CHAPTER 1

Introduction

1.1 PRINCIPLES OF FUEL CELLS

Fuel cells are one of the oldest energy conversion methods known to man since the mid-nineteenth century. Since the beginning of the twentieth century, the conversion of chemical energy into electrical energy has become more important due to an increase in the use of electricity. One of the major factors that has influenced the development of fuel cells has been the increasing concern about the environmental consequences of fossil fuel use in the production of electricity and for the propulsion of vehicles. The dependence of the industrialized countries on oil became apparent in the oil shock. Fuel cells may help reduce our dependence on fossil fuels and diminish poisonous emissions into the atmosphere, since fuel cells have higher energy conversion efficiencies compared with heat engines. Using hydrogen and oxygen, fuel cells produce only water that can eliminate the emissions caused by other methods used now for electricity production. The share of renewable energy from wind, sun, and water may also eliminate the pollution. However, these sources are not suited to cover the electrical base load due to their irregular availability. The combination of these sources, however, to produce hydrogen in cooperation with fuel cells will be an option for future power generation [1–3].

Fuel cells are galvanic cells in which the free energy of a chemical reaction is converted into electrical energy. The Gibbs free energy change of a chemical reaction is related to the cell voltage, as shown in Eq. (1.1) [4]:

$$\Delta G = -nF\Delta U_0 \tag{1.1}$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, and ΔU_0 is the voltage of the cell for thermodynamic equilibrium in the absence of a current flow. The anode reaction in fuel cells is either the direct oxidation of hydrogen or the oxidation of the hydrocarbon compounds like methanol. An indirect oxidation via a reforming step can also occur. The cathode reaction in fuel cells is the reduction of oxygen, in most cases from air.

Polymers for PEM Fuel Cells, First Edition. Hongting Pu.

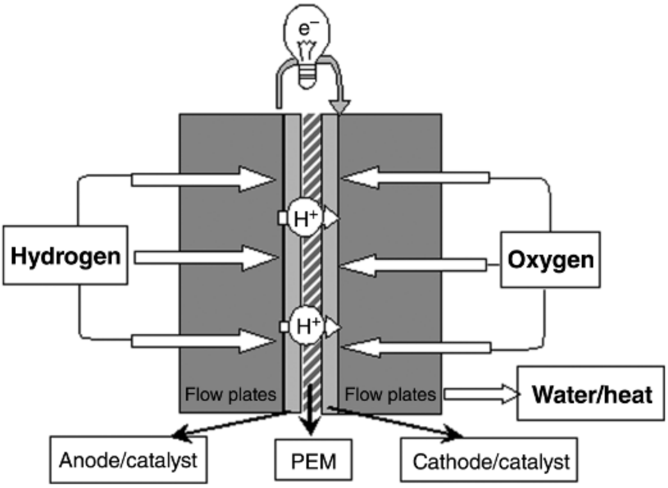

FIG. 1.1 Schematic drawing of a hydrogen/oxygen fuel cell and its reactions based on polymer electrolyte membrane fuel cell (PEMFC).

For the case of a hydrogen/oxygen fuel cell, the principle is shown in Fig. 1.1. The overall reaction is

$$H_2 + 1/2O_2 \rightarrow H_2O, \quad \text{with } \Delta G = -237\,\text{kJ/mol} \tag{1.2}$$

with an equilibrium cell voltage of ΔU_0 for standard conditions at 25 °C of $\Delta U_0 = 1.23\,\text{V}$. The equilibrium cell voltage is the difference of the equilibrium electrode potentials of cathode and anode that are determined by the electrochemical reaction taking place at the respective electrode:

$$\Delta U_0 = U_{0,\text{c}} - U_{0,\text{a}} \tag{1.3}$$

The basic structure of all fuel cells is similar: The cell consists of two electrodes that are separated by the electrolyte and that are connected with an external circuit. The electrodes are exposed to gas or liquid flows to supply the electrodes with fuel or oxidant (e.g., hydrogen or oxygen). The electrodes have to be gas or liquid permeable and, therefore, possess a porous structure. The structure and content of the gas diffusion electrodes (GDEs) are quite complex and require considerable optimization for practical application. The electrolyte should possess gas permeability as low as possible. For fuel cells with a proton-conducting electrolyte, hydrogen is oxidized at the anode (according to Eq. (1.4)) and protons enter the electrolyte and are transported to the cathode:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1.4}$$

At the cathode, the supplied oxygen reacts according to

$$O_2 + 4e^- \rightarrow 2O^{2-} \tag{1.5}$$

Electrons flow in the external circuit during these reactions. The oxygen ions recombine with protons to form water:

$$O^{2-} + 2H^+ \rightarrow H_2O \tag{1.6}$$

The product of this reaction is water that is formed at the cathode in fuel cells with proton-conducting membranes. It can be formed at the anode, if an oxygen ion (or carbonate)-conducting electrolyte is used instead, as is the case for high-temperature fuel cells.

1.2 TYPES OF FUEL CELLS

Fuel cells are usually classified by the electrolyte employed in the cell. An exception to this classification is DMFC (direct methanol fuel cell) that is a fuel cell in which methanol is directly fed to the anode. The electrolyte of this cell does not determine the class. The operating temperature for each of the fuel cells can also determine the class. There are, thus, low- and high-temperature fuel cells. Low-temperature fuel cells are alkaline fuel cells (AFCs), polymer electrolyte membrane fuel cells (PEMFCs), DMFC, and phosphoric acid fuel cells (PAFCs). The high-temperature fuel cells operate at temperatures ~600–1000 °C and two different types have been developed, molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFCs). All types of fuel cells are presented in the following sections in order of increasing operating temperature. An overview of the fuel cell types is given in Table 1.1 [1,5–7].

1.2.1 AFC

AFC has the advantage of exhibiting the highest energy conversion efficiencies of all fuel cells, but it works properly only with very pure gases, which is considered a major restraint in most applications. The KOH electrolyte that is used in AFCs (usually in concentrations of 30–45 wt%) has an advantage over acid fuel cells, which is due to the fact that the oxygen reduction kinetics are much faster in alkaline electrolyte than in acid, making AFC a very attractive system for specific applications. AFC was one of the first fuel cells used in space. It was used in Apollo missions and the Space Shuttle program.

The first technological AFC (1950s) was developed by the group of Bacon at the University of Cambridge, provided 5 kW power, and used a Ni anode, a lithiated NiO cathode, and 30 wt% aqueous KOH. Its operating temperature and pressure were 200 °C and 5 MPa, respectively. For the Apollo program, a PC3A-2 model was used that employed an 85% KOH solution at operating temperatures of 200–230 °C. In

TABLE 1.1 The Different Fuel Cells That Have Been Realized and Are Currently in Use and Development

	AFC	PEMFC	DMFC	PAFC	MCFC	SOFC
Operating temperature (°C)	<100	60–120	60–120	160–220	600–800	800–1000, lower temperature (500–600) possible
Anode reaction	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_2OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode reaction	$1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$1/2\ O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$1/2\ O_2 + 2e^- \rightarrow O^{2-}$
Application	Transportation, space, military, energy storage systems			Combined heat and power for decentralized stationary power systems	Combined heat and power for stationary decentralized systems and for transportation (trains, boats, etc.)	
Realized power	Small plants 5–150 kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small–medium sized plants, 50 kW–11 MW	Small power plants, 100 kW–2 MW	Small power plants, 100–250 kW
Charge carrier in the electrolyte	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

Space Shuttle program, the fuel cells are used for producing energy, cooling of Shuttle compartments, and producing potable water. Three plant modules are used, each with a maximum power output of 12 kW. AFCs are now normally run at operating temperatures below 100 °C, as a higher temperature is not needed to improve oxygen reduction kinetics (although higher temperatures are still advantageous for the hydrogen oxidation kinetics).

AFC electrodes used to be Ni-based catalysts and were sometimes activated with Pt. Pt/C gas diffusion electrodes are now generally used for both the anode and the cathode (see PEM), although other possibilities are being pursued, for example, Pt–Co alloys have been suggested [8] and have proved to have a superior activity than Pt for oxygen reduction due to a higher exchange current density. A Pt–Pd anode was tested for stability characteristics in comparison with Raney Ni [9]. It is known that Raney Ni electrodes have a high activity for hydrogen oxidation, but due to the wettability of the inner pores and changes in chemical structure under operation conditions, a decay in performance occurs. The Pt/Pd activity was also seen to have a very rapid decay initially, but after a short time the decay stopped and the performance remained constant.

KOH in a stabilized matrix as a liquid electrolyte for the space model of AFC is disadvantageous for such applications. It has been found that a much longer operating lifetime can be obtained when using circulating KOH [10,11]. A circulating electrolyte provides a good barrier against gas leakage and it can be used as a cooling liquid in the cell or stack. An early demonstration of AFC with circulating electrolyte was brought about by Kordesch in the 1970s [11]. He combined a hydrogen/air AFC with a lead–acid battery in a hybrid vehicle. In between operations, the complete cell was shut down by draining KOH electrolyte. This improved the life expectancy enormously as normally when the cell is under no load (open circuit) and the cell voltage is very high, carbon oxidation processes are induced that produce carbonates that can destroy the matrix/electrolyte.

The formation of carbonates that can destroy the electrolyte is one of the most controversial issues in AFC. It is generally accepted that the CO_2 in the air and the CO_2 formed by reaction of the carbon support interact with the electrolyte in the following reaction:

$$CO_2 + 2OH^- \rightarrow (CO_3)^{2-} + H_2O \tag{1.7}$$

The formation of carbonates is destructive to the electrolyte and the cell performance will decrease rapidly. One way to solve this problem suggested early was by circulating KOH instead of using a stabilized matrix; in this way the electrolyte can be pumped out of the system in between cycles. This avoids the buildup of carbonates.

CO_2 can be removed cost-effectively from both the hydrogen feed and the airflow by an iron sponge system, which is similar to the shift reaction in a reformer. This process is used in most NH_3 production plants for the same purpose and can be used in AFC applications. Other processes to remove CO_2 are swing adsorption or the water gas shift reaction, both of which are being used in fuel cell systems [10–12].

1.2.2 PAFC

Phosphoric acid fuel cell is mainly used in stationary power plants ranging from dispersed power to *in situ* generation plants. Power plants based on PAFCs are being installed worldwide with outputs ranging from 5 to 20 MW supplying towns, cities, shopping malls, or hospitals with electricity, heat, and hot water [13].

The advantages of PAFC are its simple construction, thermal, chemical, and electrochemical stability, and the low volatility of the electrolyte at operating temperatures (150–200 °C). These factors probably assisted the earlier deployment into commercial systems compared with the other fuel cell types.

At the beginning of PAFC development, diluted phosphoric acid was used in PAFCs to avoid corrosion of some of the cell components. Nowadays with improved materials available for cell construction, the concentration of the acid is nearly 100%. The acid is usually stabilized in a matrix based on SiC. The higher concentration of the acid increases the conductivity of the electrolyte and reduces the corrosion of the carbon-supported electrodes.

The electrodes used in PAFCs are generally Pt-based catalysts dispersed on a carbon-based support. For the cathode, a relatively high loading of Pt is necessary for the promotion of the O_2 reduction reaction. The hydrogen oxidation reaction at the anode occurs readily over a Pt/C catalyst.

In PAFCs, it is extremely important to have a hydrophobic backing layer (more than in PEMFCs where the water source is derived from humidifying the gases) as a liquid electrolyte is used. To provide hydrophobicity, the backing layer can be immersed in a dispersion of polytetrafluoroethylene (PTFE). Also, the catalyst layer must be prevented from pore flooding that can be obtained by binding the electrode with PTFE. It is difficult, however, to find the optimum amount of PTFE in the electrode as there is a fine balance between low wettability/good gas diffusion and high wettability/poor gas diffusion [14].

