

# Hybrid ion-exchange membranes for fuel cells and separation processes

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## Abstract

This work reports the preparation and characterization of hybrid membranes cast from dispersions of inorganic fillers in sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene solutions. Silica gel, SBA-15 and sepiolite, all of them functionalized with phenylsulfonic acid groups, were used as fillers. For comparative purposes, the performance of composite membranes cast from dispersions of functionalized inorganic fillers in Nafion<sup>®</sup> solutions was investigated. Inspection of the texture of the membranes by using SEM techniques shows that the fillers are better dispersed in sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene than in Nafion<sup>®</sup>. The value of the water uptake for the membranes prepared from the former polyelectrolyte is in most cases at least three times that measured for hybrid Nafion<sup>®</sup> membranes. The conductivity of the membranes was measured at 80 °C by impedance spectroscopy obtaining values of 3.44, 6.90 and 3.54 S m<sup>-1</sup> for the hybrid membranes based on the triblock copolymer containing functionalized silica gel, SBA-15 and sepiolite fillers, respectively. These results compare very favourably with those obtained at 80 °C for Nafion<sup>®</sup> hybrid membranes containing silica gel, SBA-15 and sepiolite, all of them functionalized with phenylsulfonic acid groups, whose conductivities are, 2.84, 6.75 and 3.31 S m<sup>-1</sup>, respectively. Resistance measurements carried out under controlled humidity conditions show that the conductivity of sulfonated triblock copolymer membranes containing functionalized SBA-15 filler undergoes a rather sharp increase when they are conditioned under an atmosphere of 75%, or larger, relative humidity.  
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## 1. Introduction

The characterization of proton transport in ion-exchange membranes using impedance spectroscopy is a flourishing field of research which complements other well-documented studies reported in the literature related to concentration potentials, determination of counterion and coion transport numbers, diffusion coefficients, electro-osmotic permeability, etc. [1]. A better understanding of the relationship between structure and both conductivity and permselectivity is paramount to optimize the application of ion-exchange membranes as electrolytes for both low temperature fuel cells and ionic separation processes.

The relatively low protonic conductivity under low humidity conditions and the relatively high permeability to methanol are the main drawbacks that commercial cation exchange mem-

branes present in their use as polyelectrolytes in fuel cells technology. Moreover, good performance fuel cells require that membranes combine good mechanical properties and thermal stability, at moderately high temperatures. However, even high thermal stability ion-exchange membranes may undergo oxidative processes that preclude their use in the unfriendly working conditions of fuel cells. Several strategies, mainly focused in reducing the methanol uptake while preserving the water content and the high proton conductivity at working temperatures of about 150 °C, were used in the development of organic polyelectrolytes in recent years [2–5]. The strategies involve reinforcement of commercial ion-exchange membranes, such as Nafion<sup>®</sup>, and synthesis of new membranes. The incorporation of suitable inorganic fillers into commercial cation exchange membranes seems to be a promising way of obtaining solid electrolytes for medium temperature fuel cells [2–4,6–9]. Fillers, such as silica, heteropolyacids, laminar metallic phosphates particularly layered zirconium phosphates [10–12] and phosphonates (phosphates functionalized by acid organic substituent [13]) improve the high temperature conductivity of Nafion<sup>®</sup> membranes.

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Aside high permeability to methanol, high cost is one of the major disadvantages of membranes based on perfluorocarbon ionomers. Hence, efforts are being made to develop cation-exchange membranes based on cheap materials. Block copolymers made up of hard and soft components are obvious candidates [14–19]. In this context, the preparation of cation-exchange membranes from poly(styrene-block-ethylene-co-propylene) [20] and hydrogenated poly(butadiene–styrene) copolymers [21,22] has been reported. Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (PSEBS) is a triblock copolymer made up of a thermoplastic phase (polystyrene) dispersed in an elastomeric matrix (polyethylene/butylene). Polyelectrolytes can be obtained by direct and selective sulfonation of the phenyl groups of the polystyrene component of the copolymer [23,24]. Recently Sangeetha [25] reported a thorough study on the conductivity and thermal properties of sulfonated PSEBS (SPSEBS) showing that fully hydrated membranes exhibit an excellent conductivity, of the order of  $10 \text{ S m}^{-1}$ . Moreover the thermal stability of SPSEBS membranes seems to improve by impregnating them with tetraethyl orthosilicate [26].

Pursuing in this line of research, this work reports the preparation of inorganic–organic hybrid membranes by incorporating inorganic materials containing phenylsulfonic acid groups into SPSEBS membranes. Attention is paid to the study of the effect of the fillers on the conductivity and mechanical and thermal stability of the membranes. For comparative purposes, the performance of Nafion<sup>®</sup>/fillers composite membranes is also investigated.

In this study, the membranes were characterized by measuring water uptake, ion-exchange capacity and conductivity. The homogeneity of the dispersion of the fillers in the membranes was analysed by SEM techniques, and the dynamic mechanical behaviour of the composites was studied at several frequencies in a wide temperature window. Comparison of the conductivities of the SPSEBS membranes with those of Nafion<sup>®</sup> leads to conclude that the former membranes exhibit interesting transport properties as solid electrolytes for fuel cells, as well as for separation processes based on membranes technology.

