Ionomeric membranes for proton exchange membrane fuel cell (PEMFC): sulfonated polysulfone associated with phosphatoantimonic acid

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Abstract

Sulfonation of polysulfone strongly affects both protonic conductivity and lifetime of composite polyelectrolytes. Viscosimetric comparisons showed the effect of the sulfonating agent. Indeed, chlorosulfonic acid leads to chain cleavage while its trimethyl silyl ester does not affect the polymer backbone. Sampling aliquots allowed the sulfonation yield to be followed by ^{1}H NMR. From this study, one might infer that the conversion should not exceed 70% of the theoretical yield. Viscosimetric measurements performed on the same aliquots demonstrated that, even after 72 h reaction time, chain cleavage did not occur. Filling of sulfonated polysulfone with 8% of phosphatoantimonic acid resulted in a conductivity trebling 0.06 versus 0.02 S cm^{-1} at 80°C and 98% of relative humidity (RH). Electrochemical performances, thermo-mechanical stability and low cost make this composite membrane an attractive material for proton exchange membrane fuel cell (PEMFC). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sulfonation; Sulfonated polysulfone; Phosphatoantimonic acid; Composite membrane; Fuel cell

1. Introduction

With the liberalisation of the energy market and owing to their high efficiency in heat/electricity co-generation, fuel cells are envisaged as power stations. A proton exchange membrane fuel cell (PEMFC) appears well-adapted to this application. In addition, car, bus and truck electrification should increase in the next decade, on the one hand to supply the extra electricity required by the car evolution: air conditioning, TV, etc. on the other hand, to meet the future environmental constraints. PEMFC, in particular in association with power batteries and perhaps supercapacitors, could be a mid-term alternative for electrical or hybrid vehicles [1,2]. The main advantage of fuel cells in this application is that they do not need to be recharged, as batteries and can be used continuously. The combustive, oxygen, is provided by ambient air while the fuel, hydrogen in PEMFC has to be stored in the vehicle or can be produced in situ by methanol (or fuel) reforming.

PEMFC power depends on the current density delivered, mainly controlled by the catalyst efficiency

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at the electrodes and the ohmic drop in the electrolyte, i.e. the protonic conductivity of the polymeric electrolyte and the membrane thickness. PEMFC lifetime is a critical parameter and must exceed at least 3000 h; that is to say roughly 150,000 km in an electrical car. This lifetime depends on the electrode efficiency and on the catalyst poisoning. But above all PEMFC lifetime depends on the membrane. Another critical parameter for PEMFC development is related to their price which must be drastically cut. Here again the price of commercially available membranes based on perfluorinated ionomers is too high at present.

Many approaches have been carried out, often in R&D laboratories, to provide cheaper alternatives to these membranes. The Ballard company has successfully developed its own membranes for several years [3], while radiation grafted fluorinated polymers have been proposed by Paul Scherrer Institute in Switzerland [4] and by Solvay–Morgane in Belgium. Sulfonated polyaromatic thermoplastic polysulfones [5] and polyaryl ether ketone [6] as well as sulfonated polyimides [7,8] have also been proposed. Previously, we proposed to use membranes based on modified hybrid polysiloxane which associate [9,10] an inorganic polysiloxane backbone to organic moieties consisting in dangling organic functional groups inducing either protonic conductivity — benzylsulfonic function or an internal plasticizing effect — octyl and perfluorooctyl radicals or enabling further cross-linking. Although these materials met some specifications of fuel cell membranes, namely high protonic conductivities and thermal stability, their mechanical behaviour was unsatisfactory as compared to Nafion membranes. But maintaining the idea of associating organic and inorganic material, we moved towards composite materials consisting of an inorganic proton-conducting material, acting as a filler and a polymer matrix.

Several inorganic proton-conducting materials, such as zirconium/tin phosphates, laponite, tin mordenites and phosphatoantimonic acids $H_n Sb_n P_2 O_{(3n+5)}, x H_2 O$ ($n = 1$ and 3) may show high protonic conductivities, depending on relative humidity (RH). We selected the layered phosphatoantimonic acid H3 ($n = 3$) because of its swelling behaviour and its stronger acidity [11–13]. H3 conductivity reaches $20 \, mS \, cm^{-1}$ at $25°C$ and 100% RH [13]. However, whatever the proton-conducting inorganic material,

it does not meet the specifications to be shaped into membrane and requires the use of a polymeric binder. Our efforts to find the most appropriate polymer included using nitrile–butadiene rubber (NBR), polyisobutylene (PIB), polyvinylidene fluoride (PVDF) and ethylene–propylene–diene terpolymer (EPDM) [14]. Despite the fact that some of these membranes reached high conductivities (see Section 3.4), they did not meet the specifications of the application. Moreover, all these polymers consist of polyalkylene backbones of which long-term stability in oxidation has not been demonstrated. So, we moved towards polyaromatic ionomers as polymer matrix for H3.

It is well known that comparative durability tests of polymers are time-consuming, especially in the complex environment of operating fuel cell, containing an aqueous acid, oxydants (O_2, H_2O_2), reductant (H_2). Also, tests performed on EME-electrode/membrane/electrode-module require between several hundred and several thousand hours and the end of test may obviously result from a membrane tear or leak but also from a poor membrane/electrode assembly. So a chemical a priori approach of the main industrial speciality polymers might enable a selection to be made. Thus, for instance, polyesters must obviously be avoided, as the ester instability in aqueous acids is well known. A common feature between the sulfonated polyaromatics often proposed for this application is the thermostability of the starting material. However, the aromatic sulfonic acids are also well known for undergoing reversible desulfonation at temperatures higher than $180°C$ in aqueous acid solutions [15]. Thus, the loss of the ionic groups occurs at temperatures markedly lower than the degradation of the polyaromatic backbone. The main advantage of these high temperature speciality polymers is, therefore, not related to their thermostability but to their expected stability versus oxydant, reducing agent and acidic environment. Among these speciality polymers we would highlight polyimides, polyetherketones and polysulfones. Polyimides are able to endure high temperatures but they are known to be sensitive to hydrolysis. If the use of naphtalenic moieties seems to prevent this degradation, the lifetime of sulfonated polyimides has still to be demonstrated above $100°C$. Polyetherketone (PEK) and polyetheretherketone (PEEK) are semi-crystalline thermoplastics with a melting point ranging between

330 and 370°C [16]. On one hand, the crystallinity of PEEK slows down and even vanishes upon sulfonation of the aromatic rings. On the other hand, ketones might be reduced in contact with platinum catalysts and hydrogen leading to benzylic groups.