Pt–Co alloys were investigated for oxygen reduction in PAFCs; it was found, however, that Co leaches out from the alloy in two stages. A fast dissolution occurs at the particle surfaces after which a slow dissolution removes the Co from the bulk. Also, a “ripening” of the Pt particles occurs that decreases the performance of the catalyst [15]. Pt–WO_3 electrode was found to have an increase in performance over plain Pt/C electrodes by about twice the current density for the same voltage. It was seen, however, that the addition of WO_3 induces an increase only in electrochemically active surface area, which accounts for the increase in performance [16]. A model for PAFC cathodes is described in the literature [17]. PtRu catalysts were found to be better than Pt catalysts for hydrogen oxidation when using reformate hydrogen as it contains CO that is more easily oxidized with Ru as a secondary metal. Additions of W and Pd also improved the CO tolerance of the system. It is important to note, however, that at very high overpotentials, Ru is not completely stable and an aging of the catalysts is significant.

1.2.3 MCFC

The development of molten carbonate fuel cells started about the mid-twentieth century [18]. The advantages of MCFC are that it allows internal reforming due to the high operating temperatures (600–700 °C) and using the waste heat in combined cycle power plants. The high temperatures improve the oxygen reduction kinetics dramatically and eliminate the need for high loadings of precious metal catalysts. The molten carbonate (usually a LiK or LiNa carbonate) is stabilized in a matrix ($LiAlO_2$) that can be supported with Al_2O_3 fibers for mechanical strength.

Molten carbonate fuel cell systems can have the energy conversion efficiencies up to 50%, or up to 70% when combining the fuel cell with other power generators [19]. MCFCs can operate on a wide range of different fuels and are not prone to CO or CO_2 contamination as is the case for low-temperature cells. For stationary power, molten carbonate fuel cells can play an important role in power conversion units.

Cathodes for MCFCs are usually NiO made by an anodic oxidation of a Ni sinter or by an *in situ* oxidation of Ni metal during the cell start-up time [18,20]. NiO cathodes are active enough for oxygen reduction at high temperatures, so a Pt-based metal is not necessary. A problem with the NiO cathode occurs as over time the NiO particles grow as they creep into the molten carbonate melt that reduces the active surface area and can cause short-circuiting of the cell. One of the solutions for this problem is the addition of small amounts of magnesium metal to the cathode and the electrolyte for stability. Also, the use of a different electrolyte that decreases the dissolution of the NiO cathode is possible.

Alternatives for MCFC cathodes have been found in doped lithium oxide materials such as $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$ and also in combination with NiO materials to form double-layered electrodes. A tape casting of a NiO/$LiCoO_2$ double layer electrode improved the stability tremendously. The oxygen reduction reaction is improved at these double layer cathodes and the resistance is reduced [21].

NiAl or NiCr metals have been employed as MCFC anodes. These materials are used because Ni metal anodes are not stable enough under MCFC operating conditions as Ni creeps out [18,20]. Cermet (ceramic metal) materials avoid sintering, pore growth, and shrinkage of the Ni metal so that a loss of surface area does not occur. A low- cost process needs to be found, however, as these materials are still expensive to fabricate.

The electrolyte for MCFCs is a molten carbonate that is stabilized by an alumina-based matrix. Initially, Li_2CO_3/K_2CO_3 (Li/K) carbonate materials were used as electrolytes. Degradation of electrode materials is a problem in this electrolyte. A Li/Na melt provides the advantage of a slightly more alkaline system in which the cathode and anode dissolution is lower as it prevents a dendritic growth of Ni metal. Li/Na electrolytes are expected to have a longer endurance and a lower decay rate than Li/K melts.

The matrix that stabilizes the electrolyte consists of either an alumina phase or a ceria-based material. Usually γ-$LiAlO_2$ phase is used, whereby a transformation into α variant during operation is observed. The stability of α variant was investigated and it was suggested that α variant may actually be more stable for long-term operation than γ-$LiAlO_2$ phase. Ceria-based materials are more stable than alumina-based matrices, but they are also more expensive. Reinforcements can be built into the matrix in the form of particulates or fibers. These reinforcements act as crack deflectors for the matrix to avoid dissolution in the carbonate melt [19,21,22]. The formation of the interfaces between electrolyte and electrodes can be obtained by several different techniques.

Material selection is far more important in high-temperature fuel cells due to the degradation, sealing, and thermal expansion properties. There are some high-temperature stainless steel (SS) alloys available for use in fuel cells. Ni-, Co-, and Fe-based alloys or Cr/Al alloys have proven to be more stable than normal SS. A Fe–Cr ferritic SS material was used in fuel cell components as the materials are low cost, but it was found that the corrosion resistance was not sufficient. A Fe–Ni–Cr austenitic material was also used and found to be very resistant for the cathodic reduction but not for anodic oxidation. A nickel coating is necessary for the abatement of anodic corrosion. The Cr content in the stainless steel compound influences the corrosion resistance the most. The higher the Cr content, the lower the corrosion rate. Cr-containing stainless steels form a $LiCrO_2$ inner layer under operating conditions, which is a barrier against Fe^+ diffusion, thus decreasing the corrosion [21,23]. Cost reduction is still a major factor in the fabrication of fuel cell components.

1.2.4 SOFC

Solid oxide fuel cells employ a solid oxide material as electrolyte and are, thus, more stable than the molten carbonate fuel cells as no leakage problems due to a liquid electrolyte can occur. SOFC is a straightforward two-phase gas–solid system, so it has no problems with water management, flooding of the catalyst layer, or slow redox kinetics. On the other hand, it is difficult to find suitable materials that have the necessary thermal and stability properties for operating at high temperatures.

As for MCFC, internal reforming in SOFCs is possible over the anode catalyst; partial oxidation reactions and direct oxidation of the fuel have also been found to occur [24–28]. Different concepts for solid oxide fuel cells have been developed over the years. Flat plates have an easier stack possibility, while tubular designs have a smaller sealing problem. Monolithic plates and even single-chamber designs have been considered and investigated for SOFC use [29–31].

Due to the high power density of SOFCs, compact designs are feasible. An important advantage of SOFCs is the internal reforming. Due to the high temperature of the exhaust gases, a combination with other power generation systems (e.g., gas turbines) is also possible, which can provide high overall energy conversion efficiency (up to 70% in a combined cycle system).

Different SOFC designs have been developed over the years to implement the fuel cell and reformers into the stack and ultimately the complete system. The tubular design is probably the best-known design. It has been developed by Westinghouse (now Siemens Westinghouse). Tubular designs have a self-sealing structure that improves thermal stability and eliminates the need for good thermal-resistant sealants. The tubular design can be split into two systems: one where the gas flow is along the axis of the tube and the other where the flow is perpendicular to the axis. The first concept was pursued by Westinghouse and consisted of an air electrode-supported (AES) fuel cell [29]. In earlier days, the tubes were made from a calcium-stabilized zirconia on which the active cell components were sprayed. Nowadays the porous supported tube (PST) is replaced by a doped lanthanum manganite air electrode tube (AES) that increases the power density by about 35%. The LaMn tubes are extruded and sintered and serve as the air electrode. The other cell components are thin layered on this construction by electrochemical vapor deposition (EVD). Electrochemical vapor deposition of the electrolyte produces a gastight film with a uniform thickness, but other depositions such as colloidal electrophoresis are also under investigation [29].

A different type of SOFC design is under development by SulzerHexis. The HEXIS (heat exchanger integrated stack) can be used for small cogeneration plants. The interconnect in this case serves as a heat exchanger as well as a current collector and is made by Plansee (Reutte, Austria) (see interconnect materials (ICMs)). Thermal spray coatings on the current collector can improve the stability of the system and performances were tested up to 3000 h [32].

The planar design is more efficient and cheaper than the tubular as the current path is shorter and easier to stack than the tubular design [33]. It is, however, still a problem to find good sealants and interconnect materials. Interconnect materials for planar SOFCs have been investigated. For lower temperatures, it was found that stainless steel had the best performance (also better stabilities were reported when doping the stainless steel). For higher temperatures, an alloyed metal or a La chromite material has to be used [30]. Heat removal in a planar design can be achieved by a direct heat dissipation to air preheater coils, small-size cells make this heat exchange easier.

The components of SOFC can be made in different ways. The main differences between the preparation techniques consist of the fact that the whole cell can be made self-supporting (i.e., the electrode/electrolyte assembly supports the structure of the cell and no substrate is used) or supported whereby the electrodes and electrolyte are cast onto a substrate. In the anode-supported planar SOFC concept, with a 20 μm thin electrolyte layer, the operation temperature can be reduced significantly, for example, to 800 °C [34]. This reduces the material requirements considerably.

From the beginning of SOFC development, it was found that $LaSrMnO_3$ (LSM) electrodes had a high activity for oxygen reduction at high temperatures and were stable under SOFC operation conditions. These LSM cathodes have been improved over time and it has been seen that an yttria stabilization of the cathodes improves the performance [35]. Single-phase LSM cathodes show a low oxide diffusion coefficient, so it is better to use a two-phase cathode that results in a lower overpotential for the oxygen reduction reaction.

Perovskite-type materials have also been investigated as cathodes for SOFCs. Lanthanide-based perovskites showed a high conductivity and a high catalytic activity for oxygen reduction. Applying a thin porous layer of YSZ particles on LSM electrodes also increased the performance as the polarization resistance is reduced. Especially for operating at lower temperatures (650–700 °C), it is important to have an efficient cathode [36].

Anodes for SOFC are again based on Ni, usually Ni cermet materials are used that are more stable than plain Ni metal. NiO anodes are slightly soluble in YSZ electrolyte, but this stabilizes the cubic phase of the electrolyte. A NiO powder mixed with a YSZ powder together with a resin binder produces an anode functional layer onto which YSZ electrolyte can be deposited and sintered. The cathode can then be sprayed onto this layer and form an anode-supported planar SOFC structure [33]. YSZNi anodes can also be produced by vacuum plasma spraying. To fit the thermal expansion mismatch that can occur between the anode and the electrolyte, a zirconia-stabilized anode is preferable. The performance of plasma-sprayed electrodes is similar to that of the more common screen-printed anodes [37].

For high-temperature operations, most ceramics are conductive enough to give a good overall cell performance. ZrO_2-supported electrolytes have been found to be stable and they give a reasonable conductivity. Special metallic or ceramic materials are investigated to lower the operating temperatures. At these temperatures, however, better cathodes and more conductive electrolytes need to be considered. CeO_2-based electrolytes are more conductive than yttria-stabilized electrolytes and in conjunction with ferritic stainless steel materials, they can provide a competitive model for solid oxide fuel cells [38,39]. However, the advantages of the well-studied ZrO_2-based electrolytes are that thermal expansion of all components of the system has been matched by careful development and there is considerable resistance to change to completely new ceramic systems.

The interconnect material is another important issue in SOFC development. It forms the connection between the anode of one cell and the cathode of the next in a stack arrangement. The ICM has to be electronically conductive, but it must also seal the gas chambers for the feed of oxygen and fuel gases at either the anode or the cathode. Different possibilities for the material depending on the stack design are possible. However, no systematic procedures exist to determine the suitability of a material in a fuel cell or stack as hardly any data on the degradation of interconnect and sealant materials are available [40]. Ni-based alloys that are mostly used nowadays have a tendency to evaporate, so silver alloys were investigated instead for operating temperatures under 900 °C. Cheaper options were found in highly conductive metal oxides [41].

Bipolar plates fabricated from ceramics based on $LaCrO_3$ have a heat expansion coefficient similar to ZrO_2, but can provide a high enough conductivity only if a Cr_2O_3 layer is formed on the surface of the material [42]. A new metallic ceramic alloy made by Plansee (Reutte, Austria) has been found to have a high corrosion resistance and good thermal conductivity combined with a high mechanical strength and a low expansion coefficient. The metal/cermet alloy is based on a CrFe stainless steel metallic component mixed with an yttrium oxide ceramic.

