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Nanostructured Proton-Conducting Membranes for Fuel Cell Applications

*Ai Ren Tan, Luisa Magno de Carvalho, Ailton de Souza Gomes**

Summary: Composite polymer membranes based on sulfonated poly(arylene ether sulfone) (SPSU) containing benzimidazole derivatives (BIzD) and heteropolyacid for use in fuel cells were prepared. The effects of both the increment in BBIzD component and the procedure of mixing on the morphology and proton conductivity were investigated. The heteropolyacid (HPA) extracted in water decreased with the addition of BBIzD in the composite. The interactions developed among the sulfonate groups, the benzimidazole derivatives and the HPA were verified by Fourier transform infrared (FTIR). The network of interactions established in the composite membrane based on SPSU containing benzimidazole derivatives and phosphotungstic acid (HPW) in the ratio of SPSU/BBIzC$_4$(8:1) in equivalents and SPSU/HPW(7:3) in mass resulted in a very high proton conductivity at 110 °C.

Keywords: benzimidazole derivatives; composite membranes; nanocomposites; proton conductivity; sulfonated poly(arylene ether sulfone)

Introduction

Fuel cells have been considered as promising alternative power sources due to the high conversion efficiency of the chemical energy of fuel to electrical energy with low emission of pollutants. In particular, the polymer electrolyte fuel cell (PEMFC) using polymer electrolyte membranes (PEM) have been received much attention as electric power source in transportation vehicles.[1] Perfluorinated membranes from the DuPont (Nafion), Dow and Asahi Chemical Companies possess good chemical and mechanical stabilities and also high proton conductivity. Up to now these membranes have been almost the only effective membranes used in commercial systems fed by hydrogen fuel. However, their high cost and some additional disadvantages, such as dehydration at temperatures above 100 °C limits the PEMFC performance, once the kinetics of electrochemical reactions rises with temperature, and the poisoning catalysts problems caused by the presence of the traces of CO in the fuel could be reduced at higher operating temperatures. Besides, in direct methanol fuel cell (DMFC) use, one of the major drawbacks is the methanol crossover, which reduces the overall cell performance. Many efforts have been undertaken to develop new proton conductive membranes less expensive than Nafion, preserving its electrochemical properties and improving its performance in Polymer electrolyte fuel cells (PEFCs). Polymer electrolytes based on partially fluorinated ionomers and non-fluorinated ionomers are being developed by several groups around the world.[2] Sulfonated aromatic polymers such as polyketones and polysulfones have been developed[3,4] however, the proton conductivity at elevated temperatures is not yet satisfactory. The use of heteropolyacids as inorganic modifier in sulfonated polymer composites is very attractive, due its high conductivity

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Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Centro de Tecnologia Bloco J, Cidade Universitária, Cx. Postal 68525, CEP 21945-900, Rio de Janeiro, RJ, Brazil
Fax: (+55) 21 2270 1317
E-mail: asgomes@ima.ufrj.br

and thermal stability. It was observed that specific interactions between HPAs and sulfonated polymers had important influence on fuel cell performance at elevated temperatures.[5] This class of additives present however a problem of bleeding out from composite membranes when immersed in hot water, specially above 55 °C[6] which reduces the cell performance.

In this paper we studied the properties of composite membranes based on sulfonated poly(arylene ether sulfone) (SPSU) containing phosphotungstic acid (HPW) as inorganic modifier to improve the conductivity and benzimidazole derivatives as crosslinking agent by ionic interactions. One expect that the crosslink effect in this composite membranes can improve the ionic conductivity by reduction of HPW bleeding out of membrane, besides promoting a reinforcement of membrane in swelled state at high temperatures.[7] The effect of ionic interactions over the reduction of HPW leaking from composite membranes was inspected by ultraviolet spectrometry and by weighting of extracted HPW fraction. The dispersion of HPW domains, the proton conductivity and the water uptake of membranes were also evaluated.

Experimental Part

Materials

Poly(arylene ether sulfone) (PSU) Ultrason S6010 ($\overline{M}_w = 60\,000$, $T_g = 187$ °C, $d = 1.24$) was kindly supplied by BASF; trimethylsilil chlorosulfonate (TMSiClS) was purchased from Aldrich Chemicals; phosphotungstic acid (HPW) from Aldrich Chemicals; benzimidazole from Acros Organics; 1,4-dibromobutane from Acros Organics; 1,10-dibromodecane from Acros Organics; potassium hydroxide, sodium hydroxide, 1,2-dichloroethane, ethanol, 1-methyl-2-pyrrolidone (NMP); sodium sulfate and dimethyl acetamide (DMAC) from Vetec.