Polyethersulfone thermoplastics, widely used as membranes in dialysers, in micro-, nano- and ultrafiltration and for reverse osmosis, exhibit an extremely high resistance to hydrolysis. The repeat unit of polysulfone consists of diphenylene sulfone, diphenylene ether and aromatic isopropylidene. Aromatic polyether part, also present in polyimides and in PEEK, induces some flexibility in the backbone, moderately augmented by the isopropylidene link. Sulfones are insensitive to hydrogenation and diphenylene sulfone moiety must confer thermal stability and oxidative resistance to the polymer backbone [17]. The easiness of the polysulfone chemical modification and the expected processing via casting of the resulting polyelectrolytes were decisive in selecting this polymer.

This paper focuses on mastering PSF sulfonation and its composite performance optimisation.

2. Experimental

2.1. Materials

2.1.1. Bisphenol-A-polysulfone (PSF)

Known under the commercial name UDEL-P1700 — provided by AMOCO Chemical is dried at 80°C, under vacuum (5 mmHg) for 24 h before sulfonation. PSF is an amorphous, transparent, rigid polymer with a $T_g = 185°C$, thermostable, redox stable, easily sulfonated in low boiling point solvents, easily handled and with a low cost. It is soluble in numerous organic solvents as methylene chloride, 1,2-dichloroethane, dimethyl formamide (DMF), dimethyl acetamide (DMAc), N-methylpyrrolidone (NMP). It is stable up to 400°C in air, above 500°C it loses weight quickly.

$(CH_3)_3SiSO_3Cl$ (TMSCS) from Aldrich was used as received.

2.1.2. Sulfonated polysulfone (SPSF)

The dried PSF is dissolved (10% in weight) in anhydrous dichloroethane, under argon, in a glove-box (1 ppm H_2O). The resulting solution is poured in a three-necked flask. Then, still in the glove-box, $(CH_3)_3SiSO_3Cl$, is dissolved (30% in weight) in dichloroethane and introduced into a dropping-funnel equipped with a pressure-equalisation arm [18]. Then the flask is withdrawn from the glove-box and put under an argon draft before starting the next step of the chemical reaction. After that the dropping-funnel is connected to the flask and the sulfonating reagent is dropped carefully, under argon, to the stirred PSF solution.

Sulfonation is carried out in anhydrous conditions under Ar, which carries the gaseous HCl generated by the substitution. $ClSO_3H$ leads directly to the acidic form while $(CH_3)_3SiSO_3Cl$ provides the sulfonate ester $PSF-SO_3Si(CH_3)_3$, from which the sulfonic acid or the alkaline sulfonate forms could easily be obtained further.

After 24 h stirring at ambient temperature, the reaction mixture is poured in a large methanol excess to precipitate the polymer into the acidic form SPSF. After filtration, the polymer is successively washed with methanol and water and dried under vacuum at 80°C for 24 h. For higher sulfonated polymer isopropanol or 2-methyl-2-propanol is used for precipitation because of SPSF solubility. An alternative consists in precipitating the polyelectrolyte into its sodium salt SPSF-Na, using a methanolic solution of sodium methoxide in a 4/1 ratio versus the initial concentration of sulfonating reagent. After filtration the polyelectrolyte is thoroughly washed with methanol and water until a neutral pH, and dried under vacuum at 80°C for 24 h. Polyelectrolyte storage as a sodium form — SPSF-Na — is convenient, as the acidic form can easily be recovered by precipitating a DMF solution of SPSF-Na in an aqueous HCl solution (0.5 M), followed by filtration, washing and drying of SPSF.

PSF and SPSF are characterised by ^{1}H NMR [19].

2.1.3. Phosphatoantimonic acid (H3)

The synthesis as well as the proton-conductivity, toxicity and other properties of H3 [$H_nSb_nP_2O_{(3n+5)} \cdot xH_2O (n = 1$ and $3)$] are already reported [11–13]. H3 is toxic as an acid but it is not soluble in an acid field; in addition, the Sb content in it is low. The size distribution of the H3 powder is determined by sieving

on polyamide filtration membrane so that the average particle size of H3 is less than 10 μm.

2.1.4. Membrane preparation

Filled membranes are prepared from 20% SPSF solutions in diethylenglycol-monoethyl-ether $C_5H_{12}O_3$ ($H_3C–O–CH_2CH_2O–CH_2CH_2OH$) (DGME) or in a mixture of isopropanol (IP) and dichlorethane (DCE) IP/DCE. H3 is used as aqueous gel 2.5% in weight. The desired amounts of H3 gel and SPSF solutions are mixed, under stirring at ambient temperature. Then, water is partially (as much as possible) removed at 80°C under vacuum (water pump) and the viscous suspension is cast on a flat glass surface, using a film coating machine Erichsen. The film is then heated at a moderate temperature (about 50°C) in a ventilated oven for several hours when DGME as a solvent is partially removed. The flat glass is left at room temperature, the polymer film is peeled by water and kept in cold water which removes DGME totally. The obtained membranes are about 150–200 μm thick and about 10 cm wide. They are completely uniform in thickness and transparent in the case of pure polymer; in the composite films there is some uniformity due to the larger particle size of the additive and as a consequence — they are translucent. The membrane sample size depends on the test requirements (see below).

