Reviews

Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100 °C

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The state-of-the-art of polymer electrolyte membrane fuel cell (PEMFC) technology is based on perfluorosulfonic acid (PFSA) polymer membranes operating at a typical temperature of 80 °C. Some of the key issues and shortcomings of the PFSA-based PEMFC technology are briefly discussed. These include water management, CO poisoning, hydrogen, reformate and methanol as fuels, cooling, and heat recovery. As a means to solve these shortcomings, high-temperature polymer electrolyte membranes for operation above 100 °C are under active development. This treatise is devoted to a review of the area encompassing modified PFSA membranes, alternative sulfonated polymer and their composite membranes, and acid−base complex membranes. PFSA membranes have been modified by swelling with nonvolatile solvents and preparing composites with hydrophilic oxides and solid proton conductors. DMFC and H_2/O_2(air) cells based on modified PFSA membranes have been successfully operated at temperatures up to 120 °C under ambient pressure and up to 150 °C under 3−5 atm. Alternative polymers are selected from silicon- and fluorine-containing inorganic polymers or aromatic hydrocarbon polymers and functionalized by sulfonation. The sulfonated hydrocarbons and their inorganic composites are potentially promising for high-temperature operation. High conductivities have been obtained at temperatures up to 180 °C. Acid−base complex membranes constitute another class of electrolyte membranes. A high-temperature PEMFC based on H_3PO_4-doped PBI has been demonstrated for operation at temperatures up to 200 °C under ambient pressure. The advanced features include high CO tolerance, simple thermal and water management, and possible integration with the fuel processing unit.

1. Introduction: Why High Temperatures?

1.1. PFSA Membranes and Related Technologies. The currently well-developed PEMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion) as electrolyte.[1,2] PFSA membranes are composed of carbon−fluorine backbone chains with perfluoro side chains containing sulfonic acid groups. Some typical commercial PFSA membranes and their structures are listed in Table 1. Review articles with emphasis on transport processes,[3] structure and properties,[4,5] and applications[6] of PFSA membranes are available and recently updated for fuel cell applications.[7]

The Teflon-like molecular backbone gives these materials excellent long-term stability in both oxidative and reductive environments. A lifetime of over 60 000 hours under fuel cell conditions has been achieved with commercial Nafion membranes. These membranes exhibit a protonic conductivity as high as 0.10 S·cm^{-1} under fully hydrated conditions. For a membrane thickness of, say, 175 μm (Nafion 117), this conductivity corresponds to a real resistance of 0.2 ohm (Ω)·cm^2, i.e., a voltage loss of about 150 mV at a practical current density of 750 mA·cm^{-2}.

As an electrolyte, the polymer membrane provides an environment for electrode reactions at the electrolyte−electrode interfaces. Compared with phosphoric acid, for example, the catalytic activity of carbon-supported noble metal catalysts for oxygen reduction is high in the PFSA electrolyte, due to the nonadsorbing nature of the sulfonic acid anions on the Pt catalyst surface. Solubility of hydrogen[8] and oxygen[9] are also found to be 20−30 times higher than that in phosphoric acid. As a result of the fast electrode reaction kinetics, the performance of PEMFCs is high, especially at low noble metal loadings.

Such a thin membrane serves, at the same time, as a catalyst support and an effective gas separator. This is fulfilled by its good mechanical properties and low gas permeability. At 23 °C and 50% relative humidity (RH), for example, the tensile strength of Nafion membranes is about 40 MPa and the elongation is larger than 200%.[7] The permeability of both oxygen and hydrogen through the membrane is of the order of 10^{-11} to 10^{-10}

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Table 1. Commercial PFSA Membranes by Producer

$$—(CF_2—CF_2)_x—(CF_2—CF)_y—$$
$$|$$
$$(O—CF_2—CF)_m—O—(CF_2)_n—SO_3H$$
$$|$$
$$CF_3$$

structure parameter	trade name and type	equivalent weight	thickness (μm)
	DuPont		
$m = 1$; $x = 5–13.5$; $n = 2$; $y = 1$	Nafion 120	1200	260
	Nafion 117	1100	175
	Nafion 115	1100	125
	Nafion 112	1100	80
	Asashi Glass		
$m = 0, 1$; $n = 1–5$	Flemion-T	1000	120
	Flemion-S	1000	80
	Flemion-R	1000	50
	Asashi Chemicals		
$m = 0$; $n = 2–5$; $x = 1.5–14$	Aciplex-S	1000–1200	25–100
	Dow Chemical		
$m = 0$; $n = 2$; $x = 3.6–10$	Dow	800	125

mol·cm^{-1}·s^{-1}·atm^{-1}, corresponding to an equivalent current loss of 1–10 mA·cm^{-2}, ca. 1% of the performance. However, when methanol is directly used as fuel, this type of membrane suffers from a high crossover rate of methanol.[10]

Great success has been achieved with the PFSA membranes, though the membrane cost is high, amounting to about 100–200 US$ per kW. The following is a brief review on the technical achievements and challenges for the PFSA-based PEMFC technologies, with more emphasis being placed on their association with low operational temperatures.

1.1.1. Water Management. Being equilibrated with 100% RH vapor or with liquid water, the drag coefficient results were found to range from 0.9 to 3.2 at room temperature.[7] Under fuel cell operating conditions, especially at higher temperatures and equilibrated with a water–methanol mixture, this value will be even higher.[11–13] During operation of a PEMFC, the electroosmotic drag causes dehydration of the membrane of the anode side and consequently a dramatic decrease of the conductivity. Moreover, any change in the water content will result in swelling and shrinkage of membranes, which can lead to the deterioration of the membrane–catalyst interface or even membrane breakage. As a result, an effective and intensive humidification of both the fuel steam and the oxidant is needed.

The presence of water limits the operational temperature to below 100 °C under atmospheric pressure, typically around 80 °C. Operation of a PEMFC at such a temperature close to the boiling point of water involves a dual-phase water system. When the humidification is too high, water condenses and the gas diffusion electrodes are flooded. Careful management of the water balance is therefore one of the key issues for the system design and operation. For a high-temperature operation, a high water vapor pressure in the feed-gas stream is a necessity, which in turn requires a high total pressure because otherwise a low reactant-gas partial pressure

results in increased concentration overpotential. At a certain partial pressure (of 0.5 atm, for example) of the reactant gases in a water-saturated feed stream, to maintain 90% of the relative humidity at 150 °C requires pressurization of at least 8 atm.

1.1.2. CO Poisoning Effect. Another critical effect associated with a low operational temperature is the reduced tolerance to fuel impurities, e.g., CO in the hydrogen steam. This poisoning effect has been shown to be very temperature-dependent, i.e., CO adsorption is less pronounced with increasing temperature.[14] For example, at 80 °C, the typical operational temperature of a PFSA polymer membrane electrolyte fuel cell, a CO content as low as 20 ppm in the fuel steam will result in a significant loss in the cell performance.[15] As a consequence very pure hydrogen is needed for operation of PEMFCs.

1.1.3. Direct Hydrogen. With pure hydrogen as fuel, the PEMFC exhibits a single-cell performance higher than 0.6 W·cm^{-2} under atmospheric pressure or over 1 W·cm^{-2} at higher pressures. The PEMFC stacks have achieved specific power output higher than 1 kW·kg^{-1} or 1 kW·L^{-1} at a practical cell voltage, i.e., a system efficiency above, say, 40%. This technology has weight, volume, and other features competitive with those of internal-combustion-engine propulsion systems. However, the development of a new hydrogen infrastructure faces unsolved technological problems and economic uncertainties such as compact and lightweight hydrogen storage, hydrogen supply, and distribution and refueling systems. It is interesting to mention that recent results of hydrogen storage based on complex hydrides such as NaAlH$_4$ show a significant increase in the storage capacity from 1–2 wt % to 4–5 wt % or higher.[16,17] One fundamental requirement is that heat for hydrogen desorption should be provided in a temperature range of 100–200 °C. Though the amount of heat needed is estimated to be only about one-fourth of the excess heat from a fuel cell stack (at an efficiency of 50%), such a high-capacity H$_2$ storage tank cannot be integrated into a PEMFC system because of the low operational temperature.

1.1.4. Methanol Reformate. The use of methanol is an efficient and economical way to bring hydrogen into a fuel cell system because its storage and refueling need little infrastructure change. Currently, methanol is used in an indirect way, i.e., via reforming. The reformate gas contains hydrogen, carbon dioxide, carbon monoxide, and residual water and methanol as well.[18,19] Because of the above-mentioned CO poisoning effect, considerable efforts have been made to develop CO-tolerant electrocatalysts, with PtRu alloys being the most promising candidates.[20] Even with PtRu catalysts, however, a significant performance loss is still observed at a CO concentration above 100 ppm at 80 °C. Therefore, careful purification of the reformed hydrogen is necessary to remove the CO traces. This is carried out by means of a water–gas shift reaction, preferential oxidation, membrane separation, or methanation. For a small dynamic load as in a vehicle, the main challenge for an on-board fuel processing system is the complexity, which not only requires increased cost, weight, and volume but also reduces the start-up time, transient response capacity, reliability, or maintance-free operation of the

system. Such a fuel processing system generally covers 40−50% of the total cost for a fuel cell power system and the CO-cleanup unit counts for the major part of weight, volume, and cost of the fuel processing system. A CO-tolerant PEMFC will decisively simplify the power system.

1.1.5. Direct Methanol. Direct use of methanol as fuel is a preferable option for propulsion of vehicles and other purposes. However, the direct methanol fuel cell (DMFC) technology is far from satisfactory, mainly because of two technical challenges.[21,22] As mentioned above,[10] the PFSA membranes have a large methanol crossover rate of about 10^{-6} mol·cm^{-2}·s^{-1}, corresponding to a performance loss of current density of 50−100 mA·cm^{-2}. This results in not only waste of fuel but also considerably lowered energy efficiency and cell performance due to the mixed electrode potential.[23] Secondly, the anodic catalyst is not sufficiently active, leading to a high anodic over-potential loss of ca. 350 mV, compared to ca. 60 mV for hydrogen. Taking into account the elimination of a fuel processing system, it is believed that a power density as low as 0.2 W·cm^{-2} at a cell voltage above 0.5 V for a direct methanol fuel cell would be competitive with a power density of 0.5−0.6 W·cm^{-2} for a direct hydrogen fuel cell. However, such a power density target can hardly be achieved even at high operational pressures (3−5 atm) and high noble metal loadings (2−8 mg·cm^{-2}). From a kinetic point of view, the insufficient activity of the anode catalyst is due to the slow kinetics of the methanol oxidation and the strong poisoning effect of the intermediate species (CO) from methanol oxidation. Both effects could be considerably improved by increasing the operational temperature of DMFC.

1.1.6. Thermal Balance. Another complication with PEMFCs is the cooling of the system. A PEMFC operating at 80 °C with an efficiency of 40−50% produces a large amount of heat that has to be removed in order to maintain the working temperature. As recently rationalized by Frank,[24] the existing cooling systems of modern vehicles reject less than 40% of the waste heat, whereas the high-temperature exhaust gases carry away the rest. As a comparison, a PEMFC stack at 80 °C has to reject all the heat via the cooling loop. On the basis of such a system at an ambient temperature of 40 °C, it was estimated that a PEMFC operating at an efficiency of 56% would require a stack temperature above 145 °C. Even with an advanced cooling system, a stack temperature above 100 °C would be necessary.[24]

1.1.7. Heat Recovery. The heat energy from a PEMFC stack at around 80 °C is of little value to recover, either for stationary or for mobile applications. If the operational temperature is elevated to, for example, 200 °C, water steam of up to 15 atm can be produced from a fuel cell stack. This heat can be directly used for heating so that the overall efficiency will be improved for stationary purposes. It can also be used to operate the system at high pressures or to produce steam for fuel reforming. For steam reforming of both natural gas at 800 °C and methanol at 300 °C, preheating fuels and water up to 200 °C will significantly improve the overall system energy efficiency.

