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This is an **author produced version** of a paper published in:

Renewable Energy 127 (2018): 883-895

DOI: <http://doi.org/10.1016/j.renene.2018.05.020>

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Poly (vinyl alcohol) and Poly (benzimidazole) blend membranes for high performance alkaline direct ethanol fuel cells

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Abstract:

A series of poly(vinyl alcohol)-*blend*-poly(benzimidazole) (PVA:PBI) membranes are synthesized with different ratios of PVA and PBI (2:1, 4:1, 6:1 and 8:1) using the casting method. These materials are doped in KOH 6M solution in order to study their suitability for fuel cell applications. The Infra-red (IR) and Raman spectra confirm the successful doping of the membranes and the dimensional changes due to water and KOH uptakes during the doping are similar to other PBI-based membranes. XPS measurements are performed to evaluate the characteristics of these materials after the doping process. The thermal stability of the membranes is excellent in the range of desired temperatures (below 100 °C) and the conductivity values found are between 10^{-2} and 10^{-1} S cm⁻¹. These results are optimal to consider these membranes as candidates for anion exchange membranes (AEMs) and they are

tested in a single cell with ethanol as fuel. The PVA:PBI 4:1 membrane have the best behaviour in fuel cell, reaching a power density of 76 mW cm^{-2} , approximately 50% better than the doped PBI in the same conditions. These important results can be considered highly promising for the future application of these membranes in alkaline polymer electrolyte membrane fuel cells (APEMFC).

Keywords:

Fuel cells; alkaline; blend membrane; PBI; PVA; ethanol.

1. Introduction

In recent years, polymer exchange membrane fuel cells (PEMFC) are attracting great interest due to the high power densities that are capable of reaching at relatively low temperatures [1–3]. Hydrogen and methanol have been the most common fuels used in these devices but both have certain drawbacks. Hydrogen has problems of production, storage and distribution, and methanol issues due its toxicity [4]. Nowadays, one of the best alternatives to these fuels is the use of ethanol, easy to store and distribute, cheaper and less toxic than methanol. The main advantages are the high energy density of this fuel, in addition to the fact that ethanol is considered a green chemical. It can be produced as a renewable biofuel from the fermentation of biomass in large quantities and, in addition, both ethanol and its final oxidation products are relatively non-toxic.

Direct ethanol fuel cells (DEFC) meet some requirements for a sustainable energy conversion technology, such as high electrical efficiency, easy handling of ethanol, or low operation temperature, and they are attractive power sources for portable electronic devices. However, this technology have important drawbacks as the slow electrode kinetics of ethanol electrooxidation (EOR), the poisoning of catalyst materials and high cost of

electrocatalysts[5,6] especially when Nafion[®] is used as proton exchange electrolyte. Besides, with Pt or Pt alloys nanoparticles a very low conversion is carried out, the C-C bond rupture during the EOR is most likely not occurring and the complete conversion to CO₂ is very low. Nevertheless, the higher pH of alkaline membranes can improve the reaction kinetics of both processes, EOR and ORR (oxygen reduction reaction), with respect to acidic media. It facilitates the use of a range of non-precious metal catalysts in the cathode and in the anode, reducing the dependence of platinum [7–9]. On the other hand, anion exchange membranes present an important decrease of alcohol permeability [10,11]. It is necessary to take into account that the ionic current is now in reverse direction in comparison with proton conducting membranes[12]. These advantages are the main reason to change the common type of PEMFC devices to others with anion exchange membranes as electrolytes. However, the main issue of the improvement of the performance of these fuel cells was the limited development of the anion exchange polymeric membranes (AEM).

At the present, many groups have made important researches looking for materials capable to exchange anions as well as Nafion[®] for acid media[13,14]. The main objectives for these membranes for DEFCs applications are to increase the ionic conductivity and to decrease the ethanol permeability through the electrolyte. Some important groups at membrane research collaborated in one of the more important reviews on this topic in 2014[12]. This article collects the most representative kind of anion exchange membranes that are being investigated nowadays. The main ways to prepare AEMs according to S. Maurya et al. [15] are: i) by polymerization of monomers [16], ii) by the solution casting method[17] or iii) by the grafting method of conventional polymers[18], and iv) by using composites or blends[19]. Despite all the studies that are being carried out, AEMs are still in an early stage of development, with conductivity values lower than the standard membrane in acid medium, Nafion[®]. This is related to the lower conductivity of the OH⁻ anion used in AEMs compared to the H⁺ cation used in cation exchange membranes (CEM)[12].

One of the most studied materials for this type of exchange membranes is the polybenzimidazole (PBI)[20–22], but it is necessary to dope it in alkaline medium for several days and, even after this process, its conductivity is still about 10 times lower than Nafion®[23]. Other material that has been used for this application was the polyvinyl alcohol (PVA)[24,25]. This polymer has a hydrophilic nature which is considered as an advantage for some applications but in most cases it becomes a problem because of the high swelling capacity of the membranes in water. To enhance the stability and performance of PVA membranes different modifications have been carried out. The strategy followed in this paper has been to blend it with other polymer, in this case PBI.

