Preface

Fuel cell is considered to be one of the most promising clean energy sources since it does not generate toxic gases and other hazardous compounds. It is currently an important research topic in all leading automobile and energy industries. Fuel cells will provide an urgently needed solution to the increasing impact of vehicles pollution. Among various kinds of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) are easy to be miniaturized and suited as energy sources for automobiles as well as domestic applications and potable devices. Fuel cell is also currently considered as reaching the threshold of commercialization. The center of PEMFC is the polymer electrolyte membrane, as it defines the properties needed for other components of fuel cell and is the key component of a fuel cell system. The membrane component of a fuel cell stack may account for as much as 30% of the total material cost. Their properties are paramount to the successful operation and commercialization of fuel cells. The most widely used solid polymer electrolyte membranes in fuel cells are perfluorosulfonic acid membranes such as Nafion, Acipex and Flemion. However, they have some drawbacks that should be overcome before their practical applications will be achieved. The most significant drawbacks of these membranes are their relatively high cost in the range of US $ 800/m^2, and their limited stability at temperatures substantially in excess of 100°C. Moreover, there is a problem of methanol crossover when used in direct methanol fuel cell. Hence, there is a need to develop less expensive polymeric membranes with improved performance. More specifically, it is currently targeted to develop membranes with high proton conductivity (above 10^{-2} S cm^{-1} at 120°C), preventing excessive methanol crossover, and with durability of 5000 hours for transportation and 4000 hours for stationary devices.

During the past two decades many attempts have been made all over the world to improve the performance of presently available membranes and develop new ones for PEMFC. The fuel cell membrane field is growing with such a fast pace that it will emerge as one of the most important membrane technologies. A literature search on fuel cell membranes over the years 1990–2006 revealed more than 2500 patents only in addition to thousands of journal publications, which clearly indicate the importance of the subject. It seems most timely to summarize the results of such research efforts. Hence, this book is focused on the development of polymeric and polymeric/inorganic hybrid membranes for PEMFC.

Although each chapter is independent from the other chapters, attempts were made to give some cohesiveness between chapters.

The first five chapters are general description of the strategies adopted to improve the membrane properties and status of the PEMFC technology.

Chapter 1 and 2 outline the principle of PEMFC and its desired properties. The general trend in recent R & D efforts and the future outlook is also summarized. It would be a good start to read these two chapters before entering any other chosen chapter.

Chapter 3 presents an overview of fuel cell technology, potential applications of fuel cell technology, current research and development in fuel cells, key technology players in fuel cells, and provides directions for fuel cell research.

Chapter 4 presents an overview of the synthesis, chemical properties, and polymer electrolyte fuel cell applications of new proton-conducting polymer electrolyte membranes based on sulfonated poly(arylene ether ether ketone) polymers and copolymers.

In chapter 5, a comprehensive review was made of the attempts to prepare alternative proton conductive membranes (PCMs) by radiation-induced graft polymerization.

Chapters 6 and 7 deal with the hydrocarbon polymers and composites targeted for high temperature PEM fuel cell applications. Specifically, chapter 6 deals with a series of high molecular weight, highly sulfonated poly(arylenethioethersulfone) (SPTES) polymers synthesized by polycondensation. They were characterized by different methods and tested for proton conductivity. Finally, membrane electrode assemblies (MEAs) were fabricated.

Chapter 7 emphasizes polymer/inorganic composite membranes to increase thermal stability. More specifically, polymers include perfluoronated polymers, sulfonated poly(arylene ether)s, polybenzimidazoles (PBIs), and others. The inorganic proton conductors are silica, heteropolyacids (HPAs), layered zirconium phosphates, and liquid phosphoric acid.

In the next five chapters more specific classes of macromolecules and other materials are shown for the design of improved PCMs.

Chapter 8 describes a strategy to improve the membrane properties by blending polymer electrolytes with other polymers. Different types of interactions are involved when cross-linking between polymers is formed.

In chapter 9 the general strategy involved in the preparation of organic-inorganic membranes for fuel cell applications is described and its advantages and disadvantages are discussed.

In Chapter 10 efforts have been made to highlight the response of thermal and mechanical properties with variation of different parameters characteristic of a typical fuel cell environment.

Chapter 11 also includes the polymer inorganic membranes consisting of Nafion and zirconium phosphates, heteropolyacids, metal hydrogen sulfates and metal oxides. Moreover, this chapter includes the design of thin film electrodes for MEA.

Chapter 12 deals with carbon nanotube (CNT) filled membranes for PCMs. CNT-filled polyethylene terephthalate was blended with various polymers, injection molded and characterized by different methods.

The next four chapters are for direct methanol fuel cells (DMFC).

In Chapter 13 critical issues for the commercialization of DMFCs are discussed thoroughly. Functions, current status and technical approaches have been discussed in terms of proton conductivity, methanol permeability, water permeability, life cycle and processing cost as well as the interaction with other compartments.

Chapter 14 presents a brief literature survey of such modifications, along with recent experimental results (membrane properties and fuel cell performance curves) for: (i) thick Nafion films, (ii) Nafion blended with Teflon®-FEP or Teflon®-PFA, and (iii) Nafion doped with polybenzimidazole.

Chapter 15 is a general overview of DMFC research to develop membranes with low methanol permeability without sacrificing other important qualities.

Chapter 16 presents a unique membrane design and development using the concept of pore-filling. The membranes are used for both polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).

And finally, chapter 17 was written to summarize the whole chapters. Attempts were also made to show the future direction of the fuel cell R & D.

The editors believe that this book is the first book exclusively dedicated on fuel cell membranes in which the experts of the field are brought together to review the development of polymeric membranes for PEFC in all their aspects. The book was written for engineers, scientists, professors, graduate students as well as general readers in universities, research institutions and industry who are engaged in R & D of synthetic polymeric membranes for PEMFC. It is therefore the editors' wish to contribute to the further development of PEMFC by showing the future directions in its R & D.

