From polymer chemistry to membrane elaboration
A global approach of fuel cell polymeric electrolytes

C. Iojoiu [a], F. Chabert [b,c], M. Maréchal [b], N.El. Kissi [c],
J. Guindet [b], J.-Y. Sanchez [b,*]

[a] ERAS-Labo, 222 RN 90, F-38330 St. Nazaire-les-Eymes, France
[b] LEPMI ENSEEG, Domaine Universitaire, BP 75, F-38402 St. Martin d'Hères Cedex, France
[c] Laboratoire de Rhéologie, ENSHMG, Domaine Universitaire, BP 95,
F-38402 St. Martin d'Hères Cedex, France

Available online 11 July 2005

Abstract

The paper tries to make a critical inventory of Ionomers, free of fluorine or fluorine less, which can be used as alternatives to Nafion® in polymer electrolytes fuel cells, as Ionomer is indisputably one of the main bolts of these technologies. All the Ionomer families are discussed, with their main advantages and drawbacks, in particular in terms of their possible industrial scale-up. Special attention has been paid to the discussions about the choice of the ionic functions and that of polymeric backbones of the Ionomers, with regard to the required electrochemical properties and also to their thermomechanical behaviour. It has been emphasized that a global approach of the polymer electrolytes is essential to progress. This must involve (i) a control of the syntheses up to the pilot scale, (ii) thorough characterizations, (iii) attention to the membrane and the MEA assembly and (iv) durability investigations, including post-mortem characterizations.
© 2005 Elsevier B.V. All rights reserved.

Keywords: PEMFC; AFC; Membrane; Non-fluorinated Ionomers; Proton-conducting polymer; Composites

1. Introduction

At the beginning of the 1990's, policies put together on a voluntary basis in California led to the implementation of federal programmes that aimed to develop the use of electrical vehicles. The USABC part of USCAR funded several programmes on rechargeable batteries. Mid-term and long-term performances, i.e. specific and volumetric energy, cyclability at 80% DOD, peak power and price per kWh were required. Later with hybrid vehicles, the PNGV programme was aimed at decreasing the energy consumption of thermal vehicles and provide alternatives to traditional vehicles. As, at present (i) the autonomy of batteries does not satisfy the long-term goals of the USABC, (ii) the safety of large lithium batteries is not yet fully guaranteed and (iii) there are still severe limitations with the rate of charge of the best batteries, fuel cells appear as a promising alternative for cleaner vehicles. In addition to

environmental issues, one must consider that oil will run out during the second half the present century and fuel cells based on renewable chemicals, such as ethanol as energy sources might be a solution.

Along with the need to have cleaner cars, intermediary power stations are also necessary. Due to their efficiency and the possibility of thermal/electrical energy co-generation, fuel cells, in particular solid oxide fuel cells, should be well-adapted to this application. More recently, fuel cells also appear to compete with batteries for the 4 C (computers, camcorders, cellular phones, cordless tools) market.

Because of their modularity, proton exchange membrane fuel cells (PEMFC), seem at present to be the most promising fuel cell for all the applications, including electricity production. Many problems have to be solved, however, in particular price, operating temperature range, fuel selection and supplies. If PEMFC have a prevalent position nowadays, many members of the scientific community are looking at direct methanol fuel cell (DMFC) [1,2], suitable for portable electronics. The main interest here lies in the use of a liquid

---

fuel which can easily be stored, for instance in cartridges. More recently, anion-conducting polymer electrolytes have also been used to replace alkaline aqueous solutions in alkaline fuel cells [3,4].

The performances of polymer electrolyte fuel cells closely depend on the performances of the elementary unit membrane-electrode-assembly (MEA) even if other components such as the bipolar plates, play an essential role in the MEA's stacking. According to Garche et al. [5], quoting a report of D. Little [6], the price of the MEA, in a market perspective, ranks in first position with roughly 75% of the overall price of PEMFC. The efforts currently concentrate on new ion-conducting membranes, although a large number of the scientific contributions still deal with Nafion® membranes. Several well-documented papers relate the different possible Ionomers for PEM fuel cell [7–9]. In this paper, part of a special issue of IBA 2004, our purpose is not to produce an additional and exhaustive review but to make a critical inventory of various possibilities, emphasizing their respective advantages and drawbacks.

2. Fuel cell versus batteries

Except perhaps for some electronic devices, while competing with batteries, fuel cells might be associated to other electrochemical energy sources, such as supercapacitors and (or) batteries. The advantages of fuel cells with respect to batteries are mainly: (i) the recharge time which is just equal to the filling time of the tank, (ii) the absence of self-discharge; while their main drawbacks lie (i) in the complexity of the system, (ii) in the low voltage, close to 0.7 V, of the MEA. It is therefore attractive to associate these complementary electrochemical energy sources while avoiding: (i) too many complex devices and (ii) enhanced costs.

Indeed, contrary to batteries which, with a thermodynamical approach, may roughly be seen as a closed system that should not exchange matter with the external medium, fuel cells are unambiguously open systems. Thus, in PEMFC operating at $T < 100\,°C$, liquid water is continuously produced and removed. This means that a polymeric membrane, intended to be used for several thousand hours, cannot be made up of polymer/liquid acid or a polymer/base complex. Therefore, one of the ionic groups must be attached to the macromolecular backbone as in Ionomers which are single-ion conductors. For that reason, polymer electrolytes complexes between polymers with basic character, such as polybenzimidazole, and inorganic or organic molecular acids will not be considered in this paper.

3. Alkaline fuel cells based on polymer electrolytes

Alkaline fuel cells, on the NASA space flights between 1960 and 1970 [10], are interesting fuel cells which operate according to Fig. 1.

Among its advantages is the possible substitution of expensive and rare platinum by catalysts based on silver. One of its main drawbacks is related to the formation, when air is used instead of oxygen, of K_2CO_3 which precipitates in the electrolyte and may, in addition, affect the behaviour of the electrodes. It has been proposed to use an anion-conducting polymer electrolyte to fully or partially replace the potassium hydroxide solution. Thus, polyethers such as polyepichlorhydrin have been used as starting polymers to create anion-conducting Ionomers [3]. Indeed if aliphatic polyethers, due to their sensitivity to strong aqueous acids, must be avoided in PEMFC they are chemically stable in alkaline medium. The nucleophilic substitution of methylene chloride by a cyclic diamine 1,4-diazabicyclo[2,2,2]octane (DABCO), insures the formation of quaternary ammonium chloride along the polymer chain, according to Scheme 1.
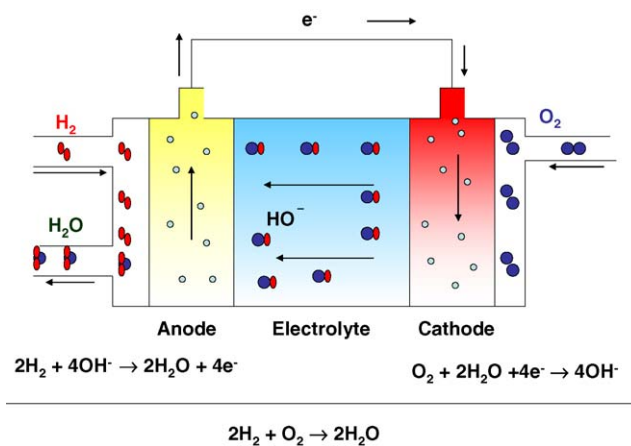
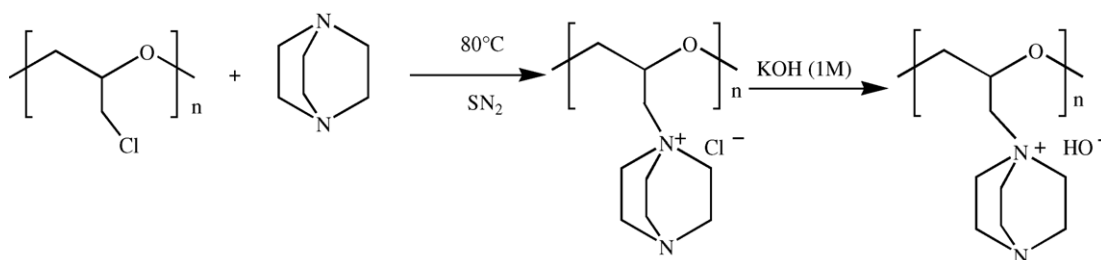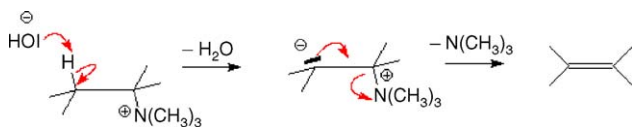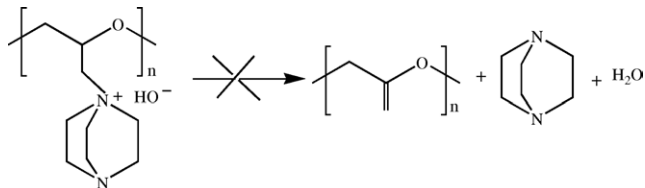Then, chlorine anion has to be replaced by OH^-.

