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Synthesis and characterization of novel hybrid polysulfone/silica membranes doped with phosphomolybdic acid for fuel cell applications

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A B S T R A C T

Novel proton conducting composite membranes based on sulfonated polysulfone (sPSU)/SiO₂ doped with phosphomolybdic acid (PMoA) were synthesized, and their proton conductivity in acid solutions was evaluated. The hybrid membranes were prepared by casting and the characterization by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X ray diffraction (XRD) confirmed the presence of the inorganic charges into the polymer. Thermal properties and proton conductivity were also studied by means of thermogravimetric analysis (TGA) and electrochemical impedance spectroscopy (EIS), respectively. The incorporation of the inorganic particles modified the thermal and mechanical properties of the sPSU as well as its proton conductivity. Taking into account that a compromise between these properties is necessary, the hybrid membrane with 2%SiO₂ and 20%PMoA seems to be a promising candidate for its application in proton exchange membrane in fuel cells (PEMFCs) operated at high temperatures.

Keywords:

Proton-exchange membrane fuel cell
Polysulfone
Silicon oxide
Heteropolyacid
Electrochemical impedance spectroscopy

1. Introduction

Nowadays, clean energy technologies play an important role in overcoming fossil fuel exhaustion and global pollution. Among these technologies, fuel cells are electrochemical energy systems that convert energy from a chemical reaction into electrical energy without emitting pollutants. In particular, the polymer fuel cells based on proton exchange membranes (PEMFCs) are of great importance in the automotive field because of its higher energy efficiency and no emission compared to the combustion engines [1]. Currently, the most commonly used polymer electrolyte in PEMFC is based on expensive perfluorinated membranes, such as Nafion[®], which present high proton conductivity, good mechanical strength and excellent stability. However, these membranes show several drawbacks since to ensure good proton conduction they must be fully hydrated, limiting their working temperature range below 80 °C and 100% relative humidity [2,3]. Moreover, this type of membrane exhibits high methanol permeability and high

cost of production, which limits its further application and future commercialization.

These limitations have led to research and develop different polymers as promising alternatives to improve fuel cell performance of the current perfluorosulfonic membranes. One research line involves the sulfonation of aromatic polymers with non perfluorinated backbone such as polyaryl ether ketone [4], polystyrene [5] as well as polybenzimidazoles [6]. Among these polyaromatic materials, polysulfone (PSU) is a commercially available polymer and well known for its excellent mechanical, thermal and chemical stability [7]. Hybrid organic inorganic nanocomposites have gained considerable attention because present improved properties such as swelling capacity, water retention or operating temperature, while maintaining mechanical properties [8–10]. In this line, there are several studies that reflect the improvement of performance of several polymers due to the incorporation of inorganic particles such as SiO₂ [11], TiO₂ [12] or zeolites [13]. Also, another inorganic fillers such as heteropolyacids like phosphotungstic (PWA), phosphomolybdic (PMoA), silicotungstic (SiWA) and silicomolybdic (SiMoA) acids related to the well known Keggin structure, have recently received most attention due to their good proton conductivities [14–17]. However, it is well known that heteropolyacids itself are water soluble and may be easily extracted during the operation of fuel cell, leading to the instability of the composite membranes. For this reason, the retention of heteropolyacid into polymer matrix

Abbreviations: sPSU, Sulfonated polysulfone; PWA, Phosphotungstic acid; PMoA, Phosphomolybdic acid; SEM, Scanning electron microscopy; FTIR, Fourier transform infrared; XRD, X-ray diffraction; TGA, Thermogravimetric analysis; EIS, Impedance spectroscopy technique; PEMFC, Proton-exchange membrane fuel cells; PSU, Polysulfone; σ_m , Membrane ionic conductivity; r_m , Membrane ionic resistivity
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appears as one of the most challenge in preparing heteropolyacid containing membranes. For this purpose, inorganic particles have been incorporated together these materials to immobilize them inside a polymer matrix [18]. Thus, the incorporation of SiO₂ nanoparticles showed that it is effective to reduce PWA leaching in sulfonated polysulfone nanocomposites membranes [19]. The aim of this work was the evaluation of novel proton conducting composite electrolyte based on hybrid polysulfone/SiO₂ membranes doped with PMoA as possible alternative for current used PEMFC. Furthermore, sPSU/SiO₂ membranes containing different amounts of SiO₂, were also prepared for comparison.

2. Experimental

2.1. Materials

The polymer used in the study was polysulfone Udel (PSU) with Mn=22,000. The solvents were trimethylsilyl chlorosulfonate (TMSCS, 99%), 1,2 dichloroethane (DCE) and N,N dimethylacetamide (DMAc). For the preparation of composites two inorganic compounds were used, pyrogenic silica (fumed silica, 99.8%) with an average particle size of 11 nm and surface area of 255 ± 15 m²/g, and commercial phosphomolybdic acid (H₃PMo₁₂O₄₀·xH₂O, PMoA). All of these reagents were purchased from Sigma Aldrich. Sulfonated product purification was carried out by adding ethanol (Panreac).

2.2. Sulfonation of polysulfone

Firstly, the sulfonation process was carried out in anhydrous conditions following the method described by Chao et al. [20]. Thus, a solution of polysulfone in DCE was prepared and purged with nitrogen for one hour. Then, a solution containing the sulfonating agent (TMSCS) and DCE was slowly added drop by drop under magnetic stirring. The resulting mixture was additionally stirred for 24 h at room temperature. Once the sulfonation process was completed, the product obtained was poured into ethanol. Finally, the precipitated polymer was filtered and washed with distilled water up to neutral pH.

