



## Thermostable ionomeric filled membrane for H<sub>2</sub>/O<sub>2</sub> fuel cell

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Received 27 November 1997; accepted 9 December 1997

### Abstract

Dispersion of submicronic particles of phosphoantimonic acid fillers (H3) with a 4.3 H<sup>+</sup>/kg (4.3 eq/kg) cationic exchange capacity (cec), in a solution of sulfonated polysulfone (PSS) of 1.07 H<sup>+</sup>/kg gives viscous suspension allowing the 'filled' material to be shaped in thin films. From the conductivity measurements, a synergic effect between the acidity of PSS and H3 has been highlighted. Conductivity values close to those of the Nafion 117 have been determined in the same experimental conditions, i.e., 96% relative humidity at 80°C. Furthermore, the inorganic filler improves both the mechanical strength and the gas impermeability of the filled membrane as compared to an unfilled PSS membrane. A PSS–H3 membrane of 1.07 H<sup>+</sup>/kg cec filled with 7.1% in H3 provided 80% of Nafion performances in a H<sub>2</sub>/O<sub>2</sub> fuel cell for 500 h at 80°C and 4 bars pressure of H<sub>2</sub> and O<sub>2</sub>. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Sulfonated polysulfone; Phosphoantimonic acid; Filled membrane; Fuel cell

### 1. Introduction

Proton exchange membrane fuel cells (PEMFC) appear as a mid-term alternative to batteries for EV (Electrical Vehicle) application, above all for buses and trucks. The specificity of PEMFC is to convert the free energy  $\Delta G$  of the reaction: H<sub>2</sub> + 1/2O<sub>2</sub> into electricity and water as efficiently as possible. The PEMFC power depends on the current density also controlled by the ohmic drop in the electrolyte, i.e., the protonic conductivity of the polymeric electrolyte and the membrane thickness.

At present most PEMFC use expensive perfluorinated membranes. Despite their high performances and their lifetime, these ionomers are clearly responsible for the cost of fuel cells and compromise their development. Several approaches have been carried out, often in R&D laboratories, to provide cheaper alternatives to these membranes. Ballard have successfully developed their own membranes for several years [1,2], while radiation grafted fluorinated polymers are prepared by Paul Scherrer Institute in Switzerland [3] and by Solvay-Morgane in Belgium. Sulfonated polyaromatic thermoplastic polysulfones [4] and

polyaryl ether ketone [5] as well as sulfonated polyimides [6,7] have also been proposed. Unlike the previous ionomers, complexes were prepared by mixing a thermos table polymer (polybenzimidazole) with phosphoric acid [8] and ionomers loaded with an acidic inorganic filler [9] (this work) in France. More recently, the manufacture of thin composite membranes, consisting of a teflon tissue impregnated with a Nafion 117 solution [10] with high conductivities, has been reported by Gore.

Here we present polymeric membranes made of thermoplastic ionomers loaded with acidic inorganic fillers. These membranes are in fact the extension of an activity started within European JOULE programs [11] on solid state protonic electrolyte for DMFC (direct methanol fuel cell). They were mainly prepared by dispersing superprotonic conductors in a polymeric binder. The protonic charge carriers were provided by zirconium phosphates, laponite and tin mordenites [12]; shaping into thin film was ensured by the presence of a polymeric binder. Unfortunately, the binding resulted in an important loss of conductivity while the long term stability of the binder was questionable. In parallel our group investigated another approach by preparing sulfonated polybenzyl siloxane via a sol–gel process [13]. Despite the high thermal stability and the very high protonic conductivities of these siloxane based ionomers,

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we did not succeed in preparing membranes with good mechanical properties.

Concerning the choice of an inorganic protonic conductor, it appeared worthwhile to consider the layered phosphoantimonic acids  $H_nSb_nP_2O_{(3n+5)} \cdot xH_2O$  ( $n = 1$  and  $3$ , with  $n = 3$  the phosphoantimonic acid is called H3) which exhibit a swelling behaviour similar to that of smectite clays and have stronger acidic behaviour than the layered group (IV)  $\alpha$ -ZrP like acids [14–16]. They are good protonic conductors ( $\sigma = 0.02 \text{ S cm}^{-1}$  at  $25^\circ\text{C}$  in 100% relative humidity (RH) [14]). It appeared convenient to disperse H3 in an ionomeric binder. Indeed the loss of conductivity previously observed when dispersing the inorganic protonic conductors in a hydrophobic polymeric binder such as EPDM or PTFE should be avoided using an ionomer. To obtain the stability in oxidation observed for perfluorinated membranes a thermostable polymer was chosen. Polysulfone was selected because of its low cost, its commercial availability and the great facility of finding easily handling solvent, with a low to medium boiling point.

The filled membrane, obtained after the dispersion of the phosphoantimonic acid (hereafter called H3) in the

sulfonated polysulfone matrix, presents the protonic conductivity and the electrochemical stability of perfluorinated membranes with a considerably lower cost.