1.2. Why High-Temperature Polymer Electrolyte Membranes? As discussed above, most of the shortcomings associated with the low-temperature PEMFC technology based on PFSA membranes can be solved or avoided by developing alternative membranes operational at higher temperatures than 100 °C. These include the following: (1) The kinetics for both electrode reactions will be enhanced. This is of special importance for the direct oxidation of methanol in DMFC. (2) Above the boiling point of water, operation of PEMFCs involves only a single phase of water, i.e., the water vapor, and therefore can be simplified. (3) The required cooling system will be simple and practically possible due to the increased temperature gradient between the fuel cell stack and the coolant. (4) The heat can be recovered as, e.g., steam, which in turn can be used either for direct heating or steam reforming or for pressurized operation. In this way the overall system efficiency will be significantly increased. (5) The CO tolerance will be dramatically enhanced, from 10−20 ppm of CO at 80 °C, to 1 000 ppm at 130 °C, and up to 30 000 ppm at 200 °C.[25] This high CO tolerance makes it possible for a fuel cell to use hydrogen directly from a simple reformer, so that the water−gas−shift reactor, the selective oxidizer, and/or the membrane separator for the CO cleanup can be eliminated from the fuel processing system. (6) The operational temperature of a fuel cell around 200 °C is close to temperatures for methanol reforming and for hydrogen desorption of the newly developed high-capacity storage materials. This will allow for an integration of the fuel cell with a methanol reformer or a high-capacity hydrogen storage tank. The integration is expected to give the overall power system advanced features including higher efficiency, smaller size, lighter weight, simple construction and operation, and efficient capital and operational cost.[26] High reliability, less maintenance, and better transient response capacities can also be expected as the potential features of the high-temperature PEMFC technology.

1.3. Scope of This Review. Great efforts have been and are being made to develop proton-conducting membranes for operation at temperatures above 100 °C for fuel cells[27−33] and water electrolysis.[34−36] This paper attempts to review these efforts including approaches and potential membrane systems of the development, and the status of their applications in PEMFCs. The developed membranes are classified into three groups: (1) modified PFSA membranes, (2) alternative sulfonated polymers and their composite membranes, and (3) acid−base polymer membranes.

Developments of PFSA membranes and their applications have been reviewed.[3−7] For operation at temperatures above 100 °C, modifications of the PFSA membranes have been extensively investigated. Approaches and results of these modifications are reviewed in Section 2.

Nonperfluorosulfonated membranes have been recently reviewed by a number of authors,[37−43] especially the sulfonation[39−43] and cross-linking[37] of polyaromatic and polyheterocyclic polymers. The motivation of these developments is to substitute PFSA membranes for low-temperature operation. It is interesting that some of the sulfonated hydrocarbons exhibit high conductivity for potential operation at temperatures above 100 °C. The

discussion in Section 3, after a brief overview of polymer selection and their sulfonation, is focused on the high-temperature performance of these sulfonated membranes. To achieve high operational temperatures, more efforts are being made to develop organic–inorganic composites based on these alternative polymers, as recently reviewed.[44] Also related to the development of inorganic–organic composites, review articles on inorganic proton-conductor materials in general are available.[45–48]

Acid–base polymers are another class of proton-conducting membranes with good performance at high temperatures.[40,41] Phosphoric-acid-doped PBI and ionically cross-linked acid–base blends, among others, have received the most attention, as recently reviewed by Wainright et al.[49] and Kerres.[37] Section 4 is devoted to a general description and characterization of these membranes.

High-temperature fuel cells have been tested with modified PFSA membranes and acid–base polymer membranes. These efforts and the advanced features of the high-temperature PEMFC are summarized in Section 5. Finally, nomenclature is listed at the end of the paper.

2. Modifications of PFSA Membranes

Over the last 30 years the PEMFC technology with good and steadily increasing performance and long lifetime has been developed based on PFSA membranes. One major drawback of PFSA membranes is their low conductivity and therefore poor performance under low humidification and at elevated temperatures (above 90 °C) because of the water loss.

Considerable efforts have been made to modify the PFSA membranes to achieve high-temperature operation. To replace water with nonaqueous and low-volatile media has been explored with some success, as to be discussed in Section 2.1.

More research has been carried out to improve water management, which is necessary to simplify the low-temperature operation and enable a high-temperature operation. The water balance in a PEMFC involves the following mechanisms: (1) water supply from the fuel and oxidant (humidification); (2) water produced at the cathode (current density); (3) water drag from the anode to the cathode (current density, humidity, temperature); and (4) back-diffusion of water from the cathode to the anode (concentration gradient and capillary forces).

Accordingly, approaches have been developed for low-humidification operation at both low (80 °C) and high (above 100 °C) temperatures. These approaches include reducing the thickness of membranes (Section 2.2), impregnating the membranes with hygroscopic oxide nanoparticles (Section 2.3), and solid inorganic proton conductors (Section 2.4).

To reduce the methanol crossover rate for a DMFC option, PFSA membranes have also been modified by plasma-etching and palladium-sputtering[50] and by introducing a barrier layer of polybenzimidazole (PBI)[51] or sulfonated PBI.[52] This modification is, however, not directly related to the operational temperature and will not be discussed further in this review.

2.1. Swelling with Nonaqueous, Low Volatile Solvents. It is well-known that high ionic conductivity

of Nafion membranes can also be achieved in solvent environments other than pure water, for example, in water–organic mixtures, alcohols, organic acids, and aprotic dipolar solvents.[53–57] This opens the possibility to replace water with a nonaqueous and low volatile solvent.

The first attempt was made in 1994 by Savinell et al.,[32] who incorporated phosphoric acid in Nafion and achieved a conductivity of 0.05 S·cm^{-1} at 150 °C. As suggested, the low volatile phosphoric acid acts as a Brönsted base and solvates the proton from the strong sulfonic acid group in the same way as water does.[58] Phosphoric acid has a very low volatility and therefore allows for an extension of the operational temperature up to 200 °C. However, it should be noted that the obtained conductivity for the phosphoric-acid-swollen Nafion is lower than that of pure phosphoric acid. This may indicate that phosphoric acid is in fact the intrinsic proton conductor. Improved kinetics for oxygen reduction at the cathode has been reported[59] in the Nafion/phosphoric acid electrolyte compared to pure phosphoric acid. However, no fuel cell tests based on Nafion–H_3PO_4 membrane electrolytes have been successfully conducted, because a failure of the anode occurred after a short period of operation.[60] Savinell et al.[61] attributed this failure to the possible anion migration and the consequent electrode flooding.

The idea has been extended to impregnation of Nafion membranes with other acids or ionic liquids. Malhotra et al.[62] impregnated Nafion (117) membranes with a phosphotungstic acid (PTA) solution in acetic acid. Using a thus-obtained membrane electrolyte, a high-temperature fuel cell performance at 110 °C was compared to that with the nonimpregnated Nafion. Above 110 °C, the acetic acid evaporates. A more thermally stable molten salt solvent, tetra-*n*-butylammonium chloride (TBAC), which has a melting point of 58 °C, has also been used for impregnation of PTA into Nafion. In this way the operational temperature of the fuel cell was extended to 120 °C.

Following an idea of "polymer-in-salt" for developing polymer electrolyte for lithium batteries,[63] a rubbery gel electrolyte was prepared from room-temperature ionic liquids and poly(vinylidene fluoride)–hexafluoropropylene copolymer (PVdF(HFP)). The ionic liquids, i.e., 1-butyl,3-methyl imidazolium triflate (BMITf) and BMI tetrafluoroborate (BMIBF$_4$), have a wide liquid range, low volatility, and high thermal stability (above 300 °C). The obtained polymer gel electrolyte exhibited good thermal stability and an ionic conductivity of 4×10^{-2} S·cm^{-1} at 205 °C.[64] Doyle et al. used the same ionic liquids (i.e., BMITf and BMIBF$_4$) to swell the PFSA membranes.[31] By using these nonvolatile dipolar solvents, the treated Nafion membranes showed very high ionic (most likely protonic) conductivity of over 0.1 S·cm^{-1} at 180 °C.

Another interesting group of solvents with potential to replace water is the heterocycles (e.g., imidazole, pyrazole, or benimidazole), containing both proton donor (NH) and acceptor (N). Kreuer et al. reported an increasing conductivity for sulfuric acid mixed with the heterocycles,[65] though no increase in conductivity was observed for a mixture of phosphoric acid with the heterocycles.[66] Sun et al. prepared water-free Nafion

117 membranes by swelling them in imidazole and imidazolium salt (e.g., trifluoroacetate and trifluoromethane sulfonate) solutions.[67] They reported conductivities of about 10^{-3} S·cm^{-1} at around 100 °C.

No fuel cell test has been reported with PFSA membranes swollen in these ionic or heterocyclic media. The difficulties may arise from (1) the immobilization of the liquids, especially in the presence of water (an attempt has been made to immobilize imidazole as proton solvent[68]), and (2) adsorption of the solvent on the catalyst surface.

2.2. Thin, Reinforced PFSA Membranes. Using thinner membranes will improve water management during PEMFC operation,[69] even though the main motivation for developing thinner membranes is to lower the internal resistance and reduce the material cost. One challenge for developing thinner membranes is the reduced mechanical strength, especially under swelling and at high temperatures. Composite PFSA membranes with reinforcement either by a porous PTFE sheet (from W. L. Gore[70]) or by micro PTFE fibril (from Asahi Glass Co.[71]) make this possible. Nafion-impregnation of other substrates such as porous polypropylene,[72] expanded PTFE,[73] and polysulfone and microglass fiber fleece[74] has also been investigated.

By means of reinforcement, the thickness of PFSA membranes has been successfully reduced down to 5–30 μm with good conducting and mechanical properties.[75–77] Because of the effective back-diffusion of water from the cathode to the anode side through such thin membranes, water management and, therefore, the average conductivity are improved. Lin et al.[78] used a Gore MEA with a Nafion-like membrane of 25-μm thickness for operation at temperatures up to 120 °C under ambient pressure. With a humidifier temperature at 80 °C, they obtained performance of about 160 and 250 mA·cm^{-2} at 105 and 120 °C, respectively, at the cell voltage of 0.6 V. Although these values are much lower than the performance at 80 °C (about 700 mA·cm^{-2} at 0.6 V) under the same humidification conditions, the effect of the membrane thickness is still significant when compared with the results, for example, from Malhotra et al.,[62] who obtained a poor performance of 20 mA·cm^{-2} (0.6 V) using Nafion 117 at a cell temperature of 110 °C and humidifier temperatures of 95/90 °C.

2.3. Composites with Hygroscopic Oxides. An effective way to achieve low-humidity and high-temperature operation of PFSA membranes is to recast Nafion membranes with mixed hygroscopic oxides (e.g., SiO$_2$ and TiO$_2$). Watanabe et al.[79] presented the first report in 1994. Thereafter a number of patents have been granted.[80] It has been shown that the water uptake by the oxide-containing membrane is higher than that of the pristine Nafion. For recast Nafion membranes predried at 80 °C, the water absorbing ability by humidification with water vapor at 60 °C was found to be 17 wt %, whereas for membranes containing 3 wt % SiO$_2$ of 7-nm size, the water absorbing ability was increased to as high as 43 wt %.[81] As a result of the water adsorption on the oxide surface, the back-diffusion of the cathode-produced water is enhanced and the water electro-osmotic drag from anode to cathode is reduced. These modified Nafion membranes were developed with aims at an internal (self) humidification

at low operational temperatures.[83] High-temperature operation has also been demonstrated using a recast Nafion membrane containing 3 wt % SiO$_2$. Antonucci et al.[84] tested a DMFC at 145 °C under pressures of 4.5 atm (methanol–water)/5.5 atm (air). The obtained performance was about 350 mA·cm^{-2} at 0.5 V.

Mauritz et al.[85] developed a sol–gel technique to introduce SiO$_2$ into the fine hydrophilic channels (ca. 50 Å diam.) of PFSA membranes. Detailed investigations on microstructures and fundamental properties of the obtained composite membranes have been carried out.[86–91] A modification of the method is proposed by using a Nafion solution, instead of the preformed PFSA membranes, mixed with tetraethyl orthosilicate (TEOS) (and TMDES).[92,93] High SiO$_2$ content in Nafion has been reached up to 54%. Conductivity in the range of 10^{-7} to 10^{-5} S·cm^{-1} was reported at 100 °C under dry argon atmosphere.

Recently, efforts have been made to test these composite membranes in an H$_2$/O$_2$ PEMFC at temperatures above 100 °C.[94–97] By processing of tetraethoxysilane in the Nafion acidic medium, a mixture of SiO$_2$/siloxane polymer is formed within the PFSA membrane, with SiO$_2$ contents of up to 10 wt %. At 130 °C under a pressure of 3 atm, a PEMFC based on such a membrane delivered 4 times the current density (at 0.4 V) as obtained with unmodified Nafion 115 membranes.[96] Low equivalent weight and small thickness of the PFSA membranes further improve the performance. Under the same conditions by using Aciplex 1004 (see Table 1) membranes, the obtained current density at 0.4 V was 6 times higher than that of unmodified Nafion 115 membranes.[95]

2.4. Composites with Solid Inorganic Proton Conductors. Inclusion of the hygroscopic oxide particles in PFSA membranes is primarily single-functional, i.e., for water retention. Bifunctional particles, being both hydrophilic and proton conducting, have also been incorporated with PFSA membranes. More general discussion on inorganic–organic composite membranes based on solid inorganic proton conductors and polymers will be given in Section 3.3. In this section, inorganic solid proton conductors are first briefly reviewed, followed by a discussion on the development of composite PFSA membranes.