2.2. Methods

2.2.1. ^1H NMR spectra

The sulfonic group content in the PSS was determined by ^1H NMR in d_6 DMSO, using the Kopf method [19].

2.2.2. Viscosimetry

For this purpose a Schott Gerate AVS 310 viscosimeter, equipped with an Ubelohde capillary was used. The maximum concentration used for SPSF was $8\,g\,l^{-1}$. The solvent selected was a $0.1\,mol\,l^{-1}$ NaI in DMF and the measurements were performed at 25°C (at ±0.1°C).

2.2.3. Mechanical measurements

The stress–strain measurements were performed, using a Minimat MM 12-F from Rheometrics at ambient temperature and humidity. The samples — 5 mm broad and 50 mm long — were carefully cut using a pastry cutter designed for this purpose. The mechanical traction was applied at 25°C and at constant speed (dl/dt) $1\,mm\,min^{-1}$.

2.2.4. Conductivity measurements

They were performed under controlled relative humidity (RH) 60–100% and at temperatures 50, 70 and 80°C, on lab made equipment described elsewhere [18], using a 5 Hz–13 MHz 4192 A Hewlett-Packard analyser. Nafion 117 conductivities were measured in the same conditions to provide a reference.

3. Results and discussion

### 3.1. Sulfonation of bisphenol-A-polysulfone — comparison between two sulfonating agents

From the articles [19,20] on sulfonation it is obvious that side reactions occur in most cases: in sulfonation by HSO_3Cl and by SO_3-complex but no comparative data are available. A patent [21] first described the sulfonation of organic compounds by trimethylsilyl chlorosulfonate (TMSCS) which was then applied to poly(aryl ether sulfone) sulfonation. More recently a sulfonation procedure was described [5] based on a mixture of two reagents: HSO_3Cl and $(CH_3)_3SiCl$ with a slight excess of the latter as compared to the stoechiometry.

Within the last 5 years a new sulfonation process of poly(arylene sulfones), through an aromatic lithiation, has been proposed [15,22]. The sulfonation process consists in four successive steps: lithiation at −50 to 80°C, gassing with SO_2, oxidation of polymeric sulfinate to sulfonate. This procedure makes possible the sulfonation of the polymer in its diarylsulfone moiety, the authors claiming an increased hydrolytic stability of the sulfonated polymer as compared to that obtained by electrophilic substitution. On the other hand, the four step sulfonic conversion seems too complicated to be scaled-up.

Here, we present comparative data on the influence of two sulfonating agents on the SPSF samples. The sulfonation scheme is presented elsewhere [14,18]. The PSF might be sulfonated up to two sulfonic groups per monomer unit; the electrophilic substitutions take place at the *o*-positions of the ether function.
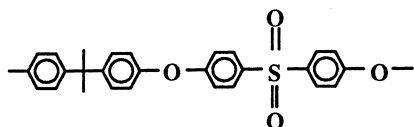
PSF monomer unit:
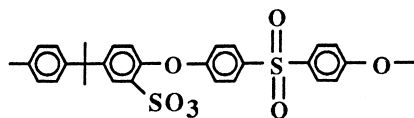
SPSF with one sulfonic group per monomer unit
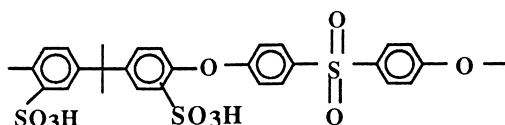
SPSF with two sulfonic groups per monomer unit

Normally SPSF sulfonation yield is expressed as a sulfonation degree, i.e. the number of moles of $-SO_3H$ groups per monomer unit. From these degrees the cation-exchange capacity (CEC, (meq g^{-1} = eq kg^{-1})) may be calculated, using the following relation [19]:

$$CEC = \frac{1000x}{442 + 80x},$$

where x is the sulfonation degree $-SO_3H/PSF$. One could point out that the CEC is roughly twice the sulfonation degree.

Usually, three different sulfonating agents could be used:

1. Chlorsulfonic acid, $ClSO_3H$;
2. Trimethylsilylchlorsulfonate, $(CH_3)_3SiSO_3Cl$ — (TMSCS);
3. Complex of SO_3 with triethylphosphate, $PO(OCH_2CH_3)_3$.

The last one, which provokes an exothermal reaction, is not recommended because of its high toxicity. The sulfonation performed with the first two reagents are compared here.

When $ClSO_3H$, a strong sulfonating agent is used, the reaction medium is not homogenous and results in a partial precipitation which must be prevented by adding several drops of dimethylformamide (DMF). On the other hand, the reaction mixture remains perfectly homogeneous with $(CH_3)_3SiSO_3Cl$. After precipitation, the acid forms of sulfonated polymers

yielded by both reagents were carefully washed, rinsed, dried and submitted to viscosimetry and mechanical stress–strain tests.

Viscosimetric measurements were conducted to detect a possible chain breaking during the electrophilic substitution. It is well known that the hydrodynamic behaviour of polyelectrolytes is completely different from that of non-ionic polymers, the chain dimensions varying with the polyelectrolyte concentration. Therefore, one may attain the limiting viscosity number or intrinsic viscosity (η) of polyelectrolytes using Fuoss and Strauss relation. An altenative consists in adding a strong electrolyte, here NaI, to the polyelectrolyte solution. In that case, the specific hydrodynamic behaviour of polyelectrolytes vanishes and enables one to access to η in a similar way as for neutral polymers. As the sulfonation degree of sulfonated polysulfones has to be varied in a wide range, the second way was selected.