## 2. Materials

### 2.1. Phosphoantimonic acid

The preparation of  $H_3Sb_3P_2O_{14} \cdot xH_2O$  (H3) involves the synthesis of  $K_3Sb_3P_2O_{14} \cdot xH_2O$  by solid state reaction at  $1000^\circ\text{C}$  and a successively  $K^+/H^+$  ion exchange in concentrated nitric acid (8 N) at  $50^\circ\text{C}$  [15]. When dispersed in water, H3 undergoes an infinite swelling leading to a gel-like solution of pH close to 2.5. Its cation exchange capacity is  $4 \text{ H}^+/\text{kg}$  (close to the theoretical cec) as determined by titration with a 0.1 M KOH solution.

H3 is hydrated at room temperature, its water content, interlayer distance and protonic conductivity are strongly dependent on the relative humidity as it is reported in Ref. [16]. The protonic conductivity is closely related to the water content of the material and presents two plateaus corresponding to two stable hydration states as well as two

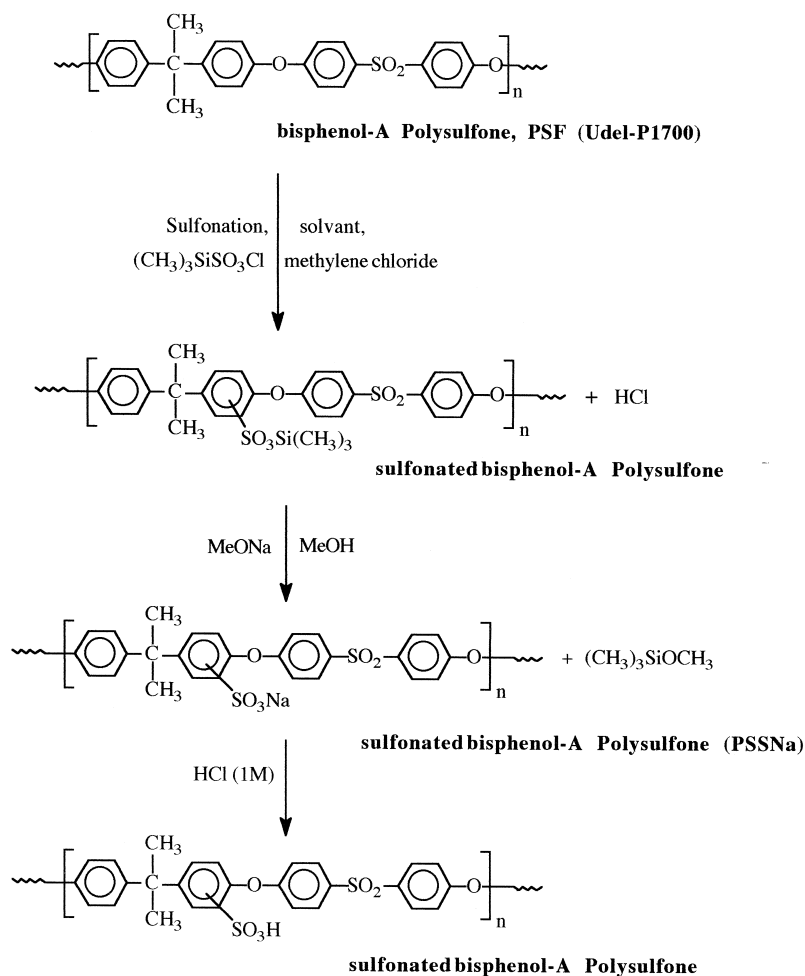


Fig. 1. PSF sulfonation with  $ClSO_3Si(CH_3)_3$ .

particular interlayer distances. The conductivity ( $2 \times 10^{-2}$  S cm<sup>-1</sup> at 100% RH and 20°C) is temperature dependent, with an activation energy of 0.18 eV [16].

## 2.2. Bisphenol-A polysulfone

The structural formula of bisphenol-A polysulfone (PSF), commercialised by AMOCO as UDEL-P1700 is given in Fig. 1. PSF is an amorphous, transparent, rigid polymer of high molecular mass, with a  $T_g = 190^\circ\text{C}$ . 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 quickly loses weight.

## 2.3. Sulfonated polysulfone (PSS)

Sulfonation of above mentioned chemical with  $[(\text{CH}_3)_3\text{SiSO}_3\text{Cl}]$  [17] leads, after treatment with sodium methoxide, to the sodium sulfonate form (PSSNa) which is dissolved in DMF and precipitated in the acidic form (PSS) with HCl (Fig. 1). PSS and PSSNa are only soluble in polar solvents as DMF, DMSO (dimethyl sulfoxide), NMP, some hydrophilic solvent and also in mixtures of DCE/IP (1–2 dichloroethane/isopropanol) or DX/MEK (dioxane/methylethyl ketone) [18]. Sulfonation leading to cationic exchange capacity from 1 to 2.5 H<sup>+</sup>/kg were carried out.

PSF and PSSNa were characterised by <sup>1</sup>H and <sup>13</sup>C NMR [18,19] and IR spectroscopy [20–24]. Sulfonation rate determination was performed using the sulphur content obtained by chemical analysis and the results of both spectroscopic techniques were analysed by the method proposed by Johnson et al. [20]. The detailed analysis of NMR and IR spectra is presented elsewhere [25]. Uncertainty on the cec values may be roughly estimated at  $\pm 8\%$ .

