its derivatives have been standard materials for polymeric electrolyte fuel cells [63, 64]. Figure 6 shows the chemical structures of representative PFSIs [64].
Alternative polymer membranes are almost invariably compared to Nafion®. Generally, such ionomers are free radical initiated amphiphilic copolymers, consisting of hydrophobic polytetrafluoroethylene (PTFE) backbones and regular spaced long perfluorovinylether pedant side chains terminated by a hydrophilic sulphonate ionic group. Table 2 summarizes the most popular available Nafion® membrane types provided by DuPont. Table 2: Thickness and basis weight property measurements taken with membrane conditioned to 23°C, 50 % RH [65, 66].

<table>
<thead>
<tr>
<th>Nafion® membrane type</th>
<th>Typical thickness [µm]</th>
<th>Basis weight [g m⁻²]</th>
<th>EWa [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR111</td>
<td>25.4</td>
<td>50</td>
<td>1100</td>
</tr>
<tr>
<td>NR112</td>
<td>50.8</td>
<td>100</td>
<td>1100</td>
</tr>
<tr>
<td>N112</td>
<td>50.8</td>
<td>100</td>
<td>1100</td>
</tr>
<tr>
<td>NE1135</td>
<td>88.9</td>
<td>190</td>
<td>1100</td>
</tr>
<tr>
<td>N1035</td>
<td>88.9</td>
<td>175</td>
<td>1000</td>
</tr>
<tr>
<td>N115</td>
<td>127.0</td>
<td>250</td>
<td>1100</td>
</tr>
<tr>
<td>N105</td>
<td>127.0</td>
<td>n.a.</td>
<td>1000</td>
</tr>
<tr>
<td>N117</td>
<td>177.8</td>
<td>360</td>
<td>1100</td>
</tr>
<tr>
<td>N1110</td>
<td>254.0</td>
<td>500</td>
<td>1100</td>
</tr>
</tbody>
</table>

Note: equivalent weight, mass of dry ionized polymer (g) in the protonic acid form that would neutralize one equivalent of base.

Other world-class manufacturers have also been involved in the production of Nafion®-like structured perflourosulphonic acid ionomers, for example, Asahi Chemical Industry (Aciplex®, Aciplex® 1b) or Asahi Glass (Flemion®, Flemion® 1c), Dow Chemical Company (Dow®, Dow® 1d) or 3M Company (3M®, 3M® 1e). However, Dow® and 3M® membranes had structures with side chains reduced to tetrafluoroethylenoxysulphonic acid (–OCF₂CF₂SO₃H) and hexafluoropropyleneoxysulphonic acid (–OCF₂CF₂SO₃H) functions, respectively [67, 68]. Moreover, in China, the Shanghai Institute of Organic Chemistry has developed its own perfluorosulphonated ionomer membranes used in fuel cells (Shanghai®) [69]. Similarly to Nafion®, all of these perfluorinated sulphonic acid membranes suffer from shortcomings such as low proton conductivity at low hydration and relatively low mechanical strength at elevated temperatures. Moreover, the high cost of production has limited their use. However, Solvay-Solexis has presented a cheaper membrane named Hyflon-Ion H® [70].

Up to now, the perfluorinated sulphonic acid membranes (e.g. Nafion® membrane) have been the most advanced membrane for use in practical fuel cell systems due to their high cell performance and long lifetime over 60 000 h at 80°C. All of these polyperfluorosulphonic acid membranes are stable in oxidative and reductive environments. The polymer chain structure provides very good chemical and thermal stability and also enables production of suitable thin membranes, while the negatively charged SO₃⁻ groups are very appropriate for ion exchange, because sulphonate groups allow for the passage of cations and reject anions due to the occurrence of electrostatic interactions [71, 72].

The water sorption behaviour in PFSI membranes is very important since they can conduct protons only in the humid conditions. With increasing water content, Nafion®-like membrane constituents are characteristically separated into hydrophobic PTFE-region and hydrophilic ionic clusters which contain water, solvated SO₃⁻ heads and counterions (mainly H⁺ but depending on pre-treatment also some Na⁺ or K⁺). Water-filled clusters are connected by short and narrow nanochannels that form a random cluster network embedded in the surrounding, sponge-like hydrophobic fluorocarbon backbones [73]. The level of hydration is a critical parameter in Nafion®-type membranes, since at temperatures above 100°C, the water evaporates and these materials significantly decrease in performance [72]. Furthermore, during the production process, strongly toxic and
environmment-unfriendly intermediates can be formed. One of the main shortcomings of Nafion® series PEMs is their high price due to expensive fluoroorganic compound having to be employed in their synthesis (cost of membrane amounting even to US$ 2500 per square meter for Nafion® N1110 [74]).

4.1.1 The proton conduction mechanism in perfluorosulphonic acid ionomers (PFSIs)

Proton conduction is a crucial feature for proton exchange membrane fuel cells to assure high current density. At the molecular level, the proton transfer in hydrated conditions can be described through two principal mechanisms: the proton hopping of the generally named Grotthuss mechanism or a diffusion mechanism.

In the proton hopping mechanism, the protons jump from one hydrolysed ionic site (SO$_3^-$·H$_3$O$^+$) to another across the membrane. The proton formed in the oxidation reaction of hydrogen gas at the anode adheres to water molecules and forms provisional hydronium ions. Subsequently, one different proton from the same hydronium ion hops onto the other water molecule. In this mechanism, an ionic region forms specific hydrophilic clusters which swell in the presence of water. As a result, the percolation mechanism for protons can occur [64, 75].

In vehicular mechanisms, the hydrated proton (hydronium ion) diffuses through an aqueous medium in response to an electrochemical difference. The protons attach themselves to a vehicle such as water and diffuse through the medium. In other words, the protons treat the water as a carrier. The rate of such transport depends on the existence of the free volumes within the polymeric chains, as well as on the rate of vehicular diffusion [76]. Moreover, water plays an important role in the proton conductivity by impacting the formation, size, connectivity and strength of the ionic pathways and clusters in the PEMs [75]. When the cluster sizes increase in aqueous conditions, the proton conductivity also increases along with the humidity [59].

The important parameter in the case of membranes based on sulphonated perfluoropolymers, which describes the hydration extent of the proton exchange, is the total number of exchangeable sites for the protons. The parameter indicates the overall proton activity, thus defining the total number of water molecules coordinated per sulphonate group (denoted $\lambda$). The hydration extent can be described at a few levels. At the beginning ($\lambda<2$), only small water clusters are observed and Nafion®-based membranes behave like insulators. If $\lambda$ reaches ~2, the percolation threshold of the proton conductivity occurs and the water molecules bond with sulphonate groups on the inner side of the channels and clusters forming specific solvation shells. When the conditions become more humid ($\lambda$ from 2 to 5), the water clusters and channels become bigger and broader, respectively. With this extent of hydration, some of the water molecules exist in a free form; however, they are strictly limited due to the coordination of hydronium ions by sulphonate groups caused by electrostatic interaction. Subsequently, with more water content (between 5 and 7), structural reorganization is observed. The swelling clusters and expanded channels become a partially interconnected network. The continuous path for the conduction of protons begins to be expanded. Furthermore, the existence of free water in the membrane increases, and therefore, an increase in proton conductivity is also noticed. Lastly, the maximum hydration extent is observed, and the distance between SO$_3^-$ groups becomes larger. The Nafion®-like membrane swells, and a well-developed proton transfer network with markedly increased free water content is obtained, as illustrated in Figure 7 [23, 77–80].