Fig. 1 gathers the viscosimetric measurements, η and "Huggins" coefficient values being reported in Table 1. From this Fig. 1 and Table 1, it is obvious that SPSF intrinsic viscosity depends on the sulfonation reagent used. Thus, η of SPSF prepared using $ClSO_3H$
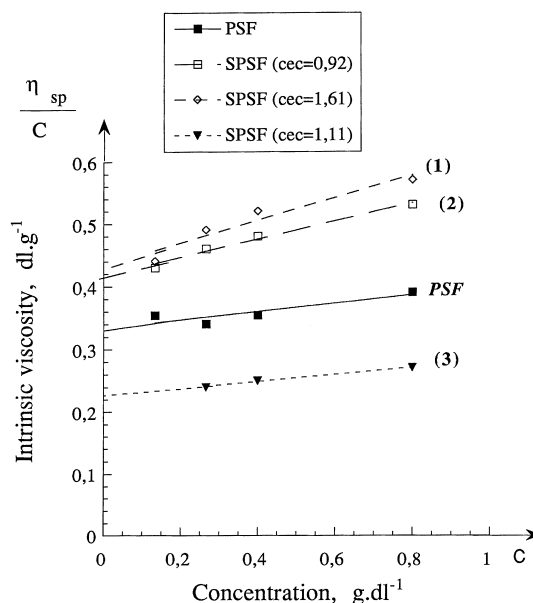

Fig. 1. Reduced viscosity plots of PSF and SPSF samples, obtained by $ClSO_3H$ (curve 3) and by TMSCS (curves 1 and 2) with different CEC: 0.92, 1.11 and 1.61 meq g^{-1}.

Table 1
Viscosimetric data on PSF and SPSF with different sulfonation degrees obtained by two sulfonating agents: $ClSO_3H$ and TMSCS

CEC ($eq\,kg^{-1}$)	Sulfonating agent	Intrinsic viscosity (η) ($dl\,g^{-1}$)	K' (Huggins coefficient)
PSF			
0	–	0.33	0.68
SPSF			
0.92	$(CH_3)_3SiSO_3Cl$	0.42	0.77
1.61	$(CH_3)_3SiSO_3Cl$	0.44	0.90
1.11	$ClSO_3H$	0.23	0.94

is almost twice as low as that of SPSF obtained using $(CH_3)_3SiSO_3Cl$. A decrease in η means a decrease in average viscosimetric molecular weight. From these results it may be inferred that the superacid $ClSO_3H$ provokes chain cleavages. In the case of a mild sulfonating agent as the chlorosulfonic ester $(CH_3)_3SiSO_3Cl$ the intrinsic viscosity of the two SPSF samples 0.92 and 1.61 is similar which reflects almost the same hydrodynamic behaviour. These results imply that neither cleavage nor branching takes place during the sulfonation. DMF/NaI used as a solvent is probably a better solvent for sulfonated polysulfone PSS than for the starting polysulfone PSF as shown by the comparison between their intrinsic viscosities.

Comparative mechanical stress–strain tests of SPSF specimens, prepared with the two previous sulfonating agents (Fig. 2), show that elongation at break is higher with SPSF sulfonated by $(CH_3)_3SiSO_3Cl$. Viscosimetric and mechanical measurements are, therefore, in agreement and allowed $(CH_3)_3SiSO_3Cl$ to be selected as the sulfonating reagent rather than $ClSO_3H$.

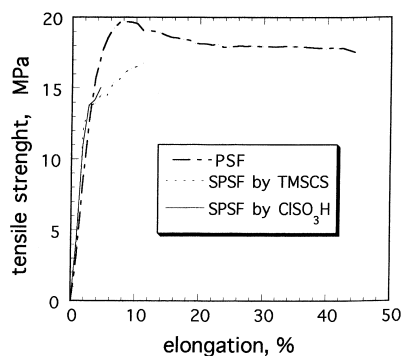### 3.2. Sulfonation conversion of PSF into SPSF

Whatever the selected reagent, the conversion yield is not quantitative as shown by a comparison between the theoretical and real sulfonation degree of SPSF (Fig. 3). To the best of our knowledge a critical investigation of that reaction was never reported in the case of polysulfone, reports mainly paying attention to the final properties of the polyelectrolyte.

In order to check the sulfonation efficiency, several experiments were carried out using the same typical procedure, i.e. solvent, concentration, inert atmosphere — but varying the reagent concentration and the reaction time. Two sets of values were obtained at 40°C for 4 h and at 35°C for 24 h. Fig. 3 plots the real sulfonation degree versus the theoretical one leading to a straight line for a 24 h/35°C

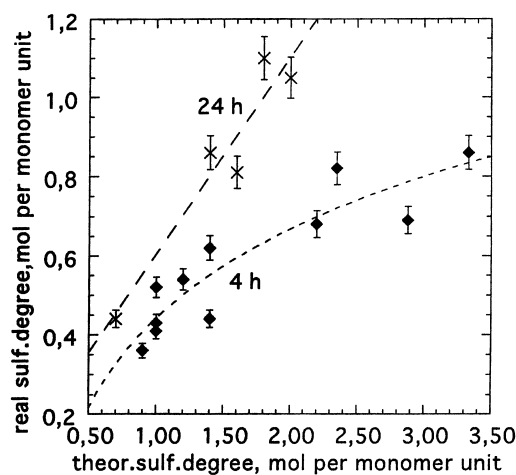Fig. 2. Stress–strain plots of PSF and SPSF specimens, obtained by $ClSO_3H$ and TMSCS.

Fig. 3. Conversion plots of sulfonation of PSF into SPSF at two different conditions: for 4 h at 40°C and for 24 h at 35°C.

reaction process and to a curve for a 4 h/40°C sulfonation. In fact, these plots reflect the efficiency of the sulfonation, the straight line shows an average efficiency of about 60% with respect to the sulfoning reagent introduced. In the case of 4 h sulfonation, the efficiency is less and decreases with the increase of the theoretical sulfonation degree. Moreover, the real sulfonation degree is limited to about 0.85 even when the target exceeds 3. A 4 h reaction time is obviously insufficient to achieve a high sulfonation level.

