

Emerging membranes for electrochemical systems Part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications[☆]

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Abstract

This paper shows an exhaustive presentation and complementary discussions on various aspects of works done recently on the developments of composite membranes for polymer electrolyte fuel cell (PEFC) applications. The limitations of per-fluorinated polymer electrolyte membranes to low temperature (<80 °C) PEFC applications are discussed. Research on alternative proton conducting membranes to the per-fluorinated membranes for high temperature PEFC applications are shown. The development of the bis[(perfluoroalkyl)sulfonyl]imide as an alternative membrane to the per-fluorinated family is indicated. The concept of synergetic composite membranes for high temperature PEFC applications is introduced. Recent approaches and concepts for the elaboration of new composites membranes are described. The following aspects of the researches on proton conducting proton membranes are discussed: (i) macro- and nano-composites per-fluorinated ionomer composite membranes (PFICMs); (ii) partially per-fluorinated composite membranes; and (iii) non-per-fluorinated composite membranes. Results based on our original works are also presented. In each case, the type of the composite membrane is well described. Accordingly, organic–inorganic, organic–organic, organic–acid and organic–base complexes composite membranes are considered. The challenges related to these developments are discussed. Prospective for future developments on effective composite membranes for high temperatures PEFC applications are discussed.

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1. Introduction

Instead of the well established per-fluorinated polymer electrolytes (Nafion[®], Flemion[®], and Aciplex[®] families), various new modified per-fluorinated, partially per-fluorinated and non-per-fluorinated polymer electrolytes are under development for PEFC applications. One of the key arguments for the development of new polymer electrolytes is the necessity to operate the cell under high temperatures conditions. The operation of polymer electrolyte fuel cells at temperature above 140 °C is receiving world-wide attention because the selection of the fuel is still straightforward and a number of fuels including reformed hydrogen with high CO content and light hydrocarbons (alcohol, natural gas, propane, etc.) are still in consideration for PEMFC application. Accordingly, cell temperature op-

eration at temperature more than 140 °C is very interesting because at this range of temperatures, anode catalyst poisoning by CO is less important and the kinetics of the fuel oxidation will be improved and the efficiency of the cell be significantly enhanced. High temperature cell operation will contribute to reduce the complexity of the hydrocarbon fuel cell systems. This work is based on the status of recent developments made on various composite membranes and their potential use in high temperatures (more than 140 °C) PEFC. Original works on some concepts we developed on new composite membranes based on various commercial polymer will be also presented. The possible candidates of composite membranes to be developed for commercial applications will be discussed and future prospects related to membranes development will be presented. The advantages and limitations of per-fluorinated polymer electrolytes for PEFC applications will be analyzed. Development of the bis[(perfluoroalkyl)sulfonyl]imide as an alternative membrane to the per-fluorinated family will be described. Development of macro- and nano-composite per-fluorinated membranes will be shown. The various concepts and studies

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of partially per-fluorinated and non-per-fluorinated membranes will be extensively presented.

2. Advantages and limitations of per-fluorinated polymer electrolytes

The technical challenges related to the development of commercial polymer electrolyte fuel cells (PEFC) are the following: (i) mass production and cost reduction of components (bipolar plates, membranes, catalysts, etc.); (ii) installation of the infrastructure for low-cost, clean and efficient fuel; (iii) simplification of the stack and system; (iv) introduction of low-cost/high-volume and environmentally friendly materials processes; and (v) automation of materials processes; while at the same time maintaining or increasing performance and reliability. Accordingly, for the components, the main aspects to be developed are thin films and surface modification technologies. Membrane electrode assembly (MEA) is the basic component of the single cell of a stack. From the point of view of low-cost production, the best approach is to produce the layered structures of the MEA using continuous processes; for example, by casting the constituent materials as films at a very much lower cost than is the case today. The proton exchange membrane (PEM) is the key element of this component, which separates the electrode structures to prevent the mixing of reactant gases and the formation of an electrical short. This makes its properties, functionality, cost and reliability very important for real cell operations. The main properties required for PEFC applications which are to be used in electrochemical systems are [1–3]:

- (i) good mechanical and chemical stability (over long periods) in a strongly oxidative environment;
- (ii) high proton conductivity, which can be obtained by increasing the proton exchange capacity and the water content, and decreasing membrane thickness (the proton conductivity may be due to the existence of ionic domains which swell in the presence of water);
- (iii) high perm-selectivity for non-ionized molecules and anions, although conductivity decreases when selectivity increases and a compromise must be found.

To meet the needs of mass production of PEFC components, these requirements must be met at very much lower cost than that of today. In addition, viable membranes will have to be compatible with volume-manufacturing processes. The most commonly used membranes for low temperature fuel cell applications are per-fluorinated sulphonic acid membranes (PFSAs). Their development by DuPont [4,5] with continuous improvements up to the present time [1,2] and Dow (the co-monomer structure is $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$) [6], as well as the Flemion[®] membrane from the Asahi Glass Corporation and the Aciplex[®] membrane from Asahi Chemicals have made a significant contribution to the use of these membranes in fuel cell

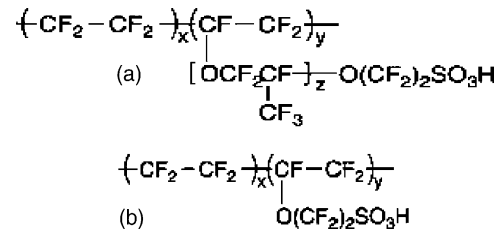


Fig. 1. (a) The general structure of the per-fluorinated membrane: $X = 6-10$; $y = z = 1$ (Nafion[®], Flemion[®] and Aciplex[®] membranes). (b) The general structure of the Dow[®] membrane: $X = 3-10$; $y = 1$ and $z = 0$.

applications (Fig. 1). DuPont has made great strides in improving the durability and power densities of PEFC by decreasing the equivalent weight (EW) and thickness of their membranes. The Nafion[®] (the co-monomer structure is: $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$) EW for PEFC applications ranges from 1100 to 1000 or less and their thickness is in the 175–25 μm range. The Flemion[®] (the co-monomer structure is $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$) [7] and Aciplex[®] (the co-monomer structure is $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$) [8] membranes may have the same ranges of EW and thickness. These have been the most studied membranes in the literature of PEFC development activities for almost 20 years now, both industrially and academically. Their conditions of preparation, their properties and their fuel-cell performance have been published elsewhere [1–9].

The continuing development of the knowledge related to the properties of per-fluorinated should be of particular importance because we still do not understand the multifunctional behavior of these membranes in PEFC. As an example, it is only recently that an important property of ion cluster in Nafion[®] has been shown [10]. The minimum and maximum distances of separation between surfaces and two adjacent hydrated clusters are 0.30 and 0.88 nm, respectively. This may be an indication that we can spatially control them. Up to now, these membranes have been the best choice for commercial low temperature polymer products ($<80^\circ\text{C}$). The advantages of PFSAs are: (i) their strong stability in oxidative and reduction media due to the structure of the polytetrafluoroethylene backbone; and (ii) their proton conductivity, which can be as high as 0.2 S cm^{-1} in polymer electrolyte fuel cells. When used at elevated temperatures, however, PEFC performances decrease. This decrease is related to: dehydration of the membrane; reduction of ionic conductivity; decrease in affinity with water; loss of mechanical strength through a softening of the polymer backbone; and parasitic losses (the high level of gas permeation).

There are several reasons for the development of new membranes:

- (i) The operation of PEFC at temperature above 140°C is receiving world-wide attention because fuel selection remains straightforward, and a number of fuels, including reformed hydrogen with a high CO content

- and light hydrocarbons (alcohol, natural gas, propane, etc.) are still being considered for PEMFC application. Accordingly, cell temperature operation at temperatures above 140 °C is of great interest because, in this temperature range, anode catalyst poisoning by CO is less important and the kinetics of fuel oxidation will be improved and the efficiency of the cell significantly enhanced. High temperature cell operation will contribute to reducing the complexity of the hydrocarbon fuel cell system. Some other advantages of operating PEFC at high temperatures are: a reduction in the use of expensive catalysts; and minimization of the problems related to electrode flooding. Light hydrocarbons may be potential energy vectors for PEFC, which may lead to the development of suitable membranes that are stable in high temperature operating conditions and prevent fuel cross-over. These membranes are poor hydrocarbon barriers, so significant quantities of these fuels may diffuse through the membrane where they reduce the efficiency of the cathode. They also allow high water permeability; and the presence of these fuels at the cathodes could affect the gas diffusion structure of the electrode.
- (ii) Enhancement of gas transport in the electrode layers is also expected because no liquid water will be present in the cell at these temperatures. Membrane proton conductivity should be dependent on water content at these temperatures; consequently, it is not necessary to humidify the gas before it enters the stack. This may help improve the kinetics of mass transport and simplify the fuel cell system. In particular, the kinetics of the oxygen reduction reaction could be improved, by at least three orders of magnitude, if we increase the operating temperature from 25 to 130 °C. Per-fluorinated membranes cannot be used in PEFC operating above temperatures around 100 °C, because at these temperatures they will lose their mechanical properties and their swelling properties will be lowered. They do not perform well above 90 °C in a hydrocarbon PEMFC and above 85 °C in hydrogen PEMFC. The boiling point of water can be raised by increasing the operating pressure above 3 bar, which may correspond to a boiling point of water of about 135 °C. But raising the pressure of PEFC is undesirable from an efficiency point of view. Accordingly, the development of polymer electrolytes which may permit operations at higher temperatures and lower water vapor pressure is a very important and interesting approach to improve PEMFC technology.
- (iii) Consideration of the environmental friendliness of materials processes may favor the use of protonated rather than fluorinated membranes, in particular in the case of the mass production of membranes;
- (iv) Reduction of membrane costs related to mass production would not be enough to cut the current price (US\$ ~650 m⁻² or less) by at least one order of magnitude for PEMFC application in electrical vehicles, where a

membrane surface area of at least 5–12 m² is necessary to get 40–60 kW power for a mid-sized electrical car. We must point out that reasonable price reductions have been made in recent years in the well-established proton exchange membranes, e.g. Nafion[®], Flemion[®] and Aciplex[®] and their related products. High-volume fabrication of PEMFC products will be seriously limited if the process of making available viable and reliable materials for the industry is not accelerated. It is essential that the focus be placed on the development and production of low-cost ionomer membranes;

- (v) Instead of per-fluorinated ionomer membranes, several approaches are currently used to develop new membranes:
- per-fluorinated ionomer composite membranes;
 - partially per-fluorinated ionomer membranes;
 - partially per-fluorinated ionomer composite membranes;
 - non-per-fluorinated ionomer membranes; and
 - non-per-fluorinated composite membranes.

Accordingly, development of high-temperature membranes are based on the following concepts:

- improvement of water uptake of the polymer electrolyte; or
- achievement of proton conductivity independently of membrane humidification.

A new class of ionomer materials being developed for polymer electrolyte fuel cell applications is based upon the bis[(perfluoroalkyl)sulfonyl imide acid group whose structure is illustrated in Fig. 2 [10–13]. The bis[(perfluoroalkyl)sulfonyl]imide group has been shown to exhibit greater thermal stability and stronger gas phase acidity [13] than the perfluorosulfonic acid group which suggests that ionomers based on that acid group may be well suited for use in polymer electrolyte fuel cells. The effect of ionomer EW on water absorption and ionic conductivity for the bis[(perfluoroalkyl)sulfonyl]imide ionomers. Strong correlations among ionomer EW, water absorption, and ionic conductivity were found. It was also found that both water absorption and ionic conductivity are greater for low equivalent weight materials. The strong similarities in water absorption and ionic conductivity between Nafion[®], and the sulfonyl imide ionomers suggest that the two materials possess similar phase-separated ionomer structures and water absorption mechanisms. When copolymerized with tetrafluoroethylene, these materials produce ionomers with a primary structure that is very similar to Nafion[®], except

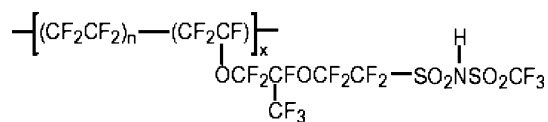


Fig. 2. Chemical structure of bis[(perfluoroalkyl)sulfonyl]imide (from [14]).

Table 1
Water absorption of sulfonyl imide ionomers and Nafion™ 1100 [14]

Relative humidity (%)	Water absorption (# H ₂ O per acid site)			
	Imide 1470	Imide 1200	Imide 1075	Nafion™ 1100
100	21	28	48	19
81	8	8	17	10
58	4	5	3	5
31	3	4	2	3
9	2	1	1	1

Table 2
Ionic conductivity of sulfonyl imide ionomers and Nafion™ 1100 [14]

Relative humidity (%)	Conductivity (S cm ⁻¹)			
	Imide 1470	Imide 1200	Imide 1075	Nafion™ 1100
100	1.1e – 2	5.3e – 2	5.2e – 2	6.2e – 2
81	2.1e – 3	8.5e – 3	2.1e – 2	2.1e – 2
58	2.3e – 4	2.7e – 3	5.1e – 3	8.0e – 3
31	2.9e – 6	3.8e – 4	4.6e – 4	1.4e – 3
9	1.0e – 8	5.9e – 5	6.2e – 5	1.1e – 4

that the perfluoroalkylsulfonic acid group in Nafion[®], is replaced with a bis[(perfluoroalkyl)sulfonyl]imide group in the new materials [14]. The observed dependencies of water absorption and ionic conductivity on RH and ionomer equivalent weight for the bis[(perfluoroalkyl)sulfonyl]imide ionomers are similar to that which has been reported for Nafion[®] (Tables 1 and 2), which suggests that the phase-separated ionomer structures and the effect of water sorption on the phase-separated structure are qualitatively similar for the two ionomer classes. Even these two polymers exhibited similar behavior, the difference between the sulphonated group of the Nafion ionomer and the bis[(perfluoroalkyl)sulfonyl]imide monomer may support the investigation of the characteristics at high temperatures of PEFC and direct methanol fuel cells (DMFC) based on this polymer electrolyte.

3. General aspects of synergetic composite membranes

A synergetic composite membrane may be defined as one in which a mixed membrane is more effective for at least one property (water uptake, conductivity, mechanical properties, etc.) than either material of the composite system alone. Many cases may exist, for example:

- (i) some percentage of an organic or inorganic component (A) is dispersed into an organic or inorganic electrolyte support (B), producing a synergetic membrane A–B;
- (ii) some percentage of A and some percentage of a component other than A indicated in (i) (named C) is dispersed into the support B, producing a synergetic composite system A–C–B;

- (iii) suitable functional groups are attached to a support, producing synergetic functional-group-support systems; and
- (iv) more complex synergetic systems constructed with more than two organic or inorganic components dispersed into the same support B.

