Nanostructured Membranes Based on Sulfonated Poly(aryl ether sulfone) and Silica for Fuel-Cell Applications

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ABSTRACT: Nanostructured sulfonated poly(aryl ether sulfone) (SPSU) membranes were made from SPSU/silica composites through the addition of amorphous, precipitated, and micronized silica particles (Tixosil 333) and short or segmented linear structures. Linear and branched segments of silica were obtained from the *in situ* reaction of tetraethoxysilane (TEOS) in an SPSU solution through a sol–gel acid-catalyzed process. Different amounts of silica in the SPSU composites were prepared to evaluate their influence on the ionic conductivity, the water and alcohol solution sorption capacities, and the stability in an ethanol medium. The effect of silica (Tixosil) on the conductivity was higher than that of the silica made from TEOS in SPSU composites. The conductivities of the membranes containing 10% Tixosil and 6.6% silica prepared from TEOS were measured at 80°C; their values were 60 and 33 mS/cm, respectively. Furthermore, a membrane made of a silica blend (5% Tixosil and 3% TEOS) in SPSU attained a value of 92 mS/cm, whereas the commercial membrane Nafion 117, used as a reference, had a conductivity of 54 mS/cm measured under the same conditions. All those composites membranes could be used as components in hydrogen fuel cell. However, only the SPSU/2% Tixosil composite could be used in both hydrogen and ethanol direct fuel cells. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1690–1698, 2008

Key words: membranes; nanocomposites; poly(ether sulfones); silicas; structure-property relations

INTRODUCTION

Fuel cells efficiently convert the chemical energy of a fuel into electrical energy with low emissions of pollutants. Proton-exchange membrane fuel cells (PEMFCs) use a proton-conducting polymer as a support for the ionic transportation, and this results in devices with high power density. This promising power source, compact and environmentally friendly, has stimulated the development of efficient PEMFCs, particularly for mobile applications.

Hydrogen is the classic fuel used in fuel cells and is generally obtained by the re-formation of hydrocarbons or alcohols. It presents good electrochemical reactivity in the cell and almost no pollutant emissions. Direct alcohol fuel cell (DAFC) technology uses direct feeding of alcohol in the cell, avoiding reformer use or complex and hazardous procedures for the storage and handling of hydrogen, and it is suitable for portable devices or transport applications.[1]

The current membranes used in PEMFCs are perfluorinated polymers containing sulfonic acid, such as Nafion (produced by Dupont). Although the hydrated membrane of Nafion has excellent properties, such as high proton conductivity and good chemical, mechanical, and thermal stability, it presents several disadvantages. Cell operation at temperatures above 100°C is required to avoid the poisoning of the catalyst by carbon monoxide present in hydrogen. However, dehydration problems of the Nafion membrane limit its use at temperatures above 80°C because the conductivity of the membrane decreases sharply with the loss of water. Besides this, Nafion has a high cost and high alcohol (methanol and ethanol) permeability, and this constrains its applications.[2]

Different approaches employing many sulfonated organic polymers have been adopted to develop proton-conducting membranes for fuel-cell applications in the last years. Some examples include poly(arylene ether sulfone) (PSU),[3,4] poly(ether ketones),[5,6] and polyimides,[7] which try to meet the general requirements of proton-conducting membranes for PEMFC applications. These requirements involve a high level of conductivity under the operation
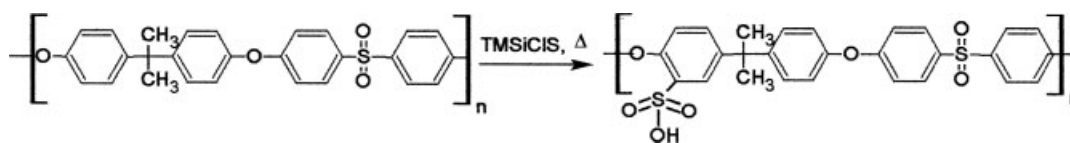
Scheme 1 Sulfonation reaction of PSU.

conditions, thermal, chemical, and mechanical stability, good barrier properties (to avoid the permeability of fuel and gas), the absence of electronic conductivity, and low cost. Among the distinct attempts in the development of polymer electrolyte membranes, organic–inorganic composite materials have been extensively studied, with special focus on DAFC applications. These inorganic materials are layer silicates,[8] heteropolyacids,[9] zirconium phosphates,[10] and silicas.[11–13]

The challenge of attaining proton-conducting membranes for DAFCs consists of obtaining stable membranes with low permeability to alcohol and a high level of conductivity. The alcohol crossover through the membrane in the cell drastically reduces its efficiency.[14] The hybrid organic–inorganic membranes present very attractive characteristics for this purpose. This allows adjusting important properties of the membrane through the control of the organic and inorganic phases. The presence of silica nanoparticles in proton-exchange membranes helps to maintain the water content of polymers and improves their thermal stability. The ethanol crossover of polyelectrolyte–silica nanocomposites is also reduced with the depression of their swelling degree in ethanol fuel solutions.

In this article, composite membranes based on a sulfonated polymer with silica in a particle form were prepared. The adsorption properties, stability of the membranes in ethanol solutions, and conductivity of the composites were evaluated to select suitable membranes for applications in water or an ethanol medium.