3.3. PSF sulfonation rate

Based on the previous results, it would be interesting to know (1) whether an increase in reaction time causes a chain length decrease; (2) whether better sulfonation level and conversion can be reached and (3) what the kinetic features of this reaction are.

To elucidate these points, several PSF sulfonations were carried out at 35°C, up to 72 h, using the same theoretical sulfonation degree = 2.0. Sampling aliquots at different reaction times allows one to follow the evolution of sulfonation levels.

It was expected that the sulfonation could take place relatively smoothly up to a sulfonation degree = 2 which corresponds to two sulfonic groups per monomer unit. However, a clear decrease in the reaction rate was observed beyond sulfonation degrees of 0.74 and 1.35.

Fig. 4, which plots the real sulfonation degree versus time displays three main stages of the reaction. A somewhat fast sulfonation occurs in the first 5 h. Then, up to a 48 h reaction time, the rate decreases markedly and the sulfonation level reaches 1.35, namely 67% of the theoretical conversion. A closer look at the graph shows that the sulfonation of the second benzene ring proceeds at almost the same rate. Indeed, after reaching a real sulfonation degee of 1 the PSF sulfonation process proceeds with the same rate as shown by the slope of the reaction-time plot. After 48 h, the sulfonation level reaches a plateau. As the solution remains homogeneous (neither precipitation, nor cloudy) and keeps apparently the same viscosity, this decrease should be related to a lesser reactivity of the polysulfone already sulfonated at a sulfonation degree roughly equal to 1.37. Despite the induced electron-withdrawing effect on the aromatic ring related to the monosulfonation, this effect should
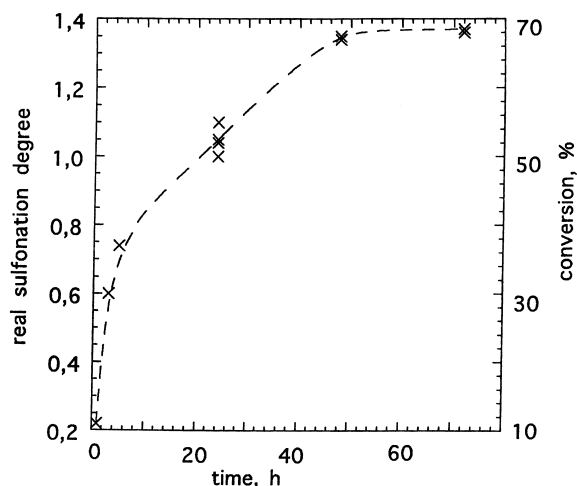

Fig. 4. Time-conversion plot of sulfonation of PSF into SPSF up to 72 h.

be confined to the sulfonated ring and should not extend to the neighbouring phenoxy ring. So we cannot provide, at present, sound explanations for this rate decrease. Nevertheless, one may assume that, despite the gaseous purging (argon), a part of HCl, produced in high yield by the electrophilic substitution, might interact with the phenoxy group weakening the ether + M effect.

In an attempt to follow up the sulfonation rate and assuming a second order reaction, 1/C versus time was plotted in Fig. 5. In this case C, concentration of the ring positions available for sulfonation, is based on the measured real sulfonation degree.

Although the plot is linear up to 5 h, we cannot conclude on the mechanism of the first substitution. In a further study we will focus on the sulfonation kinetic.

In addition to the determination of their sulfonation level the aliquots were submitted to viscosimetric measurements — η values being gathered in Fig. 6 and Table 2. We may point out the reliability of the experimental data. At the beginning of sulfonation, η increases and then remains roughly independent of the sulfonation degree. From these viscosimetric data we may assume the absence of chain cleavage, even at high sulfonation degree, confirming, once again, the efficiency of $(CH_3)_3SiSO_3Cl$ in the sulfonation of polysulfone.
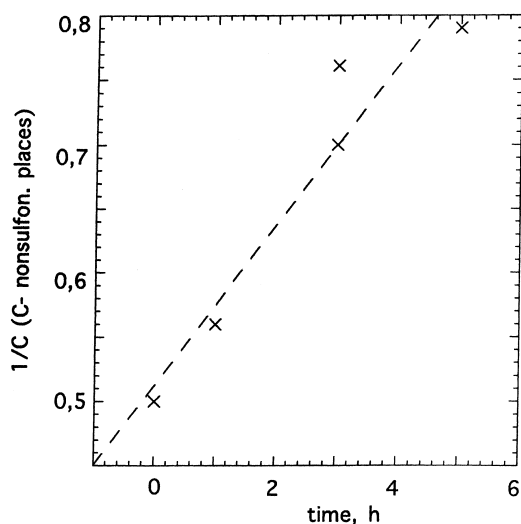
Fig. 5. Initial rate velocity vs. sulfonation time of SPSF.

3.4. Membrane-composite based on SPSF and its conductivity

PEMFC application of a polymeric membrane requires high proton-conductivity comparable to Nafion 117.

Prior to analysing the conductivities of a composite membrane which associates two kinds of proton-conducting materials, i.e. H3 and a polyelectrolyte, each contribution must be investigated separately.

