

Composite Membranes

SPEEK/Zelite/Ionic-Liquid Anhydrous Polymer Membranes for Fuel-Cell Applications

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Abstract: Sulfonated poly(ether ether ketone) (SPEEK)/zeolite/ionic-liquid composite membranes were prepared with different amounts of 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[\text{C}_4\text{MI}]\text{CF}_3\text{SO}_3$) or 1-decyl-3-methylimidazolium trifluoromethanesulfonate ($[\text{C}_{10}\text{MI}]\text{CF}_3\text{SO}_3$) ionic liquids (ILs). The structure of the composite membranes was investigated by FTIR-ATR spectroscopy, X-ray diffraction, atomic force microscopy, and by thermogravimetric analyses. The introduction of

the IL, encapsulated in zeolite, into the SPEEK polymer leads to improvement of the water uptake, thermal stability, and proton conductivity of the composite membranes, compared with pristine SPEEK. The proton conductivity of the membranes with 1.5 % and 2.0 % $[\text{C}_4\text{MI}]\text{CF}_3\text{SO}_3$ IL showed values of 3.34 mS cm^{-1} and 5.98 mS cm^{-1} , respectively, under anhydrous conditions at $80 \text{ }^\circ\text{C}$. The conductivity obtained for these membranes is about 100 times higher than for pristine SPEEK (0.038 mS cm^{-1}).

Introduction

In recent years, the world has been faced with an energy concern, due to the depletion of natural resources and an increase in environmental pollution.^[1] This is why, in the ranking of the world's top ten problems for the next 50 years, energy is proposed to be in first position.^[2] Since the 1973 oil crisis, considerable progress has been made in the search for alternative energy sources, such as solar, wind, ocean-wave, and biomass energies, and hydropower.^[3] All of these renewable sources involve the generation of electricity. Among the candidates, hydrogen has a prominent position, because of its high energy content and low environmental impact. Its use is a long-term alternative for reducing CO_2 emissions, and it presents great potential in being the preferred fuel of the future, because it is clean and renewable. The primary interest in using hydrogen as a fuel is based on a simple fact: when it produces energy, the reaction products are only water and heat. This is why it is expected that, by the end of this century, hydrogen will replace fossil fuels as the preferred one for the transportation industry.^[4]

Fuel cells correspond to a technology of electric power generation that has been intensively developed in recent years.^[5] They are devices operating in a way similar to conventional batteries in converting chemical energy into electrical energy. Fuel cells that use hydrogen as the fuel are the most studied ones. They are called proton exchange membrane fuel cells (PEMFCs), and they operate at low temperatures, high power density, and high efficiency, without any negative emission to the environment. The only reaction product is water in the form of vapor.^[6,7]

Significant advancement has been made in the development of PEMFCs, searching for low cost and high performance. This can be achieved by alloying Pt with inexpensive metals, such as Ni,^[8] Co, and others.^[9] The other way is to develop electrocatalytic materials based on nonprecious metals.^[10]

In these cells, the most commonly used polymeric membrane is Nafion[®]. Its extensive use is due to its high proton conductivity, excellent mechanical and thermal properties, and high chemical and electrochemical stability. However, Nafion[®] is very expensive, with a manufacturing cost of approximately $800 \text{ US\$ m}^{-2}$. Also, Nafion[®] membranes must be humidified to obtain high proton conductivity, and the main drawback is its rapid dehydration at temperatures above $100 \text{ }^\circ\text{C}$, leading to a rapid drop in proton conductivity.^[11,12]

In recent years, sulfonated poly(ether ether ketone) (SPEEK) has been proposed for developing membranes for different applications, such as CO_2 separation,^[13] methanol fuel cells,^[14] and PEMFCs.^[15] Several studies consider SPEEK a strong candidate to replace Nafion[®], due to its low cost, and in particular, its good thermal and chemical stabilities,^[16] which may allow PEMFCs to operate at higher temperatures than with Nafion[®]. Studies confirm that SPEEK membranes can be durable under fuel-cell operating conditions, with a lifetime of over 3000 h.^[17] On the other hand, SPEEK membrane conductivity and water absorption increase as their degree of sulfonation (DS) increases.^[18] However, depending on the variation of the level of sulfonation, the mechanical properties of the SPEEK membranes may deteriorate progressively. With an increasing DS, the long-term stability of SPEEK membranes is considerably affected, due to degradation initiated by the hydroxyl radical. Small sulfonated SPEEK membranes show high thermal and chemical stability, but, unfortunately, they have low proton conductivity. Under optimized conditions of temperature and degree of sulfonation, the SPEEK conductivity at high moisture levels exceeds that of Nafion[®] (ca. 0.1 S cm^{-1}).^[19]

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The primary needs to develop new PEMFC membranes are cost reduction, high proton conductivity and impermeability to fuel, high thermal and chemical stability, and also mechanical strength. Therefore, the choice of SPEEK instead of Nafion[®] would be primarily due to electrochemical considerations, and also due to its lower cost and higher physical/chemical stability.