Sulfonation of Polymer

Dried PSU was dissolved in 1,2-dichloroethane (DCE) under mechanical stirring and nitrogen atmosphere. Trimethylsilyl chlorosulfonate dissolved in DCE was added in drops by using an addition funnel for half an hour. The reaction mixture was stirred at 30 °C for a given time, which varied in function of the desired sulfonation degree. The polymer solution was poured into a large excess of cold methanol under vigorous stirring, to precipitate the polymer. After washing with water the sulfonated polymer was dried in vacuum oven. The procedure of sulfonation was based in literature works.[8]

The determination of ion exchange capacity (IEC) and sulfonation degree was done by titration method. The sample was dissolved in NMP and a little amount of water was added before titration with solution of 0.1 N NaOH. The following expressions were used to determine the IEC and the sulfonation degree, respectively:

$$\mathrm{IEC} = \frac{n^{\circ}\mathrm{meq}_{\mathrm{SO_3H}}}{\mathrm{weight}_{\mathrm{SPEEK}}} \qquad (1)$$

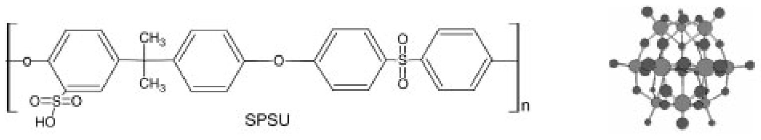
where IEC, n°meq are ion exchange capacity ($\mathrm{meq \cdot g^{-1}}$) and miliequivalents number respectively. The unit of weight is in grams.

$$\mathrm{SD} = \frac{\mathrm{MW_p} \times \mathrm{IEC}}{1\,000 - (80 \times \mathrm{IEC})} \times 100 \qquad (2)$$

where SD, $\mathrm{MW_p}$ are sulfonation degree (%) and molecular weight of mero unit of polymer, respectively.

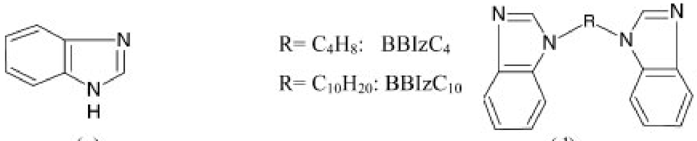
Synthesis of Benzimidazole Derivatives

Benzimidazole and dibromo n-alcane were added to a solution of KOH and ethanol and the reaction mixture was refluxed for 3 h. The mixture was then cooled and the potassium bromide was filtered. The filtrate was dried and treated with chloroform. The chloroform solution was washed with NaOH solution and with water, and dried over anhydrous sodium sulfate overnight. After filtration of the salt, the oil residue was crystallized from toluene/hexane (2:1) solution. The obtained crystals were dried under vacuum (m.p. $\mathrm{BBIzC_4} = 170.7$ °C and m.p. $\mathrm{BBIzC_{10}} = 98.9$ °C).



(a)
Sulfonated polysulfone (SPSU)

(b)
Keggin Structure of HPW anion-$PW_{12}O_{40}^{-3}$



(c)
Benzimidazole

(d)
Benzimidazole derivatives

Figure 1.
Components of composite membranes: (a) sulfonated polymer (SPSU); (b) inorganic component, Keggin structure of anion of HPW; (c) crosslinking promoters- benzimidazole and its derivatives (d).

Preparation of Composite Membranes

The composite membranes were prepared by casting solution of SPSU, HPW and benzimidazole derivatives onto a glass plate. All of components of composite membranes are represented in Figure 1.

The HPW was dried at 120 °C in vacuum oven before use to obtain the secondary structure $H_3PW_{12}O_{40} \cdot 6H_2O$. The components of blend were mixed in one or in two steps in DMAC. The SPSU concentration in DMAC was 10 wt.-%. Mixing the components in two steps, the third component is added onto solution with the two first components previously prepared for 12 h at 80 °C. Before the third component addition, the solution was submitted to the same time and temperature conditions, and casting onto glass plate, and it was dried at 60 °C for 24 h under dried nitrogen flow followed by vacuum over at 80 °C for 24 h. The compositions were calculated in relation to SPSU. The ratio SPSU:BBIz is referred in equivalents and the ratio SPSU:HPW is referred in mass.