3.4.1. SPSF conductivities

Proton-conductivity of polyelectrolytes depends on the concentration in charge carriers, i.e. protons as $t+ = 1$, and on their mobility which is mainly ensured by water molecules. In Nafion membranes
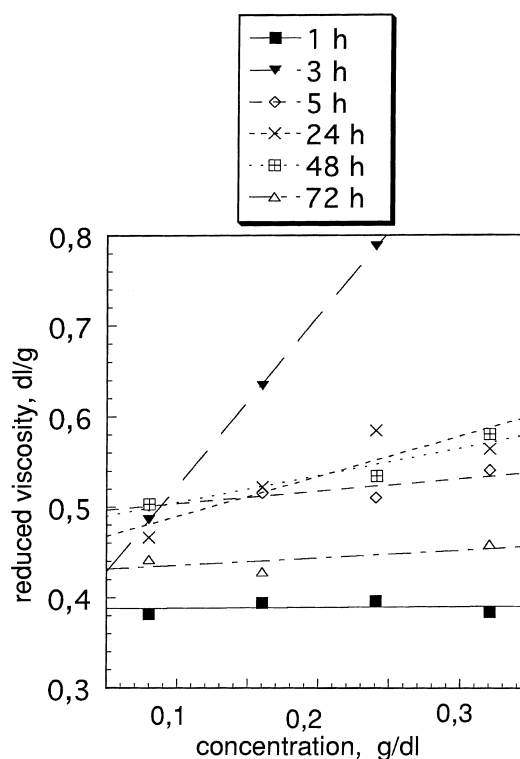

Fig. 6. Reduced viscosity plots of SPSF, sulfonated in different periods of time: 1, 3, 5, 24, 48 and 72 h.

the perfluorosulfonic acid groups may be classified as superacids and have, therefore, a great ability to dissociation, while aryl sulfonic acids have pK_a close to −6 as compared to −12 for a superacid [23]. To get from SPSF a concentration in charge carriers similar to that in Nafion requires a higher content in sulfonic groups, namely greater than 1.5 mol of H^+ per kilogram. Although viscosimetric measurements

Table 2
Viscosimetric data on SPSF, supplied after different sulfonation times

Time (h)	Sulfonation degree (mol-SO$_3$H/m.u.)	CEC (eq kg^{-1})	Intrinsic viscosity (dl g^{-1})	K' (Huggins coefficient)
0	0	0	0.33	0.68
1	0.22	0.46	0.375	0.06
3	0.60	1.24	0.427	0.716
5	0.74	1.56	0.492	0.055
24	1.00	2.05	0.440	0.276
48	1.35	2.76		
72	1.36	2.79	0.435	0.020

demonstrated that such high concentrations can be obtained without chain cleavage, the resulting poly-electrolytes swelled markedly and even dissolved partially in hot water (80°C).

3.4.2. H3 conductivities

H3 conductivities versus relative humidity were already reported (see Section 1). Nevertheless, no report dealt with the conductivities of H3 scattered in a polymeric binder. Several binders such as NBR, PIB, PVDF and EPDM were investigated [14]. High content of fillers must be incorporated to provide conductivity levels compatible with the application. EPDM and PVDF composite membranes were found to keep appropriate mechanical properties at these H3 rates. Fig. 7 gathers the Arrhenius conductivity plots, at 92% RH, of three composite membranes whose H3 content (in wt.%) and distribution size have been varied (up to 10 or 1 mm). An increase from 60 to 72%, results in an increase by a factor 10 of the conductivity which reaches $5\,mS\,cm^{-1}$ at 85°C. We may point out that the conductivity is thermally activated for an H3 rate of 60% but seems almost temperature-independent for higher rates. The particle size also affects conductivity which doubles and reaches $12\,mS\,cm^{-1}$ at 85°C upon decreasing particle size. Although this conductivity is among the best one obtained with self-supporting

membranes this value still remains too low as compared to Nafion.

3.4.3. SPSF/H3 composite membranes

The filled membranes were firstly prepared by dispersing H3 of average particle size larger than $10\,\mu m$ in a SPSF solution based on dichloroethane–isopropanol (DCE–IP) rather hydrophobic mixture [19]. Solvent evaporation after casting drove the H3 particles to the upper face of the membrane, inducing a heterogeneous H3 distribution. This rough material, exhibited a maxima conductivity for 8% H3 and a SPSF CEC of $1.1\,meq\,g^{-1}$. Its permeability to oxygen becomes about twice as low as that of Nafion. Lastly, an electrode/membrane/electrode assembly was able to run for 500 h at 80°C under 4 bar of H_2 and O_2, while reaching about 80% of the Nafion performances (using a $1.1\,meq\,g^{-1}$ SPSF). Water swelling determinations showed the respective influence of the sulfonation rate, H3 content, and temperature. Thus, H3 increases the water content and improves the insolubility of the composite based on SPSF up to $1.4\,meq\,g^{-1}$ CEC [24,25]. Conductivity measurements performed under controlled temperature and relative humidity showed that 8% in H3 fillers doubled (trebled) the proton conductvity (Fig. 8). But at
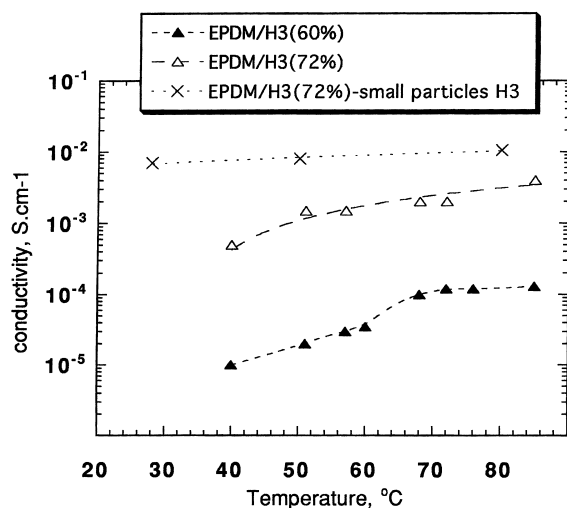