Many studies were carried out in the modification of polymeric membranes to achieve high thermal stability and high conductivity. Some of them focused on the use of ionic liquids (ILs) to improve their performance by incorporating less volatile solvents.^[20–23] ILs are salts with a melting point below 100 °C and a low vapor pressure. Composed of ions, they are characterized by weak interactions due to the combination of a large cation with an anion of delocalized charge, which usually has an excellent conductivity. Due to their particular characteristics, ILs are being applied in many scientific and technological fields (catalysis, CO₂ capture devices, energy conversion, batteries, and fuel cells).^[24,25]

The literature shows that the most commonly used IL for modifying PEMFC polymeric membranes consists of large asymmetric ions, such as imidazolium salts. The choice of the imidazolium salt is due to its unusual properties, such as: (i) low vapor pressure; (ii) high ionic conductivity due to high viscosity; and (iii) wide electrochemical window. Besides that, the imidazolium salt keeps its fluidity at low temperatures and has a low glass transition temperature, which facilitates its solubility in a variety of organic solvents.^[26,27]

In addition to their good chemical characteristics, ILs have good structural features, which can make them promising additives for the incorporation into a polymeric matrix.^[28] Their structure helps in the transport of mobile cations in polymer electrolytes, leading to high ionic conductivity. This is attributed to the presence of polar groups in their structure, which provides for additional local traffic for the mobile ions along its polymer backbone.^[29]

On the other hand, zeolites are hydrophilic and have excellent heat resistance. These two qualities make them promising additives for improving the water absorption of PEMFC polymeric membranes at high temperatures.^[30] In contrast to silicates, zeolites exhibit intrinsic protonic conductivity.^[31] Holmberg et al.^[32] demonstrated that acid functionalization of zeolite nanocrystals increases their hydrophilicity and also improves their proton conductivity at room temperature, up to 12 mS cm⁻¹. It was shown that the mechanical, thermal, and barrier properties of polymer electrolyte membranes were enhanced by the addition of zeolite as the silicate-based inorganic filler.^[33] Increased absorption, water retention, and conductivity were also achieved.^[34–36] Because of their above-mentioned intrinsic properties, the combination of ILs and zeolites can result in composites with high water retention, and it promotes the proton conductivity of the polymeric membranes. A recent study evaluated the combination of the IL bis(trifluoro sulfonyl)imide H-3-methylimidazolium (TFSI) with the NaY zeolite in the Nafion[®] membrane at different concentrations. It was observed that the proton conductivity of the Nafion[®]/zeolite/IL composite membrane in a dry atmosphere increased with temperature.^[37]

Considering the discussion above, in this work we report the preparation and characterization of new proton-conductive SPEEK/zeolite/ionic-liquid membranes for their potential use in PEMFCs in under low-humidity conditions. The 1-butyl-3-methylimidazolium trifluoromethanesulfonate and 1-decyl-3-methylimidazolium trifluoromethanesulfonate ionic liquids were encapsulated in the NaY zeolite (3 % of the mass) in different proportions, and they were then incorporated into the SPEEK polymer membranes.

Results and Discussion

ATR-FTIR spectra of zeolite, SPEEK, and the composite membranes were measured to understand the reactions that occur among the components. Figure 1 shows the spectra of zeolite, pristine SPEEK, and the composite membranes. Figure 1 demonstrates that the original bands of this zeolite at (464 ± 4), (576 ± 4), and (995 ± 4) cm⁻¹ (corresponding to the bending and stretching vibrations of Si–Al–O, respectively), are present. Furthermore, the band at 576 cm⁻¹ is less intense than those at 995 cm⁻¹, which is also a characteristic of this material. The stretching of the hydrogen atom bonded to the oxygen ions (Si–O–H), is characterized by a broad band at (3397 ± 4) cm⁻¹ in the zeolite spectrum.^[38] The pristine SPEEK spectrum shows a characteristic wide band at 3418 cm⁻¹ (assigned to the vibration of the O–H subgroups in the –SO₃H groups), bands at 1230 and 1078 cm⁻¹ (associated with O=S=O stretching vibrations), and an absorption peak at 1649 cm⁻¹ (corresponding to the carbonyl band of SPEEK).^[39] The ATR-FTIR spectra of the composite membranes, modified by the addition of different amounts of ionic liquid, show that the composite membranes preserve those characteristic bands.

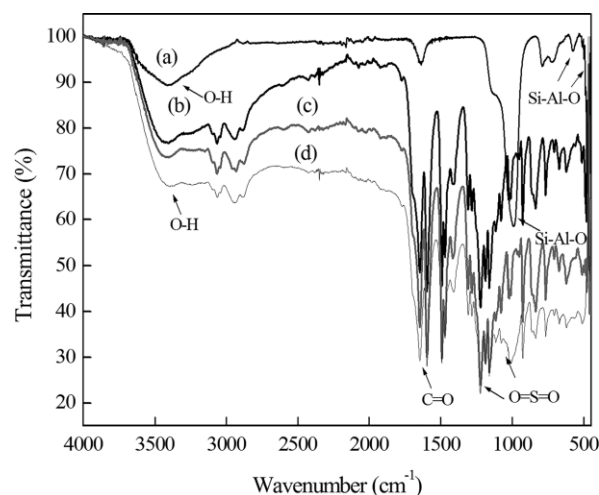


Figure 1. ATR-FTIR spectra of: (a) zeolite, (b) the pristine SPEEK membrane, (c) SP-Z15C4, and (d) SP-Z15C10.