Measurements

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were measured in absorbance mode in a Perkin Elmer spectrometer model 1720X, at a resolution of 2 cm^{-1}, and 20 scans.

Water Uptake of Membranes

Samples previously dried and weighted were immersed in deionized water at different temperatures and weighted each 2 h. The excess of water on surface was removed by an absorbent paper, then the membranes were weighted again, and the water uptake (%) was calculated by the relation:

$$\text{Water\_uptake} = \left[\left(\frac{W_{\text{wet}}}{W_{\text{dry}}}\right) - 1\right] \times 100$$

where W_{wet} and W_{dry} are weight of wet membrane wet and dried membrane, respectively.

HPW Extraction from Composite Membranes

The procedure of HPW extraction from the composite membranes was to immerse the membranes previously weighted onto water vapor at 100 °C for 4.5 h, or in deionized water at 80 °C for 6 h. In the case of water vapor extraction, the membranes were placed in the upper space above liquid water, in a reflux system. The loss of HPW was determined by gravimetric method (from the difference of weight of extracted membrane and the membrane before

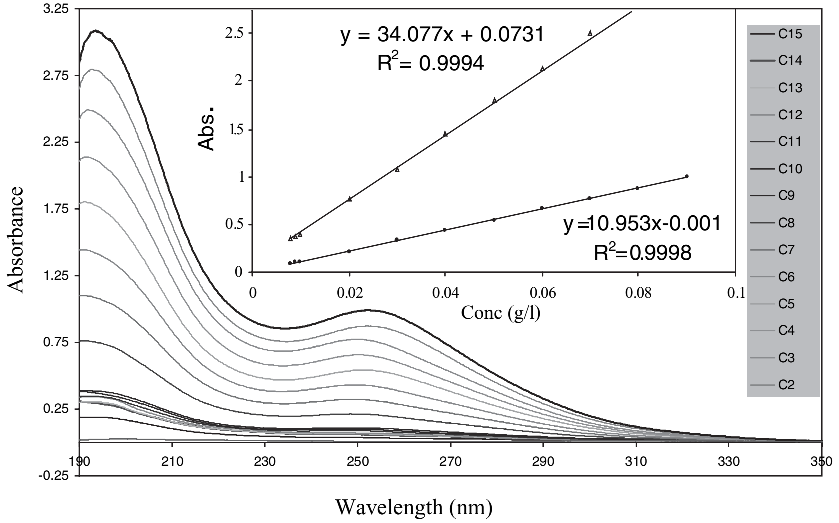


Figure 2.

Calibration curves of HPW content by UV spectrometry and equations relating absorbance intensity and HPW concentration at $\lambda = 190$ and 250 nm.

extraction) and by ultraviolet absorption spectroscopy of the extracted solution. In this case, it was used a calibration curves of HPW solution for wavelengths of 190 and 250 nm, as illustrated in Figure 2 (the HPW concentration changed from 9×10^{-2} to 3×10^{-3} $g \cdot l^{-1}$). The 250 nm wavelength was associated to the absorption band of PW_{12} in the solution. The inserted illustration shows the linear relationships between the absorbance intensity and the HPW concentration of solution at 190 and 250 nm wavelength, respectively. Where y, x, and R are absorbance intensity, concentration in ($g \cdot l^{-1}$) and linear co-relation coefficient of fitting curve.

Scanning Electron Microscope (SEM)

Samples were fractured under cryogenic conditions and vacuum sputtered with a thin layer of gold before imaging by scanning electron microscopy (SEM) JEOL model JSM-5610LV.

X-ray Diffraction (XRD)

Analysis were made on membranes using a diffractometer Rigaku Miniflex RIX3100 with Cu radiation (30 kV, 15 mA), CuKα, $\lambda = 1.5406$ Å, the scanning speed of 0.05° per 2 s, the step width of 0.05°. The samples were scanned at angular range of 1.5° and 20°.

Proton Conductivity

All membranes were pre-treated at 90 °C for 1 h, and kept in water until the analysis moment. Nafion membrane was boiled for 1 h.

Proton conductivities were measured in transverse direction. The membranes were sandwiched within stainless steel electrodes. When submitted to temperatures up to 80 °C, membranes were under full hydration conditions. Measurements were performed using Autolab PGSTAT-30, over a frequency range of 10 Hz–1 MHz. At temperature of 110 °C, measurements were conducted in water vapor in a sealed vessel.