![Figure 7: Evolution of the membrane structure as a function of water content, $\lambda$ (moles of water per mole of sulphonic acid sites).](image)

4.2 Partially fluorinated and non-fluorinated polystyrene-based membranes

Chemical synthesis of poly(perfluorosulphonic acid) membranes is challenging due to the safety concerns of the tetrafluoroethylene (TFE) and their high cost combined with the limited availability of perfluorovinylethers. One alternative to the PFSA membranes is the use of styrene or its partially fluorinated derivatives to prepare...
PEMs. Polystyrene-sulphonic acid (PSSA) membranes are the oldest commercial polymer materials and their evolution began in 1955, when General Electric tested the first polystyrene membranes for PEMFCs [81–83]. Polystyrene-sulphonic acid (PSSA) membranes were used to produce the operational PEM fuel cells that were first ever employed in one of the Gemini programme space flights organized by NASA. The system, however, exhibited low power density, a short lifetime and low mechanical strength. In the practical FC operating conditions, under chemical attack by free radicals, local depolymerization of the polystyrene backbone occurred, resulting in interrupted regularity in the structure, and thus rapid degradation of the membrane material [84]. Reactive intermediates, mainly hydroxyl radicals (OH•) formed during electrochemical conversion in PEMFC, can react with PSSA via abstraction of the labile tertiary α-protons of the polymeric chain 2 leading to the formation of a benzyl radical 3 (Figure 8, reaction A) and follow-up chain scission and polymer degradation [85]. However, OH• may add very rapidly to the ortho position of the aromatic rings, producing the isomeric hydroxycyclohexadienyl radicals 4 (Figure 8, reaction B). The resulting OH-adduct 4 may subsequently form additional highly reactive radicals [86–88].

Figure 8: The main degradation reactions occur in polystyrene membranes.

Despite the fact that PSSA membranes are relatively inexpensive, the conductivity loss occurring during degradation caused that the emergence of Nafion® in the late 1960s reduced interest in the development of polystyrene-based membranes. The call for alternative materials, however, has reinstated the interest in polystyrene-sulphonic acid membranes for FC application. Relatively stable materials were developed by using styrenic monomers that possess substituents other than a labile proton at the α-position to the aromatic ring [89]. The preparation of α-methylstyrene-based membranes (PMSSAs) and the study of the effect of tertiary hydrogens on their stability in oxidatively aggressive environments by comparison with styrene-based membranes (PSSAs) were first reported by Assink et al. The PMSSAs exhibited higher energy efficiencies and stronger resistance to oxidative degradation conditions [90, 91].

Another strategy involving the introduction of fluorine substituents allowed for the production of various phosphonated or sulphonated poly(α,β,β-trifluorostyrene) membranes. The α,β,β-trifluorostyrene (TFS) monomer synthesis was first reported in 1949 by Cohen et al. [92]. A few years later, the TFS monomer was successfully homopolymerized under radical conditions [93]. The first sulphonated poly(α,β,β-trifluorostyrene) with an applicability to fuel cells was presented by Hodgdon [94]. Moreover, Ballard Advanced Materials Corporation developed sulphonated α,β,β-trifluorostyrene membranes under the trade name BAM1G and BAM2G (Ballard Advanced Materials 1st and 2nd Generation, respectively). The durability of these ionomeric polymers was limited to approximately 500 h under practical fuel cell operating conditions [71]. Based on previous achievements, Ballard provided a series of sulphonated copolymers of α,β,β-trifluorostyrene with selected α,β,β-trifluorostyrene analogues such as m-trifluoromethyl-α,β,β-trifluorostyrene, p-sulphonyl fluoride-α,β,β-trifluorostyrene or p-fluoro-α,β,β-trifluorostyrene – a group of materials referred to as BAM3G (Ballard Advanced Material 3rd Generation) [95]. BAM3G membranes exhibited performances superior to the Nafion® and Dow® membranes [71]. The main disadvantages of these membranes, however, include the complicated production process for the α,β,β-trifluorostyrene monomer and the difficult post-sulphonation procedures [94, 96]. Furthermore, the Ballard Company decided to investigate the potential of phosphonic acid-based PEMs. They presented a preparation of phosphonated α,β,β-trifluorostyrene polymers, their characterization, and indications of their fuel cell performance capabilities [97]. The sulphonated materials showed outstanding perfor-
mance in both oxygen and air conditions, while the phosphonic acid-type membranes showed excellent performance only in the oxygen fuel cells. The BAM membranes demonstrated good stability, and conductivity values ranging from $5 \times 10^{-2}$ to $9 \times 10^{-2}$ S cm$^{-1}$. In order to improve the thermal stability of the targeted polystyrene-sulphonic acid membranes, attempts were made to modify the initial physical and chemical properties of the polystyrene via the introduction of various fluorinated styrenic comonomers into the polymer chain. The studies were mostly focused on copolymerization of the styrene with comonomer such as: $\beta$-fluorostyrene, $\alpha,\beta,\beta$-trifluorostyrene, 3-methyl-$\alpha,\beta,\beta$-trifluorostyrene, 4-methyl-$\alpha,\beta,\beta$-trifluorostyrene, $\alpha$-fluoromethylstyrene, $\alpha$-difluoromethylstyrene and $\alpha$-trifluoromethylstyrene [98–100]. The polymeric materials produced in the copolymerizations of fluorinated $\alpha$-methylstyrenes with styrene exhibited enhanced thermal properties in comparison with the polystyrene homopolymers. An increase of the thermal stability might be attributed to the thermo-oxidative resistance of the styrene carbon $\alpha$ bearing fluorinated methyl groups [101].

The above-presented ionomers are believed to be random systems, both in the chemical composition of the copolymer backbone and with regard to their sulphonic acid attachment. The comparison with sulphonated multiblock copolymers revealed, however, that the latter exhibit a higher proton conducting ability with less dependence on relative humidity. Until recently, many PEMs that contain various block-copolymers with a styrene function were developed including sulphonated poly(styrene-block-isobutylene-block-styrene) triblock copolymers [102–104], sulphonated polystyrene-block-(ethylene-ran-butylene)-block-polystyrene [105, 106], sulphonated styrene-ethylene copolymers [107], sulphonated polystyrene(ethylene-butylene)-polystyrene triblock copolymers [108] and poly-[norbornenyl-ethylstyrene-$s$-styrene]-poly[$\alpha$-propyl-$p$-styrenesulphonate] (PNS-PSSP) block polymers [109]. The Dais Analytic produced semi-commercial sulphonated styrene-ethylene-butylenestyrene (SSEBS) membranes that are based on the well-known commercial block copolymers containing SEBS blocks (e.g. Kraton® G1650). Unlike the perfluorinated or partially fluorinated ionomers, the Dais membranes suffer from low resistance to an oxidative condition due to the partially aliphatic character of the hydrocarbon backbone structure. Therefore, its operational temperatures should not exceed 60°C. Nevertheless, they are considerably cheaper to produce than Nafion® and, as a result, offer an affordable alternative for lower cost portable electronics and other low power ($\leq 1kW$), room temperature applications [110].

Another strategy involves the modification of existing polymer backbones through chemical or radiation-induced grafting polymerization. Such modification affects the most inherent characteristics only to a small extent and thus offers an effortless route for the preparation of PEMs with desirable properties. The partially fluorinated acid ionomer membranes were typically fabricated by the radiation-induced grafting of a versatile monomer such as styrene onto a highly stable fluoropolymeric matrix with subsequent sulphonic acid functionalization [111]. The common base polymer films employed in the preparation of polystyrene-sulphonic acid-grafted membranes include polytetrafluoroethylene (PTFE, Teflon®), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEF), poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA), polyvinylene fluoride (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HEP), poly(ethylene-alt-tetrafluoroethylene) (ETFE), polyvinyl fluoride (PVF), or polyethylene (PE) [112]. Such membranes offer a higher ion exchange capacity than block membranes and often have physical and electrochemical properties superior to Nafion® but also an inferior fuel cell performance due to the degradation of the ionic domains while operating in a fuel cell environment. As a result, a loss of ion exchange capacity and thus a loss in conductivity were observed. In order to improve the intrinsic chemical stability and extend the durability of the grafted membranes, materials grafted with a substituted styrene sulphonic acid: $\alpha,\beta,\beta$-trifluorostyrene and $\alpha$-methylstyrene were developed. However, the preparation of such membranes is limited due to their low grafting rate [113]. To address this problem, the substituted styrene sulphonic acid was grafted with other monomers (co-grafted membranes). The most popular non-cross-linking comonomers for such co-grafting procedure were methacrylonitrile (MAN), acrylonitrile (AN), methyl methacrylate (MMA) and methyl acrylic acid (MAA) [114]. An attractive skeleton structure for the co-grafted membranes preparation was provided by poly(ethylene-alt-tetrafluoroethylene) (ETFE) [115]. However, all the co-grafted membranes exhibited an increase in membrane water uptake with but a similar ion exchange capacity without any improvement of the conductivity, which was obviously undesirable.