In all these cases, the dispersed materials or suitable functional groups may, of course, be at low concentrations compared to the support. For example, composite membranes cast from silicotungstic acid dispersed in Nafion[®] or Flemion[®] may be considered synergetic composite membranes for PEFC applications, because this membrane is more effective than either silicotungstic acid and Nafion[®] or Flemion[®] alone for these applications. The nature of a synergetic system is to create active functional groups for the desired properties of the membranes. These active functional groups come from the interaction between the support and the dispersed components of the system. An active functional group is the site of the composite membrane where the desired membrane properties can act effectively [15].

The characteristics of a composite membrane can be improved by varying the parameters of the support and/or the additive components (i.e. concentration of the active additive components, etc.). Performance of the synergetic effect of the composite membrane can be estimated by the values of the single fuel cell current densities at 900 mV (i_{900}) and/or at 600 mV (i_{600}), when the other parameters of the MEA and fuel cell operating parameters are kept constant. These current densities can be determined with respect to the concentrations of the additive components. The variation of the water uptake and/or the conductivity of the membranes with the concentrations of the additive components can also be considered as probes for the synergetic behavior of the composite membranes. These characteristics are as follows:

- (i) In the case of an A–B synergetic composite membrane, where A is the additive and B the support, a variation in the current densities i_{900} and/or i_{600} of a single-cell PEMFC based on this composite membrane, with the A loading concentration, will indicate evidence of the maximum in the curve of i_{900} and/or i_{600} against the A concentration.
- (ii) In the case of an A–C–B-synergetic composite membrane, where A and C are the additives and B the support, a variation in the current densities i_{900} and/or i_{600} of a single-cell PEMFC based on this composite membrane, with the A and C concentrations respectively, will indicate evidence of the maximum in the curve of i_{900} and/or i_{600} against the A and C concentrations.
- (iii) In the case of synergetic composite membranes composed of more than two different materials dispersed into the same support, a variation in current densities i_{900} and/or i_{600} of a single-cell PEMFC based on this

composite membrane, with each material concentration, will indicate evidence of the maximum in the curve of current densities i_{900} and/or i_{600} against each dispersed material concentration.

- (iv) If a dispersed material or a number of functional groups constitute the only active component and variation of its (their) concentration(s) in the support has no effect on the membrane performance, the system is not a synergetic one and the current densities i_{900} and/or i_{600} will remain constant as a function of each dispersed material's concentration.
- (v) If two different materials or functional groups A and C are dispersed, into or attached on, the same support to form a synergetic composite membrane material, current densities i_{900} and/or i_{600} of a single-cell PEMFC based on this composite membrane, will apparently increase (decrease) as the A(C) concentration decreases (increases) to an optimum value.
- (vi) The interaction between the support and the dispersed elements of each synergetic composite membrane material may create neutral, positive or negative active sites at the membrane–electrode interface. The quantitative analysis of these active sites will give an explanation of the catalytic activity of the MEA.
- (vii) The synergetic composite membrane will exhibit at least one of these two properties:
 - An ionic effect due to the interaction between the dispersed materials or functional groups and the polymer matrix support. In this case, the synergetic effect may induce a decrease in the activation energy of the proton conduction mechanism.
 - An increase in the number of active sites at the composite membrane surface. In this case, the synergetic effect may induce a non-variation in the activation energy of the proton conduction mechanism.
- (viii) The exact process responsible for the synergetic effect in a composite membrane may be identified by studying the effect of the nature of the dispersed materials and the support on the true heat of activation (E_0) and on the order of the reaction between the additives and the support. These basic studies may help in understanding and in designing new composite membranes for PEMFC applications. Accordingly, appropriate composite membranes can be developed using various combinations of supports and additives.

The term “composite membranes” can be used to describe any membrane made from: (a) organic and inorganic components (at least one of each of the organic and inorganic components); (b) several organic components (at least two different organic components which may have complementary properties). This can be done in macro- or nano-meter scale. The term “hybrid” is also used for membranes characterized by nano-scale mixing, which may involve covalent,

ionic or hydrogen bonding, or weak or physical interactions between the inorganic components and the polymer electrolyte [16,17]. As the term “hybrid” covers a range from a discrete nano-meter-scale particle dispersed in the polymer electrolyte to more continuous inorganic and organic networks, we will use the term “nano-composite” to describe this class of composite membranes. Accordingly, we will consider that a composite membrane can be described as:

- (i) a macro-composite membrane, which is a combination of the polymer with an organic and inorganic structure of micro-meter scale;
- (ii) a nano-composite membrane, which is a combination of the polymer with an organic or inorganic component of nano-meter scale.

Synergetic composite membranes are composite membranes which should exhibit higher ionic conductivity and mechanical strength than other membranes. They will also resist dehydration and fuel non-permeation. Their use in fuel-cell systems is very attractive because they will enhance the efficiency of the cell significantly. The development of synergetic composite membranes must be the most important aspect to be considered if we want to get membranes suitable for high temperature PEMFC applications. Below, we will consider the various types of composite membranes under development for these applications.

4. Per-fluorinated ionomer composite membranes (PFICMs)

Composite membranes must exhibit high ionic conductivity and mechanical strength. They must also resist dehydration and exhibit fuel non-permeation. Their use in fuel-cell systems is very attractive because they will enhance the efficiency of the cell significantly. Two types of PFICMs are currently being developed: (i) the macro-composite membrane, which is a combination of the polymer with an organic or inorganic structure of micro-meter scale; and (ii) the nano-composite membrane, which is a combination of the polymer with an organic or inorganic piece of nano-meter scale.

4.1. Macro-composite membranes

The most important macro-composite membrane of the PFICM type fabricated today is based on a woven and a non-woven matrix filled with a proton-conducting polymer. Per-fluorinated membranes reinforced with Owen polytetrafluorethylene (PTFE) are known in many electrochemical industry plants (for example, Nafion[®] 324 and 417). Unfortunately, these membranes exhibit very limited performance for fuel-cell applications ([1] and references therein). Based on formulations of non-woven PTFE–fluorinated ionomers [1,18–29], progress in materials and processing technology,

Table 3
Identification of the various membranes [29]

Membrane type	Thickness (μm)	Mechanical reinforcement	Process	MEA
Standard GSM A	25	ePTFE	–	PRIMEA [®] Series 5510
GSM B	35	ePTFE	–	PRIMEA [®] Series 5620
FSM	25	None	Solution Casting	–
Nafion [®] 101	25	None	Extrusion	–
Nafion [®] 1035	88	None	Extrusion	–

three types of PTFE reinforcement technologies for per-fluorinated membranes for PEFC are now available [18]:

- (i) reinforcement based on PTFE porous sheet (content of reinforcement material is 20–30 wt.%);
- (ii) reinforcement based on PTFE-yarn embedded (content of reinforcement is 10 wt.%); and
- (iii) reinforcement based on PTFE-fibril dispersed (content of reinforcement material is 2–5 wt.%).

This provides good properties such as tear strength, dimensional stability, low membrane resistance and durability under PEFC operating conditions for automobile applications. A new family of PTFE–fluorinated ionomer composite membranes based on PTFE porous sheet reinforcement is being developed by Gore and Associates Inc., under the trademark Gore-Select[®]. These composite membranes are made according to the concept of micro-reinforcement, by which a non-ionically functional micro-porous medium is combined with ion-exchange material. Accordingly, Gore-Select[®] membranes are very thin (5–20 μm) composite membranes which consist of porous PTFE sheets impregnated with Nafion[®]. The types of the composite membranes and the principle of their fabrication are shown in Table 3.

The relatively high performances of these membranes compared to those of Nafion[®] are:

- (i) low shrinkage upon dehydration;
- (ii) high mechanical strength; and
- (iii) more effective water management.

But, as we indicate elsewhere [1], the PTFE may increase the specific resistance, i.e. lower the ionic conductivity, of the membranes. The tensile strengths of Nafion[®] and Gore-Select[®] were found to be similar, but, upon dehydration, Nafion[®] membranes losses over one-half its strength, while the loss in hydrated Gore-Select[®] is quite modest. This is not surprising, since the PTFE matrix makes the composite membrane more hydrophobic than conventional Nafion[®]. The effect of the reinforcement on water management is not well established, but it can be anticipated that, for the same thickness, more effective water management in the composite membrane might result in the hydrophobic character of the PTFE matrix. For membranes of different EW and/or thickness, water management would essentially be related to their EW and/or thickness. By contrast, accelerated fuel cell life tests performed to understand the

factors that may control the durability of composite membranes versus non-composite membranes [29] have shown that the most significant effect influencing membrane durability in these tests was mechanical strength, i.e. reinforced versus non-reinforced membranes. The Gore-Select[®] membrane exhibited a life-time which is an order of magnitude longer than that of a non-reinforced membrane of comparable thickness (Fig. 3). Furthermore, a 25 μm Gore-Select[®] membrane outlasted commercial membranes three times its thickness, while providing higher power density by a significant margin. Membrane failure characteristics, exhibited by an increase in H₂ cross-over rate, also showed a significant difference: non-reinforced commercial membranes exhibited immediate and sudden failure, while Gore-Select[®] membranes showed gradual increases in gas cross-over until pinhole failures occurred. It was also concluded, from fluoride release analysis of product water, that membrane failure in the testing hardware was highly localized. The ionomer degradation rate does not correlate with the membrane's life-time, and, since reinforcement may provide effective barriers against defect propagation, it was concluded that e-PTFE reinforcement in Gore-Select[®] membranes plays a very important role in membrane durability. For a clearer understanding of the behavior of these macro-composite membranes and their technological development, it would be of great interest to conduct extensive studies on their use in direct methanol fuel cells (DMFC), in particular to analyze how they can reduce methanol permeation. As we have previously indicated [1], it would be important to apply this concept to other types of matrices. It could probably help in the ongoing development of membranes which are less sensitive to dehydration and permeation and more suitable for high temperature fuel cell application. In such respects, it is probable that some macro-composite membranes based on the other per-fluorinated membranes are under development. This is for example the case of Flemion[®] composite membrane based on PTFE-fibril dispersed reinforcement developed by Asahi Glass Corporation [7,18]. Even with the small content in material reinforcement (2–5 wt.%), improvement in the performances of the mechanical properties and fuel cell characteristics of the composite membranes were obtained. One of the advantages of this type of reinforcement is the decrease of the membrane thickness from >100 to <50 μm . New approaches related to fabrication of these composite membranes are under active investigation.

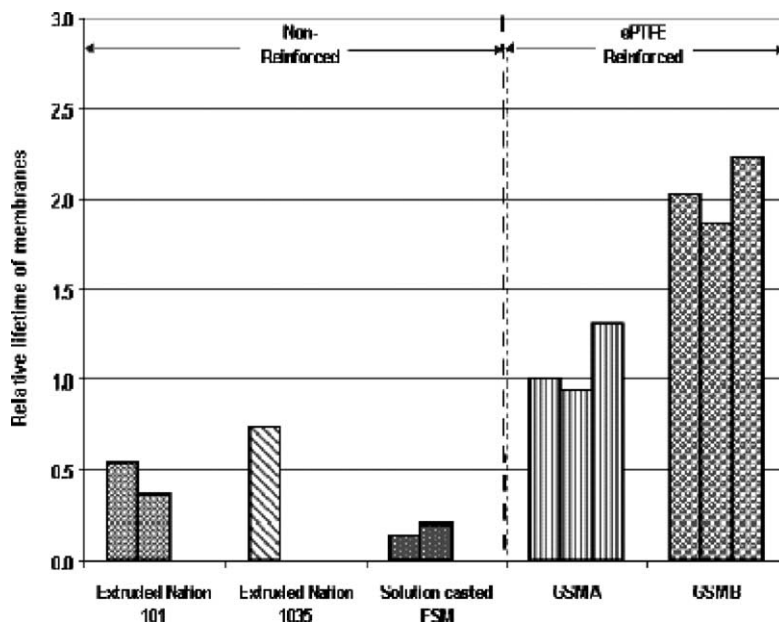


Fig. 3. Lifetime of various membranes in accelerated fuel cell conditions (from [29]; the identification of the various membranes are shown in Table 3).

Macro-composite membranes which have also been investigated include the polybenzimidazole (PBI)–Nafion composite membrane [30] which consists of:

- (i) films of Nafion[®] 112 membranes sprayed with a 10% (weight) PBI solution in a dimethylacetimide (DMA) yielding PBI films about 20 μm thick; and
- (ii) cast films of PBI from a similar solution on a Nafion[®] membrane to eliminate methanol cross-over. It was found that the methanol cross-over was at least one-tenth that of Nafion[®] 112. It was also shown that Nafion[®]–PBI (PBI on the cathode side of the MEA) exhibited less permeation than Nafion[®]–PBI (PBI on the anode side of the MEA).

The advantage of this approach is that the methanol cross-over can be reduced by using PBI and a good proton conductor by using Nafion[®]. The main problems related to this composite membrane are as follows:

- (i) fabrication of a cast PBI which adheres well to Nafion[®] with a very stable interface;
- (ii) a PBI–Nafion[®] interface which is stable in the long term; and
- (iii) a technological application of the composite which is related to the limited performances of PBI–phosphoric acid doped for PEMFC applications.

The use of a metal hydride foil as a macrostructure electrolyte to eliminate methanol crossover has been investigated [31]. This composite system consists of a three-layer structure of a (25 μm) palladium foil sandwiched between two Nafion[®] membranes. The moderate performances of this macro-composite in eliminating methanol cross-over and the anticipated high cost of the system may signifi-

cantly limit its use in fuel-cell applications. A very recent and interesting approach to minimizing the permeation of methanol through the fluorinated membrane for PEFC has been introduced [32]. It was found that the deposition of a plasma polymer barrier layer of a thickness of 0.3–0.15 μm on Nafion[®] membranes can reduce the methanol permeation by a factor of 20. The permeation barrier layers are deposited from hydrocarbons like CH_4 and C_6H_{14} or from fluorohydrocarbons like CF_3H and $\text{C}_2\text{F}_4\text{H}_2$. However, all treatments and layers which reduce methanol permeation through Nafion[®] also reduce the swelling of the membrane. Finally, the proton conductivity of treated membranes is reduced by a factor of 7. This is an indication that the plasma polymer layer is not only a barrier to the methanol molecules, but it might also be a barrier to the protons. No direct methanol single cell performance data is available at present, but work is planned to provide such data.

4.2. Nano-composite materials

In comparison with macro-composite materials, more types of nano-composite materials have been developed. The following approaches may permit operation at higher temperatures by modifying the per-fluorinated acid ionomer membrane (PFAM) to improve water retention and/or water uptake at temperatures above 100 $^\circ\text{C}$.

4.2.1. Fluorinated-HPA recast composite membranes

This concept is based on the properties that a non-volatile acid may have in a composite non-volatile/acid per-fluorinated–sulphonated acid electrolyte. If the pK_a of the non-volatile acid is higher than that of the per-fluorinated–sulphonated acid electrolyte, it will solvate the proton of the stronger sulphonic acid, creating the ion network clusters

for conduction. The non-volatile acid should have the same function as water in conventional per-sulphonated acid electrolyte. This is very interesting because this type of acid does not have the volatility problems of water, and the free acids in the electrolyte composite pores will also conduct protons through self-ionization. The non-volatile acid may also aid in water retention and could help reduce fuel cross-over. The mechanical properties of the membranes should also be modified by the acid content.