2.3. Composite membrane preparation

All membranes were prepared by casting procedure. A solution consisting of 5 wt% of sPSU in DMAc was stirred for 2 h at room temperature and subsequently was filtered. For the preparation of sPSU/SiO₂ membranes, different amounts of SiO₂ nanoparticles (0.5, 1, 2, 4 and 6 wt%) were added and the resulting mixture was stirred for 1 h at 60 °C. Afterward, the solutions were placed in an ultrasonic bath at 60 °C for 1 h and finally they were magnetically stirred for an additional 1 h at room temperature. Subsequently, the solutions were filtered, added to a Petri dish and heated in order to remove the solvent.

On the other hand, for some SiO₂ doped membranes (2 and 4 wt%), the effect of the addition of the heteropolyacid was studied. In this case, different amounts of PMoA (10 and 20 wt%) were dispersed with SiO₂ in water. The resulting suspension was dried at room temperature and the obtained solid was crushed using an agate mortar with the aim to obtain a fine powder. After that, the preparation of sPSU/SiO₂/PMoA composite membranes was carried out by the same mixing and thermal procedure used in preparation of sPSU/SiO₂ membranes aforementioned. As result, thick membranes between 80 and 140 microns were obtained.

2.4. Methods

2.4.1. ¹H NMR analysis

The sulfonation degree of sPSU was estimated by means of liquid ¹H NMR [21]. The analysis was performed on a Bruker Avance DPX 300MHz spectrometer using dimethylsulfoxide (DMSO d₆) as the solvent and tetramethylsilane (TMS) as internal reference.

2.4.2. SEM

The morphology of prepared membranes was analyzed with a Philips XL30 scanning electron microscope operating at 15 kV and equipped with a backscattered electron detector (BSE) and an energy dispersive analyzer (EDAX 4i). In order to examine the cross sections, the membrane samples were fractured cryogenically by immersion into liquid nitrogen and then coated with gold.

2.4.3. Infrared spectroscopy

Infrared characterization was performed using a Perkin Elmer Spectrum GX Instrument (resolution 4 cm⁻¹) in the range of 4000 400 cm⁻¹. The infrared spectra of SiO₂ and PMoA powder were recorded in KBr pellets and composites membranes slices of about 50 microns of thickness were used for the analysis.

2.4.4. X ray diffraction

X ray diffraction (XRD) patterns were recorded on a Philips X'Pert diffractometer equipped with a CuKα radiation source. This instrument has a (θ/2θ) Bragg Brentano geometry and is equipped with a curved graphite monochromator. The 2θ range analyzed was 5 55° with a step scan of 0.02° and a counting time of 2.8 s per step. Finally, the experiments were carried out at an excitation voltage of 40 kV and a current of 40 mA.

2.4.5. PMoA extraction

To evaluate the ability of silica nanoparticles to reduce the leaching of heteropolyacid in water, we have estimated the extraction of PMoA by means of UV vis spectroscopy. The study was carried out in a Jasco V 650 UV vis spectrophotometer. The sPSU/SiO₂/PMoA composites membranes were immersed in deionized water at room temperature for 72 h. After that, the solvent with extracted PMoA was placed into a quartz cell and then measured at 253 nm, which correspond to the maximum absorption of the studied heteropolyacid. Thus, the PMoA extraction (%) was determined by using the following equation [19]:

$$\text{PMoA}_{\text{extraction}}(\%) = \frac{C \times V}{M_{\text{PMoA}}} \times 100 \quad (1)$$

where C is the extracted PMoA concentration obtained from the concentration absorption graph.

2.4.6. Water uptake

Given that the water content affects the proton conductivity and mechanical properties of the membranes, the water uptake percentage was determined. For this purpose, the membranes were dried in a vacuum oven at 60 °C for 24 h until constant weight. Each dried membrane was subsequently weighed (W_{dry}) and soaked in distilled water at room temperature for 72 h. After that, the membranes were taken out and immediately weighed (W_{wet}) after removing the surface water. Water uptake was calculated using the following equation:

$$W_{\text{uptake}}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2)$$

where W_{wet} and W_{dry} are the weights of the wet and dry membrane, respectively.

In case of the sPSU/SiO₂/HPA membranes, the measure of the water uptake values was calculated taking into account the loss of HPA produced during the immersion in water. Thus, the loss mass of this component was considered in the obtained W_{dry} values.

2.4.7. Thermogravimetric analysis

Thermogravimetric experiments were performed in a Perkin Elmer TGA1 analyzer from 30 °C to 900 °C at a heating rate of 10 °C/min in air atmosphere. The initial sample weight was approximately 8 mg.

2.4.8. Mechanical properties

Uniaxial tensile tests were carried out at room temperature. The 5 mm × 10 mm samples were tested to failure at a crosshead speed of 0.5 mm/min in a Universal Testing Machine (Shimadzu model AG 1) with an operating load cell of 1 kN. The number of samples tested for each membrane was at least three. Prior to the measurements, the membranes were stabilized in distilled water at 50 °C for 3 h.

2.4.9. Ionic conductivity

The conductivity of the membranes was determined by means of electrochemical impedance spectroscopy technique (EIS). The characterization was carried out using a cell constituted by two compartments separated by two O rings where membrane was sandwiched [22]. The measurements were performed with the membrane samples in contact with aqueous HCl solutions at different concentrations ($4 \times 10^{-4} \text{ M} \leq c \leq 0.1 \text{ M}$) at room temperature. Before testing, the membranes were immersed for at least 12 h in a solution of the appropriated HCl concentration.