### 4.3 Polybenzimidazole/H$_3$PO$_4$ membranes

Generally, the high temperature PEMFCs are known to be very attractive due to their improved catalyst activity, high tolerance to impurities present in the hydrogen fuel such as carbon monoxide, and simplified thermal and water management. In order to obtain a fuel cell system that can operate in limited humidification, above 100 °C, many research groups focus their efforts on producing polymeric membranes for HT-MEA [116]. The use of Nafion® requires humidified conditions, but at an elevated temperature, the water evaporates from the membrane. Under such conditions, Nafion® converts to insulator and becomes useless for the fuel stack. To
solve this problem, an aromatic heterocyclic polymer, called polybenzimidazole (PBI), was synthesized by Vogel and Marvel [117]. The PBI consists of an aromatic backbone, which provides excellent thermal stability (with a glass transition temperature reach of 430 °C), good chemical inertness and high mechanical strength. The PBI in and of itself is not a proton conducting polymer and cannot be used as a PEM. In order to ensure the proton conductivity, Savinell et al. presented polybenzimidazole impregnated with phosphoric acid (PA) [118–120]. The use of phosphoric acid was determined due to its thermal stability at a temperature above 100 °C and its ability to conduct protons [121]. So far, such polymers doped with H₃PO₄ are one of the most attractive alternatives to Nafion® for high temperature polymer electrolyte membrane fuel cells [122]. Without humidification, phosphoric acid (PA)-doped m-polybenzimidazole (PBI) membranes perform well. Moreover, increase of the temperature and humidity of the reaction gases result in a much improved performance, even above 100 °C.

Fully aromatic PBIs are a well-known group of polybenzimidazoles. Among them, the most popular are the para-type poly[2,2′-(p-phenylene)-5,5-bisbenzimidazole]] (pPBI) 5 and the meta-type poly[2,2′-(m-phenylene)-5,5-bisbenzimidazole]] (mPBI) 6 (Figure 9). Such PBIs are mainly synthesized via the polycondensation reactions of aromatic amines and aromatic acids (or their derivatives) and self-condensation reactions involving 3,4-diamino acids [123].

![Figure 9: Chemical structures of polybenzimidazole polymers.](image)

The most systematically studied polybenzimidazoles are those of the mPBI, which has been commercially produced by the Celanese Corporation since 1983 under the trade name PBI®, and poly(2,5-benzimidazole) (ABPBI). Nonetheless, it is well known that the first one has a very rigid molecular structure so its processability is limited [124]. To date, BASF has introduced other commercially available polybenzimidazole/H₃PO₄ membranes, for example, CeltecL®, CeltecP1000® or CeltecV®.

The proton conductivity mechanism of phosphoric acid (PA)-doped m-polybenzimidazole (PBI) membranes (poly-salts) is mainly by the Grotthuss mechanism. Phosphoric acid has an amphoteric character, so it can act as either a proton donor (acid) or a proton acceptor (base). As a result of the dynamic hydrogen bond network, where protons can transfer through the formation and cleavage of bonds, a so-called hopping mechanism is formed (Figure 10) [125]. The PBI polymer chain has two basic nitrogen atoms per repeating unit, which may trap two phosphoric molecules. Additional acid molecules absorbed during the doping process accumulate in the free volume of the polymer network. These “free phosphoric acids” are responsible for the proton conductivity of the material.

![Figure 10: Proton conducting mechanism in phosphoric acid (PA) doped polybenzimidazole (PBI).](image)

The conductivity of (PBI/H₃PO₄) poly salts depends on the acid content. A low acid content (up to 2.4 H₃PO₄ per PBI monomer unit) yields conductivities of less than approximately 10⁻⁴ S cm⁻¹ at 160 °C, while a high acid content (11 acid molecules per repeating polymer unit) provides high conductivity values of up to 0.15 S cm⁻¹ at 160–180 °C [126, 127].

An increasing phosphoric acid content may encounter several disadvantages, however, including leaching out of H₃PO₄, poisoning of the catalyst, or the inducing of corrosion of the electrodes and bipolar plates in the FC stack [128]. Furthermore, with the increasing acid content, the mechanical properties of the membranes such as their tensile strength and homogeneity become significantly deteriorated [129, 130]. An optimal
phosphoric acid content depends on the structure of the membrane polymeric matrix. Improved mechanical properties and enhanced conductivity can be obtained via: cross-linking modification of the linear PBI (using e.g. \(\gamma\)-(2,3-epoxypropoxy)propyltrimethoxysilane (KH560) \[131\], poly(vinylbenzyl chloride) \[132\], 1,3-bis(2,3-epoxypropoxy)-2,2-dimethylpropane (NGDE) \[133\] or dichloromethylphosphinic acid (DCMP) \[134\] as cross-linkers), modification of the main PBI chain (e.g. using partially fluorinated polybenzimidazoles containing \(-\text{C}(\text{F}_3)_2-\) junctional groups) \[135\], or using nanofibres to reinforce the PBI/H\(\text{}_{3}\)PO\(\text{\textsubscript{4}}\) membranes \[136\].

The phosphoric acid (PA)-doped \(n\)-polybenzimidazole (PBI) membranes are vulnerable to attack by radicals \[126\]. The PBI membrane exhibits higher weight loss than Nafion\textsuperscript{TM} in reaction with Fenton’s reagent. However, the oxidative stability of the PBI membranes was improved as the molecular weight of the PBI polymers increased \[137\].

4.4 Polyphosphazene membranes

An alternative class of polymers for proton exchange membranes is polyphosphazenes. Polyphosphazenes (PPZs) are very unique hybrid polymers that contain a backbone of alternating phosphorus and nitrogen atoms with two organic, inorganic, or organometallic side groups attached to each phosphorus atom (Figure 11).

Figure 11: General polyphosphazenes structure.

The polymers are of interest to many research groups because of the opportunities they provide for structural diversification via the introduction of a vast range of side groups, which allows obtaining an unprecedented and largely controlled variety of desirable properties \[138-140\].

PPZs have numerous advantages over conventional hydrocarbon-based polymers. One of the most important is their thermal and chemical stability. Due to the highest oxidation states of nitrogen and phosphorus atoms in the \(-\text{P} = \text{N} -\) backbone, the polyphosphazenes are particularly stable in aggressive oxidative conditions. Moreover, PPZs are characterized by a low glass-transition temperature due to their low barrier to the skeletal free rotation of each phosphorus–nitrogen bond and their high torsional mobility \[141\]. Other very important advantages of polyphosphazenes are their relatively low cost and facile synthesis routes. The most widely used method is the thermal ring-opening polymerization of chlorophosphazene cyclic trimer, presented by Allcock and Kugel \[142-146\]. The cyclic trimer – hexachlorocyclotriphosphazene – is polymerized to linear poly(dichlorophosphazene). The subsequent macromolecular substitution with the appropriate nucleophilic reagent allows to obtain polyphosphazene (Figure 12). The PPZs containing aryloxy substituents exhibit the best combination of properties \[138\].

In order to be qualified as typical ion-conducting materials for MEA applications, the phosphazenes polymers need to have acid functionality, which is incorporated into the polymer structure. Polyphosphazenes can be classified according to the type of acidic function they have. Literature reports present that the sulphonic and phosphonic groups can ensure the proton conductivity of PPZs. The first attempt to develop the polyphosphazene solid electrolyte took place in 1984 and was published by Blonsky and Shiver \[145\]. It was Allcock et al. who reported the first synthesis of polyphosphazenes with sulphonic groups (S-PPZs) which would be a proton-conducting material for fuel cell applications. The authors synthesized the polyphosphazenearylsulphonic acid derivatives. The sulphonation reactions were developed initially with cyclic trimers, then polymers in solution, and, finally, with surfaces made of solid S-PPZs \[146\].
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Pintauro and co-workers showed sulphonation reaction for poly[(3-methylphenoxy)(phenoxy)phosphazene] [147] and poly[bis(3-methylphenoxy)phosphazene] [141]. In result, they obtained a stable material with high ion exchange capacity values (near 2 mmol/g). Furthermore, they developed PEMs with sulphonated poly[bis(3-methylphenoxy)phosphazene] characterized by their high IEC (1.4 mmol/g) [148]. The poly[bis(3-methylphenoxy)phosphazene] with SO$_3^-$ groups allow to understand the specific proton conductivity mechanism. The ion exchange capacity and proton conductivity of the sulphonated membrane increased with increasing water content, finally reaching the maximum conductivity of 0.1 S cm$^{-1}$ at the IEC of 1.6 mmol/g. Moreover, the results clearly indicated that sulphonated PPZs are good proton conductors (comparable to Nafion®) when they swell in water. The hydrophilicity of the –N=P– backbone demonstrated that in this type of a conductor, the proton migration proceeds primarily according to the Grotthuss mechanism [149]. For such a mechanism, the activation energy for proton conduction should vary from 14 to 40 kJmol$^{-1}$ [150].