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Chapter 2
Research Trends in Polymer Electrolyte Membranes for PEMFC

S.M. Javaid Zaidi

Abstract In this chapter research trends followed by various scientific groups for the development of polymeric membranes have been described and reviewed. Most notably, the developments made at Ballard Advanced Materials (BAM) and some of their results are discussed. In general three different approaches have been followed worldwide by various research groups for the development and conception of alternative membranes. These approaches include: (1) modifying perfluorinated ionomer membranes; (2) functionalization of aromatic hydrocarbon polymers/membranes; and (3) composite membranes based on solid inorganic proton conducting materials and the organic polymer matrix or prepare acid-base blends and their composite to improve their water retention properties. The current trend is for the composite and hybrid membranes, which combines the properties of both the polymeric component and inorganic part. The most widely studied polymer after Nafion is the sulfonated polyether-ether ketone (SPEEK), as it has a high potential for commercialization. A number of research projects are currently undergoing dealing with the SPEEK polymer in various research labs.

2.1 Introduction

Fuel cells have been in development for over 150 years, ever since their invention in 1839 by William Robert Grove. The fuel cell became a real option for a wider application base in the late 1980s and early 1990s, although structural improvements are still needed to accommodate the increasing demands of fuel cell systems for specific applications. The research in this area gained momentum in the 1980s due to increased awareness of energy and environmental concerns. Also, some pivotal innovations (e.g., low platinum catalyst loading, thin film electrodes) drove down the cost of the fuel cell, which made the development of PEMFC more realistic.

The center of the fuel cell is the polymer electrolyte membrane, as it defines the properties needed for other components of the fuel cell. However, fuel cells' efficiency and power density also strongly depend on the conductance of electrolytes, and only acidic electrolyte can be used to aid carbon dioxide rejection for DMFC. The performance of polymer electrolyte fuel cells is closely related to the

performance of MEA. The price of MEA ranks first in market position, roughly 75% of the overall price of PEMFC. Historically, the progress in PEMFC performance in terms of efficiency and lifetime was related to the development of proton-conducting membranes. Currently, efforts concentrate on the development of new proton-conducting polymer membranes, although a large number of scientific contributions still deal with Nafion membrates.

The desired properties for a membrane to be used as a proton conductor in a fuel cell are listed in the following:

 1. Chemical and electrochemical stability in fuel cell operating conditions
 2. Elevated proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity
 3. Good water uptakes at high temperatures of approximately 100°C
 4. Thermal and hydrolytic stability
 5. Chemical properties compatible with the bonding requirements of membrane electrode assembly
 6. Extremely low permeability to reactant species to maximize efficiency
 7. Mechanical strength and stability in the operating conditions. (The membrane must be resistant to the reducing environment at the anode as well as the harsh oxidative environment at the cathode.)
 8. Resistance of fuel transport through it. (This is a concern in a DMFC, in which methanol crossover takes place, and gets oxidized at the cathode. This reduces the cell voltage by formation of mixed potential at the cathode.)
 9. High durability
10. Facilitation of rapid electrode kinetics
11. Flexibility to operate with a wide range of fuels
12. Production cost compatible with the commercial requirements of the fuel cell

In addition to the preceding properties, hydration of the membrane (water management) and thickness also play important roles in affecting the overall performance of fuel cells.

The advances made in fuel cell performance have been closely associated with advances in polymer electrolyte technology. Until now, perfluorinated ionomer (PFI) membranes, Nafion (DuPont de Nemours), and Dow membranes (Dow Chemical Co.) have been useful in practical fuel cell systems and are currently the only ones being used commercially. The performance of Dow membranes is superior to that of Nafion 117, but they are more expensive than Nafion. In spite of the outstanding properties of these membranes, such as high proton conductivity and high chemical inertness, these membranes cost US$800–2,000 m^{-2} and suffer from serious drawbacks, such as high methanol permeation and water balance problems. Moreover, lack of safety during manufacturing and use, requirements of supporting equipment, and temperature-related limitations are some other drawbacks. Degradation of Nafion membranes at high temperatures is a serious drawback. Conductivity at 80°C is reduced by more than 10-fold relative to that at 60°C. Safety concerns rise from evolution of toxic intermediates and corrosive gases liberated at elevated temperatures above 150°C. Degradation products could be a

concern during the manufacturing process or vehicle accidents and could limit fuel cell recycling options [1]. Thus PFI membranes, which have a number of limitations, are not the ideal choice today, and their cost is a major drawback for the commercialization of PEMFC and DMFC technology. For fuel cells to be commercially feasible for transportation devices, the projected membrane cost has to be reduced significantly, to a range of US$5–15 ft^{-2}.

Thus began the search for an alternative low-cost polymer material. The current challenge is to improve the membrane properties in terms of thermal stability and proton conductivity while reducing methanol crossover. This may be achieved by the creation of new low-cost membranes. It has been mentioned by Smitha et al. [1] in their study that Gilpa and Hogarth identified 60 alternatives to the PFI membranes. Among these, 15 membranes showed potential for replacing Nafion membranes. To develop new polymer membrane with similar and improved properties by a less expensive route, the properties of Nafion polymers need to be understood; consequently, research on Nafion membranes was carried out.