2.4.1. Inorganic Solid Proton Conductors. Among the inorganic solid proton conductors,[47,48,98] zirconium phosphates, heteropolyacids, metal hydrogen sulfate, and a few others are of special interest for developing high-temperature composite membranes for PEMFC.

Zirconium phosphates have long been known as interesting inorganic ion exchangers,[99,100] especially after their crystalline form of Zr(HPO$_4$)$_2$·H$_2$O was prepared in the 1960s.[101] This group of compounds can be expressed as M^{IV}(RXO$_3$)$_2$·nS, where M is a tetravalent metal such as Zr, Ti, Ce, Th, or Sn; R is an inorganic or organic group such as −H, −OH, −CH$_3$-OH, or (CH$_2$)$_n$; X is P or As; and S is a solvent, i.e., H$_2$O. They form two types of layered structures, named α and γ.[47,102,103] These compounds exhibit good proton conductivity in a temperature range up to 300 °C. In the form of glassy plates or films, a room-temperature conductivity of 10^{-2} S·cm^{-1} has been reported.[104] And the conductivity can be enhanced by composite formation

Table 2. Conductivity of Zirconium Phosphates and Phosphonates At and Above 100 °C

compound	conductivity, S·cm^{-1}	ref
α-Zr(O$_3$POH)$_2$·H$_2$O	5×10^{-6}, 100 °C, 60% RH	29
	1×10^{-4}, 100 °C, 95% RH	29
α-Zr(O$_3$PC$_2$H$_5$)$_{1.15}$(O$_3$PC$_6$H$_4$SO$_3$H)$_{0.85}$	$5-12 \times 10^{-6}$, 180 °C, dry N$_2$	110
α-Zr(O$_3$PCH$_2$OH)$_{1.27}$(O$_3$PC$_6$H$_4$SO$_3$H)$_{0.73}$·nH$_2$O	8×10^{-3}, 100 °C, 60% RH	111
α-Zr(O$_3$PC$_6$H$_4$SO$_3$H)$_2$·3.6H$_2$O	2.1×10^{-2}, 105 °C, 85% RH	112
γ-Zr(PO$_4$)(H$_2$PO$_4$)$_{0.54}$(HO$_3$PC$_6$H$_4$SO$_3$H)$_{0.46}$·nH$_2$O	5×10^{-2}, 100 °C, 95% RH	113

with SiO$_2$ or Al$_2$O$_3$.[105] Because of their ability to undergo infinite swelling in appropriate solvents, these materials can be incorporated into polymeric proton-conducting membranes.[103]

It is interesting to remark that organic derivatives of the α-zirconium phosphate[106] and γ-zirconium phosphate[107,108] have been prepared since the 1970s. These are a group of inorganic polymers where the O$_3$POH groups of the α-type Zr(O$_3$POH)$_2$·nH$_2$O and the O$_2$P-(OH)$_2$ groups of γ-type ZrPO$_4$·O$_3$P(OH)$_2$·nH$_2$O are replaced with O$_3$POR or O$_2$PR′R$-$ groups. In these structures, R and R′ are organic groups, bridging through phosphorus atoms to an inorganic two-dimension matrix.[109] When the organic moieties R contain a proton-generating function such as $-$COOH, $-$PO$_3$H, $-$SO$_3$H, or NH$_3^+$, these compounds become proton conductors. Some of the mixed zirconium alkyl$-$sulphophenyl phosphates exhibit proton conductivity as high as 5×10^{-2} S·cm^{-1} at about 100 °C with good thermal stability at temperatures up to 200 °C. Table 2 lists some of the conductivity measurements at and above 100 °C. The possible uses of these membranes for medium-temperature sensors and fuel cells have been recently reviewed.[29]

Heteropolyacids, as known more than a century ago,[114] exist in a series of hydrate phases. The basic structure unit of these acids is a special [PM$_{12}$O$_{40}$]$^{3+}$ cluster, the so-called Keggin unit.[115] Typical compounds include H$_3$PW$_{12}$O$_{40}$·nH$_2$O (PWA), H$_3$PMo$_{12}$O$_{40}$·nH$_2$O (PMoA), and H$_4$SiW$_{12}$O$_{40}$·nH$_2$O (SiWA). In their crystalline forms hydrated with 29 water molecules, these acids exhibit high proton conductivities;[116] for example, 0.18 S·cm^{-1} for H$_3$PW$_{12}$O$_{40}$·29H$_2$O and 0.17 S·cm^{-1} for H$_3$PMo$_{12}$O$_{40}$·29H$_2$O.[117] Aqueous solutions of heteropolyacids, e.g., SiWA[118] and PWA,[119-121] have been explored as fuel cell electrolytes, showing fast electrode kinetics and less CO poisoning at the electrode$-$electrolyte interface. Solid electrolyte fuel cells have also been proposed.[122] Of more interest in recent years is the development of composite membranes.

Another group of inorganic solid proton conductors is *hydrogen sulfates*, MHXO$_4$, where M is large alkali species Rb, Cs, or NH$_4^+$, and X is S, Se, P, or As. Among these compounds is CsHSO$_4$, the most interesting. It undergoes several phase transitions and the high-temperature phase above 141 °C exhibits a high proton conductivity about 10^{-2} S·cm^{-1},[123] due to the dynamically disordered network of hydrogen bonds. Compared with other low-temperature hydrate proton conductors, this compound has relatively high thermal (decomposition temperature 212 °C) and electrochemical stability, as it does not contain water molecules in its structure. Its conductivity does not depend on atmospheric humidity. By introducing metal oxides of high surface area, inorganic composites of CsHSO$_4$ with SiO$_2$ [124,125] and TiO$_2$ [126] have been found to exhibit higher conductivity

and low transition temperature. New solid compounds CsHSO$_4$·CsH$_2$PO$_4$ and 2CsHSO$_4$·CsH$_2$PO$_4$ have been prepared and shown to have lower transition temperatures and high proton conductivity.[127,128] Suffering from poor mechanical properties and water solubility, as well as extreme ductility and volume expansion at raised temperatures, however, these compounds have not yet found practical applications, though an attempt was recently made to assemble an H$_2$/O$_2$ fuel cell with a solid CsHSO$_4$ acid electrolyte.[129] It has been suggested to prepare composite membranes for the fuel cell purpose.[130]

Recently a high-proton-conducting salt, boron phosphate (BPO$_4$), has been prepared[131] and its stability has been improved by aluminum substitution.[132]

2.4.2. Composite Membranes with Inorganic Solid Proton Conductors. PFSA composites with heteropolyacids[133-135] and zirconium phosphate[28,136,137] have been the subject of active development aimed at improving the hydration characteristics and raising the operational temperature.

A simple method to prepare inorganic$-$PFSA composite membranes is membrane recasting from an ionomer solution containing one or more inorganic components, e.g., heteropolyacids, preferably supported on high-surface-area silica.[133] Similarly to the method for in-situ growth of silica in PFSA membranes, zirconium phosphate has been successfully incorporated in PFSA membranes by an exchange$-$precipitation process.[138] The membrane is first swollen in a boiling methanol$-$water mixture and then transferred into a zirconyl chloride solution at 80 °C. In this way Zr^{4+} ions are introduced to the ionic sites of the membranes by ion exchange. The metal ions act as a center for the particle growth during precipitation of zirconium phosphate when the membrane is then immersed in H$_3$PO$_4$.[28,136]

As hydrophilic additives, the presence of these inorganic compounds decreases the chemical potential of the water inside the membrane and therefore creates an additional pathway for the proton conduction. At the same time, they provide hydrogen-bonding sites for water in the membrane so that the hydration of the membrane will be increased and the transport and evaporation of water will be reduced.[95] The enhanced water retention enables low humidification and high-temperature operation of both DMFC and H$_2$/O$_2$(air) fuel cells.

Staiti et al.[133] recast Nafion membranes from a mixture of Nafion ionomer with silica-supported phosphotungstic acid (PWA$-$SiO$_2$) and silicotungstic acid (SiWA$-$SiO$_2$). They applied the composite membranes in DMFC at temperatures up to 145 °C, and obtained a maximum power density of 400 mW·cm^{-2} with O$_2$ and of 250 mW·cm^{-2} with air.

Table 3. Summary of Modifications of PFSA Membranes

polymer	modifiers	remarks	ref
Nafion	H_3PO_4	0.05 S·cm^{-1} at 150 °C	32
Nafion	PTA−acetic acid	H_2/O_2 cell, 110 °C, 660 mA·cm^{-2} at 0.6 V, 1/1 atm, humidifier 50/50 °C	62
Nafion	PTA−TBAC	H_2/O_2 cell, 120 °C, 700 mA·cm^{-2} at 0.6 V, 1/1 atm, humidifier 50/50 °C	62
Nafion	SiO_2	>0.2 S·cm^{-1}, 100 °C, 100% RH	83
Nafion	SiO_2	DMFC, 145 °C, 4.5/5.5 atm (air), 350 mA·cm^{-2} at 0.5 V	84
Nafion	SiO_2/siloxane	H_2/O_2, 130 °C, 3/3 atm	95
Aciplex	SiO_2/siloxane	H_2/O_2, 130 °C, 3/3 atm	96
Nafion	Teflon + PTA	H_2/O_2 cell, 120 °C, 400 mA·cm^{-2} at 0.6 V, 1/1 atm, humidifier 90/84 °C	78
Nafion	ZrP	DMFC, 150 °C, 4/4 atm, 380 mW·cm^{-2} (O_2), 260 mW·cm^{-2} (air)	28
Nafion	ZrP	H_2/O_2 cell, 1.5 A·cm^{-2} at 0.45 V, 130 °C, 3 atm	136
Nafion	di-isopropyl phosphate	0.4 S·cm^{-1} at 25 °C	139
Nafion	SiP−PMA/PWA	0.005 S·cm^{-1} at 23 °C, fully hydrated	140
Nafion	SiWA (+ thiophene)	fuel cell test at 80 °C	141
Nafion	SiO_2, PWA−SiO_2, SiWA−SiO_2	140 °C, 3/4 atm, DMFC, 400 mW·cm^{-2} (O_2), 250 mW·cm^{-2} (air)	133
Nafion	PMoA + SiO_2	> 0.3 S·cm^{-1} at 90 °C	142

Using the exchange−precipitation method, Yang et al.[28] prepared Nafion 115 composites from an extruded film for DMFC. At temperatures up to 150 °C under pressures of 4/4 atm, they obtained a maximum power density of 380 mW·cm^{-2} for O_2 and 260 mW·cm^{-2} for air. Similar composite membranes have been prepared from both commercial membranes and recast Nafion.[136] H_2/O_2 cell tests were conducted at 130 °C and 3 atm. At a cell voltage of 0.45 V, the commercial membrane composites had a performance of 1000 mA·cm^{-2} and the recast composite membranes had a performance of 1500 mA·cm^{-2}, whereas the unmodified Nafion membranes had a performance of only 250 mA·cm^{-2}.

Table 3 summarizes these efforts as well as other modifications of PFSA-based membranes.

3. Alternative Sulfonated Polymer Membranes and Their Composites

Development of sulfonated polymer membranes as alternatives to PFSA has been another active area in the field. A great number of polymer materials have been prepared and functionalized as membrane electrolytes for PEMFC. A brief overview of selection and functionalization of the polymers is given in Section 3.1. These developments are principally motivated to lower the material cost for low-temperature operation, as recently reviewed.[37−43] Some of these materials, especially the sulfonated hydrocarbons, show interesting features for a possible high-temperature operation (Section 3.2). To achieve high operational temperatures, more efforts are being made to develop organic−inorganic composites based on these alternative polymers (Section 3.3).

3.1. Types of Polymers and Their Sulfonation. The essential requirements for polymer membrane electrolyte materials of PEMFC include (1) proton conductivity; (2) chemical stability; (3) thermal stability; (4) mechanical properties (strength, flexibility, and processability); (5) low gas permeability; (6) low water drag; (7) fast kinetics for electrode reactions; and (8) low cost and ready availability.

As starting materials, basic polymers should have high chemical and thermal stability. Two main groups of polymers have been widely investigated for this purpose. One group is polymers containing inorganic elements, i.e., fluorine in fluoropolymers and silicon in polysiloxanes. The other group is aromatic polymers with phenylene backbones.

3.1.1. Fluoropolymers. Sulfonated polystyrenes (structure 1 in Figure 2) were investigated in the 1960s as the first generation of polymer electrolytes for fuel cells.[143,144] Extensive studies[145−148] on the membranes have contributed greatly to the understanding of sulfonated polymers as electrolytes for fuel cells. This type of polymer membrane, however, suffers from a short lifetime because the tertiary C−H bonds in the styrene chains are sensitive to oxidation by oxygen and hydrogen peroxide.