One type of nano-composite membrane is based on the in situ casting of fluorinated membranes with heteropoly-acid (HPA) [33–38]. The use of HPAs is increasing because of their broad application in catalysis [39,40], analytical chemistry [41], electronics [42], solid-state cells and electrochromic devices [42–47]. They are also being used for nano-porous TiO₂ electrode surface modification [48], semiconductor and metal surface modification [49,50] and polyaniline surface modification [51]. We have introduced the concept of in situ modification of per-fluorinated membranes with HPAs with a view to increasing our knowledge of the behavior of materials modified by these compounds. This knowledge comes from our laboratory's long experience in the electrochemistry of various materials (e.g. metals and semi-conductors) modified in situ and ex situ with HPAs. Significant improvements in the properties of the modified electrodes have been observed in the following cases:

- (i) the hydrogen evolution reaction on electro-deposited metals, or modified at their surface [52–55];
- (ii) the photo-electrochemical properties of deposited semi-conductors, or modified at their surface [56,57];
- (iii) the photo-voltaic properties of chemically deposited semi-conductors with and without HPAs [57–61].

The main features of interest of these catalysts are their structure and their strong acidity [62]. They have a well-defined local structure, the most common of which is the Keggin form. This structure is formed by a central atom (Si or P) tetrahedrally linked to oxygen and surrounded by oxygen-linked peripheral metal atoms (Mo, W, V, Nb, Ta) or a combination of these atoms. The structure has a three charge, which requires three cations to satisfy the condition of electro-neutrality. If these cations are protons, the material functions as an acid catalyst. The membrane can be modified either by soaking a commercial membrane in HPA electrolytes or by in situ casting from the ionomer solution containing HPA. After some years of research on the experimental conditions for both methods, it appears that soaking does not give satisfactory results, and so our efforts have been devoted to the fabrication of membranes from in situ casting. The sequence for doing so is the following: The volume of a commercial 5% Nafion[®] solution (from Dupont de Nemours, Inc.) is reduced by 50% and mixed with the appropriate concentration of HPA: silicotungstic acid (STA), phosphotungstic acid (PTA) or phosphomolybdic acid (PMA) (from BDH, Inc.), to produce NaSTA, NaPTA and NaPMA membranes respectively. Membranes

of various thicknesses (15–500 μm) were made by solvent evaporation from different amounts of solution in a glass beaker with a 100% optically flat bottom. After solvent evaporation at room temperature, the membranes were dried on a plate at 45 °C–60 °C for 24 h and then in an oven at 130–170 °C for 4 h. The resulting films were peeled off the beakers, washed with de-ionized water and then stored in de-ionized water. The mechanism of membrane polymerization is not known. Results on the measurement of membrane hydration, conductivity, chemical and mechanical properties, and fuel-cell performances can be summarized as follows: Various new cation exchange membranes based on a Nafion[®] solution and HPA such as silicotungstic acid (STA), phosphotungstic acid (PTA) and phosphomolybdic acid (PMA) were developed for H₂/O₂ PEMFC. The parameters for the preparation of the membranes were determined: 5–30 ml of 5% Nafion[®] 117 solution was reduced by 50% and mixed with 10⁻²–10⁻⁶ M, STA, PTA and PMA to produce a NaSTA-, a NaPTA- and a NaPMA-based membrane respectively. The ionic conductivity, water uptake, tensile strength and thermal properties of NaSTA, NaPTA and NaPMA were compared with those of Nafion[®] 117. The effect of membrane thickness and the HPA concentration used during the preparation of NaSTA, NaPTA and NaPMA on their physico-chemical properties were determined. It was shown that the water uptake of the various membranes increases in this order: Nafion[®] 117 (27%) < NaSTA (60%) < NaPTA (70%) < NaPMA (95%). The water uptake of the composite membrane was also correlated to the membrane preparation parameters (Table 4).

The ionic conductivity increases in the order: Nafion[®] 117 (1.3 × 10⁻² S cm⁻¹) < NaPMA (1.5 × 10⁻² S cm⁻¹) < NaPTA (2.5 × 10⁻² S cm⁻¹) < NaSTA (9.5 × 10⁻² S cm⁻¹). The tensile strength of the membranes decreases in the order: Nafion[®] 117 (15000 Pa) < NaSTA (14000 Pa) < NaPMA (8000 Pa) < NaPTA (3000 Pa), while their deformation (ε_{max}) changes in the order: NaSTA (45%) < NaPMA (70%) < NaPTA (170%) < Nafion[®] 117 (384%). The voltage–current characteristics of polymer electrolyte fuel cells (PEFC) were determined. The fuel-cell parameters

Table 4
Variation of NaSTA membrane water uptake with the pre-treatment temperature of the membrane [38]

Membrane identification	Membrane pre-treatment temperature (°C)	Pre-treatment time (h)	Maximum water uptake (%)
Nafion [®] 117	80	6	27
Nafion [®] 117	135	6	5
NaSTA-1	105	6	50
NaSTA-2	110	6	60
NaSTA-3	120	6	45
NaSTA-4	130	6	30
NaSTA-5	135	6	28
NaSTA-6	80	6	65

The water uptake was measured at 90 °C on membranes of the same thickness (180 μm) [38].

Table 5

Physico-chemical characteristics and kinetic electrode parameters of Nafion® 112, 115 and 117 membranes and composite membranes based on Nafion® and HPA [38]

Membrane identification	Thickness in dry state (μm)	Water uptake (%)	i_{900} (mA cm^{-2})	i_{600} (mA cm^{-2})
Nafion® 117	180	30	14	640
NaSTA	175	60	136	695
NaPTA	165	70	140	810
NaPMA	160	95	145	940
Nafion® 112	100	36	40	1100
Nafion® 115	125	35	40	800

were correlated to water uptake and ionic conductivity. From the cell voltage–current plots, the current density at 0.600 V of the PEMFCs based on the various membranes varies in the order: Nafion® 117 (640 mA cm^{-2}) < NaSTA (695 mA cm^{-2}) < NaPTA (810 mA cm^{-2}) < NaPMA (940 mA cm^{-2}) (Table 5). It can be pointed out that NaSTA with a high water content (60%) does not exhibit better electro-catalytic parameters than NaSTATHI, the water content of which is lower (40%) (Table 6). It was also shown that the modification has a beneficial effect on the resistance of the membrane to contaminant effects [63]. Table 7 shows that the current densities of hydrogen/oxygen PEM cells decrease significantly for MEA based on non-modified membranes soaked in electrolyte containing metal ion contaminants (Fe^{2+} , Co^{2+}). But the current densities of the cells are the same for MEA based on soaked and NaSTA or NaSTATHI in contaminant metal ion electrolytes (Table 7). The fundamental reason for this behavior is not known, but it may be associated with the role of the modification by the HPA species, which may block the membrane sites for subsequent contamination by the metallic ions. It was also shown that the highest current density is obtained with the NaPMA membrane. Accordingly, the following conclusions were made:

- (i) the ionic conductivity and conductance of the NaSTA membranes are higher than those of the Nafion® 117, NaPMA and NaPTA membrane;
- (ii) the water uptake of the NaSTA, NaPTA and NaPMA membranes is greater than that of the Nafion® 117 membranes;

Table 6

Physico-chemical characteristics and kinetic electrode parameters of modified perfluorinated membranes in H_2/O_2 [63]

Membranes	Thickness in dry rate (μm)	Equiv. weight ($\text{g mol}^{-1} \text{SO}_3^1$)	Water uptake (%)	i_{900} (mA cm^{-2})	i_{600} (mA cm^{-2})	R (Ωcm^{-2})
Nafion® 117	180	1100	34	14	640	0.35
Nafion® 115	125	1100	25	40	800	0.15
Nafion® 112	100	1100	36	40	1100	0.15
Aciplex®	120	1000	43	50	1000	0.16
Dow®	125	800	54	25	900	0.14
NaSTA	175	1100	60	136	694	0.1
NaSTATHI	170	1100	40	156	810	0.08

PEMFCs at 90°C and with a pressure ratio of 3/5. For comparison, the H_2/O_2 parameters of PEMFC using Nafion® 112 or 115 are indicated [63].

Table 7

Effect of membrane contamination on current densities at 900 mV (i_{900} mV) and at 600 mV (i_{600} mV) for Nafion® 117 and Nafion® modified with silicotungstic acid (STA) [63]

Membrane treated with or without contaminant agents	i_{900} mV (mA cm^{-2})	i_{600} mV (mA cm^{-2})
Nafion® 117	17	540
Nafion® 117 + $[\text{Fe}^{2+}]$	0.1	400
Nafion® 117 + $[\text{Co}^{2+}]$	5	470
NaSTAI	138	694
NaSTAI + $[\text{Fe}^{2+}]$	60	640
NaSTAI + $[\text{Co}^{2+}]$	80	660
NaSTATHI	156	808
NaSTATHI + $[\text{Fe}^{2+}]$	110	760
NaSTATHI + $[\text{Co}^{2+}]$	130	780

Membranes were soaked in sulphuric acid containing different contaminant agents [63].

- (iii) for membranes made with the same HPA, the water uptake increases when the time and temperature of the pre-treatment and also the thickness of the cast membranes decreases;
- (iv) the NaSTA membrane has similar mechanical properties to the Nafion® 117 membrane, but better thermal properties;
- (v) the characteristics of SPEFC based on NaSTA, NaPTA and NaPMA membranes are better than those obtained in fuel cells based on the Nafion® 117 membrane;
- (vi) STA insertion in a Nafion® membrane increases the number of active sites in the membrane, as well as the number of water molecules by the addition of hydrophilic groups, which results in improvements to proton transport through the membrane and the electrochemical properties of the membrane.

These results are very interesting and open the way for the development of fluorinated HPA composite membranes for PEFC applications. Accordingly, many aspects related to the development of the knowledge and technology of these membranes are under active study. Some of these aspects are:

- (i) determination of why and how using HPA increases the water uptake;

- (ii) determination of the chemical composition of the membrane fabricated with HPA and treated in various experimental conditions using XRD and XPS (this may help in determining the stability of HPA species incorporated into the membrane);
- (iii) determination of how HPAs interact with the polymer backbone to improve its properties;
- (iv) determination of the mechanism of proton conductivity in the fluorinated HPA composite membranes and comparison with that of fluorinated membranes;
- (v) determination of the effect of the casting solvent on the membrane properties and stability;
- (vi) application of this approach to the preparation of low-cost polymer electrolyte membranes.

The mass transfer parameters for oxygen transport (solubility, diffusion coefficient, permeability) and membrane water uptake were determined [64] and their values were compared to those of Nafion[®] 117, BAM3G 407 (Ballard Advanced Membranes 3rd Generation, with an Equivalent Weight of 407) (Table 8). From the results indicated in Table 6, it can be seen that BAM3G 407, which has a higher sulphonic acid content, and, of course, a lower equivalent weight, a high water content, low oxygen solubility and a high oxygen diffusion coefficient, exhibited the highest fuel cell current densities at 600 mV and 60 °C. Our results have also indicated that, when the casting temperatures decrease from 120 °C to 80 °C, the oxygen diffusion coefficient increases from 17.4×10^{-6} to 25.7×10^{-6} cm² S⁻¹ and the current density at 600 mV increases from 810 to 902 mA cm⁻² (Table 8). This is an indication that better performances of low-temperature PEFC are obtained when the composite membranes are recast at low temperatures.

These results indicate that recast membranes have many advantages: (i) very thin membranes (less than 50 μm) can be fabricated easily; (ii) the desired properties can be controlled more easily and the effect of various parameters on fuel-cell performances can be studied; and (iii) optimized parameters of the membrane casting can be determined very rapidly.

4.2.2. Metal oxide-recast Nafion[®] composite membrane

This concept was suggested by Watanabe et al. [67,68] and is based on the development of self-humidifying composite membranes. The membranes are fabricated from the high dispersion of nano-particles of Pt and/or metal oxides in a thin Nafion[®] film (~50 μm). Membranes fabricated based on this concept should not require external humidification and should suppress the cross-over of H₂ and O₂. The dispersed particles should catalyze the oxidation and the reduction of the crossover H₂ and O₂ respectively. Water from this reaction is directly used to humidify the membrane. This is supposed to result in a more stable operation of the cell at 80 °C without any external humidification of the membrane [69]. In the case of platinum, loadings as small as 0.07–0.09 mg cm⁻² were used. More interesting results are claimed using nano-oxides like SiO₂ or TiO₂ (3% weight compared to dried Nafion[®]) in very hot drying conditions. This helps in retaining the cell water in the composite membranes. The weak point of this approach is the risk of hot spots in the membranes due to the platinum particle size. Similar to Watanabe's approach, Antonucci et al. presented results on the direct liquid methanol fuel cell (DMFC) based on composite silica-recast Nafion[®] 117 membranes [69]. Also, the amount of silica introduced into the composite was 3% (weight) compared to dried Nafion[®]. The operating temperature of the cell (145 °C) was significantly higher than those indicated by Watanabe. The beneficial effect of the composite membranes is very difficult to evaluate because the performance of a recast membrane with the same thickness and without silica was not indicated. This benefit in performance improvement is also difficult to evaluate when we compare the results of this approach to the better data obtained elsewhere [70] with MEAs based on standard Nafion[®] 112 at similar operating conditions (pressure and temperature in a liquid-feed DMFC). For example, the voltage at a current density of 500 mA cm⁻² was 420 mV with a maximum power density of 240 mW cm⁻² for a Nafion[®] silica composite [69], whereas it was 560 mV with a maximum power density of 400 mW cm⁻² for Nafion[®] 112 [70].

Table 8
Mass transfer parameters for oxygen transport properties and membrane properties

Membrane	Nafion [®] 117* (100% RH, 30 °C, 3 atm O ₂)	Nafion [®] 117 (100% RH, 30 °C, 3 atm O ₂)	BAM3G 407 (100% RH, 30 °C, 3 atm O ₂)	NaSTATH (100% RH, 30 °C, 3 atm O ₂)
EW (g mol ⁻¹)	1100	1100	407	11000
Water content (wt.%)	17	19	87	45
Solubility (mol cm ⁻³)	9.3	9.2	2.1	4.2
Diffusion coefficient $D \times 10^{-6}$ (cm ² S ⁻¹)	1.0	6.0	26.4	17.5
Permeability (mol cm ⁻¹ S ⁻¹ × 10 ¹²)	9.3	54.8	54.9	52.6
i_{600} (mA cm ⁻²)	–	640**	892**	810***

(i) In Nafion[®] 117 and in BAM3G 407 membranes [65]; (ii) in Nafion[®] modified with silicotungstic acid and thiophene recast in aqueous solutions (NaSTATH) [64]. For comparison, the parameters obtained on Nafion[®] 117* by [66] are indicated in the first column of data in this table. The values of i_{600} (mA cm⁻²) for Nafion[®] 117 and BAM3G 407 are deduced from [3] and the value of i_{600} (mA cm⁻²) for NaSTATH is deduced from [36].