## 2. Experimental

### 2.1. Materials

Tetraethoxy silane (TEOS) (ABCR), phenyl-tri-ethoxy-silane (ABCR), triblock copolymer Pluronic 123 (Aldrich), silica gel 0.04–0.063 mm size (Merck), sepiolite Pansil-2 (Tolsa), toluene (Merck), hydrochloric acid (Merck), isopropanol (Scharlau), fuming sulfuric acid 65%  $\text{SO}_3$  (Merck) were used as received.

Calprene H6120, a linear triblock copolymer of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (styrene 32%), was a gift from RepsolYPF (Spain). A 5% solution of Nafion 117 in low molecular weight alcohol was supplied by Fluka.

### 2.2. Functionalization of inorganic materials

Phenyl residues were anchored to inorganic fillers by reaction of their hydroxyl groups with phenyl-tri-ethoxy-silane. In the case of silica gel, 5 g of this product were dispersed in 150 ml of toluene. Then 2.4 g of phenyl-tri-ethoxy-silane ( $2 \text{ mmol g}^{-1}$  silica) and 250  $\mu\text{l}$  of distilled water were added to the dispersion, and the mixture was stirred at  $100^\circ\text{C}$ , under reflux, for 24 h. The solid was filtered and successively washed with petroleum ether and ethylic ether, and finally dried in vacuum.

Anchorage of phenyl groups to SBA-15 was carried out by dissolving 4 g of Pluronic123 surfactant in 160 ml of an aqueous solution of hydrochloric acid (pH 1.5). Then the solution was added dropwise to a mixture of 8.41 g of TEOS and 1.06 g of phenyl-tri-ethoxy-silane, under vigorous stirring, until a transparent solution appeared. The solution obtained was transferred to a Teflon bottle, and 76 mg of NaF and 1 ml of distilled water were added to the solution, at  $70^\circ\text{C}$ , under stirring. The polycondensation reaction started immediately, and it was allowed to proceed for 2 days, under heating and stirring. The solid obtained was filtered and washed. The template was removed by Soxhlet extraction with ethanol during 24 h [27].

The first step of the functionalization of sepiolite was carried out by successively adding 2.5 mmol of phenyl-tri-ethoxy-silane and 1 g of sepiolite to 10 ml of a solution (1:1, v/v) of HCl in isopropanol, under stirring. After 15 h of reaction at  $65^\circ\text{C}$ , the solid was filtered and washed with methanol, methanol/water, distilled water, and dried at  $90^\circ\text{C}$  [28].

The phenyl groups of the moieties anchored to the fillers were finally sulfonated with fuming sulfuric acid as illustrated in the reaction scheme shown in Fig. 1.

### 2.3. Sulfonation of PSEBS

PSEBS was sulfonated with acetyl sulfate prepared *in situ* by reaction of acetic anhydride with sulfuric acid in dichloroethane (DCE), at  $0^\circ\text{C}$  [29]. Acetyl sulfate was added dropwise to a 10% solution of the polymer in DCE, under nitrogen and vigorous stirring, keeping the temperature of the reaction at  $80^\circ\text{C}$ . The sulfonation reaction was stopped after 4 h by adding isopropanol to the reaction medium. The polyelectrolyte obtained (SPSEBS) was recovered by steam stripping using boiling water for the evaporation of DCE. Then the polyelectrolyte was filtered, washed with distilled water and dried in vacuum, at room

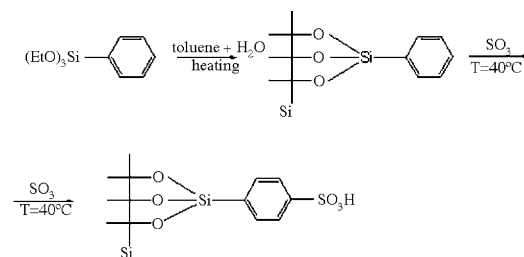


Fig. 1. Scheme showing the reaction of the  $-\text{OH}$  groups of both silica gel and SBA-15 with phenyl-triethyl-siloxane and further sulfonation of the phenyl groups.

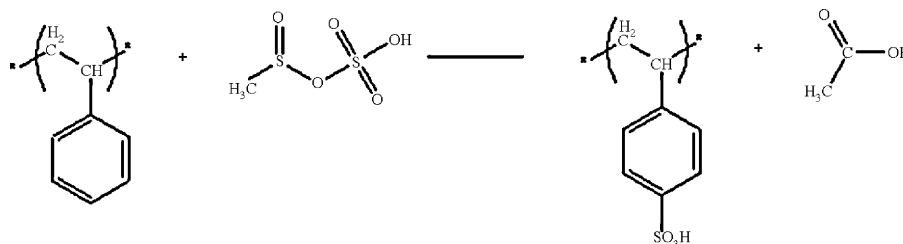


Fig. 2. Scheme of the sulfonation of PSEBS.

temperature, for 48 h. The scheme of the sulfonation reaction of PSEBS is illustrated in Fig. 2.

#### 2.4. Preparation of ion-exchange membranes

Hybrid membranes based on Nafion<sup>®</sup> and SPSEBS, containing 10% of solid fillers, were prepared by two procedures. In the first method, the required amount of sulfonated filler was added to a commercial Nafion<sup>®</sup> solution under stirring. After 6 h of ultrasonic dispersion, the apparently homogeneous dispersion was cast on a smooth Petri dish, and solvent evaporation proceeded at room temperature. Finally the composite Nafion<sup>®</sup> membrane was dried under vacuum. In the second method, evaporation of the solvent from the apparently homogeneous dispersion was carried out at 70 °C for 2 h, and then at room temperature, until total solvent elimination [30,31].