Results and Discussion

Infrared Studies

Infrared spectra were used to elucidate the ionic interactions developed in the composite membranes. It was observed interactions between sulfonic groups of the SPSU and imidazole groups of benzimidazole compounds. In addition, HPW also established ionic interactions with benzimidazole compounds and with sulfonic groups of polymer matrix. So, a real network of ionic interactions seems to have been developed in the composite membranes. This ionic crosslinking system occurred specially due to interactions between nitrogen from benzimidazole compounds which had unshared pair of electrons, and the electron pair acceptor of acid groups. Sulfonated polymer composites presenting donor-acceptor (acid-base) interactions for use in fuel cells have been described in literature.[9]

Specific Interactions between Sulfonated Polymer and HPW

The phosphotungstic acid (HPW), in the dehydrated state or in polar solvents produces stable Keggin type anions such as $PW_{12}O_{40}^{3-}$, which requires three protons to satisfy the condition of electron-neutrality $H_3PW_{12}O_{40}$. This structure is denominated primary structure, and is formed by a central atom of phosphorus tetrahedrically linked to oxygen atoms surrounded by eleven other oxygen atoms linked to a tungsten atom. When hydrated water molecules are present in HPW, the terminal oxygen atoms of the anions are associated with $H_5O_2^+$ generating a secondary structure that presents characteristic peaks in the FTIR spectroscopy.[5] Vibrational band of the terminal oxygen, $W{=}O_t$ interacting with the protonated water dimmer is found at 980 cm^{-1}. There are two kinds of bridging oxygen, one corresponds to symmetric stretching band of corner-shared octahedral, $W–O_c–W$ at 887 cm^{-1}. The other is associated to symmetric stretching band edge-shared octahedral, $W–O_e–W$ at 795 cm^{-1}. The central tetrahedral P–O band is observed at 1 080 cm^{-1}. Figure 3 shows the spectra of SPSU/HPW composites at different compositions (7:3 and 5:5 in w/w) and those of pure SPSU and pure HPW. One can observe that the composites spectra presented higher absorbance intensities than those of pure components. The vibrational band of the terminal oxygen in the secondary structure at 979 cm^{-1} in the composites spectra suggests that specific interactions occurred between this terminal oxygen and a group from SPSU. Probably the sulfonic group interacts with this terminal oxygen, once that band associated

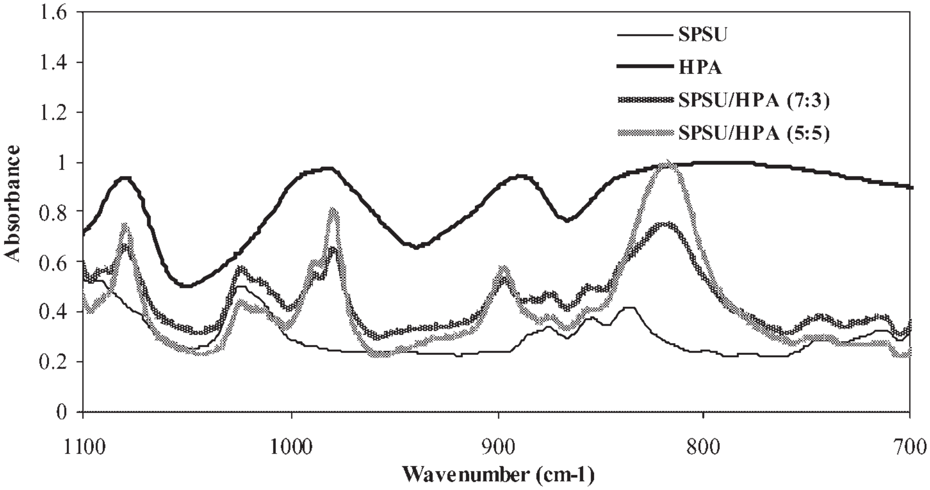


Figure 3.
FTIR spectra of pure SPSU, pure HPW and SPSU/ HPW composite membranes observed in membranes of SPSU containing HPW 7:3 and 5:5 in (w:w).

to symmetric stretching of SO_3 observed at 1 029 cm^{-1} for pure SPSU was shifted to 1 023 cm^{-1} in the presence of HPW. The high intensity of bands at 816 cm^{-1} for both SPSU/HPW composites seem to be associated to symmetric stretching band of edge-shared octahedral, W–Oe–W of HPW shifted due the interactions with the sulfonated component.

Specific Interactions between Sulfonated Polymer and Benzimidazole Derivatives

The protonation of imide raises electron density on carbon of the heterocycle, shifting and intensifying the band of ring vibration C–N at 1 602–1 622 cm^{-1} and also intensifying the band of aromatic C–C at 1 585 cm^{-1}[10] as observed in Figure 4.