Fig. 1. Alkaline fuel cell.

Scheme 1. Anion-exchange Ionomer prepared from polyepichlorhydrin.

Scheme 2. Hoffman degradation.

Scheme 3. Impossibility of Hoffman degradation.

One of the main requirements for these membranes is to avoid the well-known Hoffman degradation of the quaternary ammoniums which occurs according to Scheme 2.

DABCO moiety cannot undergo Hoffman degradation but the reaction may originate from the polyether backbone, according to Scheme 3.

However, the abstraction of the proton in beta position clearly depends on the steric hindrance, the order of reactivity being ethyl > $n$propyl > $n$butyl > $n$amyl > isoamyl > isobutyl. In the previous Ionomer the beta position is located on a secondary carbon, also hindered by its bond with the oxygen. It may be assumed therefore that the Hoffman reaction impact by attack on the polyether backbone is negligible.

Although DABCO is a diamine, it may lead surprisingly to unidimensional anion-conducting polyether, provided appropriate conditions of temperature are used. But by increasing the reaction temperature, it may also lead to cross-linked Ionomers, as shown in Scheme 4.

Due to their polyether backbone, these Ionomers undergo a high swelling in water. This is, to some extent, an advantage in terms of conductivity, but affects the mechanical properties of the membrane. Despite the cross-linking induced by DABCO, the resulting thermomechanical properties are not sufficient and the polymer must be reinforced. As for the conductivity, the diffusion coefficient of OH$^-$ is about

four times lower than that of H$^+$ [4]. Therefore, even assuming a high dissociation of ammonium hydroxide, it will be impossible to reach the highest conductivities obtained with proton-conducting Ionomers. The previous authors added KOH solutions to the anion-conducting Ionomer. They did not observe any degradation at KOH concentrations lower than 1M and obtained conductivities higher than 10^{-2} S cm^{-1} at 25 °C for KOH concentrations close to 0.5 M. Using Henderson and Hittorf methods, they found transport numbers ranging between 0.93 and 1 for the Ionomer doped by KOH solutions. However, despite this high transport number, KOH solution should be gradually eliminated by the water produced by the AFC. Encouraging tests were performed on MEA free of KOH solutions. This preliminary research is promising and a French programme PALCAM, carried out by our laboratory, has just started on this revisited AFC. Moreover, according to Jolli [11], an important programme has also started in the UK on direct methanol AFC based on polymer electrolytes.

4. Polymer electrolytes for PEMFC

Contrary to the previous ones, polymer electrolytes usable in PEMFC must be chemically resistant to strong acids. In addition they must exhibit high thermal and mechanical stabilities and a low permeability to oxygen. Obviously they must meet the electrochemical requirements both in terms of conductivity and of electrochemical stability.

The best known membranes are obviously Nafion® membranes which, as their Aciplex® or Dow® counterparts, consist of perfluorinated polymers. These polymers combine remarkable properties: (i) conductivity, (ii) chemical, thermal and electrochemical stabilities, and good mechanical properties. On the other hand, the whole environmental impact of the active cycle of life from the monomer to the co-polymer syntheses up to the membrane recycling raises serious questions about their mass production. In addition, the behaviour of this type of membrane at temperatures higher than 75–80 °C, limits its use, in particular for the electric traction. Finally the cost of Nafion® type membranes, currently close to US$
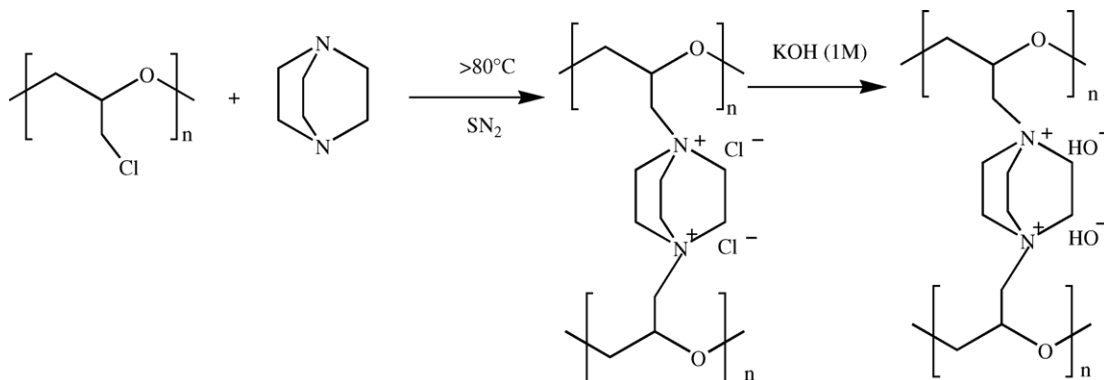
Scheme 4. Cross-link of anionic Ionomer by DABCO.

3000 kg^{-1} is crippling for any application, other than military and spatial ones. It is clear that within the framework of a mass production, the price of the membranes could fall, but the cost of chemistry, processes, recycling, would maintain it at too high a level.

Attempts to lower the number of perfluorinated Ionomers in the membrane through a decrease in their thickness or by use of a macroporous perfluorinated separator is only a temporary solution and, from an environmental point of view, alternative solutions to perfluorinated Ionomers are absolutely essential.

Perfluorinated Ionomers based on sulfonic acids, in addition to the advantage provided by the perfluorinated skeleton have an asset, namely superacid dangling groups. We must therefore consider both the choice of the ionic function and that of polymer skeleton.

4.1. Selection of anionic functions

Special attention has to be paid to the selection of the anionic group which must be both electrochemically stable and must provide high conductivity. By definition, acidic solid-state Ionomers, even if swollen by water, have a cationic transport number t_+ equal to 1. This is not true for Ionomer solutions. As in any electrolyte the conductivity depends on the concentration in charge carriers and their mobility. Proton mobility in water is the highest cationic mobility. Contrary to most of the salts, the cationic transport number t_+ in aqueous solutions of Bronstedt acids is close to 0.9 [12]. The anion immobilization, in the Ionomer, should not therefore be too detrimental to the conductivity if enough water molecules are available to insure the proton mobility. The conductivity also depends on proton concentration which is proportional to the acid concentration and its dissociation. In Ionomers this concentration also indirectly affects the conductivity as the acidic functions simultaneously modify the Ionomer hydrophily. In order to optimize the dissociation, the organic anions have to be selected from among the conjugated bases of strong acids to superacids.