Sealing the SOFC compartments is still a major problem due to the high temperature for which not many sealing materials are available. The most commonly used material for this purpose is glass (SiO_2). Normal glass, however, can evaporate and soften with a higher likelihood of leakages as a result. Pyrex seals can be used to avoid evaporation and glass ceramic sealants have been proven to have the necessary stability at high temperatures and pressures so that the probability of leakages can be reduced dramatically [43]. Ceramic foams consisting of Co-doped LSM materials have been found to have a high electronic conductivity and reasonable compression strength, but most of the materials do not creep [44]. A survey of materials for electrolytes and interconnect materials for ceramic fuel cells has been published [38].

1.2.5 PEMFC

Polymer electrolyte membrane fuel cells, also called proton exchange membrane (PEM) fuel cells, use a proton exchange membrane as an electrolyte. They are low-temperature fuel cells, generally operating below 80 °C and were the first to be used in Space. The Gemini program employed a 1 kW fuel cell stack as an auxiliary power source. The historical development of PEM fuel cells has been described recently [45]. It was also used to provide the astronauts with clean drinking water. The membrane used was a sulfonated polystyrene (sPS) polymer, which however did not prove stable enough. This was one of the major reasons for NASA to opt for the AFC system for its further missions.

A major breakthrough in the field of PEM fuel cells came with the use of Nafion® membranes by DuPont. These membranes possess a higher acidity and also a higher conductivity and are far more stable than the polystyrene sulfonate membranes. The Nafion® consists of a PTFE-based structure that is chemically inert in reducing and oxidizing environments. The characteristic value of proton-conducting polymer membranes is the equivalent weight that is defined as the weight of polymer that will neutralize 1 equiv of base and is inversely proportional to the ion exchange capacity (IEC).

In 1987, Ballard started using a different membrane in their PEM fuel cells that gave about four times higher current densities at the same voltage than Nafion®. The Dow® membrane (Dow Chemicals) together with Nafion® and some other PTFE-based polymers is still under scrutinous investigation by several research groups. A general overview of polymer electrolytes was published in 1997 [46].

The first PEM stack was employed in Gemini space program. The unit provided the spacecraft with 1 kW power. The most famous applications of PEM fuel cells nowadays are the cars and buses from Ballard, DaimlerChrysler, Toyota, Ford, General Motors, and other motor companies. Ballard also constructed a power plant operating on by-product hydrogen, which provided 10 kW. A 250 kW commercial prototype was commissioned in 1997 and focused on weight reduction. Field trials of this prototype are being carried out around the world today.

Plug Power installed a 7 kW residential power system that provides electricity, heat, and hot water to a house in upstate New York. Residential fuel cells are in essence miniature power plants that provide electrical power efficiently, reliably, and most of all quietly to a house or to a block of houses. One of Plug Power's fuel cells has cleared a milestone of 10,000 h and the company has announced the completion of 52 fuel cell systems, 37 of which are operated on natural gas and the other 15 on synthetic fuels.

A fuel cell stack with internal humidifier has proven to exhibit similar performances as external humidification for PEM fuel cell applications. In an internal humidification configuration, water is supplied to the stack through a water flow channel and serves to provide both cooling for the stack and humidifying of the gases. Water and reactant gases flow on opposite sides of the membrane and water can permeate through the membrane. External humidifying serves only as humidification of the gases and cannot take part in the cooling of the stack.

It was found that the mass transfer behavior of reactants and products of the stack is more complicated compared with a single cell because of the heat exchange, humidity, and reactant supply effects. Some of the produced water was lost by evaporation, while self-humidifying was found to be more efficient at temperatures above 30 °C. Under laboratory conditions, humidification can be lowered if cooling power is improved to compensate for the heat released by the electrode reactions. In applications, however, cooling power is limited and humidification is a necessity.

1.2.6 DMFC

The direct methanol fuel cell is a special form of low-temperature fuel cells based on PEM technology. It operates at temperatures similar to PEMFC, although it is usually operated at slightly higher temperatures in order to improve the power density. In DMFC, methanol is directly fed into the fuel cell without the intermediate step of reforming the alcohol into hydrogen. Methanol is an attractive fuel option because it can be produced from natural gas or renewable biomass resources. It has the advantage of a high specific energy density (since it is liquid at operating conditions) and it is assumed that the existing infrastructure for fuels may be adapted to methanol. DMFC can be operated with liquid or gaseous methanol–water mixtures.

The liquid DMFC generally uses diluted methanol in water mixture (typically 12 M) and only a fraction of the methanol is used at the anode. It is, therefore, important to recycle the effluent and replenish it to keep the concentration in the fuel feed constant. To be able to achieve this, methanol sensors play a very important part in the fuel cell system. Methanol sensors are usually based on an electrochemical system that measures the current from the electrooxidation of methanol [47,48]. Gaseous feed of the methanol–water mixture is also possible.

Catalysts for methanol oxidation need to be improved, as the reaction is comparatively sluggish on Pt-based compounds. Compared with hydrogen oxidation, the catalytic activity for methanol oxidation is not very effective. It was found early on that additions of other metals to Pt could enhance the activity of the catalyst dramatically. Species such as Re, Ru, Os, Rh, Mo, Pb, Bi, and Sn have been found to have a promoting effect on the catalytic activity for methanol oxidation [49–55]. For all these species, it was found that the determining factor for promotion is the formation of an adsorbed oxygen-containing species on the secondary metal at potentials lower than for Pt. The oxygen-containing species are needed for the oxidation of intermediate adsorbates. It is still necessary, however, to employ higher loadings for the catalysts than are needed for H_2 oxidation. PtRu alloys are the most widely used anode catalysts for DMFC.

Other factors that influence the catalytic activity of the electrode are the support [56], the ionomer content in the active layer [57], the preparation method, and the fuel feed. It was found that the specific activity of supported PtRu/C is much higher than for a PtRu black. The maximum attainable voltage in the cell is, however, much lower for the supported catalyst. The cell employing the unsupported catalyst also features a lower crossover rate suggesting higher methanol utilization. The advantage of using a supported metal catalyst lies in the possibility to reduce the metal loadings drastically. The difference in performance may be due to the difference in morphology between the two types of catalysts. It is, therefore, necessary to improve the stability of both supported and unsupported metal catalysts [58,59].

The ionomer content in the catalyst layer can greatly influence the performance of the electrodes as was seen before for PEM fuel cells. Electrodes for methanol oxidation are usually bound together with Nafion® to improve the ionic conductivity in the catalyst layer.

A vapor feed methanol fuel cell minimizes the crossover effect and can, in principle, improve the overall performance of the cell using gas diffusion electrodes due to the higher temperature of operation (the highest power densities so far are reached with liquid DMFCs) [60]. Using a liquid feed arrangement that simplifies the design as no humidification system is needed, it is necessary to optimize the hydrophobicity of the backing layer and methanol crossover and water permeation are more significant due to the importance of electroosmotic drag through the membrane and the large gradient in chemical potential [61,62].

Catalysts for oxygen reduction for DMFC are mostly identical to those for PEM fuel cells. The operating conditions for both fuel cells are similar, although one major problem arises for DMFC is the crossover of methanol from the anode to the cathode. At present, most DMFC research is concentrated on PEM technology. The membranes used in DMFCs were developed for PEM application (thus optimizing the proton conductivity was the priority), although these membranes are not advantageous regarding methanol blocking. The proton movement in the membrane is associated with the water content of the membrane. Due to the similar properties of methanol as compared with water (e.g., dipole moment), methanol molecules as well as water molecules are transported to the cathode by the electroosmotic drag and diffusion. At the cathode, methanol causes a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction. As a consequence, the cell performance decreases.

Methanol crossover depends on a number of factors, the most important ones being the membrane permeability/thickness, the concentration of methanol in the fuel feed, the operating temperature, and the performance of the anode itself. The membrane is a very important factor regarding the methanol crossover problem. Thinner membranes give lower resistances in the cell, but tend to have a higher permeability for liquid methanol. For methanol fuel cells, a thicker membrane such as Nafion®120 is advantageous [63].

The crossover effect is dependent on the methanol concentration in the feed. The optimum concentration was considered to be around 1–2 M methanol in water (around 6% methanol in water). A higher concentration as well as a higher temperature in the cell increases the diffusion of methanol through the membrane [64–66] and, thus, lowers the cell performance. An optimized anode will oxidize much methanol from the feed and the methanol available for crossover decreases leaving another factor to optimize in DMFC [24]. A different approach to cope with the methanol crossover problem is the investigation of methanol-tolerant cathodes. In this concept, the methanol diffusion is not prevented, but at the cathode catalysts that are inactive regarding methanol oxidation are used. Thus, the establishment of a mixed potential at the cathode is prevented. Different methanol-tolerant cathodes have been investigated [67,68]. Although a $Mo_2Ru_5S_5$ catalyst (Chevrel phase) exhibits inferior performance than Pt for pure oxygen reduction activity, in the presence of methanol the reactivity of MoRuS-based catalysts is superior to Pt. A sulfur treatment of the carbon support also increased the performance of the mixed transition metal sulfides (whereas the same treatment for a Pt/C catalyst inhibits the performance).

Other methanol-tolerant catalysts have been found in iron porphyrine-type materials supported on high surface area carbon [69,70]. These catalysts were tested in fuel cell conditions and it was found that no deterioration of the electrode performance could be seen when utilizing methanol in the cell. The catalysts are insensitive to methanol. These catalysts were also combined with a new cell concept whereby the anode and the cathode reside in the same compartment. Both electrodes are in contact with the same side of the membrane, thus eliminating most of the ohmic resistance in the cell. The fuel efficiency in the cell at low current densities was much higher than for a normal bipolar plate design. A methanol-tolerant cathode is a prerequisite to make this concept feasible.

For DMFC, two alternatives can be used as approaches for the fuel feed: the methanol–water mixture can be fed into the cell/stack as a liquid or as a vapor. Gas feeding of the fuel minimizes the crossover problem, but it can give more problems with humidification of the cell. Both systems have been investigated and no conclusive arguments have been found as to which of the two systems is better. Methanol crossover is still the main problem for both configurations, so the development of methanol-tolerant cathodes and better membranes remains the biggest issue for these systems [61].

At LANL (Los Alamos National Laboratories) a DMFC stack was produced that attained a 90% fuel utilization and produced 2.25 kW/kg. The stack temperature was 60 °C and the air pressure was the atmospheric pressure at the LANL site. The width of each cell was 1.8 mm and the pressure drop across the cells was minimized. A stoichiometric airflow was achieved and a maximum power density of 1 kW/l (0.3 W/cm^2) was reached. It was found, however, that the concentration of methanol in the fuel flow must be kept as constant as possible for which a methanol sensor was essential.

1.3 APPLICATIONS

Fuel cells will make a valuable contribution to future power generation facilities. They improve the flexibility and increase the options for many applications, such as distributed power, vehicle propulsion, and portable devices. Their main property is the high electrical efficiency compared with other energy conversion devices. Both the low- and the high-temperature fuel cells have their advantages and disadvantages depending on the application. Sometimes they both can be implemented in similar applications. The modularity of fuel cells makes them quite flexible as the power needed can be easily attained by changing the number of modules.

1.3.1 Stationary Power

The most important attributes of fuel cells for stationary power generation are the high efficiencies and the possibility for distributed power generation. Both low- and high-temperature fuel cells could, in principle, be utilized for stationary applications. The low-temperature fuel cells have the advantage that usually a faster start-up time can be achieved. The needed operating time for the stationary application is about 40,000 h, which may be a challenge for fuel cell systems. The high-temperature systems such as SOFC and MCFC generate high-grade heat that can be directly used in a heat cycle or indirectly used by incorporating the fuel cell system into a combined cycle. SOFCs and MCFCs also have the advantage that they can operate directly on available fuels without the need for external reforming.

For a small distributed power system, for example, single or multiple house power generation, a PEM, SOFC, or PAFC combined with a heat cycle could be used to meet all the needs of a home. The PAFC start-up time is much lower than this for high temperature systems, which makes it more attractive for small power generation. The heat generated by the fuel cell system can be employed for heating and providing the house with hot water. The PAFC produces enough steam to operate a steam reforming system, whereas the PEM system due to its lower operation temperature is not able to supply the necessary heat.