## 2.4. Membranes preparation

Filled membranes were prepared from a solution of PSS in a mixture of DiChloroEthane–IsoPropanol (DCE–IP 4:1) in which the selected weight of H3 was dispersed; the membranes were shaped by evaporating the suspension in a ring glued on a Teflon flat surface and drying for 4 h at room temperature.

# 3. Experimental

## 3.1. Physico-chemical characterisation

TGA measurements were performed on a NETZSCH STA 409 analyser, under helium flow for PSF, and argon

flow for PSS and PSSNa, from ambient temperature to 600°C at 10 K/min. FTIR spectra were recorded with a 710 FTIR from NICOLET, from thin PSS films deposited on ZnSe disks by transmission or from membranes of 100  $\mu\text{m}$  thickness, with six reflections 45° ATR equipment using a KRS5 crystal. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on AC200 and AC250 BRUCKER spectrometers from PSF or PSS solution, respectively, in CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub>. Chemical shifts were measured according to TMS. Dispersion of the inorganic particles in the membrane was studied by XRD and scanning electronic microscopy. XRD diagrams were performed with a Siemens D5000 diffractometer, using the Cu K<sub>α</sub> radiation on thin samples deposited onto a flat surface. SEM investigations were performed with a LEICA LEO 440 microscope. Samples were coated with a thin carbon layer obtained by vacuum evaporation then analysed on the surface and in bulk. Two types of analysis were in parallel performed: secondary electrons images analysis giving access to the membrane morphology, back scattered electrons analysis providing a chemical composition contrast on a 0.5  $\mu\text{m}$  thickness.

## 3.2. Conductivity measurements

The ionic conductivity of the protonic ionomers is water content dependent. The water content itself is controlled by the hydration equilibrium with the surrounding atmosphere. To obtain reproducibility, the conductivity measurements have to be performed using a suitable system having controlled temperature and relative humidity. A nitrogen flux goes through a temperature regulated water tank, where it becomes water vapour saturated. The hydrated nitrogen flux is driven through 110°C heated tubes to the conductivity measurements cell maintained in a temperature controlled oven. The conductivity cell is composed of two disks of 13 mm diameter fixed on the top of two empty alumina cylinders. These small cylinders are included in a larger alumina cylinder of 15 mm diameter allowing both electrodes to remain joined and pressed on each side of the sample by the pressure produced by a spring. The sample lies in between two flat circular electrodes: one is a 13 mm diameter porous graphite, the second a 13 mm diameter sintered glass surrounding a 1 mm diameter silver electrode. Increasing the  $e/S$  ratio (membrane thickness to silver electrode area, respectively) results in an improvement of the resistance value accuracy of the 100  $\mu\text{m}$  thin membrane. It is swept by the humid nitrogen flux driven in the cell by a metallic tube going through the oven inside the cell, which is enclosed in a tight metallic container. The relative humidity and temperature near the sample are checked with a digitalized thermometer–hygrometer (VAISALA HMI31). Conductivity measurements were performed by impedance spectroscopy using a 4192A Hewlett Packard Impedance meter moni-

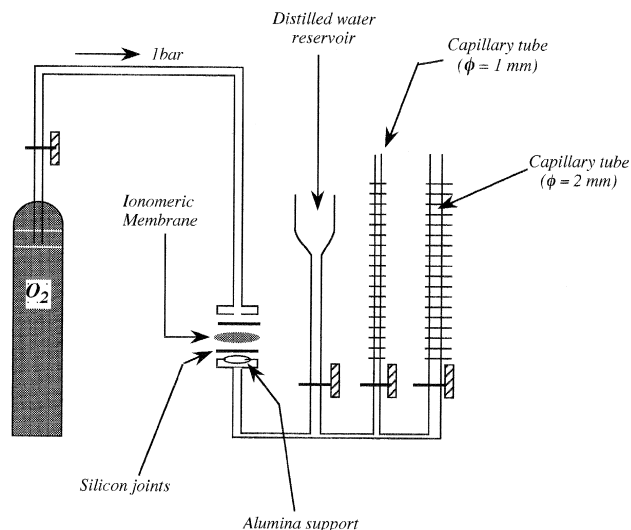


Fig. 2. Scheme of the gas permeability measurement cell.

tored by a 9340 HP computer driven by a self made program [26].

### 3.3. Gas permeability measurements

The gas permeability of the membrane is controlled by its swollen water. Indeed, the gas is dissolved in water and it diffuses with water throughout the membrane [27–29]. For this reason, the gas permeability measurements have to be carried out on fully hydrated membranes. The oxygen permeability measurements were performed with the apparatus described in Fig. 2. The gas permeability throughout a 2 cm diameter, 100  $\mu\text{m}$  thick membrane is controlled by a diffusion mechanism. A well hydrated membrane is put in between the two O-rings of the cell drawn in Fig. 2. A one bar oxygen pressure is applied on the top part of the membrane. The system is filled with water from the lower face of the membrane up to the capillary tube. The bottom part lies on a porous alumina pellet covered by water introduced from the reservoir tube, isolated from the cell during the measurement. The cell is connected to the capillary tube in which the water can move up when oxygen crosses the membrane. When the gas crosses over the membrane, it pushes the water column in the tube; its displacement is measured with respect to time and compared to that measured in the same conditions with a Nafion membrane.