4.1.1. Carboxylic acids

Carboxylic acids are weak acids, thus at 25 °C, pK_a of acetic acid is close to 4.8 and, although slightly more acidic, that of benzoic acid is 4.19. Despite trifluoroacetic acid being a much stronger acid with a pK_a of 0.23, perfluorinated Ionomers bearing carboxylic acids as Flemion® are not conductive enough.

4.1.2. Phosphonic acids

Ionomers based on phosphonic acid have been reported earlier. More recently several groups have reported the use of such Ionomers as PEMFC membranes [13]. The main advantage is the increased stability of aryl phosphonic acids with regard to aryl sulfonic ones. Unfortunately acidity of phosphonic acids is lower than that of sulfonic acids.

4.1.3. Aryl and alkyl sulfonic acids

Sulfonic acids are much more acidic than carboxylic ones. Cerfontain and Schnitger reported [14] negative pK_a values ranging between −6.85 and −6.3 for aryl sulfonic acids substituted by electron-donating and electron-withdrawing groups. They ranked their acidity between that of the first acidity of H$_2$SO$_4$ and that of HCl. The acidity of aryl sulfonic acid should be increased by electron-withdrawing substituents but a weak value 0.7 was reported for the slope ρ of the ρ σ relation of Hammett. This surprising result indicates that dissociation of aryl sulfonic acids is only slightly dependent on the electronic effect of the substituents located on the aromatic ring.

We assume that dissociation of aryl sulfonic acids is probably higher than that of alkyl sulfonic acids. Although no data based on acidic Ionomers may support this assumption at present, results reported by Xu and Angell [15] and Ito and Ohno [16] on similar lithium Ionomers, respectively, on lithium oligoetheralkylsulfonates and lithium oligoether-arylsulfonates, clearly show that the former are much less conductive.

However, similar conductivities have been reported for polymers bearing either a dangling alkyl sulfonic acid or an aryl sulfonic acid located on the main-chain of an Ionomer [17]. This is probably due to the spacer between the aromatic chain and the acidic function.

The electrochemical stability of sodium arylsulfonates has been investigated, using cyclic voltammetry, in sulfolane [18] to widen the electrochemical stability explored with regard to the electrochemical stability window of water. Whatever the temperature, RT till 80 °C and the atmosphere (Ar, H$_2$ or O$_2$), no instability was detected.

4.1.4. Perfluorosulfonyl imide acids

Use of perfluorinated Ionomers based on perfluorosulfonyl imide acids (Scheme 5) has been proposed as an alternative to Nafion® membranes [19].

High conductivities were obtained and these imide based Ionomers seem to retain water more easily than Nafion 117 at high relative humidity [20]. Taking into account on the one hand the chemical, thermal and electrochemical stabilities of LiTFSI, acronym of lithium trifluoromethylsulfonylimide (CF$_3$-SO$_2$)$_2$NLi, on the other hand its high conductivities obtained in dry polymer electrolytes or in liquid electrolytes it seems indeed a good idea to attach this kind of anion to a polymer backbone. Despite the nice synthesis performed by Desmarteau and co-workers [19] the results must be evaluated in terms of additional cost of the Ionomer with regard
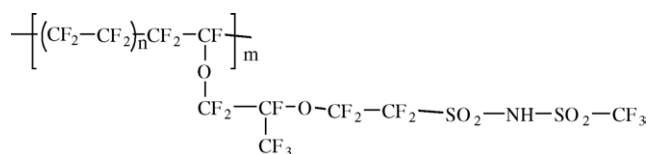
Scheme 5. Perfluosulfonylimide based Ionomer.

to its advantages. First of all, comparative ab initio calculations [21,22] show that the extent of the delocalization of the negative charge is higher in TFSI$^-$ anion than in triflate and that TFSI$^-$ has a very high flexibility. This is a clear advantage in aprotic solvents with a low AN value such as aprotic poly(oxyethylene) or aprotic liquid solvents and must be an asset in fuel cell membranes free of water. On the other hand, comparative studies of cationic transport in polyether complexes show that in LiTFSI based complexes, anionic conductivity is widely prevalent and that their cationic conductivities, i.e. $\sigma_+ = \sigma t_+$, are lower than for example that of LiClO$_4$ or LiI complexes in the same polyether [23] and of that obtained with a single-cation polyether based on a perfluorosulfonate anion similar to that of Nafion® [24]. From these data it may be inferred that immobilization of such a bulky perfluorinated anion in an acidic Ionomer, supposed to operate in hydrated membranes, might not lead to an actual advantage in light of the plausible increase in cost.
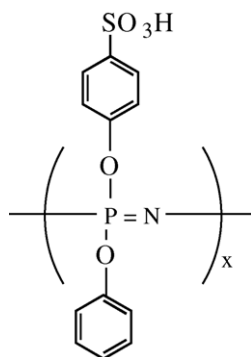
4.1.5. Improvement of ionic dissociation?

Due to its high permittivity, high DN and AN, water to some extent exerts a levelling effect on the ionic function. However, aqueous equivalent concentrations, calculated from the swelling data of membranes in water, would correspond to highly concentrated solutions of acid in water. So the search of more dissociated ionic functions might allow high conductivity levels to be maintained while decreasing the ionic exchange capacity and preventing the membrane of too huge a swelling.

4.2. Inventory of Ionomers alternative to Nafion®

4.2.1. Ionomers based on polyphosphazene

These Ionomers are obtained by nucleophilic modification of polydichlorophosphazene as the sulfonated polyphosphazene shown in Scheme 6 [25].

Earlier Allcock proposed to use comb type polyphosphazene bearing polyether dangling chains as lithium polymer electrolyte [26]. Polyphosphazene has one of the lowest glass transitions among the elastomers and a high limiting oxygen index (LOI). However, both properties are modified by the substitutions. Allcock developed a very attractive chemistry to modify the polyphosphazene (PPZ). If the electrochemical stability of PPZ skeleton versus lithium metal is probably questionable [27] it should be adapted to fuel cell application. Several ionic groups were grafted to the PPZ backbone, namely arylsulfonic [28], arylphosphonic [13,28], partially fluorinated imides [29]. The main concern of PPZ Ionomers deals with its mechanical properties. Pintauro and co-workers [28] cross-linked PPZ by UV using a huge amount of BP as photo-initiator. More recently cross-linking has been achieved by gamma radiation [30].

4.2.2. Ionomers based on polysiloxane

Like polyphosphazene, polydimethylsiloxane has a very low glass transition temperature. As for silicone, a high permeability to oxygen may be expected of Ionomers based on polysiloxane backbone, but this aspect is not catastrophic insofar as the Ionomer is swollen by water. Other specific properties of polysiloxane are their thermal and oxidative stabilities. However, polysiloxane are sensitive both to acid medium and alkaline medium. Anhydrous proton-conducting networks [31] and Ionomers based on organic–inorganic hybrid polymers were prepared through a sol–gel route, using, for instance, benzyltrialkoxy silica [32–34] Scheme 7.

High conductivities, high electrochemical and thermal stabilities but, unfortunately, poor mechanical properties for free-standing membranes, were obtained. More recently, microporous silicon filled with polysiloxane based Ionomers were successfully tested for micro fuel cells [35]. Other approaches, involving polysiloxane Ionomers prepared by sol–gel, were reported by Slade and Varcoe [36] and Jacob et al. [37].