Hybrid PSEBSS membranes were prepared by dissolving the desired amount of the sulfonated copolymer in chloroform/ethanol (80/20), at room temperature. A viscous solution containing 5% (w/w) of PSEBSS was obtained after approximately 2 h. Then the required amount of sulfonated filler was added to the polyelectrolyte solution under stirring. After 6 h of ultrasonic dispersion, the apparently homogeneous composite mixture was cast on a smooth Petri dish, at 70 °C.

The membranes were transformed to the acid form by immersion in a 1 M sulfuric acid solution. Then they were washed several times with distilled water to remove the excess of acid and stored in deionised water.

#### 2.5. Chemical and thermal characterization of fillers and ion-exchange membranes

The amount of sulfonic acid groups in the fillers was determined by both elemental analysis and titration with a 0.01 M hydroxide sodium solution. The results obtained are given in Table 1. The thermogravimetric analysis of the fillers was carried out at a heating rate of 10 °C min<sup>-1</sup> with a Metler TGA/SDTA 851 apparatus, under an oxygen atmosphere. The thermal sta-

bility of the membranes was measured with a TA TGA Q500 thermogravimetric apparatus under a nitrogen atmosphere.

#### 2.6. Mechanical characterization of the membranes

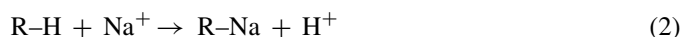
The mechanical properties of the composites were measured with a dynamic mechanical analyser (DMA 2980, TA Instruments), at a heating rate of 2 K min<sup>-1</sup>. The complex relaxation modulus of the membranes was obtained in dry nitrogen, from -150 °C to 200 °C, at the frequency of 0.3, 1, 3, 10 and 30 Hz. The stress and elongation ratio at the breaking point, together with the Young's modulus of the membranes, were determined at 23 °C (50% RH) with a mechanical analyser Instron Mod. 4301, at a crosshead speed of 10 mm min<sup>-1</sup>.

#### 2.7. Water uptake, ion-exchange capacity and conductivity of the membranes

Weighed dry membranes were immersed in distilled deionised water overnight. The membranes were removed from water, gently blotted between filter paper to remove surface water and weighed. This operation was repeated three times. Water uptake was obtained by means of the expression:

$$\text{water uptake (\%)} = \frac{\text{weight of wet membrane} - \text{weight of dry membrane}}{\text{weight of dry membrane}} \times 100 \quad (1)$$

The ion-exchange capacity (IEC) was obtained by immersing the membranes in the acid form in 1 M NaCl solution. The hydrochloric acid liberated in the interchange reaction:



was titrated with a 0.01 M NaOH solution.

The conductivity of the membranes was obtained by ac measurements performed in the frequency range  $10^{-2} < f < 10^7$  Hz, using a voltage amplitude of 0.1 V. The membranes previously equilibrated with water were placed between two gold electrodes coupled to a Novocontrol Broadband Dielectric Spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface. The temperature was controlled by nitrogen jet (QUATRO from Novocontrol) with a temperature error of  $\approx 0.1$  K during every single sweep in frequency. Membranes were sandwiched between the electrodes in a BDS 1308 liquid sample filled with distilled water to simulate a 100% RH atmosphere [32].

Table 1  
Sulfur content of fillers obtained by elemental analysis and acid groups titration

Sample	S (elemental analysis) (mmol g <sup>-1</sup> )	S (neutralization) (mmol g <sup>-1</sup> )
Silica	0.063	0.072
SBA-15-f	0.33	0.34
Sepiolite	0.26	0.23

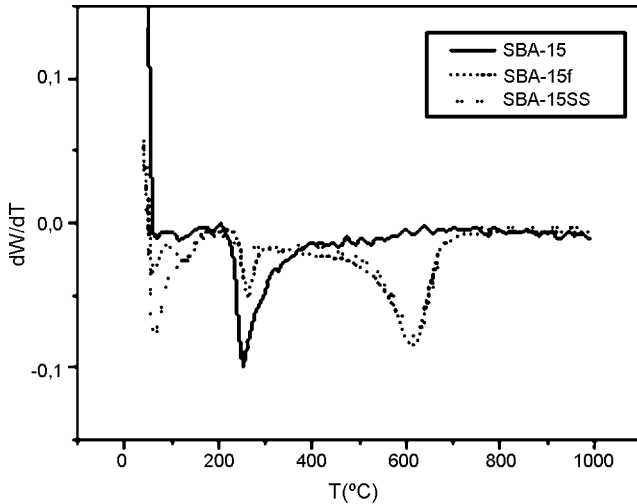


Fig. 3. Differential thermogravimetric diagram showing the loss of water as a function of temperature for the fillers indicated in the inset.

The conductivity of ion-exchange membranes was also measured by dc with a four-point probe arrangement, where the current  $I$  between two adjacent points, generated by the voltage drop  $\Delta V$  across the other two points, was measured. Prior to the experiments, the membranes were equilibrated under the RH atmosphere of interest, and that atmosphere was kept during the electrical measurements.