### 3.4. Tests in fuel cell

Tests in fuel cell were performed using humidified  $\text{H}_2$  and  $\text{O}_2$  driven on the anode and on the cathode sides over 4 bars with a flow of 2.9 and 2.4 l/h, respectively. E-Tek electrodes covered with 0.35  $\text{mg cm}^{-2}$  of thin Platinum particles are impregnated with 0.85  $\text{mg cm}^{-2}$  of an alcoholic Nafion solution and heated at 120°C. Electrodes were

applied on each side of the membrane in between two graphite plates, ensuring the gas distribution throughout the electrodes. The assembly graphite plates electrode–membrane–electrode is pressed under controlled conditions. The running temperature is 80°C. The electrode planar area is 25  $\text{cm}^2$ . Current density, cell voltage, humidifier and cell temperatures and gas pressures are recorded vs. time.

## 4. Results

### 4.1. Thermal stability

Thermal stability of PSS, in argon, is observed up to 245°C where a first weight loss occurs, a second weight loss is observed at 450°C corresponding to the polymeric backbone degradation (Fig. 3). The former is assigned to sulfonic group elimination as already observed by Gupta and Scherer [30], Gupta et al. [31] and Samms et al. [32]; the latter was already identified by Rose [33].

### 4.2. Sulfonation rate and water swelling properties

#### 4.2.1. Sulfonation rate and water swelling properties of PSS

Weight increase due to swelling in water was measured after 72 h at 25°C and after a stay of 24 h at 80°C for PSS with cec from 0.76 to 1.4  $\text{meq g}^{-1}$ . Fig. 4 shows the evolution of the water swelling with the sulfonation rate at both temperatures. The number of water molecules associated to a sulfonic group ranges from 2.5 molecules for a 0.76  $\text{meq g}^{-1}$  cec to 12 molecules for a 1.4  $\text{meq g}^{-1}$  cec at 25°C, corresponding to a weight increase of 30%.

#### 4.2.2. Sulfonation rate and water swelling properties of PSS-H3: influence of the H3 content on the membrane swelling

Three PSS with the cec 1.07, 1.26 and 1.38  $\text{meq g}^{-1}$ , respectively, were loaded with increasing amount of H3.

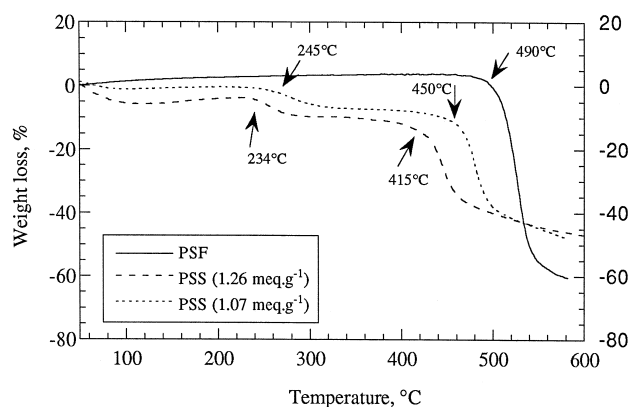


Fig. 3. TGA recordings under helium for PSF and under argon for PSS with a cec of 1.07 and 1.26  $\text{meq g}^{-1}$ , respectively.

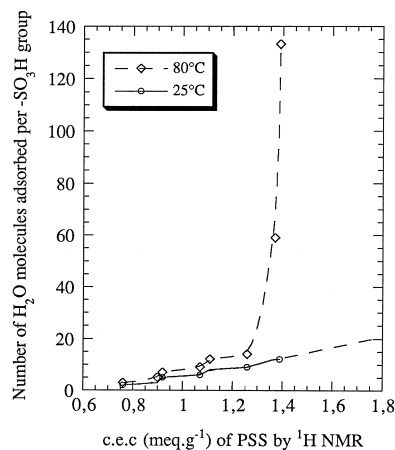


Fig. 4. Water content dependence vs. cec of PSS at 25°C and 80°C.

The water swelling or water content, expressed in weight% is plotted vs. H3% in Fig. 5 at 25 and 75°C, respectively. The influence of H3 amount, sulfonation rate and temperature are observed.

#### 4.3. Gas permeability

##### 4.3.1. Gas permeability of pristine materials (Nafion, PSS)

Fig. 6 compares the permeability of PSS (1.38 meq g<sup>-1</sup>) and Nafion 117 obtained from our measurements: they show the same trend. PSS with a lower exchange capacity has a lower gas permeability, as reported in Table 1. PSS with a 1.07 meq g<sup>-1</sup> cec exhibits a gas permeability 5 times lower than those of Nafion 117. For cec higher than 1.4 meq g<sup>-1</sup>, PSS swells too much, and becomes more permeable than Nafion 117 to oxygen.