4.2.3. Polystyrene based Ionomers

Polystyrene and above all its networks, obtained by styrene/divinyl benzene co-polymerization, provide, after sulfonation, cation-exchange resins. They were therefore tested very early as membranes for PEMFC. Unfortunately, as for any alkylbenzene, the benzylic position is very sensitive to oxidation and any free-radical created on the carbon1 of the monomer repeat unit will benefit from a double stabilization: (i) as tertiary radical, (ii) as delocalized by resonance

Scheme 6. Sulfonated polyphosphazene.
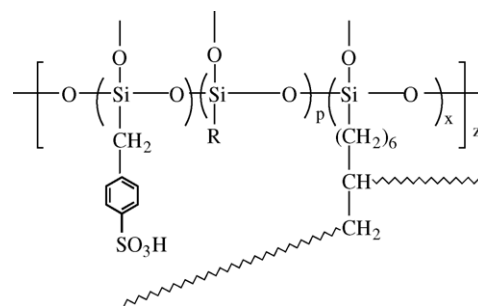
Scheme 7. Polysiloxane based Ionomers.

effect on the aromatic ring. Yu et al. [38] recently reported investigations on the degradation mechanisms of sulfonated polystyrene in PEMFC and showed that the degradation occurred at the cathode. The use of composite Nafion®-sulfonated polystyrene at the cathode results in an increase in the membrane lifespan. However, the free-radical formed at the cathode may migrate and lead to the degradation of the polystyrene sulfonic membrane.

4.2.4. PVdF-sulfonated polystyrene networks

One of the ways to improve the lifespan of sulfonated polystyrene deals with its cross-linking into a PVDF polymer [39]. PVdF films are first radiated (gamma rays) to create free-radicals on the fluorinated chains which can eventually be frozen inside the film by cooling it. Then the film is immersed in styrene or in a mixture of styrene and divinyl benzene. The polymerization starts from the free-radical located onto the PVdF chains. As in any free-radical polymerization, transfer to the monomer should create polystyrene networks non-attached to the PVdF backbone. Afterwards, (i) the remaining monomer is removed, (ii) swelling in a chlorinated solvent followed by sulfonation are performed and (iii) the membrane is washed to remove the by-products. Such materials are not really interpenetrated networks but rather graft cross-linked co-polymers. Their main advantage is to associate, (i) the high thermo-mechanical properties of PVdF, probably slightly affected by the loss of crystallinity, (ii) its resistance to oxidants and (iii) its hydrophobic character, to the three-dimensional polystyrene Ionomers. Although only delayed, the polystyrene degradation does not drastically affect the membrane performances. However, despite its advantage, the industrial scale-up of such membranes seems questionable.

4.2.5. Triblock polystyrene Ionomers

In such an approach a triblock polystyrene-co-polyethylene-butylene-co-polystyrene is modified by sulfonation of the lateral block of polystyrene. The central block insures both the mechanical properties, at least up to its melting temperature, and a hydrophobic character [40]. This polymer is manufactured at present by Dais-Analytic Corporation.

Yet again, the sensitivity to oxidation and free-radicals of polystyrene remains, even if their impact on the mechanical properties is markedly lower than in polystyrene homopolymers and networks. Although much less sensitive to oxidants than polypropylene, or polystyrene, polyethylene-butylene, as any alkane, may be sensitive to oxidants. Lastly there is the cost of the starting triblock co-polymer.

4.2.6. Partially fluorinated polystyrene Ionomers

To prevent the oxidation in benzylic position, the Ballard group [41] proposed to use 1,2,2-trifluorostyrene monomers substituted, or not, on the aromatic ring. Their co-polymerization leads to polystyrene with a perfectly stable perfluorinated backbone and aromatic side groups which allow sulfonation and other chemical modifica-
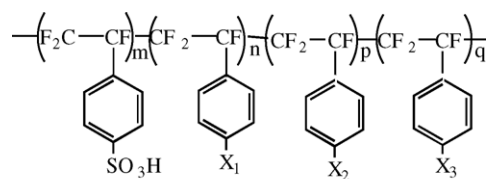
X_1, X_2, X_3 = alkyls, halogens, O-R, CF=CF$_2$, CN, NO$_2$, OH

Scheme 8. BAM 3G membrane.

tions to be easily performed by electrophilic substitution (Scheme 8).

As compared to Nafion® the fluorine content is decreased in such Ionomers. However, it is well-known by polymer chemists that trifluorostyrene can be polymerized neither by anionic nor cationic polymerization and has a very low reactivity in free-radical polymerization. As the Ballard group did not provide information about molecular weights or thermomechanical properties of these Ionomers, we cannot conclude that it is suitable for PEMFC application. Basura et al. [42] who reported the behaviour in oxygen reduction of BAM3G®407 membranes from Ballard found that its permeability to oxygen is close to that of Nafion®117.

4.2.7. Ionomers with polyaromatic backbone

High performance non-fluorinated polymers are based on polyaromatic backbones. These provide both high mechanical strength and high chemical, thermal and oxidative stabilities, make most of them thermostable polymers. Even if their thermostability is not retained after the chemical modifications which lead to the Ionomers, these polymers keep most of their mechanical, chemical and oxidative stabilities. Some of these Ionomers are preferentially prepared by chemical modifications of available polymers while others are prepared by polycondensation from ionic monomers.

4.2.7.1. Polyimide based Ionomers.
Polyimides such as, for instance, Kapton, are high performance thermostable polymers with exceptional mechanical properties. However, polyimides are very sensitive to hydrolysis. Mercier et al. [43,44] performed the syntheses of polyimide sulfonate starting from sulfonated monomers, leading to Scheme 9.

In order to decrease the sensitivity of polyimide to hydrolysis they used naphthalene dianhydride rather than benzene oxydiphtalic anhydride [43,44]. Then by co-polycondensation from ionic pre-polymers and neutral ones, they succeeded in preparing block sulfonated polyimide with hydrophobic and hydrophilic domains. Thereafter, many patents and papers deal with sulfonated polyimides, for instance Yin et al. [45]. However, despite the improvements, the main drawback of polyimide Ionomers for utilization in fuel cells remains their sensitivity to hydrolysis. Lastly, polyimides are relatively costly polymers.
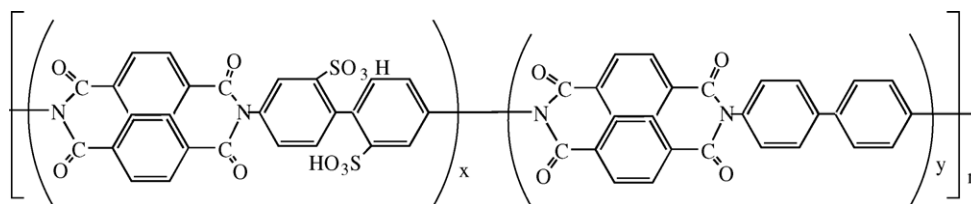
Scheme 9. Polyimide sulfonated Ionomer.

4.2.7.2. High performance thermoplastic Ionomers. These commercial polymers are obtained by polycondensation and, therefore, have a fairly low molecular weight with Mn values around 30,000 g mol^{-1} and a polydispersity index close to 2. According to whether they are intended to be elaborated by injection molding or by extrusion, they have slightly different molecular weights. They can be shared between semi-crystalline polymers, such as polyphenylene sulfide (PPS), polyetherketone (PEK) and polyether-ether-ketones (PEEK) and amorphous polymers such as aromatic polysulfones (PSU) (UDEL® from Solvay) and polyphenylsulfones (PPSU) (RADEL® from Solvay) Scheme 10.