### 3. Results and discussion

Figs. 3 and 4 depict the thermal stability of the fillers. The pertinent thermograms for SBA-15 and sepiolite exhibit a loss of weight in the vicinity of 100 °C attributed to the evaporation of the absorbed water. The solids with channel structure, SBA-15 and sepiolite, also lose mass in the vicinity of 200 °C caused by desorption of the water adsorbed in the channels. At temperatures above 600 °C, loss of the organic mass takes place. Finally, loss of mass is observed at 800 °C in raw sepiolite as a result of

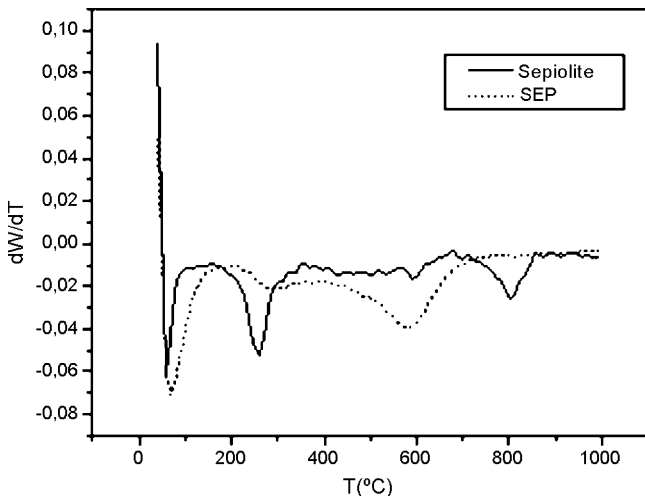


Fig. 4. Differential thermogravimetric diagram showing the loss of water as a function of temperature for the fillers indicated in the inset.

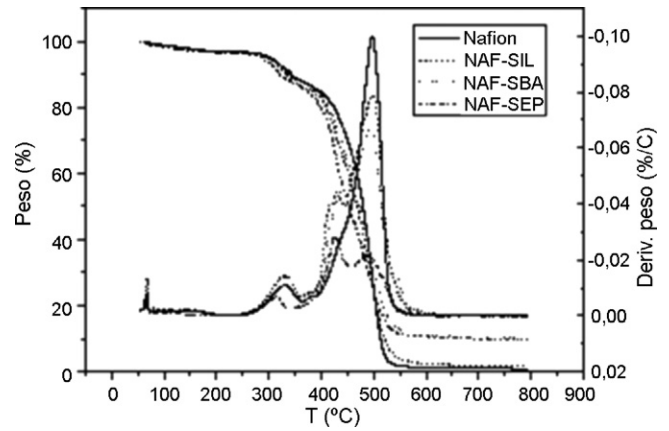


Fig. 5. TGA diagrams for Nafion, NAF-SIL, NAF-SBA and NAF-SEP membranes.

the dehydroxylation of the filler [33], loss not observed in the functionalized sepiolite because the *o*-silyl phenyl groups have already been degraded at lower temperatures.

The thermal stability of the membranes is described in Figs. 5 and 6 for Nafion® and SPEBS membranes, respectively. The thermograms for Nafion® membranes exhibit a loss of weight in the vicinity of 100 °C attributed to the evaporation of the absorbed water. Desulfonation around 280 °C takes place for the hybrid and pristine membranes, followed by polymer degradation that occurs at lower temperature in the composite membranes. Accordingly, inorganic fillers reduce the thermal stability of Nafion® membranes, in agreement with results reported in the literature [34]. Therefore weight of loss in these membranes involves more than a single stage due to complex mechanisms that imply a certain number of series–parallel degradation reactions [35–37].

The thermograms represented in Fig. 6 show that the loss of weight for the PSEBS copolymer is negligible below 400 °C. However, above this temperature, PSEBS undergoes a massive degradation as temperature increases. The loss of weight observed in the thermograms of the pristine and hybrid SPSEBS membranes between 50 and 150 °C presumably is associated

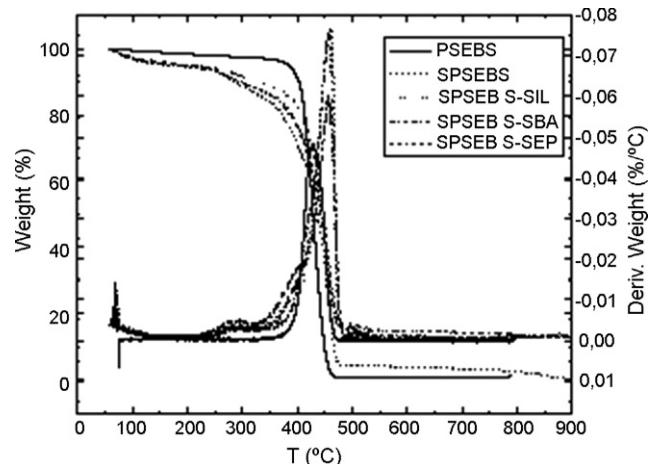


Fig. 6. TGA diagrams for SPSEBS, SPSEBS-SIL, SPSEBS-F-SBA and SPSEBS-F-SEP membranes.



