Synthesis and characterization of anion-exchange membranes with various functional groups

M.T. Pérez-Prior, T. García-García, A. Várez, B. Levenfeld*

Department of Materials Science and Engineering and Chemical Engineering, Universidad Carlos III de Madrid, Avda. Universidad, 30, E-28911-Leganés, Spain

* Corresponding e-mail address: bll@ing.uc3m.es

ABSTRACT

Purpose: In the current study anion-exchange membranes comprised of different functional groups were prepared to be used as electrolyte in fuel cells.

Design/methodology/approach: Polysulfone was firstly chloromethylated followed by nucleophilic substitution reaction with the corresponding N-compound, trimethylamine and 1-methylbenzimidazole to obtain the resulting quaternary ammonium and benzimidazolium functionalized membranes, respectively. The membranes thus prepared as well as the starting polymers were characterized by ^{1}H-NMR and FTIR analysis.

Findings: The thermal stability of the membranes was lower than the original polymers. However, both membranes exhibited high thermal stability for typical fuel cell operation temperatures below 100°C. The capacity of these materials to absorb water was more favored when benzimidazolium groups were inserted to the polymer instead of quaternary ammonium ones. The ionic conductivity of the membranes in dilute aqueous solution of potassium hydroxide was studied by means of impedance spectroscopy. The results show a clear correlation between the membrane's electrochemical behaviour with the electrolyte solution embedded in the membrane. In addition, the nature of the functional group modifies the membrane ionic conductivity. So, the membrane ionic conductivity was more than twice as high when the quaternary ammonium groups were replaced by the benzimidazolium ones.

Research limitations/implications: The nature of the functional group as well as the number of exchangeable groups plays an important role on the ionic transport through the membrane. Therefore, the membrane ionic conductivity could be significantly improved by modifying the chemical structure of the polymer.

Originality/value: The current study describes the main properties of benzimidazolium functionalized membranes. The electrochemical characteristics of this material as well as the thermal stability have been compared to the most commonly used comprising quaternary ammonium groups.

Keywords: Fuel Cells; Electrical properties; Polysulfone; Anion-exchange membranes

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MATERIALS

1. Introduction

Over the last decade, there has been increasing interest in the development of new technologies that avoid the consumption of fossil fuels including coal and oil, and that are considered environmentally sustainable. Fuel cells are among these devices because they are able to operate with H_2 as the fuel and the only by-product for H_2/O_2 fuel cell is water, which makes the process more eco-friendly [1].

Proton-exchange membrane fuel cells (PEMFCs) have been extensively investigated due to the large number of potential applications including vehicles and mobile devices [2]. For many years, the commonly used polymer electrolytes have been limited to proton-exchange membranes, typically Nafion, a high-performance polymer produced by DuPont. Nafion has been considered a reference material due to its high ionic conductivity, thermal stability and chemical resistance. However, PEMFCs exhibit some drawbacks due to its high cost since the use of Pt or precious metals as catalysts has become necessary, and, in addition, these catalysts exhibit low durability under acidic conditions [3]. In this scenario, anion-exchange membrane fuel cells (AEMFCs) are gaining attention as environmental sustainable energy generation technology primarily because of they aim to overcome the drawbacks showing proton-exchange membrane fuel cells (PEMFCs) [4]. The high durability [5], the enhancement of the reaction kinetics for both oxygen reduction and fuel oxidation [6], or the potential to use non-precious metal-based electrocatalysts such as silver [7], or nickel [8] instead of platinum ones, are some of the most significant advantages of these kinds of fuel cells versus traditional PEMFCs.

In these electrochemical devices, the anion exchange membrane (AEM) plays an important role as barrier to hydrogen and oxygen. Therefore, polymers, such as polybenzimidazole (PBI) [9], poly(arylene ether sulfone) (PES) [10], poly(2,6-dimethyl-1.4-phenylene oxide) (PPO) [11], and polysulfone (PSU) [12] have been extensively used as polymeric backbones in the synthesis of membranes.