It is difficult to check the electrochemical aging of a polymer electrolyte used as a film because when degradation occurs at the interface with the electrode, the film is not renewed. We have already used an approach on model molecules mimicking the repeat units of polymers to show the higher stability in reduction of polymethacrylonitrile as compared to polyacrylonitrile [46]. A comparative electrochemical study of model molecules which mimic the repeat unit of PPS, PEEK, PSU and PPSU, has also been undertaken in our laboratory Scheme 11.
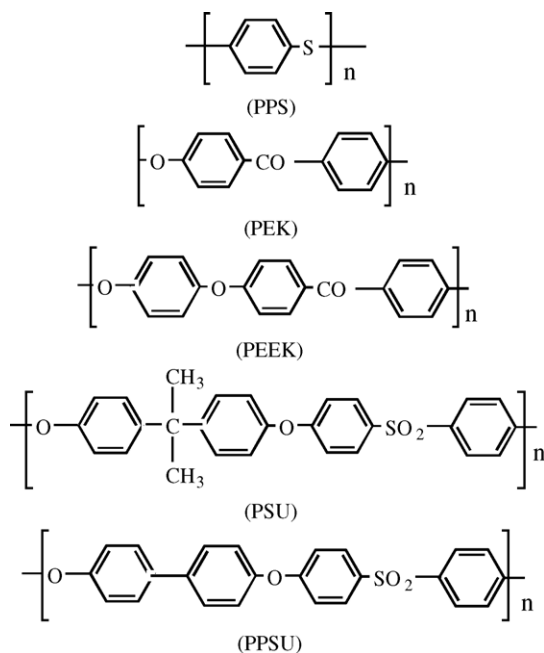

Scheme 10. Thermoplastic polymers precursors of Ionomers.

Sulfolane was selected as a solvent of these molecules and cyclic voltammetry performed at 30 and 80 °C, under argon, hydrogen and oxygen atmospheres, using platinum rotating disc electrode, as working electrode [18]. Within the electrochemical window of sulfolane, much wider than that of water, only PSU and PPSU are perfectly stable. PPS, due to its diphenyl sulfide moiety, is sensitive to oxidation so, according to this criterion, sulfonated PPS [47] should not be a good candidate for PEM fuel cells. On the contrary the model molecule of PEEK appears perfectly stable in oxidation but, due probably to the diphenyl ketone moiety, PEEK appears unstable in reduction. However, as this instability appears at low potential, it should not be detrimental to a sulfonated PEEK.

4.2.7.2.1. PEEK Ionomers. PEEK is a high performance thermoplastic, the crystallinity of which results in remarkable thermomechanical properties. Now this cristallinity makes it difficult to undergo any chemical modification. Thus, the sulfonation of PEEK in concentrated sulfuric acid is the only known method [48–50] to perform the sulfonation of PEEK which is insoluble in organic solvents. The reaction is performed at 5–10% in weight and requires the use of at least 30 times more water than the initial amount of acid in order to recover the sPEEK. In addition, the control of exchange capacity is not easy and often the reaction leads to the formation of water soluble polymers. If PEEK has no solvent except H$_2$SO$_4$, the resulting Ionomer is soluble in various polar organic solvents as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, *N*-methylpyrrolidone, allowing membrane to be elaborated by a film casting method. It may be pointed out that one of the main advantages of PEEK, i.e. its high melting temperature, disappears when reaching the IEC required to obtain a high conductivity level.

4.2.7.2.2. PSU and PPSU Ionomers. As previously reported, the polysulfone backbone exhibits a wide electrochemical stability window in a wide temperature range [18]. In addition these polymers have high glass-transition temperatures and a great thermal stability, while their solubility in usual organic solvents enabling chemical modifications, is an indisputable asset. Moreover, as contrary to PEK, PEEK and PPS, these polymers are fully amorphous; their mechanical strength does not depend on cristallinity ratios and on melting temperatures which are very sensitive to the nature of chemical modifications and to their content. Lastly, polysulfones have been widely used in membrane
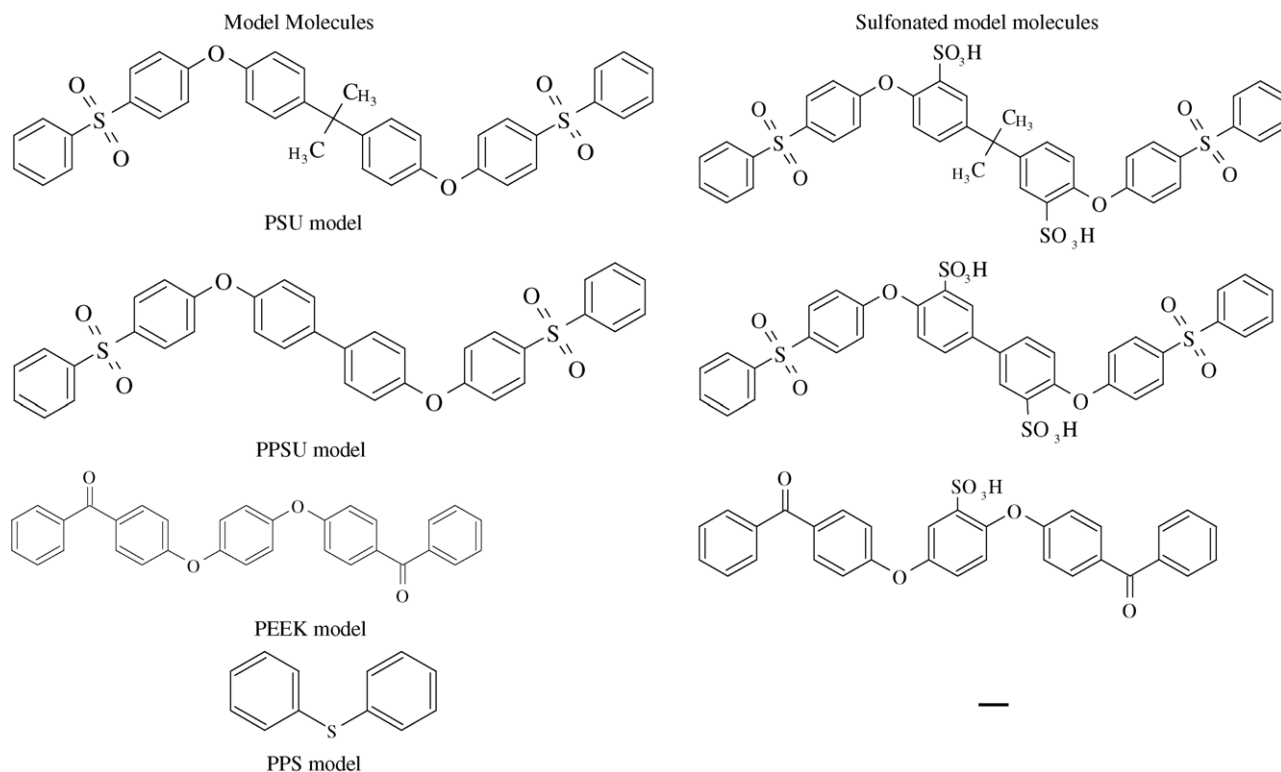
Scheme 11. Model molecules and their sulfonated forms.

applications, e.g. filtration, ultrafiltration, pervaporation, electrodialysis.

As in PEEK, the diaryl ether provides flexibility to the polymer chains. In addition, due to their lone pair, oxygen atoms may interact both with protons and water. According to the application and its constraints, commercial polysulfone used either isopropylidene moiety, which provides flexibility to the polymer but, above all, enables the polymer to be dissolved in various solvents or diphenyl moiety which improves thermomechanical properties.

Syntheses of sulfonated polysulfones can be performed by chemical modification of the polymers by two routes: (i) electrophilic substitution and (ii) aromatic nucleophilic substitution. An alternative consists in step-growth polymerization performed from ionic monomers.

4.2.7.2.2.1. Electrophilic substitution. Contrary to PEEK, PSU and PPSU are soluble in chlorinated solvents well-adapted to carry out electrophilic substitutions. This therefore allows the sulfonation to be carried out in homogeneous media using trimethylsilyle chlorosulfonate [51,52] (Scheme 12) or a SO_3-triethylphosphate complex [53,54]. Particular attention has to be paid to the scale-up of the syntheses which may lead to chain breakings which dramatically affect the lifespan of the membranes.

4.2.7.2.2.2. Nucleophilic aromatic substitutions. An electrophilic route does not allow sulfonic groups to be located on the phenyl sulfone moiety while the sulfonic acid in ortho position of the sulfone should be, at least slightly, more dissociated than a sulfonic acid located in ortho position of an ether.