EXPERIMENTAL

Materials

PSU, a bisphenol A polysulfone (Ultrason S6010), was kindly supplied by BASF; trimethylsilyl chlorosulfonate (TMSiClS) was purchased from Aldrich Chemical Co. and used as received. Tixosil 333 was kindly supplied by Rhodia. The Nafion 117 membrane was purchased from Sigma–Aldrich and used after being treated in boiling water for 1 h.

Preparation of sulfonated poly(ether sulfone)

The synthesis of sulfonated poly(aryl ether sulfone) (SPSU) was based on a literature procedure.[4,15] Dried PSU was dissolved in 1,2-dichloroethane and reacted with TMSiClS under a nitrogen atmosphere

at 50°C for 6 h. The sulfonated polymer was precipitated in methanol, washed in cold water until the washing water became neutral, and dried in vacuo at 70°C. The chemical equation for this reaction is presented in Scheme 1.

The determination of the ion-exchange capacity (IEC) and sulfonation degree (SD) of the final product was performed by a titration method. The polymer was dissolved in N-methylpyrrolidone (NMP) and titrated against a 0.1N NaOH solution, and phenolphthalein as an indicator was added. IEC (mequiv/g) was calculated as the ratio of the total charge determined by titration divided by the dried polymer weight. SD was calculated from IEC as follows:

$$SD = (MW_P \times IEC)/[1000 - (80 \times IEC)] \qquad (1)$$

where MW_P is the molecular weight of the mer unit of the PSU polymer.

In this study, SPSU with IEC = 1.35 mequiv/g was prepared.

The presence of the sulfonic group in SPSU was confirmed by Fourier transform infrared (FTIR), which detected one band at 2800 cm^{-1} characteristic of —OH stretching that belonged to the sulfonic acid group, two bands at 1024 and 118 cm^{-1} associated with symmetric and unsymmetrical O=S=O stretching of the sulfonated group, respectively, and a band at 624 cm^{-1} characteristic of vibrations of C—S bonds.[16–18]

Preparation of the SPSU/silica composite membranes

SPSU/Tixosil composite membranes

The SPSU/silica (Tixosil) membranes were obtained directly from the SPSU solution. A certain amount of silica dispersed in NMP was added to the polymer solution also in NMP (20%), and the mixture was stirred for 24 h; this promoted a uniform and transparent dispersion. The films were obtained through casting onto a heated glass plate at 60°C for 24 h under a controlled atmosphere. Then, the films were dried at 70°C in a vacuum oven for 48 h.

SPSU/silica [tetraethoxysilane (TEOS)] composite membranes

The SPSU/silica (TEOS) hybrid membranes were prepared by a sol–gel process through the acid
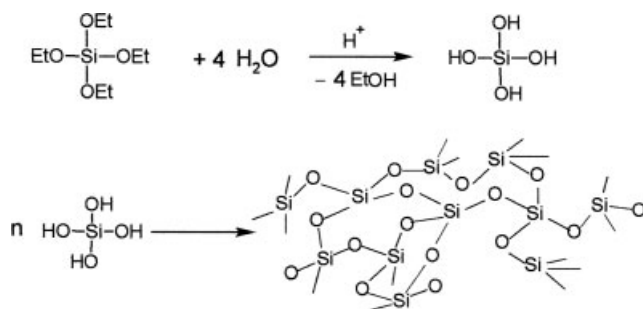
Scheme 2 Hydrolysis and condensation steps of acid-catalyzed TEOS.

catalysis condensation reaction of TEOS in the SPSU solution. The hydrolysis and condensation reaction steps of the sol–gel starting from TEOS are presented in Scheme 2. A dispersion of TEOS in ethanol and water was prepared with a molar ratio of 1 : 4 : 10. This solution was maintained at room temperature for 2 h under stirring. Then, it was added to an SPSU solution in NMP (20 wt %). The suspension was adjusted to pH 1.8 and stirred at 40°C for 24 h. The resultant dispersion was poured onto a heated glass plate at 60°C and left to evaporate for 48 h. The solid film was dried in a vacuum oven at 70°C for 48 h.

Characterization

FTIR spectroscopy

Infrared spectra of thin films were collected on a PerkinElmer model 1720X spectrometer in the absorbance mode and taken in the wavelength range of 4000–400 cm^{-1} with an average of 64 scans at a resolution of 2 cm^{-1}.

Thermogravimetric analysis (TGA)

The silica content in the composites was determined with a PerkinElmer model 7 thermogravimetric analyzer at a high temperature. The membrane samples were heated from 30 to 1100°C at a heating rate of 20°C/min and analyzed under an atmosphere of synthetic air fed at 20 mL/min.

Scanning electron microscopy (SEM)

A JEOL model JSM-6460LV was coupled with a microprobe of a Noran System Six-200 energy-dispersive spectroscopy (EDS) apparatus. The scanning electron microscope was mounted with tungsten filament and set at an accelerating voltage of 15 kV. Samples of cross-section surfaces were prepared, strips of membranes being fractured under cryogenic conditions and gold-coated before imaging by SEM.