However, the functionalization of these polymers by introducing cationic groups capable of transporting OH⁻ in the AEMFC is needed. Therefore, many functional groups have been employed [13]. Although quaternary ammonium groups appear to be the most commonly used [14], quaternary phosphonium, tertiary sulfonium, guanidinium [15] and imidazolium (Im) [16] groups have also been used in AEM synthesis.

In the current study, we synthesized anion-exchange membranes based on polysulfone. PSU has been extensively used in AEMs synthesis due to its high thermal stability, good chemical resistance, and excellent mechanical properties. The most distinctive feature of PSU is the diphenylene sulfone group. The contribution of this group becomes evident when its electronic characteristics are studied. The sulfone group tends to draw electrons from the adjacent benzene rings, making them electron deficient. Thus, this group confers on PSU oxidative resistance [17]. In addition, the sulfone group is located in a conjugated system showing a high degree of resonance stabilization. Therefore, large amounts of incident energy in the form of heat or ionizing radiation can be dissipated without chain scission or cross-linking taking place. So, thermal stability of PSU can be provided by the high strength of the chemical bonds in the diphenylene sulfone group.

Different anion-exchangeable functional groups like benzimidazolium (BIm) and quaternary ammonium (QA) were used in the present work to prepared the corresponding functionalized membranes based on PSU (PSU-BIm-OH and QAPSU-OH, respectively). BIm group shows a chemical structure similar to that of Im consisting on an imidazolium ring fused to benzene. Benzimidazole is part of PBI, a polymer known to exhibit high thermal and chemical stability as well as satisfactory mechanical properties [18]. It is important to note that BIm groups can also be attached to the polymer chain and act as cationic groups in AEMs, thereby favoring the mobility and consequently the membrane ionic conductivity with respect to PBI. Quaternary ammonium group is the most commonly used as electrolyte in AEMFCs [14,19]. This functional group shows better alkaline stability and fuel cell performance than the diammonium and quaternary phosphonium groups (QP).

This study involves the synthesis and characterization of AEMs using ^{1}H-NMR and FTIR, analyses. The water uptake, swelling degree, thermal stability, and ionic conductivity were also evaluated to determine if these materials could be successfully employed as electrolytes in AEMFCs. Subsequently, we have discussed their structural relationships according to the type of functional groups.

2. Experimental

2.1. Materials and reagents

Polysulfone, tin (IV) chloride (99%), paraform-aldehyde (95.0-100-5%), chlorotrimethylsilane (≥98%),

trimethylamine solution (TMA) (25 wt.% in H$_2$O), 1-methylbenzimidazole (mBIm) (99%), 1-methyl-2-pyrrolidone (NMP) (ACS reagent, ≥99%), dimethylformamide-d$_7$ (DMF-d$_7$) (99.5% D), dimethyl sulfoxide-d$_6$ (DMSO-d$_6$) (99.9% D), All of the other reagents were of analytical grade.

2.2. Chloromethylation of PSU

To avoid the use of chloromethyl methyl ether that is considered carcinogenic, the chloromethylation reaction of PSU was performed by using a mixture of paraformaldehyde/chlorotrimethylsilane as chloromethylating agent, tin (IV) chloride as catalyst, and chloroform as solvent [20].

PSU (5 g) was dissolved in chloroform (250 mL) with mechanical stirring in a three-neck round bottom flask and, after adding stannic chloride (0.27 mL) and paraformaldehyde (6.79 g) to the solution, chlorotrimethylsilane (28.64 mL) was added dropwise. This solution was stirred at 55°C for a certain time which varied from 24 to 72 h in order to obtain different degrees of chloromethylation (DC) of polysulfone. As shown in Fig. 1 substitution takes place on the bisphenol-A units, firstly in the position 1 leading to monosubstituted product and then in the position 2 when disubstituted product is obtained [21]. The obtained chloromethylated polysulfone (CMPSU) was precipitated into ethanol, washed with deionized water, and dried at room temperature.