Chemically the bond strength for C−F is about 485 kJ·mol^{-1}, higher than that for C−H bonds (typically 350−435 kJ·mol^{-1}) or C−C bonds (typically 350−410 kJ·mol^{-1}). Polymers containing C−F bonds have been demonstrated to give high thermal and chemical stability. Poly(tetrafluoroethylene) (PTFE), for example, consisting of the repeat unit −[CF_2−CF_2]−, has an excellent chemical stability and a high melting temperature around 370 °C.

In addition to the well-developed PFSA membranes discussed above, partially fluorinated polymer membranes have also been actively investigated. Poly(tetrafluoroethylene−hexafluoropropylene) (FEP) films have been adapted, mainly by Scherer's group.[149−152] The FEP film is first irradiated, and then styrene groups are grafted on with, e.g., divinylbenzene (DVB) as a cross-linker. The proton conductivity is introduced by sulfonating the aryl groups. A recent work reported a fuel cell lifetime over 5000 hours at 85 °C based on this type of membrane.[153] Poly(vinylidene fluoride)- (PVDF) based polymer membranes have also been prepared by grafting and then sulfonating the styrene groups, mainly by Sundholm's group.[154−162] The combination of the good physical stability and chemical resistance of PVDF with the good conductive properties of sulfonated polystyrene seems to give high water uptake[158] and high proton conductivity.[155−157] Partially fluorinated polymer membranes based on α,β,β-trifluorostyrenes have been prepared by either sulfonation[163] or phosphonation.[164] Fuel cell tests showed promising performance, though the tests were perfomed at low temperatures.[165]

3.1.2. Polysiloxanes. Another type of temperature-resistant polymers of interest contains the chemical bond of Si−O, which has a chemical bond strength of
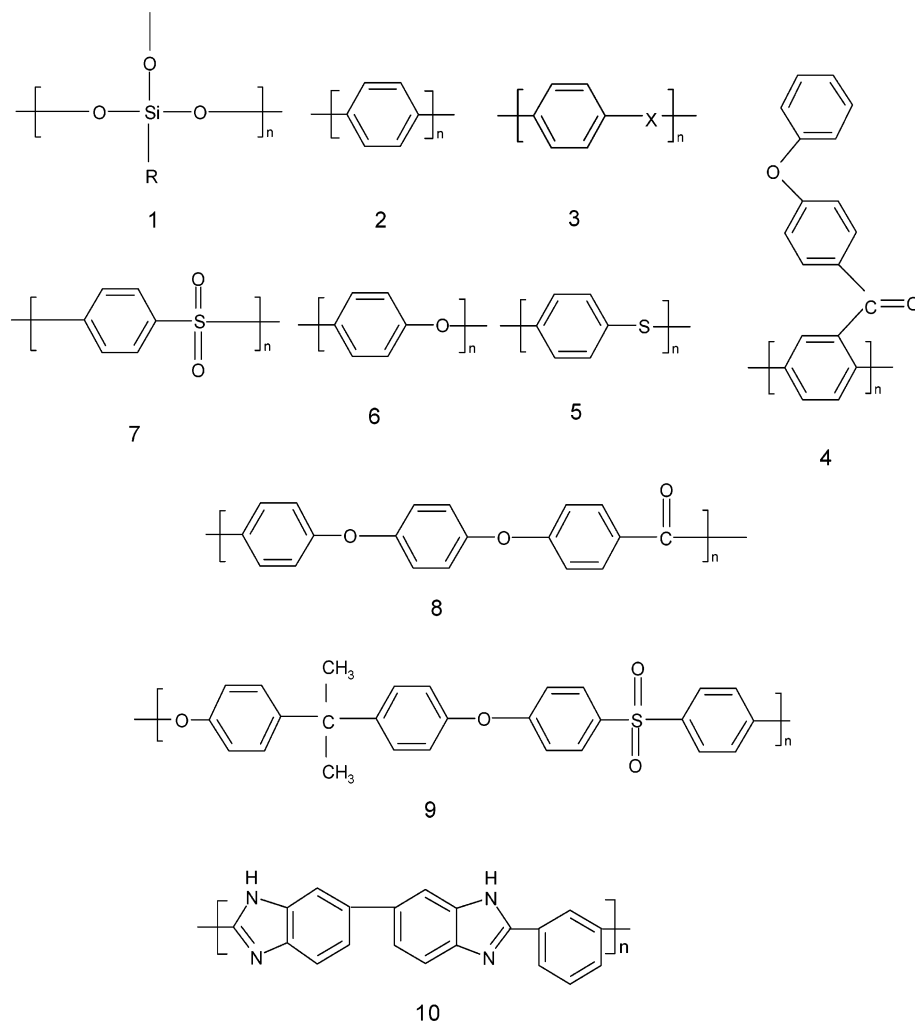
Figure 1. Polymer structures of interest for developing the temperature-resistant PEM: 1, polysiloxane; 2, poly-*p*-phenylene; 3, poly-*p*-phenylene with a flexiblizing group; 4, poly(4-phenoxybenzoyl-1,4-phenylene); 5, polyphenylene sulfide; 6, polyphenylene oxide; 7, poly-*p*-phenylene sulfone; 8, polyetheretherketone; 9, Udel polysulfone; 10, poly(2,2′-*m*-(phenylene)-5,5′-bibenzimidazole.

about 445 kJ·mol^{-1}. An example is the silicone polymers, e.g. polysiloxanes, as shown in structure 1, Figure 1, where R represents either methyl or mixed methylphenyl groups.

Normally inorganic Si–O networks (ceramics) are formed at high temperatures. By the sol–gel process,[166,167] the inorganic network can be developed at low temperatures in organic or aqueous solutions. In this way, organic groups can be chemically bonded to the silica matrix. Thus-obtained products are termed organic-modified silicates (ORMOSIL) or organic-modified ceramics (ORMOCER).[168] By functionalizing the inserted organic group, a large family of polymer electrolytes have been prepared, sometimes named organic modified silicate electrolyte (ORMOLYTE) and used primarily as electrolytic membranes for lithium batteries.[169−175] Attempts have been made to develop proton-conducting membranes for fuel cell applications by using arylsulfonic anions[176] or alkylsulfonic anions[177,178] grafted to the benzyl group. The poly(benzylsulfonic acid siloxane) (structure 2, Figure 2) membranes can be cross-linked via hydrosilylation, and they have been reported to exhibit a proton conductivity of 10^{-2} S·cm^{-1} at room temperature and a thermal stability of the amorphous network up to 200 °C with optical transparency and chemical stability.

No report on fuel cell tests based on the silicone polymer membranes seems available so far. Interestingly, these polymers have been used for PFSA modification (see Section 2.3) and for preparation of composites with inorganic components (see Section 3.3).

3.1.3. Aromatic Hydrocarbons. 3.1.3.1. Selection of Polymers. Aromatic hydrocarbons represent a large group of polymers that are low in cost and available commercially. From the chemical point of view, the good oxidation resistance of aromatic hydrocarbons is due to the fact that the C–H bonds of the benzene ring have a typical bond strength of around 435 kJ·mol^{-1}, compared with aliphatic C–H bond strengths around 350 kJ·mol^{-1}.

Polymers consisting entirely of linked benzene rings, e.g., poly-*p*-phenylene (PP) (structure 2, Figure 1), are superbly resistant to oxidation with a softening point over 500 °C. They are, however, stiff rigid-rod polymers. Polyelectrolytes based on these rigid rod poly-*p*-phenylenes have recently been developed.[179,180] Commercial polymers from the aromatic family are more often of the type shown in structure 3 in Figure 1, where X is an atom or group of atoms, giving the polymer chains a certain degree of flexibility and hence processability.[181]

Most simply, X is a single atom such as S in *polyphenylene sulfide (PPS)* (structure 5, Figure 1) or O in *polyphenylene oxide (PPO)* (structure 6, Figure 1). PPS
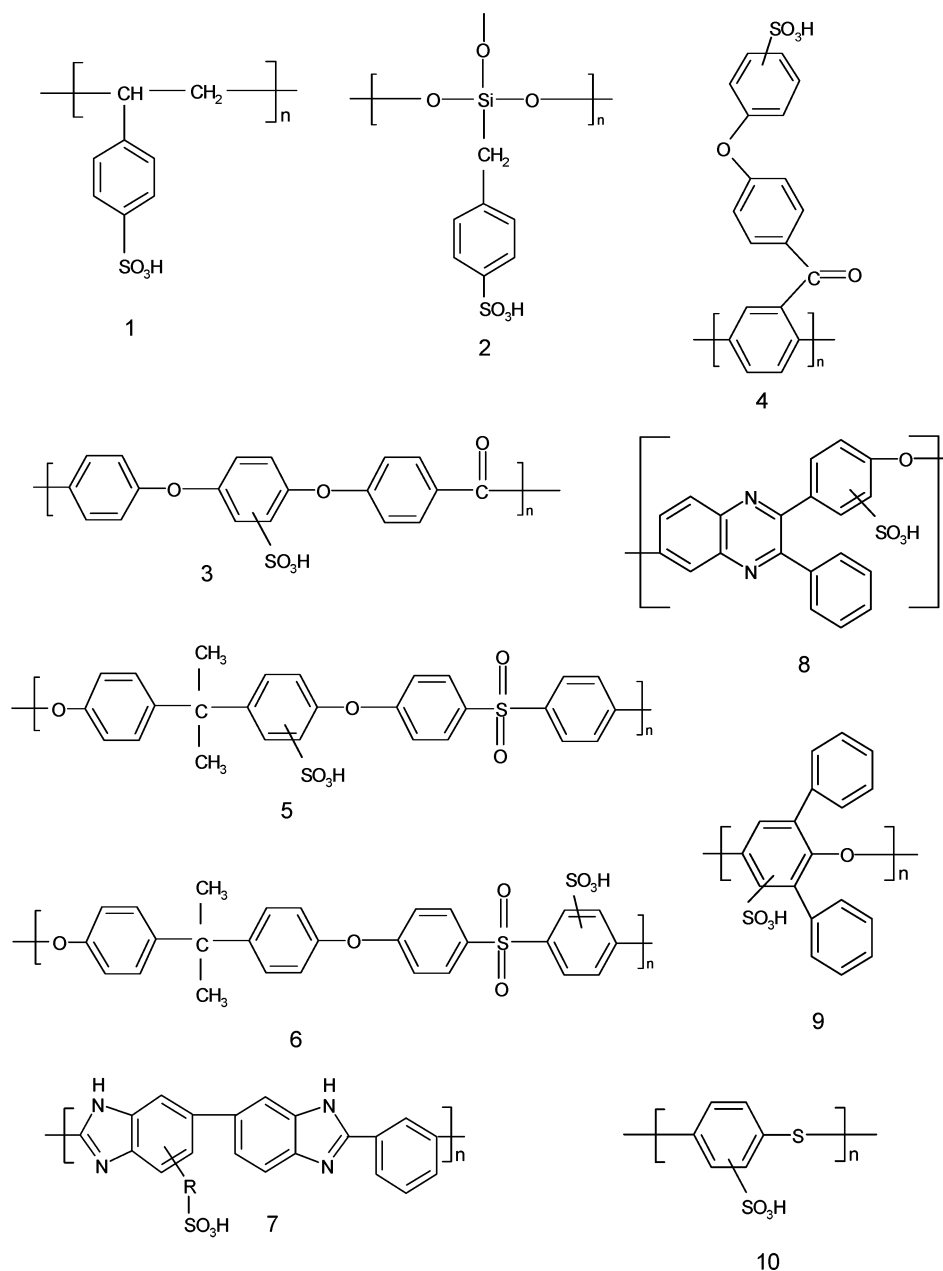
Figure 2. Chemical structures of sulfonated polymers: 1, sulfonated polystyrene; 2, poly(benzylsulfonic acid siloxane); 3, sulfonated PEEK; 4, sulfonated PPBP; 5, sulfonated PSF; 6, sulfonated PSF; 7, sulfonated PBI; 8, sulfonated poly(phenylquinoxalines); 9, sulfonated poly(2,6-diphenyl-4-phenylene oxide); 10, sulfonated PPS.

is normally crystalline, having a melting point of 285 °C with good thermal and oxidative stability at continuous working temperatures above 200 °C. Ether links provide a very good choice of functional groups as the −C−O−C− link itself is very flexible and also is highly resistant to thermal oxidation. An example is poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP, structure 4, Figure 1). In the development of polymer electrolyte membranes, aromatic polymers containing ether links have been widely investigated, e.g., *polyetheretherketones* (Victrex PEEK, structure 8, Figure 1). Being fully aromatic, this polymer has excellent thermal oxidation resistance with a glass transition temperature of 143 °C.