The impedance system consisted of a frequency response analyzer (Solartron 1260) and electrochemical interface (Solartron 1287). The measurements were carried out between 10^{-1} Hz and 1 MHz and an oscillating voltage of 10 mV. Tests were also performed at different temperatures (30–80 °C) and for this purpose, a Binder KMF 115(E5.2) temperature chamber was used. In this case, the conductivity was measured after 15 min of equilibration at each temperature.

The proton conductivity was calculated from the following equation: $\sigma = d/RS$, where d and S are the thickness and the surface area of the sample, respectively. The resistance of the membrane (R) was estimated from the Nyquist plot and considering the corresponding geometric factors.

3. Results and discussion

3.1. Sulfonation degree

The sulfonation reaction was evaluated by means of ¹H NMR spectroscopy. Fig. 1 shows the chemical structure as well as the ¹H NMR spectra corresponding to polysulfone (PSU) and sulfonated polysulfone (sPSU).

The proton resonance in sPSU spectra which appear at ~7.7 ppm was assigned to the proton adjacent to the incorporated acid group (SO₃H). Thus, the presence of this peak confirmed the success of the sulfonation process. The sulfonation degree of sPSU was calculated using a modified formula reported elsewhere [23], taking into account that the polysulfone might be sulfonated up to two sulfonic group per monomer unit. Thus, a sulfonation degree of 30% was obtained.

3.2. Membrane morphology

With the aim to study the dispersion of the inorganic particles in the composite membranes, SEM micrographs of the cross

section of the studied membranes were obtained. The SEM images and the EDS analysis of the silica doped polysulfone membranes indicated a uniform and homogeneous distribution of inorganic oxide up to 4 wt% through the polymer matrix (Fig. 2a–c). It can be observed that no cavities are present, showing a good adhesion between inorganic particles and the polysulfone. However, for the highest concentration (6 wt%), the SEM micrographs showed evidence of agglomeration of SiO₂ nanoparticles on the bottom surface of the membrane (Fig. 2c). This fact might be related with a silica migration by gravity toward the membrane bottom surface produced during the membrane preparation. On the other hand, the sPSU/SiO₂/PMoA composite membranes showed uniform dispersion of the inorganic solids throughout the membrane without presence of agglomerates (Fig. 2d).

3.3. FTIR analysis

The FTIR spectra of inorganic materials, PSU, sPSU and sPSU/SiO₂/PMoA membranes are shown in Fig. 3.

The SiO₂ powder showed a characteristic band at 805 cm⁻¹ associated to the symmetric Si–O–Si stretch, at 1090 cm⁻¹ and 1220 cm⁻¹ corresponding to the asymmetric Si–O–Si stretch and another one at 960 cm⁻¹ characteristic of the Si–OH stretch (Fig. 3a) [24,25]. On the other hand, the FTIR spectrum of PMoA showed the characteristic bands of this Keggin type heteropolyacid. Thus, the vibration modes at 1065, 960, 869 and 782 cm⁻¹ correspond to the asymmetric stretching vibrations of P–O, Mo=O, Mo–O_b–Mo and Mo–O_c–Mo, respectively [26–28].

Regarding to the membranes, the spectrum of sPSU (Fig. 3b) showed the characteristic peak at 1024 cm⁻¹ which are assigned to the symmetric stretching of the sulfonate group [29]. The presence of this signal, which is not shown on PSU spectrum, confirmed the success of the sulfonation reaction. On the other hand, although the peaks of polysulfone are masking some vibration modes of SiO₂ and PMoA, it was possible to observe additional absorption bands associated to these materials on sPSU/SiO₂/PMoA composites (Fig. 3b). Also, it can be noticed that the band assigned to the edge shared octahedral of Keggin unit (Mo–O_b–Mo) at 869 cm⁻¹ in pure PMoA, was shifted to higher wavenumber in the doped membrane, around to 907 cm⁻¹. This frequency shift was attributed to the interaction of oxygens of PMoA with hydroxyl groups from hydrated oxide structure, which reflects the ability of the silica oxide to retain the PMoA into polymer matrix [27], improving the stability of this material inside the hybrid material. Another consequence of this interaction is the appearance of several and broader bands in the 800–900 cm⁻¹ range. It is worth to note that the peak at 1024 cm⁻¹ of sPSU was slightly shifted to higher wavenumber when the SiO₂ were incorporated, indicating weak interactions between the inorganic particles and the sulfonated group, which probably corresponds to hydrogen bonding. This effect was more pronounced with the subsequent addition of heteropolyacid.

3.4. XRD analysis

The X Ray diffraction patterns of inorganic powders as well as sPSU and sPSU/SiO₂/PMoA membranes are illustrated in Fig. 4.