Due to the opportunity to incorporate the acidic groups into the polymer structure without the harsh conditions required in the sulphonation process, the phosphonic acid functionalized polyphosphazenes (P-PPZs) are a promising alternative to the sulphonated PPZs. Nonetheless, the literature data show that P-PPZs membranes have a lower conductivity than S-PPZs [138]. Another alternative is the use of polyphosphazenes with the sulphonamide group incorporated. Such derivatives have good conductivity and are excellent candidates for MEAs [151].

PEMs containing pure polyphosphazene films have relatively poor mechanical behaviour due to the necessary hydrated conditions. In order to improve such properties, polymer blends were produced. The membranes were synthesized either by cross-linking (e.g. with segments of polybenzimidazole [152] or polyacrylonitrile [153]), or other re-enforcement via a physical mixture (e.g. with PVDF [154]).

4.5 Sulphonated polyimide membranes

The aromatic polyimides are compounds containing an imide heterocyclic structure in their backbone. They have found a vast range of applications in many industrial fields due to their excellent thermal stability, high mechanical strength, membranability (good film-forming ability) and significant chemical resistance. These values are required for the electrolyte membrane for proton exchange fuel cells, and thus, sulphonated polyimides (SPIs) have been developed as promising candidates for PEMFCs [155]. Generally, the opportunity to produce significantly less expensive membranes than Nafion® successfully contributed to the polyimide-based materials development. The use of polyimide membranes in FCs applications was first presented by Faure et al. [156]. The most interesting are the more hydrolytically stable six-membered ring (naphthalenic) sulphonated polyimides-based membranes (Figure 13) [157, 158].

![Figure 13: Naphthalenic type polyimides containing sulphonic acid moieties attached directly to the polymer main chain 7 and with sulphonated side-chains 8.](image)

Five-membered heterocyclic (phthalic) polyimides have been also investigated for many years, but under practical fuel cell operating humidity conditions they quickly degrade via hydrolysis due to the lower electron density of the carbonyl carbon atom [71]. Such a step in the degradation of imide is caused by the nucleophilic attack of a hydroxyl anion from water on the electrophilic carbon atom of the carbonyl group. Hydrolytic cleavage of phthalic polyimides results in polyimide chain scission and the formation of units with dicarboxylic acid and...
free amine functions [159]. Due to the fact that the sulphonic acid group is strongly electron-withdrawing, the distancing its position from the imide moiety is also expected to result in an increase in the hydrolytic stability of the polyimide main chain (Figure 13). The polyimide membranes containing sulphonic acid groups attached directly to the polymer backbone (7, Figure 13) are less stable compared to the polyimides with sulphonated side-chains (8, Figure 13). In contrast to the SO$_3$H groups, to improve oxidative and hydrolytic stability of the six-membered ring polyimides-based membranes, sulphonated polyimides bearing trifluoromethyl groups were successfully synthesized. The hydrophobic character of CF$_3$ moieties protect the imide ring from being attacked by water or radical molecules, despite its strong electron-withdrawing behaviours [160]. Furthermore, the addition of bulky aliphatic groups into the main and side chains of the ionomers significantly improves the hydrolytic stability [161–163]. The addition of a cross-linker or constructing network structure can also increase the resistance to hydrolysis while simultaneously improving the dimensional stability. This may be because cross-linking can reduce the swelling to a greater extent. Sundar et al. used a series of dibromoalkanes (dibromobutane, dibromohexane and dibromodecane) as cross-linking compounds. The cross-linked sulphonated polyimides exhibited higher hydrolytic stability than un-cross-linked ones. However, this feature decreased with an increase in the chain length of the cross-linker. This may be due to the higher swelling of the polymers with longer alkyl chain lengths [164]. Other cross-linkers used to obtain membranes with high hydrolysis resistance are as follows: various diols (1,2-ethanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol or 1,10-decanediol) [165], poly(ethylene glycol) diacylate [166] or 1,3,5-tris(4-aminophenoxy) benzene (TAPB) [167]. Another possibility to enhance the water stability of SPIs for fuel cells is to use the SPI membranes employing 4,4’-binaphthyl-1,1’,8,8’-tetracarboxylic dianhydride (BTDA) that contains binaphthyl units instead of conventional 1,4,5,8-naphtalenecarboxylic dianhydride (NTDA) with a common aromatic naphthyl function. The improved stability of BTDA-based polyimides was attributed to its unique binaphthalimide structure, which effectively decreases the possibility of a nucleophilic attack leading to hydrolysis [168, 169]. Electron-donating phenoxy [170] or benzophenone groups [171] at the meta-position of the imido groups positively impact the hydrolytic stability of producing SPI materials. The naphthalenic SPI membranes are much more resistant to hydrolysis, but they also have a few drawbacks. They show rather low water stability, which limits their further use in FCs technology [163]. Moreover, the proton conductivity of SPI membranes is low at low humidity levels [172]. Accordingly, in order to overcome the above disadvantages, many researchers have been endeavouring to prepare novel and improved SPI membranes for the proton exchange fuel cells.

4.6 Sulphonated poly(arylene ether ketone)-based membranes

The sulphonated poly(arylene ether ketone)-based (SPAEEK-based) membranes are a family of sulphonated aromatic main-chain polymers. They are a promising alternative to PEMs due to their wide range of advantages such as good mechanical properties, outstanding thermal and chemical stability, facile processability, high availability and also low cost. The PAEK polymer family includes poly(ether ketone)s (PEKs), poly(ether ketone ketone)s (PEKKs), poly(ether ether ketone)s (PEEKs), poly(ether ether ketone ketone)s (PEEKKs) and poly(ether ketone ether ketone ketone)s (PEKEKKs). The exemplified general structures of the PAEK polymer group are presented in Figure 14.
Poly(arylene ether ketone)s are very rigid, inflexible polymers with bulky aromatic rings. These features result in a high glass transition temperature exceeding 200 °C. The aromatic rings support various electrophilic or nucleophilic modifications. To produce membranes for MEAs for fuel cells, active proton exchange sites, such as sulphonic groups, have to be introduced to the poly(arylene ether)s [173]. Of all these suitable materials, the sulphonated poly(ether ether ketone)s (SPEEK) are the focus of many investigations in preparing membranes (Figure 15).

The literature reports that sulphonated poly(arylene ether ketone)-based (SPAEEK-based) membranes are durable under fuel cell operating conditions and sometimes their lifetime exceeds 3000 h. However, while the higher degree of sulphonation (DS) offers higher proton conductivity, the mechanical stability decreases. Such membranes are vulnerable to radical attacks and degradation processes [174, 175]. The radicals generated during PEMFC operation (mainly HO•) may degrade with the detachment of the sulphonic acid groups and the scission of the polymer chain [176]. Further studies suggested that HO• may either attack the aromatic ring in the ortho position to the alkyl and RO substituents (Figure 16, sites A), or cause the C–O–C scission (Figure 16, site B) [177].
Attempts to improve the stability of SPAEK have included optimization of the position of \(\text{SO}_2\text{H}\). When such an electron-withdrawing group is attached directly to the aromatic ring, it may reduce the electron density of the neighboring ether function via resonance and increase the susceptibility to hydrolysis of ether linkage [178].