Measurement of the water and ethanol uptake

The membrane samples were vacuum-dried at 120°C before testing. The sample films were soaked in deionized water or in an ethanol solution at a concentration of 20% at different temperatures until swelling equilibrium was attained. The dry weight and equilibrated swollen weight of the membranes were determined. Swollen membranes were wiped with tissue paper before weight measurements. The apparent water or ethanol uptakes of the membranes were determined as follows:

$$\text{Uptake content} (\%) = [(W_s - W_d)/W_d] \times 100 \quad (2)$$

where W_s and W_d are the weights of the swollen and dried samples, respectively.

Proton conductivity

The proton conductivity was measured by the alternating-current impedance spectroscopy technique and scanned over a frequency range of 10 Hz to 1 MHz at an amplitude of 5 mV with a system based on an Autolab PGSTAT30 frequency analyzer. Prehydrated samples in deionized water were measured while immersed in water in a sealed cell compressed between two stainless steel blocking electrodes (1.0 cm^2). The measurements were performed in the direction transverse to the plane of the membranes. The conductivity of the membranes (σ) was calculated from the impedance data:

$$\sigma = d/RS \quad (3)$$

where d and S are the thickness of the membrane and the face area of the contact membrane electrodes, respectively; and R was derived from the low intersection on a complex impedance plane with the Re (z) axis.

RESULTS AND DISCUSSION

FTIR analysis

Typical spectra of PSU and SPSU are provided in Figure 1. The presence of the sulfonic group is confirmed by the appearance of one band at 2800 cm^{-1} assigned to ─OH stretching of the sulfonic group,[16] two bands at 1024 and 1169 cm^{-1} associated with symmetric and asymmetric O=S=O stretching of the sulfonate group, respectively; and one band at 624 cm^{-1} characteristic of stretching vibrations of C─S bonds.[16–18] Curve 1 in Figure 1 is the PSU infrared spectrum. It has bands at 1583 and 1484 cm^{-1} related to aromatic C=C stretching; bands at 1012, 1152, and 1237 cm^{-1} are characteristics of the ring vibration of p-substituted aryl ether,
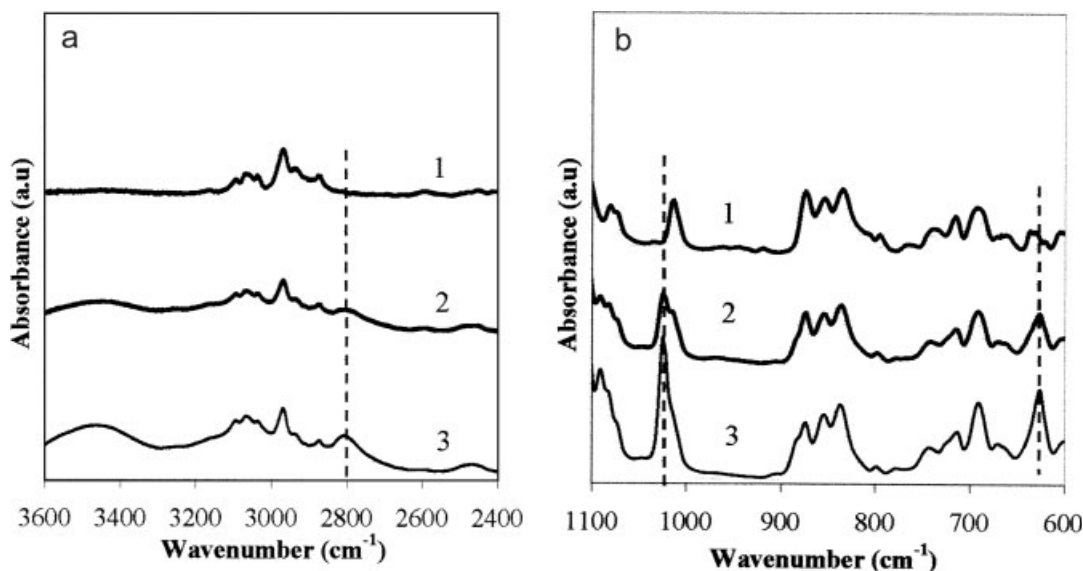
Figure 1 FTIR spectra of SPSU with different SDs: (1) PSU, (2) SPSU with SD = 48.5%, and (3) SPSU with SD = 87%.

symmetric O=S=O stretching of the sulfone group, and asymmetric C—O—C stretching of the aryl ether sulfone group, respectively.[17,18] The band of PSU at 1012 cm^{-1} tends to disappear as sulfonation proceeds. Curve 2 is the spectrum of SPSU of a low SD (48.5%), and curve 3 is the spectrum of SPSU of a high SD (87%); all of them were previously determined by titration. The level of sulfonation may be estimated if we take into account the relative intensities. The peak of O=S=O stretching of the sulfonate group located at 1024 cm^{-1} represents the intensity of the sulfonated unit. This peak is normalized against internal standard intensities, such as the

diphenyl ether units (1246 cm^{-1}) and/or aliphatic isopropylidene unit (1393 and 1368 cm^{-1}) contained in the bisphenol A portion of the macromolecules, as mentioned in the literature.[17]