2.2 Early Developments: Nafion Membranes

The concept of using ion exchange membranes as electrolytes was first reported by General Electric (GE) in 1955. The idea of using organic cation exchange membranes as solid electrolytes was first described by William Thomas Grubb and Lee Niedrach in 1959. NASA's interest in fuel cells as power sources for space applications gave great impetus to polymer fuel cell development with the testing of phenolic membranes [2]. These membranes showed power densities of 0.05–0.1 kW m^{-2} and lifetimes of 300–1,000 h, as well as low mechanical strength. Later on, GE improved the power density by developing partially sulfonated poly(styrene sulfonic acid) membranes, which showed improved power densities of 0.4–0.6 kW m^{-2}. The first PEMFC used in an operational system was built by GE as a primary power source for the GEMINI series of spacecraft during the mid-1960s [3]. It was a 1-kW power plant. At that time extremely expensive materials were used and the fuel cells required very pure hydrogen and oxygen. The polymer membranes used as electrolytes were based on poly(styrene sulfonic acid). However, these membranes exhibited brittleness in the dry state and were later replaced with cross-linked polystyrene-divinyl benzene sulfonic acid membranes. This material also lacked stability and underwent degradation and suffered other problems. Also, the main problem encountered with these membranes was that proton conductivity was not sufficiently high to reach a power density even as low as 100 mW cm^{-2}. Therefore, in 1966 they were replaced by PFI Nafion membranes; this was a real breakthrough in membrane developments for PEM fuel cells. At this early stage of development the most improved membranes showed lifetimes of up to 3,000 h at low current densities and temperatures of 50°C [4, 5]. The demonstrated cell life as a function of operating temperature of various membranes is illustrated in Fig. 2.1 [4, 5]. Results are also given for a perfluorosulfonic acid membrane Nafion. The
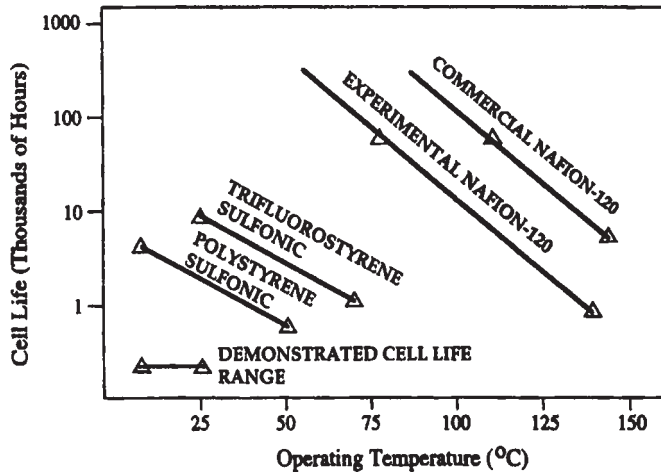
Fig. 2.1 PEM fuel cell life capacity [4]. (With the permission of Prof. Savadogo, editor and publisher of the Proceedings of the First International Symposium of New Materials for Electrochemical Systems, Montreal, Canada, 2005.)

most commonly used membrane is Nafion, which relies on liquid water for humidification of the membrane to transport proton. Nafion possessed inherent chemical, thermal, and oxidative stability and it displaced the unstable polystyrene sulfonic acid membranes. The advent of Nafion in the late 1960s gave an impetus to the PEM industry. The second GE PEFC unit, a 350 W module, powered the Biosatellite spacecraft in 1969. An improved DuPont manufactured Nafion membrane was used as an electrolyte. Nafion, a sulfonated tetrafluorethylene copolymer discovered in the late 1960s by Walther Grot (DuPont) [6], is the first of a class of synthetic polymers with ionic properties called ionomers. From the late 1960s onward, membrane requirements were best met by the Nafion family of membranes. Nafion's unique ionic properties result from incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone. Nafion received considerable attention as a proton conductor for PEM fuel cells because of its excellent thermal and mechanical stability. Nafion is a perfluorosulfonic acid (PFSA) membrane, chemically synthesized in four steps according to the DuPont process [7].

It is similar to Teflon, to which sulfonic acid groups are attached. The acid molecules are fixed to the polymer and cannot leak out, but the protons of these acid groups are free to migrate through the membrane. The chemical structure of Nafion is in Fig. 2.2.

With commercial Nafion 120, a lifetime of over 50,000 h has been achieved [7]. Nafion 120 has an equivalent repeat unit molecular weight of 1200 (x = 6–10 and y = z = 1) and a dry state thickness of 260 μm, whereas Nafion 117 and 115 have equivalent repeat unit molecular weights of 1,100 and thicknesses in the dry state of 175 and 125 μm, respectively. The Nafion family of membranes extended the lifetime by four orders of magnitude, and soon became standard for PEMFC, which it remains to this today. The Dow and Asahi Chemical companies also synthesized
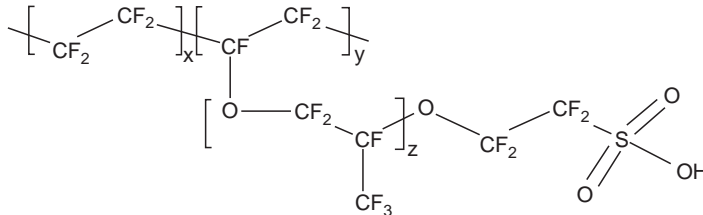
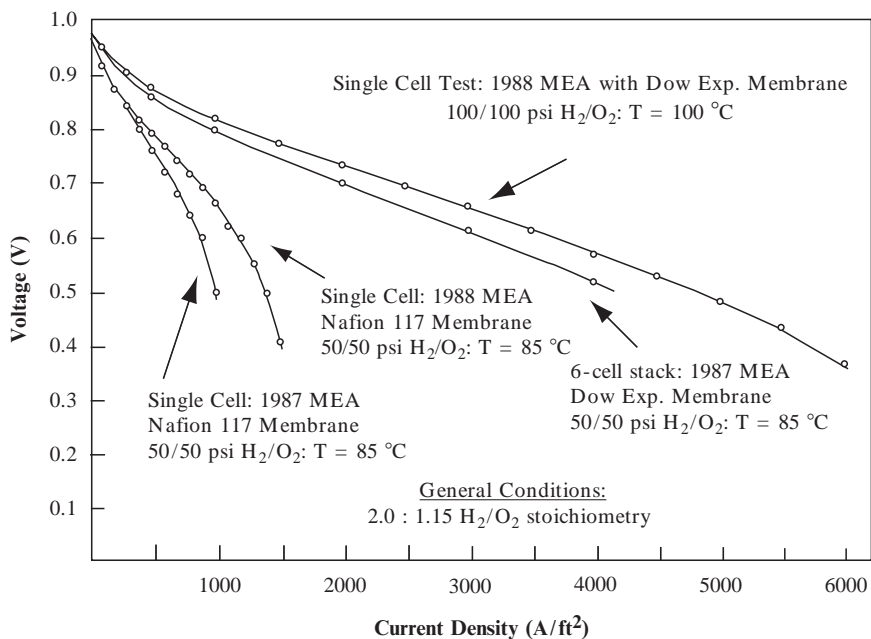**Fig. 2.2** Chemical structure of PFSA Nafion membrane

Fig. 2.3 Polarization data for Nafion and Dow membranes in Ballard Fuel cells. (With the permission of Prof. Savadogo, editor and publisher of the Proceedings of the First International Symposium on New Materials for Electrochemical Systems, Montreal, Canada, 2005.)

advanced perfluorosulfonic acid membranes with shorter side chains. The Dow polymer membrane has higher conductivity than Nafion. The Dow membranes are structurally and morphologically similar to Nafion membranes, but differ with respect to their lower equivalent weights, which are typically in the range of 800–850, and have shorter side chains (Dow $z = 0$, Nafion $z = 1$). The conductivity of 800 and 850 EW Dow membranes have been reported to be 0.2 and 0.12 S cm^{-1} [7, 8]. The best performance of Nafion in a six-cell MK 4 stack was 0.5 V at 1,400 A ft^{-2}, whereas the best performance of the DOW membrane was 0.5 V at 5,000 A/ft^2 as shown in Fig. 2.3 Although the large-side chain-perfluorinated polymer electrolytes

prolonged service life, there is no large-scale industrial electrochemical system using Dow membranes. Asahi Glass Company developed Flemion R, S, T, which has equivalent repeat unit molecular weights of 1,000 and dry state thicknesses of 50, 80, 120 μm, respectively.