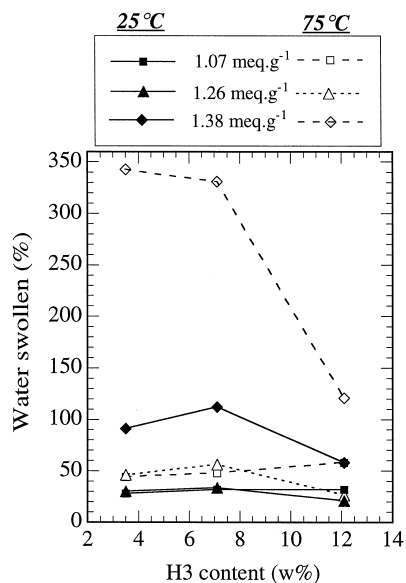


Fig. 5. Influence of H3 content on the swelling rate in water, at 25°C and 75°C, of PSS-H3 membranes.

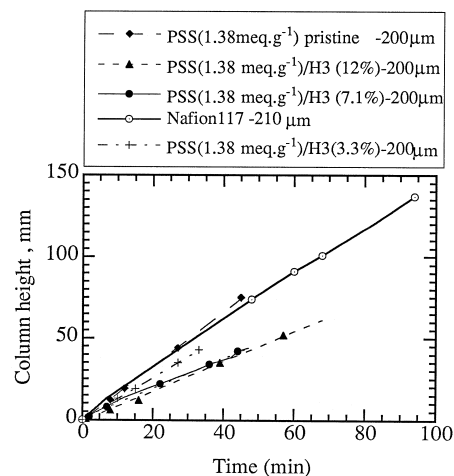


Fig. 6. Gas permeability comparison of (i) Nafion and (ii) unfilled and filled PSS with 3, 7.1 and 12% rates of H3.

##### 4.3.2. Influence of H3 content on the gas permeability of the membrane

Fig. 6 and Table 1 also compare the permeability of Nafion 117 and PSS (1.38 meq g<sup>-1</sup>) unloaded and loaded with 3.3, 7.1 and 12% in H3. The gas permeability of PSS-H3 decreases with increasing H3 content, this evolution was expected since it parallels the water swelling of membranes of the same composition. Table 1 provides a comparison between the variation of the oxygen permeability coefficient of pristine PSS (with increasing cec), of the filled PSS-H3 membranes (with increasing H3 content) and those of Nafion 117 as reference value.

#### 4.4. Conductivity measurements

##### 4.4.1. $\sigma(T, RH)$ of Nafion 117

Conductivity measurements under controlled Temperature and Relative Humidity ( $T, RH$ ) were first performed

Table 1  
Comparison of the oxygen permeability coefficients of Nafion 117, PSS and PSS-H3

Sample	Permeability coefficient $P * (\text{barrer}) = [(\text{cm}^3 (\text{STP}) \text{cm}) / (\text{s cm}^2 \text{cm Hg})]$
PSS (0.92 meq g <sup>-1</sup> )	$0.22 \times 10^{-10}$
PSS (0.92 meq g <sup>-1</sup> )/H3 (3.5%)	$0.27 \times 10^{-10}$
PSS (0.92 meq g <sup>-1</sup> )/H3 (7.1%)	$0.43 \times 10^{-10}$
PSS (1.07 meq g <sup>-1</sup> )	$0.42 \times 10^{-10}$
PSS (1.07 meq g <sup>-1</sup> )/H3 (3.5%)	$1.25 \times 10^{-10}$
PSS (1.07 meq g <sup>-1</sup> )/H3 (7.1%)	$2.52 \times 10^{-10}$
PSS (1.07 meq g <sup>-1</sup> )/H3 (12.1%)	$3.2 \times 10^{-10}$
PSS (1.38 meq g <sup>-1</sup> )	$19.4 \times 10^{-10}$
PSS (1.38 meq g <sup>-1</sup> )/H3 (3.5%)	$13.7 \times 10^{-10}$
PSS (1.38 meq g <sup>-1</sup> )/H3 (7.1%)	$10.4 \times 10^{-10}$
PSS (1.38 meq g <sup>-1</sup> )/H3 (12.1%)	$10.1 \times 10^{-10}$
Nafion® 117	$17 \times 10^{-10}$

\* Ref. [34].