2.3. Synthesis of the anion-exchange membranes

The benzimidazolium and quaternary ammonium chloride-functionalized polysulfone membranes (PSU-BIm-Cl and QAPSU-Cl, respectively) were synthesized via the nucleophilic substitution reaction of CMPSU with m-BIm and TMA, respectively. Dried CMPSU (1.9 g) was dissolved in NMP (30 mL) in a three-neck round bottom flask until complete dissolution and next the corresponding *N*-compound, m-BIm (1.3 g) or 25 wt.% trimethylamine solution (3.15 mL), was added. The reaction mixture was maintained at 60°C for 15 h. The resulting solution containing the membrane in the Cl⁻ form was cast onto a flat glass plate and dried in an oven using a temperature program containing several steps from 30 to 100°C. The membranes in the OH⁻ form (PSU-BIm-OH and QAPSU-OH) were prepared from the membrane in the Cl⁻ form by

immersion in a 1M KOH solution for 48 h to replace Cl⁻ with OH⁻. Finally, the resulting membrane was repeatedly rinsed with deionized water until the pH of the residual water was neutral.
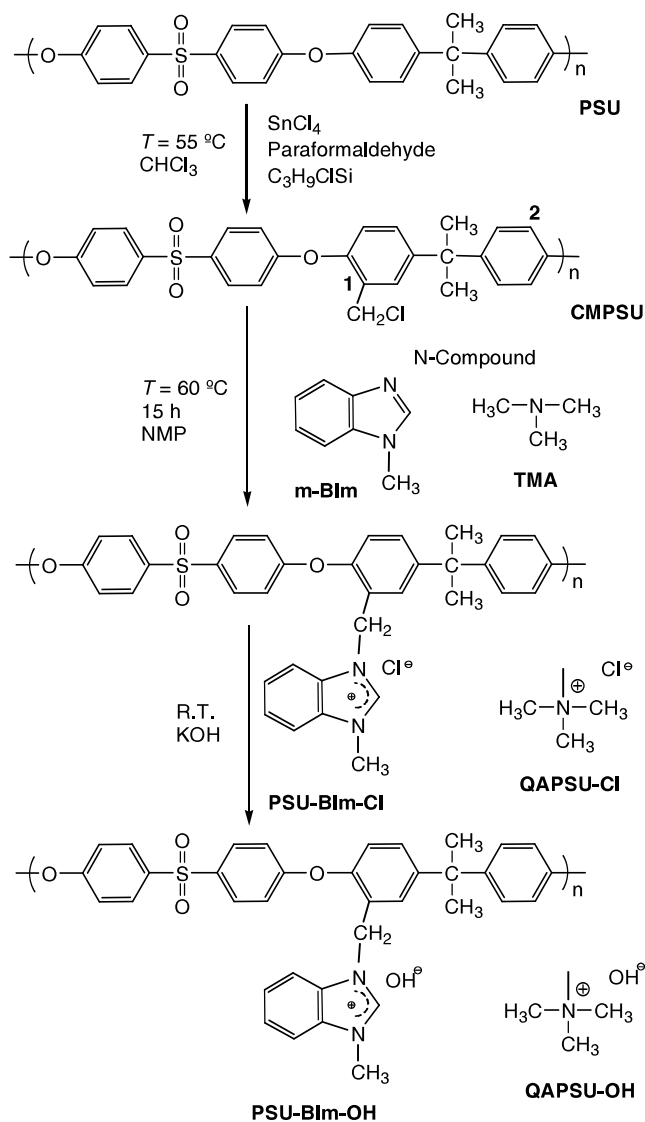

Fig. 1. Synthesis of PSU-BIm-OH and QAPSU-OH membranes

2.4. Measurements

^{1}H-NMR (300 MHz) analysis was performed on a Bruker Avance DPX-300 spectrometer using DMSO-d$_6$ as solvent, except for PSU where DMF-d$_7$ was used due to

its low solubility in DMSO-d$_6$. TMS was used as the internal reference.

The FTIR spectra were recorded on a Perkin-Elmer Spectrum GX Instrument. The measurements were performed directly on the membrane in the 4000-400 cm^{-1} range and 16 scans were taken at a resolution of 4 cm^{-1}.