To further investigate the structural changes induced by the incorporation of IL, X-ray diffraction data were collected. Figure 2 shows the X-ray diffraction crystallographic patterns of PEEK, SPEEK, and the composite membranes. PEEK is a semi-crystalline polymer, showing sharp peaks, corresponding to

the (110), (111), (200), and (211) planes, in the 2θ range of $20\text{--}30^\circ$.^[40,41] The PEEK sulfonation leads to a sharp decrease in the crystallinity, and it has been reported that highly sulfonated

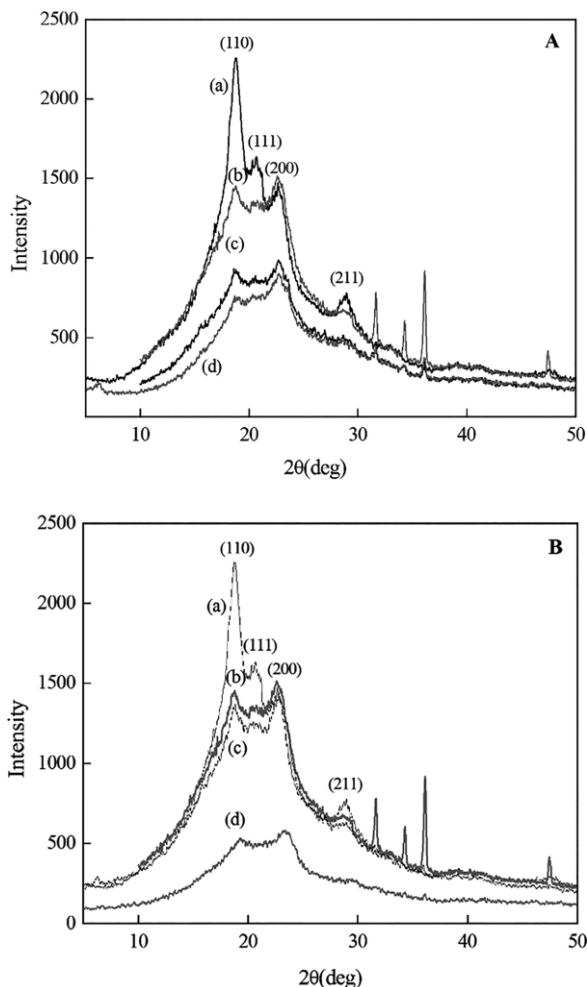


Figure 2. XRD patterns of: (a) PEEK and (b) pristine SPEEK membranes, (c) SP-Z15 and (d) SP-Z30 composite membranes with ionic liquids (A) C4MI and (B) C10MI.

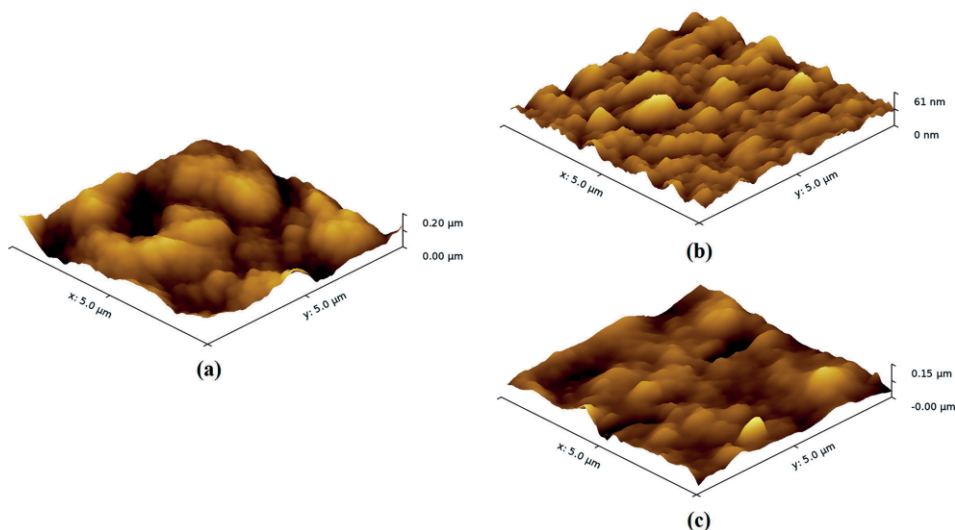


Figure 3. AFM images of: (a) pristine SPEEK membrane, (b) SP-Z15C4 and (c) SP-Z30C4 composite membranes.

PEEK is entirely amorphous.^[41] However, the XRD pattern of SPEEK, with a DS of 53 %, as used in this work, indicates the presence of two peaks, corresponding to the (110) and (200) planes. The introduction of SO_3H groups into PEEK, as well as the launch of the zeolite containing the ionic liquid, changes the chain conformation and packing, thus decreasing the crystallinity. Figure 2A shows that upon doubling the concentration of the ionic liquid C4MI, up to 3.0 %, the XRD pattern is the same. Notwithstanding, for those samples using C10MI (Figure 2B) the XRD pattern for 1.5 % of IL is almost the same as that of pristine SPEEK, but as the IL is increased to 3.0 %, the membrane shows a substantial decrease in its crystallinity.