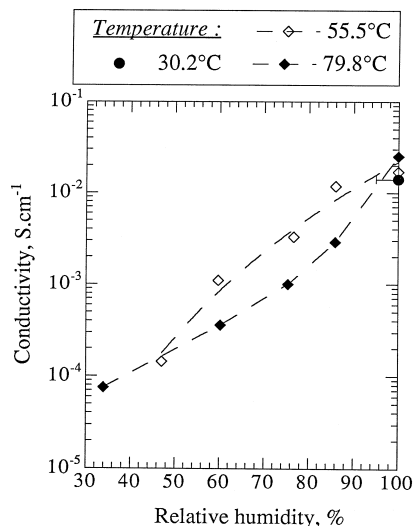


Fig. 7. Conductivity isotherms vs. RH at 30°C, 50°C and 80°C for a Nafion 117 membrane.

with Nafion 117. A Nafion 117 sample was washed in a 3 M boiling nitric acid solution for 2 h then rinsed for 24 h with distilled boiling water in order to eliminate any traces of free acid. Conductivity measurements were performed as a function of humidity (from 20 to 100% RH) and temperature (30°C, 50°C and 80.8°C) and the results are reported in Fig. 7. Conductivity values measured are  $6.7 \times 10^{-2}$  and  $9.5 \times 10^{-2}$  S cm<sup>-1</sup> at respectively 30 and 80.8°C for roughly 100% RH. The conductivity at 30°C and 100% RH is in good agreement with that measured by Zawodzinski et al. [35]. We did not observe a conductivity maxima as previously reported by Rieke and Vanderborgh [34], nevertheless we must emphasise a slight increase in conductivity with increasing temperature which is in the same order of magnitude as the accuracy of our measurements.

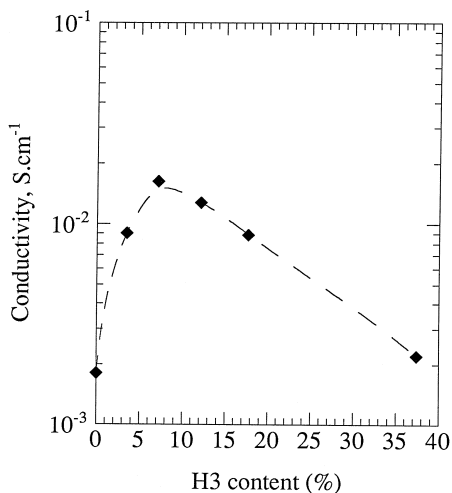


Fig. 8. Conductivity variation, at 100% RH and 35°C, of filled PSS vs. the rate of H3; cec of PSS: 1.07 meq g<sup>-1</sup>.

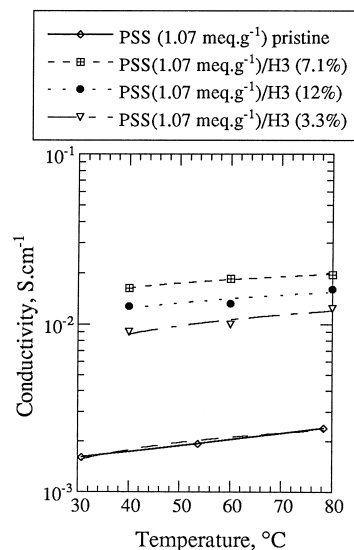


Fig. 9. Conductivity dependence with temperature for several rates of H3 dispersed in a PSS with a 1.07 meq g<sup>-1</sup> cec.

#### 4.4.2. $\sigma(T, RH)$ of PSS-H3

The conductivity vs. H3 content, in a H3 range from 0 to 20% weight, has been determined in filled PSS membranes, with a sulfonic rate corresponding to 1.07 meq g<sup>-1</sup> cec prepared from DCE/IP solution. Fig. 8 shows the conductivity vs. H3 content of the filled membranes at 35°C: conductivity values range from  $0.2 \times 10^{-2}$  S cm<sup>-1</sup> to  $1.8 \times 10^{-2}$  S cm<sup>-1</sup> for 6 to 8% content in H3. Fig. 9 provides, at 96% RH, the conductivity dependence with temperature of membranes filled with different H3 rates.

## 5. Test in fuel cell

A PSS of 1.07 meq g<sup>-1</sup> cec dissolved in DCE/IP and loaded with 7.1% w in H3 was put in the fuel cell under

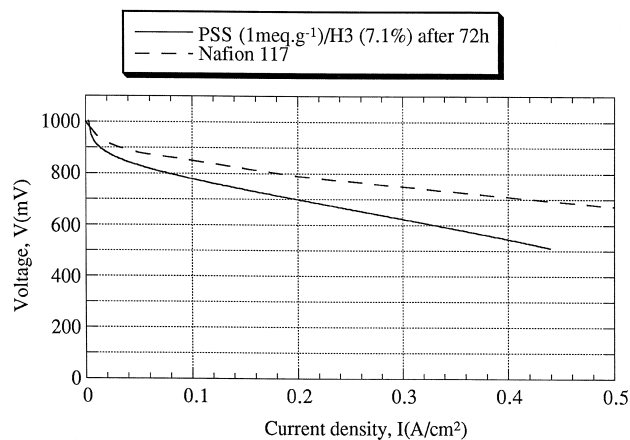


Fig. 10. Comparison between the  $V(I)$  curves of the fuel cell operating with a Nafion 117 membrane (dotted line) and a PSS (1.07 meq g<sup>-1</sup>) membrane filled with 7.1% H3 (continuous line). Cell temperature: 80°C under 4 bars of H<sub>2</sub> and O<sub>2</sub>, with a humidified gas flow respectively at 2.9 and 2.4 l/h.