2.5. Thermogravimetric analysis

Thermogravimetric analysis of the membranes was performed in a Perkin-Elmer Pyris TGA1 instrument. The measurements were conducted by heating from 40°C to 600°C at a heating rate of 10 °C/min under an air atmosphere.

2.6. Ion-exchange capacity

Ion-exchange capacity (IEC) was determined by titration using a 916 Ti-Touch titrator from Metrohm. The membrane in the OH$^-$ form was immersed in a 0.1 M HCl solution for 48 h. The resulting solution was titrated until the pH was 7 with a 0.1 M KOH solution, which was previously normalized with potassium hydrogenphthalate. To remove any remaining HCl, the membrane was washed with deionized water for 24 h. The resulting membrane was dried in an oven and then weighed to determine the dried mass of the Cl$^-$ form (m$_{dry(Cl)}$). The IEC value was calculated as follow:

$$IEC = \frac{n_{i(H^+)} - n_{f(H^+)}}{m_{dry(Cl)}} \qquad (1)$$

where $n_{i(H^+)}$ and $n_{f(H^+)}$ are the initial and the final moles of H$^+$ in the HCl solution, respectively.

2.7. Water uptake and swelling degree

The water uptake (WU%) and swelling degree (SD%) parameters were determined by measuring the change in weight and thickness of the membranes before and after hydration, respectively. The dry membrane in the Cl$^-$ form was immersed in a 1M KOH solution for 48 h to replace Cl$^-$ with OH$^-$, followed by washing with deionized water to remove the remaining KOH. Then, the WU% and SD% values were calculated as follow:

$$WU\% = \frac{m_{hyd(OH)} - m_{dry(Cl)}}{m_{dry(Cl)}} \times 100 \qquad (2)$$

$$SD\% = \frac{x_{hyd(OH)} - x_{dry(Cl)}}{x_{dry(Cl)}} \times 100 \qquad (3)$$

where $m_{dry(Cl)}$ and $x_{dry(Cl)}$ are the mass and thickness, respectively, of the dried membrane in Cl$^-$ form and $m_{hyd(OH)}$ and $x_{hyd(OH)}$ are the mass and thickness, respectively, of the wet membrane in the OH$^-$ form.

2.8. Ionic conductivity

The ionic conductivity of the prepared membranes was determined using impedance spectroscopy (EIS). The measurements were performed using an impedance analyzer (Solartron 1260) with an electrochemical interface (Solartron 1287) in a frequency range of 10^{-1} and 10^6 Hz with a 10 mV amplitude. The test cell consisted of two half-cells separated by two O-rings where the membrane was placed [22]. A conventional electrochemical setup with four electrodes involving two saturated Ag/AgCl electrodes as the reference electrodes and two graphite electrodes as the secondary electrodes was employed. The electrochemical measurements were performed in different KOH solutions ($10^{-4} \leq c \leq 10^{-1}$ M). Prior to testing, the membranes were immersed in a 10^{-4} M KOH solution for 24 h. The cell temperature was controlled in a Binder KMF 115(E5.2) constant climate chamber.

Z-View analysis impedance software (Scribner Associates, Inc., Southern Pines, NC, USA) was used to analyze the data obtained from the EIS measurements.

3. Results and Discussion

3.1. Synthesis of anion-exchange membranes

The chemical structure of the species involved in the synthesis of benzimidazolium-functionalized membranes (Fig. 1) was confirmed by ^{1}H-NMR analysis. ^{1}H-NMR spectra of PSU, CMPSU, PSU-BIm-Cl, and QAPSU-Cl are shown in Fig. 2.