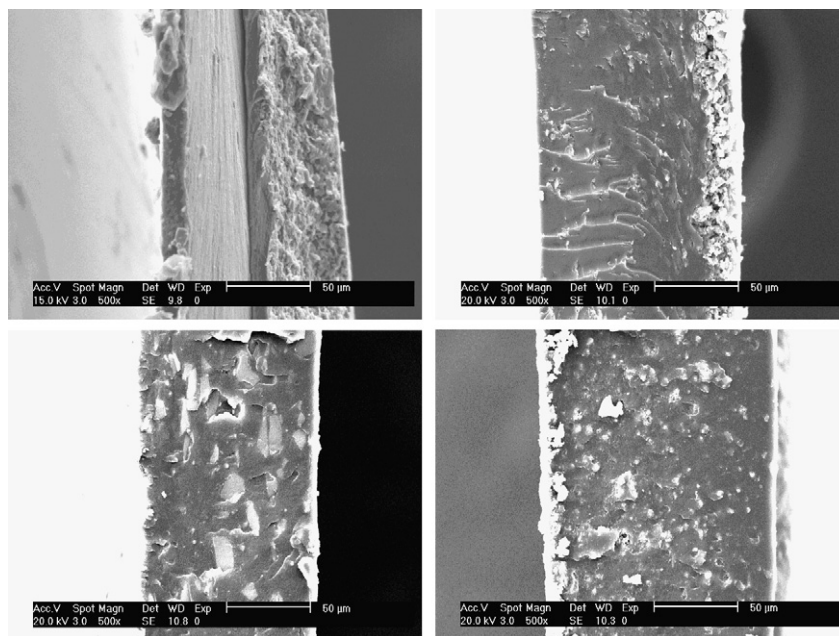


Fig. 7. (Top) Micrographs of the cross-section of Nafion hybrid membranes cast from sepiolite dispersions in Nafion 117 solutions at room temperature (left) and 70 °C (right). (Bottom) The same for SPSEBS hybrid membranes cast at 70 °C from silica dispersions (left) and SBA15 (right) in SPSEBS chloroform/ethanol solutions.

with the evaporation of water absorbed in the sulfonated polymer matrix and the fillers. The loss of weight between 250 and 370 °C corresponds to the degradation of the sulfonic acid groups in the matrix. Above 370 °C, the membranes undergo a sharp degradation. An inspection of the thermograms suggests that the fillers confer thermal stability to the hybrid SPSEBS membranes.

The distribution of fillers in the membranes was analysed using SEM techniques. The composite membranes were freeze-fractured by immersion into liquid nitrogen first, and then cracked. Illustrative micrographs showing the cross-section of the membranes are shown in Fig. 7. The micrographs at the top row of this figure correspond to Nafion<sup>®</sup>-sepiolite membranes cast, respectively, at room temperature (top left) and at 70 °C (top right). As a result of the relatively slow evaporation of solvent at room temperature, the top-left micrograph exhibits two phases, one rich in fillers and other in polymer, that reveal severe fillers sedimentation processes during solvent evaporation. At 70 °C, however, the relatively fast evaporation of the solvent rapidly increases the viscosity of the solution, hindering fillers sedimentation, and a relatively homogeneous membrane is obtained. Only the membranes cast at 70 °C were used in further experiments.

Both SPSEBS-Silica and SPSEBS-SBA 15 membranes were also cast at 70 °C, and the pertinent cross-sectional micrographs are shown at the bottom row of Fig. 7, left and right, respectively. The fillers are more homogeneously distributed in the hybrid SPSEBS membranes than in their Nafion counterparts presumably as a consequence of the higher viscosity of the evaporating solutions in the former case.

Owing to the incompatibility of the flexible and rigid components of the triblock PSEBS copolymer, the blocks of polystyrene form hard domains dispersed in the elastomeric region. As a result, raw PSEBS must exhibit two glass tran-

sition temperatures associated, respectively, with the soft and hard domains. The mechanical isochrone shown in Fig. 8 for dry PSEBS obeys this picture. The isochrone exhibits an ostensible absorption in the low temperature region and a broad relaxation at higher temperature. The low temperature absorption, centred in the vicinity of -56 °C, is associated with the glass transition temperature of the soft elastomeric block of PSEBS whilst the high temperature relaxation corresponds to the glass-rubber transition temperature of the hard domains (polystyrene domains). Since a fair dispersion of the functionalized fillers in the SPSEBS matrix is accomplished using ultrasonic

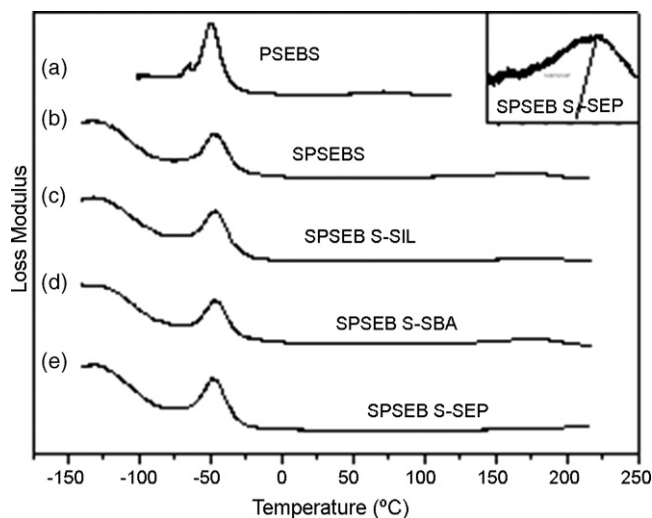


Fig. 8. DMTA results for the PSEBS membranes at 1 Hz. Isochrones (a) and (b) correspond to PSEBS and SPSEBS homogeneous membranes. Curves (c), (d) and (e) represent the temperature dependence of the loss modulus for SPSEBS-SIL, SPSEBS-SBA and SPSEBS-SEP hybrid membranes, respectively

Table 2  
Glass transition temperatures associated with the soft (PEB) and hard domains (PS) of homogeneous and hybrid PSEBS membranes obtained by DMTA

Sample	$T_g$ (°C)	
	PEB	PS
PSEBS	−54.7	70.7
SPSEBS	−48.1	168.7
SPSEBS-SIL	−47.5	179.7
SPSEBS-SBA	−47.0	178.2
SPSEBS-SEP	−48.8	236.2

dispersion techniques, one would expect that micro-Brownian motions in the soft domains of SPSEBS membranes would be restricted by the filler particles unless the interactions fillers–soft domains were negligible. The fact that the location of the low temperature absorption associated with the glass transition temperature of the soft domains is similar for PSEBS and SPSEBS composites suggests that segmental motions of the polymer chains in the soft domains are not affected by the fillers.