Figure 2 shows the FTIR spectra of the SPSU/silica composite prepared with Tixosil. The curves for SPSU were normalized with respect to the absorption band of C—H bending belonging to the methyl group (1412 cm^{-1}). In Figure 2(a), spectra of composites with different contents of Tixosil show that the characteristic peak of Si—O—Si bonds around 1100 cm^{-1} cannot be seen because of the presence of aromatic, sulfone, and sulfonate groups
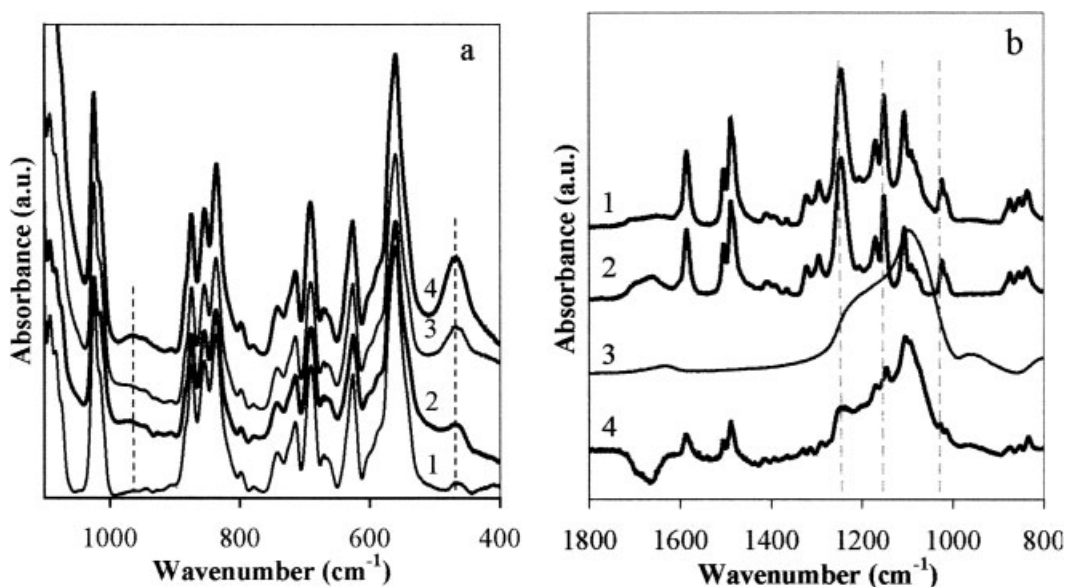

Figure 2 (a) FTIR spectra of SPSU, silica (Tixosil), and some composites: (1) plain SPSU, (2) SPSU/2% Tixosil, (3) SPSU/5% Tixosil, and (4) SPSU/10% Tixosil. (b) Spectra of (1) the SPSU/10% Tixosil composite, (2) plain SPSU, and (3) Tixosil and (4) a subtraction spectrum [(SPSU/Tixosil 10%) − plain SPSU].
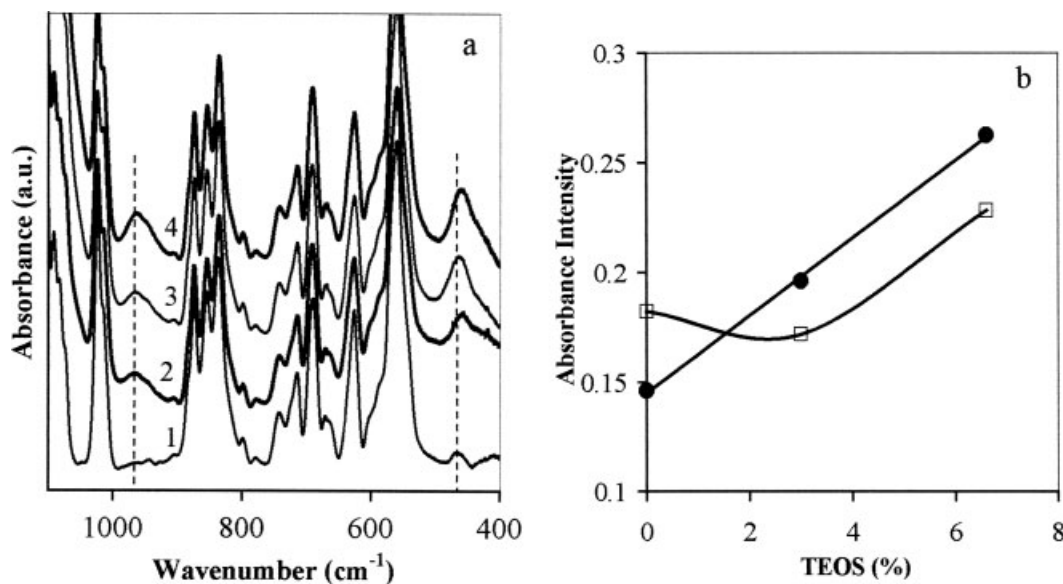
Figure 3 (a) FTIR spectra of SPSU/silica (TEOS): (1) plain SPSU, (2) SPSU/3% TEOS, (3) SPSU/6.6% TEOS, and (4) SPSU/silica (5% Tixosil + 3% TEOS). (b) Relationship of the absorbance intensities at (●) 967 and (□) 800 cm^{-1} versus the TEOS loading in the composites. The linear relation taken at the 967-cm^{-1} peak can be expressed by $y = 0.0177x + 0.1451$.

of SPSU, whose absorption bands are in the range of 1000–1180 cm^{-1}, and they overlap the Si—O—Si peak. However, other peaks assigned by dashed lines at 970 and 470 cm^{-1} are characteristic of silanol and Si—O—Si links from Tixosil, and they are sensitive to the silica content.