Polysulfone membrane and SiO₂ showed a very broad peaks located at $2\theta = 18.5^\circ$ and 22° respectively, typical of very low crystalline materials [30,26]. On the other hand, the XRD pattern of pure phosphomolybdic acid showed intense peaks due to its higher crystallinity as reported elsewhere [31]. In the case of sPSU/4%SiO₂/10%PMoA composite, the shoulder at 26° (2θ) was due to the presence of highly dispersed heteropolyacid into the polymer matrix. On the other hand, the signal associated to SiO₂ was

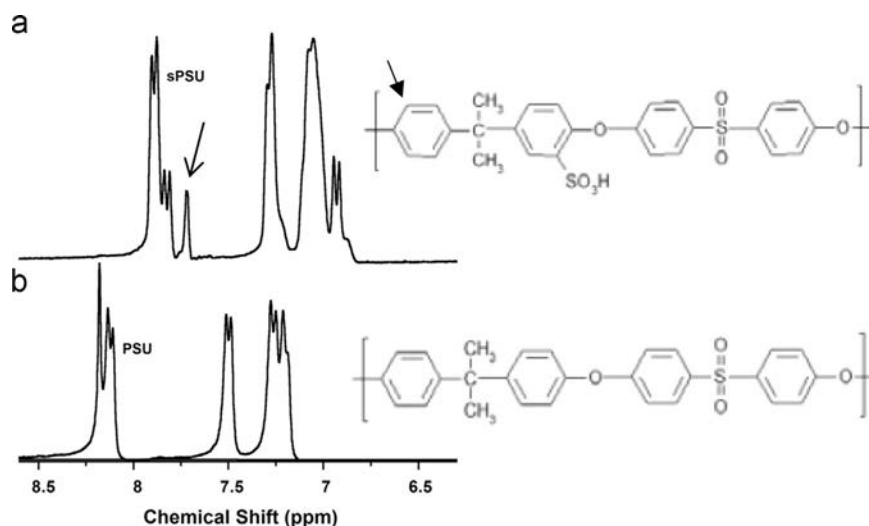


Fig. 1. Chemical structures and H-NMR spectra of polysulfone (PS) and sulfonated polysulfone (sPSU).

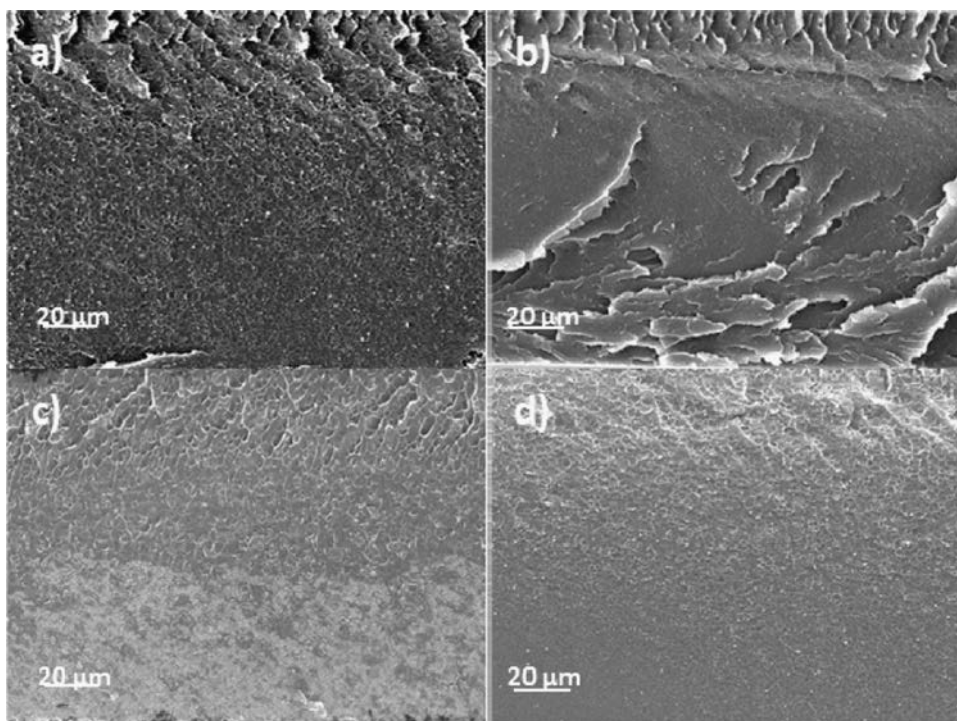


Fig. 2. SEM micrographs (x1500) of the cross section of nanocomposites membranes: (a) sPSU, (b) 1 wt% SiO₂ doped sPSU, (c) 6 wt% SiO₂ doped sPSU and (d) 1 wt% SiO₂-10% PMoA doped sPSU.

difficult to appreciate due to its amorphous character as well as its low concentration into the composite.

3.5. Heteropolyacid extraction

The extracted percentages of PMoA after water treatment from sPSU/10PMoA composites membranes with different silica content are shown in Table 1. The results showed that, in spite of the potential loss of this heteropolyacid in water, the introduction of silica content up to 1 wt% leads to PMoA stabilization within polymer backbone. However, this stabilization decreases when SiO₂ content is above 2 wt%.

Similar results were reported in the study by Zhang et al. [19], where they observed that SiO₂ content below 2% stabilizes the PWA within the sulfonated polysulfone backbone. In this case the

HPA extracted were lower due to the lower solubility of PWA in water in comparison with that of PMoA.

3.6. Water uptake

The obtained values of water uptake percentages for the different studied membranes are shown in Fig. 5. The results showed that the incorporation of the nanoparticles of SiO₂ produced an increase of the water absorption in comparison with the pristine sPSU. Similar result has been also reported by other authors using silica gel nanoparticles and it was associated with the hydrophilic nature of the silica due to the presence of Si OH groups in the composite [19] which can form bonding with H₂O molecules [32].