2.3   Ballard Advanced Material Membranes

The research efforts made at Ballard Power Systems for the development of low cost PEM membranes for fuel cell are encouraging. These membranes are the only ones among membrane development works which have gone through extensive testing in different fuel cell configurations. Ballard Advanced Materials (BAM) developed a series of membranes and designated them as BAM1G, BAM2G, and BAM3G—first-, second-, and third-generation BAM membranes, respectively. The BAM1G membranes were based on poly(phenylquinoxalene) (PPQ) polymers [4, 5]. The performance evaluation carried out in experimental size Ballard MK4 fuel cell with an active area of 50 cm^2 operated on air/hydrogen at 24/42 psig and at 70°C showed that BAM1G membranes of 39–420 EW are comparable to Nafion 117 membranes or are even better. However BAM1G membranes showed finite lifetime in an operating fuel cell when run at a constant 500 A ft^{-2} at 70°C. In all the longevity evaluations performed with BAM1G, the average time to failure was 350 h. This is particularly low compared with Nafion membranes, which show a lifetime of more than 10,000 h [8].

To overcome this problem, a second generation of polymer membrane known as BAM2G was developed, based on poly(2,6-diphenyl-4-phenylene oxide). They exhibited good mechanical properties in the dehydrated state, but for membranes less than 450 EW the hydrated membrane showed less than optimum resistance to tearing and tensile strength properties. These membranes showed superior performance to BAM1G and to both Nafion 117 and Dow membranes at current densities above 600 A ft^{-2} [Fig. 2.4]. However, these membranes also suffered from limited longevity and their operation lifetime was restricted to 500–600 h. The root cause of failure was attributed to internal transfer of reactant gases across the membrane electrode assembly.

Using α, β, β-trifluorostyrene (TFS), a novel family of sulfonated copolymer incorporating TFS series and a series of substituted TFS comonomers provided the group of materials referred to as BAM3G. Their performance was evaluated in a standard membrane electrode assembly (MEA) in an experimental size Ballard MK4 single cell hydrogen/air fuel cell at 85°C with an active area of 50 cm^2. These membranes maintained high efficiency as that of BAM2G and increased lifetime. The longevity achieved from these new membranes exceeded 15,000 h of operation. These BAM3G membranes are still in the testing stage and have not yet been commercialized as low-cost PEM membranes, so their cost information is not available, only some projections are there. Also, their performance in a DMFC, and the permeation behavior of methanol through these membranes are not known.
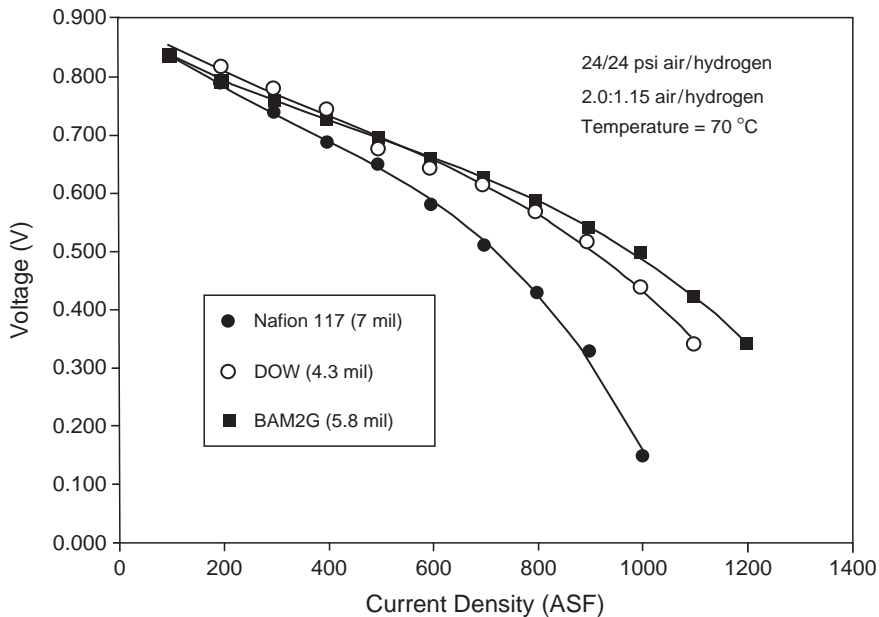
Fig. 2.4 Polarization data for Nufion 117, Dow, and BAM2G. (With the permission of Prof. Savadogo, editor and publisher of the Proceedings of the First International Symposium on New Materials for Electrochemical Systems, Montreal, Canada, 2005.)

Moreover, BAM3G being a fluorinated product will not be environmentally friendly, as when mass produced these membranes will pose a problem for their safe disposal. Apart from that, a great deal of information relating to their ionic conductivity, thickness, exact chemical composition, and mechanical strength, hydraulic permeation is proprietary and is not available in the literature.

2.4   Modification of Nafion Membranes

Some of the pioneering works will be discussed here, with important results reported in the literature. Primarily attempts have been made to modify the morphology of Nafion membranes themselves by using different processes such as plasma etching and palladium sputtering to modify the Nafion membranes. Plasma etching of Nafion membranes increases the roughness of the membrane surface and decreases the methanol permeation. The sputtering of palladium on plasma-etched Nafion further decreased methanol permeation. Apart from the decrease in methanol permeation, the open circuit voltages and current-voltage performance of fuel cells fabricated with membranes which had undergone plasma etching and palladium sputtering were also improved significantly.