The spectrum of PSU showed the peaks corresponding to phenyl and methyl groups at δ = 6.9-7.9 ppm and δ = 1.7 ppm, respectively [21]. The characteristic peak of -CH$_2$Cl, which

corresponds to the newly formed chloromethyl group, appeared at δ = 4.6 ppm (H_f). This peak confirmed the successful preparation of CMPSU [21]. In addition, the signal associated with the proton located in δ position with respect to the carbon containing the chloromethyl group was downshifted in CMPSU and it appeared at 7.5 ppm (H_g). Given that the H_a positions on PSU show the highest electron density, the electrophilic substitution is favored at these locations [16]. On the other hand, H_d positions show the lowest electron density and therefore, will not be affected by the chloromethylation reaction. So, the degree of chloromethylation (DC) could be successfully determined from the ^{1}H-NMR spectrum (Fig. 2) according to the equation:

$$DC = \frac{2A(H_f)}{A(H_d)} \quad (4)$$

where $A(H_f)$ and $A(H_d)$ are the integral area of the H_f and H_d peaks, respectively. The DC was 100% for all of the studied membranes.

The presence of BIm groups in PSU-BIm-Cl was confirmed by the appearance of a new characteristic peak at 3.8 ppm (H_j) corresponding to the proton of methyl in m-BIm. The formation of benzimidazolium increased the acidity of the proton of the methylene group located between the two N-atoms in m-BIm leading to the downshift of its signal (H_i).
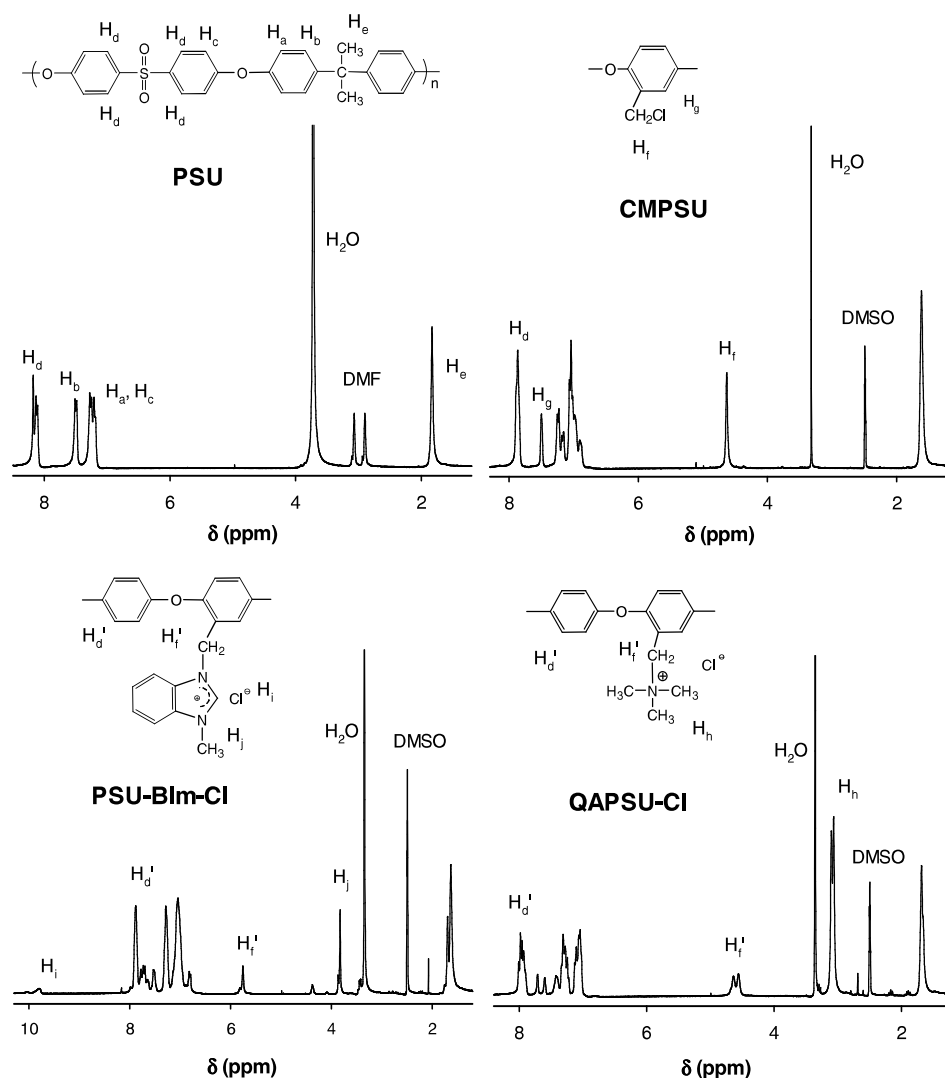