Small power plants in the range above 250 kW can be operated by high-temperature fuel cell systems. The high-grade heat obtained from these systems can be exchanged at a broad temperature range leaving the possibility of direct heat use or further electricity generation by steam engines. The start-up time for these systems are longer than for low-temperature systems, but the advantages of being able to operate the system without external reforming and the higher efficiencies of SOFCs and MCFCs make these systems more suitable for large-scale power plants.

1.3.2 Propulsion of Vehicles

For vehicular applications, fuel cell systems need to be different from stationary power generation. Available space in vehicles is much more critical and fast response times and start-up times are required.

The controversial AFC has proven to be a suitable system for hybrid vehicles as long as a circulating electrolyte is used and pure hydrogen is supplied to the fuel cell. Pure hydrogen distribution centers are not widely spread over the world and, thus, it is to be predicted that AFC vehicles will be limited to specified types (e.g., fleet buses and other centralized vehicles). For space vehicles, AFC technology is established and although the tendency to change to PEM fuel cells is also penetrating the space

FIG. 1.2 NECAR4, a fuel cell vehicle with a PEM system operated with liquid H_2 [71].

industry, it is likely that AFC systems will be employed for many more years in space. PEM systems still need to be tested concerning the stringent requirements (reliability of operation, etc.) for space applications.

Prototype fuel cell-powered vehicles (an example is shown in Fig. 1.2, NECAR4, a car from DaimlerChryler with PEM system operated with liquid H_2) have recently been demonstrated in Europe, Japan, and North America by several car manufacturers [71]. All of the various demonstration vehicles are based on a basic conceptual design combining the PEM fuel cell with an electric drive. The PEMFC is regarded as ideally suited for transportation applications due to its high power density, high energy conversion efficiency, compactness, light-weight, and low operating temperature (below 100 °C). The recent PEM-driven electric vehicles have demonstrated the technical feasibility of the concept. However, among all applications for fuel cells, the transportation application involves the most stringent requirements regarding volumetric and gravimetric power density, reliability, and costs.

Since a widespread hydrogen retail infrastructure will not be available in the near future, car manufacturers consider a liquid fuel as the best option for a short-term market introduction of a fuel cell propulsion system. Furthermore, the higher energy density of a liquid fuel guarantees a driving range similar to that of internal combustion engine vehicles. The fuel favored by many car manufacturers is methanol from which hydrogen can be produced onboard by steam reforming. The reforming of the fuel, however, leads to slower response times, and extensive gas cleanup procedures need to be carried out to supply the fuel cell with high-grade hydrogen.

Because of the difficult thermal integration and the size of the reformer and gas cleaning unit, a direct methanol fuel cell, where methanol is oxidized directly at the anode, would be more desirable for mobile systems (higher simplicity of the system). Therefore, in addition to the reformer–fuel cell combination, DMFCs using methanol–water vapor or liquid methanol–water mixtures as fuel are being investigated and developed. The development of DMFC for transportation applications, however, is less advanced as compared with the indirect PEMFC and hampered by problems of reduced power density caused by methanol permeation through the membrane and poisoning of the electrocatalysts. Recent progress regarding power density and compactness of DMFC stacks is encouraging and indicates that this concept may be competitive in vehicles.

Due to the multitude of realized demonstration vehicles with PEMFC technology, it appears a forgone conclusion that only fuel cells based on the PEM technique are suitable for transportation applications. System considerations, however, show beneficial properties of high-temperature fuel cells that could simplify the system considerably. Certainly, PEMFCs have the advantage of the low operating temperature and the high power density. Using alcohols or hydrocarbons as fuel, thermal integration is complicated. The main advantage of SOFCs compared with PEMFCs concerns the unproblematic use of hydrocarbon fuels. SOFCs do not require pure hydrogen as fuel, but can be operated on partially prereformed hydrocarbons (e.g., gasoline). They do not exhibit any significant poisoning problem. Several studies have investigated the potential of SOFC for transportation applications and have pointed out this advantage [72]. These beneficial factors have been recognized recently, leading several companies (e.g., Delphi Automotive Systems) to develop SOFCs as auxiliary power units (APU) for gasoline vehicles. BMW is implementing PEM fuel cells in their hydrogen combustion engine vehicles (BMW 7 series) and SOFCs in gasoline vehicles as auxiliary power unit [73]. The APU replaces the traditional battery and provides further electrical energy for air-conditioning and car electronics.

1.3.3 Portable Applications

For small power applications such as laptops, camcorders, and mobile phones, the requirements of the fuel cell systems are even more specific than for vehicle applications. Low temperatures are necessary and, therefore, PEM fuel cells are chosen. Possibilities for fuel cell systems are the combination of PEM with hydrogen storage by hydrides or gas cartridges or the direct methanol fuel cell. Such type of fuel cell will be employed in portable phones and can be adjusted for other portable applications. The requirements for portable applications are mostly focused on size and weight of the system (as well as on the temperature). Other fuel cells are, therefore, not suitable for this kind of applications. Portable devices need lower power than other fuel cell applications and, thus, DMFC systems may be well suited for this kind of applications. With further technological improvements and better storage systems, PEM fuel cells and DMFC systems will continue to compete in this market [74,75].

1.4 NEEDS OF FUNDAMENTAL MATERIALS FOR PEM FUEL CELLS

1.4.1 Membranes

Nafion® is probably the most studied and operated electrolyte for PEM fuel cells, but other perfluorocarbon sulfonic acid membranes from Dow, Gore, and Asahi Chemicals are also used and investigated [46,76]. Membranes usually have a small temperature range in which they are stable. The upper limit of temperature is dictated by the need of humidification of the membrane, as water is a prerequisite for conduction.

Improvements in membrane structure and conductivity are made by producing composite membranes. This can be done in several ways, one of which consists of reinforcing the perfluorosulfonic membrane by PTFE components, which is the successful approach of Gore and Asahi Chemicals (however, with different procedures). Another possibility is to impregnate a membrane with a solution or with a solid powder to decrease the permeability of the reactant gases. Yet another technique is to dissolve the membrane into an appropriate solvent and to mix it with another substance. After recasting (usually by evaporating the solvent), the composite membrane can be used in a fuel cell [77,78]. Impregnation of PTFE films with Nafion® ionomer (18 wt% Nafion® in EtOH) was carried out to make thinner membranes, thus reducing the membrane resistance in the system [79]. The conductivity of this membrane was comparable with that of Nafion® 112 (0.1 S/cm), but its permeability toward gases is higher.

Novel membranes are also prepared by new techniques such as radiation grafting or plasma polymerization [80–82]. Plasma polymerization is known to give highly cross-linked, uniform and stable thin films. Radiation grafting of PVDF films gave membranes with a lower oxygen solubility but higher diffusion than through Nafion®. These membranes are promising for PEM fuel cells as long as they prove to be mechanically and electrochemically stable.

Membranes in PEM fuel cells are generally water filled to keep the conductivity high [83], a dried out membrane possesses a lower conductivity as proton transport through a wet membrane is similar to that of an aqueous solution. Water management in the membrane is one of the major issues in PEM technology. Factors influencing the water content in the membrane are water drag through the cell (electroosmotic) (for every proton, a shell of H_2O is also transported through the membrane) and back diffusion from product water from the cathode into the membrane.

One way of improving the water management is to humidify the gases coming into the fuel cell. Another form of water management can be found in the direct hydration of the membrane by mounting porous fiber wicks [84]. Twisted threads of porous polyester fibers are placed between the membrane and a cast thin film of Nafion® ionomer and is hot pressed at 150 °C. This ensures a direct water supply from either the humidifiers or from the product water at the cathode to the membrane by using a pressure difference.

1.4.2 Electrodes

Electrodes for PEM fuel cells are generally porous gas diffusion electrodes to ensure the supply of the reactant gases to the active zones where the noble metal catalyst is in contact with the ionic and electronic conductors. The fabrication of GDE is an intricate procedure in which all details of the structure and preparation are important. The reason for this is that the function of the electrodes is far more than just catalyzing a reaction, that is carried out by the catalyst particles.

The main requirement of a good electrode is a three-phase boundary between the gas supply on the one hand and the catalyst particle and the ionic conductor on the other [85]. The particles must be in direct contact with an electronic conductor to ensure the electrons are supplied to or taken away from the reaction site. Electronic conductivity is usually provided by a carbon support onto which the catalyst particles are mounted. The three-phase boundary is made by impregnating the catalyst/support powder with an ionomeric binder (usually Nafion® solution) before pressing the electrode onto the membrane. This ensures good contact of most catalyst particles with the ionomer material that has ionic contact with the membrane.

Gas diffusion occurs through the backing layer and the carbon support to the catalyst particles. When using humidified gases or a methanol–water mixture (see DMFC), the catalyst layer must be sufficiently hydrophobic to prevent the pores from flooding. This hydrophobicity can be provided by introducing PTFE as a binder, in combination with Nafion® that is hydrophilic. Usually the catalyst is made in ink with water and isopropanol and mixed with the binder material (the optimum binder quantity depends on the type of catalyst) after which the ink can be cast straight onto the membrane. The effect of the binder content on the performance of the electrodes was studied for both the PTFE binder and the Nafion® binder [86].

1.4.2.1 Cathode Although a huge variety of catalysts have been investigated, so far Pt-based catalysts have been the superior material for the oxygen reduction reaction. Pt dispersed on carbon or other small Pt particles (such as colloids) exhibit a good performance. Due to the low temperature in PEMFC, the loadings for the oxygen catalysts are significant to compensate for the slow reaction kinetics. Because pure oxygen is seldom available, fuel cells require air for the cathode gas supply. The lower oxygen partial pressure in air leads to a decrease in activity compared with pure oxygen. Under operating conditions for longer times, a “ripening” of the Pt particles has been reported that manifests itself in a decrease of active surface area due to the formation of larger particles [87]. More information on ORR and its kinetics has been published in a review [88]. Research into less expensive materials and better catalysts for ORR is being carried out by various groups.

1.4.2.2 Anode If pure hydrogen is used as fuel, the performance of the anode is excellent with pure Pt catalyzing the oxidation of hydrogen. Unfortunately, in most practical systems, the fuel stream contains certain traces of elements or compounds such as CO, S, and NH_3. All of these substances can to a greater or lesser extent poison the anode catalysts.

CO is one of the major poisons in low-temperature fuel cells [89]. In PEMFC and PAFC, CO poisoning occurs due to adsorption of the species to the active sites of the platinum catalysts so that no, or virtually no, sites are available for reaction with H_2. To reactivate the surface, the CO can be oxidized to CO_2.

To avoid CO contamination in the cell, a gas cleanup can be built in between the reformer and the fuel cell that adds complexity to the system. Other methods to remove CO from the fuel cell are the mixing of the fuel feed with small amounts of air or oxygen (“air bleeding,” about 1% content in the gas) [89]. This stimulates the oxidation of CO over the catalyst. This method requires an extensive control system since the air content has to be closely monitored. The addition of hydrogen peroxide to the fuel stream has also been investigated as a method to minimize the CO contamination [90]. A new method of operating PEM fuel cells with reformed hydrogen with reduced requirements for gas cleaning is applying electrical pulses to the cell. The electrical pulses increase the anode potential to values at which the CO is oxidized to CO_2. In this way, the catalyst surface is continuously cleaned and the loss of cell voltage is minimized [91].

CO-tolerant catalysts are still being investigated by numerous research groups in order to reduce the importance of the problem. CO-tolerant anodes usually contain a PtRu alloy as the state-of-the-art catalyst. The mechanism of CO oxidation and CO tolerance of PtRu catalysts with well-defined surfaces has been investigated and clarified by several groups [92–94]. For example, catalysts prepared via a DC magnetron sputtering technique producing thin layers on standard fuel cell electrode substrates have been investigated [95]. PtRuW and PtRuMo showed an improved CO tolerance over Pt and PtRu catalysts.