To avoid this potential instability, the sulphonic group should be attached to the pendant chain rather than to the main chain of the polymer [179]. Another way of improving the stability is incorporating hydrophobic perfluorinated blocks in the main-chain of the multi-block aromatic polymer. Strong electron-withdrawing fluorine atoms can deactivate the aromatic ring and reduce the negative addition reactions of radicals [178]

The proton transport of SPAEK was compared to the corresponding properties of Nafion®. Due to the rigid structure of the aromatic backbone in SPAEK, the hydrophilic channels are narrower than in Nafion®. It results in a reduced dissociation level of the sulphonic groups. Moreover, the narrower channels have numerous cul-de-sacs (dead-end “pockets”) which form a slimmer and poorly connected water-filled network and significantly impede proton transfer. Scientific efforts are focused on producing SPEEK with a high proton conductivity, but maintaining the sulphonation on appropriate levels to assure also chemical stability and limited swelling [180]. Currently, SPEEK membranes with conductivity over 0.1 S cm\(^{-1}\) are reported [181].

The general approaches for the synthesis of sulphonated poly(arylene ether ketone)s include polymer post-modification and direct copolymerization of sulphonated monomers. The conditions of the first modification reaction are very harsh and sometimes incur difficulties (e.g. a lack of control over the sulphonation level and the final location of the acidic conductivity groups, as well as the possibility of side reactions or degradation of the polymeric chain). Such a transformation was used to obtain the most popular sulphonated poly(arylene ether ketone) – sulphonated Victrex® PEEK [182]. PEEK can be obtained by two main synthetic pathways – electrophilic or nucleophilic substitutions [183]. The first method employs extremely strong acidic conditions, such as a triflic acid (CF\(_3\)SO\(_3\)H) used as a solvent. Such a media limited the applicability in the industry, however, due to its safety hazards. In contrast, the nucleophilic substitution method may be performed using a wider range of solvents (e.g. dimethyl sulphoxide, sulpholane [184], diphenyl sulphone [185] or N-methylpyrrolidone [186]). In the nucleophilic substitution method of PEEK synthesis, a hydroquinone reacted with a 4,4′-dihalobenzophenone (derivative with chlorine or fluorine atoms) in the presence of a potassium carbonate as a base (Figure 17).

The direct synthesis of sulphonated monomers for SPEEK membranes seems to be more advantageous than the postsulphonation process. In such a synthesis, side reactions can be avoided or significantly reduced. Moreover, the degree of sulphonation (DS) and position of the sulphonate groups in the aromatic ring may be better controlled.

In order to improve the performance of SPAEK membranes, various modification strategies were introduced [23].

Cross-linking of poly(ether ether ketone)s improves the thermal stability, mechanical strength and oxidative stability of the membranes. Such membranes exhibit lower water uptake than non-cross-linked materials. Nonetheless, the expanded polymer network and increased cross-linking density may cause a reduction in the proton conductivity and flexibility of the PEMs [187]. Hou et al. presented an excellent review of recent advancements in the development of cross-linking strategy [188]. Literature reports show that cross-linked SPAEK membranes have limited solubility in common solvents and show improved stability. Wang and co-workers prepared an outstanding SPAEK sulphonated poly(ether ether ketone) bearing pendant amino group (Am-SPEEK) membrane with 4,4′-diglycidyl(3,3′-5,5′-tetramethylbiphenyl) (TMBP) as an epoxy resin cross-linker with a proton conductivity of 0.140 S cm\(^{-1}\) (80°C), i.e. higher than that of Nafion® (0.1 S cm\(^{-1}\)) [189]. Li et al.
used sulphonated – a novel cross-linker – carboxyl terminated benzimidazole trimer bearing sulphonic acid groups (s-BI). The series of SPEEK/s-BI-n membranes show excellent stability and a low swelling ratio. Furthermore, the authors achieved high proton conductivities exceeding 0.12 S cm⁻¹ (60 °C) [190].

The next modification is preparing branched sulphonated poly(ether ketone)s. The branched polymers are defined as materials between linear and cross-linking type polymers. Branching allows getting a larger free volume for water [191, 192] and increases the proton conductivity of the membranes.

Polymer blending is an appropriate technique for designing materials with enhanced properties. The blends often exhibit better properties than the properties of an unmixed component. The preparation of blended membranes employing organic fillers is a common way to improve the properties of SPAEKs materials due to the simplicity of preparation and easy control of different physical properties. Until now, sulphonated poly(arylene ether ketone)s have been blended with polybenzimidazole (PBI) [193–195], poly(ether sulphone) (PES) [196, 197], sulphonated and silylated polyphenylsulphone [198], sulphonated cycloextrin [199] poly(vinylidene fluoride) (PVDF) [200–202], poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) [202], phosphonated polysulphone [203], 3-aminopropyltriethoxysilane [204], poly(ether sulphone) [205], acrylic acid-co-4-vinylimidazole [206], poly(ether imide) [207, 208], polypyrrole [209], nylon 6 [210], poly(styrene-sulphonic acid) [211], polyacrylonitrile [212], or poly(vinyl alcohol) [213].

The formation of composite SPAEK-based materials with inorganic filler is another technique to enhance the proton conductivity and mechanical stability of membranes. A wide range of heteropolyacids (HPA) and their salts is used as fillers, for example, H₃PW₁₂O₄₀, H₃PMo₁₂O₄₀, Na₂HPW₁₂O₄₀ [214], Cs₃H₅PW₁₂O₄₀/Cs₃H₅SiW₁₂O₄₀ [215], CsH₅H₂O₂PW₁₀O₄₀/Pt [216], Cs₂H₅H₀.₅PW₁₂O₄₀/Pt [217], H₃PW₁₂O₄₀/SiO₂ [218], H₃PW₁₂O₄₀ and MCM-41 [219], H₃SiW₁₂O₄₀/SiO₂ or Al₂O₃ [220], γ-K₉SiW₁₆O₄₆ [221], Cs₅H₅H₃.₅PW₁₂O₄₀ [222]. Furthermore, the combination of SPAEK and non-acid zirconium, titanium or silica inorganic fillers was also reported [223–225].

4.7 Natural polymer- and bio-inspired-based membranes

Power needs to be generated using environmentally friendly natural materials, so scientists are focusing their efforts on investigating natural or bio-inspired polymeric membranes for the application of FCs. Use of eco-friendly biopolymers in designing electrical devices is not only challenging and interesting, but also important from the environmental safety point of view. Moreover, use of such polymers can significantly decrease the cost of production, often very high compared to typically synthetic materials. Currently, few natural or bio-inspired polymers have been employed as an attractive electrolyte for the membrane electrolyte assemblies [226]. Until now, only few polymers have been reported as suitable biopolymer electrolyte membranes for fuel cell applications. Such natural-based polymers include agar [227], uracil [228, 229], gelatin [230, 231], pectin [226] or cellulose [232–236].

Chitosan (CS) and its derivatives are extensively investigated as some of the most attractive “green” materials for fuel cell applications. CS is a biodegradable, biocompatible, nontoxic, and quite low-cost polymer, offering a vast range of possibilities for simple chemical modifications.

The proton conductivity of Chitosan is low, and it is necessary to enhance its conductivity. In order to produce a conducting material, proton donors may be introduced into the CS matrix by a blending method with various acidic compounds. In result of such modifications, the acid–base complexes are synthesized [111]. Until now, Chitosan has been mixed with various acidic compounds, such as a medronic acid [237], poly(vinyl phosphonic acid) [238], poly(4-styrenesulfonic acid-co-maleic acid) (PSSA-MA) [239], acrylic acid-2-acylamido-2-methylpropane sulfonic acid copolymer [240], oxalic acid [241], poly(acrylic acid) [242], or various heteropolyacids and their salts [243, 244]. Furthermore, the grafting of acidic functions to the backbone of CS may be another effective way to obtain proton conducting materials [245, 246].

The proton conducting mechanism for acid-base complexes with Chitosan in anhydrous conditions is of a Grotthuss-type character. Yamada and Honma have presented proton transfer for Chitosan and medronic acid (MA). The electrostatic interaction of the amino groups in Chitosan with the phosphate group in the MA molecule forms a proton defect site. The neighbouring proton in the acid molecule is transferred to the defect site (Figure 18) [237]. The hydrated or partially hydrated conditions contribute to the combine vehicle and Grotthuss mechanisms [240].
Figure 18: The anhydrous proton conducting mechanism of Chitosan-MP composite proposed by Yamada and Honma [237]

Recently, the model PEMFC with a CS-based natural membrane has demonstrated some possibilities but a low power density (16 mW cm\(^{-2}\) at 75 °C [237]). Therefore, the preparation of such membranes to be efficiently applied in PEMFC is still a challenge for many research groups.