The morphology of pristine SPEEK and the composite membranes were examined by AFM microscopy. Figure 3 shows the AFM images of the neat SPEEK and the composite membranes with the C4MI IL. As shown in Figure 3, the average surface roughness of the pristine SPEEK membrane was reduced from (1.97 ± 0.12) to (1.25 ± 0.12) nm by the addition of 1.5 % of IL. Besides, doubling the amount of ionic liquid, the roughness increases again to (1.64 ± 0.14) nm. The same behavior was observed for C10MI samples; that is, the average roughness decreases from (1.97 ± 0.12) to (1.37 ± 0.11) nm and then increases again to (1.52 ± 0.13) nm. All of these morphological changes may be associated with phase rearrangement of hydrophilic and hydrophobic regions in the SPEEK microstructure during the formation of homogeneous SPEEK/zeolite/IL composite membranes.^[42]

The thermal stability of pristine SPEEK and the composite membranes was investigated by TG measurements. Figure 4 shows the thermal stability of the neat SPEEK membrane and the composite membranes with the C4MI (A) or C10MI (B) ionic liquids. The SPEEK membrane and the composite membranes showed three mass-loss stages: the first stage, between 50 and 190°C , could be due to the evaporation of water and residual solvent;^[39,43] the second stage starts at 200°C and could be attributed to the sulfonic acid group degradation.^[44,45] For those samples modified with 3.0 % of C10MI, the second stage started at approximately 220°C . The mass loss which starts at

above 460 °C, the third stage, could be associated with the degradation of the polymer backbone.^[39,46] Again, for those samples modified with 3.0 % of IL, this process starts at more elevated temperatures, 500 °C. This increase in the degradation temperature may be assigned to the existence of a strong interaction between the hydrophobic SPEEK backbone and the zeolite particles.

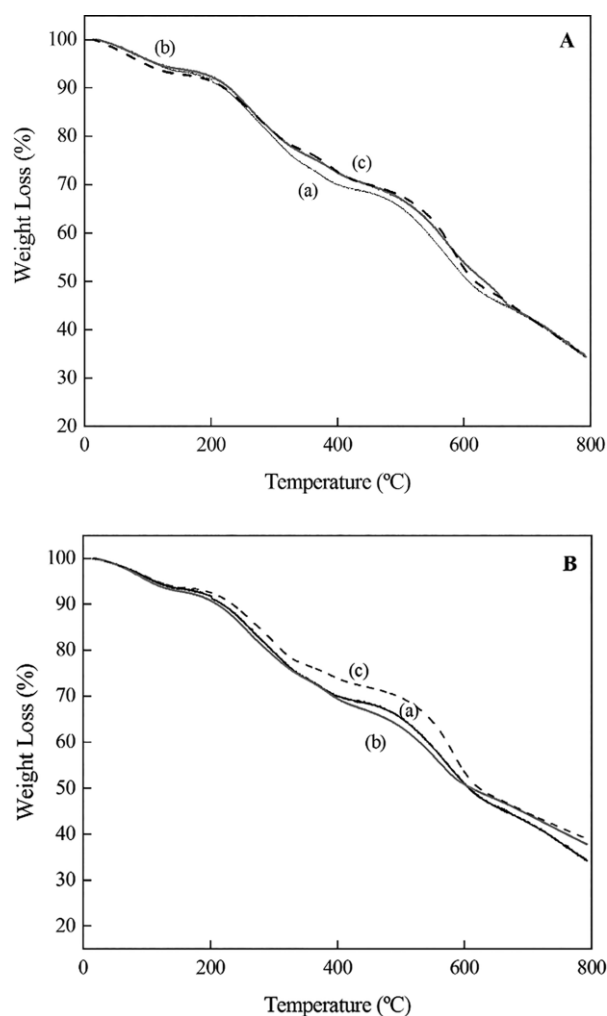


Figure 4. TG analysis of: (a) pristine SPEEK, (b) SP-Z15 and (c) SP-Z30 composite membranes with ILs (A) C4MI and (B) C10MI.

Another important property of membranes is water absorption. This property plays an important role for proton-exchange membranes, because it is related to their mechanical strength and proton conductivity.^[47] Changes in the water uptake of the pristine SPEEK and the membranes modified by the incorporation of the C4MI and C10MI ionic liquids, as a function of the temperature, are shown in Table 1.

The modification of the SPEEK membranes with the inclusion of the ILs induces an increase in water absorption by the membrane; a larger amount of IL into zeolite corresponds to a higher water uptake. The increase of water absorption by the modified membranes is attributed to the interaction of zeolite particles with the polymer, probably through hydrogen bonding between the Si-OH group of the zeolite and the SO₃H groups of

Table 1. Water uptake of pristine SPEEK and composite membranes modified by the incorporation of the C4MI and C10MI ILs, as a function of the temperature.