In Figure 2(b), the spectra of an SPSU/silica composite (10% content), plain SPSU, and pure silica (Tixosil) are presented as references. Moreover, a curve resulting from spectral subtraction of plain SPSU from the SPSU/silica composite (10%) is also included, showing a shape similar to that of the Tixosil silica.

Characteristic peaks of silica at 1100, 811, and 470 cm^{-1} have been assigned to the Si—O—Si asymmetric stretching, Si—O—Si symmetric stretching, and Si—O—Si bending mode, respectively. However, PSU peaks overlap the main peak of silica, whose peak has a large and strong intensity in the 1250–1100-cm^{-1} region. Other silica peaks can be seen and remain untouched. In addition, two peaks can be observed at 972 and 3460 cm^{-1} due to the associated silanol groups (hydrogen-bonded Si—OH) seen in the pure silica spectrum.[19,20] The spectrum resulting from subtraction involving SPSU/silica and plain SPSU [Fig. 2(b)] enhances the characteristic peaks of silica and provides evidence of some reminiscent peaks related to SPSU (1151 cm^{-1}, O=S=O symmetric stretching from sulfone; 1253 cm^{-1}, C—O—C asymmetric stretching from aryl ether; and 1024 cm^{-1}, O=S=O symmetric stretching from the sulfonate group),[17,18] suggesting that some interactions between silica and SPSU take place in the composite. These interactions involve silanol groups

from silica and sulfone and sulfonate groups from the polymer, possibly through hydrogen bonding. A slight band shift associated with sulfonate group from 1026 (plain SPSU) to 1023 cm^{-1} (SPSU composite at a 10% loading) can be observed. On the other hand, the peak associated with the silanol group of silica in the SPSU composite containing a 10% concentration (976 cm^{-1}) shifted to a higher energy with respect to the pure silica (972 cm^{-1}) and is in accordance with the suggested interactions.

Figure 3 presents results for SPSU/silica (TEOS) composites (obtained by a sol–gel reaction *in situ* of TEOS in an SPSU solution). Figure 3(a) shows the spectra of SPSU/silica (TEOS) composites with different compositions. The peaks assigned by dashed lines and centered at 967 (related to silanol groups) and 467 cm^{-1} (due to Si—O—Si chains) evidence the silica enrichment and the increase of noncondensed Si—OH, respectively, with the increment of TEOS in the composites. The relationships between the TEOS loading and intensity of the infrared absorbance peaks are shown in Figure 3(b). There is a linear relation between the intensity of the absorbance peak located at a frequency of 967 cm^{-1} and the TEOS content at all concentrations explored up to 6.6%. In contrast, the intensity of the absorbance peak located at a frequency of 800 cm^{-1} is linear only in a narrower range of 3–6.6% loaded TEOS.

TGA

The formation of a silica structure based on the TEOS reagent by a sol–gel process in the polymer
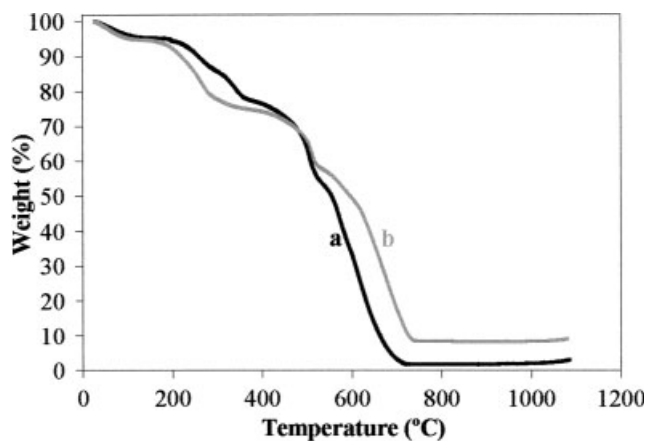
Figure 4 Thermograms of (a) pure SPSU and (b) SPSU plus silica (TEOS).

membranes was examined with TGA. Figure 4 shows the thermograms of the membranes.

Pristine SPSU and SPSU/silica membranes exhibited similar degradation patterns. The data indicate that SPSU/silica (TEOS) has 6.6% silica. The presence of silica nanoparticles might not significantly

alter the thermal degradation of the SPSU polymer.[21] However, SPSU/silica (TEOS) membranes had poorer thermal stability. The initial weight loss was attributed to water; the subsequent weight loss was due to desulfonation, which started around 167°C.[22,23] The final weight loss due to polymer chain thermal degradation started around 384°C.

Microstructure of the composite membranes

The morphology of the fractured cross-section surfaces of the composite polymer membranes was investigated with SEM. Micrographs of SPSU/silica composite membranes are presented in Figure 5.

The micrographs of membranes compounded with 2 and 10% Tixosil are presented in Figure 5(a,b), respectively. They show that the composite with a low content of Tixosil had a lot of aggregates (0.5 μm) and particles (0.1 μm) distributed over the polymer matrix. The large aggregates could not be observed in the composite containing 10% Tixosil.