1.4.3 Polymeric Materials as Components of Fuel Cell Catalytic System

Platinum and its alloys are usually used as catalysts of reactions responsible for the generation of power by FCs. It is, therefore, of great advantage from the economic viewpoint to reduce the amount of the catalyst required for efficient operation of FC. Since the efficient operation of the cathode strongly depends on the supply of protons, deposition of catalyst in contact with a conductive matrix may help achieving this goal. Indeed, alternative spattering of 5 nm platinum layers on Nafion® membrane, and of the conductive carbon ink, permits to reduce the loading of the catalyst from 0.5 to 40 mg Pt/cm^2. Similar procedures have also been tested for other catalytic systems that replaced or were alloyed with Pt. Rhodium, ruthenium, or iridium were used in such alloys [96].

Commercial MEAs are usually sprayed with Nafion® solution in methanol [97]. In order to increase the permeation of Nafion® into pores of carbon black (CB), used as Nafion®-supported Pt/CB catalyst, the uniformly mixed paste was thermally treated in an autoclave by heating it for 24 h at 200 °C [98]. Effects due to changes in Nafion® loading were investigated [99].

Various composite catalysts such as PtRu/C were prepared by mixing the catalytic powder and active carbon particles with a diluted aqueous solution of Nafion®, homogenizing the dispersion in an ultrasonic bath, and depositing it on a boron-doped diamond electrode [100]. Pt-RuO_2 was prepared by thermal decomposition of its polymeric precursors [101]. Treatment similar to the method described in Ref. [100] was used to deposit Pt/C on the anode and RuxCrySez catalyst on the cathode [102].

Catalytic inks were prepared by grafting of polymeric electrolyte onto Pt/C powders (acrylamide *t*-butylsulfonic acid was used as the monomer). Subsequent preparation and deposition of the Pt/Ru (supported on grafted carbon ink) was executed as described in Refs [100,101]. Effect of the preparation of the catalytic ink on the performance of FCs was discussed in Ref. [103].

Teflon® suspension was used for the deposition of La/Pt anode catalyst on MEA of DMFCs [104]. Teflon-bonded GDEs were modified by electropolymerization of aniline with trifluoromethane sulfonate as counterion. The use of PANI instead of Nafion® in the catalyst layer increased its utility by 18%. It provided good connection with the catalytic particles. The deposition of the homogeneously distributed electroconductive PANI increased the catalytic properties of the reactive layer and reduced the overpotential and the polarization resistance of the electrode [105].

Incorporation of single-wall nanotubes (SWNTs) into PANI matrix reduced significantly the defects in PANI structure and improved efficiency of the catalytic oxidation of methanol [106].

Ni/Mo alloy deposited on PANI was shown to act as an efficient catalyst for hydrogen evolution from water using PEM-type hydrogen generators analogous to PEMFCs [107].

Another conductive polymer-polypyrrole (PPy) has been found to provide efficient protective coatings against corrosion. Such coatings may enable introduction of certain inexpensive metal oxides (which dissolve under acidic PEMFC conditions) instead of platinum as slow oxygen reduction catalysts (ORC). Remarkable stability was achieved by simultaneous deposition of PPy and $Na_{0.3}Co_{2.7}O_4$ onto carbon. The same was true for CoF_2O_4 sandwiched between PPy layers [108]. The introduction of a layer of polypyrrole in contact with PEM and with current collector greatly enhanced the catalytic oxidation of hydrogen [109].

Poly(3,4-ethylenedioxythiophene) (PDOT) was investigated as the Pt/PDOT/polystyrene sulfonic acid electrode for DMFCs. It influenced the activity of DMFCs in three different ways. It could be introduced into the anode, cathode, or the gas diffusion layer [110].

A patent application describing pyrolysis of poly(phenylene ether) (PPE) leading to the formation of highly electrically conductive and permeable gaseous carbons, which could be used as base materials for catalysts and for the preparation of the fuel cell gas diffusion electrodes, was submitted in 2003 by Cabasso et al. [111]. This was achieved by oxidization of PPE in an oxygen-containing atmosphere, at a temperature close to its T_g, followed by its carbonization in an inert atmosphere at high temperatures [111].

1.4.4 Bipolar Plates

Bipolar plates uniformly distribute air and fuel supplied to FCs. They remove heat from the active area and carry current from cell to cell. Since they should not be too heavy, they are usually made from aluminum or other light metals. However, they are heavily corroded because of harsh conditions to FCs operation. Problems related to materials used for construction of PEMFCs were reviewed by Hermann et al. [112]. One of the solutions proposed in order to solve problems related to bipolar plates was coating them with various polymer–carbon-based composites. However, electric conductivity of such coatings may not be sufficient. Another approach proposed to solve this problem involved the use of conductive polymers [112]; electrodeposition of polypyrrole coating for corrosion protection of bipolar plates was investigated by García and Smit [113]. They found that although initially the surface of stainless plates was effectively passivated by such treatment and oxidation rates at PEM potentials were reduced by several orders of magnitude, the protective coatings were lost with increasing time of immersion, even when up to 0.14 g/cm^2 of PP was deposited in up to eight consecutive cycles [113].

The use of Nylon 6/CB blend for construction of dipolar plates was proposed as an inexpensive economically attractive solution. However, it is unsatisfactory for automotive applications. Even at 35% of CB load, the resistance is as high as 80 mV/cm^2. Moreover, Nylon 6 cannot be used at temperatures higher than 120 °C [114]. Bipolar plates used for automotive application of FCs should be thin and light and their electrical resistance should not exceed 20 mV/cm^2. High load of highly conductive carbon such as graphite, at which they become brittle, is required to achieve this goal with the currently used polymer–carbon blends. Therefore, there is a need to develop materials with high conductivity, but low loading of the filler, which will enable fabrication of thin, ductile, and highly conductive plates [115]. The recently proposed novel concept of triple-continuous structure may help to achieve this goal. An increase of 2500% in electrical conductivity, 36% increase in tensile strength, and 320% increase in elongation were achieved when carbon nanotubes, combined with the poly(ethylene terephthalate)–polyvinylidene fluoride blend were tested [116].

1.5 MEMBRANES FOR PEM FUEL CELLS

1.5.1 Proton Exchange Membranes

Nafion®, the fluorosulfonated copolymer of the perfluorinated ethylene and propylene oxide, has been extensively investigated as polymeric electrolyte for fuel cell systems (PEFCs). Water concentrates in the bulk of Nafion® pores, where efficient proton diffusion occurs, but because of the hydrophobic nature of its backbone it avoids their surfaces. This, apparently, may be the reason for some of the excellent characteristics of Nafion® as PEM [117]. The ionic conductance of hydrated Nafion®, at 80 °C, is quite high and its chemical and mechanical stability is very good. However, it is too expensive for large-scale applications. Moreover, due to the dehydration at higher temperatures, a sharp decline in its conductivity takes place above 100 °C. The use of Nafion® for DMFC is also questionable, because of its permeability to methanol that reduces significantly the efficiency of DMFCs in which Nafion® has been used as PEM.

Recasting of the commercial Nafion® membranes has recently been investigated [118]. Slight improvement in the ionic conductivity at 80 °C of the recast Nafion® has been observed. The investigators believe that the technology described by them may be useful for the development of membranes for FCs operated at higher temperatures. The performance of membranes has also been improved by blending Nafion® with titanium dioxide. The conductivity of the hydrated, unstressed, and stressed Nafion® membranes blended with 3 wt% TiO_2 increased by ~20%. It was also noted that the decrease in elastic modulus, as a result of water absorption, was less pronounced and the decrease of plastic modulus was more pronounced for such membranes. The mechanical properties of the composite membranes were more affected by hydration than by the increase in temperature. Clear correlation between improvement in performance of FCs due to addition of TiO_2 and its effect on the mechanical properties of such membranes was, however, not yet established [119].

Methods of preparation of various functional fluoropolymers suitable for fuel cell applications have been discussed by Ameduri and coworkers [120]. They claimed that in spite of the high cost of Nafion® and its permeability to methanol, it still remains the fluorinated polymer of choice for the preparation of the proton exchange membranes for FCs.

Styrene with divinylbenzene as cross-linker in a 9:1 ratio has been radiation grafted onto poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) membranes. It is subsequently chlorosulfonated in CH_2Cl_2 at room temperature (RT) with chlorosulfonic acid. Optimal graft level was found to be 24.2%. Membranes with graft levels below 19% did not show any ionic conductivity and those above 30% degraded during cell operation. Fuel cells with ~30 mm thick membranes, grafted to 24.2% graft level, produced a current of 500 mA at 0.6 V, when fueled with H_2 versus O_2 at 80 °C. No signs of deterioration could be detected during 770 h of operation. At its end, they remained leak tight. Their ohmic resistance was constant at 280 V/cm^2. The performance of the radiation-grafted, sulfonated PETFE membranes has been found to be nearly as good as that of Nafion®, while they are much less expensive than the former material. It should be pointed out that water content at RT of such water-swollen membranes is only around four molecules of water per sulfonic acid group, while for Nafion® it is $18H_2O/SO_3^-$. Poly(tetrafluoroethylene-*co*-hexafluoropropylene) membranes, similarly prepared by radiation grafting, behave in analogous fashion to the grafted, sulfonated PETFE membranes. Such membranes may also be suitable for direct methanol FCs [121]. A novel process for the preparation of ETFE-based membranes for PEMFCs was recently developed. It is based on the UV-induced photografting of styrene into ETFE followed by cross-linking of the grafted film by electron beam irradiation and then by sulfonation. Liquid-phase photografting showed uniform distribution of the subsequently sulfonated polystyrene chains and resulted in relatively high proton conductivities, even at lower IECs. Cross-linking reduced the conductivity slightly, but greatly improved the chemical stability of the membrane. Moreover, concentration of the sulfonic groups after cross-linking maintained its high level. This is of great importance for performance of MEA since it affects favorably the resistance of the connections [122].

Self-humidifying Pt-SiO_2-PEM membranes have been prepared by soaking Nafion® 112 membrane with tetraethoxysilane (TEOS). Stable SiO_2 nanoparticles, uniformly dispersed in Nafion® matrix, were formed when TEOS was hydrolyzed by raising the temperature to 70 °C. The size of the hydrophilic clusters increased when they absorbed water. Subsequent ion exchange reaction with $[Pt(NH_3)_4]Cl_2$ followed by reduction with 1-pentanol at 125 °C for 2 h yielded Pt particles uniformly dispersed on SiO_2-PEM. When H_2 and O_2 are supplied to such membranes, the *in situ* formed water humidify them. The performance of FCs equipped with such membranes was similar to the performance of FCs supplied with externally humidified fuels. Utilization of hydrogen may also increase in such systems, since it is not diluted by an externally introduced H_2O [123]. A similar self-humidifying arrangement was used for the composite of Nafion® with reinforced Teflon [124].

Composite Nafion®/aZrP and Nafion®/silica can be operated above 140 °C. Their conductivity at 160 °C and 34% RH was demonstrated to be 0.1 S/cm. Composite sulfonated poly(ether ether ketone) (sPEEK) may also be operated at such temperatures. However, its conductivity is much lower [125]. Stable operation at 120 °C was also reported for blends of Zr phosphate with sulfonated poly(fluorinated arylene ether(s)) [126].

Nafion®-layered sulfonated polysulfone (sPSU) membranes have been prepared by pressing thin Nafion® 115 layers on sPSU. Nafion® layers on sPSU prevent washing out of the water-soluble sPSU. Such membranes are stable during FCs operation at 120 °C. sPSU with high ion conductivity and high IEC has been prepared by sulfonation of polysulfone with trimethylsilyl chlorosulfonate. The silicon-containing compound, formed during such synthesis, was removed by evaporation. The conductivity of sPSU increased exponentially with the increase in relative humidity. It reached the value of 0.1 S/cm at RH > 70%. At 65 °C, power production of FCs equipped with Nafion®-layered sPSU membranes has been found to be four times larger than that of analogous FCs equipped with Nafion® [127].

Synthetic procedures leading to the preparation of the sulfonated polysulfones have been reviewed by Guan et al [128]. These authors believe that they are the most promising materials for the proton transfer membranes for FCs [128].