Compositing Nafion polymer with various inorganic materials, such as zirconium phosphate, boron phosphate, and heteropolyacids at high temperature has been reported and tested. Composite membranes thus prepared at operating temperatures up to about 150°C with dry oxidant, under mild preheating conditions (85°C) showed better performance in DMFC. Typical cell resistances of 0.08 Ω-cm^2 were observed under cell operation at 140–150°C [6, 9, 10]. Composite membranes of Nafion with silicon oxide for use in fuel cell operating at 80–140°C were also reported in literature. The membranes showed better water retention, proton conductivity at elevated temperatures, and thermomechanical stability were also improved as compared with unmodified Nafion membranes [11–13]. Further, hybrid Nafion-silica membranes doped with heteropolyacids for application in direct methanol fuel cells have also been reported. Nafion-silica composite membranes doped with phosphotungstic and silicotungstic acids showed better performance at higher temperatures for DMFC operations at 145°C. These membranes showed significant enhancement in the operating range of a direct methanol fuel cell; also, the kinetics of methanol oxidation was improved due to high temperature operation [14].

Savadogo and Tazi prepared and studied Nafion composite membranes with the help of Nafion and heteropolyacids. The heteropolyacids used in this study were silicotungstic acid, phosphotungstic acid, and phosphomolybdic acid. The ionic conductivities of composite membranes were found to be higher than those of pure Nafion membranes. The composite membrane prepared from Nafion and silicotungstic acid was found to be most conductive of all other membranes prepared [15]. In another study, Ramani et al. has prepared and investigated Nafion/HPA composite membranes for high temperature and low relative humidity fuel cell operation. The decomposition temperature of the composite membrane was extended to 150°C, permitting more stringent operating conditions. The protonic conductivities of the composite membranes at 120°C and 35% RH were on the order of the 0.015 S cm^{-1} [13, 16]. The HPAs were water soluble and studies of their long-term stability in the membrane matrix were not investigated.

Tricoli and Nanetti [17] prepared a novel zeolite-Nafion composite membrane by embedding zeolite fillers in Nafion. The zeolites used in this study were chabazite and clinoptilolite. The presence of zeolites in the membranes caused notable changes in conductivity, methanol permeability, and selectivity with respect to pure Nafion. In another interesting study, Holmberg et al. synthesized and characterized zeolite-Y nanocrystals for Nafion-zeolite-Y composite proton exchange membranes. The composite membranes were found to be more hydrophilic and proton conductive than the base-unmodified membranes at high temperatures [18].

Blending Nafion polymer with other polymeric materials has also been tried by some researchers. In one such study, poly(1-methylpyrrole) has been impregnated with commercial Nafion membrane by in situ polymerization. A decrease of more than 90% in the permeability of the membranes to methanol is reported, although the ionic resistance of such heavily loaded membranes became too high for high-power fuel cells. At lower poly(1-methylpyrrole) loadings, a decrease in methanol permeability by as much as 50% could be realized without a significant increase in ionic

resistance [19]. In another study Nafion/polytetrafluoroethylene (PTFE) membranes have also been prepared using porous PTFE membranes as support material. The membranes were synthesized by impregnating porous PTFE membranes with Nafion solutions. Resulting membranes were found to be mechanically and thermally stable. The composite membranes thus prepared were also cost effective [20, 21].

Membrane prepared by blending sulfonated polybenzimidazole (PBI) with Nafion polymer showed a conductivity of 0.032 S cm^{-1}. The methanol permeability of the composite membrane was found to be 0.82×10^{-6} cm^2 s^{-1} as compared to Nafion, which is around 2.21×10^{-6} cm^2 s^{-1} [22]. Addressing the problem of methanol permeation, a composite membrane of Nafion with polyvinyl alcohol (PVA) for direct methanol fuel cell has been reported. It is concluded that at the weight ratio of 1:1 in PVA and Nafion, the thin film-coated Nafion membrane exhibited low methanol crossover, and the membrane protonic conductivity could be improved by the sulfonation treatment [23]. Recently, Zaidi et al. [24] prepared composite membranes of PFSA ionomer with boron phosphate and showed the conductivity of 6.2×10^{-2} S cm^{-1} at 120°C.

2.5 Hydrocarbon Composite Membranes

The approach of making composite membranes from the inorganic modification of the polymer matrix has gained momentum recently due to the exemplary success achieved by some people working on this approach. The composite membrane approach represents one of the ways to improve the properties of the polymer electrolyte membranes as the desired properties of the two components can be combined in one composite. Various polymers have been used in this approach with different inorganic materials. One of the important polymers that has drawn much attention is the sulfonated polyether ether ketone (SPEEK) polymer whose structure is shown in Fig. 2.5. SPEEK falls into the category of aromatic sulfonic acid polymers. Its advantages include low methanol permeation, high conductivity, and very good mechanical properties. Good mechanical stability provides the membrane enough flexibility, thus making the membrane thin enough to decrease the resistance offered by the thickness of the membranes [25–27].

SPEEK polymer is supposed to be a noble substitute to Nafion membranes as far as its use in DMFC is concerned. SPEEK has potential to substitute Nafion membranes but only after modification of certain properties. Mainly these properties include protonic conductivity of SPEEK membranes as compared with Nafion membranes; otherwise, SPEEK has comparable methanol permeation, high temperature stability, and low cost as compared with commercial Nafion membranes. The
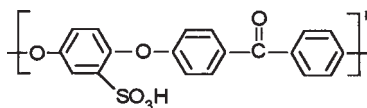

Fig. 2.5 Chemical Structure of SPEEK

electrochemical properties of a series of composite membranes prepared by incorporation of boron phosphate into the polymeric matrix of SPEEK were studied. The proton conductivity of the composites was found to be higher than the pure SPEEK polymer. The mechanical stability was also in the satisfactory range for use in DMFC at moderately high temperatures [26, 28].