4.2.3. Zirconium phosphate–Nafion[®] composite membrane

Zirconium phosphate is an inorganic proton conductor ($\text{Zr}(\text{HPO}_4)$). It has been electrochemically [71] and chemically [72] precipitated in situ in the pores of a per-fluorinated ionomer membrane for PEFC applications. Zirconium phosphate is a very highly hygroscopic insoluble solid. It and some of its derivatives also exhibit very high proton conductivity properties [73]. It has been shown, for example, that zirconium phosphate glasses prepared through a sol–gel route have a proton conductivity of $10^{-2} \text{ S cm}^{-1}$ at room temperature under conditions of full humidification [74]. The composite membranes can be prepared by incorporating the zirconium phosphate into the membrane using the procedure described by Grot and Rajendra [72] or by recasting from a Nafion[®] solution with zirconium ions [75]. Zirconium phosphate was incorporated into Nafion[®] via an exchange reaction involving Zr^{4+} ions followed by precipitation of zirconium phosphate by immersion of the membrane in a phosphoric acid solution. The usual preparation sequence is as follows: (i) the membranes are swollen in a 1:1 vol methanol–water solution; (ii) they are dipped in zirconylchloride; and (iii) they are rinsed and placed in a 1 M phosphoric acid solution. This process leads to an insoluble zirconium phosphate in the nano-pores of the membrane. The properties of these membranes can be summarized as follows: (i) a composite membrane based on a commercial Nafion[®] 115 membrane exhibited a performance of 1 A cm^{-2} at 0.45 V, whereas an unmodified membrane exhibited a performance of 0.25 A cm^{-2} for an H_2/O_2 PEMFC at 130 °C and a pressure of 3 bars. With the same operating conditions, the cell performance was 1.5 A cm^{-2} at 0.45 V for the composite recast membrane. The composite recast membranes showed a stable behavior over time when maintained at 130 °C, while non-composite membranes show irreversible degradation. The proton conductivity was found to be similar for pure Nafion[®] and Nafion[®]–zirconium phosphate. The activation energy associated with the proton conduction was found to be similar for pure Nafion[®] (9.34 kJ mol^{-1}) and composite Nafion[®]–zirconium phosphate (9.82 kJ mol^{-1}). Then, it was hypothesized that the presence of zirconium phosphate does not significantly change the proton conduction mechanism and proton conduction in a well-hydrated membrane. The improvement was attributable either to the hygroscopy of the zirconium phosphate or to the reduction in the number of free spaces in the nano-pores, promoting capillary condensation and thus water retention and proton conductivity [73]. Modified Nafion[®] structures based on surface modification (surface cross-linking, etc.) and/or bulk modification (Nafion[®]-inorganic hybrid structures or barrier layer laminated composite structures) are under development at DuPont [76] for DMFC applications. One of the Nafion[®]-inorganic hybrid structures should be an “impermeable” Nafion[®]–zirconium phosphate composite membrane for methanol and water [72]. Accordingly, a new, developmental Nafion[®] 117-based composite membrane

(which should be a silica (3% (w/w))-recast Nafion[®] composite membrane) for micro-fuel-cell application, which exhibits >60% lower methanol cross-over at an equivalent power density relative to Nafion[®] 117, has been indicated. A 2 mol developmental composite membrane (probably a composite (silica 3% (w/w))-recast Nafion[®] 112 membrane) cutting down methanol cross-over by ~60% and increasing fuel cell power output >60% versus Nafion[®] 112 has also been indicated. More than 1600 h of operation with a DuPont MEA based on a composite silica (3% (w/w))-recast Nafion[®] membrane has been claimed. The recasting process of the DuPont composite membrane is not known, but the above results on a zirconium phosphate–Nafion[®] composite membrane may induce some comments for further developments:

- (i) determination of the stability of the composite membrane with time, and a study of whether or not the dopant is retained in the composite membrane over an extended period;
- (ii) the stability of cell performance based on the composite membrane, in particular at cell temperatures higher than those of the humidifiers;
- (iii) determination of the fuel-cell exhaust, and the anode and cathode catalyst compositions, and of whether or not they are contaminated by the dopant; and
- (iv) monitoring of the conductivity of the composite membrane with time.

4.2.4. Nafion[®] 117–zirconium phosphate modified with room temperature ionic liquids

Room temperature ionic liquids (RTILs) have been discovered by Cooper and Sullivan [77] and Wilkes and Zawaroko [78], RTILs are liquids at ambient temperature or even far below ambient temperature. Due to their high thermal stability, low water vapor pressure, relatively high thermal stability, and good electrochemical stability, they should be very interesting in electrochemical device applications. RTILs have been also used in polymers to make ion-conducting polymer electrolytes [79], consequently a new type of Brønsted acid–base ionic liquids was derived from a mono-proton acid and an organic base under solvent free condition. In such conditions, the reduction of oxygen could be observed at the interface between a platinum catalyst and these ionic liquids [80]. Studies of the properties of the modified membranes were conducted on room temperature ionic liquids (RTILs)–Nafion[®] 117–ZrP composite electrolytes. They were fabricated by direct incorporation of ZrP (1 and 10 wt.%, etc.) in RTILs. Room temperature ionic liquids (RTILs) are based on EMITFSI (1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulphonyl) and EMITf (1-ethyl-3-methyl-imidazolium trifluoromethanesulphate). The proton conduction of RTMS–ZrP were studied by DC loading using a two-electrode cell under a hydrogen or nitrogen atmosphere [81]. Fig. 4 shows the effect of the zirconium phosphate (ZrP) content on the conductivity

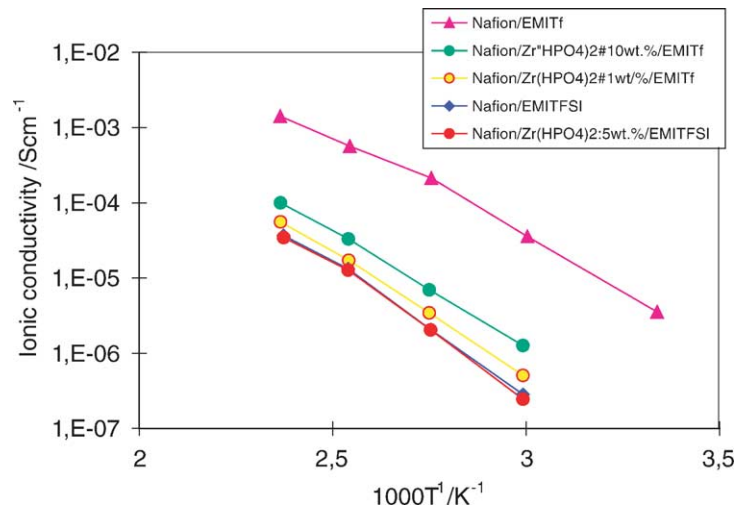


Fig. 4. Effect of zirconium phosphate (ZrP) content on the conductivity vs. temperature curves of the Nafion[®] 117–ZrP–EMITf composite membranes [75].

versus temperature curves of the Nafion[®] 117–ZrP–EMITf composite membranes. The zirconium phosphate was directly incorporated into the recast composite membrane. From the curves, it can be seen that the addition of ZrP from 1 to 40 wt.% in the composite membranes decreases the conductivities of the membrane when compared to the conductivity of pure EMITf. An optimum conductivity is obtained with Nafion[®] 117–10 wt.% ZrP–EMITf. The conductivity of the composite membrane based on ZrP is about one order of magnitude lower than the conductivity of the membrane without ZrP. These conductivities are smaller than those Nafion[®] 117–EMITf or ZrP alone. Therefore, no synergetic effect was observed between ZrP and Nafion[®] 117–EMITf, which may allow improvement of the composite membrane in the 1–40 wt.% range of ZrP added directly to Nafion[®] 117–EMITf. Even though the direct addition of 1–40 wt.% ZrP does not improve the conductivities of the Nafion[®] 117–ZrP–EMITf composite membrane, its water uptake might be improved with the presence of zirconium phosphate because of a similar improvement in water content of the Nafion[®] 117–ZrP composite membrane when compared to Nafion[®] 117 alone, as indicated in the literature [72]. Work is under way to improve our understanding of Nafion[®] 117–ZrP–EMITf composite membranes and their behavior. This concept is interesting but the challenge is to operate under anhydrous conditions and at elevated temperature this new candidate as a proton conductor in hydrogen/oxygen PEFC environment, because several of these RTILs are, of course, soluble in water.

5. Partially per-fluorinated composite membranes

5.1. Partially per-fluorinated trifluorostyrene composite membrane

A novel family of sulphonated co-polymers incorporating the α,β,β -trifluorostyrene monomer and a series of substi-

tuted α,β,β -trifluorostyrene co-monomers have been referred as Ballard Advanced Materials 3rd Generation (BAM3G) membranes for PEMFC applications [1,3,82–85]. They are partially per-fluoro-sulphonic acid (PFSA) membranes with an equivalent weight (EW) in the range of 320–920. Due to its low EW, it was shown that its water retention is higher than that of the conventional perfluorinated membranes. It was also shown that the PEFC performance based on these membranes is superior to that of conventional perfluorinated membranes [1,3].

Macro-composite BAM3G was also fabricated from sulphonated BAM3G impregnated into micro-porous film [86–91].

Accordingly, a composite membrane is provided in which a porous substrate is impregnated with a polymeric composition comprising various combinations of α,β,β -trifluorostyrene, substituted m - α,β,β -trifluorostyrene and ethylene-based monomeric units, where the polymeric composition includes ion-exchange moieties. The porous polymeric substrate comprises a polyethylene, or a polytetrafluoroethylene material. The polymeric composition is:

- (i) sulfonated α,β,β -trifluorostyrene and m -trifluoromethyl- α,β,β -trifluorostyrene;
- (ii) a sulfonated polymer of α,β,β -trifluorostyrene;
- (iii) a copolymer of α,β,β -trifluorostyrene, m -trifluoromethyl- α,β,β -trifluorostyrene and p -sulfonyl fluoride- α,β,β -trifluorostyrene;
- (iv) a sulfonated copolymer of α,β,β -trifluorostyrene and p -fluoro- α,β,β -trifluorostyrene;
- (v) a copolymer of α,β,β -trifluorostyrene, p -fluoro- α,β,β -trifluorostyrene and p -sulfonyl fluoride- α,β,β -trifluorostyrene.

This should provide further improvement to its mechanical strength in the dry state and its dimensional stability in the wet state, as well as reducing the cost compared to the

initial BA3G membrane. Unfortunately, no published data are available on the various aspects of the BAM3G:

- (i) chemical composition;
- (ii) thickness;
- (iii) mechanical strength;
- (iv) behavior in the DMFC;
- (v) behavior in a non-humidified FC system; and
- (vi) behavior at elevated temperatures (higher than 120 °C).

Membranes based on composite phosphonic proton exchange have also been developed by this group [88]. The composite membrane was prepared by impregnating a microporous support with a 5% (w/w) solution of polymer or ionomer in DMF. The impregnated substrate was allowed to air dry and another coating was applied. This process was repeated until a total of 20 ml of solution had been used, producing a semi-transparent membrane. The membrane was then dried in a vacuum oven at 60 °C for 1 h, but it was found that the PEFC characteristics of the membranes based on phosphoric proton exchange are lower than those of Nafion®. The chemistry of ionomer fabrication is well-established and, of the materials produced, it was shown that ionomers based on dimethylphosphonate-substituted α,β,β -trifluorostyrene monomer provided the best performance in a Ballard MK4B single fuel cell. It was indicated that no effort was made to determine their performance in PEFC at temperatures above 100 °C.

5.2. Partially per-fluorinated grafted membrane

The concept of preparing proton conducting membrane based radiation-grafted is widely known. The advantages of this approach related to its low preparation cost, high degree of control of process and the possibility to use pre-processed films are also well established. Typically, membranes are formed by pre-irradiating the matrix films to create reactive sites, followed by grafting with styrene and sulfonation of the grafted styrene to get a proton conductor. Various fluorine-based polymers have been modified using this technique method [1,92]. It is also well known that for commercial cell systems, the durability of these types of membranes in fuel cell operating conditions should be improved [1]. The challenge is to look for polymer components and/or grafting conditions which may help in improving the membranes performances.

Nano-composite membranes are based on polymeric membranes in which one or more trifluorovinyl aromatic monomers are radiation-graft-polymerized to a preformed polymeric base film and where the grafted polymeric chains are modified to incorporate ion-exchange groups. Accordingly, graft polymeric membranes in which one or more trifluorovinyl aromatic monomers are radiation graft polymerized to a preformed polymeric base film are provided, as well as ion-exchange membranes prepared therefrom. Preferred monomers include substituted α,β,β -trifluorostyrenes (TFS)-trifluorovinyl naphthalenes which are activated to-

wards the grafting reaction which facilitate the introduction of more than one ion-exchange group per monomer unit in the grafted chains. The preparation of the following films are indicated:

- (i) grafting of *p*-SO₂-F-TFS (trifluorostyrene) to poly(ethylene-co-tetrafluoroethylene) (Tefzel-RTM) film;
- (ii) grafting *p*-PhO (phenylene oxide)-TFS (trifluorostyrene) to poly(ethylene-co-tetrafluoroethylene) (Tefzel-RTM) film and sulfonation of the graft membrane.

These composite membranes were tested in DMFC and hydrogen/air PEFC in a Ballard Mark IV cell. The cell performances are indicated elsewhere [93].

6. Non-perfluorinated composite membranes

Non-perfluorinated membranes can theoretically be made from a large variety of polymers. This new family of polymers includes:

- (i) liquid crystal aromatic polyesters;
- (ii) polybenzimidazoles (PBIs);
- (iii) polyimides (PI);
- (iv) polyetherimides (PEI);
- (v) polyphenylene sulphides (PPS);
- (vi) polysulphones (PSU);
- (vii) polyethersulphones (PESU);
- (viii) polyetherketones (PEK);
- (ix) polyether-etherketones (PEEK);
- (x) polyphenyquinoxalines (PPQ), etc.

They were initially developed for use in extreme temperatures, atmospheres and corrosive environments. The properties that make them very appropriate and of interest for PEMFC applications are their exceptional:

- (i) thermal resistance (more than 300 °C);
- (ii) hydrolytic and/or chemical resistance; and
- (iii) stability under steam O₂ and steam H₂ atmospheres up to 200 °C.

The per-fluorinated membranes are not capable of withstanding these severe conditions. Their weak points are that:

- (i) they are not very good proton conductors, even in a water-saturated environment; and
- (ii) they can be sulphonated using two approaches: (a) direct fixation of the sulphonic acid function on the polymer backbone, either by radiation-grafting of the monomers onto the polymer backbone prior to sulphonation, or by chemical grafting of sulphonated monomers onto the polymer backbone; and (b) building the polymer from monomeric units which bear sulphonic acid groups.