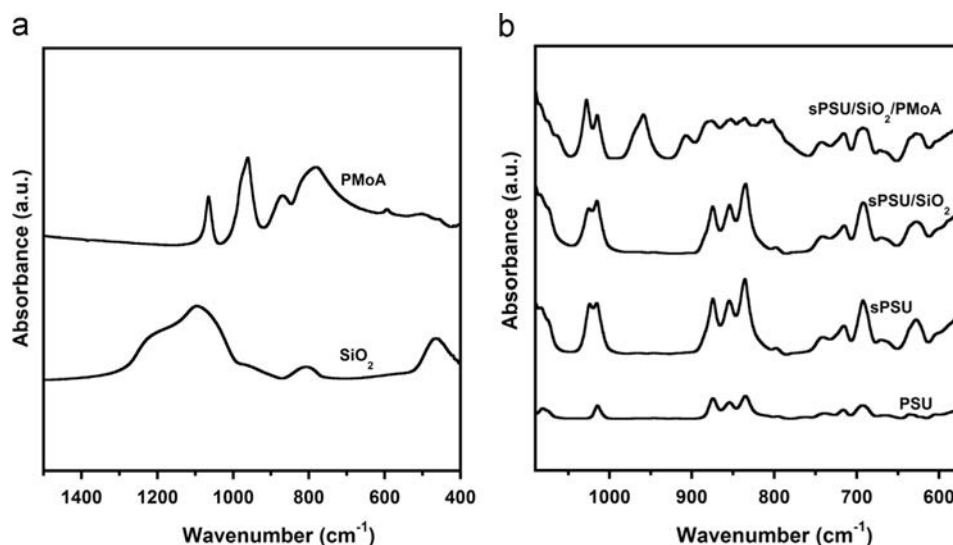


Fig. 3. FTIR spectra of (a) PMoA and SiO₂ powders (b) PSU, sPSU and doped sPSU membranes.

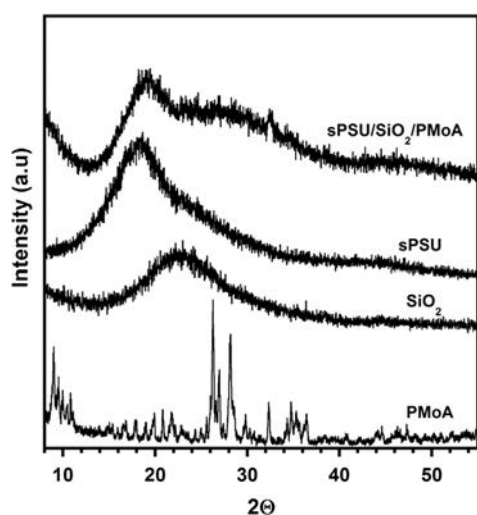


Fig. 4. XRD patterns of inorganic powders and sPSU and sPSU/4%SiO₂/10%PMoA membranes.

Table 1

PMoA extraction of different sPSU/10PMoA composite membranes in water.

Membrane	SiO ₂ (%wt)	PMoA extraction (%)
sPSU/10PMoA	0	18.0
sPSU/0.5SiO ₂ /10PMoA	0.5	9.2
sPSU/1SiO ₂ /10PMoA	1	8.8
sPSU/2SiO ₂ /10PMoA	2	13.2
sPSU/4SiO ₂ /10PMoA	4	33.1

The water uptake of the composites containing SiO₂/PMoA particles was lower in comparison with that SiO₂ doped membranes. Similar results were obtained in the study of Smitha et al. [16] with phosphotungstic acid, where the reduction of the water uptake of the polysulfone was attributed to the reduction of water absorption sites due to interactions between the heteropolyacid and the polymer, as demonstrated before in FTIR spectra.

3.7. Thermal analysis

Firstly, attention was paid to the thermogravimetric behavior of sPSU/SiO₂ composite membranes. Decomposition curves of all

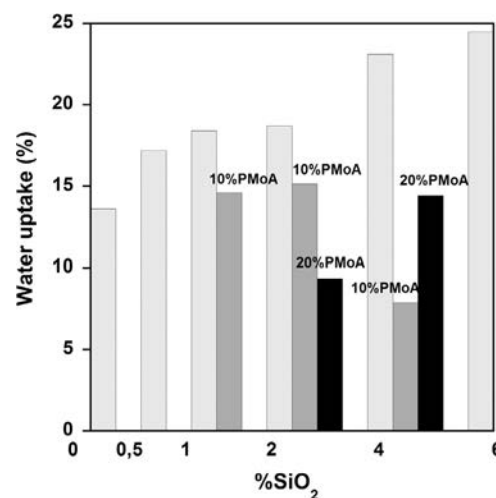


Fig. 5. Water uptake (%) of sPSU and composite membranes.

studied membranes exhibited the same pattern as is shown in Fig. 6a. The preliminary mass loss produced between 50 °C and 250 °C, corresponds to the evaporation of free water or desorption of water bonded to the hydrophilic sulfonic groups [33]. After that, in the range of 280–450 °C, the sample mass gently decreased due to the desulfonation process, which involves evolution of SO₂ and SO gases. The weight loss produced during this temperature range is critical due to its relation with the ion exchange properties of the composites [34]. On the other hand, it can be seen a slight enhancement in thermal stability of these sulfonic acid groups due to the incorporation up to 2 wt% of SiO₂ nanoparticles. Thus, the maximum degradation temperature corresponding to desulfonation process was 332 °C and 345 °C for sPSU and sPSU/2SiO₂, respectively. The final weight loss, which started at 450 °C, is attributed to the polymer backbone decomposition. In this case, the SiO₂ doped membranes with less than 4 wt% showed higher decomposition temperature due to the presence of the silica nanoparticles. The shift of this temperature can be attributed to the interaction of this inorganic oxide and polysulfone which limits the movements of polymer chain segments.