SPEEK polymer was blended with the polyetherimide (PEI) polymer and then doped with HCl and H_3PO_4 to get a better solution to the DMFC problem. Results with these membranes had mixed success. Doping of HCl was found to be more significant than that of H_3PO_4 [29]. Protonic conductivity increased moderately with boron phosphate and PEI, but the incorporation of various heteropolyacids into the SPEEK structure increased proton conductivity significantly. Room temperature conductivities on the order of 10^{-2} S/cm were reported, while the conductivity values were raised up to 10^{-1} s cm^{-1} with the same composite membrane at high temperatures of around 100°C. The composite membranes were found to be thermally stable up to 250°C [25]. Although these composite membranes showed high conductivities at elevated temperature, they had the problem of leaching of the solid heteropolyacids (HPAs). The problem of the high leaching of HPAs was found to be a detriment to the long-term use of these membranes. In order to avoid the problem of leaching, HPAs are loaded onto molecular sieve zeolite Y and mesoporous MCM-41, respectively, so that the HPAs incorporated onto these molecular sieves does not leach out of the structure. These HPA-loaded molecular sieve Y-zeolite and HPA-loaded molecular sieve MCM-41 powdered solids are embedded into SPEEK polymers to make composite membranes. These membranes exhibited conductivities on the order of 10^{-2} s cm^{-1} at 140°C and were found to be thermally and mechanically stable [30, 31].

Zirconium oxide-modified SPEEK membranes have been proposed recently for direct methanol fuel cell applications. The zirconium oxide modification affected its water swelling, chemical and mechanical stability, methanol and water permeations and, finally, proton conductivity. Depending on the amount of the inorganic component in the membrane, a good balance between high proton conductivity, good chemical stability, and low methanol permeability could be reached [32, 33]. Composite polymer membranes have prepared by embedding layered silicates (laponite and montmorillonite) into SPEEK. While the SPEEK polymer contributed partially to conductivity, layered silicates incorporated into SPEEK significantly helped to reduce swelling in hot water. Also, methanol crossover was reduced without an alarming reduction in the proton conductivity [34].

New organic-inorganic composite membranes based on sulfonated polyetherketone (SPEK) and SPEEK were synthesized with SiO_2, TiO_2, and ZrO_2. The modification of SPEK and SPEEK with ZrO_2 reduced the methanol flux by 60-fold. On the other hand, there was a big compromise on conductivity, which was reduced by 13-fold, while modification of PEK and SPEEK with silane (SiO_2) led to a 40-fold decrease of water permeability without a large decrease of protonic conductivity [35]. With some encouraging results of the modification of PEK with SiO_2, TiO_2, and ZrO_2, modification of PEK with heteropolyacid further yielded some notable results. Actually the composite membranes were prepared using an organic matrix

of SPEK, different heteropolyacids, and an inorganic network of ZrO_2 and $RSiO_{3/2}$. The bleeding out of the heteropolyacid from the membranes was also measured, in addition to water and methanol permeation and protonic conductivity tests. The presence of ZrO_2 decreased water and methanol permeability and reduced the bleeding out of heteropolyacid [36].

Apart from SPEEK polymers, some other polymer materials have also been used in order to get the appropriate candidate material for DMFC applications. Sulfonated poly(arylene ether sulfone) polymer has been incorporated with HPA. The membranes thus prepared showed excellent thermal stability (about 300°C) and good proton conductivity, especially at elevated temperatures (130°C). Infrared and dynamic thermo-gravimetric data showed that the composite membrane had much higher water retention (100–280°C) than pure sulfonated copolymer. These results also suggested that the incorporation of HPA into these proton-conducting copolymers should be good candidates for elevated temperature operation of DMFC [37]. However, these membranes showed bleeding out of heteropolyacids into the poly(arylene ether sulfone) polymer matrix. Novel composite membranes based on PVA with embedded phosphotungstic acid were prepared and measured for their protonic conductivity and methanol permeation. A marginal conductivity of the order of 6.27×10^{-3} S cm^{-1} was obtained, while the values of methanol permeation were found to be in the range of 1.28×10^{-7} and 4.54×10^{-7} cm^2 s^{-1}. From the values for methanol permeation obtained, these composite membranes had the potential to use them in direct methanol fuel cell [38].

Polybenzimidazole doped with phosphoric acid has been used to prepare the composite membranes with inorganic proton conductors such as zirconium phosphate, phosphotungstic acid, and silicotungstic acid. The conductivity of the phosphoric acid–doped PBI and PBI composite membranes was found to be dependent on the acid doping level, relative humidity (RH), and temperature [29, 39]. Apart from the direct incorporation of one component into another, a new synthetic route to synthesize organic/inorganic nanocomposites hybrid polymer membrane using SiO_2 and polymer such as modified PBI, polyethylene oxides, polypropylene oxide, polyvinylidene fluoride, etc., the composite membranes was prepared through sol-gel processes. The methanol permeation through the membranes decreased significantly and membranes showed excellent proton conductivity [40].

Different hybrid membranes with the help of inorganic/organic or organic/organic components have been reported in literature with some exciting results. Hybrid polyaryls ether ketone membranes with the help of zirconium phosphate and modified silica have been prepared and characterized for fuel cell applications. The examples were chosen to illustrate the in situ formation of inorganic particles, either on a prepared membrane, or in a polymer solution. SPEEK modified silica and SPEEK zirconium phosphate membranes provided power densities of 0.62 W cm^{-2} at 100°C. In all cases, the presence of the inorganic particles led to an increase in proton conductivity of the polymer membrane, without any harm to its flexibility [41, 42]. Zirconium carboxybutylphosphonate was synthesized to prepare inorganic/organic composite membranes based on PBI. The membrane thus prepared showed promising performance and relatively high protonic conductivities under the given

conditions. Membranes were also highly thermally stable [43]. A series of organic/ inorganic composite materials based on polyethylene glycol (PEG)/SiO_2 for use as electrolytic membrane in DMFC have been synthesized through sol-gel processes. Acidic moieties of 4-dodecylbenzene sulfonic acid (DBSA) were doped into the network structure at different levels to provide the hybrid membrane with proton conducting behavior. An increasing trend of proton conductivity with increasing DBSA doping was obtained, while the presence of an SiO_2 framework in the nanocomposite hybrid membrane provided enhanced thermal stability. Some of the hybrid membranes exhibited low methanol permeability without sacrificing their conductivities significantly, and were thus proposed to be potentially useful in DMFC [44].