Micrographs of SPSU/TEOS composites containing 3 and 6.6% silica are presented in Figure 5(c,d), respectively. They had a finer dispersion of silica in
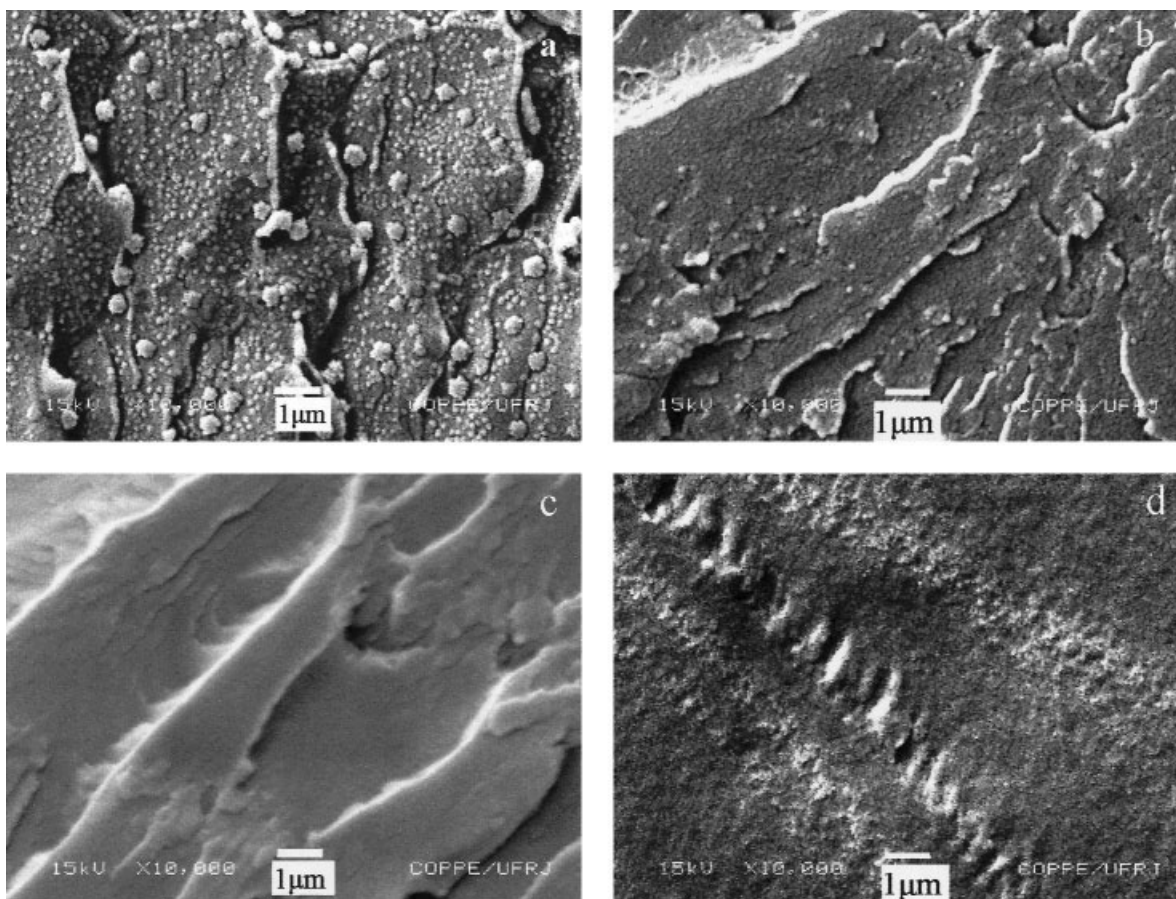

Figure 5 SEM micrographs of fractured surfaces of SPSU/silica hybrid composites based on (a) 2% Tixosil, (b) 10% Tixosil, (c) 3% silica from TEOS, and (d) 6.6% silica from TEOS.
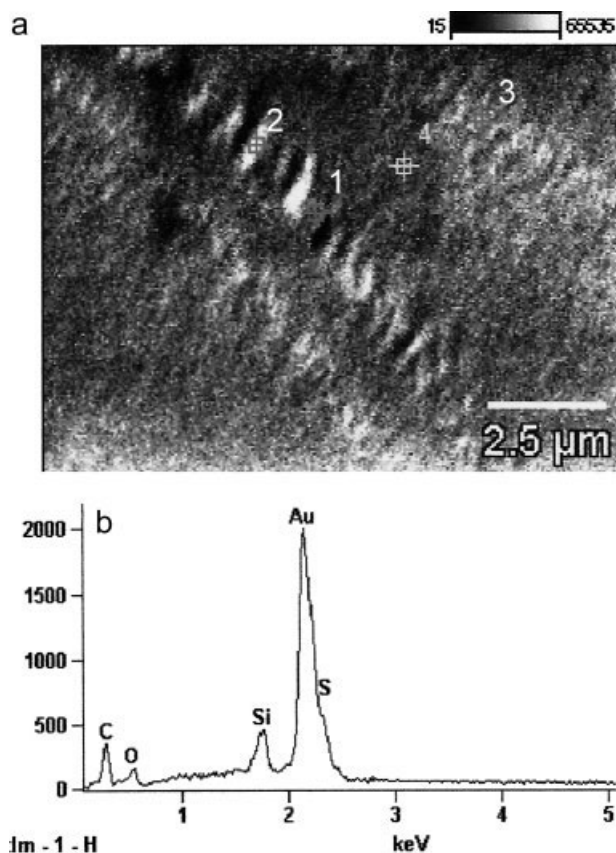
Figure 6 EDS results for an SPSU/silica hybrid composite with 6.6% TEOS (corresponding to point 1 in the micrograph).