Fig. 7. Conductivity–temperature dependance of membrane composites, based on EPDM/H3 (60%), EPDM/H3 (72%) and EPDM/H3 (72%) with a smaller size of H3 particles. RH = 92%.
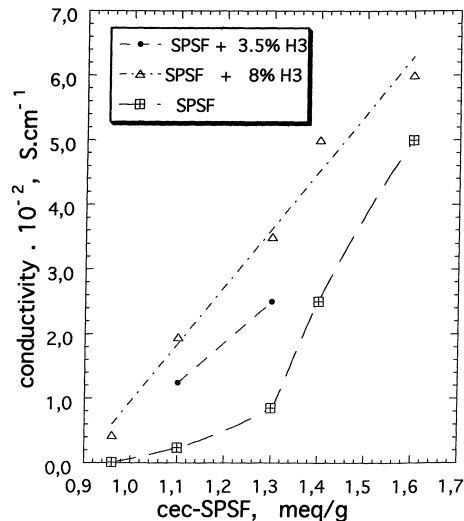

Fig. 8. Variations of conductivity vs. CEC of SPSF, concerning unfilled and filled with H3 samples at 80°C; size of H3 particles higher then $10\,\mu m$, used mixed solvent for sample preparation: isopropanol–dichloroethane, RH = 98%.

that time we did not master perfectly either the sulfonation process (reagent, titration, rate) or the selection of hydrophilic solvent allowing the membranes to be cast while keeping their hydrophilicity.

Nevertheless, we must highlight a synergetic effect between SPSF and H3 which enabled the composite conductivity to approach that of Nafion 117. Other composite membranes were prepared using the hydrophilic solvent DGME instead of the DCE/IP mixture, and H3 submicronic particles. Despite an obvious gain in homogeneity the conductivities are similar. However, we may expect, due to the homogeneity, an increase in the membrane lifetime. Other investigations on H3, SPSF and membrane processing are in progress to improve the PEMFC performance. In parallel, we are trying to understand the synergetic effect observed at low to medium sulfonation rate and the influence of H3 on water management.

3.5. Membrane-composite SPSF-H3-mechanical behaviour

The mechanical measurements were carried out, at 25°C in air, on samples consisting of pure PSS (with some sulfonation levels) and some SPSF/H3 composites. The samples were operated in two different ways, namely, samples treated in hot water at 50°C for 3 h before the tensile strength test or untreated. Unfortunately, these mechanical tests were not carried out in similar conditions to that of a PEMFC, i.e. 80°C and 100% relative humidity (RH). The apparatus available in our lab for this purpose allows the temperature to be varied, but a higher temperature was not applied in order to avoid the sample dehydration. In this way we could assess the mechanical parameters: tensile strength at break, maximum tensile strength, elongation at break and Young's modulus (YM) both of SPSF and of the composite and to predict some undesirable changes between unfilled and filled membranes. The treated samples were submitted to mechanical traction immediately after immersion in water.

It is known that the introduction of an inorganic powder in polymer results in loss of elasticity and flexibility and imparts the rigidity [26]. Shao et al. have shown [27] that the incorporation of nanoparticles of SiO_2 and TiO_2 formed by sol–gel procedure, have caused a decrease in elongation at break and an increase in elasticity modulus. Thus, it was not expected to obtain a more flexible membrane by addition of H3 to SPSF. Surprisingly, our mechanical experiments reveal another trend (Table 3).

Fig. 9 displays the plot of the tensile strength versus elongation of SPSF samples with different sulfonation levels (CEC): 0.5; 1.5 and 1.8 — unfilled and filled with 8% H3: all samples were not previously treated in hot water. From the curve analysis it appears that in unfilled membranes the highest CEC exhibits the lowest YM and the lowest tensile strength maxima. The similar correlation was found in the case of filled samples. This observation could be explained by the hydrophilic character of sulfonic groups, allowing water to act as an external plasticizer. Polymer chain mobility is, therefore, increased and as a consequence, YM decreases. From Table 4, a decrease in YM of about 20%

Table 3
Sulfonation level (CEC, eq kg^{-1}) and conductivity (σ, S cm^{-1}) at 80°C of SPSF and SPSF + H3; CEC1 — CEC of SPSF, CEC2 — CEC of SPSF + H3[a]

SPSF (CEC1)	H3 (%)	SPSF + H3 (CEC2)	CEC2/CEC1	$\sigma2/\sigma1$	$\sigma2$ (SPSF + H3)
0.92	3.3	1.0	1.08	47.1	4.24×10^{-3}
1.07	3.3	1.16	1.08	5.16	1.25×10^{-2}
	7.1	1.28	1.19	8.12	2.0×10^{-2}
	12.0	1.4	1.30	6.66	1.6×10^{-2}
1.26	3.3	1.34	1.06	2.94	2.5×10^{-2}
	7.1	1.45	1.15	4.11	3.5×10^{-2}
1.39	7.1	1.54	1.12	1.70	4.12×10^{-2}
	12.0	1.68	1.20	1.93	

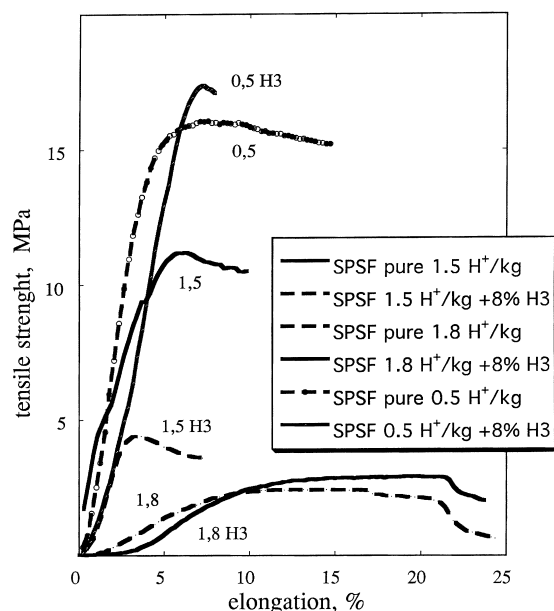[a] $\sigma1$ — σ of SPSF; $\sigma2$ — σ of SPSF + H3.