Composite membranes based on acid and alkaline polymer complexes may be fabricated according to the following concept. The doping of polymer networks containing basic (acid) sites by strong acids (bases). Polymers

which can be considered are: polybenzimidazole (PBI), poly(ethylene oxide) (PEO); polyacrylamide (PAAM); polyvinylpyrrolidone (PVP); poly(2-vinylpyridine) (P₂VP); poly(4-vinylpyridine) (P₄VP); linear poly(ethyleneimine) (LPEI); branched poly(ethyleneimine) (BLPEI), etc. Any strong acids (sulfuric acid, phosphoric acid, chlorodic acid, etc.) or bases (potassium hydroxide, sodium hydroxide, etc.) can be considered. The challenge is to look for an appropriate acid site polymer–base or basic site polymer–acid pair. Consequently, many types of composite polymers can be made by coupling sulphonated or non-sulphonated polymers, or by complexing an acidic polymer with a base or a basic polymer with an acid.

Using these approaches, the concept of macro- and nano-composite materials has also been applied to non-perfluorinated membranes. The usual approach is to form hybrid inorganic–organic membranes by using a bulk, powdered inorganic proton conductor dispersed in a polymer solution. In the case of layered proton conductors, they can form colloidal suspensions of monolayers of building blocks of very large surface area in an appropriate solvent [94,95]. Composite membranes are then cast from the mixed electrolyte formed by transfer of this colloidal suspension into a polymer solution. The mixed solution should enable the inorganic particles of nanometer size to be dispersed in the formed membrane. This concept consists of mixing strong acids or bases with basic- or acid-based polymers respectively. Accordingly, various inorganic polymer components can be used, with the result that polyetherketone, polyimide or polybenzimidazole can be used as the polymer component and metal phosphates, sulphophenylphosphates, silica, heteropoly compounds, etc. can be used as the inorganic component. Organic–organic composite membranes can also be developed as polymer blends.

6.1. Polyether-etherketone (PEEK) composite membranes

Polyether-etherketones are thermoplastic polymers with an aromatic non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by a number of linkages, –O– and –CO–. The structure of PEEK is shown in Fig. 5.

The composite membranes based on this polymer can be developed by using a reinforcement of woven and non-woven supports. Sulphonated polyether-etherketone (*S*-PEEK) with a 60% degree of sulphonation (where 100% sulphonation corresponds to one sulphonic acid group per repeat unit) was prepared as described elsewhere [96]. The sulphonation was performed at 20 °C using sulfuric acid with an SO₃ concentration of 82.4%. Membranes

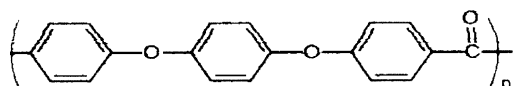


Fig. 5. Basic chemical structure of a PEEK.

were cast from an *N*-methylpyrrolidone solution prepared at 130 °C under vacuum. Woven *S*-PEEK (reinforced or non-reinforced) and fibre glass-reinforced non-woven membranes were prepared on glass plates. It was, for example, claimed that a 60 μm *S*-PEEK membrane with equivalent weight 625 g mol⁻¹ undergoes a shrinkage of 1.5% up to 140 °C and a reversible elongation of 0.6% occurs thereafter up to 180 °C. It was also indicated that the conductivity of *S*-PEEK was 0.05 S cm⁻² at 100% relative humidity and 100 °C, and increased to 0.11 S cm⁻² at 150 °C. It was further claimed that the *S*-PEEK loses water up to 150 °C and degradation of the sulphonic groups take place up to 240 °C. This last claim is important for fuel-cell applications because one of the most significant limiting factors in the use of sulphonated membranes is the loss of the SO₃ groups at high temperatures and the severe oxidative and reducing environments of PEMFC systems. In particular, the dehydration of *S*-PEEK observed at 180 °C leading to a shrinkage of 1.5% may limit the use of this membrane at high temperatures. Accordingly, *S*-PEEK might have significant limitations for high temperature PEFC applications. But recently, it was claimed that the stability of *S*-PEEK depends on the solvent used to cast it [97,98]. It was found that when dimethylformamide (DMF) was used as the casting solvent, the amide function forms a hydrogen-bonding complex with the sulphonic acid group starting at 60 °C [97]. But, when dimethyl acetamide (DMAc) was used, this hydrogen bonding occurs at 140 °C. The solvent interactions with *S*-PEEK reduce the membrane proton conductivity. The decrease in proton conductivity was more pronounced with membrane cast in DMF. From these results, it was claimed that DMF is not an appropriate solvent for the casting of proton conducting membranes based on sulphonic acid functions. It is also found that for highly sulphonated PEEK, the excess of sulfuric acid degrades DMF or DMAc, resulting in formation of dimethylaminium sulphate and corresponding carboxylic acids. This results in a decrease in the membrane proton conductivity due to a decrease in sulphonic acid concentration [98]. Accordingly, it should be important to understand the relations between these results and the performances of PEFC in low and high temperatures operating conditions when these membranes are used. As it is not well established that *S*-PEEK can be used in high temperature operating conditions, it is necessary to develop composite membranes based on *S*-PEEK. This may help to understand the behavior of *S*-PEEK in various matrices and also to sustain the development of high temperatures polymer electrolytes. Accordingly various composite membranes based on *S*-PEEK or PEEK must be developed. The electrochemical parameters derived from the polarization curves of a 16 cm² PEFC single cell based on *S*-PEEK, woven *S*-PEEK and fibre glass-reinforced *S*-PEEK are shown in Table 9. Even though the membranes did not have the same thickness and the cell measurement conditions were not the same, some general tendencies can be seen in this table. From the data indicated in Table 9, no significant

Table 9
Physico-chemical characteristics and kinetic electrode parameters of non-per-fluorinated composite membranes used in hydrogen/oxygen PEFC [96]

Membranes	Thickness (μm)	σ (S cm^{-1}) (100 °C)	V_{oc} (V)	i_{900} (mA cm^{-2})	b (mV per decade)	R (Ωcm^{-2})	i_{600} (mA cm^{-2})
S-PEEK	18	3×10^{-2}	0.95	40	25	0.20	>1200
Woven S-PEEK	110	4×10^{-2}	0.90	40	40	0.35	620
Fibre glass-reinforced S-PEEK	70	–	1.00	40	40	0.25	1000
Nafion® 115	–	–	0.92	40	25	0.25	900

difference can be observed on the values of the specific current density (i_{900} in mA cm^{-2}). The current density in the operating potential regions (i_{600} in mA cm^{-2}) in these operating conditions does not improve significantly due to the reinforcement. These results indicate that, in the practical operating potentials of the PEFC, the reinforcement of S-PEEK with fibre glass does not improve the single cell polarization curves, although it might be possible that the reinforcement could improve the long-term behavior of the cell when compared to that of the cell based on non-reinforced S-PEEK. It should also be interesting to study the performances of single-cell PEFC based on reinforced S-PEEK at intermediate temperatures.

Sulphonated polyether-etherketone has been also used as polymer matrix for composite membranes with inorganic proton conductors. [99] Membranes incorporating up to 40% (w/w) of inorganic proton conductor, including amorphous silica (S-PEEK-6), zirconium phosphate sulphenylphosphonate (S-PEEK-ZrPSPPhx) and zirconium phosphate (S-PEEK-ZrPx). It was claimed that the presence of the inorganic component leads to an increase in the conductivity of the composite membrane, without detriment to its flexibility. For example, S-PEEK membranes containing Si 10%; 30% ZrP or 40% ZrPSPPhP present conductivities in the range of 0.03–0.09 S cm^{-1} at 100 °C/100% relative humidity. Single-cell PEMFC polarization characteristics of hydrogen/oxygen cells based on S-PEEK membranes containing 25 to 14% (w/w) of zirconium phosphate were measured at 120 °C. The preliminary polarization curves of cells based on S-PEEK-ZrP25% show better results than those of S-PEEK only. More detailed studies on PEMFC performances will be helpful in gaining a better understanding of the behavior of these composite membranes for PEMFC applications.

It has also been claimed that nano-phase composite membranes with up to 50 wt.% silica can be obtained with S-PEEK cast in dimethylsulphoxide. Composite membranes cast in lower dielectric constants such as dimethylformamide are translucent and more brittle. A conductivity higher than 0.01 S cm^{-1} was obtained for S-PEEK-aminophenyl-functionalised silica membranes (50 wt.% SiO_2) at 25 °C (100% RH). This was attributed to the improvement of the proton transport properties due to the membrane micro-structure and extensive silica-membrane interfacial regions [100]. The potential existence of the interpenetration of the S-PEEK polymer and aminophenyl with

functionalized silica networks with a similar domain size of about 4 nm indicates the possible confinement of the polymer within the composite membrane. This result is very important because it should indicate that composite membranes can exhibit a micro-structure different from that of the basic polymer and the inorganic particle conductors used to make the composite membrane. This may open the way to the introduction of appropriate new concepts and methods for fabricating new composite membranes for PEMFC applications. Similar approaches have been developed by studying the behavior of the proton composite membranes made from polyether-etherketone and HPA for fuel cell applications [101]. Consequently, a series of composite membranes has been prepared by incorporation of tungstophosphoric acid, its disodium salt and molybdophosphoric acid into a partially sulphonated PEEK polymer. These membranes exhibited a rather high conductivity of 10^{-2}S cm^{-1} at ambient temperature, and up to a maximum of about 10^{-1}S cm^{-1} above 100 °C. From the DSC (differential scanning calorimeter) studies, it was indicated that the glass transition temperature of the S-PEEK-HPA composite membrane increases due to the incorporation of solid HPA into the S-PEEK membrane. This increase in the glass transition temperature (T_g) was attributed to an intermolecular interaction between S-PEEK and HPA. The following performances of the composite membranes were also indicated:

- (i) thermal stability up to 275 °C;
- (ii) good flexibility and strong mechanical properties;
- (iii) high conductivity during storage in water for several months; and
- (iv) easy preparation.

Despite these claims of interesting properties, the following comments might be made. The high content of the HPA (60 wt.%) may have an important impact on the mechanical properties (high HPA content may lead to a brittle composite) and high cost (HPAs are very costly) of the composite membrane. Composite membranes based on low content of HPA are an interesting approach to decrease the high cost of the HPA. The methods of preparation of these composite membranes are based on dispersion of an inorganic solid in the polymer. Accordingly, the particle size of the inorganic solid, the method and parameters of dispersion may, of course, have important effect on the properties of the composite membrane. Using a similar approach, S-PEEK-boron,

phosphate (BPO_4) has also been described [102]. Composite membranes prepared by incorporation of solid inorganic proton conductor boron phosphate into different *S*-PEEK matrices were studied. Composite *S*-PEEK– BPO_4 membranes were prepared by solution casting. The *S*-PEEK polymer was first dissolved in dimethylacetamide (DMAc) to form a 5–10% solution and appropriate weights of BPO_4 were then added to the solution. The method of preparation of BPO_4 has been published elsewhere [103]. The resulting *S*-PEEK– BPO_4 mixture was stirred for 16–24 h. After evaporation of most of the solvent the mixture was cast onto a glass plate using a casting knife. The cast membranes were dried at room temperature overnight and then held for 4–6 h at 60 °C and for 12 h more at 80–120 °C [104]. It was shown that solid boron phosphate has a significant effect on the conductivity of the composite membranes. The conductivity increases with the temperature and the proportion of the solid BPO_4 from 20 to 60 wt.%. The conductivity at room temperature of the composites ($2 \times 10^{-2} \text{ S cm}^{-1}$ for a composite membrane with BPO_4 60 wt.% with *S*-PEEK degree of sulfonation (DS) 80 mol%) was found to exceed largely that of pure *S*-PEEK ($4.3 \times 10^{-3} \text{ S cm}^{-1}$ for DS 80 mol%) polymer. It was however lower than predicted by the effective medium theory for these mixtures. For the same BPO_4 60 wt.% in the composite, the conductivity increases from 1.1×10^{-3} to 1.0×10^{-2} and $2.0 \times 10^{-2} \text{ S cm}^{-1}$, when the sulfonation degrees are respectively 50, 72 and 80 mol%. Comparing these results with the electrical properties of some other composite solid electrolytes reported in the literature, it was seen that the *S*-PEEK– BPO_4 membrane surpasses many of them in conductivity. For example sulfonated polysulfone–heteropolyacids (HPA) composite membranes [105] exhibited a conductivity of $2 \times 10^{-3} \text{ S cm}^{-1}$, while tin–mordenite solid electrolyte embedded into polyacrylates [106] displayed room temperature conductivity below $5 \times 10^{-4} \text{ S cm}^{-1}$. Results from *S*-PEEK–HPA membranes obtained at the same 60 wt.% loading of the inorganic solid in the composite membrane [101] showed that *S*-PEEK– BPO_4 composite at 72 mol% DS is superior to both 70 mol% DS ($3.5 \times 10^{-3} \text{ S cm}^{-1}$) and 74 mol% DS ($5.1 \times 10^{-3} \text{ S cm}^{-1}$) *S*-PEEK mixed with tungstophosphoric acid (TPA) (which is the most efficient among HPAs). The same trend was observed at 80 mol% DS for the comparison between the conductivities of *S*-PEEK– BPO_4 membrane and *S*-PEEK–TPA composite. It was also found that molybdophosphoric acid (MPA) is less efficient as inorganic solid electrolyte filler than BPO_4 . Consequently, the most important problems in developing optimized composite membranes are to:

- (i) identify the appropriate inorganic filler for the proper polymer matrix;
- (ii) determine the conditions of dispersion of the inorganic component;
- (iii) identify the optimum concentration of the filler which should be used in the composite membrane;

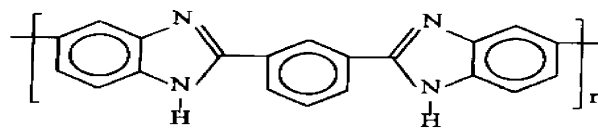


Fig. 6. Schematic of the basic chemical structure of polybenzimidazole (PBI).

- (iv) identify the preparations or casting conditions of the composite membrane;
- (v) develop knowledge related to the interactions between the filler, the polymer matrix and/or the casting solvent, etc.

These various aspects should have, of course, significant effect on the performance of the composite membranes in PEFC applications, including long term stability.

6.2. PBI composite membranes

Polybenzimidazole is an aromatic heterocyclic polymer (Fig. 6). It is a basic polymer ($\text{p}K_{\text{a}} = 5.5$) which can be complexed with strong acids or very strong bases. PBI has been suggested as a useful polymer candidate by Ahamoni and Litt [107]. It has exhibited excellent thermo-chemical stability and mechanical properties [108–113] and is much cheaper and has much lower permeability for hydrogen than Nafion[®] [1]. Blank PBI is an electronic and ionic insulator [114–117] which becomes a very good ionic conductor when it is doped with acids in the proper conditions [118–129], but remains an electronic insulator.