More commonly, X is a simple functional group such as −SO$_2$− in polysulfone, −NHCO− in polyamides, −COO− in polyesters, and −CO− in polyketones. Poly-

p-phenylene sulfone (structure 7, Figure 1) itself has too high a softening point (about 520 °C) to be processable. Aromatic polysulfone polymers containing flexibilizing groups are more preferable, for example, *polysulfone* (PSF, Udel, structure 9, Figure 1), having a glass transition temperature of 190 °C.

Polybenzimidazoles are another family of high-performance polymers. A commercial product has a chemical structure of poly(2,2′-*m*-(phenylene)-5,5′-bibenzimidazole (PBI) (structure 10, Figure 1) with a glass transition temperature of 425−435 °C. This family contains also polybenzoxazole and polybenzothiazole, which have shown a long-time thermal stability at temperatures above 350 °C.

3.1.3.2. Sulfonation of Hydrocarbons. To create the proton conductivity, charged units can be introduced into the polymer structures. This can be done by

chemical modification of the polymers (post functionalization), though a few are uniquely designed during the synthesis. The bound ion is commonly an anion, typically sulfonate ($-SO_3^-$). Sulfonation can be performed in several ways, as follows: (1) by direct sulfonation in concentrated sulfuric acid, chlorosulfonic acid,[182–185]sulfur trioxide, or its complex with tri-ethyl-phosphate[186–188]; (2) by lithiation–sulfonation–oxidation[189]; (3) by chemically grafting a group containing a sulfonic acid onto a polymer[190]; (4) by graft copolymerization using high-energy radiation followed by sulfonation of the aromatic component[151,152]; or (5) by synthesis from monomers bearing sulfonic acid groups.[191]

For developing polymer electrolytes for fuel cells, the most widely investigated systems include sulfonation of polysulfones (PSF) or polyethersulfone (PES),[189,192–196] polyetheretherketone (PEEK)[41,182,197–200] or polyetheretherketoneketone (PEEKK),[11] polybenzimidazoles (PBI),[41,43,190,201] polyimides (PI),[191,202–205] polyphenylenes (PP), poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP),[41,200,206] and rigid rod poly(*p*-phenylenes) (PP)[179,180]), and other polymers[207] (such as polyphenylenesulfide (PPS),[208,209] polyphenylene oxide (PPO),[210] polythiophenylene,[211] polyphenylquinoxaline,[212] and polyphosphazene[213]).

As a semicrystalline polymer, PEEK does not dissolve in organic solvents, but does dissolve in strong acids. PPBP dissolves in some solvents such as chloroform and dichloromethane but the sulfonated product is insoluble in these solvents. As a consequence, sulfonation of PEEK and PPBP is normally carried out by directly dissolving the polymer in concentrated sulfuric acid or oleum. Recently an amorphous form of PEEK (PEEK–WC) has been prepared,[198] which is soluble in a few aprotic polar solvents and allows a homogeneous sulfonation in, e.g., chlorosulfuric acid.

Unlike PEEK and PPBP, sulfonation of PSF can be carried out in homogeneous media because it is soluble in, e.g., dichloroethane solution. A sulfur trioxide/triethyl phosphoate (SO_3/TEP) complex was found to be more reliable with minimized side reactions.[186,187,195,214] An alternative method based on trimethylsilyl chlorosulfonate $(CH_3)_3SiSO_3Cl$ has also been recently developed.[196,215]

This direct sulfonation, either heterogeneous or homogeneous, is chemically electrophilic, i.e., the electron-donating site favors the reaction.[216] In other words, the rings that are not directly connected to the flexibilizing group are not influenced by the electron-withdrawing effect of the group, have a high electron density, and are preferably sulfonated. For PEEK, the sulfonation takes place exclusively in the phenyl rings flanked by two ethers, as shown in structure 3, Figure 2. For PPBP, it is the terminal phenyl rings that are sulfonated, as shown in structure 4, Figure 2. In the structure of PSF, the rings that are not directly connected to the sulfone group are sulfonated (see structure 5, Figure 2).

A new method was developed by lithiation followed by treatment of the metalated PSF with SO_2 to yield sulfonated PSF, and finally oxidation of the sulfonated PSF to the SPF sulfonate.[189] By this method, the sulfonic acid group is inserted into the more hydrolysis-stable part of the molecule (see structure 6, Figure 2).

PBI is difficult to sulfonate directly by using sulfuric or sulfonic acids. The resultant sulfonation degree is low and the polymer is brittle.[35] An alternative two-step method was developed: (1) activation of PBI by deprotonating the nitrogen in the benzimidazole rings of the polymer backbone with an alkali metal hydride (LiH or NaH), followed by (2) reaction with arylsulfonates[190,217] or alkyl sulfones.[218,219] The structure of sulfonated PBI is shown in structure 7, Figure 2, where R is either a benzyl or an alkyl. The introduction of arylsulfonic or alkylsulfonic acids was found to create proton conductivity with better thermal, chemical, and mechanical stabilities compared to those of sulfonic acid groups, as discussed below.

3.2. Characterizations Related To High-Temperature Operation. These sulfonated membranes, including partially fluorinated, silicone, and hydrocarbon polymers have been extensively characterized by measurements of water uptake/swelling, glass transition temperature, spectroscopy, conductivity, thermostability, gas permeability and perm-selectivity, and fuel cell performance. In general, the sulfonated polymer membranes are characterized as an alternative to PFSA membranes for low-temperature operation because of their lost cost or commercial availability or both. It is interesting to note that some of these materials, especially the sulfonated hydrocarbons, do exhibit improved performance at relatively high temperatures. The following discussion is directed to their high-temperature characteristics with emphasis on water retention, conductivity, and thermal and chemical stability.

3.2.1. Microstructures, Water Uptake, and Conductivity. In general, sulfonated aromatic polymers have different microstructures from those of PFSA membranes, as illustrated in Figure 3, according to Kreuer.[39] For PFSA membranes, the water content inside membranes is balanced by the extreme hydrophobicity of the perfluorinated polymer backbones and the extreme hydrophilicity of the terminal sulfonic acid groups. In the presence of water, only the hydrophilic domain of the nanostructure is hydrated to maintain the proton conductivity, while the hydrophobic domains provide mechanical strength. As a result the water uptake by the PFSA membranes is very high but extremely sensitive to the relative humidity.

In the case of sulfonated hydrocarbon polymers, the hydrocarbon backbones are less hydrophobic and the sulfonic acid functional groups are less acidic and polar. As a result the water molecules of hydration may be completely dispersed in the nanostructure of the sulfonated hydrocarbon polymers.[41] Generally speaking, PFSA and sulfonated hydrocarbon membranes have similar water uptakes at low water activities, whereas at high relative humidity (100%) PFSA membranes have a much higher water uptake due to the more polar character of the sulfonic acid functional groups. Consequently, the sulfonated polyaromatic membranes in general need more humidification during fuel cell operation in order to maintain the high level of conductivity. On the other hand, the less hydrophobic nature of the hydrocarbon nanostructure may result in less dependence of conductivity on humidity in the low water activity range, allowing for good proton conductivity at high temperatures. For example, by sulfonating PPS to
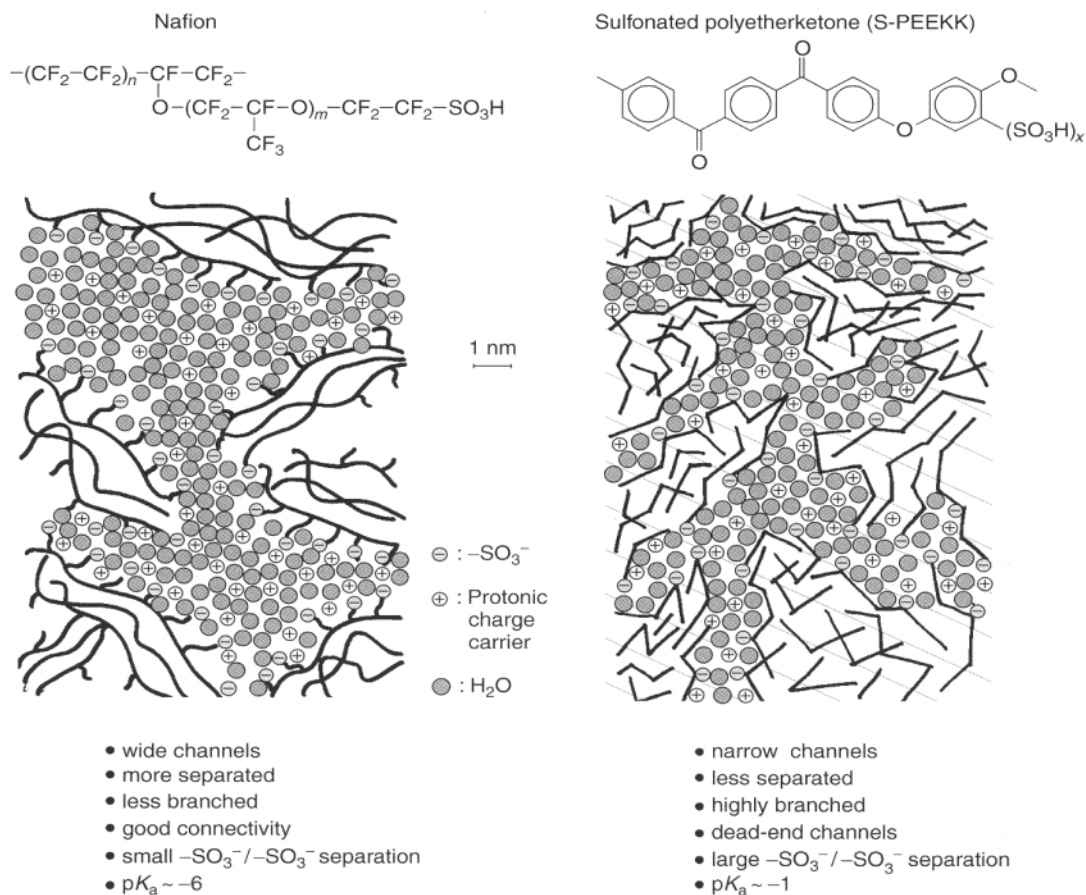
Figure 3. Schematic illustration of the microstructures of Nafion 117 and SPEEK (reproduced from ref 39 with permission of Elsevier Science).
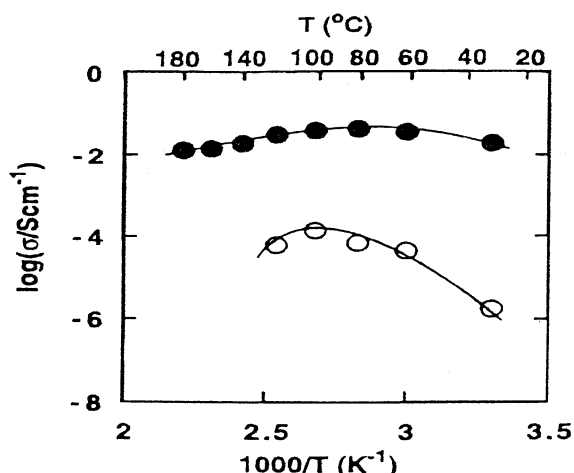

Figure 4. Temperature dependence of the conductivity of poly(thiophenylene sulfonic acid. Solid cycles, sulfonating degree of 200%; open cycles, sulfonating degree of 120% (reproduced from ref 211 with permission of the American Chemical Society).

a sulfonating degree of 200% via sulfonation of the polysulfonium salt at 120 °C, the resultant sulfonated PPS (structure 10, Figure 2) exhibits a proton conductivity of the 10^{-2} S·cm^{-1} level in a temperature range from 30 up to 180 °C, as shown in Figure 4.

It is very interesting that, by means of alkylsulfonation, the length of alkyl chains and chain branching were found to have tremendous effects on the water uptake and proton conductivity (and its temperature dependence), as well as the thermal stability of the obtained polymer membranes.[41] For example, at room temperature and 90% relative humidity, Nafion 117 membranes have a water uptake of 11 H_2O/SO_3H, and the propanesulfonated PBI (73.1 mol % sulfonation) membranes have a similar value (11.3 H_2O/SO_3H), whereas butanesulfonated PBI and methylpropane-sulfonated PBI membranes exhibit water uptakes of 19.5 and 27.5 H_2O/SO_3H, respectively, under the same conditions. It seems that the long alkyl chain and chain branching induce an increased water uptake.[41] Moreover, the absorbed water molecules and sulfonic acid groups in hydrocarbon membranes seem to be involved in stronger interactions than in PFSA membranes. As a result, the high proton conductivity of alkylsulfonated PBI membranes is maintained at temperatures above 100 °C,[41] as shown in Figure 5. Of course the stability of the alkylsulfonic acid chains is of concern, as the tertiary C−H bonds are known to be chemically unstable against H_2O_2 under fuel cell operational conditions.