Specific Interactions between Benzimidazole Derivatives and HPW Particles

The sharp peak centered at 3 412 cm^{-1} was attributed to the stretching vibration of isolated none hydrogen bonded to N–H group of $BBIzC_4$ and the broad peak approximately located between 3 100 and 3 670 cm^{-1} was assigned to the stretching vibration of the N–H groups involved in hydrogen bonding with hydrated water molecules and hydronium molecules $H_5O_2^+$ present in HPA.[10]

Higher absorbance intensities are observed mainly in peak P–O stretching at 1 077 cm^{-1}, $W{=}O_t$ terminal oxygen at 985 cm^{-1} and $W–O_e–W$ symmetric stretching band of corner-shared octahedral at 885 cm^{-1}, besides little shifts were observed to higher frequency, all these aspects suggested that cited groups interact at the same time within N–H of $BBIzC_4$ (Figure 5).

Stability to Water at High Temperature, Water Uptake and HPW Extraction

The stability of composite membranes was observed in water uptake and in water vapor tests. The loss of weight means dissolution of membrane in water and so characterizes the poor stability of the sample. Table 1 presents qualitative results of stability test. It shows that sulfonation degree (SD) of SPSU is restricted to 70%. This table also shows an increasing of the stability of SPSU/HPW membrane with the addition of BIz derivatives specially $BBIzC_4$. Figure 6 and 7 are in accordance with these described behaviors. High values of SD decrease the stability of composite membranes (Figure 6). Figure 7 shows high water caption in SPSU/HPW membranes. The addition of $BBIzC_4$ reduced the water uptake improving the stability of membrane. So, $BBIzC_4$ promoted a reinforcement of composite membranes [in Figure 7(a)]. The effect of decreasing water uptake of composite membranes containing HPW, with the $BBIZC_4$ content can be observed in Figure 7(b).

The HPW weight loss is presented in Table 2. These data show the benefit of

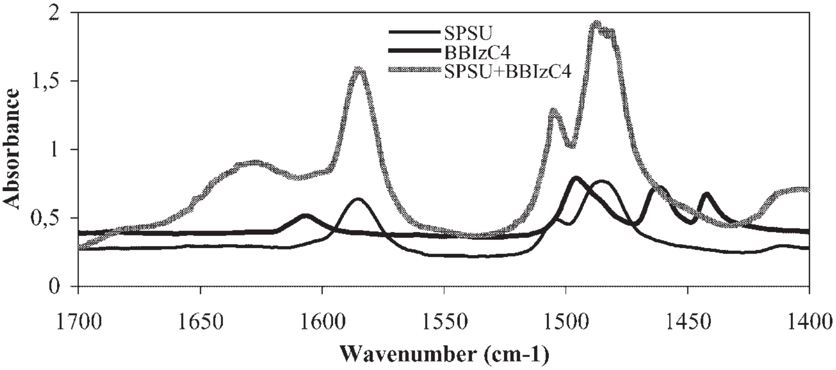


Figure 4.
Infrared spectra of pure SPSU, pure BBIzC4 and SPSU/$BBIzC_4$ composite.

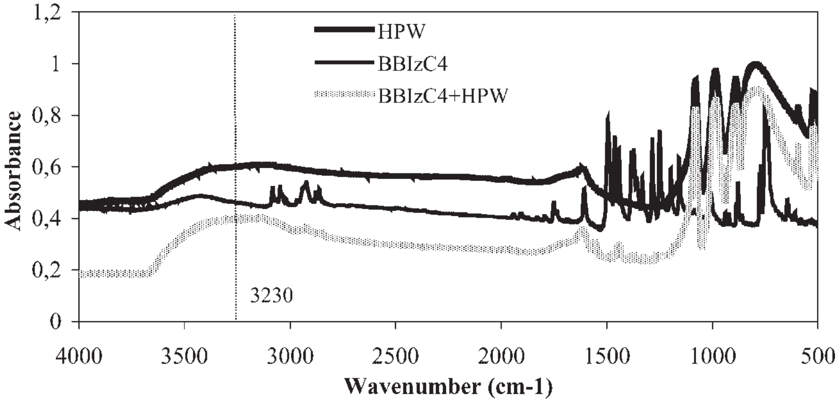


Figure 5.
Infrared spectra of pure $BBIzC_4$, pure HPW and BBIzC4 + HPW blend.