5 Synthetic methods of PEMs preparation

As illustrated in the preceding section, many polymer classes of diverse chemical structures and various strategies of the incorporation of protogenic moieties have been explored as electrolyte materials for PEM application. The sulphonic acid moieties arrangement and the acid strength and the character of the connecting unit to the polymer backbone may have a considerable impact on the morphologies of the resultant membrane and subsequently on its physical and chemical properties. Most of the synthetic methods employed in the formation of ionomeric materials lead to the statistical or random distribution of sulphonic acid groups along the backbone chain of the copolymer [22]. The following four different synthetic strategies, allowing for preparations of the ionomer membranes, can be distinguished: (i) postmodification/postsulphonation of existing fluorinated/nonfluorinated polymeric materials (Figure 19)), (ii) direct polymerization of monomers functionalized by acids (sulphonic mostly) with fluorinated or/and nonfluorinated monomeric units (Figure 19)), (iii) chemical grafting of sulphonated monomers onto the fluorinated/nonfluorinated backbone (Figure 19) and (iv) the stepwise route based on irradiation grafting of monomers onto the fluoropolymer backbone followed by a subsequent postsulphonation (Figure 19)).

One of the most commonly used and oldest methods that allow to convert the existing polymeric materials into ionomers and to confer their protonic conduction properties is the postsulphonation strategy (Figure 19(a)). Postsulphonation has been employed in the preparation of numerous ionomeric materials as PEMs, namely polystyrene-sulphonic acids (PSSA) [81–88], sulphonated poly(\(\alpha,\beta,\beta\)-trifluorostyrene) – 1\(^{\text{st}}\), 2\(^{\text{nd}}\) and 3\(^{\text{rd}}\) generation Ballard Advanced Materials (BAM1G, BAM2G, BAM3G) [71, 95–97], sulphonated poly(benzimidazole)s (SPBI) [248], sulphonated poly(phosphazane)s (S-PPZ) [148–150], sulphonated poly(arylene ether ketone)s (SPEAK) or sulphonated poly(ether ether ketone)s (SPEEK) [173–186]. The postmodification, for example, electrophilic sulphonation, is usually employed to modify polymers with aromatic functional groups either in the lateral position to the polymer backbone or incorporated directly into the polymer main chain. Aromatic polymers easily undergo sulphonation reactions in the presence of concentrated sulphuric acid, fuming sulphuric acid, chlorosulphonic acid, oleum or other sulphur trioxide complexes.
Since sulphonation is an electrophilic substitution reaction, its applicability strongly depends on the aromatic ring reactivity, that is, the electron character of the present substituents. Electron-donating groups (EDGs) activate the ring and thus favour the reaction, while electron-withdrawing groups (EWGs) deactivate the ring, so that successful introduction of a sulphonic acid moiety requires a much stronger sulphonating agent. Moreover, the sulphonylic acid substituent is preferably introduced to the activated position of the aromatic ring and usually only one –SO₂H group per repeat unit could be achieved. There are several drawbacks of the postsulphonation strategy, mainly (i) the lack of precise control over the location and degree of the functionalization that influences the ion exchange capacity, (ii) a risk of an undesired side-reaction occurrence such as cross-linking via sulphone formation that may result in the reduction of the material proton conducting properties, (iii) a degradation of the polymer chain that may contribute to deterioration of the membranes’ mechanical properties. Therefore, a direct polymerization of monomers bearing sulphonylic acid groups with nonsulphonated monomers seems to be an optional strategy allowing for the placement of ionic groups on a copolymer backbone in a controlled manner.

Synthesis of sulphonated macromolecular materials for application in PEMs by the direct copolymerization of sulphonated monomers has been alternatively applied in the preparation of nonfluorinated sulphonylic acid ionomers such as sulphonated poly(arylene ether)s [174, 249, 250] or sulphonated poly(imids) [157]. Though synthetically challenging, the direct strategy is considered to be a rigorous and repetitive method of controlling the chemical composition, acid content, and even molecular weight of the resultant sulphonated macromolecules. The direct copolymerization strategy is also commonly used in the preparation of polyfluorosulphonylic acid ionomers like Nafion®, Aciplex®, Flemion®, Dow®, or 3M®, the current state-of-the-art membranes for PEMs [62–64, 67, 68]. The perfluorinated copolymers bearing sulphonylic acid groups are synthesized in direct free radical copolymerizations of tetrafluoroethylene (TFE) with perfluorinated vinyl ethers terminated by perfluorosulphonylic acid groups (Figure 19). However, all these fluorinated membranes are expensive due to the demanding chemical synthesis and the cost or availability of perfluoroether comonomers and suffer from low conductivity at a low water content, moderate glass transition temperatures and the relatively low mechanical strength at elevated temperatures.

Chemical grafting of sulphonated monomers onto the hydrophobic polymer backbone is another approach that has been employed for the preparation of ion containing materials, such as the copolymer consisting of a polystyrene backbone and sodium styrene sulphonate graft chains (PS-g-macPSSNa) [251, 252] or a copolymer of sodium styrene sulphonate grafted to a poly(acrylonitrile) backbone (NaSS-g-PAN) [253], as well as N-benzylsulphonate poly(benzimidazole) (BzS-PBI) [254, 255] (Figure 19)). The chemical grafting strategy allows for the elaboration of ion conducting membranes formed by potentially well-defined block copolymers with sulphonated and unsulphonated blocks. The chemical structure of such materials with their blocky character results in an increased proton conductivity without an enormous increase in water swelling. Moreover, the comparison of random and graft copolymer properties (proton conductivity, water uptake, mechanical strength or thermal stability) reveals that the polymer structure, that is, selected method of synthesis, enormously impacts the morphology and, therefore, the properties of the resultant materials [22].

Poly(styrene sulphonylic acid) grafts have also been attached to per- or partially fluorinated backbones. The materials were synthesized via a stepwise route based on the irradiation grafting of monomers onto a fluoropolymer backbone followed by a subsequent post sulphonation (Figure 19)). The fluorinated polymers such as poly(tetrafluoroethylene) (PTFE) [112], poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [256–258], poly(ethylene-alt-tetrafluoroethylene) (ETFE) [259], or poly(vinylidene fluoride) (PVDF) [260] were activated by different techniques of irradiation, for example, thermally, in the presence of ozone, from swift heavy ions, electron beam or γ rays. The irradiated polymer films were immersed in styrene solution to graft polystyrene onto the fluorinated backbone, and finally, the non-conducting hydrophobic materials were sulphonated by chlorosulphonylic acid. The degree of grafting can be controlled by the concentration of styrene, choice of solvent, temperature and time of grafting.

The synthetic strategies presented above are widely used in the formation of polymers bearing functional moieties for proton conduction [23, 112]. The resulting materials are designed to serve as stand-alone PEM, although they might also be a host for inorganic compounds or organic polymer to afford a proton conducting component in a blend or composite. Preparation of such polymeric systems is a promising technique to improve the membrane ionic conductivity, mechanical strength, water retention and to decrease the fuel permeability, especially at elevated operating temperatures [261]. To overcome the most crucial problem, that is, the severe loss of conductivity at working temperatures above 100°C, two strategies have been developed. The first approach is based on systems that exhibit a high resistance to dehydration or are capable of maintaining high conductivity with low water content. The other strategy employs systems where media other than water assist the proton transport. Ionomer composite membranes include perfluorosulphonylic acid ionomer/polymer matrix membranes (e.g. PTFE/perfluorinated ionomer macrocomposite membrane from W. L. Gore and Associates, Inc. – Gore®Select [262], sulphonated FEP/Nafion hybrid membrane [263], or
Nafion/PBI composite membrane doped with phosphoric acid [264]), perfluorosulphonic acid ionomer/inorganic fillers composite membranes (e.g. Nafion/SiO₂ nanocomposite membrane [265], Nafion/TiO₂ composite membrane [266], Nafion/Zirconium phosphate (α-ZrP) composite membrane [267], or Nafion/polyphenylsilsesquioxane (PFSQ) – polysiloxane composite membrane [268]), sulphonated polymer/inorganic proton conductor systems (e.g. most widely studied SPEEK/heteropolycarboxylic (HPC) composite membranes [214, 215], 216, 217, 218, 219, 220, 221, [222]), polymer/acid complexes (e.g. PBI/H₃PO₄ based membranes [269], or poly(diallyldimethylammonium-dihydrogenphosphate (PAMA–H₂PO₄⁻)/H₃PO₄ blend membrane [270], sulphonated polymer/base complexes (e.g. SPEEK/imidazole or pyrazol complex membranes [271]), or polymer blends (e.g. SPEEK/PBI and ortho-sulphone-sulphonated poly(arylethersulphone (SPS)/BPI as the acid/base blend membranes [272], or sulphonated poly(phenylene oxide) (SPO)/PVDF [273]). The current trend is for the composite and hybrid membranes, which combine the properties of both the polymeric matrix and inorganic part.