In the present research, we report a comparative study of the behaviour of different synthesized blend membranes based on PVA and PBI and the influence of the weight ratio. Specifically, we have prepared a series of PVA:PBI membranes, with different weight ratio of polymers (2:1, 4:1, 6:1 and 8:1), using the casting method. The membranes characterization was performed by: Fourier transform Infra-red spectroscopy (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy, XPS. The mechanical properties and the ionic conductivity measured by AC impedance technique were determined. Also KOH and water uptake measurements were carried out on the PVA:PBI membranes. In addition, we evaluate the performance and applicability of these materials as solid electrolyte in alkaline membrane direct ethanol fuel cells (AMDEFC).

2. Experimental Section

2.1 Materials

The reagents used were poly(2,2'-m-(phenylene)-5,5'-bibenzimidazole) (polybenzimidazole, PBI), powder (BETWEEN, LizenzGMBH) (density 0.7-0.9 dL g⁻¹); polyvinyl alcohol (PVA), hydrolysed, powder of MW89.000-98.000, 99+% (Aldrich); dimetilsulfoxide (DMSO), 99.9%; N,N-dimethylacetamide (DMAc), 99.5% (Aldrich); and potassium hydroxide (KOH), 85% (Aldrich).

2.2 Synthesis of membranes

A series of PVA:PBI membranes was prepared from solutions of the precursors by using the following weight ratios: 2:1, 4:1, 6:1 and 8:1. A 4.76 wt. % PVA solution was obtained by heating 1g of PVA in DMSO (20 g) under continuous stirring at 85°C for 30 minutes. Similarly, a solution of 3.5 wt. % PBI was obtained by heating 3.5 g of PBI in DMAc (96.5 g) at 80°C for 48 hours. The required amounts of solved PVA and PBI, according to the weight ratio desired, were transferred to glass beakers and stirred for 40 minutes at 500 rpm at 80 °C.

Then, the solutions were placed in Petri dishes coated with PTFE liners and they were introduced in a vacuum oven (Mettmert VO200). The pressure was lowered from room pressure to 10 mbar, and the temperature was maintained at 40 °C. After, the membranes were peeled and stored (see Fig. 1). Commercial PBI membrane of the company Danish Power Systems was used for comparison purposes.

Some membranes were doped in 6M KOH at different times. Then the membranes were washed and rinsed with Milli-Q water four times, dried with filter paper and stored in sealed plastic bags until been used.

Fig.1. a) Image of a synthesized PVA: PBI membrane and b) Scheme of the original polymers.

2.3 NMR spectroscopy

High resolution solid-state ^{13}C CP NMR spectra were measured in a Bruker AV-400- WB spectrometer at ambient temperature working at ^{13}C resonance frequency of 100.61MHz. Spin-lock cross polarization with magic angle sample spinning (CPMAS) were used to obtain the solid state ^{13}C spectra. Samples were hand-compacted into ZrO rotors with Kel-F end caps. All samples were accumulated one night. Chemical shifts were reference relative to the CH_2 signal of adamantane (29.5 ppm) as secondary reference and the TMS (tetramethylsilane) as primary reference.

High resolution liquid ^1H NMR spectra were recorded using a Bruker DRX 500 MHz spectrometer at 298K, with chemical shifts relative to the TMS. The PBI and PVA powders were weighted (10 mg of each), dried in an oven at 110 °C for 15 hours and then dissolved in 0.6mL DMSO- d_6 (deuterated) highly dried separately. The powders PVA were dissolved by heating with a hot-air pistol and agitation with a Vortex machine to achieve complete dissolution. PBI couldn't be completely dissolved using the same methods but the dissolved fraction was enough to clearly color the solution. The spectrum of each one was performed and after 0.4mL of the PVA solution were mixed with 0.1mL of the PBI solution, which should give approximately a 4:1 ratio solution. Separately a piece of membrane of 10 mg was partially dissolved in 0.6mL of DMSO- d_6 highly dried. This liquid phase of the dissolved membrane was used to perform the ^1H -NMR spectrum.

2.4 TGA/DSC

Thermal stability of the membranes was studied using the thermogravimetric analysis (TGA) technique (TA Instrument 20). The samples were heated from 25 to 900 °C under nitrogen atmosphere at a rate of 10 °C min⁻¹. The differential scanning calorimetric (DSC) was measured in a TA Instrument 10, under nitrogen atmosphere, heating from 25 to 300 °C at a rate of 10 °C min⁻¹ with the samples sealed in aluminium pans.