$BBIzC_4$ in retaining HPW particles inside the composite membranes.

Morphology

The HPW dispersion was analyzed by X-ray diffraction (XRD). The diffractogram is presented in Figure 8. Basal reflection of HPW ($H_3PW_{12}O_{40} \cdot 6H_2O$) is found at $2\theta_{210} = 10.3^\circ$, $d = 8.58$ Å [Dias, Dias and Kob (2001)].

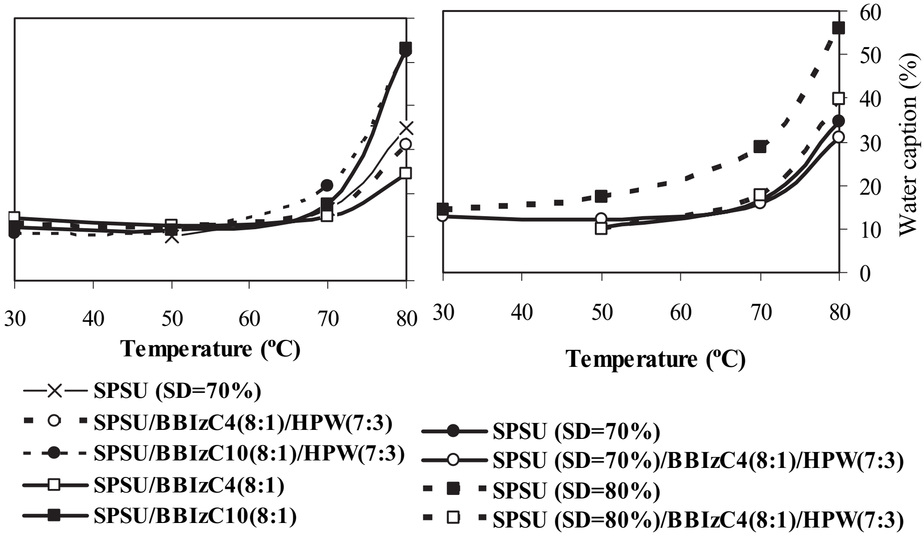
HPW presented peak in the range of $2\theta = 4–12^\circ$, while SPSU had no peak in this range. Practically no evidence of the crystalline HPW Keggin structure is found in the XRD spectra of SPSU/BBIZC4 (8:1)/HPW(7:3) composite. This suggests that HPW can be dispersed at the molecular level thus losing its own crystal structure and long-range order. If this premise is correct, the order of addition of components of composites has important role in dispersion process, as well as mixing in two steps achieve better dispersion than one step, which more groups of HPW could be exposed to form specific ionic interactions. However, the best dispersion was obtained when solution of [SPSU + BBIzC4] was mixed first and then the solution of HPW was added on, so the dispersion of particles of HPW was followed by disappearance of peak of HPW in diffractogram.

The morphology of two composite membranes can be observed in micrograph of SEM illustrated in Figure 9. These

Table 1.
Stability of membranes in water.

Samples	Water	Water	Vapor
	80 °C, 6 h	90 °C, 2 h	4.5 h
Mixing at once			
SPSU GS = 70%	R[a)]	—	NR[b)]
SPSU/HPW (7:3)	R	NR	NR
SPSU/$BBIzC_4$ (6:1)/HPW (7:3)	R	R	R
SPSU/$BBIzC_4$ (8:1)/HPW (7:3)	R	R	R
SPSU/$BBIzC_4$ (12:1)/HPW (7:3)	R	R	R
SPSU/$BBIzC_4$ (8:1)/HPW (7:3)	R	NR	NR
Mixing in two steps			
SPSU GS = 80%	R	—	NR
[SPSU + $BBIzC_4$(8:1)] + [HPW(7:3)]	R	R	NR
[SPSU + HPW(7:3)] + [$BBIzC_4$(8:1)]	R	R	NR
[$BBIzC_4$(8:1) + HPW(7:3)] + [SPSU]	R	R	NR