As indicated previously [1], PBI–phosphoric acid for high temperature DMFC applications has been extensively investigated at Case Western University, USA [118–129]. The phosphoric acid concentration used was <11 M. In an alternative preparation method, the PBI membrane is cast directly from a solution containing phosphoric acid [119]. It was shown that the PBI membrane cast in situ exhibited better performances for DMFC applications than PBI complexed with phosphoric acid by immersion of the film in a phosphoric acid solution. Conductivities in the range of 5×10^{-3} to $2 \times 10^{-2} \text{ S cm}^{-1}$ at 130 °C and 3.5 S cm^{-1} at 190 °C were reported. It was also shown that the methanol cross-over with the PBI– H_3PO_4 membrane at a thickness of 80 μm is one-tenth that of the Nafion[®] membrane at a thickness of 210 μm . Using solid-state NMR [120], they have also shown that the phosphoric acid absorbed by the PBI membrane is relatively immobile. Consequently, when PBI is complexed with PBI, the result is retention of the phosphoric acid inside the polymer matrix, probably due to the strong interaction of the phosphoric acid and the PBI. Similar results were obtained by Glipta et al. [130] who showed a proton transfer from the phosphoric acid to the imino groups of PBI. At high doping levels of PBI with phosphoric acid, the undissociated H_3PO_4 was observed by infra-red spectroscopy. The determination of the conductivity values with temperature in a wide range of acid doping levels (300–1600%) has shown

a conductivity of $5 \times 10^{-2} \text{ S cm}^{-2}$ at 165°C for a relative humidity of 85% [131]. Based on the mechanical properties and the conductivity values, they suggest that the appropriate phosphoric acid doping level should be 350–750%. This suggests that the phosphoric doping level may have a significant effect on the properties (conduction values and mechanism, water uptake, behavior at high temperature, mechanical properties, etc.) of the PBI–phosphoric acid system. Effectively, a strong interaction between the acid groups and the nitrogen atoms of the imadazolium ring in PBI may reduce proton mobility. Such interaction results in the protonation of the imino sites of the PBI and should create strong hydrogen bonding with the polymer. Consequently, a change in the acid doping level might have a significant effect on these properties. These results were confirmed by studies on sulphonated PBI [132]. A low proton conductivity $7.5 \times 10^{-5} \text{ S cm}^{-1}$ at 160°C , and 100% RH, and a high thermal stability were obtained with the sulfonated PBI [132].

We have determined the proton conductivity of PBI doped with different concentrations, including high concentrations ($>11 \text{ M}$), of various acids such as H_3PO_4 , H_2SO_4 , HNO_3 , HCl , etc. PBI film $40 \mu\text{m}$ thick was purchased from Hoechst Celanese. The film was cut into small square samples measuring $3 \text{ cm} \times 3 \text{ cm}$. The samples were washed in boiling water for more than 6 h to remove the LiCl impurities. These blank samples were kept in water. The samples were doped with sulfuric acid or phosphoric acid by immersing them in the acid solution in a glass beaker for a varying number of days. The concentration of sulfuric acid or phosphoric acid was in the 8–16 M range for sulfuric acid and the 1–16 M range for phosphoric acid. It was shown that in doping at high acid concentrations (11–16 M), high ionic conductivi-

ties at 25°C , for example, 2×10^{-3} and $6 \times 10^{-2} \text{ S cm}^{-1}$, are obtained for PBI doped with phosphoric acid and sulfuric acid respectively [133]. It was shown that the conductivity changes in the order $\text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{HCO}_4 > \text{HNO}_3 > \text{HCl}$. Accordingly, the conductivity depends on the type of doping acid and also on its concentration. The highest conductivity was obtained with sulfuric acid, which is as good as that of Nafion[®] 117. The potential–current characteristics of a H_2/O_2 PEMFC using H_2SO_4 - or H_3PO_4 -doped PBI were studied. The conditions involved in the doping of PBI with sulfuric acid or phosphoric acid and the preparation of a membrane electrode assembly (MEA) using these membranes were determined. The potential–current fuel-cell characteristics of MEA using H_2SO_4 -doped PBI were compared to those of MEA using Nafion[®] 117. The effects of membrane doping and of drying times on the fuel-cell performances of MEA based on PBI doped with sulfuric acid in various conditions were determined for the first time [134]. These results indicate that the membrane and the MEA preparation conditions are key factors in fuel-cell performance. This is supported by the following results. The characteristics of fuel cells recorded at various temperatures based on PBI doped with 16 M H_2SO_4 and dried during the same time period (7 days) (MEA0) increase in the order (Fig. 7): 70°C (curves (d)) $< 50^\circ\text{C}$ (curves (b)) $< 30^\circ\text{C}$ (curves (c)). The best characteristics obtained at lower temperature may indicate that the rate of dehydration of the membrane increases with cell temperature. However, MEA based on long doping and drying times (MEA1) exhibited better fuel cell characteristics (curve (a) of Fig. 7) than those based on short doping and drying times (MEA0) (curve (b) of Fig. 7). By contrast, it was found that the fuel-cell

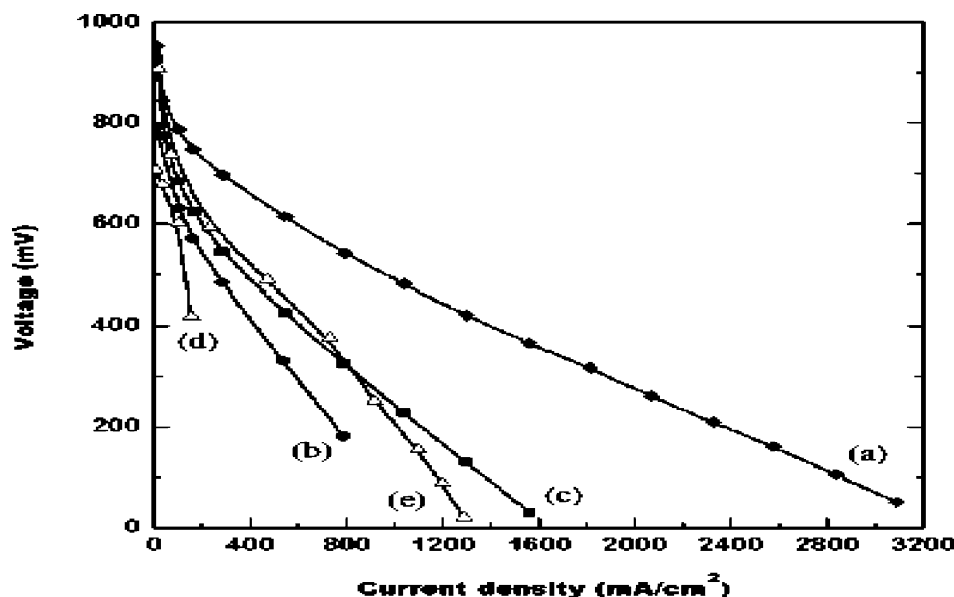


Fig. 7. Fuel cell polarization curves of MEA at various operating temperatures based on 16 M H_2SO_4 -doped PBI: (a) 50°C with 16 M H_2SO_4 -doped PBI and dried in air for a long period of time (more than 7 days); (b) 50°C with 16 M H_2SO_4 -doped PBI and dried in air for 7 days; (c) 30°C with 16 M H_2SO_4 -doped PBI and dried in air for 7 days; (d) 70°C with 16 M H_2SO_4 -doped PBI and dried in air for 7 days; (e) 70°C with 16 M H_2SO_4 -doped PBI and dried in air for a long time (more than 7 days) (from [134]).

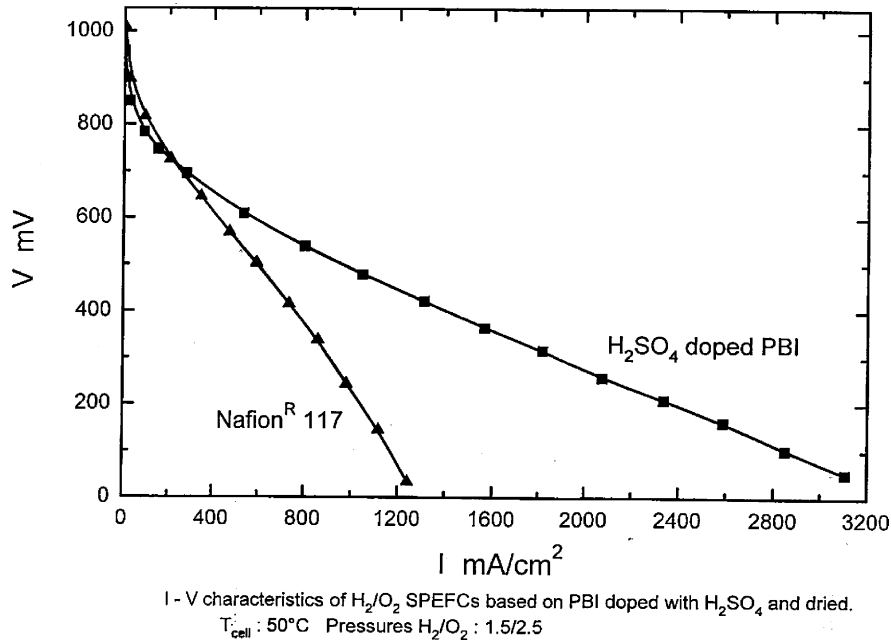


Fig. 8. H₂/O₂ fuel cell polarization curves for PBI doped with H₂SO₄ and dried in air for a long time and for Nafion[®] 117. T_{cell} = 50 °C; gas pressures H₂/O₂: 1.5/2.5 (from [121]).

characteristics did not change when the current density of 6.4 mA cm⁻² was applied to the MEA for <30 min before fuel cell characteristic curves were recorded. But, when a current of 6.4 mA cm⁻² was applied to the MEA for 125 min before the fuel-cell characteristics were recorded, the cell polarization curve decreases significantly. It was shown that MEA based on non-humidified H₂SO₄⁻ doped

PBI exhibited higher fuel-cell characteristics than MEA based on Nafion[®] 117 (Fig. 8). The fuel-cell characteristics of MEA based on phosphoric-acid-doped PBI exhibited high performance at 185 °C, even when fuelled with hydrogen-containing 3% CO (Fig. 9). These results show that the experimental conditions of acid concentration and doping time for the modification of PBI membranes with

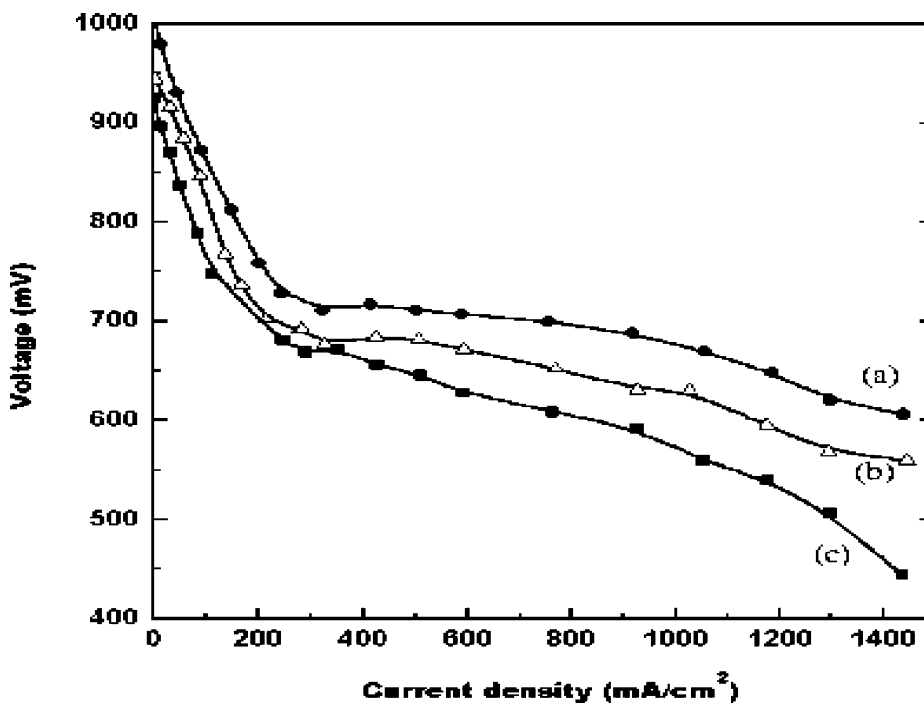


Fig. 9. Fuel-cell polarization of MEA curves at 185 °C based on phosphoric-acid-doped PBI. The fuel cell was fed with H₂/O₂ at atmospheric pressure. The hydrogen contained between 0 and 3% by volume of CO: (a) 100% H₂; (b) H₂ + 100 ppm CO; (c) H₂ + 3% CO; based on Nafion[®] 117 (from [134]).

sulfuric acid or phosphoric acid for PFC applications have been determined. The fuel cell polarization curves obtained on MEA based on sulfuric acid-doped PBI are dependent on the acid concentration and the drying time of the doped membrane. The 16M sulfuric acid-doped PBI dried for more than 7 days exhibited cell performances that were significantly better than those obtained on Nafion[®] 117. The increase in cell operating temperature from 50 °C to 185 °C significantly improves the polarization curves of fuel cells based on phosphoric acid-doped PBI. At atmospheric pressure and 185 °C, the optimum power output of 650 mW cm⁻² was obtained at 1500 mA cm⁻². Based on these promising results, the following aspects are currently under development:

- (i) determination of the relation between membrane doping conditions, water uptake, conductivity, mechanical strength, electro-osmotic drag coefficient and fuel-cell performances;
- (ii) determination of the optimum concentration of CO in hydrogen that will not trigger the CO poisoning effect on fuel-cell characteristics based on these membranes;
- (iii) determination of the long-term stability of the fuel-cell characteristics;
- (iv) utilization of this approach to develop new low-cost polymer electrolyte membranes.

These results show that PBI–acid systems exhibit promising results for high temperature utilization. This is one of the most interesting systems for high temperature polymer electrolyte fuel cell applications, and scientific and technological knowledge based on this system must be developed.

The FTIR data obtained on PBI complexes with strong acids like C₂H₅SO₃H, CH₃SO₃H or H₂SO₄ have shown a protonation of the imidazole group [135] but no protonation of this group by phosphoric acid was seen. This supports the above results, which indicate that H₃PO₄ interacts only with the imidazole group of PBI (without protonating them) by hydrogen bonding between the OH and N groups. Observation of the H₂PO₄⁻ and HPO₄²⁻ anions suggest a proton conduction based on the Grotthus mechanism. The conductivity of the PBI–H₃PO₄ was 10⁻⁵ S cm⁻² at 160 °C. This mechanism of proton conduction in PBI–H₃PO₄ has also been suggested elsewhere [136,137]. A proton conduction mechanism based on two contributions: the hopping of the proton via the hydrogen bonds between solvent molecules, and the self-diffusion mechanism of phosphate moieties and water molecules, has also been proposed [138]. Despite these interesting properties of PBI–H₃PO₄ for high temperature fuel cells, the formation of methyl esters and their diffusion throughout the phosphoric acid limits the long-term utilization of this system. There are also no durability data available on this system.