The sulfonation in ortho position of the sulfone involves three successive steps, metalation–sulfination–oxidation [55,56] (Scheme 13).

The polymer lithiation is performed, under argon, by treatment of THF solution of the polymer with highly concentrated butyl lithium. Lithiation is followed by SO_2 addition which leads to an arylsulfinate, whose oxidation leads to the sulfonate. Kerres et al. [56] reported that the hydrolytic desulfonation from ortho position to ether is easier than from ortho position to sulfone. But, is the hydrolytic desulfonation responsible for the end of life of sulfonated polyaromatic Ionomers?

Although highly sensitive to oxidants, lithium sulfinated polysulfone may be used as nucleophilic agents. Thus, some of them may therefore be used to insure the membrane cross-linking, while most of them are converted into sulfonates. An alternative consists, via the modification of all the sulfinate functions, in spacing the sulfonic function from the polyaromatic backbone by a polyalkylene spacer Scheme 14 [57].

This trimethylene or tetramethylene spacer should prevent the Ionomer from too huge a swelling in water. These synthesis routes open up a wide field of modifications. However, the industrial scale-up of these syntheses seems problematic with regard to the potential benefits.
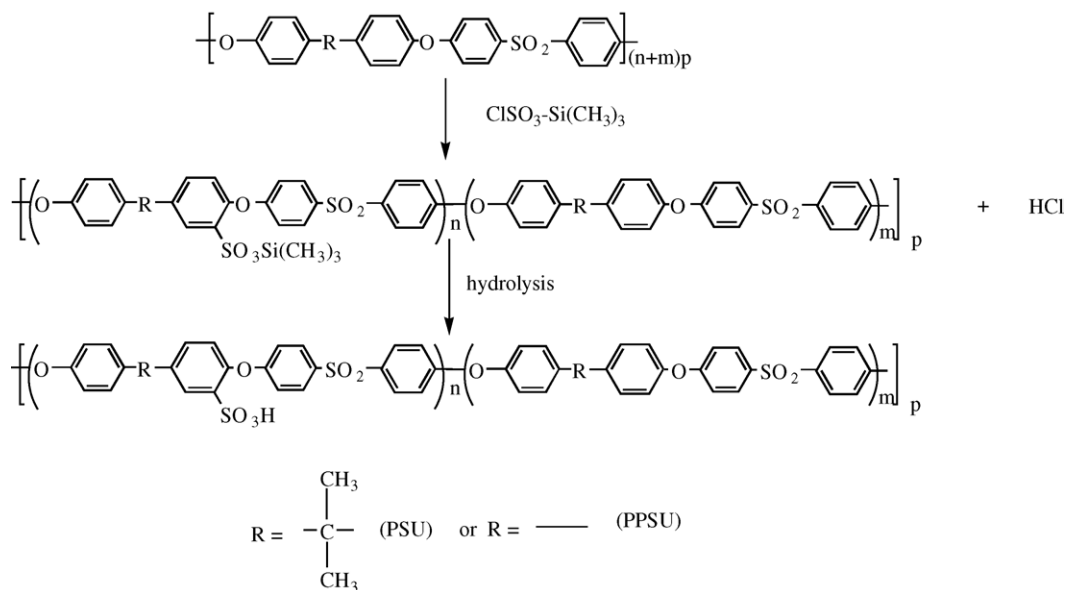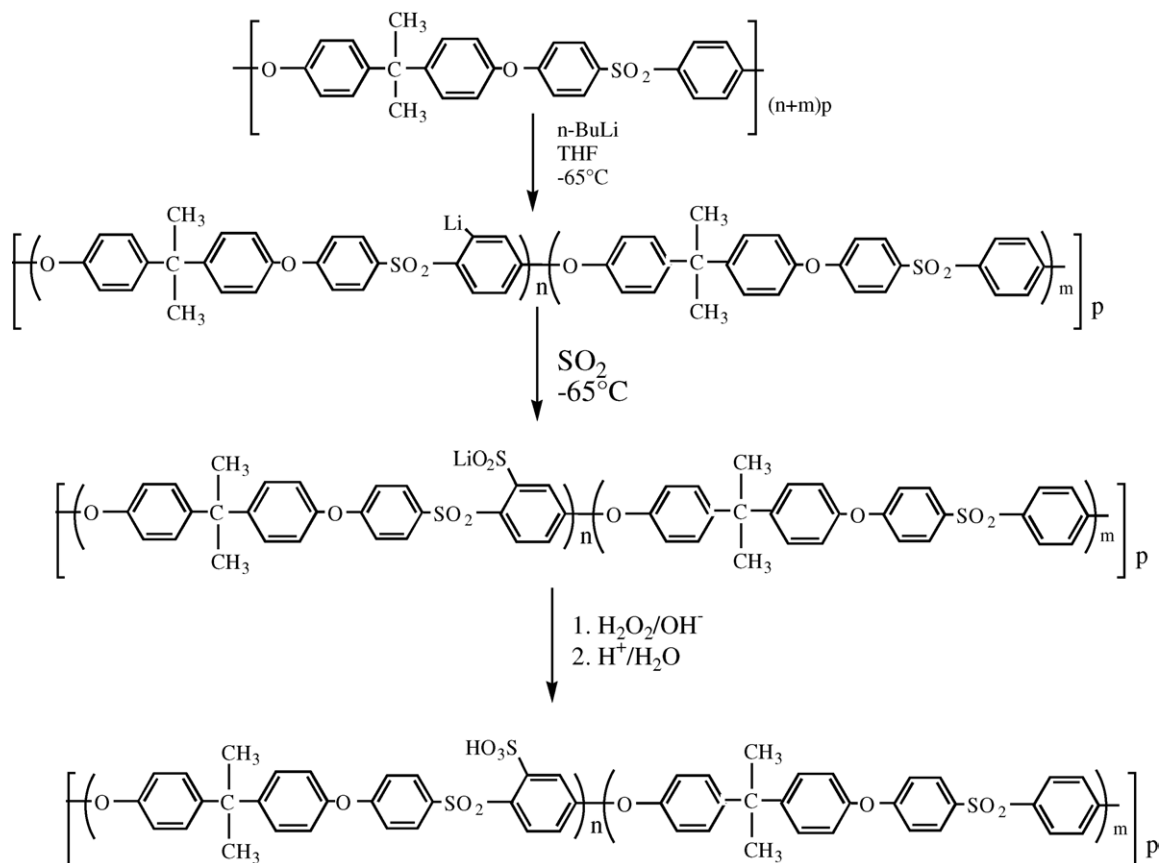
Scheme 12. Electrophilic substitution of polysulfones.

4.2.7.3. Step-growth polymerization performed from ionic monomers. Sulfonated polysulfones have been prepared by Mc Grawth et al. according to the approach developed by Mercier and co-workers for sulfonated polyimides [44].