The results of Table 2 show that the glass transition temperature of the hard domains of PSEBS is centred at 71 °C. The location of the peak shifts to 169 °C for SPSEBS as a result of both the restriction of conformational transitions about the skeletal bonds caused by the bulky phenylsulfonic side groups and the increase of intermolecular interactions between ionic groups.

Whenever sedimentation occurs, particle aggregations takes place that negatively affect the mechanical properties of the membranes [25,38]. However, the rather good mechanical properties of the hybrid membranes suggest a fair good dis-

persion of the fillers in the composites. The results presented in Table 3 show that sepiolite containing phenylsulfonic acid groups dramatically increases the Young’s modulus of the Nafion® membranes. The increase of the Young’s modulus is more moderate for SPSEBS membranes. Although the fillers do not significantly change the stress at the breaking point, they augment the deformation reached by the SPEBS membranes at the rupture point.

The conductivity of acidic membranes involves dissociation of protons from  $-\text{SO}_3\text{H}$  groups and their transport across water and  $-\text{SO}_3^-$  ionic fixed groups. Then the conductivity depends on the water uptake and the ion-exchange capacity. Values of the water uptake and the ion-exchange capacity of the membranes are given in the second and third columns of Table 4, respectively. In general, the water uptake of Nafion membranes is 1/3 to 1/4 that of SPSEBS membranes. Although the ion-exchange capacity of the latter membranes is somewhat larger than that of Nafion, the number of moles of water per fixed ionic group in SPSEBS based membranes is roughly three times the value of this parameter for both Nafion® and hybrid Nafion® membranes.

The conductivity of the membranes was obtained from impedance measurements using the equivalent circuit of Fig. 9 made up of an inductance  $j\omega L$  arising from the inductivity of the connectors in series with the protonic resistance  $R_0$  of the membrane. The resulting impedance is also in series with a circuit made up of an element  $R_1$ , which represents the charge transfer resistance at the membrane/electrode interface, in parallel with a constant phase element representing the membrane/electrode double layers connected in series. By assuming that the phase element admittance is  $Y^* = Y_0(j\omega\tau)^n$ ,  $0 < n \leq 1$ , the real and imaginary components of the complex impedance of the circuit are

Table 3  
Ultimate properties for homogeneous and inorganic–organic hybrid membranes based on SPSEBS and Nafion materials

Sample	Stress at the breaking point (MPa)	Maximum deformation (%)	Young modulus (MPa)
NAF <sup>35</sup>	–	–	170
NAF-SIL	12.8	43.5	268.4
NAF-SBA	–	–	–
NAF-SEP	23.7	25.1	604.6
SPSEBS	11.7	295.2	87.1
SPSEBS-SIL	13.0	468.1	75.8
SPSEBS-SBA	–	–	–
SPSEBS-SEP	13.4	449.8	148.1

Table 4  
Water uptake and ion-exchange capacity for homogeneous and inorganic–organic hybrid membranes based on Nafion and SPSEBS materials

Sample	Water uptake (%)	Ion-exchange capacity	
		(mmol H <sup>+</sup> )(g dry membrane) <sup>−1</sup>	(mol water)(mol SO <sub>3</sub> H <sup>−</sup> ) <sup>−1</sup>
Nafion	36.60	1.48	13.74
NAF-SIL	24.11	1.44	9.27
NAF-SBA	31.67	1.55	11.33
NAF-SEP	22.28	1.50	8.24
SPSEBS	154.06	1.78	48.19
SPSEBS-SIL	124.10	1.67	41.32
SPSEBS-SBA	104.23	2.15	26.90
SPSEBS-SEP	119.37	2.15	30.82

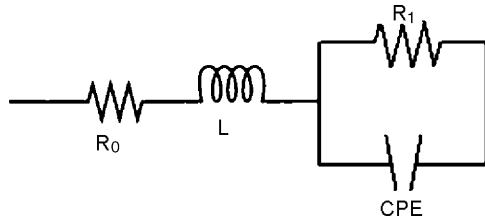


Fig. 9. Equivalent circuit showing the protonic resistance of a membrane in series with an inductance element and in parallel with a RC circuit containing a constant phase element that accounts for the departure of the relaxation behaviour of the membrane from Debye behaviour.