Polybenzimidazole–propesulfone or polybenzimidazole–butanesulphone composite membranes have been also fabricated and some of their characteristics determined [139]. The performances of the membranes were deter-

mined at 80 °C and a relative humidity of 100%. The current–potential curves of hydrogen/oxygen cells based on 0.4 mg Pt cm⁻² exhibited 0.7 A cm² and 0.3 V. Composite membranes based on PBI with phosphotungstic acid (PWA) adsorbed on SiO₂ have been studied [140]. It was shown that the membranes of non-sulphonated PBI loaded with 60 wt.% of 30 wt.% silica-supported tungstophosphoric acid exhibited 1.5 × 10⁻³ S cm⁻¹ at 150 °C and 100% relative humidity. But, this value is 100 times lower than the conductivity of Nafion[®] 117 measured at 100% RH and 100 °C. All these works are based on a PBI–acid system. But different results have been obtained from author to author. This is due to the various methods of PBI material preparation and different sources, as well as non-standardized conditions of testing (humidifier temperatures, cell temperature, MEA preparation conditions, membrane treatment, catalyst loading, electrode surface area, pressure, fuel and oxidant rates, etc.) for all the authors. This seemingly universal lack of non-standardized conditions for fuel-cell testing is one of the most critical problems that fuel-cell development is facing. The development of appropriate membranes by various groups world-wide requires that all the results be compared in the same conditions of preparation and testing. PBI has also been used in various other applications, for example, the PBI-impregnated zirconium separator was used in the Ni–Cd battery [141]. This cell was capable of being operated at 80% depth of discharge (DOD), and it was about 30% lighter than other alternatives. In all test regimes, at any DOD and temperature, the cell demonstrated three times the life cycle of the state-of-the-art Ni–Cd cell. PBI fibre has been used as the matrix material in alkaline fuel cells [142,143] which continue to perform well (>0.9 V at *i* = 1 A cm⁻²) after over 13,000 h of operation. However, the level of corrosion of the system is high in 42% KOH. PBI has also been used in the alkaline cadmium battery to increase the capacity and life cycle of the cadmium anode [144]. Even though PBI has been added to the alkaline solutions used in some applications, in none of these cases was a PEMFC based on an alkali-doped PBI film membrane involved. Furthermore, fundamental studies on the doping of PBI films (net PBI 100%) in an alkaline solution are lacking in the literature. We investigated the effects of the type and concentration of the alkaline solution on the conductivity of PBI and the mechanism of diffusion of alkaline species in PBI [145]. Fig. 10 shows the variation of the conductivity, measured in the doping electrolyte, of alkali-doped PBI with OH⁻ with the doping electrolyte concentration for various alkaline electrolytes. When complexed with an alkali such as potassium hydroxide, sodium hydroxide or lithium hydroxide, films (40 μm thick) of polybenzimidazole (PBI) show conductivity in the 5 × 10⁻⁵ to 10⁻¹ S cm⁻¹ range, depending on the type of alkali, the time of immersion in the corresponding base bath and the temperature of immersion. It has been shown that PBI has a remarkable capacity to concentrate KOH, even in an alkaline bath of concentration 3 M. The highest conductivity of KOH-doped PBI (9

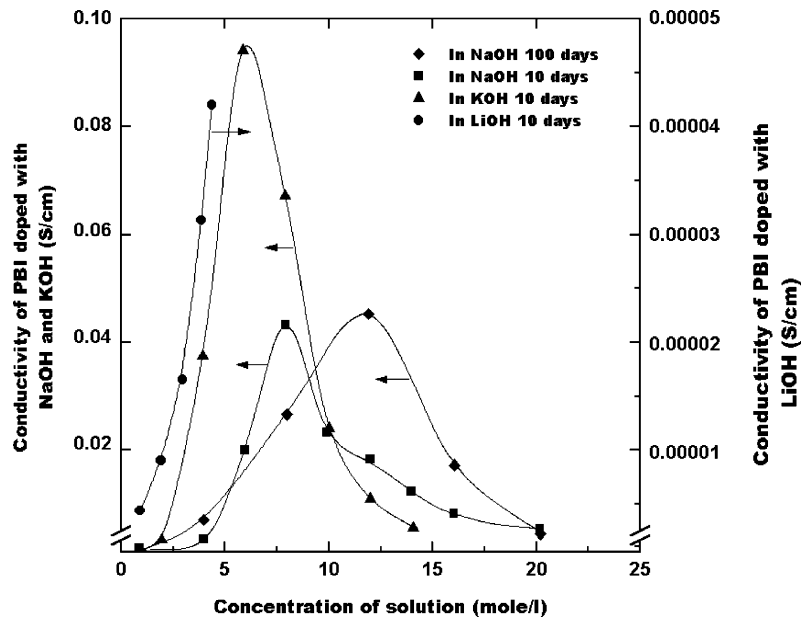


Fig. 10. Variation of the alkali-doped PBI with OH^- conductivity with the doping electrolyte concentration for various alkaline electrolytes. The conductivity was measured in the doping electrolyte (from [145]).

$\times 10^{-2} \text{ S cm}^{-1}$) at 25°C obtained in this work is higher than what we had obtained previously as optimum values for H_2SO_4 -doped PBI ($5 \times 10^{-2} \text{ S cm}^{-1}$ at 25°C) and H_3PO_4 -doped PBI ($2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C).

The optimum alkaline concentration, that which gives the highest conductivity, increases with doping time. As can be seen in Table 10, the optimum concentration of sodium hydroxide is 8 M for 0.1 day of doping and 12 M for 12 days of doping. The optimum conductivity corresponding to the optimum concentration of NaOH decreases when the doping time is <10 days. For a doping time longer than 10 days, conductivity is stable. This is related to the increase in the alkaline species in the membrane with time. After 10 days, the membrane is saturated with the alkaline species and the conductivity becomes stable.

The effect of carbonate concentration on the conductivity of doped PBI in a binary solution of KOH and K_2CO_3 decreases from 0.095 to 0.016 S cm^{-1} when the K_2CO_3 concentration increases. The conductivity of PBI doped in the solution decreases very rapidly when the concentration of K_2CO_3 is <0.3 M. Above 0.3 M K_2CO_3 , it decreases slowly. Even at a very high K_2CO_3 concentration, e.g. 3 M, which is almost the saturated concentration of K_2CO_3 in 6 M KOH,

the PBI doped in the solution still has a high conductivity (0.016 S cm^{-1}) higher than that of Nafion[®] 117 (without K_2CO_3) (0.012 S cm^{-1}). These results show a decrease in the conductivity of the PBI doped with KOH + K_2CO_3 . The explanation of the difference in the mechanism of the conductivity of the alkali-carbonate-doped-PBI is under active investigation.

This decrease in conductivity may affect the characteristics of fuel cells based on such a membrane. By contrast, carbonates would block electrolyte pathways and electrode pores on platinum-based electrodes. Fig. 11 shows the potential–current polarization curves of 6.25 cm^2 MEA obtained using a Globe station. The H_2 and O_2 gases were not humidified, the H_2/O_2 pressure ratio was 3/5 and the polarization curves were carried out at 50°C . As may be seen in Fig. 11, the fuel cell based on the KOH-doped PBI membrane exhibited 0.62 A cm^{-2} at 0.6 V . This value is similar to what we obtained on H_2/O_2 PEMFC based on the Nafion[®] 117 membrane [145]. Thus, H_2/O_2 PEMFC based on the KOH-doped PBI membrane performs as well as H_2/O_2 PEMFC based on the Nafion[®] 117 membranes.

Development related to the alkali-doped PBI membranes for PEMFC applications will necessitate continuing study of the following aspects:

- (i) determination of the mechanism of ionic conductivity in alkali-doped PBI and in alkali-carbonate-doped PBI;
- (ii) determination of the effect of alkali concentration on membrane water uptake;
- (iii) determination of the chemical composition of alkali-doped PBI in various experimental conditions;
- (iv) determination of the effect of modification of the doped membrane on water uptake;

Table 10
Variation of the alkaline concentration corresponding to a maximum conductivity with doping time

	Time (day)		
	0.1	10	100
Concentration of NaOH (M)	8	10	12
Conductivity (S cm^{-1})	0.00637	0.0425	0.0444

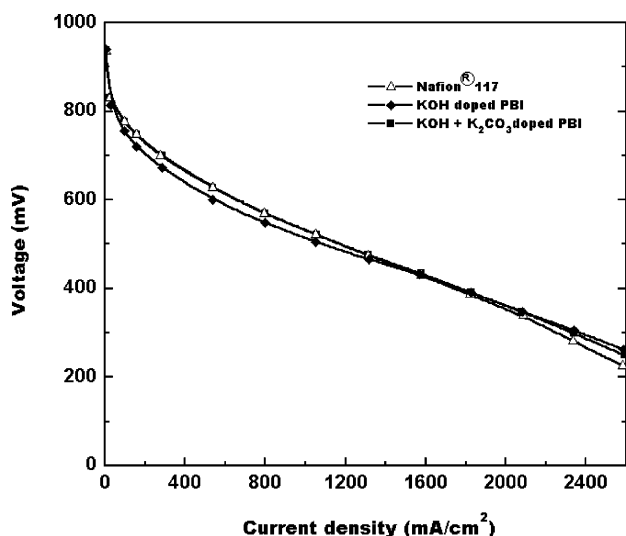


Fig. 11. Potential–current polarization curves of H_2/O_2 fuel cells using a KOH-doped PBI membrane (thickness = $40\ \mu\text{m}$), with the anode and cathode based on $0.35\ \text{mg Pt cm}^{-2}$ from 20% Pt/C catalysts, pressure ca ratio = 3/5. For comparison, the polarization curves of H_2/O_2 fuel cells using Nafion[®] 117 membrane and a KOH + K_2CO_3 -doped PBI membrane (from [145]).

- (v) development of PEFC based on these membranes; and
- (vi) application of this approach to the preparation of low-cost PEFC.

Their development is currently under active investigation. In particular, the mechanism of ionic conductivity in this system is of particular importance. These advantages, which support the research on the development of PBI composite membranes for high temperature PEFC applications are:

- (i) the high temperature oxidative stability of the blank PBI ($\sim 300\ ^\circ\text{C}$);
- (ii) the good chemical stability and mechanical properties of the blank PBI;
- (iii) the high ionic conductivity for PBI– H_2SO_4 ,
- (iv) the ease of fabrication of the composite;
- (v) the exhibition by the composite membrane of less methanol cross-over than Nafion[®] 117; and
- (vi) water management in fuel cells based on PBI composite membranes might be easier than that of cells based on Nafion[®] 117.

Despite these advantages, PBI composites exhibit some disadvantages, among them:

- (i) the long-term stability and reliability of PEMFCs based on composite PBI membranes must be proven;
- (ii) the conductivity of PBI– H_3PO_4 is 10 times less than that of Nafion[®] 117;
- (iii) the methanol cross-over must cause cathode depolarization in DMFC;
- (iv) the diffusion of H_3PO_4 on basic imidazole- N and the diffusion of methyl esters out of the PBI limit membrane performances; and

- (v) the formation of phosphoric acid methyl esters causes the degradation of the composite membrane.

Some other comments should be made on these composite membranes. PBI–phosphoric acid has been studied for almost ten years for high temperature PEFC applications. Other PBI–acid systems are emerging in the literature for fuel-cell applications, however many aspects related to the development of PBI–acid systems for this application remain unclear:

- (i) the proton conduction mechanism at high temperatures with acid doping levels and relative humidity close to such conditions should be important;
- (ii) comparison of these studies to those of the PBI–sulphuric acid system; and
- (iii) the conditions under which these membranes are tested are not standardized.

More attention must be paid to the PBI–alkaline system because it opens the way to a new area of PBI modification and the development of solid polymer alkaline fuel cell (SPAFC).

6.3. Polyimide or polyetherimide composite membranes

Polyimides are thermoplastic polymers, the basic structure of which is shown in Fig. 12. As indicated in our previous work [1], properties and hydrogen/oxygen PEMFC performances using membranes of sulphonated polyimides (S -PI) based on 4,4'-diaminobiphenyl-2,2'-disulphonic acid (BDSA), 4,4'-oxydianiline (ODA), 4,4'-oxydiphthalic anhydride (OPDA) and 1,4,5,8-naphthalene tetracarboxylic dianhydride (DNTA) have been extensively developed by the CEA group (Grenoble, France) [146–150]. It was shown that stability was significantly improved using naphthalene dianhydride momomers, since a life time in fuel cells of more than 3000 h was obtained [147]. They have shown in particular that S -PI membranes can be considered as a new class of ion exchange membranes, for the following reasons [150]:

- (i) they show very little sensitivity to external conditions due to the vitreous nature of their polymer chain (this property is very useful in the development of commercial PEFC products);
- (ii) unlike most of the membranes, the number of water molecules per ionic group is independent of equivalent weight;
- (iii) conductivity is not related to the water content in the membrane;

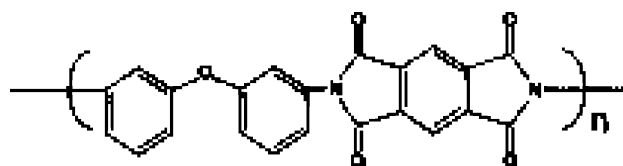


Fig. 12. Basic chemical structure of a polyimide.

- (iv) the monomers contain an internal structure of ionic domains which are not water droplets, but an ionic part of the polymer chain; and
- (v) the microstructure of the membrane is probably lamellar or disc-like, and fundamentally different from the other ion exchange membranes which are essentially spherical ionic domains.

In conclusion, this is an interesting new class of ion exchange membranes, because of the anisotropy of the microstructure, the existence of nano-scale porosity and the fact that this microstructure is formed of hydrophobic domains embedded in a continuous ionic phase composed of ionic sticks and a large quantity of free volume. These results show that the new class of ion exchange membranes may have properties which are fundamentally different from those of per-fluorinated membranes.

The development of other types of sulphonated polyimides which are different from those developed above will help in the research of new ion exchange membranes for PEMFC applications. We are developing some composite membranes based on commercial polyimide polymers purchased from Goodfellow, USA. Polyimide (regular Kapton or PIKJ) and thermoplastic polyimide or PIHN [151]. The glass transition of the PIKJ is 230 °C and that of PIHN is over 300 °C. Modification consisted of an acid doping process (with sulfuric acid, chlorosulphonic acid, phosphoric acid) or an alkaline doping process. Conductivity was achieved using two-terminal impedance spectroscopy, which consists of measuring the complex impedance of doped film (electrolyte) between two metallic electrodes. The ionic conductivity of the polyimide type PIKJ polymer doped in potassium hydroxide is 10^{-4} S cm⁻¹. The ionic conductivity of the polyimide type PIHN polymer was not measured because it dissolved in the alkaline solution. The polymer was also doped in an acid medium (ClSO₃H, H₂SO₄, H₃PO₄). They exhibited very small resistance in concentrated sulfuric acid. The polyimide films doped in 75% (volume) sulfuric acid presented very good mechanical properties, but their conductivity is very low ($<10^{-8}$ S cm⁻¹). The PIHN-type polyimide polymer was soaked in diluted solutions of ClSO₃H in dichloro-ethane (DCE) at 40 °C. When this polymer was doped with 0.1 M ClSO₃H in DCE for 18 h, it exhibited a conductivity of 2.4×10^{-4} S cm⁻¹. The conductivity of the PIKJ-type polyimide soaked in the same conditions is 7.7×10^{-7} S cm⁻¹. These results show that it is possible to complex polyimide film with the appropriate alkaline or acid agents to make

them good ionic conductors for PEFC applications. The continuing development of the modifications and characterization of these films are under active consideration.