Fig. 2. ^{1}H-NMR spectra of PSU, CMPSU, PSU-BIm-Cl, and QAPSU-Cl

The complete conversion from a chloromethyl group to a benzimidazolium one was tested by the displacement of the proton signal of methylene from 4.6 ppm (H_f) in CMPSU to 5.8 ppm (H_f') in PSU-BIm-Cl [12].

The conversion from a chloromethyl group to a quaternary ammonium group was confirmed by the appearance of the peak at $\delta = 3.0$ ppm associated with the methyl groups of the amine [14,19] and the split peak at $\delta = 4.6$ ppm.

FTIR analysis was also used to confirm the presence of the functional groups in the polymer (data not shown). A characteristic peak at 750 cm^{-1} in PSU-BIm spectrum, which was not observed in CMPSU [12], was associated with the bending vibrations of the imidazolium groups [23], indicating the existence of these functional groups in the membrane. In the case of quaternary ammonium functionalized membranes, the stretching vibration peaks of the quaternary ammonium groups were located at 1648 and 1480 cm^{-1} [24].

3.2. Thermal stability of functionalized polysulfones

To evaluate the thermal stability of the functionalized polysulfones, thermogravimetric analysis was performed. Fig. 3 shows the TGA curves of the PSU, CMPSU, PSU-BIm-OH and QAPSU-OH under an air atmosphere.

PSU exhibits high thermal stability due to its rigid aromatic structure, the degradation of the polymer backbone begins at 500ºC [21]. Regarding to the chemical structure of PSU, the carbon-sulfur bond between the aromatic ring and the sulfone group, and the carbon-carbon bond between the methyl group and the central carbon of the isopropylidene moiety are the weakest links [25]. So, the degradation products identified by means of mass spectrometry include benzene, toluene, octane, ethylbenzene, styrene, diphenyl ether, dibenzofuran, phenol, and sulfur dioxide.

CMPSU showed a lower thermal stability than the original PSU with a weight loss at approximately 300ºC. By comparing the TGA curve of CMPSU to that of functionalized polysulfones containing QA or BIm groups, the presence of functional groups in the membrane decreased the thermal stability of the polymeric membrane [12,14]. So, the TGA curves of the membranes exhibited three weight losses. The first loss, from 40ºC to 200ºC was due to the adsorbed water (this loss was more pronounced in QAPSU-OH membrane). The weight loss at around 200ºC corresponded to the cleavage of the functional groups. The weight loss associated with the BIm and QA

groups was observed below 200ºC and at around 220ºC [26], respectively. The third weight loss at temperatures higher than 450ºC was due to the degradation of the polymer backbone.

By comparing the TGA curve of QAPSU-OH to that of PSU-BIm-OH, the temperature at which the weight loss of the functional groups begins was lower in PSU-BIm-OH. Therefore the chemical structure of BIm group which comprises an aromatic ring seems to favor the thermal stability of the membrane.
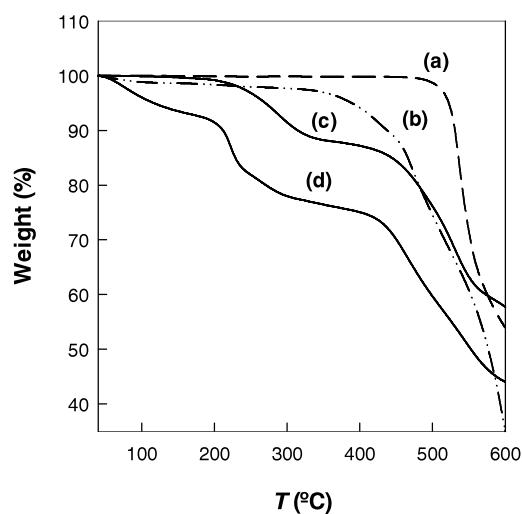