The sPSU/SiO₂ composite membranes containing inorganic heteropolyacid showed lower weight loss than sPSU/SiO₂ in the temperature range associated to elimination of absorbed water (Fig. 6b). Thus, at 150 °C a weight loss of ~6%, 4% and 2% for sPSU

2%SiO₂, sPSU/2%SiO₂/10%PMoA and sPSU/2%SiO₂/20%PMoA was obtained, respectively. Also, the onset temperature of the decomposition of sPSU backbone was lower in the case of sPSU/2%SiO₂/20%PMoA than the sPSU/SiO₂, indicating that this inorganic acid can accelerate the degradation of the polymer. Furtado and Gomes [35] showed that the incorporation of tungstophosphoric acid into bisphenol A polysulfone produced an increase of main chain degradation of the polymer. This effect was assigned to the presence of radicals originated from the decomposition of the inorganic acid. Finally, the residual mass above 750 °C is related to PMoA content. To sum up, all the synthesized membranes showed adequate thermal stability for fuel cell applications at temperatures below 100 °C.

3.8. Mechanical properties

The tensile strength and % elongation at break of all studied membranes are shown in Table 2.

The sPSU/SiO₂ membranes exhibited higher strength at break than the sulfonated polymer up to 4 wt% SiO₂. This fact shows that SiO₂ particles act as reinforcing agents for very low amount of particles and can be related with an interaction between SiO₂ and sulfonated matrix which results in the formation of crosslinked network within the polymer matrix. This interaction produces an enhance of the energy of breaking down of the polymer main chains [12]. At the highest concentration, the excessive oxide content produced a weakness of both properties tensile strength and % elongation of sPSU [19]. This could be related to the heterogeneous microstructure of this membrane.

The decrease on the elongation at break of sPSU at the higher concentrations of SiO₂ nanoparticles (> 2 wt%) was related to the brittle nature of the composite due to the incorporation of the filler and the formation of SiO₂ nanoparticles clusters which results in a restriction of ductile matrix deformation. These results are in agreement with the studies that show a loss of flexibility of polymer due to the incorporation of inorganic particles [36].

On the other hand, the results showed that the incorporation of PMoA produced a decrease in the tensile strength, being this effect

less pronounced at higher SiO₂ content. However, sPSU/SiO₂/20% PMoA membranes exhibited higher elongation at break in comparison with sPS/SiO₂ composites. Thus, sPSU/4%SiO₂ composites showed around 68% increase in % elongation at break due to the addition of 20 wt% PMoA. In the study performed by Genova et al. [37], tensile test shows an improvement of mechanical properties of phosphoantimonic acid filled sPSU membranes. However, Smitha et al. [16] observed a reduction in the elongation at break of polysulfone with increasing concentration of phosphotungstic acid (> 40% PWA). This difference in the mechanical property might be associated with the heteropolyacid content and the homogeneity of the dispersion.

3.9. Ionic conductivity

The electrical characterization of the studied membranes was performed by electrochemical impedance spectroscopy. The resistance values were obtained from the intercept on the real axis at the high frequency end of the Nyquist plot (Fig. 7a).

All spectra consisted of a semicircle (Fig. 7a), which was associated to the membrane capacitance (or constant phase element of the membrane) acting in parallel with its resistance. The size of this semicircle changes with the HCl concentration of the solution. Also, the fact that semicircle did not intercept the origin of the graph, showed the existence of a resistive element which should be related to the electrolyte solution. The experimental data of the studied membranes were fitted to different equivalent circuits, obtaining the best fit to that shown in the inset of Fig. 7a. R₁ is associated with the resistance of the electrolyte solution and the distance between electrodes, R₂ represents the ionic resistance of the membrane and CPE is assigned to the geometric capacitance of the membrane.

As expected, the resistivity associated to the membrane decreased as HCl concentration increased in all studied concentration range (Fig. 7b) showing a possible dependence of this parameter with the electrolyte solution embedded in the polymer matrix [30]. This behavior was observed in all membranes of this study.

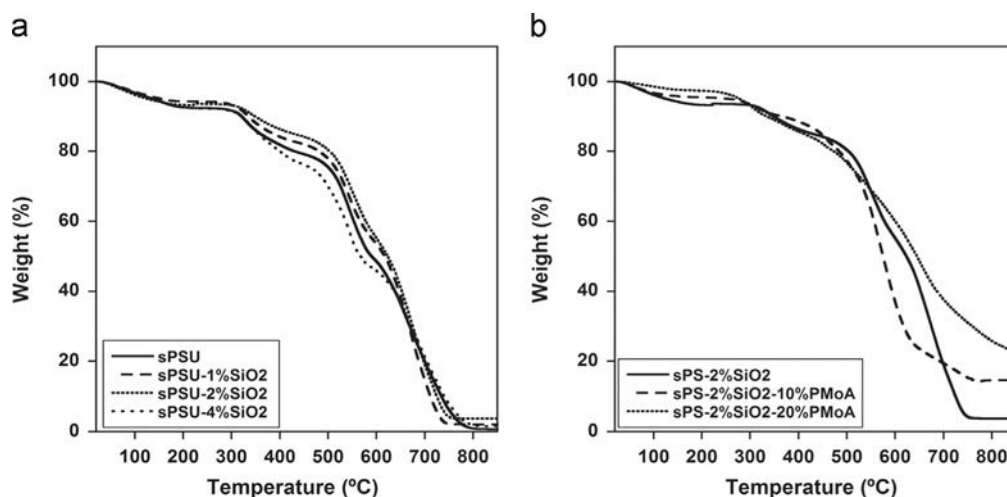


Fig. 6. Decomposition curves of (a) silica doped sulfonated polysulfone and (b) SiO₂/PMoA sulfonated polysulfone.