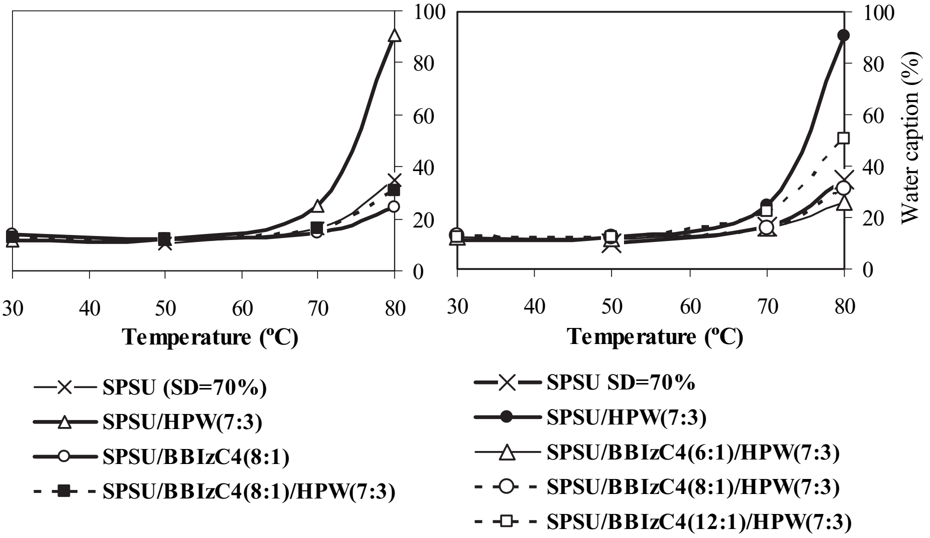
a) R—Resistant.
b) NR—Non-resistant.



(a) (b)

Figure 6.

Curves of water caption with temperature: (a) for pure SPSU and SPSU composites containing different chain length as spacer in BBIzDs components; (b) for pure SPSU and SPSU composites at different sulfonation degrees (SD = 70 and 80%).



(a) (b)

Figure 7.

Curves of water caption with temperature: (a) for pure SPSU and different SPSU composites (SD = 70%); (b) for pure SPSU and SPSU composites at different BBIzC4 content.

Table 2.
HPW weight loss in water.

Samples	Water	Water vapor
	80 °C, 14 h	4.5 h (UV λ = 190 nm)
SPSU/HPW(7:3)	15	—
SPSU/BBIzC$_4$(6:1)/HPW(7:3)	2	17.5
SPSU/BBIzC$_4$(8:1)/HPW(7:3)	3	11.7
SPSU/BBIzC$_4$(12:1)/HPW(7:3)	7	21.8

Data of weight loss in %.

micrographs confirm the good dispersion of components for membrane [SPSU + BBIzC4] + HPW prepared in two steps. The micrograph of this membrane suggests dispersion in nanometer scale. Both micrographs presented in Figure 9 have the composition [SPSU/BBIzC$_4$(8:1)/HPW(7:3)]. The difference is just the way to prepare the mixture.

Conductance

Outstanding results were achieved in the membrane with composition SPSU/BBIzC$_4$ (12:1)/HPW(7:3). The conductivity value at 70 °C was twofold of the Nafion117 in the same conditions, and threefold at higher temperatures. The high value was favored by higher swelling about 300%, when the sample was left immersed in water for 20 h after the pre-treatment. Conductance is plotted versus temperature in Figure 10.

The high conductivity of the composite SPSU/BBIzC$_4$(12:1)/HPW(7:3) was obtained in detriment of dimension stability, once that the membrane swelled 300% in water. This shows the role of water on the conductivity in this system. The composite that had the best morphology and stability presented a gain in the conductivity level, comparatively to that similar, made in one step. The conductivity of composite membranes [SPSU + BBIzC$_4$(8:1)] + HPW(7:3) prepared in one step was 76 mS · cm^{-1}, the prepared in two steps was 118 mS · cm^{-1} and the conductivity of Nafion was 119 mS · cm^{-1}, at 80 °C (132 mS · cm^{-1} at 100 °C). At 110 °C the conductivities were 84 mS · cm^{-1} and 159 mS · cm^{-1} for the composites obtained in one and two steps respectively.

Conclusion

The use of BBIzC4 and HPW in sulfonated polymer to generate ionic crosslinks seems to be a promising way to improve membrane stability at higher temperature and promotes the reduction of leaking of HPW from the composite membrane. Looser nets