Fig. 3. TGA curves obtained under an air atmosphere for the PSU (a), CMPSU (b), PSU-BIm-OH (c), and QAPSU-OH (d) membranes

Membranes containing imidazolium groups showed higher thermal stability than PSU-BIm-OH and QAPSU-OH membranes. Thus the degradation of Im groups begins to degrade at 258ºC [16]. However, the decomposition temperature of the phosphonium [27] and guanidinium [15] groups was 186 and 185ºC, respectively.

3.3. Ion exchange capacity, water uptake and swelling degree

The IEC for the different functionalized membranes here studied is shown in Table 1. PSU-BIm-OH showed an IEC higher than that obtained for QAPSU-OH which value (0.7 mmol g^{-1}) is in agreement with that previously reported [28].

The IEC reflects the amount of exchangeable groups in the membrane and consequently, it is directly related to the

ionic conductivity. Therefore it is expected that PSU-BIm-OH showed higher ionic conductivity than QAPSU-OH.

The water uptake and swelling degree were also determined in these membranes. The results indicated that the capacity of PSU-BIm membrane to absorb water was more favored when benzimidazolium groups were inserted in the polymer.

Table 1.
IEC, WU%, and SD% values of AEMs

Membrane	IEC (mmol g^{-1})	WU%[a]	SD%[a]
PSU-BIm-OH[b]	0.84	9.9	14.8
QAPSU-OH[c]	0.70	5.7	10.0

[a]Room temperature; [b]Ref [12]; [c]Ref [14]

3.4. Ionic conductivity

The ionic conductivity of the different membranes was determined using impedance spectroscopy. Measurements were performed in aqueous solution of potassium hydroxide (10^{-4}-10^{-1} M). Therefore, it is important to consider the effect that the electrolyte solution has on the membrane electrical properties.

The evolution of the membrane ionic resistivity (r_m) with KOH concentration is shown in Fig. 4.
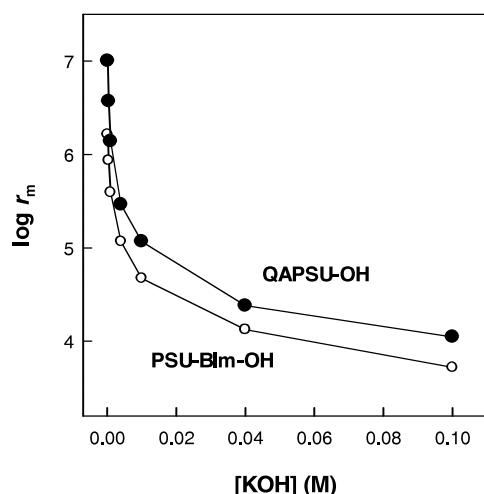

Fig. 4. Evolution of the ionic resistivity values of PSU-BIm-OH (○) and QAPSU-OH (●) with KOH concentration at room temperature

For both membranes, r_m decreased as KOH concentration increased in the 10^{-4}-10^{-1} M range. However, PSU-BIm-OH membranes showed lower r_m values over the concentration range studied here. This fact reflects the great influence that the electrolyte solution embedded in the membrane network has on the electrochemical properties of this polymeric material [22,29].

Therefore, the membrane ionic conductivity (σ_m) seems to be strongly influenced by the nature of the functional group. As can be seen in Table 2, the membrane ionic conductivity was more than twice as high when the quaternary ammonium groups were replaced by the benzimidazolium ones.