Polyetherimide is a thermoplastic, amorphous polymer with excellent mechanical properties and good thermal stability. Its glass transition temperature is 216 °C. The basic structure of the polyetherimide is shown in Fig. 13. We have previously indicated that the polymer should be modified for commercial PEFC applications [1], and we are currently doing this [151]. The polymer was purchased from Goodfellow, USA, and soaked in alkaline or acid solutions as indicated above for polyimide polymers.

The conductivity of the alkali-doped PEI at room temperature increases from 2.7×10^{-7} to 3.4×10^{-4} S cm⁻¹ when the OH⁻ concentration increases from 20 to 100 M. Fig. 14 shows the variation with time of the ionic conductivity of polyetherimide soaked in 100 M KOH. The conductivity of the soaked polymer increases with doping time. This suggests a volume modification of the membrane.

This behavior was not observed with PBI doped with alkali where the change in conductivity with time shows two plateau. This is probably related to the interaction between the amino groups of the PBI and the OH [134]. Composite membrane based on PEI–(H-chabazite, phosphotungstic acid (PTA) or boron phosphate (BPO₄)) has been also investigated. The membranes were fabricated using the phase inversion or the casting method [152]. For phase inversion method the polymer is dissolved in an appropriate solvent and the appropriate inorganic filler is added to this mixture and cast and then quickly immersed in a water bath to induce a phase inversion. The highest proton conductivity (3×10^{-4} S cm⁻¹) was obtained for the PEI–BPO₄ composite membrane prepared from inversion method. It should be important to measure water diffusion coefficient through the composite membranes, and to evaluate the performance of composite membranes in H₂/O₂ and in direct alcohol fuel cell.

6.4. Organic–organic composite membranes

Concepts using other proton-transporting vehicles instead of water are under development [153–157]. This approach is very similar to that of the acid–polymer or base–polymer composite membranes described above. These composite membranes are synthesized by a combination of polymeric nitrogen-containing bases (N-bases) with polymeric sulphonic acids. The formation and properties of the composite membranes are based on the interaction

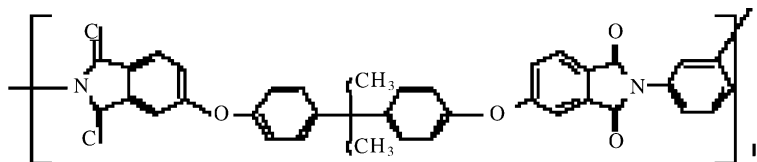


Fig. 13. Structure of polyetherimide.

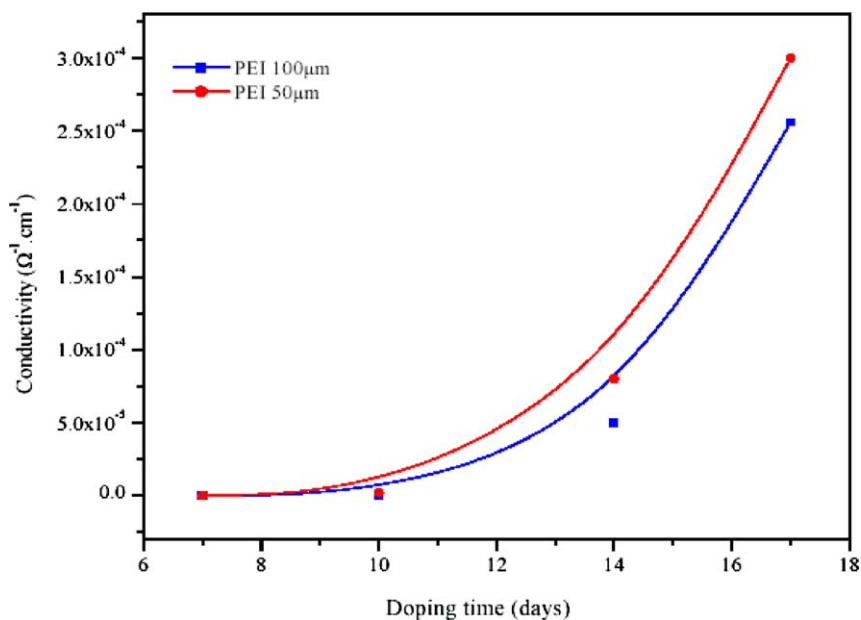


Fig. 14. Variation of conductivity with doping time for PEI membranes (100 and 50 μm thickness) doped with 100M KOH at room temperature [151].

between the sulphonic group acids and the N-bases. This may lead to the a formation of hydrogen bonds or the protonation of the basic N-sites. According to: (a) (polymer 1)–SO₃ ··· H ··· N–(polymer 2), which leads to a hydrogen bond; and (b) (polymer 1)–SO₃ + N-polymer 2 [polymer 1–SO₃] + ⁺[H–N-polymer 2]. Today, this family of blended polymers includes:

- (i) ionically cross-linked polymer composite membranes from sulphonated and basic polymers, such as membranes containing a sulphonated polyaryletherketone, polybenzimidazole PBI and, optionally, a second basic component;
- (ii) covalently cross-linked composite membranes from polymeric sulphochlorides and sulphonated polymers;
- (iii) covalent ionically cross-linked composite membranes from polymeric sulphonates and polymers containing both sulphonate and amino groups.

Consequently, the ionic cross-linked membrane can be formed by mixing the sulphonated poly(etherketones) (S-PEK) and two different basic polysulphone (PSU) polymers. The covalently cross-linked membranes can be synthesized by mixing S-PEK with S-PSU (sulphonated PSU). The covalently and ionically cross-linked composite membrane can be prepared by mixing an S-PEK with an S-PSU and a basic PSU [154].

Similar approach has been used also used to fabricate blend polymer electrolytes by mixing PBI with S-PSU to [158]. It was shown that this composite membrane exhibited a high performance for direct methanol fuel cell. A high temperature operation of 200 °C of the cell containing 1–3% CO was indicated with success.

It was shown that these different types of blended membranes exhibit thermal stability between 250 and 270 °C.

Homogeneous membrane morphology was obtained with the covalently and ionically cross-linked membrane, and a micro-phase-reported was obtained with covalently ionically cross-linked membranes. The three types of cross-linked membranes exhibited similar ionic conductivity and ion-exchange capacity. It was indicated that the swing degree of the covalently cross-linked membranes is 50% of that of the other types of cross-linked membranes. The methanol cross-over through the three cross-linked membranes is half that of Nafion[®] 105. DMFC performances based on the cross-linked membranes are similar for the three types of cross-linking. These performances are also similar to those of Nafion[®] 105. The limitations of the cell performances for cross-linked membranes were attributed to a non-optimized contact between the membrane and the electrode. This is due to the use of Nafion[®] solution in the catalyst ink preparation. The development of catalyst ink based on the cross-linked polymer might help improve the contact between the electrode and the membrane. Another interesting aspect of this approach is the possibility of an ionic or a covalent cross-linking of a sulphonated or an acid-complexed part of a polymer (PBI-acid) to its aminated or basic complexed part (PBI-base). This approach opens the way to new combinations of acidic and basic polymers to make new families of composite membranes for PEFC applications. But the most important issues related to the use of these composite membranes for PEFC applications remain the improvements to mechanical properties, fuel cell performances, long-term stability, fuel cross-over and materials processed in a low-cost and environmentally friendly way. Macro-composite membranes produced by filling a porous polymer matrix with a non-fluorinated ionomer [159] are another series of organic–organic composite membranes. The composite membrane will exhibit

the strength of the matrix while ionic conductivity is provided by the non-fluorinated ionomer material. The matrix is usually a thermo stable aromatic polymer such as polyimide, poly(phenylquinoxaline), poly(phenylene oxide), poly(arylether sulfone), poly(arylether ketone) or polybenzimidazole. The ion-conducting polymer is usually a sulfonated (or phosphonated or carboxylated) derivative of one of the above materials. As an example, composite membranes based on the mixing of a sulfonated poly(phenylene oxide) (S-PPO) and poly(vinylidene fluoride) (PVDF) [160] were also fabricated. These blend membranes show a significant increase in the conductivity of S-PPO–PVDF when compared to that of S-PPO. Some combinations of S-PPO–PVDF have higher ionic conductivity than pure S-PPO. Consequently, a surprising effect of the non-conducting component (PVDF) in the enhancement of the intrinsic conductivity of the S-PPO was observed. The composite membranes require less water than S-PPO while attaining the same conductivity. A specific hydration number (ratio of $\text{H}_2\text{O}:\text{SO}_3$) of 9.9 for the best S-PPO–PVDF blends was obtained. Unfortunately they are suitable for PEFC applications only up to 130°C . The performances of these membranes in direct hydrogen fuel cells at 45°C was reported to be much higher than that of Nafion[®] 112 membrane. It should be interesting to know the behavior of these blends in DMFC. Although this is a very interesting approach to prepare novel high temperature membranes, the fuel cell performance data for this family of materials in the literature are seriously limited. This does however appear to be a very promising approach.

6.5. Other types of non-per-fluorinated composite membranes

Poly(ethylene oxide)– H_3PO_4 , poly(vinylalcohol)– H_3PO_4 and poly(acrylamide) hydrogels doped with H_3PO_4 have been reported in the literature [161–163]. The inorganic–organic polymer blends have been reviewed by Lassegue [164].

Blends consisting of a cationic polyelectrolyte and phosphoric acid have also been reported [165]. Accordingly, polydiallyl-dimethylammonium-dihydrogenosulphate (PAMA + H_2PO_4^-) has been synthesized and its conductivity measured. The electrolyte is blended with H_3PO_4 to give (PAMA + H_3PO_4^-)– H_3PO_4 , which is stable up to about 150°C . Its conductivity increases with $[\text{H}_3\text{PO}_4]$ and can reach 10^{-2} S cm^{-1} at 100°C . This may open up new avenues for developing advanced proton conducting polymers. Proton conducting blends of poly(4-vinylimidazole) (P-4VI) with phosphoric acid have already been synthesized and characterized. It was shown that H bridges exist between aryl–N–H and aryl–N in the pure P-4VI. Upon blending of P-4VI with phosphoric acid concentration, of protonated aryl–N increases. The increases of phosphoric acid concentration content plasticizes the membrane and shifts the glass transition temperature (T_g) to lower temper-

atures. It was assumed that the dc conductivity of the blends is mainly based on proton transfer between the phosphate moieties, and also a self diffusion of these species [166]. It was found that for 2 mol of phosphoric acid per polymer unit, the conductivity was 10^{-4} S cm^{-1} . It was also shown that the conductivity of P-4VI blended with sulfuric acid exhibited higher conductivity than P-4VI blended with phosphoric acid [167]. This is similar to the results we have obtained with PBI–acid blends [134]. Proton conducting poly(vinylpyrrolidone)–polyphosphoric acid has been also investigated [168]. When the polymer is blended with 3 mol of acid per polymer unit, the glass transition temperature shifts from 180°C for the blank polymer to -23°C for the blend membrane and the conductivity was 10^{-5} S cm^{-1} . The conduction was mainly due to the proton transfer between the phosphate moieties. The values of these conductivities are lower than those obtained on Nafion or composite membranes based on PBI, PSU or PEEK. Composite membranes based on PSU or polymethyl methacrylate (PMMA) and H-chabazine, phosphoric, tungstic acid or boron phosphate as fillers have been investigated [104]. The highest conductivity ($2 \times 10^{-3}\text{ S cm}^{-1}$) was obtained for PMMA–BPO₄ composite membrane. The various composite membranes have not been tested in PEFC. These tests are very important to evaluate the performance of composite membrane in PEFC operating conditions.

Hybrid organic–inorganic nano-composite membranes consisting of SiO_2 –poly(ethylene oxide) (PEO) has been also synthesized through sol–gel processing [169,170]. They were prepared by the hydrolysis and condensation reaction of poly(ethylene oxide), end capped with triethoxysilane and monophenyl-triethoxysilane. The hybrid membranes doped with acidic molecules such as phosphotungstic acid (PWA) show good protonic conductivities at high temperatures above 100°C . These materials show good thermal stability because the SiO_2 framework in the composite matrix is stable due to the controlled mixture of polymer–silica–dopant at the nanometer level. The conductivity depends on the humidification level and the dopant (PWA) concentration in the composite materials. The conductivity is $1 \times 10^{-4}\text{ S cm}^{-1}$ at 160°C , with humidification. The advantage of this composite is the strong immobilization of the dopant in the matrix by its incorporation in the PEO domains or its chemical binding to the hydrolyzed silica matrix.

7. Conclusion

Composite membranes are very interesting and promising as suitable electrolytes for PEFC applications. They are based on non-sulphonated or sulphonated per-fluorinated, partially per-fluorinated and non-per-fluorinated polymers filled by conducting or non-conducting organic or inorganic materials. The composite membranes can be macro-, nano-composite and/or hybrid organic–inorganic membranes.

They can be fabricated by: (i) dispersion in the inorganic solid powder in the polymer matrix; (ii) filling the polymer matrix with a solid inorganic powder filler; (iii) filling a porous polymer matrix with a non-fluorinated monomer, etc. The last type of composite membrane should exhibit the strength of the matrix while ionic conductivity is provided by the non-fluorinated ionomer material. The matrix is usually a thermo stable per-fluorinated polymer (Nafion, Flemion or Aciplex, type), partially per-fluorinated (α,β,β -trifluostyrene monomer) or a non-per-fluorinated polymer based on an aromatic polymer such as polyimide, poly(phenylquinoxaline), poly(phenylene oxide), poly(arylether sulfone), poly(arylether ketone) or polybenzimidazole. In the case of the non-per-fluorinated polymer, the ion-conducting polymer is usually a sulfonated (or phosphonated or carboxylated) derivative of one of the above materials. Although, new concepts were developed for proton conducting composite membranes fabrication, the utilization of these membranes for PEFC applications is still very limited. These do however appear to be very promising approaches. We have shown that the PBI–sulphuric acid complex is promising proton conductor for high temperature PEFC applications. Even PBI–acid has been identified as an interesting system for high temperature PEFC applications. Significant studies and developments of this composite membrane are still needed. We have also shown that the PBI–alkaline and other polymer–alkaline or organic–organic blends are very interesting approaches to develop appropriate high temperature composite membranes for PEFC applications. The development of composite membranes is an important aspect to be continued worldwide. Aspects related to the characterization and aging of composite membranes are also very important for further developments of appropriate systems for commercial applications. This may sustain the global research activities on cheap proton conducting composite membranes offering stability up to 150 °C.

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