New sulfonated polysulfones were thus synthesised by co-polycondensation between sulfonated and non-sulfonated monomers [58]. The synthesis from functional monomers, in particular, allows the Ionomer to be shared between

Scheme 13. Nucleophilic substitution of polysulfones.
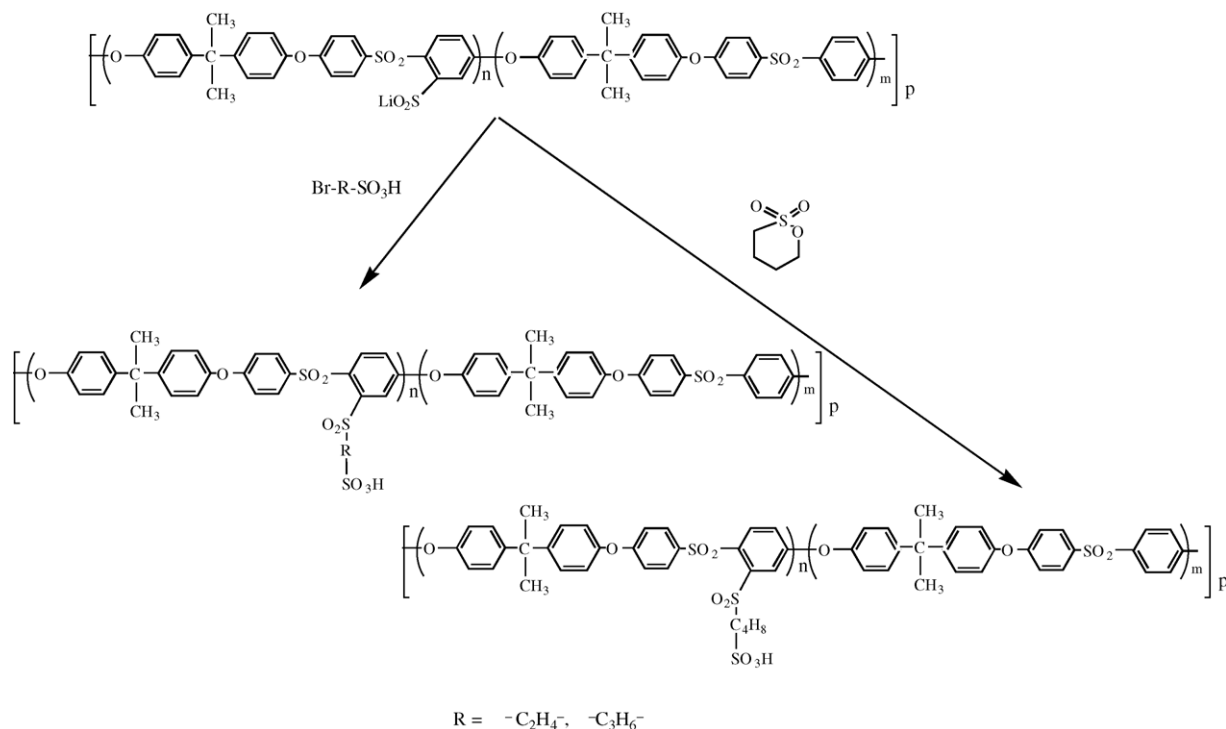
Scheme 14. Sulfonic polysulfone Ionomers with an aliphatic spacer.

hydrophobic and hydrophilic blocks, while the chemical modification of polymers results in functional groups perfectly distributed along the macromolecular backbone. As a result, this synthesis route should limit the swelling of the membrane. But whatever the advantages and the variety of Ionomers which can be produced using the polycondensation route, its main disadvantage with regard to the polymer sulfonation is that the latter starts from commercially available polymers.

4.3. Composite Ionomers

A very well-documented review, covering nano, micro and macrocomposite membranes has recently been published by Alberti and Casciola [7]. In this paper we would therefore like to attract attention to some specific aspects of these composite membranes. The composites are widely used in structure material, generally to reinforce polymers and in that case are mainly used as single fibres or tissues. Other composites deal with powders, e.g. carbon, mica, silica, etc. which are generally called fillers. Obviously such composites can be used in membrane fuel cells, but the term is generally used to indicate a contribution to the electrochemical properties. Indeed, some solid inorganic materials display high conductivities but their mechanical properties do not allow them to be shaped into thin membranes. One of the solutions is to use a polymeric binder. In this case fairly high conductivities were obtained using layered phosphatoantimonic acid $H_nSb_nP_2O(3n+5) \cdot xH_2O$ (with $n = 1$ or 3) and several binders NBR, EPDM, PVdF [52]. Conductivities as high as

10^{-2} S cm^{-1} are obtained but at high content of acid, i.e. 72% in weight. According to Alberti and Casciola [7] the dispersion of inorganic acids in Ionomers has previously been tested but, to the best of our knowledge, for applications other than fuel cell membranes. The use of inorganic insoluble acids in Ionomers for fuel cell membranes was claimed in 1996 [59]. Addition of these fillers to Ionomers allow satisfactory conductivities [60,52] to be obtained while keeping a moderate IEC and preventing, therefore, the membrane of too huge a swelling. Used in high performance Ionomers such as sulfonated polysulfone, they do not noticeably increase the mechanical properties. On the other hand, addition of phosphatoantimonic acid to Nafion® resulted in a doubling of the storage modulus [61]. During the last 5–6 years, many research groups have studied composite Ionomers, using for instance αZrP [62] or heteropolyacids [63,64], in particular to improve the operating temperature of the membranes. Some key points must be emphasized:

- the conductive filler must be electrochemically stable. Thus, cyclic voltammetry performed on phosphatoantimonic acid showed a stability adapted to fuel cell;
- it must improve the conductivity;
- it must not induce any degradation of the Ionomer matrix. Thus, we checked that the previous acid even heated at 300 °C with polysulfone does not induce chain breakings;
- it must not be removed with water.

Lastly attention must be paid to the elaboration, by film casting, of composite Ionomers. Indeed, due to its density,

generally much higher than that of the solvent and Ionomer, it often deposits at least partially. Then, the evaporation of the solvent may generate a microporosity around the filler particles.

5. Conclusion

Voluntary scientific and technological programmes in the US, Japan and Europe are at present mobilizing a significant part of the research potential of the planet. The polymer electrolyte figures indisputably among the bolts of PEMFC technology. On the one hand, a global approach of the polymer electrolytes is essential to progress. This implies: (i) a good control of the syntheses, not only at the laboratory scale but also, at least, at the pilot scale, (ii) characterizations as complete as possible and (iii) attention to the membrane elaboration and in particular at the assembly between electrode and membrane. On the other hand, durability investigations, including post-mortem characterizations should be performed in order to understand the degradation mechanisms and therefore to increase the fuel cell lifetime and performances.