Sample designation	Water uptake [wt.-%]				
	25 °C	40 °C	60 °C	75 °C	90 °C
SPEEK	1.91	7.76	20.5	22.6	25.0
SP-Z15C4	2.03	7.85	21.0	23.3	26.5
SP-Z20C4	8.81	15.6	22.6	25.0	31.3
SP-Z25C4	11.1	15.7	23.5	25.8	35.3
SP-Z30C4	12.4	16.2	24.1	26.4	38.3
SP-Z15C10	7.10	19.3	24.0	25.0	26.3
SP-Z20C10	7.40	21.7	24.5	25.0	26.7
SP-Z25C10	7.50	22.0	24.8	25.2	27.1
SP-Z30C10	7.70	22.2	25.1	26.4	28.0

the polymer, which, when combined, contribute to increased water retention and water mobility.^[48,49] The same behavior was observed for the Nafion®/zeolite composite membranes, with zeolite ranging from 0 to 12.5 wt.-%. The water uptake increased with the increase of the amount of zeolite, ranging from 32.3 to 45.2 % at ambient temperature.^[50]

To evaluate how much ionic liquid within the zeolite these modified membranes retain, leaching tests were carried out. This experiment was performed, because water is produced at the cathode during the operation of a fuel cell, and in the presence of water, leaching of the ionic liquid encapsulated in the zeolite may occur. This test was performed by immersing modified membranes in deionized water for 48 h at two different temperatures (25 °C and 80 °C), and the mass-loss percentage was calculated. Figure 5 shows the leaching of C4MI (A) and C10MI (B) ionic liquids at two different temperatures.

By increasing the temperature from 25 to 80 °C, there is a growth in mass loss, because the free volume increases with temperature. Another possibility for the increase in IL mass loss with temperature is that the viscosity of the ionic liquids decreases, thus increasing its fluidity. However, increasing the concentration of the C4MI IL substantially decreases the leaching process. This can be explained in the following way: by increasing the amount of ionic liquid, the pore of the zeolite is filled, thereby making it difficult to leach, since, as found in the literature, when the SPEEK membrane is modified with the same ionic liquid, increasing the amount of IL and the temperature results in a larger membrane mass loss.^[39] However, it is observed that when the zeolite is filled with C10MI (Figure 5B) there is a larger mass loss, larger than that for C4MI, which may be explained, because the size of the IL cation is increased and it is not securely attached to the pore of the zeolite, which would facilitate its exit. The results of the oxidative stability tests also show that the stability of SPEEK with the C10MI is lower, showing it exits more easily from the pore of the zeolite.

As the chemical stability of proton exchange membranes is affected during operation of the fuel cell, because radicals like HO[•] and HOO[•], which can induce membrane degradation, are produced inside,^[51] Fenton's test was performed to evaluate the chemical stability of the membranes. This test consists of soaking the membrane in Fenton's reagent (3 % H₂O₂, 4 ppm

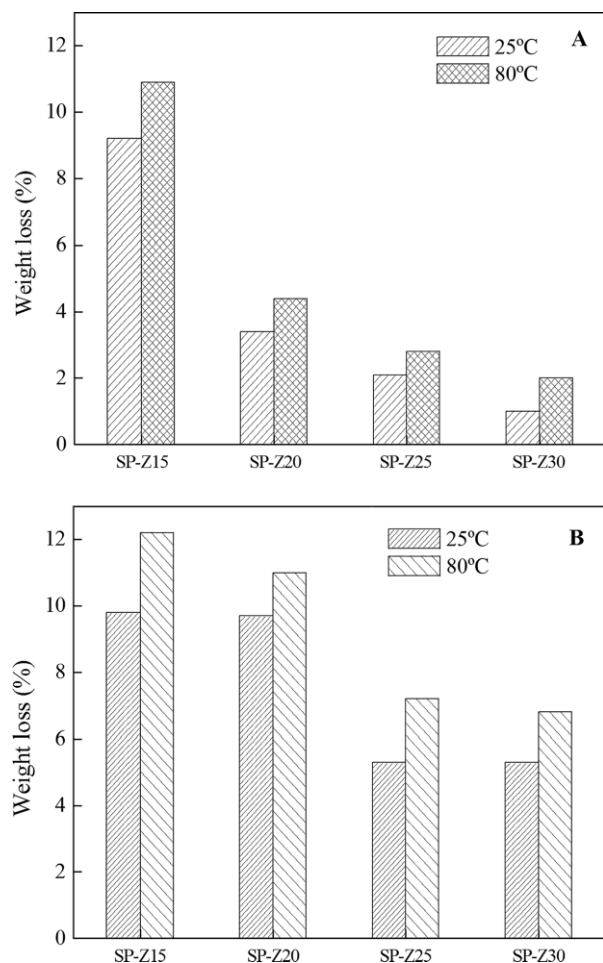


Figure 5. Leaching of SP-Z15, SP-Z20, SP-Z25, and SP-Z30 composite membranes with ionic liquids (A) C4MI and (B) C10MI at different temperatures.

Fe²⁺); the membranes were left in the reagent at 80 °C for 24 h. Figure 6 shows the oxidation stability of pristine SPEEK and the composite membranes.