Cross-linking is another efficient strategy to improve the thermal stability, mechanical strength and oxidative stability, as well as to lower the water uptake of ionomeric membranes. It has been widely employed in modifying the structure of sulphonated aromatic polymers in particular [188, 274]. A cross-linking reaction can be defined as a process where a polymer becomes a dense three-dimensional network by varied interactions, such as covalent bonds, as a result of the chemical reaction (e.g. esterification, addition, Friedel–Crafts reactions and the formation of sulphone –SO₂– bridges), ionic bonds or hydrogen bonds, as well as a combination of covalent and ionic bonds [275]. Chemical cross-linking was employed to modify a wide range of aromatic polymers of potential FC applications including polybenzimidazoles (PBIs) [131–134], polyphosphazenes (PPZs) [152, 153], sulphonated polyimides (SPIs) [164–167], and sulphonated poly(ether ether ketone)s (SPEEKs) [187–190]. Nonetheless, the expanded polymer network and increased cross-linking density may cause a decrease in the proton conductivity and flexibility of the PEMs [187].

## 6 Applications of PEM fuel cell technology

Fuel cells have the potential to replace such conventional power sources as internal combustion engines or batteries due to their high energy efficiencies and low emissions. The efficiency can reach as much as 60% in electrical energy conversion and an overall 80% in the cogeneration of electrical and thermal energies. Additionally, fuel cells can significantly reduce (by more than 90%) or even eliminate pollution – such as in the case of hydrogen-fuelled FCs, where the water forms as a non-polluting by-product, which can further be reused as potable water. Use of the FCs can also eliminate the emission of greenhouse gases, since hydrogen fuel can be produced in an environmentally friendly manner such as through the electrolysis of water driven by renewable energy, and not generated by burning fossil fuels, mostly coal and natural gas. As a consequence, avoiding the need for the usage of conventional carbon-based fuels’ (coal, oil and gas) can significantly decrease economic dependence on oil producing countries and, therefore, also provide greater security of energy supply for the user nation. Moreover, most of the fuel cells operate with a low noise level compared to conventional combustion engines, and therefore, they are ideally suited for use within buildings and readily accepted in residential areas. The availability of stationary fuel cells at any location with access to a source of power and water supply essential for producing the hydrogen fuel may result in a decentralization of power grids, the reduction of transmission and distribution losses, and, thus, considerable decrease the grid dependence. Furthermore, unlike batteries, fuel cells exhibit longer operating times that depend on the amount of fuel supplied and not on the capacity of the unit itself, quick recharge by fuelling, no "memory effect" during refuelling – no gradual energy capacity loss after repeated recharging or partial discharging – and a modular design allowing for the easy exchange of cells’ parts, and low maintenance costs. Although fuel cells feature outstanding properties, such features as high initial cost and relatively low durability still remain the greatest obstacle to their commercial implementation. Nevertheless, fuel cell technology can compete with the conventional, well-established technologies (internal combustion engines or batteries) in practically all applications [276].

The three major areas of application for fuel cell technology are portable power generation, stationary power generation and power for transportation. A fuel cell’s power output parameters depend on several factors, including the type, size, operating temperature and pressure of the supplied gases. As already presented, most often the various types of fuel cells are classified by the electrolyte used. It determines the potential for their application in certain FC technologies through their working temperature (T) profile. The profile impacts such vital characteristics as: (i) efficiency (η): the higher the temperature, the lower the internal resistivity and polarization, and offsetting of the voltage drop in result of the temperature increase, (ii) start-up time (the time needed for reaching the cell’s optimal operating temperature) is longer for higher temperatures, (iii) dynamic behaviour: fluctuating temperatures following the changing load lead to a repeated stack material shrinking.
or expanding and the resultant mechanical stress reduces the fuel cells’ lifetime, especially in the case of high temperature units (HTFC) that have ceramic components [277].

The three latter parameters above determine the applicability of specific FC technologies. Figure 20 illustrates the dependence quite well: for large stationary applications that require, most of all, high efficiency (with the start-up time and load-following dynamics being less important), MCFC or SOFC are the most suitable types. Mobile and portable equipment, on the other hand, needs short start-up times in any, also sub-zero, temperatures, so PEMFCs would be preferred.

Figure 20: Typical applications of different fuel cells’ types.

Another criterion for FC technology selection is fuel availability. From the electrochemical point of view, hydrogen is the best fuel; its direct reaction ensures the system’s high power density. However, being a gas, the fuel is difficult to handle. As for much easier to manage liquids, only methanol reacts directly at acceptable rates, but its power density is less than 20% of direct hydrogen fuel cells. Other liquid fuels require reforming into H₂-rich gases. This applies also to natural gas (NG), although in this case the advantage is the already existing dense supply network. The conversion process produces catalyst poisons, such as carbon monoxide (CO), that are desorbed in high temperatures, which makes high temperature fuel cells (HT-FCs) the preferred type for the overall reduced cell complexity and ease of handling.

Portable fuel cells can be defined as low power systems being an integral part, or external charging up, of products designed to be moved. Prime candidates for FCs application are small personal electronics (mp3 players, mobile phones, cameras), large personal electronics (laptops, printers, radios), or education kits and toys. Fuel cells also earn much attention as power supply for military applications in portable soldier’s appliances or skid mounted generators, or auxiliary power units (APU) for the leisure and trucking industries, as well as portable products (torches, trimmers) or emergency equipment [278]. The typical power range for portable electronic devices is from less than 5 W (micro power application) to 500 W. Portable/micro fuel cells are generally an alternative to batteries and typically are based on either PEM or DMFC technology. These FC applications are mostly driven by the capability of higher energy density, extending a device’s operating time, the reduction of noise and emissions, and a short charging time [279]. The market of portable fuel cells is led by the following players: Horizon, myFC, IntelligeEnergy, eZelleron, EnyMotion, Truma, Acumtrics, Thoshiba, NEC, Hitachi, Panasonic, Samsung, Sanyo, or LG [277].

Stationary fuel cells are units providing electricity (and sometimes heat), but not designed to be moved. As the prime power source, they are mostly used in large cogenerated heat and power (CHP) systems, residential applications (resCHP) and uninterrupted power supply solutions (UPS). Development works continue on expanding their functionality by adding absorption chillers to make tri-generation systems that provide heat, power, and a cooling capacity [280]. These would be of particular interest in situations characterized by comparable, seasonally fluctuating demand for heat and cooling power. An additional benefit would be the suitability of oxygen-free exhaust gases for fire prevention. An important feature of this type of FC is their resilience, that is, their ability to mitigate drops and peaks in the demand/supply, which is particularly useful in distributed power grids for absorbing local events, such as blackouts, or for stabilization and backing-up purposes. Stationary FCs make up the body of global FC sales. As reported by Navigant Research, they amounted to over 70% of the total FC turnover in 2014 [281]. The type is expected to remain most popular, with the annual volume growing from approximately 40,000 in 2014 to 1.25 million in 2022, which translates into a 51.7% compound annual growth rate (CAGR). One of the most popular types of FCs used for stationary purposes is CHP units. They generate not only power, but also heat that otherwise would be wasted, which increases their total efficiency to 80–95%. Both types of energy find use in residential applications. Based on either PEM or
SOFC technology, the fuel cells have the power output range of 0.5 kW to 10 kW. Residential CHPs are popular in Japan (over 10,000 cumulative units deployed by the end of 2010) and South Korea, although in the second case, their purchase still relies on government subsidies. Another type of stationary FC units belongs to UPS systems. They are used for continuous power supply in case of blackouts, for instance. As for the fuel type used, it differs by region: in Asia the most common fuel is natural gas and LPG, in the United States it is hydrogen, while, in Europe, there have been attempts of fuelling with methanol. Finally, there is a wide range of large stationary primary power source units ranging from 1 to 50 MW. Their main purpose is to take over the power grid function in areas with little or no network, or to extend it by additional nodes in such cases. Based on four FC types (SOFC, MCFC, PEMFC, and PAFC), the systems are mostly provided by manufactures in the United States and Japan. The prime power market of large stationary fuel cells is led by three players such as: Fuel Cell Energy (MCFC systems), Bloom Energy (SOFC systems), and Doosan (prior ClearEdge Power, PAFC systems). Moreover, commercially available PEMFC systems include units for back-up and off-grid power applications from Axane, Ballard, Power Cell, Electro Power Systems, Heliocentris, Horizon, Hydrogenics or ReliOn-Plug Power, as well as for residential CHP usage from Ene-Farm [277].