Table 2
Tensile strength and % elongation at break of sPSU and sPSU/SiO₂ and sPSU/SiO₂/PMoA composite membranes. The deviation standard of the three tests is also included.

Membrane	sPSU	2SiO ₂	4SiO ₂	6SiO ₂	2SiO ₂ /10PMoA	2SiO ₂ /20PMoA	4SiO ₂ /10PMoA	4SiO ₂ /20PMoA
Tensile Strength (MPa)	26.5 ± 4.8	41.7 ± 6.2	31.6 ± 3.9	18 ± 2	25.2 ± 1.6	21.0 ± 2.1	21.6 ± 5.0	26.9 ± 0.7
Elongation at break (%)	18.8 ± 4.5	21.9 ± 1.3	15.7 ± 3.3	9.2 ± 0.2	20.2 ± 6.0	24.8 ± 2.8	12.7 ± 1.7	26 ± 4

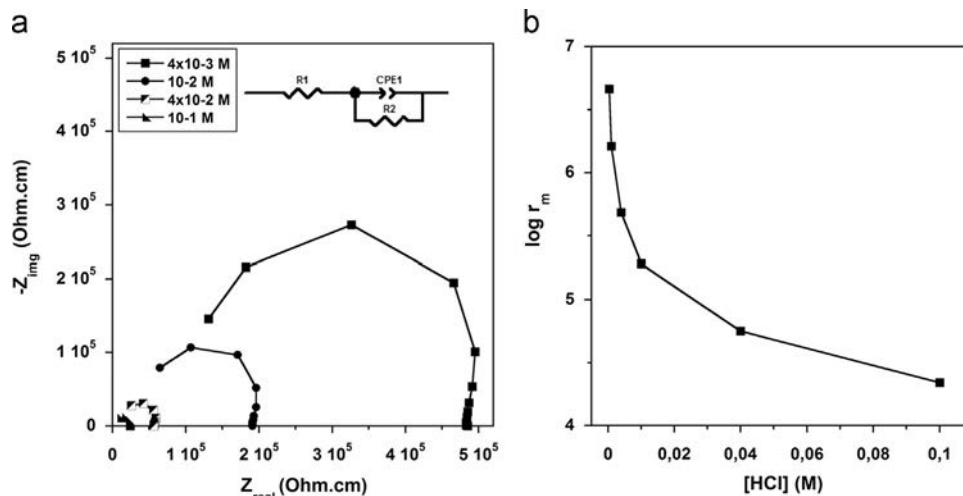


Fig. 7. (a) Complex impedance plot of sPSU/2%SiO₂/10%PMoA composite at different HCl concentrations. The equivalent circuit used for fitting is displayed in the inset and (b) ionic resistivity of this membrane for different HCl solutions.

The conductivity of sPSU and different sPSU/SiO₂ composite membranes measured at room temperature is shown in Fig. 8. All membranes showed conductivity values of the same order of magnitude than Nafion (1.36×10^{-6} and 2.09×10^{-6} S/cm for Nafion 112 and sPSU, respectively), which has been taken as reference.

The results pointed out that the sPSU/SiO₂ membranes slightly improved their ionic conductivity as the amount of SiO₂ increases up to 4 wt% (Fig. 8). This fact has been related with the hydrophilic nature of silica nanoparticles and the ability of this material to retain water even at high temperature as reported elsewhere [36]. The decrease on the conductivity for the highest values of SiO₂, may be related to the high heterogeneity of this membrane, where the most of the SiO₂ was accumulated on one side of the membrane (see Fig. 2d).

On the other hand, the incorporation of the heteropolyacid produced a decreased of the conductivity of sPSU/SiO₂ membranes at room temperature (Table 3). This fact can be correlated with the decrease of the water uptake observed previously (Fig. 5).

However, a different trend was observed when the temperature was increased. The proton conductivity values of sPSU/SiO₂/PMoA were close or even greater than sPSU/SiO₂ membranes at high temperature range (Fig. 9). Thus, for a concentration of 2 wt% SiO₂, the incorporation of 10% PMoA showed similar conductivity than PMoA free composite at 80 °C (Fig. 9a). Furthermore, when the concentration of PMoA is increased to 20 wt%, the conductivity of the sPSU/2SiO₂/PMoA composite becomes higher in comparison with the SiO₂ doped membrane above 50 °C. This increase of the conductivity showed for the composites is the results of synergic effect, that is, the higher water uptake provided for the silica oxide as well as acidity of the heteropolyacid particles. A similar behavior was observed for the sPSU/SiO₂/PMoA composites with 4 wt% SiO₂ (Fig. 9b). These results are in the line of the obtained by Zhao [19], where it was observed that the proton conductivity of Nafion/silicon oxide/PWA composite membranes was lower than Nafion membrane at low temperatures and found to be higher to that the Nafion and Nafion/SiO₂ at high temperatures.