The results show that when C4MI IL was encapsulated in the zeolite, the mass loss of neat SPEEK, SP-Z15, SP-Z20, SP-Z25, and SP-Z30 was 42.6 %, 34.5 %, 32.8 %, 30.5 %, and 29.7 %, respectively. When the ionic liquid encapsulated was C10MI, the mass loss of SP-Z15, SP-Z20, SP-Z25, and SP-Z30 was 38.3 %, 36.0 %, 34.8 %, and 32 %, respectively. With the increasing amount of ionic liquid, the oxidation stability of the composite membranes increased. Compared with the neat SPEEK, composite membranes exhibited better oxidation resistance. The reason could be the role of the zeolite in the interaction of the sulfonic acid group against the diffusion of H₂O₂.

The most important factor influencing the performance of the proton exchange membrane fuel cell is the proton conductivity. The proton conductivities of SPEEK and the composite membranes were measured in the temperature range 25–80 °C under anhydrous conditions. Figure 7 shows the conductivities of the composite membranes with varying amounts of the C4MI (A) and C10MI (B) ionic liquids, as a function of temperature, under anhydrous conditions.

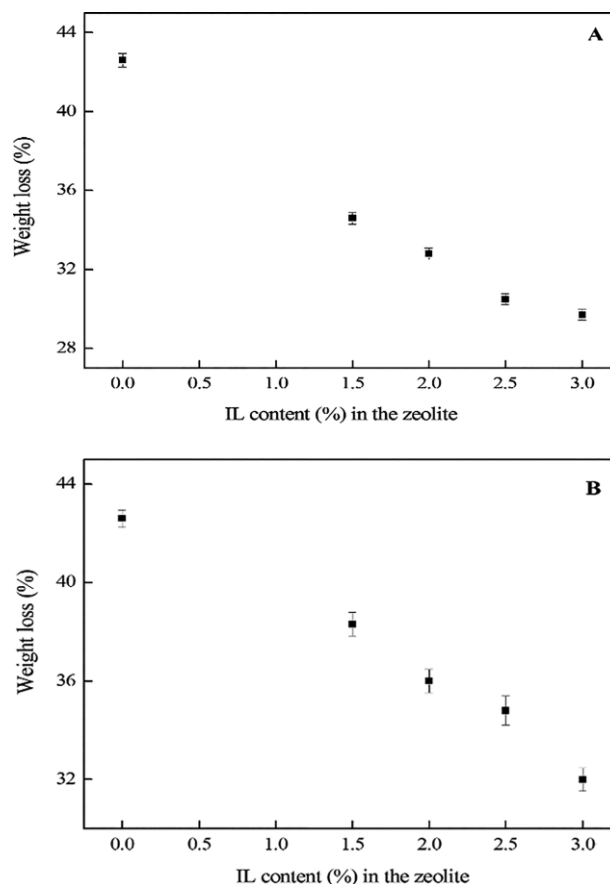


Figure 6. Oxidation stability of SPEEK, SP-Z15, SP-Z20, SP-Z25, and SP-Z30 composite membranes with ionic liquids (A) C4MI and (B) C10MI in Fenton's reagent at 80 °C for 24 h.

Figure 7 shows that the proton conductivity of the pristine SPEEK membrane increases with increasing temperature, but not significantly. This behavior can be explained by the evaporation of water at high temperatures and the mobile phase; that is, the water is not available, and under anhydrous conditions, the sulfonic acid groups in the SPEEK and composite membranes contribute little to the conductivity or become immobile. The low conductivity presented by the membranes with 2.5 and 3.0 % of ionic liquids, in comparison with the membranes with 1.5 % and 2.0 % of ionic liquids (Figure 7A and B) can be attributed to competitive effects between zeolite and the ionic liquid with respect to the water molecules, blocking the migration of the protons, causing the composite membranes to show low conductivity under anhydrous conditions. The lowest conductivity shown, when the ionic liquid encapsulated in zeolite was C10MI, can be explained by the fact that the increase in the chain substituent in position 1 of the ring leads to a gradual decrease in ionic conductivity,^[52] but even though it is less conductive than C4MI, it has good conductivity at 80 °C (4.92 mS cm⁻¹) when the zeolite is filled with 1.5 % of this IL. The best conductivity values found for C4MI were 3.34 and 5.98 mS cm⁻¹ when the zeolite was filled with 1.5 and 2.0 % of this IL, respectively. These values show that the conductivity has been improved by encapsulating the ionic liquid in the zeolite. Values of approximately 4.0 mS cm⁻¹ were found in the