High conductivity can be obtained at high sulfonation degree, but high sulfonation results in high swelling and therefore poor mechanical properties, especially at higher operating temperatures. As an example,[184] below 30% of sulfonation, sulfonated polyetheretherketone (SPEEK) and sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP) are soluble only in strong acids. Above 30% sulfonation, they are soluble in several organic media. Above 65−70% sulfonation, they are soluble in methanol, and at 100%, SPEEK is soluble in
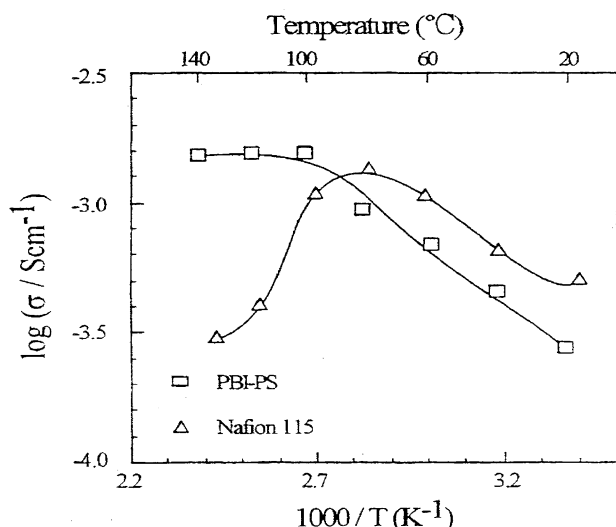
Figure 5. Conductivity of propanesulfonated PBI membranes and Nafion membranes as a function of temperature (reproduced from ref 41 with permission of Elsevier Science).

water. For sulfonated PBI, the water uptake was found to be 4, 7, 9, and 11 mol H_2O/PBI repeat unit for SPBI of sulfonation degree 0, 50, 65, and 75%, respectively.[190] Great efforts have been made to reduce the swelling by cross-linking.[185,220,221] Ionic cross-linking has been investigated by Kerres et al.,[37] as to be discussed in Section 4.3. Another way to compromise the conductivity and swelling is to prepare inorganic–organic composites. The sulfonated hydrocarbon polymers have been widely used as host matrix for preparation of such composites, aiming at high operational temperatures, as will be discussed in Section 3.3.

3.2.2. Stability and Lifetime Under Fuel Cell Conditions. For developing polymer electrolyte membranes operational at temperatures above 100 °C, another concern is the thermal stability, which is primarily due to the desulfonation of the sulfonic acid side chains.[33] The desulfonation of PFSA membranes has been widely studied [222–224] by means of TGA, DTA, FT-IR, and TGA-MS measurements. It was found that the sulfonic acid group in Nafion was stable at temperatures up to 280 °C in air.[223,224] This also seems to apply to most of the sulfonated hydrocarbons. Degradation temperatures of 240–330 and 250 °C, respectively, were reported for SPEEK[43,182,197,226,225] and sulfonated polysulfone (SPSF),[196,215] though Trotta et al.[198] reported a decomposition temperature of the SO_3H group at about 400 °C for the sulfonated PEEK–WC.

Although these thermal stability data are in general obtained by heating in nitrogen or air at a heating rate of 1–10 °C·min^{-1}, a comparison of them with the desulfonation temperature of arylsulfonic acids in aqueous solution (at around 175 °C) may suggest the positive effect of the backbone structure. This is also supported by the fact that the desulfonation temperature of sulfonic acid groups decreases with increasing degree of sulfonation.[41,226]

It is interesting to note that the degradation temperatures of the sulfonic acid groups was found to be up to 370 °C for the methylbenzenesulfonated polymers[190] and up to 400 °C for alkylsulfonated polymers,[41] compared with 280 °C for the perfluorinated sulfonic acid polymers. It seems that the strong chemical bond between

phenyl rings/alkyl chain and the sulfonic groups can improve the thermal stability of the sulfonated polymer. Another example is the highly sulfonated polyphenylene sulfide (200%), which exhibits a higher thermal stability than the lowly sulfonated polymer (60%), probably attributable to the strong C–S bond.[208] In addition, Kerres et al.[37,193] found that the acid–base blend polymer membranes (Section 4.3) also exhibit better thermal stability than the covalently cross-linked ionomer membranes.

Although informative, these thermal stability results can hardly be used to predict the long-term durability of these membranes. The chemical stability is of more concern to the lifetime of a membrane in PEMFC. The formation of H_2O_2 and radicals (–OH or –OOH) from its decomposition are believed to attack the hydrogen-containing terminal bonds in polymer membranes. This is assumed to be the principal degradation mechanism. Experimentally the generation of these radicals can be achieved by Fe^{2+}-catalyzed H_2O_2 decomposition. Based on this method, the so-called Fenton test is widely used for the stability evaluation of PFSA and other polymer membranes.[227] The results showed that membranes based on the saturated and perfluorinated Nafion exhibit higher chemical stability than those based on polyaromatic hydrocarbons. And this peroxy radical attack is believed to be much more aggressive at temperatures exceeding 100 °C. However, it should be noted that some hydrocarbon membranes, for example polybenzimidazoles, cannot stand the Fenton test at all, but as to be seen in Section 5, the membrane has been demonstrated with a fuel cell lifetime over 5000 hours at 150 °C by continuous operation.

So far, very limited information is available concerning the long-term durability of the sulfonated polymer membranes under fuel cell operations. Steck et al.[165] reported the longevity up to 500 h for the nonfluorinated polymers based on sulfonated poly(phenylquinoxalines) (SPPQ, structure 8, Figure 2) and sulfonated poly(2,6-diphenyl-4-phenylene oxide) (SP₃O, structure 9, Figure 2), as well as sulfonated poly(arylethersulfone). Based on SPEEK membranes, Bouer et al.[197] performed a discontinuous test (shut-down overnight) at temperatures of 90–110 °C for several days. Faure et al.[228] performed fuel cell tests at 70 °C with a naphthalenic sulfonated polyimide membrane, reporting a stability of at least 3000 hours.

3.3. Inorganic–Organic Composite Membranes. In addition to PFSA, sulfonated hydrocarbon polymers have been widely used as a host matrix for preparation of inorganic/organic composites, aiming at high operating temperatures. The justification of the development of inorganic–organic composite membranes may include the following: (1) improving the self-humidification of the membrane at the anode side by dispersing a hydrophilic inorganic component homogeneously in the polymer; (2) reducing the electro-osmotic drag and therefore the drying-out of the membrane at the anode side; (3) suppressing the fuel crossover, e.g. methanol in DMFC; (4) improving the mechanical strength of membranes without sacrificing proton conductivity. In sulfonated polymers, for example, a high sulfonating degree is desirable for high conductivity, however, this will be accompanied by undesirable swelling (or even solubility

Table 4. Summary of Inorganic−Organic Composite Membranes Under Development

organic component	inorganic component	comments	ref
SPEK, SPEEK	ZrP + (SiO$_2$, TiO$_2$, ZrO$_2$)	reduced methanol crossover	238
SPEEK	SiO$_2$, ZrP, Zr−SPP	0.09 S·cm^{-1} at 100 °C, 100% RH, H$_2$/O$_2$ fuel cell test at 95 °C	27
SPEEK	HPA	10^{-1} S·cm^{-1} above 100 °C	225
SPEEK	BPO$_4$	5 × 10^{-1} S·cm^{-1}, 160 °C, fully hydrated	239
SPEEK	SiO$_2$	3−4 × 10^{-2} S·cm^{-1} at 100 °C, 100% RH	240
SPSF	PWA	0.15 S·cm^{-1} at 130 °C, 100% RH	241
SPSF	PAA	0.135 S·cm^{-1} at 50 °C, 100% RH	237, 242
SPSF	PAA	2 × 10^{-2} S·cm^{-1}, 80 °C, 98% RH	214
SPSF	PAA	H$_2$/O$_2$ cell, 500 h at 80 °C and 4 atm	215
PBI	ZrP + H$_3$PO$_4$	9 × 10^{-2} S·cm^{-1} at 200 °C, 5% RH	243
	PWA/SiWA + H$_3$PO$_4$	3−4 × 10^{-2} S·cm^{-1} at 200 °C, 5% RH	
PBI	SiWA + SiO$_2$	2.2 × 10^{-3} S·cm^{-1} at 160 °C, 100% RH	234
PBI	PWA + SiO$_2$ + H$_3$PO$_4$	T_d > 400 °C; 1.5 × 10^{-3} S·cm^{-1} at 150 °C, 100% RH	233
PVDF	SiO$_2$,TiO$_2$, Al$_2$O$_3$, doping acids	>0.2 S·cm^{-1} at 25 °C	244
		>0.45 S·cm^{-1} (25 °C), DMFC at 80 °C	245
PVDF	CsHSO$_4$	10^{-2} S·cm^{-1}, >150 °C, 80% RH	130
PVDF−SPS	AA	high-dimensional stability	246
GPTS	SiWA + SiO$_2$; SiWA + ZrP	1.9 × 10^{-2} S·cm^{-1} at 100 °C, 100% RH	247
ICS−PPG	PWA, SiWA, and W−PTA	10^{-6} to 10^{-3} S·cm^{-1}	248
polysilsesquioxanes	PWA	3 × 10^{-2} S·cm^{-1} at 140 °C	249
ORMOSIL	HPA	10^{-3} S·cm^{-1} at 25 °C; DMFC test	250
PEO	tungsten acid	10^{-2} S·cm^{-1} at 120 °C; 1.4 × 10^{-2} 80 °C	230
PEO, PPO, PTMO	PWA	T_d = 250 °C; 10^{-2} S·cm^{-1} at 140 °C	231, 232
PVA/glycerin	ZrP + AA	10^{-3} to 10^{-4} S·cm^{-1} at 25 °C; T_d >110 °C	251
PTFE	zeolites	DMFC test	252
PTFE	ZrP	4 × 10^{-2} S·cm^{-1}	253, 254

in water) of the membrane and therefore reduced mechanical strength. Introduction of an inorganic component into the polymer will compensate for the mechanical behavior; (5) assisting the improvement of the thermal stability; and (6) enhancing the proton conductivity when solid inorganic proton conductors are used. This may allow for use of sulfonated polymers at a low sulfonation degree.

For preparing organic−inorganic composite membranes, the used polymer components include, besides PFSA, those without functional groups such as poly-(ethylene oxide)s (PEO)[229−232] and PBI,[233−235] and those with functional groups such as sulfonated polystyrene,[236] sulfonated polysulfone (SPSF),[214,215,237] sulfonated polyetheretherketone (SPEEK),[27,225,238−240] and many others.[244−254]

The solid inorganic compounds include oxides such as amorphous silica, inorganic proton conductors, and in many cases silica-supported inorganic proton conductors. The solid inorganic proton conductors of interest are discussed in Section 2.4.1. These compounds are in crystalline form and therefore mechanically poor when used alone in the form of membranes. Combination of these inorganic proton conductors with a polymer component will provide flexibility.

Extensive efforts have been made to develop inorganic−organic composite membranes based on these solid inorganic proton conductors. Table 4 summarizes these developments with brief comments.

As recently reviewed by Jones et al.[40] and discussed in Sections 2.3 and 2.4 for PFSA membranes, inorganic−organic composite membranes can be prepared by (1) casting a bulk mixture of powder or colloidal inorganic components with a polymer solution, or (2) in-situ formation of inorganic components in a polymer membrane or in a polymer solution.

For bulk mixing, the inorganic components should be prepared in the form of powders or dispersions. Examples include silica, titania, alumina, tungstophosphoric acid, tungstomolybdic acid, antimonic acid, phos-phoantimonic acid, boron phosphate, and silica-supported tungstophosphoric acid. To prepare uniform and nonporous membranes, size and dispersion of the solid particles are of special importance. Another method for bulk mixing is to use colloidal suspensions of phosphates and phosphonates in some solvents.[103,109] The suspensions enable the nanosized particles to be dispersed in the formed membranes.[27,29] Using this method, Bonnet et al.[27] prepared composite membranes from SPEEK and zirconium phosphate, sulfophenyl phosphonate (Zr(HPO$_4$)$_{0.5}$(O$_3$PC$_6$H$_4$SO$_3$H)$_{1.5}$ or Zr(HPO$_4$)-(O$_3$PC$_6$H$_4$SO$_3$H)). Conductivities of 0.09 S·cm^{-1} at 100 °C and 0.04 S·cm^{-1} at 150 °C under 100% RH were reported for these membranes. H$_2$/O$_2$ and H$_2$/air cell tests were performed at temperatures up to 120 °C.