4,4′-Difluorodiphenylsulfone was sulfonated by reacting it at 160 °C for 12 h with 30 wt% fuming sulfuric acid. 3,3′-Disodium salt of sulfate of 4,4′-difluorodiphenylsulfone was isolated after neutralization with NaOH, salting out with NaCl and recrystallization. It was condensed at RT in sulfolane with 4,4′-thiobisbenzenethiol. The reaction mixture was heated to 100 °C. To complete the polycondensation, it was kept for 1 h at this temperature. Thus prepared, sulfonated poly(arylenethioether sulfone) (sPTES) polymer was acidified and endcapped by reacting it for 4–5 h at 180 °C with 4-fluorobenzophenone (Fig. 1.3). It can be fabricated into tough, flexible membranes from dimethyl acetamide that show high thermal stability up to 300 °C and excellent mechanical integrity. Their proton conductivity (σ) at 65 °C and 85%

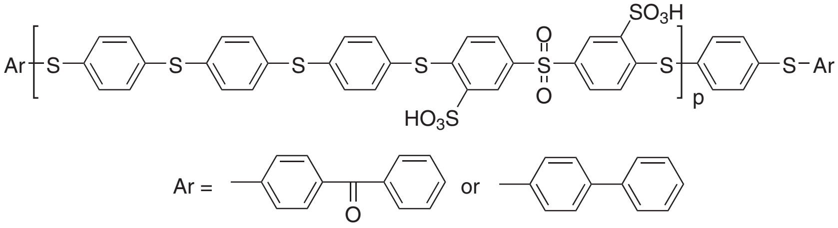

FIG. 1.3 3,3′-Sulfonated poly(arylenethioether sulfone) (sPTES).

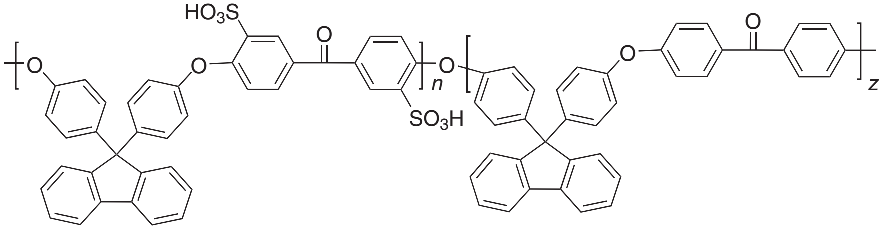

FIG. 1.4 Sulfonated poly(fluorenyl ether ketone) (sPFEK).

RH was found to be 0.36 S/cm, four times as high as that of Nafion® 117. Endcapping sPTES with unsubstituted monomers improved their oxidative stability, but decreased their conductivity [129].

The high molecular weight sulfonated poly(fluorenyl ether ketone(s)) (Fig. 1.4) have been prepared by a nucleophilic polycondensation in DMSO of the bisphenol fluorene (BPF) with difluorobisphenone (FBPO) and its sulfonated derivative. The reaction was conducted under nitrogen in the presence of anhydrous K_2CO_3. After 3 h at 150 °C, the reaction mixture was heated for 20 h at 175 °C. The degree of sulfonation could be controlled by changing the molar ratio between sulfonated and nonsulfonated FBPO. The high degree of sulfonation and high water uptake endow a relatively reasonable proton conductivity of 0.03–0.045 S/cm at 25 °C and 100% RH to membranes prepared with such polymers (the conductivity of Nafion® 117 at the same conditions was 0.0418 S/cm) [130].

Block copolymers of the sulfonated aromatic poly(ether ether ketone(s)) (sPEEKs) with various ratios of the length of the hydrophobic to the hydrophilic blocks have been prepared in order to find structures characterized by a relatively low IEC, and at the same time relatively high proton conductivity. The results of the investigation of Zhao et al. [131] revealed that at 4:1 ratio of the hydrophobic to the hydrophilic parts of sPEEK, the IEC was equal to 0.488 meq/g, the conductivity at 80 °C was 0.03 S/cm, and water uptake was 18%. At the same time, the conductivity of Nafion® 117 with IEC = 0.92 meq/g was equal to 0.1 S/cm and its water uptake was 38%. Membranes prepared from sPEEK are tough and have good thermal and mechanical stability [131]. Initiated by BuLi, sPEEK was silylated by cross-linking with $SiCl_4$. The silylated sPEEK was used for the preparation of hybrid organic–inorganic proton exchange membranes. The application of such membranes as PEM for FCs is currently investigated [132].

Sulfonated poly(arylene ether ketone(s)) were synthesized by condensation of 2,2′-bi[2-(4-flurophenyl)benzo-xazole-6-yl]hexafluoropropane with sodium 5,5′-carbonylbis(2-fluorobenzosulfonate). Copolymers were soluble in polar aprotic solvents and formed tough, flexible membranes. They were resistant to oxidation and thermally stable up to 290 °C. Their proton conductivity at 80 °C depended on their composition and could be as high as 0.055 S/cm, at RH = 95%. At 120 °C, it is more than double at high benzoxazole content [133].

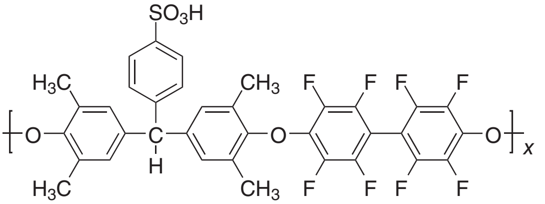

FIG. 1.5 Poly(fluorinated-arylene ether) with sulfonated triphenyl methane moiety [135,136].

The solubility parameters of sPEEK were found to be 26.4 and 35.7 $J^{0.5}$ $cm^{1.5}$. The lower value is close to its theoretical value (26.1 $J^{0.5}$ $cm^{1.5}$). For solvents with solubility parameters lower than 35 $J^{0.5}$ $cm^{1.5}$, the experimentally determined volume fraction of sPEEK in a solvent compares quite well with the theoretical predictions [134].

Various sulfonated poly(arylene ether(s)) containing either triphenyl methane or biphenyl moiety have been synthesized and characterized by Meng and coauthors. The sulfonated polymers are soluble in polar organic solvents and can be used for the preparation of tough and smooth membranes that exhibit water affinity, very good mechanical strength, and reasonable proton conductivities. Highest conductivity was observed for the polymer shown in Fig. 1.5, which contained a tetrafluoro-biphenyl segment in its main chain. Its conductivity at RT and 100% RH was found to be 0.075 S/cm [135].

Sulfonated aromatic polyimides (sPI) were used for the preparation of PEMs for FCs. Such membranes have excellent mechanical strength and low swelling. The performance at 90 °C of a fuel cell, loaded with sPI, was nearly as good as that for Nafion® 112. Their performance in DMFCs was also reasonable. At 50 wt% of methanol, they still yielded 69 mW/cm^2 [137]. Polymers were prepared with linear 4,4′-sulfonyldiamines and with angled 3.4′-sulfonyldiamines. Membranes with IECs up to 2.75 meq/g were thermally stable in air up to 300 °C. Their proton conductivities increased with the increase in temperature up to 0.1–0.2 S/cm. Angled polymers were characterized by higher proton conductivities than the linear one, while their water uptake was lower. This was attributed to their greater entanglement that limits the degree of swelling [138]. The proton conductivity of sulfonated poly(arylene-*co*-naphthalimide(s)) shown in Fig. 1.6 depends strongly

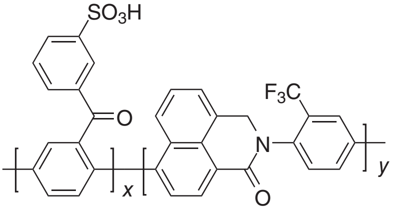

FIG. 1.6 Structures of sPIMs (in series I).

on their ion exchange capacity. The proton conductivity of membranes prepared from such sPIs, with structures belonging to series I, has been as high as 0.26 S/cm at 80 °C. $\sigma_{\text{Nafion}^{\circledR}\ 117} = 0.15$ S/cm (at the same temperature). Its mechanical properties were almost unchanged after 196 h in boiling water. Its oxidative stability was found to be very good [139].

Sulfonated aliphatic/aromatic polyimides were investigated by Watanabe and coworkers [140]. An aliphatic segment introduced in both the main and the side chains improved the hydrolytic stability of the polyimide ionomers and did not affect adversely their proton conductivity or oxidative and mechanical stability. Flexible, transparent, and docile membranes with IECs ranging from 1.78 to 2.33 meq/g could be prepared from the branched copolymers obtained by the two-stage polycondensation. Their proton conductivity below 100 °C was slightly lower than that of Nafion®, but comparable when at higher temperatures. Their permeability to both hydrogen and oxygen, at temperatures ranging from 40 to 120 °C and RH ranging from 0 to 90%, was orders of magnitude lower than that of Nafion®. The FC operated with PEM prepared from such branched sulfonated aliphatic/aromatic polyimide was durable for 5000 h of operation, as evidenced by little changes in its open-circuit voltage. Studies of the morphology of these membranes revealed that branching suppressed aggregation of ionic groups and favored homogeneous dispersion of smaller than 5 nm hydrophilic domains. Dependence of the conductivity of such membranes on their water content was significantly reduced. Their superior mechanical strength was also better than that of Nafion®. The above-outlined characteristics of such membranes seem to indicate that they may be a candidate for PEMs for H_2/O_2-fueled FCs [140].

Mechanical stability of sulfonated poly(ether ketone ketone) (sPEKK) membrane was improved by blending it with poly(ether imide) (PEI). However, the conductivity of sPEKK decreased, when blended with PEI. The morphology of such membranes can be controlled by varying the casting procedure and by high-temperature annealing, above T_g of the blend at 200 °C and below desulfonation temperature of sPEKK at 250 °C. For the 2.5/97.5–25/75 contents of PEI in the blends, it was dispersed as small particles in a continuous matrix of sPEKK. The size of these particles increased with increasing fraction of PEI in the blends. Development of cocontinuous morphologies of blends of sPEKK with other polymers is currently investigated by these researchers (Fig. 1.7a) [141].

These investigators also prepared copolymers of sPEKK with PEKK. It is thermally stable up to 250 °C. At 80 °C, the conductivity of such a copolymer with IEC of 1.8 meq/g was 0.05 S/cm and crossover of methanol through membrane in contact with 1 M methanol was equivalent to 0.22 A/cm^2. Current density of ~0.6 A/cm^2 was observed for membranes with IEC = 2 meq/g [142].

Preparation of homopolymers of the *ortho*- and *para*-acrylaminoarsonic acids by a radical polymerization of respective monomers was described by Pal and coworkers [143]. The monomers were synthesized by condensation of acryloyl chloride with corresponding arsenic acids. The thermal stability of both polymers was quite high. TGA measurements indicated that up to 205 °C they were losing only 7.7% of their weight. Thanks to the thermal stability and high ion exchange capacity of these

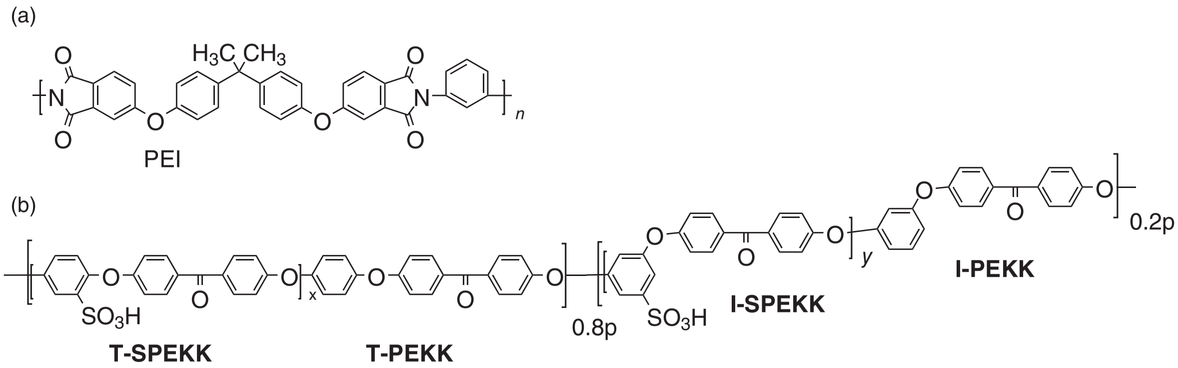

FIG. 1.7 (a) Poly(ether imide). (b) Sulfonated T-(PEKK-*co*-PEKK)-*co*-I-(PEKK-*co*-PEKK).