The blending of two organic components to get a hybrid membrane has always been a point of attraction for almost all researchers. Basically the flexibility of playing with the microstructure of the organic polymer candidates and easy handling have paved the way to explore a suitable hybrid membrane. As in one study, novel acid-base polymer blends have been characterized for application in membrane fuel cells. The membranes synthesized are composed of SPEEK Victrex or polyether sulfone (PES) as well as sulfonated polysulfone (sPSU) Udel as the acidic compounds, and of PSU CELAZOLE, or poly(ethyleneimine) PEI (Aldrich) as the basic compounds. The membrane showed good proton conductivities and excellent thermal stabilities and showed good performance [45]. In another contribution, different types of acid-base composite membranes have been prepared and characterized for their use in DMFC at high temperatures. In this study, sulfonated polyetherketone and sulfonated polysulfone are used as acidic blend components, while $PSU(NH_2)_2$, poly (4-vinylpyridine), and polybenzimidazole are used as basic components [46]. Multilayered polyphosphazene membranes have been suggested as a new series of hybrid membranes, with improved protonic conductivity and low methanol permeation. A phosphagenic polymer was used for membrane synthesis, in which the polyphosphazene was sulfonated, blended with an uncharged polymer, and then cross-linked. Poly[bis(3-methylphenoxy)phosphazene] has also been reported as a promising material for fuel cell applications. Polymer cross-linking was carried out by the use of UV light and photoinitiator. The results showed that there was a significant decrease in methanol crossover (the methanol flux was about 10 times lower than Nafion 117) [47]. Membranes from polybenzimidazole/ sulfonated polysulfone have been studied and compared with homopolymer membranes made from sulfonated polysulfone, blends of polyether sulfone with sulfonated polysulfone, and Nafion 117. Also an improved behavior of these membranes toward methanol permeation was observed [48]. In another study, blended membranes were prepared by the blending of SPEEK and polyether sulfone. The transport properties of membranes with SPEEK content in the range of 50–80 wt% were found to be comparable to those known for commercial ion exchange membranes [49].

Novel methanol barrier polymer electrolyte membranes for direct methanol fuel cells were proposed and characterized from PVA blend–polystyrene sulfonic acid (PSSA). The effects of curing temperature, methanol concentration, and membrane composition on the ionic conductivity and the methanol permeability of the membranes were also investigated [50]. In an interesting study, a new proton exchange

membrane from the sulfonation of poly(phthalazinone ether ketone) has been synthesized. Membrane performances were directly related to the degree of sulfonation (DS). Proton conductivity increased with degree of sulfonation and temperature up to 95°C, reaching up to 10^{-2} S cm^{-1} [51]. Composite membranes were synthesized with the help of polyvinyl alcohol membranes loaded with mordenite or tin mordenite. It was observed that a single layer of these materials had poor mechanical strength with noticeable cracks and also with poor conductivity, but some encouraging results were obtained when they sandwiched these layers, and membranes were prepared with many layers of the polyvinyl alcohol and tin mordenite [52].

2.6   Other Relevant Developments in the Last Decade

Several studies reported the preparation of membranes for PEM fuel cells by the radiation grafting technique. Most of these studies involve grafting of styrene or α, β, β-trifluorostyrene on to a fluorine-containing polymer, followed by sulfonation of the grafted film. The results obtained are encouraging, but these membranes are partially fluorinated and are not environmentally friendly. Furthermore, these membranes showed good performance in hydrogen fuel cells, but no information is available for methanol fuel cell. The sulfonic acid-based polymer membranes prepared by Lee et al. [53] showed a specific resistivity of 24 Ωcm, which is comparable to Nafion 117 (16 Ωcm). The data for stability of these membranes are not available and these are not tested in actual fuel cells, so nothing can be said about their long-term stability and methanol permeation [54].

Membranes having grafted poly(styrene sulfonic acid) and three different backbone polymers, and low-density polystyrene, poly(tetrafluoroethylene), and a copolymer of tetrafluoroethylene and hexafluoroethylene showed similar conductivities to those found for Nafion and Dow membranes [7]. However, the oxidative stability of these membranes was poor. Only poly(tetrafluoroethylene) showed some promise as a candidate material. The stability of these membranes in fuel cell systems for applications above 60–70°C was not investigated.

There is considerable methanol permeation through Nafion, which affects the fuel cell performance in a DMFC. Using doped PBI the same proton conductivity as Nafion can be maintained while virtually eliminating the crossover of methanol. PBI is doped with a conducting solid, usually phosphoric acid, to make it suitable for DMFC applications [55, 56]. In another attempt PBI is modified by sulfonation to make it an intrinsic proton conductor and is deposited onto a layer of Nafion membrane. This gives a composite polymer electrolyte that is a reasonable proton conductor and reduces the crossover of methanol [57].

Several materials have been studied on the goal of producing cost-effective PEMs [55–62]. Some of these are PBI-based membranes, polysterene membranes, sulfonated polyimide, cross-linked poly(vinyl alcohol), and phosphobenzene, sulfonated poly(aryl ether ketone) —based membranes. Sulfonation of aromatic thermoplastics such as polyether sulfone, polybenzimidazole, polyimides, and poly(ether ether ketone) makes them proton conductive suitable for fuel cell

applications. In a recent study, Zaidi [63] used blends of SPEEK and PBI with solid boron phosphate to prepare composite membranes. These membranes showed conductivity on the order of 0.5×10^{-2} S cm^{-1} and are thermally stable up to 150°C.

Although PBI or phosphoric acid membranes can reach up to 220°C without using any water management, higher temperatures allow for better efficiencies, power densities, ease of cooling, and controllability. These types of membranes are not common; most researchers and labs still use Nafion. It has been pointed out by Smitha et al. [1] that hydrogen permeation data and diffusion parameters at elevated temperatures are important for the selection of new materials for fuel cells operating at low temperatures. To investigate hydrogen permeation rates with varying temperatures across polymer membranes, hydrogen radiotracers such as tritium were used. Permeation and diffusion coefficients were determined for Viton, Teflon, etc., and these gave very low values. Today in most cases the membrane is made by a perfluorosulfonic ionic polymer, whereas the electrodes with a mixture of Pt supported on carbon and a dispersion of generally the same ionomer of the membrane. Making durable membranes and cost reduction of MEA is one of the main targets of fuel cell research today. Solvey Solexis is developing Hyflon ion ionomers for producing membranes and dispersing for MEA manufacture [64]. Hyflon ion is similar in structure to Nafion ionomer, except that it contains a shorter side chain compared with that of Nafion [Fig. 2.6].