Other techniques such as the exchange−precipitation process[28,136] and sol−gel reactions,[85] as discussed for PFSA composites (Sections 2.3 and 2.4), have also been employed for preparation composite membranes with sulfonated polymers.

As can be seen from Table 4, some of these composite membranes exhibit promising conductivities at temperatures above 100 °C. However, most of these composite membranes have not been tested in fuel cells.

4. Acid−Base Polymer Membranes

Acid−base complexation represents an effective approach to development of proton-conducting membranes.[255] Basic polymers can be doped with an amphoteric acid, which acts both as a donor and an acceptor in proton transfer and therefore allows for the proton migration (Section 4.1.). H$_3$PO$_4$-doped PBI has received much attention in the past few years[40,49] (Section 4.2). Another type of acid−base polymer membranes was developed by Kerres' group.[37] In their efforts to reduce polymer swelling, they found that the base protonation and hydrogen bridging in acid−base blend membranes markedly reduce the swelling. The resulting acid−base blends constitute a new class of proton-conducting

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membranes with high conductivity, thermal stability, and mechanical flexibility and strength (Section 4.3).

4.1. Acid−Base Polymer Membranes in General. Polymers bearing basic sites such as ether, alcohol, imine, amide, or imide groups react with strong acids such as phosphoric acid or sulfuric acid. The basicity of polymers enables the establishment of hydrogen bonds with the acid. In other words, the basic polymers act as a solvent in which the acid undergoes to some extent dissociation.

Because of their unique proton conduction mechanism by self-ionization and self-dehydration,[256] H_3PO_4 and H_2SO_4 exhibit effective proton conductivity even in an anhydrous (100%) form. When a basic polymer is present, the interaction between these acids and the polymer through hydrogen bonding or potonation would increase the acid dissociation, compared to that of anhydrous acids.

A number of basic polymers have been investigated for preparing acid−base electrolytes, such as PEO,[257,258] PVA,[259] polyacrylamide (PAAM),[257,260−262] and polyethylenimine (PEI).[263] Recently Nylon[264] and poly(diallyldimethylammonium-dihydrogen phosphate, $PAMA^+−H_2PO_4^-$)[265] have also been investigated.

Most of these acid−polymer blends exhibit proton conductivity less than 10^{-3} S·cm^{-1} at room temperature. When plotted as a function of the acid content, the conductivity seems to have a minimum at the composition where the maximum protonation is reached.[255,266] High acid contents result in high conductivity but sacrifice mechanical stability, especially at temperatures above 100 °C. Another concern is the oxidative stability of the tertiary C−H bonds in applications for fuel cells. To improve the mechanical strength, efforts in this field have been made by (1) cross-linking of polymers (e.g., PEI[263]); (2) using high T_g polymers such as PBI and polyoxadiazole (POD);[267] and (3) adding inorganic filler or/and plasticizer,[268] as recently reviewed by Lasségues et al.[268] Phosphoric-acid-doped PBI has received the most attention and will be discussed in Section 4.2.

The combination of the acid and polymer forms a solid polycation at low acid contents. When the acid content is higher, the plastifying effect of the excessive acid sometimes leads to the formation of a soft paste, which is unable to be processed into membranes. Addition of an inorganic filler such as high-surface-area SiO_2 would make the materials stiffer, as demonstrated in systems of $PEI−H_3PO_4−SiO_2$,[266] $SiO_2−PVDF−acid$,[269] and $Nylon−H_3PO_4/H_2SO_4−SiO_2$.[268] The latter was reported to exhibit a room-temperature conductivity as high as 10^{-1} S·cm^{-1}.

Most of the studied acid/polymer systems are not entirely anhydrous, as water is present as a necessary plasticizer for improving conductivity and mechanical properties. Gel electrolytes, as often termed, are obtained by introduction of organic plasticizers such as propylene carbonate (PC), dimethylformamide (DMF), and glycols.[270] DMF[271] and PC/DMF[261,272] have also been used as plasticizers in $H_3PO_4−PVDF$ and acid−PMMA systems.

4.2. Acid-Doped PBI Membranes. Polybenizimidazole (PBI, structure 10 in Figure 1) is an amorphous thermoplastic polymer with a glass transition temperature of 425−436 °C. It has a good chemical resistance

and excellent textile fiber properties.[273] In the form of a membrane PBI has received much attention mainly for use in blood dialysis and reverse osmosis at high temperature and in harsh environments.[274,275] In addition to the commercially available PBI, AB−PBI in a short form has also been prepared.[49] When doped with acids[276] as well as strong bases[277,278] the PBI polymeric electrolyte has been proposed for use as fuel cell membrane electrolytes at temperatures above 100 °C. A number of patents have been granted.[279] Here below are some main issues concerning the development.

4.2.1. Membrane Casting and Acid Doping. PBI dissolves in strong acids, bases, and a few organic solvents. Membranes can be cast from their solutions accordingly. Among the organic solvents that are able to dissolve PBI, N,N-dimethyl acetamide (DMAc) is the most widely used. PBI membranes can be cast from solutions of different concentrations. PBI membranes have also been prepared from a 2.5−3.0% solution in a mixture of NaOH and ethanol.[282] PBI membranes cast from DMAc and NaOH solution need to be doped with, e.g., H_3PO_4 in order to obtain sufficient conductivity. When immersed in, e.g., 11 M phosphoric acid at room temperature, the equilibrium uptake is about 5 molecules of H_3PO_4 per repeat unit of PBI.[276,280,283,285] Of the doping acid, about 2 molecules of phosphoric acid are bonded to each repeat unit of PBI, in good agreement with the fact that there are two nitrogen sites for the hydrogen bonding in a PBI monomer unit. The rest of the acid is un-bonded "free acid", which can be easily washed away.[280] A direct method to cast the PBI and acid was developed by mixing PBI with fluoroacetic acid and H_3PO_4.[281,282]

4.2.2. Conductivity. The proton conductivities of acid-doped PBI have been investigated.[283−286] The conductivity of acid-doped PBI electrolyte is found to be strongly dependent on the acid-doping level, temperature, and atmospheric humidity. The conductivity follows the Arrhenius law, suggesting a hopping-like conduction mechanism. In an acid doping range from 2.0 to 5.6 mol H_3PO_4 per repeat unit, the activation energies were found to be in a range of 18−25 kJ·mol^{-1}.

The proton hopping from one N−H site to another contributes little to the conductivity, as pure PBI is not conducting. Proton hopping from one N−H site to phosphoric acid anions contributes significantly to the conductivity. At a doping level of 2 mol H_3PO_4 per repeat unit, the conductivity of the membrane is about 2.5×10^{-2} S·cm^{-1} at 200 °C.[243] The presence of the free or unbounded acid is necessary to improve the conductivity. At an acid-doping level of 5.7 mol H_3PO_4, the measured conductivity is 4.6×10^{-3} S·cm^{-1} at room temperature, 4.8×10^{-2} S·cm^{-1} at 170 °C, and 7.9×10^{-2} S·cm^{-1} at 200 °C.[243] This indicates that the successive proton transfer along the mixed anionic chain contributes the major part of the conductivity, as recently shown for the $PAMA^+H_2PO4^-$ system.[265] Further improvement of conductivity was observed by increasing the relative humidity, indicating the bridging effect of water molecules in the proton conduction.

4.2.3. Electro-Osmotic Drag of Water. An electro-osmotic drag due to the proton movement is defined as the number of water molecules moved with each proton in the absence of a concentration gradient. As a com-

Table 5. Summary of H$_2$/O$_2$ (Air) and DMFC Tests at High Temperatures

cell	types/membranes		test results	ref
H$_2$/O$_2$ or H$_2$/Air	modified PFSA	Nafion−ZrP	130 °C, 3 atm	136
		Nafion−SiO$_2$	140 °C, 3 atm	95, 96
	hydrocarbon polymers	SPEEK	H$_2$/air 3.5/4 atm, 90−110 °C	197
		SPEEK−ZrP	50−70 μm, 120 °C, 2.6/2.6 atm, 4/4 atm (air)	27
	acid−base polymers	PBI−H$_3$PO$_4$	55−200 °C, 1/1 atm, 0.45 mg Pt	13
		PBI−H$_3$PO$_4$	1/1 atm, 150 °C, 200 h	291
		PBI−H$_3$PO$_4$	50−185 °C, 1/1 atm, 3% CO	299
		PBI−SPSF−H$_3$PO$_4$	130−170 °C, 1/1 atm, 0.45 mg Pt	194
		PBI−SPSF−H$_3$PO$_4$	190 °C, 1/1 atm, 0.45 mg Pt	298
		PBI−SPSF−H$_3$PO$_4$	Quasi-DMFC at 200 °C, 1/1 atm	26
	others	solid CsHSO$_4$	ambient pressure, 150−160 °C	129
DMFC	modified PFSA	Nafion−Teflon−PWA	H$_2$/O$_2$ (air), ambient pressure, 120 °C, humidification 90/84 °C	78
		Nafion + HPA	145 °C, 3/4 atm	133
		Nafion−ZrP	up to 150 °C, 4/4 atm	28
		Nafion−SiO$_2$	145 °C, 0.6 A·cm^{-2} at 0.4 V	84, 97
	acid−base polymers	SPEEK−PBI	80−100 °C, 1.5/1.5 atm	295
		SPSU−P$_4$VP		
		SPEEK−P$_4$VP		
		SPSU−PBI		
		SPEEK−PBI−PSU	110 °C, 2.5/4.0 atm, air	297
		PBI−H$_3$PO$_4$	1/1 atm, O$_2$, 200 °C	276
		PBI−H$_3$PO$_4$	150−200 °C, O$_2$/air 1/1 atm, 4 mg·cm^{-2}, 0.1 W·cm^{-2}	293

parison, the electro-osmotic drag coefficient for vapor- or liquid-equilibrated Nafion membranes ranges from 0.9 to 3.2 at room temperature.[7] For PBI membranes, however, the water drag coefficient is found to be close to zero,[13,287] indicating that the conductivity of the acid-doped PBI membranes is less demanding on the fuel humidification during the fuel cell operation.

4.2.4. Other Properties. Methanol crossover rate,[288] thermal stability,[289] mechanical properties,[282] and kinetics of oxygen reduction[59,290] have also been studied. Fuel cell tests have been performed with hydrogen[291,292] and methanol[276,293] as fuel.

4.3. Organic Acid−Base Blends. Flexible ionomer networks can be prepared from acid−base polymers by ionic cross-linking of polymeric acids and polymeric bases.[37,294,295] The used acidic polymers are sulfonated polysulfone (SPSF), sulfonated polyethersulfone (SPES), or sulfonated polyetheretherketone (SPEEK). Some basic polymers are commercially available, such as PBI, polyethyleneimine (PEI), and poly(4-vinylpyridine) (P$_4$-VP). New basic polymers have been synthesized by modifying the PSF backbones with NH$_2^-$ or N(CH$_3$)$_2^-$ groups.[296] Combinations of SPEEK/PBI, SPEEK/P$_4$VP, SPEEK/PSF(NH$_2$)$_2$, SPSF/PBI, and SPSF/P$_4$VP have been explored.[294−297] Good fuel cell performance has been achieved at a temperature of 110 °C and pressure of 1.5 atm. Further doped SPSF/PBI membranes with phosphoric acid[26,194,195,298] have been investigated and exhibit excellent chemical and thermal stability, and good proton conductivity.

5. Demonstration of High Temperature PEMFCs

High-temperature operation of both DMFC and H$_2$/O$_2$(air) PEMFC has been demonstrated with the developed polymer electrolyte membranes. Modified PFSA membranes have been tested at temperatures up to 120 °C under ambient pressure and up to 150 °C under pressures of 3−4 atm. The temperature range for phosphoric-acid-doped PBI membranes is up to 200 °C under ambient pressures. Table 5 summarizes these efforts according to the fuel cell mode and membrane type.