the matrix. The membrane compounded with 3% silica had an even and smooth surface, and no phases were observed. As the silica loading rose to 6.6%, one could notice that the dispersion of silica was well distributed over the polymer matrix, and the particle growth of segmented silica was uniform

over the membrane. The particle size of silica derived from TEOS was estimated to be as small as 10 nm in the composite containing 6.6% silica.

To go further into the investigation of the SPSU/ TEOS nanocomposites, EDS was used to analyze the dispersion of 6.6% silica based on TEOS, as shown at Figure 6. The EDS results showed a compositional analysis of silicon, carbon, oxygen, and sulfur almost identical for all points analyzed (1–4), so just one point is presented. The uniform compositions suggested that the silica structures were refined and well distributed in the composites.

Both types of silicas produced transparent and homogeneous composite membranes at low silica contents ($<5\%$), whereas the TEOS composite membrane was still transparent up to the highest content (6.6%) loaded in this study.

Water and ethanol solution uptake

The results for the water and ethanol solution uptake of the hybrid composites are shown in Table I.

The data were obtained after 24 h of isothermal immersion of the membranes in the solution. The concentration of the ethanol solution was 20 wt %. All membranes had acceptable sorption in the water medium heated to 90°C. However, only the composite with 2 wt % Tixosil resisted at the highest temperature in the ethanol medium. The Nafion membrane (reference) presented an interesting sorption behavior; it showed almost no effect of temperature on the uptake of both liquids. On the other hand, most sulfonated poly(aryl ether)s need the incorporation of some component to enhance their barrier properties to reduce excessive sorption at higher temperatures, especially in an alcohol medium. The silica obtained by the sol–gel process from TEOS was not efficient in reinforcing the SPSU

TABLE I
Water and Ethanol Solution Uptake Data for the SPSU/Silica Composites

Membrane composition	Temperature			
	Water concentration (wt %)		Ethanol solution uptake concentration (wt %)	
	80°C	90°	50°C	90°
Nafion 117	25	28	39	39
SPSU (IEC = 135 mequiv/g)	22	27	320	nr
SPSU + 2% SiO$_2$ (Tixosil)	23	41	54	62
SPSU + 5% SiO$_2$ (Tixosil)	13	22	30	nr
SPSU + 10% SiO$_2$ (Tixosil)	4	6	39	nr
SPSU + 3% SiO$_2$ (TEOS)	4	10	328	nr
SPSU + 6.6% SiO$_2$ (TEOS)	8	31	16	nr
SPSU + 3% SiO$_2$ (TEOS) + 5% SiO$_2$ (Tixosil)	2	2	111	nr

nr, not resistant.

TABLE II
Conductivity Data for SPSU/Silica Hybrid Composites

Membrane composition	Silica (wt %)	Thickness (μm)	Conductivity (mS/cm) 40°C	80°C
Nafion 117	0	200	38.6	54.4
SPSU (IEC = 135 mequiv/g)	0	75	10.8	14.3
SPSU/SiO$_2$ (Tixosil)	2	76	6.8	22.4
SPSU/SiO$_2$ (Tixosil)	5	79	20.7	40.1
SPSU/SiO$_2$ (Tixosil)	10	123	35.8	60.0
SPSU/SiO$_2$ (TEOS)	3	136	20.3	23.8
SPSU/SiO$_2$ (TEOS)	6.6	98	32.6	33.5
SPSU/3% SiO$_2$ (TEOS) + 5% SiO$_2$ (Tixosil)	8	172	58.3	91.8

membrane in an alcohol medium, as expected, probably because of the silanol groups detected by FTIR; this suggests an uncompleted condensation step in the sol–gel reaction. The composite membranes loaded with Tixosil presented higher water sorption than composites prepared from TEOS, whereas the composite based on a blend of the two silicas showed the lowest water sorption. Among these results, only one formulation prepared with 2% Tixosil presented good stability in water and in an ethanol medium.