References

[1] C. Lamy, A. Lima, V. Le Rhun, F. Delime, C. Coutanceau, J.-M. Léger, J. Power Sources 105 (2002) 283–296.
[2] E. Peled, T. Duvdevani, V. Livshits, A. Aharon, A. Blum, S. Reichmann, M. Philosoph, Extended Abstracts of the Battery and Fuel Cell Materials, Symposium 2004, pp. 93–94.
[3] E. Agel, J. Bouet, J.F. Fauvarque, J. Power Sources 101 (2001) 267–274.
[4] E. Agel, J. Bouet, J.F. Fauvarque, Second Workshop on Polymer Electrolyte Fuel Cells, Japan–France, 2003, pp. 14–27.
[5] J.Garche, L.Jörissen, A.Friedrich, Extended Abstracts of the Battery and Fuel Cell Materials, Symposium 2004, pp. 91–92.
[6] E.J.Carlson et al., DOE report, Ref. No. 49739 SFAA. No. DESC 02-98EE50526.
[7] G. Alberti, M. Casciola, Annu. Rev. Mater. Res. 33 (2003) 129–154.
[8] J. Rozières, D.J. Jones, Annu. Rev. Mater. Res. 33 (2003) 503–555.
[9] P. Jannash, Curr. Opin. Colloid Interface Sci. 8 (2003) 96–102.
[10] K.V. Kordesch, G.R. Simader, Chem. Rev. 95 (1995) 191–207.
[11] D. Jollie, Fuel Cell Today (2004) 1–3.
[12] J.O'M. Bockris, A.K.N. Reddy, Modern Electrochemistry 1, Ionics, second ed., Plenum Press, New-York, 1998.
[13] H.R. Allcock, M.A. Hofmann, C.M. Ambler, S.N. Lvov, X.Y. Zhou, E. Chalkova, J. Weston, J. Membr. Sci. 201 (2002) 47–54.
[14] H. Cerfontain, B.W. Schnitger, Recl. Trav. Chim. Pays-Bas 91 (1972) 199–208.
[15] K. Xu, C. Angell, Electrochim. Acta 40 (1995) 2401–2403.
[16] K. Ito, H. Ohno, Solid State Ionics 79 (1995) 300–305.
[17] L.E. Karlsson, P. Jannasch, J. Membr. Sci. 230 (2004) 61–70.
[18] M. Maréchal, J. Guindet, J.-P. Diard, J.-Y. Sanchez, ECS Spring Meeting, Paris, 2003.
[19] A.J. Appleby, O.A. VElev, J.-G. Lehelloco, A. Parthasarthy, S. Srinivasan, D.D. Desmarteau, M.S. Gillette, J.K. Ghosh, J. Electrochem. Soc. 140 (1993) 109–111.
[20] S.C. Savett, J.R. Atkins, C.R. Sides, J.L. Harris, B.H. Thomas, S.E. Creager, W.T. Pennington, D.D. Desmarteau, J. Electrochem. Soc. 149 (2002) 1527–1532.
[21] D. Benrabah, R. Arnaud, J.-Y. Sanchez, Electrochim. Acta 40 (13–14) (1995) 2437–2443.
[22] R. Arnaud, D. Benrabah, J.-Y. Sanchez, J. Phys. Chem. 100 (26) (1996) 10882–10891.
[23] F. Alloin, D. Benrabah, J.-Y. Sanchez, J. Power Sources 68 (1997) 372–376;
F. Alloin, J.-Y. Sanchez, J. Power Sources 81–82 (1999) 795–804.
[24] D. Benrabah, S. Sylla, F. Alloin, J.-Y. Sanchez, M. Armand, Electrochim. Acta 40 (13–14) (1995) 2259–2264.
[25] A.K. Adrianov, A. Marin, J. Chen, J. Sargent, N. Corbett, Macromolecules 37 (2004) 4075–4080.
[26] P.N. Blomsky, D.F. Shriver, P. Austin, H.R. Allcock, J. Am. Chem. Soc. 106 (1984) 6854–6855.
[27] M. Armand, J.-Y. Sanchez, M. Gauthier, Y. Choquette, in: J. Lipkowski, P.N. Ross (Eds.), The Electrochemistry of Novel Materials, vol. III, VCH Publishers, 1993, pp. 65–110.
[28] Q. Guo, P.N. Pintauro, H. Tang, S. O'Connor, J. Membr. Sci. 154 (1999) 175–181.
[29] M.A. Hofmann, C.M. Ambler, A.E. Maher, Macromolecules 35 (2002) 6490–6493.
[30] X.Y. Zhou, J. Weston, E. Chalkova, M.A. Hofmann, C.M. Ambler, H.R. Allcock, S.N. Lvov, Electrochim. Acta 48 (2003) 2173–2180.
[31] F. Rousseau, M. Popäll, H. Schmidt, C. Poinsignon, J.-Y. Sanchez, M. Armand, in: B. Scrosati (Ed.), ISPE-2, Elsevier, 1990, pp. 325–337.
[32] A. Denoyelle, C. Poinsignon, J.-Y.Sanchez. EU Patent, 929 017 564 (1993).
[33] I. Gautier-Luneau, C. Poinsignon, J.-Y. Sanchez, Electrochim. Acta 37 (9) (1992) 1615–1618.
[34] J.-Y. Sanchez, A. Denoyelle, C. Poinsignon, Polym. Adv. Technol. 4 (1993) 99–106.
[35] P. Curlier, J.-l. Bergamasco, B. Gauthier-Manuel, T. Pichonat, M. Maréchal, J.-Y. Sanchez. US Patent No. 10/407 069 (2003).
[36] S.R.C.T. Slade, J.R. Varcoe, Solid State Ionics 145 (2001) 127–133.
[37] S. Jacob, S. Cochet, C. Poinsignon, M. Popall, Electrochim. Acta 48 (2003) 2181–2186.
[38] J. Yu, B. Yi, D. Xing, F. Liu, Z. Chao, Y. Fu, H. Zhang, Phys. Chem. Chem. Phys. 5 (2003) 611–615.
[39] F.N. Büchi, B. Gupta, O. Haas, G.G. Scherer, Electrochim. Acta 40 (1995) 345–353.
[40] C.A. Edmondson, J.J. Fontanella, S.H. Chung, S.G. Greenbaum, G.E. Wnek, Electrochim. Acta 46 (2001) 1623–1628.
[41] J. Wei, C. Stone, A.E. Steck, US Patent 5,422,411 (1995).
[42] V.I. Basura, P.D. Battie, S. Holdcroft, J. Electroanal. Chem. 458 (1998) 1–5.
[43] S. Faure, N. Cornet, G. Gebel, R. Mercier, M. Pineri, B. Sillon, in: O. Savadogo, P.R. Robergé, A. Valeriu (Eds.), Symposium New Materials for Fuel Cell Systems, 1997, pp. 818–827.
[44] E. Vallejo, G. Pourcelly, C. Gavach, R. Mercier, M. Pineri, J. Membr. Sci. 160 (1999) 127–137.
[45] Y. Yin, J. Fang, Y. Cui, K. Tanaka, H. Kita, K.-I. Okamoto, Polymer 44 (2003) 4509–4518.
[46] N. Chaix, F. Alloin, J.-P. Bélières, J. Saunier, J.-Y. Sanchez, Electrochim. Acta 47 (8) (2002) 1327–1334.
[47] K. Miyatake, H. Iyotani, K. Yamamoto, E. Tsuchida, Macromolecules 29 (1996) 6969–6970.
[48] F. Helmer-Metzmann, F. Osan, A. Schneller, H. Ritter, K. Ledjeff, R. Nolte, R. Thorwirth, US Patent 5 438 082 (1995).
[49] D. Daoust, J. Devaux, P. Godard, Polym. Int. 50 (2001) 925–931.
[50] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, J. Membr. Sci. 229 (2004) 95–106.
[51] H.S. Chao, D.R. Kesly, US Patent 4 625 000 (1986).
[52] P. Genova-Dimitrova, B. Baradie, D. Foscallo, C. Poisignon, J.Y. Sanchez, J. Membr. Sci. 185 (2001) 59–71.
[53] S.G. Ehrenberg, J. Serpico, G.E. Wneck, J.N. Rider, US Patent No. 5 468 574 (1995).

[54] A. Noshay, L.M. Robeson, J. Appl. Polym. Sci. 20 (1976) 1885–1903.

[55] M.D. Guiver, J.W. Apsimon, O. Kutowy, US Patent 4 833 219 (1989).

[56] J.A. Keres, W. Cui, S. Reichle, J. Polym. Sci.: Part A: Polym. Chem. 43 (1996) 2421–2438.

[57] L.E. Karlsson, P. Jannasch, J. Membr. Sci. 230 (2004) 61–70.

[58] Y.S. Kim, L. Dong, M.A. Hickner, B.S. Pivovar, J.E. McGrath, Polymer 44 (2003) 5729–5736.

[59] B. Baradie, A. Denoyelle, Y. Piffard, C. Poinsignon, J.-Y. Sanchez, G. Vitter. French Patent FR2751119 (1996), EU Patent EP0818841 (1997).

[60] B. Baradie, C. Poinsignon, J.Y. Sanchez, Y. Piffard, D. Foscallo, G. Vitter, N. Bestaoui, A. Denoyelle, D. Delabouglise, J. Power Sources 74 (1998) 8–16.

[61] F. Alloin, J. Guindet, C. Iojoiu, J-Y. Sanchez, International Conference on Electro-active Polymers, Dalhousie, 1–5 November 2004.

[62] D.J. Jones, J. Rozières, J. Membr. Sci. 185 (2001) 41–58.

[63] B. Tazi, O. Savadogo, Electrochim. Acta 46 (2000) 4329–4339.

[64] Y.S. Kim, F. Wang, M. Hickner, T.A. Zawondzinski, J.E. McGrawth, J. Membr. Sci. 212 (2003) 263–282.