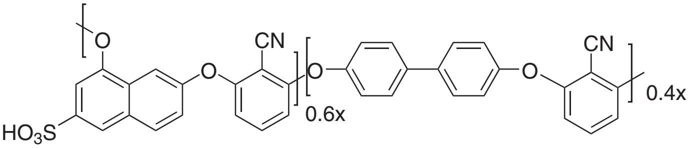

FIG. 1.8 The sPAEEN copolymer with 60% of naphthalenic units.

homopolymers, these investigators believe that they may be a promising candidate as PEM membranes for FCs (Fig. 1.7b) [143].

Proton conductivities of the terpolymers prepared by free-radical copolymerization of vinylidene fluoride with 8-bromo-perfluorinated-1-octene and sulfonated methyldioctene have been found to be orders of magnitude lower than those of Nafion® [144].

Wholly aromatic sulfonated copoly(aryl ether nitrile(s)) (sPAEENs) were prepared from commercially available inexpensive monomers by nucleophilic substitution of 2,6-difluorobenzonitrile with 4,4′-bisphenol and 2,8-dihydroxynaphthlene-6-sulfonated sodium (DHNS). Their preparation involved a one-step polycondensation reaction at 130 °C. The sulfonic acid group in the thus prepared copolymer was in the *meta*-position to the ether. The highest proton conductivity was obtained for the copolymer containing 60% of the NS units (Fig. 1.8). The proton conductivity of its membrane, swollen with water by immersion in hot water for 36 h, was found to be 0.14 and 0.15 S/cm at 80 and 100 °C, respectively, compared with 0.096 and 0.16 S/cm for Nafion® 117 at these temperatures. Its tensile strength is five times larger than that of Nafion® 117 and its elongation at break is two orders of magnitude smaller. Thanks to their good thermal stability ($T_g \approx 230\,°C$ and $T_d \approx 260\,°C$), high proton conductivity, tensile strength several times higher than Nafion®, and low-dimensional swelling, they appear to be an attractive candidate for FCs [145].

Preparation of PEMs from a blend of sulfonated to a high charge density poly (phenylene oxide) with the poly(vinylidene fluoride) was patented by Cabasso et al. [146]. This patent application describing preparation of PEMs from polybenzimidazole modified by substitution with phosphor and/or sulfur and/or halide-containing groups, blended with derivatives of polysulfonic acid, was submitted in 2004 by these investigators. Membranes of 1–250 μm thickness were prepared by casting solutions of such blends. Subsequently, they were dried to remove the solvent. Their performance was tested in H_2/O_2-fueled FCs at temperatures up to 130 °C. The recorded power densities could be as high as 1000 mW/cm^2, depending on IEC of a membrane, its thickness, composition, H_2 and O_2 pressure, catalytic system, and the temperature [147]. Effects of temperature and humidity changes on proton conductivity of PBI membranes, doped with various amounts of phosphoric acid, were investigated in Refs [148–150].

1.5.2 PEMs for DMFCs

Methanol can be synthesized in the presence of catalysts from water and carbon oxides. It can also be prepared by pyrolysis of wood. Its combustion produces both water and the environment-harmful CO_2. However, the molar amount of the generated H_2O is twice as large as CO_2. Commercial application of Nafion® as PEM for DMFCs is questionable, not only because of the high cost of Nafion® but also because of significant losses in Faradic and energy efficiency due to crossover of methanol to the cathode compartment of DMFCs, equipped with Nafion® membranes as PEM [151]; various treatments of Nafion® have been recently proposed to correct this situation. Matsuguchi and Takahashi prepared semi-IPNs of Nafion® cross-linked with divinyl benzene (DVB). Their preliminary results were not very encouraging [152]. However, Deluca and Elabd reported recently that annealing at 230 °C a blend of Nafion® with 5% PVA caused a threefold increase in its selectivity to methanol, without affecting significantly its conductivity [153]. The diffusion and the electroosmotic drug of methanol in Nafion® membranes have been discussed and tabulated by Schaffer et al. [154].

Jiang et al. [155] modified the surface of Nafion® membranes by self-assembling on it a monolayer of Pt-PDDA nanoparticles (where PDDA stands for the positively charged poly(diallyldimethylammonium chloride), which act as catalyst for methanol oxidation. Such a surface modification of Nafion® membranes enhanced the power output of DMFC by as much as 34% [155].

Novel nanoporous membranes have recently been developed by Peled and coauthors [156]. Such membranes consisted of PTFE as the backbone with a nanosized ceramic powder (Aerosil®200 or Aerosil®130) dispersed in it. An aqueous solution of sulfuric acid adsorbed inside the pores of such membranes acted as an ionic conductor. Thus prepared membranes consisted of 50–200 nm spherical particles with nanovoids between them. They have been found to be quite elastic. Preliminary tests conducted using FCs with ~250 μm thick nanoporous membrane, with electrodes on which 4 mg Pt/cm^2 was dispersed on both the anode and the cathode, and fueled by 1 M methanol (in 3 M aq. H_2SO_4) flowing at the rate of 180 ml/min, against 3 atm of dry air, yielded 50 and 130 mW/cm^2 at 80 °C and at 130 °C, respectively. The crossover of methanol in these relatively inexpensive membranes was 0.27 and 0.56 A/cm^2 at 80 and 130 °C, respectively. Its selectivity to methanol was estimated to be in the same range as PVDF-ceramic powder hybrid [157].

In view of the relatively high permeability of the currently available PEMs to methanol, several sulfonated aromatic and aliphatic polymers were tested as possible alternative PEMs that will significantly reduce the crossover of methanol to the cathode compartment of DMFCs. Sulfonated copolymers of arylene ether sulfones with carboxylic and sulfonic acid groups have been prepared by polycondensation of 4,4′-dichlorodiphenyl sulfone and of sulfonated 4,4′-dichlorodiphenyl sulfone with phenolphthalein (sDCPDS) (Fig. 1.9). For compositions of such copolymers equal to or higher than percolation thresholds (sDCPDS = 20 mol%), their permeability to methanol (calculated as its diffusion coefficient) is much lower than that of Nafion® and their selectivity at 30 °C (conductivity to protons versus permeability to methanol) is nearly five times higher than that of Nafion® [158].

Fluorinated poly(aryl ether) and its phosphonated derivative, containing the 4-bromophenyl pendant group, was prepared with high conversion yield. It had

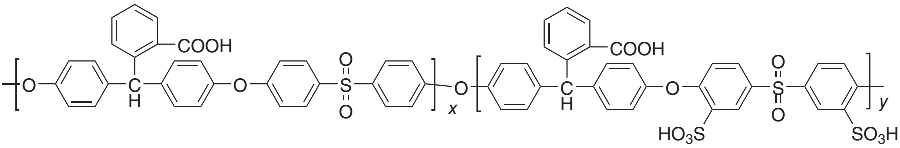

FIG. 1.9 Copolymer of diphenyl sulfone with phenolphthalein or with its sulfonated derivative (sDCPDS).

low methanol permeability, reasonable proton conductivity, and high thermal, oxidative, and dimensional stability [159].

Chemically cross-linked polymer blends of poly(vinyl alcohol), 2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS), and poly(vinyl pyrrolidone) (PVP) have been used by Qiao et al. [160] for preparation of ion exchange membranes. Their cross-linking was achieved by reaction between glutaraldehyde and the adjacent hydroxyls of PVA. The conductivity at 25 °C of cross-linked membrane prepared with PVA/PAMPS/PVP at 1:11:0.5 ratio was found to be 0.088 S/cm, hence comparable with that of a commercially available Nafion® 117. At the same time, its permeability to methanol was much lower than that of Nafion®. Moreover, these PVP blend membranes showed excellent water stability at RT and relatively high oxidative stability at 60 °C. PVP plays an important role in determining the membrane performance [160]; PVA/PAMPS membranes were also prepared as blends with the methoxy-terminated PEG oligomers or with its dimethoxy variant, which replaced the previously used PVP. The proton conductivity of such membranes at 60 °C was 0.113 S/cm and their selectivity toward methanol was 2.5 times higher than that of Nafion® 117 [161]; blends of PVP with chitosan have also been investigated and their selectivity to methanol (proton conductivity versus methanol permeability), after cross-linking, was found to be at 30 °C, three times higher than that of Nafion® 117. Absolute value of its proton conductivity at 60 °C was, however, lower by a factor of 2 than that of Nafion®. Unfortunately, these investigators did not determine permeability of methanol at 60 °C. Therefore, it is impossible to make a meaningful comparison of the methanol selectivities of the two membranes at the working temperature of a DMFC [162].

Sulfonated poly(ether ether ketone(s)) (PEEKs) and their blends, synthesized in several research laboratories, were used for casting of membranes and were evaluated as PEMs for DMFCs [163–166]. PEEK was sulfonated to various degrees of sulfonation (DS) with concentrated sulfuric acid. Both its proton conductivity and its permeability to methanol increased with increasing DS. However, a maximum in its selectivity to methanol versus proton conductivity was observed for DSs in the 57–61% range. Maximal efficiency of DMFCs with sPEEK as PEM was obtained for DS = 52%. Methanol uptake of such DMFCs increased with increasing molarity in the cathode compartment of the cell [163,164]. Blends of sPEEK with PVP as PEMs were investigated by Ma and coauthors. The conductivity of such blends decreased with the increase in fraction of PVP in the blend. Optimal value of the proton conductivity was observed for 80:20 ratio of sPEEK/PVP, DS = 69%, and $M_{n\_PVP} = 1300$ kDa [165]. Blending of sPEEK with sulfonated diphenylsilandiole in

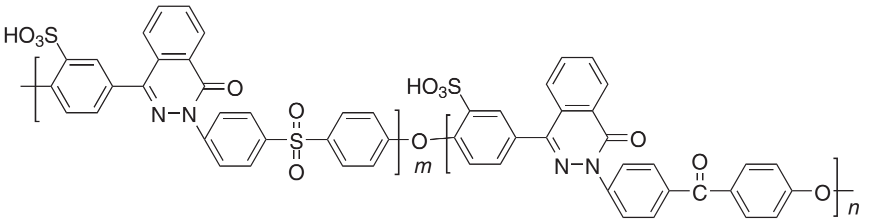

FIG. 1.10 sPPESK.

a 70:30 w/w ratio greatly increased its proton conductivity. At 70 °C, and water uptake at equilibrium of 21%, it was slightly higher than 0.1 S/cm [166].

Blends of sPEEKK with polyaniline (PANI) as PEMs for DMFCs were investigated by Na and coworkers. The sPEEKK copolymers were prepared by polycondensation of the aromatic ketone or its sulfonated derivative with 2,6-dimethyl-4-bisphenol. Water uptake and methanol permeability of such blends were lower than that of sPEEKK copolymer, while their proton conductivities were nearly equal to it. The density of the material increased and its permeability to methanol decreased, as a result of the hydrogen bonding between amino groups of PANI and hydrogens of SO_3H groups of PEEKK. Moreover, the formation of hydrogen bonds may favor proton transfer [167].

Sulfonated poly(phthalazinone ether sulfone ketone) (sPPESK) (Fig. 1.10) was prepared by sulfonation of PPESK with fuming H_2SO_4. The proton conductivity of sPPESK (DS of 81%) was 0.013 at 80 °C (not much lower than that of Nafion® 115). On the other hand, its permeability to methanol at 15 °C was apparently nearly 40 times less than that of Nafion® 115. These results seem to indicate that the Faraday efficiency of DMFCs may be good, if sPPESK membranes are used as PEMs [168].