**Fuel cells for transport applications** are units designed as the power source for vehicles or for extending their drive range. Their advantages include their zero emissions and considerably higher efficiency than ICE or battery-powered vehicles. The use of FCs has increased the range of electric vehicles (EVs) and reduced the refuelling time (sometimes to as little as a few minutes) compared to battery-based vehicles. Because of the power demand characteristics (short start-up time and high load dynamics), the cell type most often applied is PEMFC. The preferred fuel is hydrogen compressed to 350 or 700 bars, although the availability of fuelling stations is limited. The reason is a lack of feasible technology for on-board processing systems that would produce hydrogen from such liquid fuels as methanol, LPG, gasoline, or diesel. In transport, fuel cells are applied mainly in passenger cars, buses and cargo vehicles but H\textsubscript{2} and O\textsubscript{2}-fueled PEMFCs are also successfully used in military submarines, allowing silent underwater operations for up to three weeks without surfacing [279]. Development works continue for light traction vehicles such as golf cars, airport carts, wheelchairs, and motorcycles, bicycles, ships, airplanes, trams and locomotives. Although FC-powered light duty vehicles (LDVs) have not been commonly used so far, the situation started to change in 2014, with Toyota’s launch of its Mirai model. The deployment commenced at a few nodes with the required refuelling infrastructure in Germany, Japan, and the United States, but it is expected to spread from these centres as the market grows. Another sector for fuel cells is bus transport. It keeps growing with every new model presented successfully in Europe, Japan, Canada and USA. The capital cost remains high, although it is expected to become comparable to the prices of hybrid diesel buses in the near future. There are also a few niche transport applications, some successfully marketed, such as PEMFC-powered materials handling vehicles, popular in the United States and making up about 90 % of the category, as well as other applications less commercialized and still under development, such as unmanned aerial vehicles (UAV), e-bikes or trains.

In unit shipment terms, PEM has been the most popular fuel cell technology for a number of years because of its versatility and sizeability. Measured in megawatts, the distribution between various types is more even due to the contribution from the limited applicability but high power MCFCs and SOFCs commonly used for large stationary applications as the primary source of power. The medium versatility range is characterized by the SOFCs applied in stationary and some portable equipment, while DMFCs, similar to PEMs, are the most “dedicated” technology means useful in small transport units and for power grid extension or back-up purposes (Figure 21) [282, 283].

![Figure 21: Market development of various fuel cell types based on sales from 2010 to 2015 in units and by power output (MW). * Uncorrected Fuel Cell Today forecast from 2013 [282]. ** Uncorrected E4tech forecast from 2015 [283].](image-url)
half of the total fuel cell technology turnover. The sales increased due to the launch of fuel cell electric cars, mostly two models manufactured by Toyota and Hyundai. The growth trend is expected to sustain, especially in that the figures are easy to attribute, knowing the vehicles’ power rating of 114 and 100 kW, respectively, and considering the contribution from forklift trucks’ (FLT) and buses’ stacks as well as other transport applications. The impact of the few hundred vehicles on the global sales structure clearly illustrates the size of the current fuel cells market [283].

Nonetheless, the automotive sector is not the only source of the sector’s growth: micro-CHPs continue to gain in popularity in Japan and, to an extent, in Europe, as UPS solutions or grid extension nodes. Although dominated by Japanese and Canadian companies, the market is being entered into by new players such as American Altergy or ReliOn. Japanese PEM technology finds its use also in European micro-CHPs (Viessmann and Baxi/Senertec), although there are companies that prefer other solutions, such as Elcore marketing its own patented high temperature PEMs [283].

Fuel cell technology has proven feasible in a number of applications: as CHPs, remote or back-up sources of power, or for vehicle propulsion. It has successfully handled such challenges as the matter of having sufficient power density or problems with the durability of specific applications. Nonetheless, the cost of the inevitable technology is still too high, and its further reduction requires significant research and investment in its development.

7 Summary and future perspectives

This review presents the most important research on alternative polymer membranes with ionic groups attached, provides examples of materials with a well-defined chemical structure that are described in the literature, and elaborates on the synthetic methods used for preparing PEMs and the current status of fuel cell technology and its application. It also briefly discusses the development the PEMFC market.

The growing FC market is a clear driver for the scientific community to continue working on the development of inexpensive and efficient materials for the membranes. The two main barriers to global commercialization of PEM fuel cells are their durability and cost of production. Recently, we have seen considerable progress in this respect, and the two attributes can be successfully used for illustrating the current status of PEMFC technology, as set in the targets of the U.S. Department of Energy for: (1) durability: (i) for transportation applications, 5000 h by 2020, and, ultimately, 8000 h, (ii) for distributed generation and micro-CHP fuel cell systems on natural gas or liquid petroleum gas (5kW), 60,000 h by 2020 and (iii) for medium-sized CHP systems (100 kW–3 MW), 80,000 h by 2020 [284]; the currently achieved figures for the three applications are: less than 4000 h (2015, 285], 6000 h (2011) and 30,000 h (2011), respectively [286] and (2) the cost: (i) for transportation applications, $40/kW in 2020, and, ultimately $30/kW, and (ii) for the distributed power and CHP, $1000/kW to $1500/kW by 2020, depending on the size and application [284]. The cost of power in fuel cell transport systems was $53/kW in 2015 [285]. Moreover, DOE completed the set of targets with the maximum efficiency: 65% for transportation, 45% electric efficiency for micro-CHP systems, and 50% electric efficiency and 90% CHP efficiency for medium-sized combined heat and power fuel cell stacks.

The cost of FCs needs to be reduced by over 40%, but for the manufacturing plants the current figure of $53/kW translates into as much as over a half of the total system cost, and it has not been reduced considerably in the recent years [284]. The biggest cost component of the overall FC system is the membrane, followed by the catalyst. The only way to make catalyst production less expensive is to reduce the content of the platinum, but no significant progress has been reported recently in this respect. That makes lowering the cost of membranes the main method of limiting the total FC cost, that is, the change required for global marketing and popularization of the inevitable solution [287].

Although for availability and applicability reasons Nafion and similar polyperfluorosulphonic acid membranes still remain the best researched materials in properties’ terms, little is known about their manners of synthesizing, chemical composition and molecular weight. Even if they exceed their alternatives with regard to many vital properties, it might be required to compromise such attributes as a favourable conductivity profile, and develop alternative membranes that could well offset the loss with potential other advantages, such as thermal stability, durability, applicability in a wider range of conditions (especially humidity), limited swelling, lower fuel crossover, and, especially, lower cost of production and operation. Given the current status of research on and interest in PEM membranes, they remain the most promising, certainly in the short run, future solution to the challenges presently faced.
Acknowledgment

This article is also available in: Tylkowski, Polymer Engineering. De Gruyter (2017), isbn 978-3-11-046828-1.

References


[149] Tang H, Pintauro PN. Polyphosphazene membranes. IV. Polymer morphology and proton conductivity in sulphonated poly[bis(3-


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