The activation energies of sPSU, sPSU/SiO₂ and sPSU/SiO₂/PMoA were calculated from the linear fitting of data of Fig. 9 (Arrhenius plot). The obtained values were 9.1, 11.8, 16.6 and 20.7 kJ/mol corresponding to sPSU/2 wt% SiO₂, sPSU/4 wt% SiO₂, sPSU/2 wt% SiO₂/10%PMoA and sPSU/2 wt% SiO₂/20%PMoA, respectively. The low values obtained for the activation energies pointed that the predominant mechanism of proton transport in the studied

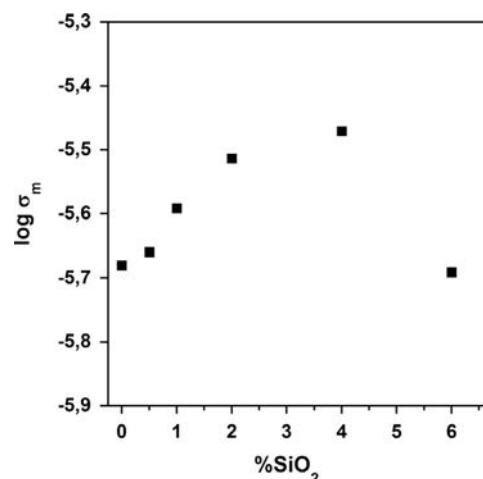


Fig. 8. Ionic conductivity of sPSU and sPSU/SiO₂ membranes measured at room temperature ([HCl] 4×10^{-3} M).

Table 3

Ionic conductivity obtained for sPSU/SiO₂/PMoA hybrid membranes measured at room temperature ([HCl] 4×10^{-3} M).

Membrane	1SiO ₂	1SiO ₂ / 10PMoA	2SiO ₂	2SiO ₂ / 10PMoA	2SiO ₂ / 20PMoA	4SiO ₂ / 10PMoA
$10^6 \times \sigma_m$ (S cm ⁻¹)	2.56	1.76	3.06	1.67	2.15	2.06

membranes was the vehicular mechanism [38]. The higher activation energies obtained for the composites membranes in comparison with the neat polysulfone could be attributed to a change on the proton transport mechanism.

4. Conclusions

In this study, SiO₂ and PMoA were used as proton inorganic additives to prepare polysulfone nanocomposites as possible polymer electrolytes for fuel cells. The composites were prepared using solvent casting technique. The presence of inorganic particles into the polymer as well as the interactions between them and

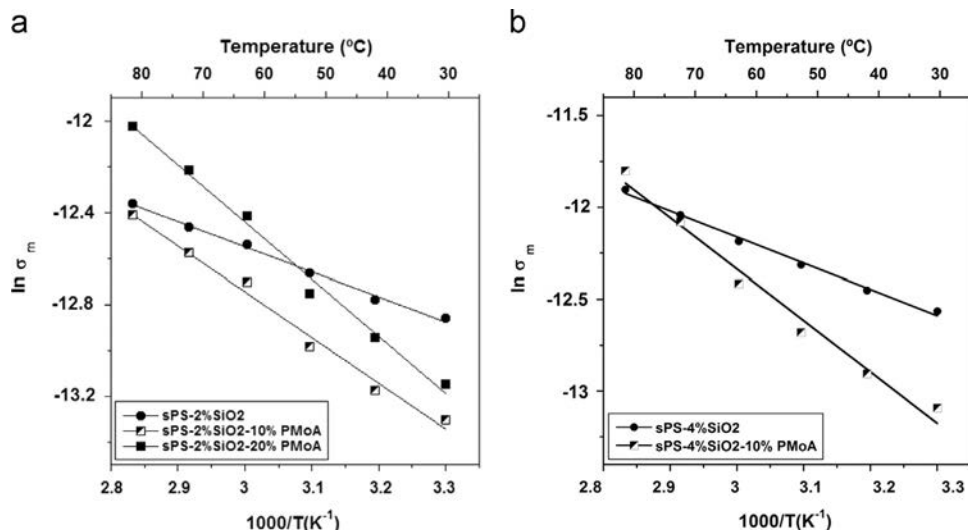


Fig. 9. Arrhenius plot for proton conductivity corresponding to sPSU/SiO₂ membranes and sPSU/SiO₂/PMoA composites.

the sulfonated polysulfone were confirmed by SEM, FTIR spectroscopy and XRD. In addition, interactions between the inorganic particles resulted in the retention of the heteropolyacid in the polymer matrix.

In general, the incorporation of inorganic material produced a decrease of both, the tensile strength and % elongation at break of the composite membranes. However, the addition of 20% PMoA improved the ductile behavior of the composites for both studied sPSU/SiO₂ membranes. Also, the results pointed that the synthesized hybrid membranes show good thermal stability at temperatures up to 200 °C. On the other hand, the electrochemical study showed that the conductivity value at room temperature of sPSU was improved with the incorporation of SiO₂ nanoparticles, while sPSU/SiO₂/PMoA composites showed lower conductivity than SiO₂ doped membranes at room temperature. However, at higher temperatures the conductivity of these nanocomposites increased showing higher values than those observed for sPSU/SiO₂ membranes. This increase was more appreciable when the amount of PMoA increased from 10% to 20%, and can be attributed to the surface functional sites for proton transfer provided by PMoA particles. Finally, the results of the present study show that the hybrid membrane with 2%SiO₂ and 20%PMoA seems to be a promising candidate for application in PEMFCs operated at high temperature.

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