Fig. 9. Stress–strain curves of non-treated in hot water unfilled and filled (8% H3) SPSF samples, CEC: 0.5, 1.5 and 1.8; solvent used for sample preparation — DGME.
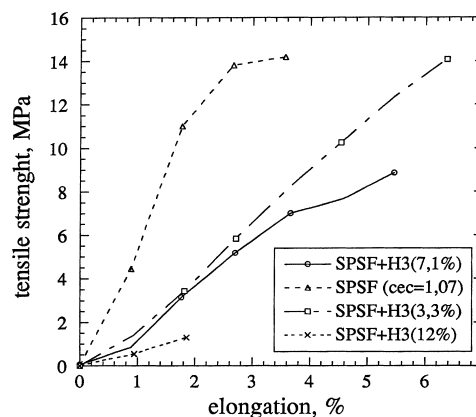

Fig. 10. Stress–strain curves of non-treated in hot water unfilled and filled SPSF (CEC 1.07) samples, containing 3.3, 7.1 and 12% H3. Solvent used for sample preparation — DCE/IP.

may be seen for filled samples based on SPSF (CEC 0.5 and 1.5) in comparison to the unfilled ones (same CEC). However, the composite based on higher sulfonated SPSF (CEC 1.8) shows a very slight increase in its YM Results on pure SPSF accord well with other published data on sulfonated polysulfones [28].

Filling SPSF (CEC 0.5) with 8% H3 does not affect the mechanical properties. On the other hand, the tensile strength of highly sulfonated SPSF and its composite is too low, in comparison to Nafion 117, to use these membranes in fuel cells. As a long-time

test in fuel cell was performed on a composite: SPSF (CEC 1.07) and 8% H3, we paid special attention to this SPSF. The mechanical curves in Fig. 10 show the plastification induced by H3 which increases with the filler amount from 3 to 12%. This result which was not expected is a pleasant surprise and confirms the previous assumption about the water plasticizer effect.

Furthermore, from Fig. 11, one can compare tensile strength versus elongation curves of unfilled and filled (8% H3) SPSF samples, after a hot water treatment (50°C) which humidifies the membranes. These kinds of measurements are, therefore, close to real working conditions of a fuel cell membrane. From the curves it is obvious that all compositions manifest higher elongation at break and the similar values of the maximum tensile strength in comparison to non-treated samples. The mechanical behaviour of filled (8% H3) SPSF (CEC 1.5) seems similar to that of Nafion 117.

Table 4
Young's modulus values extracted from mechanical measurements of unfilled SPSF and filled SPSF of different CEC

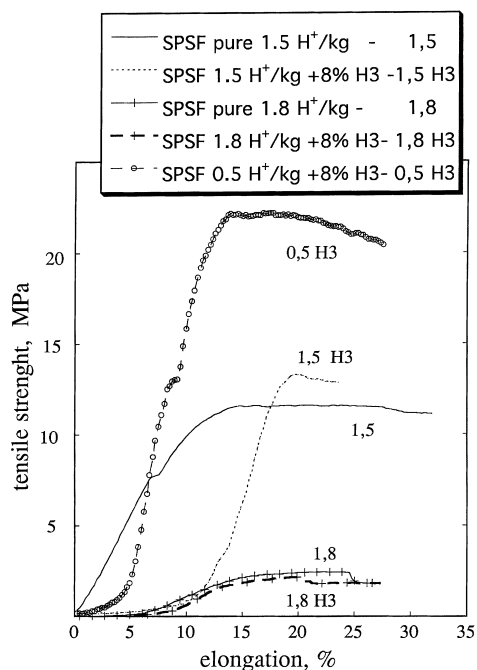| Samples — CEC	Young's modulus (Mpa) unactivated SPSF	Young's modulus (Mpa) activated SPSF
SPSF (0.5 H$^+$/kg)	426	
SPSF (0.5 H$^+$/kg) + 8% H3	298	316
SPSF (1.5 H$^+$/kg)	212	116
SPSF (1.5 H$^+$/kg) + 8% H3	192	187
SPSF (1.8 H$^+$/kg)	34	24
SPSF (1.8 H$^+$/kg) + 8% H3	41	32

Fig. 11. Stress–strain curves of treated in hot water unfilled and filled (8% H3) SPSF samples, CEC: 0.5, 1.5 and 1.8. Solvent used for sample preparation — DGME.

However, we should keep in mind that the investigated samples are not completely homogeneous and that some H3 particles might have provoked an early mechanical break.

From the conductivity and mechanical data, we would further investigate the composition associating around 8% H3 and SPSF with CEC ranging between 1 and 1.5. Nevertheless, it should not rule out the rest because there is not yet any available information on mechanical behaviour of the composites in real working conditions, i.e. 80 and 100% RH.

4. Conclusions

Sulfonating conditions, i.e. reagent, temperature, solvent, reaction time govern the polyelectrolyte adequation to PEMFC application. In particular, the reagent nature greatly affects the polymer chain length. TMSCS does not induce chain cleavage, even after a 72 h reaction time, allowing, therefore, SPSF with a wide concentration range in sulfonic groups

to be synthesised. High conductivities were obtained from pure SPSF but at too high a rate in sulfonic groups, inducing membrane swelling and even partial dissolution.

On the other hand composite membranes, consisting of phosphatoantimonic acid H3 and of moderately sulfonated polysulfone, provided conductivities close to Nafion membranes, while avoiding dissolution or excessive water swelling at 80°C. In addition a synergy was observed on the conductivity between H3 and SPSF, provided the sulfonic group concentration in SPSF remains lower than 1.5–1.6 mol kg^{-1}. Lastly, some composites showed an improvement of mechanical properties as compared to pure SPSF of the same exchange capacity, notably after hot water treatment. Future works will deal on the one hand with the composite membrane processing, on the other hand with the understanding of H3/SPSF interaction and synergy.

Acknowledgements

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