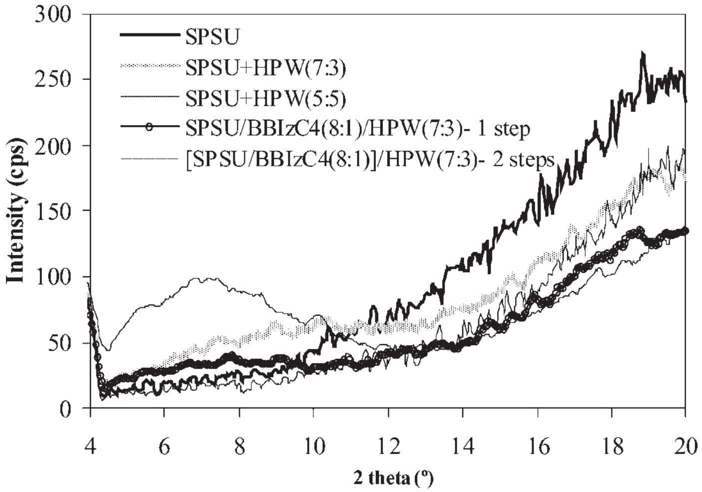


Figure 8.
XRD diffractogram of composite membranes.

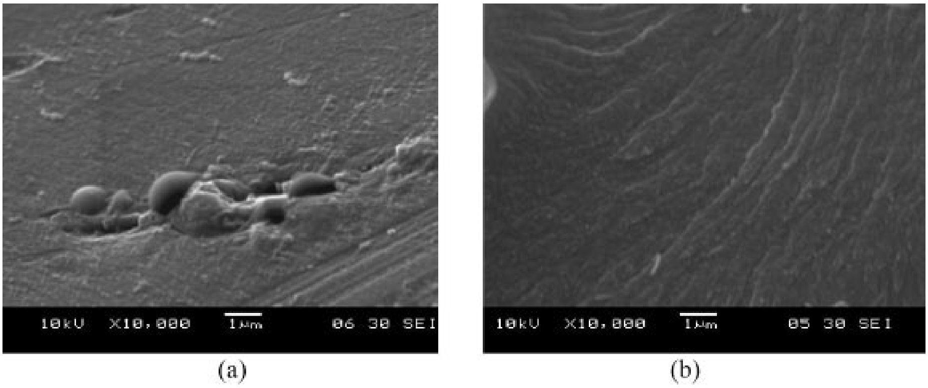


Figure 9.
SEM images of transversal section morphology for composite membranes (a) one step of mix: [SPSU + BBIzC4 + HPW] and (b) two steps: [SPSU + BBIzC4] + [HPW].

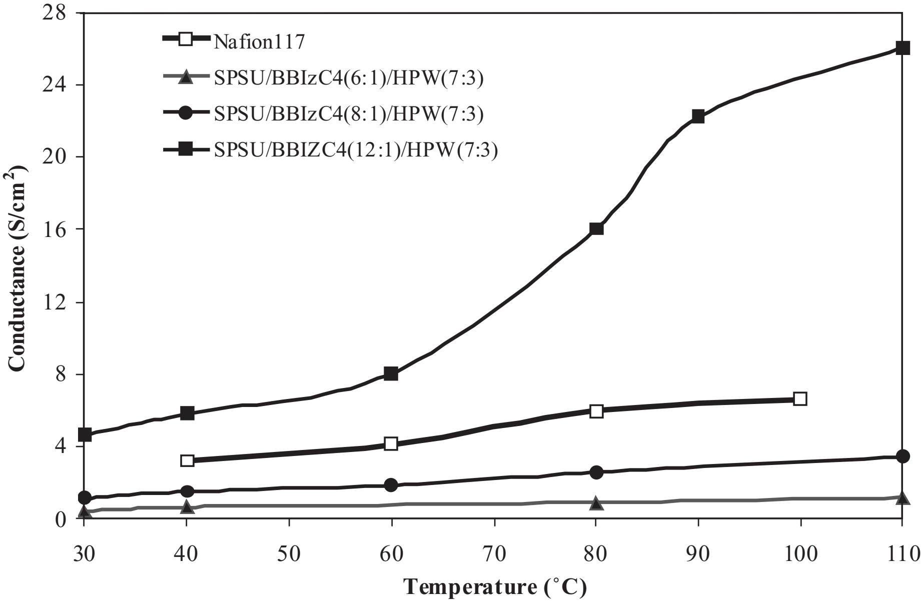


Figure 10.
Conductance of composite membranes SPSU/BBIzC4/HPW.

of ionic crosslinking allow higher water caption, which is the key to achieve high conductivity. The surprising results of conductivity for the composite with reduced content of BBIzC4 (in the proportion SPSU/BBIzD of 12:1 in equivalents) at elevated hydration level needs still to be best understood. A good compromise needs to be assumed between the water caption and the dimensional stability, by tailoring the components of composite, in order to optimize the conductivity and mechanical properties.

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