Conductivity analysis

The conductivity data for the composite membranes based on SPSU/silica are presented in Table II. All the composites had higher conductivities than those of plain SPSU (IEC = 1.35 mequiv/g). The conductivities of plain SPSU at 40 and 80°C were 10.8 and 14.3 mS/cm, respectively. Hybrid composites based on silica (5 and 10% Tixosil) had conductivity values of 20.7 and 35.8 mS/cm, whereas membranes compounded with 3 and 6.6% TEOS had values of 20.3 and 32.6 mS/cm, respectively; all were measured at 40°C. Higher values were found for Tixosil (5–10%) based composites measured at 80°C than for those obtained with TEOS (3–6.6%). At this temperature, SPSU/silica loaded with 10 wt % Tixosil attained a value of 60 mS/cm, whereas the membrane made of 6.6% TEOS presented a value of 33.5 mS/cm, and the Nafion membrane, taken as a standard reference, had a value of 54.4 mS/cm. This improvement in
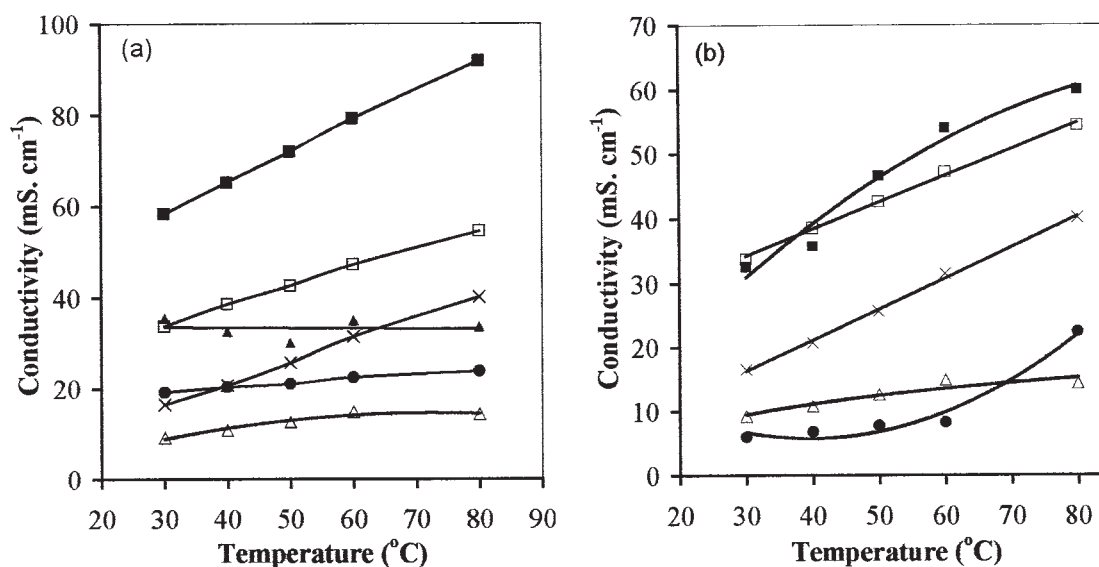

Figure 7 Proton conductivity of SPSU/silica composites. (a) Addition of Tixosil and TEOS and blends of both silicas: (△) SPSU, (□) Nafion 117, (×) SPSU/Tixosil (5%), (●) SPSU/TEOS (3%), (▲) SPSU/TEOS (6.6%), and (■) SPSU/Tixosil (5%) + TEOS (3%). (b) Different contents of Tixosil: (△) SPSU, (□) Nafion 117, (●) SPSU/Tixosil (2%), (×) SPSU/Tixosil (5%), and (■) SPSU/Tixosil (10%).

conductivity was probably due to the nanoporous particles of hydrophilic Tixosil, which could preserve a higher humidity level in the membrane than in the segmented silica from TEOS at elevated temperatures. Moreover, morphological contributions could facilitate proton transportation in composites based on Tixosil silica.

The behavior of the conductivity with the temperature can be better observed in Figure 7. The influence of temperature, measured in the range of 30–80°C, on the conductivity was more significant for the Tixosil-based composites than those based on TEOS, as presented in Figure 7(a). The conductivity curve of plain SPSU showed a slight upward slope, and this inclination was practically the same for SPSU/TEOS (3 wt %), so these curves were separated by a constant gap. The addition of TEOS had little effect on the conductivity level. The subsequent addition of Tixosil (5 wt %) resulted in an SPSU/(silica blend) composite, and the mixture of both silicas promoted a synergistic effect, increasing the conductivity intensively with a steeper ascent as the temperature rose; the formulation containing an 8 wt % silica blend attained a value of 91.8 mS/cm at 80°C. The SPSU/Tixosil (5%) composite kept this sharp slope, but at lower conductivity values.

Figure 7(b) shows the effect of silica (Tixosil) incorporated inside the SPSU polymer on enhancing the conductivity as the temperature was increased.

These composite membranes, however, were stable only in water and not in an ethanol medium, as observed from the sorption results. The composite resistant to alcohol was one that contained 2 wt % Tixosil, the conductivity of which was 22 mS/cm at 80°C.

CONCLUSIONS

SPSU/silica hybrid composites based on Tixosil had their conductivities enhanced with an increase in silica, and their conductivity was affected intensively by temperature; this was probably caused by the high capacity for hydration retention in the membranes at elevated temperatures. A synergistic effect was observed with both silica types (5 wt % each) in composites to improve the conductivity, a value of 91 mS/cm being attained at 80°C. All the membranes were stable in a water medium (90°C/24 h), and only one composition containing 2 wt % Tixosil was stable in an ethanol medium, the conductivity of which was 22 mS/cm at 80°C.

The results indicated that silica particles such as Tixosil, although they are highly hydrophilic, can be used to enhance the conductivity at high temperatures while preserving the membrane stability of composites in water.

Reinforcing membranes with a refined structure distribution of silica formed from TEOS made no contribution to stability in an ethanol medium and had little effect on conductivity.

However, hybrid composites based on a blend of Tixosil and silica produced *in situ* from a sol–gel reaction of TEOS could be tailored to optimize their properties for fuel-cell applications.

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