given by

$$Z' = R_0 + \frac{R_1 [1 + R_1 Y_0 (\omega \tau_0)^n \cos(n\pi/2)]}{1 + R_1^2 Y_0^2 (\omega \tau_0)^{2n} + 2R_1 Y_0 (\omega \tau_0)^n \cos(n\pi/2)} \quad (3)$$

and

$$Z'' = j\omega L - \frac{R_1 Y_0 (\omega \tau_0)^n \sin(n\pi/2)}{1 + R_1^2 Y_0^2 (\omega \tau_0)^{2n} + 2R_1 Y_0 (\omega \tau_0)^n \cos(n\pi/2)} \quad (4)$$

where  $\omega$  is the frequency and  $\tau_0$  is a characteristic relaxation time. Notice that at the limits  $\omega \rightarrow \infty$  and  $\omega \rightarrow 0$ ,  $Z' \rightarrow R_0$  and  $Z' \rightarrow R_0 + R_1$ , respectively. At the limit  $\omega \rightarrow 0$ ,  $Z'' \rightarrow 0$ , and  $Z'' \rightarrow \omega L$  at  $\omega \rightarrow \infty$ ; obviously,  $Z'' \rightarrow 0$  if  $L=0$ . If inductive effects are absent, the  $Z''$  versus  $Z'$  plot (Nysquit diagram) gives a curve that intersects the abscissa axis at  $Z' = R_0$ , at high frequencies. Also, since  $\lim |Z^*| \rightarrow R_0$  and  $\tan^{-1}(Z''/Z') \rightarrow 0$  at  $\omega \rightarrow \infty$ , where  $|Z^*|$  is the modulus of the complex impedance, the protonic resistance is equal to  $|Z^*|$  at  $\tan^{-1}(Z''/Z') = 0$ .

The conductivity of the membranes was calculated from the protonic resistance  $R_0$  by means of the following expression:

$$\sigma = \frac{l}{R_0 S} \quad (5)$$

where  $l$  and  $S$  are, respectively, the thickness and area of the membrane in contact with the electrodes.

Illustrative complex impedance plots for Nafion<sup>®</sup> 117, SPSEBS, Nafion<sup>®</sup>-SBA and SPSEBS-SBA membranes, at 80 °C, are shown in Fig. 10. The fact that the plots in the high frequency region are arcs that intersect the abscissa axis at high frequencies seems to rule out inductive contributions to the impedance. A zoom of the Nysquit plots for Nafion<sup>®</sup> 117, SPSEBS, Nafion<sup>®</sup>-SBA and SPSEBS-SBA membranes, equilibrated with distilled water, are shown in Fig. 11. The plots allow the determination of the protonic resistance,  $R_0$ , from the intersect of the Nysquit arc with the abscissa axis.

The interpretation of the experimental results in terms of the equivalent circuit containing a constant phase element shows that Eqs. (3) and (4) fit the complex plots by assuming that  $n = 0.6$ . The exponent of the phase element in the circuit accounts for the complexity of the polarization processes in such a way that the higher the complexity, the lower the  $n$ . The values of  $n$  and the conductivity for Nafion<sup>®</sup> 117 and SPSEBS membranes at 80 °C, under 100% of humidity, are shown in Table 5. It can be seen that the conductivity of the SPSEBS membrane is

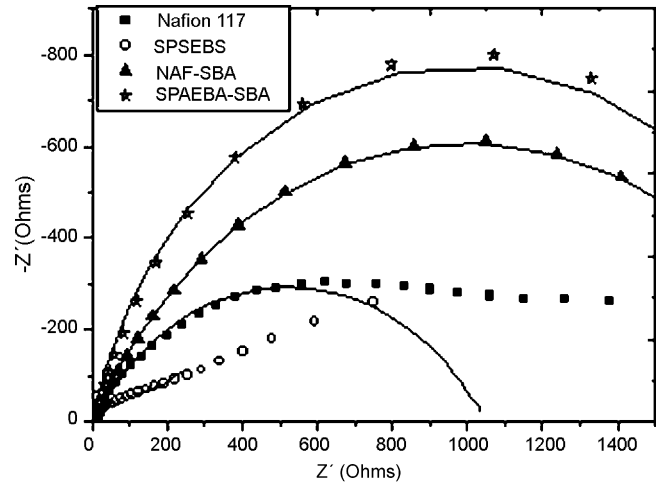


Fig. 10. Nyquist plots at 80 °C for the membranes indicated in the inset.

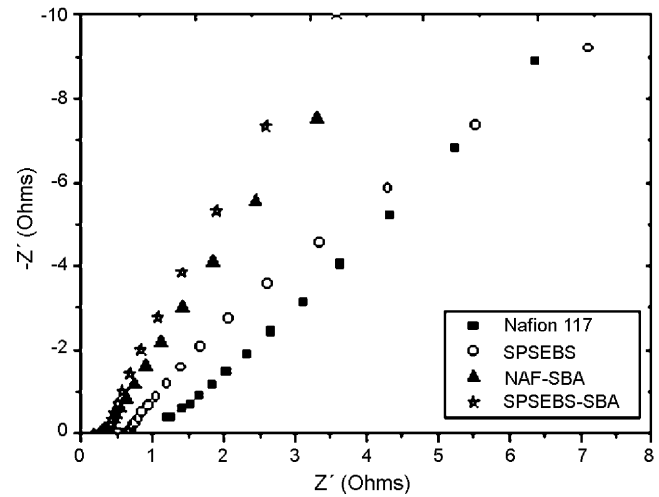


Fig. 11. Zoom of the Nysquit plot given in Fig. 10 to show in detail the intersection of the arc with the abscissa axis at the high frequency region.