The precursor can be used in the production of extruded films in the thickness range of 20–200 microns. These films are hydrolyzed by acid exchange to reach the final functional form [Fig. 2.7].

This is dispersed in polar solvents, usually water-alcohol mixtures for film processing. The concentration, viscosity, and particle size of the dispersion is controlled by changing the operating parameters (temperature, mixing, and solvent composition) during dissolution. The ionomer dispersion is then used for the production of membranes by the casting or impregnation process. This is also used for the preparation of catalyst inks that are used for the preparation of fuel cell electrodes or catalyst-coated membranes. The thickness of the cast membranes is usually in the range of 10–50 microns. These membranes are partly
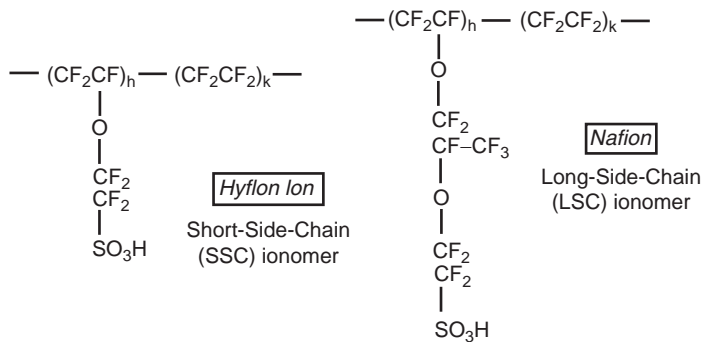

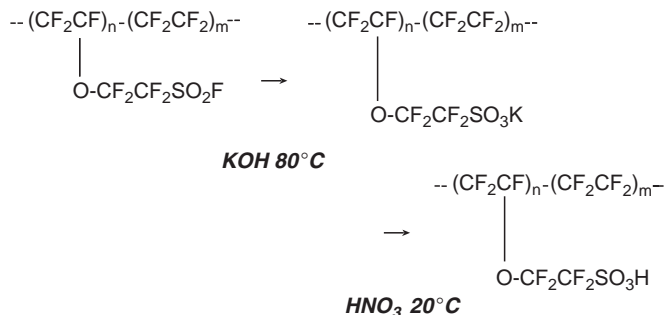**Fig. 2.6** Chemical structure of Hyflon Ion and Nafion

-- $(CF_2CF)_n$-$(CF_2CF_2)_m$--   -- $(CF_2CF)_n$-$(CF_2CF_2)_m$--

O-$CF_2CF_2SO_2F$ $\rightarrow$

O-$CF_2CF_2SO_3K$

KOH 80°C

-- $(CF_2CF)_n$-$(CF_2CF_2)_m$–

$\rightarrow$

O-$CF_2CF_2SO_3H$

HNO$_3$ 20°C

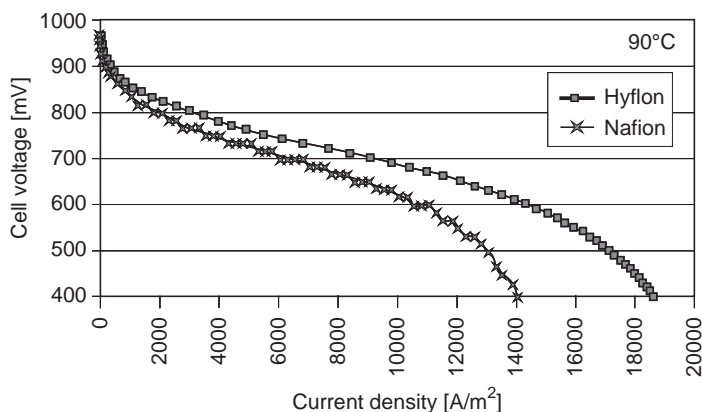**Fig. 2.7** Hydrolysis of the precursor

Fig. 2.8 Polarization curve comparison between Hyflon and Nafion at 90°C. (From: V. Arcella, A. Ghielmi, L. Merlo and M. Gebert, Membrane electrode assemblies based on perfluorosulfonic ionomers for an evolving fuel cell technology, *Desalination* **199**, 6–8 (2006).)[1]

crystalline (responsible for mechanical stability), and partly amorphous (responsible for proton conduction). Although Hyflon ion has lower equivalent weight (gram of polymer per mole of functional group) than Nafion, both have the same crystallinity and therefore mechanical properties. Sometimes crystallinity is expressed in terms of heat of fusion. That is why Hyflon ion shows more proton conductivity and therefore higher fuel cell performance. A 60°C increase in glass transition temperature for Hyflon ion gives the option of using this membrane at higher temperatures without mechanical failure. The resistance of Hyflon ion is lower than that of Nafion at all operating conditions [Fig. 2.8]. Requirements of 5,000 and 50,000 h are specified for automotive and stationary applications, and

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[1] This figure was published in V. Arcella, A. Ghielmi, L. Merlo and M. Gebert, Membrane electrode assemblies based on perfluorosulfonic ionomers for an evolving fuel cell technology, Desalination 199, 6–8 (2006), copyright Elsevier.

long-term durability. Single-cell durability tests in stationary conditions (fixed current) for several thousand h showed no notable performance degradation.

2.7 Conclusions

Following the research trends globally for the development of alternative membranes for PEM fuel cell, it can be seen that three different approaches have been used. These are: (1) modifying perfluorinated ionomer membranes; (2) functionality of aromatic hydrocarbon membranes to improve conductivity; and (3) preparing new polymer electrolyte composite membranes based on solid inorganic proton–conducting materials or prepare acid-base blends and their composite to improve their water retention properties at temperature above 100°C. The most studied polymeric material after Nafion is the sulfonated polyether-ether ketone, which holds strong potential to replace Nafion membranes. And a number of studies have been reported using SPEEK or its blend to prepare composite membranes. The current focus is on the development of temperature stable membranes in the range of 100–150°C and methanol-resistant membranes. To meet these goals, most of the work is based on the composite membrane approach to reduce the methanol crossover and improve the conductivity and water management at high temperature. The membranes prepared by BAM—BAM1G, BAM2G, and BAM3—are also promising and have undergone extensive testing in their hardware. Most probably these are the only ones that have undergone field testing for different applications, but most of the literature is patented and proprietary. In spite of the extensive research efforts worldwide, the need still exists for new polymer membranes that could satisfactorily replace Nafion.

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