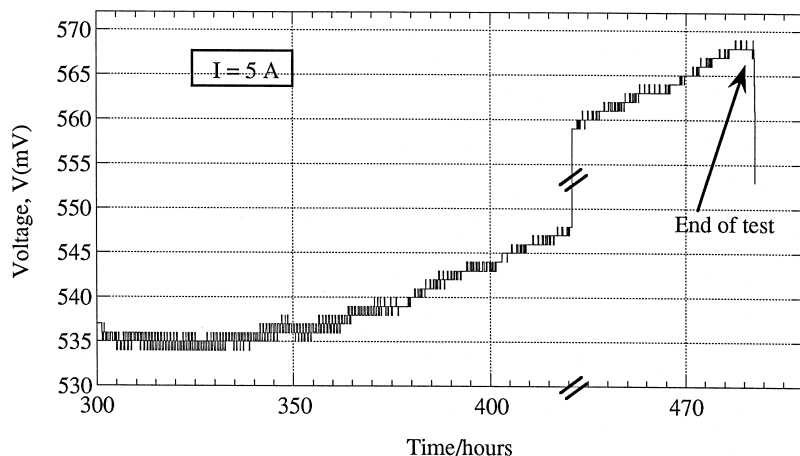


Fig. 11. Variation of the fuel cell potential  $V$  with time during the last part of the 500-h test:  $80^{\circ}\text{C}$  under 4 bars of gas pressure ( $\text{H}_2\text{-O}_2$ ).

the conditions of gas and flow pressure previously defined. The cell temperature was progressively increased to  $80^{\circ}\text{C}$ . The current was progressively increased up to 8 A ( $400\text{ mA/cm}^2$ ) and kept for 12 h in order to well humidify the membrane with the water generated by the electrochemical reaction. Then a 5 A ( $250\text{ mA/cm}^2$ ) DC is imposed again. After 3 days, the  $I$ - $V$  characterisation was performed. Fig. 10 provides a comparison between the  $I(V)$  characteristics of PSS-H3 and Nafion 117 membranes, operating in the same experimental conditions.

Fig. 11 presents the voltage evolution during the second part of a 500 h test, performed with a PSS of  $1\text{ meq g}^{-1}$  cec and 7.1% in H3. One must emphasise a continuous voltage increase with time, probably due to the progressive hydration of the badly dispersed H3 in the membrane, prepared from a DCE/IP solution. Short circuit ended the test. After membrane removal, no chemical degradation is observed: the visual aspect of the membrane is unchanged, IR spectra recorded by ATR are similar to those of the starting material. After resolubilisation, any cec decrease is observed: IR spectra do not exhibit any differences from the starting membrane material.

## 6. Discussion

From the analysis of the results gained with pristine PSS membranes and filled membranes, it appears that the way to prepare this type of membrane is of great importance: it controls their main properties. First of all, one must be careful in using strong acids as chlorosulfonic acid as well as  $\text{SO}_3$  sulfonating agent. Indeed they damage the polymer by hydrolysing the polymeric skeleton inducing the detriment of mechanical properties; this does not occur with a milder sulfonation agent as  $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$  which preserves the chain length of the starting PSF.

The second important step deals with drying conditions which must be always the same to gain reproducible samples. The membrane must retain just enough quantity

of solvent to prevent the polymer chains collapsing and to maintain place to water.

The role of H3 appears very advantageous comparing water swelling, gas permeability and conductivity properties of Nafion, PSS and PSS-H3 membranes. In fact, for PSS having a cec higher than  $1.3\text{ meq g}^{-1}$  as well as for Nafion, water swelling, gas permeation and protonic conductivity are controlled by the hydrophilic properties of sulfonic groups. Filled with H3 this membrane has higher conductivity, lower water swelling and lower gas permeability. These differences are probably induced by the interaction between H3 and the polymeric backbone, which controls water adsorption. Structural and spectroscopic investigations at different time scales are at present scheduled. They should be useful to elucidate the state of adsorbed water in PSS-H3 and the influence of H3 content on the water and proton dynamics, responsible for the

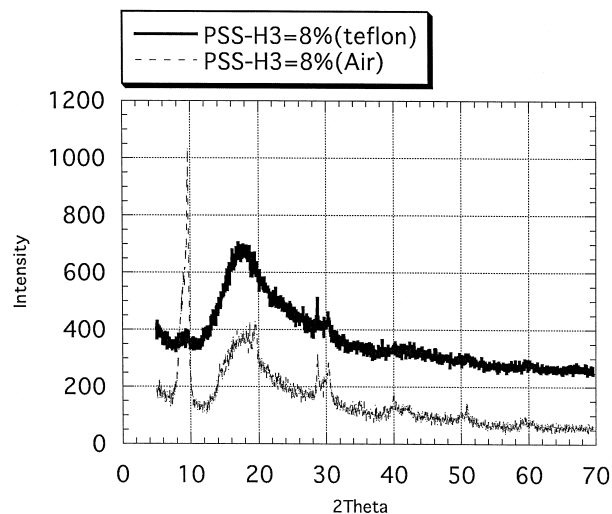


Fig. 12. XRD patterns ( $\text{Cu K}\alpha$ ) of PSS-H3 samples prepared from a DCE/IP solution. In continuous line: lower face in contact with TFE; in dotted line: upper face in contact with air. The diffraction lines of H3 are perfectly resolved, especially the 001.