The proton conductivity of poly(phthalazinone ether ketone) (sPPEK) at 20 °C was 0.0106 S/cm, as compared with 0.02 S/cm for Nafion® 115. However, its electrochemical performance at 50 °C was superior to that of Nafion® 115. It also showed good thermal and hydrolytic stability and moderate strength [169]; sPPEK blends with 12-phosphotungstenic acid (PWA) and with zirconium hydrogen phosphate (ZrP) were investigated. Blending of sPPEK with PWA caused significant increase in proton conductivity up to 0.17 S/cm at 80 °C, without weakening the mechanical properties. On one hand, blending of sPPEK with ZrP did not improve the conductivity. Conductivity of the composite obtained by incorporating up to 40 wt% of zirconium phosphate in a copolymer of bisphenol with disulfonated diphenylsulfone (PSDS) can be as high as 0.16 S/cm, when its IEC approaches 3 mmol/g. Such a composite was obtained by a precipitation method. Namely, the PSDS membrane was immersed, at 80 °C, in an aqueous solution of $ZrOCl_2$, to which 1 M H_3PO_4 was added. $ZrHPO_4$ (ZrP) precipitates for 24 h in the water-swollen pores of the membrane [170].

Physicochemical characteristics and electrical performance of sulfonated and grafted poly(*para*-phenylene(s)) have been investigated by Ninivin et al. [171]. It was expected that the permeability to methanol of some of such compounds would be very low. However, results of these studies revealed that they are comparable with that of Nafion®, while conductivities of protons are much lower. The performance of the tested DMFCs was judged to be inadequate [171].

Asymmetric PEMs with a loosely cross-linked proton conductive layer sandwiched between two primarily hydrophobic layers with limiting methanol swelling have been prepared. A three-component polymer blend (TCB) consisting of poly(4-vinylphenol-*co*-methacrylate) (PVPMA), poly(butyl methacrylate) (PBM), and acrylic copolymer resin Polaroid® B-82 acted as a methanol barrier layer. The proton conductive hydrophilic layer consisted of a random copolymer of 2-hydroxy-2-acrylamido-2-methyl propanesulfonic acid (AMPS) and HEMA, loosely cross-linked by poly(ethylene glycol) dimethacrylate (PEG-DMA) oligomer. TGA analysis showed that these membranes are thermally stable up to 270 °C. However, their proton conductivity was rather low [172]. Thermoplastic PVDF-SEBS blends compatibilized with MMA block copolymers can be used for solventless fabrication of PEMs [173].

In a review of the properties and structure of the polymer electrolyte membranes for direct methanol FCs, Deluca and Elabd mentioned that some of the proposed replacements of Nafion® as PEM for DMFC have higher methanol selectivities and comparable proton conductivities to Nafion® [174]. Montmorillonite dispersed in Nafion®, described by Song et al. [175] in 2003, and blend of PVA with the copolymer of PS-sulfonic and maleic acids, described by Kang et al. [176], seem to be the most promising ones. However, longitudinal proton conductivities of the respective membranes cited in these references may by different from horizontal conductivities of these membranes.

In principle, an interesting approach to the problem posed by the requirement of low methanol permeability of a highly proton conductive membrane was proposed by Won and coauthors [177]. They prepared cross-linked PVA membranes in which sulfonated, well-dispersed, rod-like polyrotaxenes (PRs) were supposed to provide pathways for proton transport, while blocking crossover of methanol. The inclusion complex of an oligomeric poly(ethylene glycol) (PEG) with the α-cyclodextrin (α-CD) acted as PR. The size of PR was controlled by the molecular weight of PEG. Permeability to methanol of such membranes was indeed more than an order of magnitude lower than that of Nafion®, but their proton conductivity was disappointing [177]; subsequently, somewhat better conductivities have been obtained, when these investigators replaced α-CDs by sulfonated β-cyclodextrins [178].

Polysilsesquioxane hybrid materials were prepared by adding aminopropyl trimethoxy silane and imidazole glycidoxypropyl trimethoxysilane monomers to the solution of sPEEK (with DS = 67% in NMP). $RSiO_{1.5}$ network in a polymer matrix was generated in this way by a sol–gel process. The proton conductivity of the resulting hybrid ionomers was low and, in the temperature range of 50–90 °C, did exceed a few mS/cm [179].

Nafion® was modified by blending it with Teflon FEP resin. Swelling by water and permeability of such blends to methanol was much lower than that of unmodified Nafion®. The proton conductivity of this material was less affected by this treatment [180].

Poly(ethylene-*co*-vinyl alcohol) (EVOH) was grafted with the subsequently sulfonated oligomers of ethylene glycol. Ionic conductivity of this comb-like graft polymer was in the 10^{-4} range. It decreased with the increase in the length of the oligo-glycol chains [181].

Multilayered membrane systems consisting of one inner sPPEK membrane and two outer Nafion® membranes were shown to decrease the crossover of methanol by nearly 40% [182].

The relation between the crossovers of methanol and its concentration in the anode compartment of DMFCs equipped with Nafion® membranes was explored and its effect on the efficiency and power density generation was investigated [183].

Mechanical endurance of polymeric ionomers, their chemical degradation, and their effect on the performance of FCs were recently discussed by Huang et al. [184].

1.5.3 Anion Exchange Membranes (AEMs)

Various previously developed AEMs were discussed in Ref. [185]. Advantages of using AEMs for FC systems were discussed by its authors. They pointed out that the use of AEMs makes possible operation in alkaline media, which facilitate oxidation of methanol and enable the use of less expensive catalytic systems. However, when CO_2 generated by oxidation of methanol reacts with alkali metal cations, carbonate crystals may be formed. Such crystals interfere with the activity of the catalysts and affect adversely the performance of FC. Varcoe and Slade [185] suggested that attachment of fixed tertiary amines instead of the mobile alkali metal cations to an AEM may solve this problem. They prepared such AEM membranes by polymerizing vinyl benzyl chloride and cross-linking it with *N*,*N*,*N*′,*N*′-tetramethyl hexane-1,6-diamine. Stable, low- efficiency performance of FCs equipped with these AEMs was achieved. On the other hand, FCs with commercial AEMs, initially doped with aqueous KOH, performed in the beginning much better, although their performance deteriorated with time [186]. Subsequently, electron beam irradiation technique was used by these investigators to graft vinyl benzyl chloride into ETFE. They irradiated, in air, a 25 μm ETFE membrane to a total dose of 7 Mrad. The irradiated membrane was immersed under nitrogen in vinyl benzyl chloride and kept in it at 60 °C for 120 h. The grafted membrane was immersed for 4 h at RT in aqueous trimethyl amine, and finally immersed for 1 h in 1 M KOH to replace chlorine anions by hydroxyls. The membrane electrode assembly (MEA) was pretreated in a somewhat analogous fashion, namely, Pt/C electrodes with ETFE as binder were spray treated with ethyl acetate solution of poly(vinyl benzyl chloride), immersed for 24 h in tetra-methyl-hexane diamine, and finally immersed for 1 h in 1 M KOH. Thus prepared FCs generated power densities of 0.09 and 0.11–0.13 W/cm^2 at 50 and 60 °C, respectively. Such performance was inferior to the performance of PEFC equipped with Nafion® membrane, which at 60 °C produces 0.480 W/cm^2. However, Varcoe et al. [187] claimed that they would be able to improve considerably the performance of their system by proper optimization. They also claimed that the use of such systems may be advantageous for FCs fueled with ethanol or by the much cheaper methanol ammonia, which is an environment-friendly fuel for FCs [188].

Stability and performance of AEM prepared using poly(4-vinyl pyridine-*co*-styrene), quaternized with 1-bromooctane, and deposited on fibrous woven paper was unsatisfactory [189]. Sanchez and coauthors [190] discussed problems related to the use of certain AEMs. They pointed out that the so-called Hoffman degradation that involves attack of a hydroxyl on α-hydrogen in β-position to a quaternary ammonium attached to an aliphatic chain may cause its removal, followed by release of a tertiary amine and formation of a double bond at the end of a broken chain. Attachment of DABCO on short leash prevented chain break due to Hoffman degradation, but release of DABCO and generation of a double bond attached to the chain could take place. Perhaps thermal cross-linking by DABCO of poly(vinyl benzyl chloride) may solve this problem. Sulfonated polymers prepared by polymerization or copolymerization of phosphazene, siloxans, styrene, vinylidene fluoride, and various monomers with aromatic backbones, and possibly with aliphatic spacers, have been used. Various imides as well as PPS, PEK, PEEK, PSU, PEEKK, and PPSU can also be used [190,191].

1.5.4 Organic–Inorganic Composites

Various polymeric ionomers were blended with porous inorganic powders. The prepared hybrids were used for the preparation of relatively thick membranes for FC. By adding 3% metal oxide to the commercial 5% Nafion® solution, mixed with an equal volume of isopropyl alcohol, 125 μm thick composite membranes were prepared after stirring the suspension for about 3 h. They were dried overnight. Crude membranes were treated with H_2O_2 and 1 N H_2SO_4. After the treatment, they were immersed in boiling water to remove organic impurities, oxide impurities, and residual acid. Such composite membranes prepared with 0.2–0.3 μm particles of SiO_2 did not show any significant change in their resistance at 130 °C when RH of the reacting gases was decreased from 100 to 75% humidity. Composites with the acid-treated, degassed TiO_2 behaved in the same way. Such membranes could be used in PEMFCs operated above 90 °C [192]. A nanocomposite membrane based on PVDF filled with Al_2O_3 and immersed in aqueous poly(2-acrylamido-2-methyl propylene sulfonic) acid (PAMPS) showed high thermal stability (it started to degrade around 300 °C), reasonable conductivity at RT (0.02 S/cm at 16% of Al_2O_3), and low permeability to methanol. It is believed by its investigators to be a good candidate for DMFC [193].

Some hybrid membranes prepared by mixing various polymeric ionomers with Al_2O_3 or with SiO_2 ceramic powders were described in Ref. [194]. Some improvements due to the mixing of PVDF with Al_2O_3 were noted. However, neither proton conductivity nor permeability to methanol changed dramatically as a result of such treatment [194]. The proton conductivity of hybrids prepared by mixing sPEEK with a zeolite did not exceed 8 mS/cm, even at 140 °C [195].

1.6 TESTING OF PEMs

During the last 2 years, the performance of the perfluorosulfonic acid PEMs, its instabilities, water absorption, diffusion, and activities of water in it as well as effects due to chain flexibility were investigated by several research teams [196–200]. Thermal and hydrolytic stability of sulfonated polyimides was investigated by Han and coworkers [201].

Durability of such membranes was evaluated and compared with Nafion® by Watanabe and coauthors [202]. This research group also investigated the durability of a sulfonated poly(arylene ether) membrane [203]. The durability of perfluorinated membranes was also investigated by Schiraldi [204]. Aging mechanism of sulfonated polyimides was investigated and their lifespan estimated by Perrot et al. [205]. Degradation of sPEEK and sPU membranes by hydroxy radicals was investigated by Panchenko [206], and decomposition of pefluorosulfonic acid electrolyte was investigated by Watanabe and coauthors [203]. Long-term performance of the commercially available PEMFCs was tested by Cleghorn et al. [207]. Effects of gas dilution on the performance and impedance response of commercially available PEMFC were discussed at a meeting dedicated to electroosmotic coefficient and were determined by Yi and coauthors [208].

Water transport in PEMFC was analyzed by NMR [209]. Water saturation of PEMFC was quantified by X-ray microtomography [210]. An electrode/Nafion® interface was investigated *in situ* by surface-enhanced FTIR [211]; flow phenomena in PEMFC were studied by neutron imaging [212]; ultrafast magic angle spinning NMR was used in the study of the effect of hydrogen bonding on proton conductivity of phosphoric acid attached to decane-1,10-(1-*H*-imidazol-5-yl) [213].

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