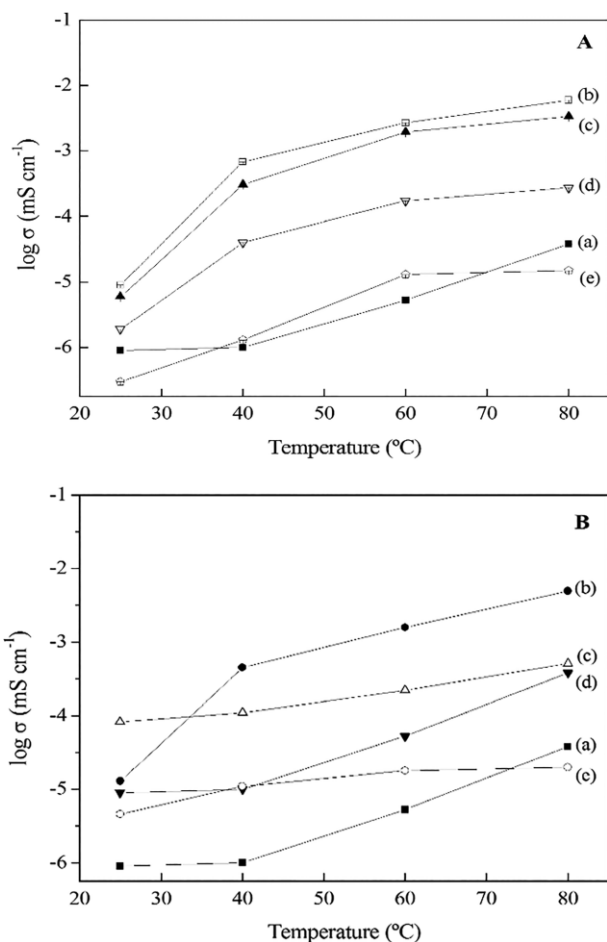


Figure 7. Proton conductivity of pristine SPEEK (a), SP-Z15 (b), SP-Z20 (c), SP-Z25 (d), and SP-Z30 (e) composite membranes with the ILs C4MI (A) and C10MI (B) at different temperatures under anhydrous conditions.

literature for SPEEK membranes (DS 70 %) with 70 % of the mass of this IL under anhydrous conditions at 80 °C;^[39] a value of approximately 1.0 mS cm⁻¹ was found for Nafion® 117 under anhydrous conditions at 80 °C.^[53]

Conclusion

SPEEK/zeolite/ionic-liquid polymer membranes were prepared and characterized for future use in PEMFCs operating at elevated temperatures and under anhydrous conditions. FTIR spectroscopy, X-ray diffraction analysis, and AFM analysis confirmed the incorporation of ILs encapsulated in zeolite into the polymers, and TG analyses indicated an improvement in the thermal stability of the modified membranes. From the conductivity measurements, we concluded that membranes modified with 1.5 % and 2.0 % of C4MI IL in zeolite have the potential to be used in PEMFCs, to maintain proton conduction at temperatures higher than 80 °C under anhydrous conditions.

Experimental Section

Materials: PEEK polymer 450 PF (Victrex), sulfuric acid (98 %, Merck), *N*-methylpyrrolidone (NMP) (Sigma–Aldrich), and zeolite

NaY (Sigma–Aldrich) were used as received. The ionic liquids 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C₄MI]-CF₃SO₃) and 1-decyl-3-methylimidazolium trifluoromethanesulfonate ([C₁₀MI]CF₃SO₃) were synthesized as described previously in the literature.^[54,55]

Sulfonation of PEEK: The sulfonated poly(ether ether ketone) was prepared by dissolving PEEK (10 g), previously dried in an oven at 80 °C for 24 h, in sulfuric acid (200 mL, 98 %) under nitrogen; the solution was vigorously stirred at room temperature for 18 h. Then, the polymer solution was precipitated with a large excess of ice-cold Milli-Q® water under continuous stirring. The precipitate (SPEEK) was washed several times, until the pH of the wash water reached 5. Then the polymer was dried in air at room temperature for 48 h, and after this step, it was dried in a vacuum oven at 60 °C, until its color changed from white to yellow.^[56,57] The degree of sulfonation (DS) of the SPEEK was obtained by ¹H NMR spectroscopy; a Varian Inova spectrometer, at a resonance frequency of 300 MHz, was used. Figure 8 shows the ¹H NMR spectrum of the SPEEK polymer and its structure, with aromatic proton numbering. The degree of sulfonation obtained was 53 %, which was calculated according to the method described in the literature.^[58,59]

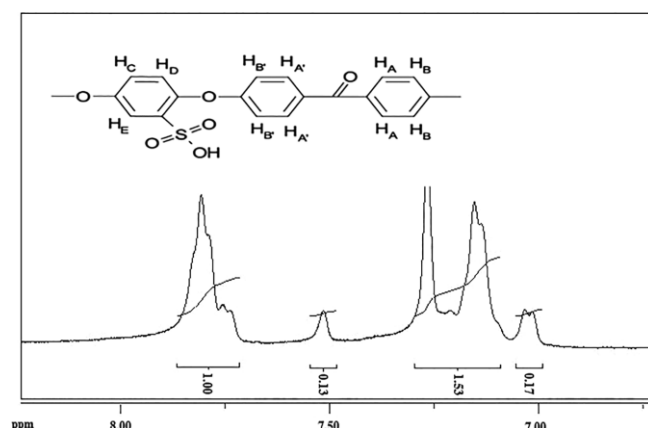


Figure 8. ¹H NMR spectrum of the SPEEK polymer.