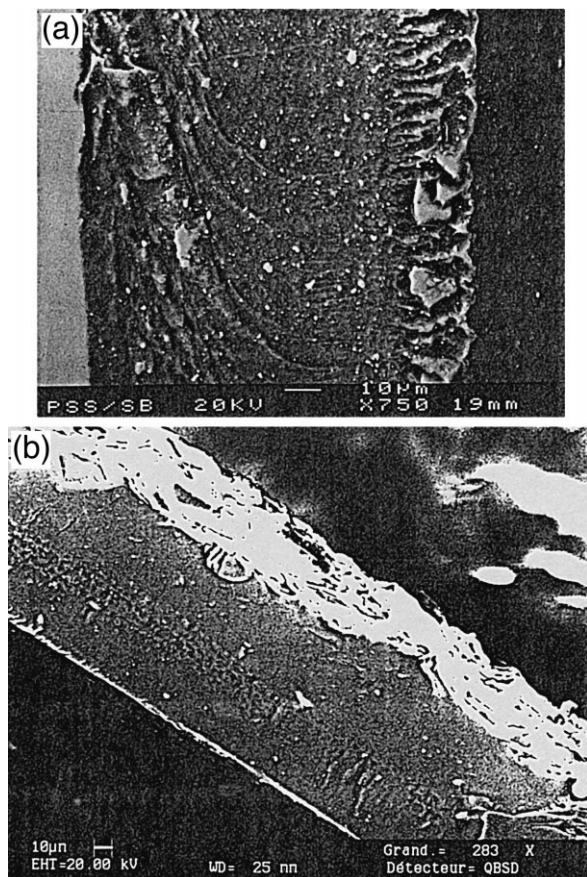


Fig. 13. SEM photographs of PSS-H3 membranes obtained (a) from hydrophilic solvent solution, (b) from DCE/IP solution.

protonic conductivity performances observed on this material.

The preparation method with DCE/IP does not provide a homogenous dispersion of H3 in all the membrane volume: we assume that the solvent evaporation drains H3 particles from the bulk on the upper face of the membrane leading to a dissymmetric dispersion, as shown on the XRD diagrams given in Fig. 12. Moreover, in a poor hydrophilic solvent such as DCE/IP, H3 particles, of initial size lower than  $10 \mu\text{m}$ , aggregate into larger particles. Attempts recently made with a hydrophilic solvent, to insure a homogenous dispersion of the hydrophilic and hydrated filler H3 in the PSS solution were successful. The comparison of SEM pictures given in Fig. 13 shows the regular dispersion of H3 in the film, obtained by casting a dispersion of H3 in the hydrophilic solvent solution of PSS, which leads to homogenous, transparent and plastified membranes.

Chemical and spectroscopic analyses of fuel cell running membranes have not given evidence of a chemical degradation of the filled PSS membrane, which lifetime in fuel cell has reached 500 h. We assume therefore that the short-circuit which ended the test was due to a mechanical failure of the membrane, related to the heterogeneous and dissymmetric dispersion of H3. Thus gas bubbles may be

trapped between H3 particles during the preparation, and explode under the influence of heat and water flow in the running fuel cell.

## 7. Conclusion

Ionomeric filled membranes have been prepared by dispersing phosphoantimonic acid particles in an industrial thermoplastic, i.e., a polyaryl sulfone carefully sulfonated. These ionomers are soluble in easily handling solvents such as DCE/IP or hydrophilic solvents, these latter enabling a homogenous dispersion of the inorganic particles in the polymeric matrix. When the pristine ionomer has a cec close to  $1.4 \text{ meq g}^{-1}$  it presents the same impermeability to oxygen as Nafion. The addition of filler intensifies this property, decreases the water swelling while increasing the protonic conductivity as compared to unfilled membranes.

Despite a heterogeneous dispersion of the inorganic phase in the ionomeric matrix, validation of a filled membrane of  $1.07 \text{ meq g}^{-1}$  cec for 500 h in a fuel cell at  $80^\circ\text{C}$  under 4 bars of  $\text{H}_2$  and  $\text{O}_2$ , with 80% of Nafion performances was gained without cec degradation. This first test leaves us hopeful of very soon increasing the membrane lifetime, taking account of the improvements made in the membrane preparation. Thanks to the use of an adapted solvent and thanks to improvements performed in the H3 synthesis leading to a submicronic grain size distribution, the homogenous dispersion of H3 in PSS is now controlled. Improvements are also made on the water swelling control of the filled membrane, which will be presented in forthcoming paper [25].

## Acknowledgements

This work was funded by the CNRS Department ECOTECH for the program VPE-PAC. The authors are grateful to T. Alleau, B. Bador, P. Baurens and G. Terrier for their efficient help during the tests of filled membranes in fuel cell.

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