4.1 S m<sup>-1</sup>, significantly higher than the conductivity of Nafion<sup>®</sup>, 1.3 S m<sup>-1</sup>.

The microstructure of fully hydrated SPSEBS membranes presumably displays hydrophilic domains of polystyrene sulfonated ionomers dispersed in the hydrophobic ethylene/butylene matrix. The hydrated ionomer clusters form percolation paths

Table 5

Proton conductivity and  $n$  values (departure of polarization processes from Debye behaviour), and 100% RH, for homogeneous and inorganic–organic hybrid membranes based on Nafion and SPSEBS materials

Sample	$\sigma$ (S m <sup>-1</sup> )	$n$
Nafion	1.33	0.65
NAF-SIL	2.84	0.61
NAF-SBA	6.75	0.70
NAF-SEP	3.31	0.64
SPSEBS	4.13	0.50
SPSEBS-SIL	3.44	0.84
SPSEBS-SBA	6.90	0.85
SPSEBS-SEP	3.54	0.84

through which the proton transport occurs. The mechanical stability of the SPSEBS membranes is provided by the non-sulfonated elastomeric phase as well as by poorly sulfonated polystyrene domains. The hydrophobic character of the skeletal bonds of perfluorocarbon polymers provides mechanical stability to Nafion<sup>®</sup> membranes, whereas the ionic clusters facilitate ionic and water transport in the membranes. The microstructure of the clusters or pores consists of an interfacial region of solvated perfluoroether side chains separating the polymer matrix from bulk-like water located in the pores. The size of the pores in the membranes is determined by the equilibrium between the internal osmotic pressure of the clusters and the counteracting elasticity of the organic matrix [39].

The similarity of the conductivity of SPSEBS membranes equilibrated with distilled water and that of the fully hydrated hybrid membranes indicates that the functionalized phenylsulfonic fillers do not disrupt the percolation path of fully hydrated SPSEBS membranes. Actually, owing to the procedure used in the preparation of the membranes, the fillers are randomly distributed across the hydrophilic and hydrophobic domains. The hydrophilic fillers dispersed in the hydrophobic domains may contribute in a significant way to ionic transport. The conductivity of the Nafion<sup>®</sup> composites seems to be somewhat affected by the phenylsulfonic inorganic fillers as a result of their presence in the hydrophobic part of the composite where they may act like hydrophilic bridges between hydrophilic clusters, thus facilitating proton transport.

The conductivity of ion-exchange membranes was also measured by dc using a four-point probe arrangement. The current  $I$  between two adjacent points, generated by the voltage drop  $\Delta V$  across the other two points, was measured. By plotting  $\Delta V$  versus  $I$  for different values of  $\Delta V$ , a straight line is obtained from whose slope the protonic resistance is obtained. The conductivity obtained by this method for the composites equilibrated with different humidity atmospheres are shown in Fig. 12. It can be seen that the conductivity is rather poor for membranes equilibrated in an atmosphere of low relative humidity. However, the conductivity sharply increases when the membranes are

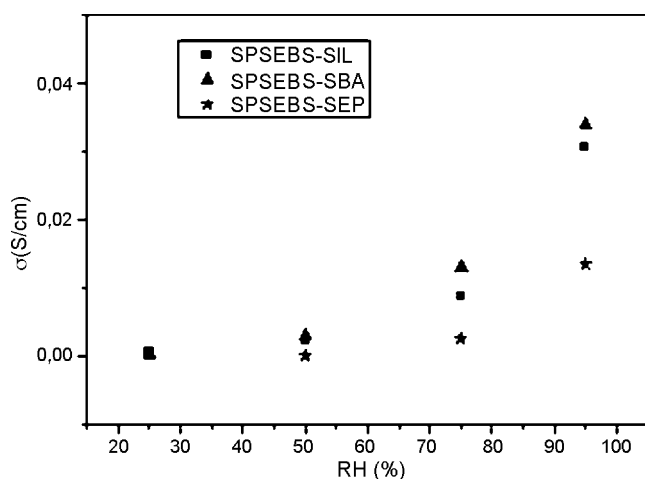


Fig. 12. dc conductivity of membranes indicated in the inset at equilibrium with atmospheres of different relative humidity.

Table 6

Comparison of ac and dc conductivities, at 80 °C and 100% RH, for inorganic–organic hybrid membranes based on SPSEBS materials

Sample	$\sigma$ (S m <sup>-1</sup> )	
	ac	dc
SPSEBS-SIL	3.44	3.07
SPSEBS-SBA	6.90	3.39
SPSEBS-SEP	3.54	1.35

conditioned under an atmosphere with RH higher than 70%, suggesting that a critical amount of water is necessary in the membranes in order that significant protonic transport across the membrane occurs. Percolation ionic paths seem to be absent in hybrid membranes equilibrated in atmospheres with relative humidity below 70%.

Comparison between ac and dc conductivities for fully hydrated membranes is shown in Table 6. It can be seen that the dc conductivity is somewhat lower than the ac conductivity for water saturated membranes. Electrodes polarization in dc measurements may be responsible for this fact.

#### 4. Conclusions

Fillers are more homogeneously dispersed in SPSEBS hybrid membranes than in their Nafion<sup>®</sup> counterparts.

The water uptake of fully hydrated SPSEBS hybrid membranes is about three times that measured for Nafion<sup>®</sup> composites.

The similarities between the conductivities of the hybrid membranes containing functionalized sepiolite and silica gel fillers and those of the respective pristine membranes suggests that fillers do not disrupt the conductivity percolation paths of the composite membranes. On the other hand, the fact that the conductivity of hybrid membranes containing functionalized SBA-15 is larger than that of the pristine membranes suggesting that particles of this hydrophilic inorganic filler may also be present in the hydrophobic regions of the membranes facilitating protonic transport.

Finally, SPSEBS hybrid membranes containing SBA-15 functionalized fillers equilibrated in an atmosphere containing 75% of relative humidity, or larger, undergo a sharp increase in conductivity.

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