Table 2.
Ionic conductivity and activation energy of AEMs

Membrane	$10^6 \times \sigma_m$ (S cm^{-1})[a]	E_a (kJ mol^{-1})[b]
PSU-BIm-OH[c]	21.2	24 ± 1
QAPSU-OH[d]	8.5	63 ± 1
Nafion 117	17[e]	12[f]

[a]Room temperature and [KOH] = 10^{-2} M; [b][KOH] = 10^{-3} M; [c]Ref [12]; [d]Ref [14]; [e][HCl] = 10^{-2} M; [f]Ref [30]

Measurements performed under similar experimental conditions ([HCl] = 10^{-2} M at room temperature) using Nafion 117 as reference material, revealed that the ionic conductivity of this polymer was the same order of magnitude as that obtained for the AEMs studied here.

The influence that temperature has on the membrane ionic conductivity was also evaluated. The experimental data obeyed Arrhenius law and the apparent activation energy (E_a) associated with the OH$^-$ transport through the membrane was easily obtained from the slope of the lnσ_m-1/T plot. Table 2 shows the calculated E_a for the AEMs studied here.

The quaternary ammonium-functionalized polysulfones showed a higher value of E_a than the obtained for the membranes which contain benzimidazolium groups. Therefore, the nature of the functional groups plays an important role on the ionic process through the membrane. In addition, these AEMs showed higher E_a values than that observed for Nafion 117. This fact can be attributed to that the diffusion coefficient of H$^+$ is usually four times higher than for OH$^-$ and, consequently, in order to get the same results, it would be necessary to have a concentration of OH$^-$ ions in the alkaline membrane four times higher than in the acidic one [31].

In view of the obtaining results, different strategies could be adopted to improve the ionic conductivity of the membranes. One of them could be focused on evaluating the number of cationic groups presented in the polymer backbone. In a previous work [12] the influence that the amount of benzimidazolium groups attached to the polymer, has on the membrane ionic conductivity was studied. The results showed that the ionic conductivity increased more than two orders of magnitude when the degree of chloromethylation (that is directly related to the number of functional groups present in the membrane) increased from 40 to 140%. Yan et al., [16] observed a similar behavior with membranes which contain imidazolium groups. This fact is easily explained since the cationic group is responsible of the ionic transport through the membrane. The other alternative to optimize the membrane electrical properties consist of incorporating inorganic charges into the polymeric matrix. When ZrO_2 nanoparticles were incorporated into quaternized polysulfone, the resulting composite membrane exhibited better electrochemical properties than that observed in the absence of zirconia [28]. The effect that the presence of Al_2O_3 nanocomposites has on the polymer properties was also evaluated in our research group [14]. The results revealed that the ionic conductivity was twice as high when a loading of 4% Al_2O_3 was added. Therefore, for AEMs, the addition of some inorganic charges can enhance the electrochemical performance.

4. Conclusions

In the present work, different functionalized polysulfones were successfully synthesized and characterized. Polysulfone was firstly chloromethylated followed by nucleophilic substitution reaction with the corresponding *N*-compound, trimethylamine and 1-methylbenzimidazole to obtain the quaternary ammonium and benzimidazolium functionalized membranes, respectively. The membranes thus prepared as well as the starting polymers were characterized by ^{1}H-NMR and FTIR analysis. The thermal stability of the membranes was lower than the original polymers. The decomposition temperature of the benzimidazolium group was higher than the quaternary ammonium one. However, both membranes exhibited high thermal stability for typical fuel cell operation temperatures below 100°C. The capacity of these materials to absorb water was more favored when benzimidazolium groups were inserted to the polymer instead of quaternary ammonium ones. The ionic conductivity of the membranes in dilute aqueous solution of potassium hydroxide was studied by means of impedance spectroscopy. The results show a clear correlation between the membrane's electrochemical behaviour with the electrolyte solution embedded in the membrane. In addition, the nature of the functional group modifies the membrane ionic conductivity. So, the membrane ionic conductivity was more than twice as high when the quaternary ammonium groups were replaced by the benzimidazolium ones. Nevertheless, these values were the same order of magnitude as that obtained for the Nafion 117 which was used as reference material.

Therefore, the membranes here studied could be considered promising materials for being satisfactorily used as electrolytes in AEMFCs.

Acknowledgements

Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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