Membrane Preparation: The SPEEK membranes were prepared by dissolving SPEEK (0.5 g) in NMP (4 mL) at 80 °C under continuous stirring. After this step, the solution was poured onto glass plate molds, the solvent was evaporated under an exhaust at room temperature for one week, and then the polymers were transferred to a vacuum oven at 80 °C for 72 h. For the preparation of the composite membranes, the first step was the encapsulation of the ionic liquid in the zeolite. This procedure was performed as follows: (a) the zeolite was evacuated at 100 °C and 1 Torr for 20 min; (b) IL was dissolved in methanol at the ratio of 1:9 (w/w); (c) the zeolite was added to the IL solution in preset proportions, and the mixture was stirred vigorously at room temperature for 24 h; (d) the IL excess was removed by performing a Soxhlet extraction with methanol, at the solvent reflux temperature (65 °C) for 2 h; and (e) the product was finally dried at 100 °C in an oven overnight.^[60] Then the composite membranes were prepared by dissolving the SPEEK in NMP, followed by addition of the required IL encapsulated in zeolite, at 80 °C under continuous stirring, followed by ultrasonication to make the solution homogeneous. In Table 2, details of the composite compositions and sample designations are presented.

Table 2. Composition and sample designation of the composite membranes.

Sample designation	SPEEK [g]	Zeolite [wt.-%]	Ionic liquid [wt.-%]
SPEEK	0.5000	0	0
SP-Z15C4	0.4850	3	1.5
SP-Z20C4	0.4850	3	2.0
SP-Z25C4	0.4850	3	2.5
SP-Z30C4	0.4850	3	3.0
SP-Z15C10	0.4850	3	1.5
SP-Z20C10	0.4850	3	2.0
SP-Z25C10	0.4850	3	2.5
SP-Z30C10	0.4850	3	3.0

Characterization: The structures of the pristine SPEEK and the composite membranes were analyzed by Fourier transform infrared (FTIR-ATR) spectra with a Bruker Alpha-P spectrometer in the scanning range 4000–500 cm^{-1} . X-ray diffraction crystallography was used to identify the crystalline structure of the pristine membrane and the composites; the analyses were made with an X-ray diffractometer by Rigaku, with a solid detector and a $\text{Cu-K}\alpha$ radiation source at 40 kV and 40 mA. The 2θ value varied between 5 and 60°. The membrane morphologies of pristine SPEEK and the composite membranes were analyzed by atomic force microscopy (AFM) with a scanning probe microscope (SPM)-9600 (Shimadzu) and PicoView 1.14 software (Keysight Technologies). The thermal stability of the polymers was measured by using thermogravimetric analysis (TGA) with a TA Instruments Q-50 apparatus in the temperature range 15–800 °C under nitrogen at a heating rate of 20 °C min^{-1} . The water uptake (WU) of the SPEEK and the composite membranes in the temperature range 25–90 °C was determined by the mass difference between the fully hydrated membrane and the completely dry membrane.^[61] The membranes were dried at 70 °C under vacuum for 6 h, weighed and immersed in deionized water for 24 h. After this time, the membranes were wiped with blotting paper to remove the surface water and were quickly weighed. The water uptake (WU) was calculated gravimetrically, using Equation (1):

$$WU(\%) = \frac{W_s - W_d}{W_d} \cdot 100 \quad (1)$$

where W_s is the mass of the wet membrane, and W_d is the mass of the dry membrane.

We tested the samples for leaching of the ILs. The membranes were dried at 70 °C under vacuum for 6 h and then immersed in deionized water at two different temperatures (25 °C and 80 °C) for 48 h. After this time, the membranes were dried using tissue paper and then dried in a vacuum oven at 70 °C for 6 h and weighed. The mass loss of the composite membranes was calculated gravimetrically using Equation (2):

$$\%Loss = \frac{W_i - W_f}{W_i} \quad (2)$$

where W_i is initial mass and W_f is the mass after immersion in deionized water.

The oxidation stability was also measured for the samples. For this test, we used a H_2O_2 (3 %) solution and Fe^{II} (4 ppm). The membranes were cut into pieces of size 1.0 × 2.0 cm and mass O_1 , placed in the solution (20 mL), and kept at 80 °C for 24 h. After this time, the sample was collected by filtering, cleaned with deionized water several times, and dried in a vacuum oven at 70 °C for 24 h. Then the membrane was weighed (O_2). The oxidative stability (OS) was calculated using Equation (3):^[62]

$$OS = \frac{O_1 - O_2}{O_1} \cdot 100 \quad (3)$$

Finally, the proton conductivity of the pristine membrane and the composites was determined as a function of the temperature in the range 25–80 °C using electrochemical impedance spectroscopy with an Autolab PGSTAT 30 potentiostat. Membranes were placed between two stainless-steel electrodes in a cell kept in a thermostat jacket connected to a thermostat. The proton conductivity was measured under anhydrous conditions, using an open-circuit potential with an amplitude of 0.01 V and a frequency range from 10 Hz to 100 kHz. The conductivities (σ) of the membranes were calculated using Equation (4):^[63]

$$\sigma = \frac{d}{AR} \quad (4)$$

where d is the membrane thickness [cm], R is the resistance value [Ω] obtained at the maximum frequency value, where imaginary Z tends to zero, and A is the sample surface area [cm^2] in contact with the stainless-steel electrodes.

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Keywords: Polymers · Zeolites · Ionic liquids · Fuel cells

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