Significant improvements in H$_2$/O$_2$ cells have been observed in comparison with the unmodified PFSA. An
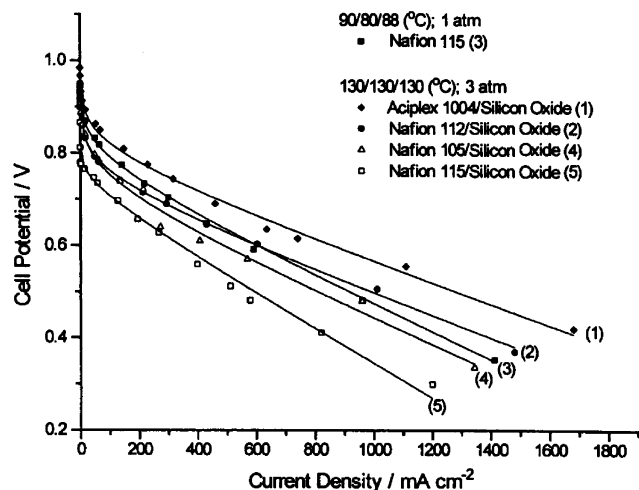

Figure 6. H$_2$/O$_2$ cell performance with unmodified and modified PFSA membranes (taken from ref 95). Temperatures indicated in the figure are hydrogen humidifier temperature/ cell temperature/oxygen humidifier temperature (reproduced from ref 95 with permission of Elsevier Science).
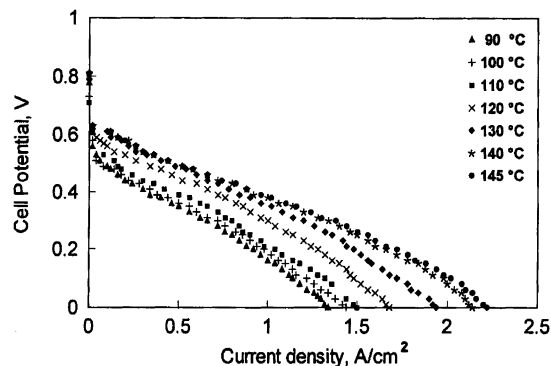

Figure 7. DMFC cell performance with recast Nafion membranes containing SiO$_2$−PWA (reproduced from ref 133 with permission of Elsevier Science).

example is shown in Figure 6, where the reference was unmodified Nafion 115 membrane, operating at 80 °C under ambient pressure with humidifier temperatures of 90/80 °C.[95] The modified PFSA membranes were Aciplex 1004/SiO$_2$, Nafion112/SiO$_2$, Nafion105/SiO$_2$, and
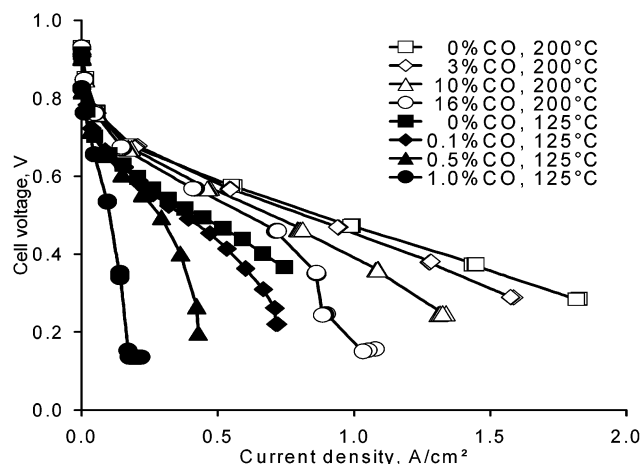
Figure 8. Polarization curves of a PBI-based PEMFC with oxygen and hydrogen or hydrogen containing CO at 125 and 200 °C under ambient pressure (adapted from ref 25).

Nafion115/SiO$_2$. Operation conditions of the fuel cell were 130 °C and 3 atm with humidifier temperatures of 130/130 °C.

Figure 7 shows DMFC performance based on the recast Nafion membrane modified with SiO$_2$-supported PWA.[133] The test temperature range was from 90 to 145 °C and the pressure was 3 and 4 atm at anode and cathode side, respectively. A cell voltage gain of about 100 mV was observed in the whole range of current density, indicating the enhanced kinetics of the methanol electro-oxidation process at high temperatures.

The CO poisoning effect has been investigated with phosphoric-acid-doped PBI membranes in a temperature range up to 200 °C.[13,25,299] Figure 8 shows polarization curves of a PBI-based PEMFC with pure hydrogen and hydrogen containing CO at 125 and 200 °C.[25] At 125 °C, no significant performance loss was observed with 0.1% CO (1000 ppm). At 200 °C, 3% CO in

hydrogen results in no significant performance loss at current densities up to 1.0 A·cm^{-2} or at cell voltage above 0.5 V. This should be compared to the tolerance of 10–20 ppm CO for PEMFCs operating at 80 °C. It should be noted that this PBI-based PEMFC operates with no humidification of the reactant gases.

The high tolerance to CO by the high-temperature PEMFC technology allows the PEMFC to operate with reformed methanol directly from a simple reformer. A direct methanol fuel cell test system is modified by filling the fuel vaporizer with methanol-reforming catalysts.[26] Figure 9 shows the fuel cell performance with hydrogen and methanol reformate as fuel. Throughout the whole current density range, up to 1.3 A·cm^{-2}, a voltage loss of about 30–70 mV is observed by using the methanol reformate instead of pure hydrogen. A peak power density as high as 500 mW·cm^{-2} was obtained at a noble metal loading of 0.45 mgPt·cm^{-2} and under the atmospheric pressure.

The lifetime of the high-temperature membranes under fuel cell conditions has been a critical issue of their development. Concerning the modified PFSA membranes, one may expect a long lifetime in a temperature range up to 150 °C due to the perfluorinated nature of the polymer, though no report has been published. No information is available for hydrocarbon-based membranes at temperatures above 100 °C. Acid-doped PBI membranes contain "unbounded" acid and therefore have received much concern with respect to their lifetime. Our research[300] showed that lifetimes of more than 3500 and 5000 h at 120 and 150 °C, respectively, have been achieved under continuous H$_2$/ O$_2$ operation. A similar result was obtained by Celanese, i.e., 6000 h at 160 °C with a small voltage decay rate.[24] This continuous operation at temperatures above 100 °C involves no liquid water formation and therefore minimizes the possible acid leakage. A thermal cycling
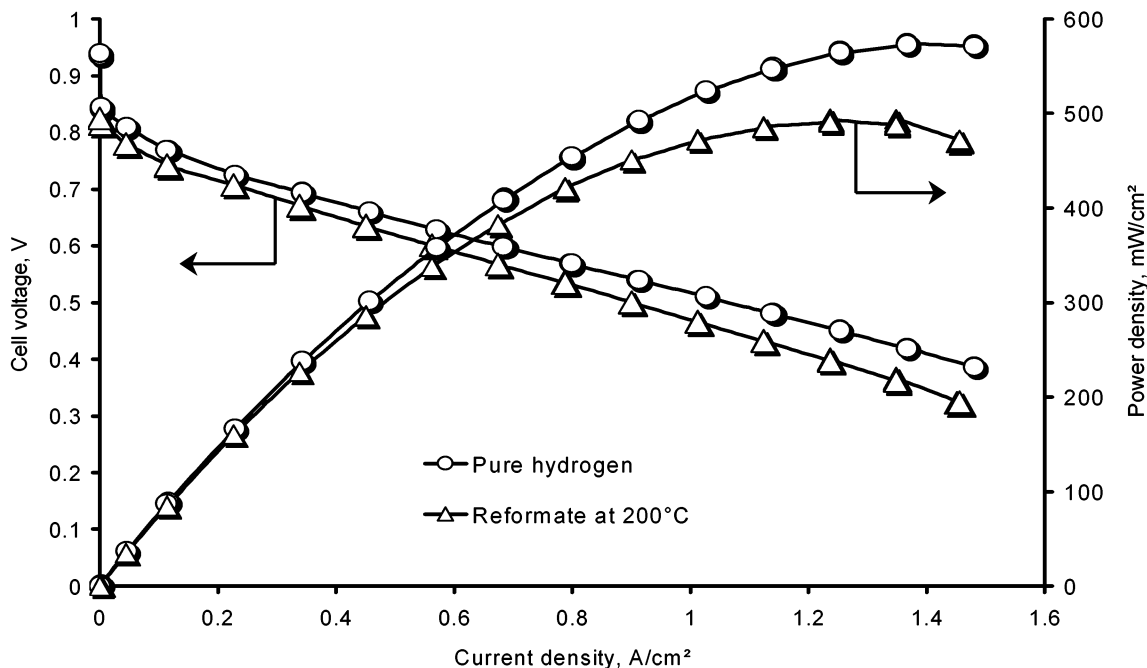

Figure 9. Cell voltage and power density versus current density of a PBI cell at 200 °C under ambient pressure. The membrane was a PBI–SPSF blend doped with H$_3$PO$_4$. The fuel was pure hydrogen and reformed hydrogen-rich gas directly from a methanol reformer (reproduced from ref 26 with permission of The Electrochemical Society, Inc.).

test with frequent shutdown and restart will be of more interest for the evaluation and is underway in our group.

6. Conclusive Remarks

The currently well-developed PEMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes operating at a typical temperature of 80 °C. The newest development in the field is temperature-resistant polymer membranes. Approaches and recent progress of the development are reviewed. The newly developed polymer membranes are classified into three groups: modified PFSA membranes, alternative sulfonated polymers and their inorganic composite membranes, and acid−base complex membranes. DMFC and H_2/O_2(air) cells based on modified PFSA membranes have been successfully operated at temperatures up to 120 °C under ambient pressure and up to 150 °C under pressures of 3−5 atm. The sulfonated hydrocarbons and their inorganic composites exhibit promising conductivity and thermal stability at temperatures above 100 °C. More evaluation is needed for their applications in high-temperature PEMFC. Acid−base polymer membranes, especially H_3PO_4-doped PBI, have been demonstrated for DMFC and H_2/O_2(air) PEMFC at temperatures up to 200 °C under ambient pressure. The advanced features include high CO tolerance, simple water management, and possible integration with the fuel processing unit.

Nomenclature

AA, Antimonic acid; AMPSA, 2-acrylamido-2-methyl-1-propanesulfonic acid; BMI, 1-butyl, 3-methyl imidazolium; BMITf, 1-butyl, 3-methyl imidazolium triflate; BMIBF4, 1-butyl, 3-methyl imidazolium tetrafluoroborate; DMF, dimethylformamide; DMFC, direct methanol fuel cell; DTA, differential thermal analysis; DVB, divinylbenzene; FEP, fluoroethylene-*co*-hexafluoropropylene; FT-IR, Fourier transform infrared spectrometer; GPTS, 3-glycidoxypropyltrimethoxysilane; HPA, heteropolyacids; ICS−PPG, 3-isocyanatopropyltriethoxy silane with poly-(propyleneglycol)-bis-(2-aminopropyl ether); Kynar, polyvinylidene fluoride; ORMOLYTE, organically modified electrolyte; ORMOSIL, organically modified silicate; PAA, phosphatoantimonic acid; PAAM, polyacrylamide; PAMA, poly(diallyldimethylammonium); PBI, poly [2,2'-(*m*-phenylene)-5,5'-benzimidazole]; PC, propylene carbonate; PEEK, polyetheretherketone; PEI, polyethyleneimine; PEM, proton exchange membrane (polymer electrolyte membrane); PEMFC, proton exchange membrane fuel cell (polymer electrolyte membrane fuel cell); PEO, poly(ethylene oxide)s; PES, polyethersulfone; PFSA, perfluorosulfonic acid; PI, polyimides; PMMA, poly(methyl methacrylate); PMoA, $H_3PMo_{12}O_{40} \cdot nH_2O$; POD, polyoxadiazole; PP, poly(*p*-phenylene); PPBP, poly(4-phenoxybenzoyl-1,4-phenylene); PPO, polyphenylene oxide, especially poly(2,6-dimethyl-1,4-phenylene oxide); PPS, polyphenylene sulfide; PSF,

polysulfone; PSU, polysulfone Udel; PTA (PWA), phosphotungstic acid; PTFE, polytetrafluoroethylene; PTMO, polytetramethylene oxide; PVA, poly(vinyl acetate); PVDF, poly(vinylidene fluoride); PVdF(HFP), poly(vinylidene fluoride)-hexafluoropropylene; P_4VP, poly(4-vinylpyridine); PWA (PTA), phosphotungstic acid; SiWA (STA), silicotungstic acid; SPBI, sulfonated poly [2,2'-(*m*-phenylene)-5,5'-benzimidazole]; SPEEK, sulfonated polyetheretherketone; SPEK, sulfonated polyetherketone; SPES, polyethersulfone; SP_3O, poly(2,6-diphenyl-4-phenylene oxide); SPPBP, sulfonated poly(4-phenoxybenzoyl-1,4-phenylene); SPPO, sulfonated polyphenylene oxide, especially poly(2,6-dimethyl-1,4-phenylene oxide); SPPQ, poly(phenylquinoxalines); SPS, sulfonated polystyrene; SPSF, sulfonated polysulfone; SPSU, sulfonated polysulfone Udel; TBAC, tetra-*n*-butylammonium chloride; TEOS, tetraethyl orthosilicate; TEP, triethyl phosphate; T_g, glass transition temperature; TGA, thermogravimetric analysis; TGA-MS, thermogravimetric mass spectrometric analysis; TMDES, 1,1,3,3-tetramethyl-1,3-diethoxydisiloxane; VPA, vinylphosphonic acid; ZrP, zirconium hydrogen phosphate.

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