2.5 IR and Raman spectroscopy

The FT-IR/ATR spectra were carried out on a Jasco FT-IR 410 spectrophotometer with an attenuated total reflectance accessory (ATR) between 500 and 4000 cm⁻¹ with a resolution of 2cm⁻¹. The Raman spectra were measured in a Via Raman spectrometer (Renishaw) with an excitation wavelength of 785 nm. The measurements were performed over a range of 100–3500 cm⁻¹ employing 10 scans and an exposure time of 10 s per measurement. The sharp silicon line located at 520 cm⁻¹ was employed as reference in the Raman shift scale.

2.6 Mechanical properties

Mechanical tensile tests were performed using a MTS® QTest1/L Elite testing machine equipped with a 100 N load cell. Type 4 dumbbell test pieces (according to ISO 37) were tested. The crosshead speed used was 10 mm min⁻¹ with an initial width of 2 mm and an initial gauge length of 20 mm. At least 3 pieces were used for each sample.

2.7 SEM/EDX measurements

Morphology of the membranes surface and cross-section was studied with a Hitachi S-300 scanning electron microscope (SEM). The membrane was first placed in a brass holder and sputtered with a thin gold coat under vacuum. The atomic composition was investigated with

an INCAxsight (Oxford Instruments) energy-dispersive X-ray spectroscopy (EDX) system equipped in the scanning electron microscope.

2.8 KOH and water uptake

Three pieces of each type of membrane, 2:1, 4:1, 6:1 and 8:1, were cut in rectangular shape of approximately 10 mm x 15 mm. Length, width, thickness, and weight of the samples were accurately measured before drying them in a vacuum oven at 40 °C and 10 mbar for 15 hours. Then, they were weighted (W_0) and dimensioned again. After that, the samples were immersed in separate baths of KOH 6 M for the doping process. Each membrane was kept in the bath for the number of days required to achieve the maximum conductivity (PVA:PBI 8:1, 1 day; 6:1, 2 days; 2:1 and 4:1, 3 days). Then, the membranes were dried in the vacuum oven, weighted (W_d) and dimensioned. Water and KOH uptake of the membranes were calculated as follows:

$$\text{Water uptake (\%)} = \frac{W_d - W_{dd}}{W_0} \cdot 100$$

$$\text{KOH uptake (\%)} = \frac{W_{dd} - W_0}{W_0} \cdot 100$$

where W_d , W_{dd} and W_0 are weight of the doped (water + KOH), dried doped (KOH), and dry membranes, respectively.

2.9 XPS Measurements

The XPS spectra were measured in an ultrahigh vacuum system (UHV) at a base pressure below 1×10^{-9} mbar using a hemispherical analyser (SPECS Phoibos 100 MCD-5). The pass energy was 9 eV, giving a constant resolution of 0.9 eV. The Au 4f_{7/2}, Ag 3d_{5/2} and Cu 2p_{3/2} lines of reference samples at 84.0, 368.3 and 932.7 eV, respectively, were used to calibrate binding energies. A twin anode (Mg and Al) X-ray source was operated at a constant power of 300 W using Mg K α radiation ($h\nu = 1253.6$ eV). Although charging was observed due to the insulating character of the samples, this effect was corrected peaking the C 1s band attributed to C–C bonds at 285.0 eV and shifting accordingly all other core levels.

2.10 Conductivity measurements

Through plane ionic conductivity of the membranes was measured using a cell composed of two stainless steel plates. The membrane was sandwiched between two stainless steel electrodes of known area (0.36 cm²). An AUTOLAB equipment (PGSTAT 302 N) equipped with a Frequency Response Analyzer (FRA) was used to perform the impedance measurements of KOH doped membranes. The applied dc bias voltage was 0 V, and 10mV rms. Data collected were in the range from 10⁶ to 1Hz. Membrane resistance, R, was calculated from the intercept on the real axis of the Nyquist plot[26]. The conductivity (σ) was calculated as follows:

$$\sigma = \frac{l}{A \cdot R}$$

where l and A are the thickness and the area between the electrodes. The measurements were conducted at 25, 40, 60, 80 and 90 °C. The measurement was carried out in chamber without additional humidification, only the temperature was controlled. Just after the doping process, the membranes were washed with Mili-Q water and superficially dried with filter paper before been sandwiched between the electrodes.

2.11 Performance evaluation of different membranes in single-cell

The membrane-electrode assembly (MEA) was formed with: carbon cloth (LT 1200W ELAT, ETEK), a catalytic layer sprayed on it, and an anion exchange membrane as solid electrolyte. The ink was obtained dispersing Pt/C (Johnson Matthey, 40 wt. %) and PtRu/C (Johnson Matthey, 45 wt. %) at cathode and anode, respectively, with isopropanol, Milli-Q water and Nafion® ionomer (Dupont, 5wt. %). The final amount of platinum was 1 and 1.33 mg cm⁻² at cathode and anode, respectively. As electrolyte, synthesized (40-60µm) PVA:PBI membranes and commercial 50 µm polybenzimidazole (PBI) membrane (Danish Power Systems) were used. All membranes were doped in 6 M KOH solution until their best conductivity was reached. FCTS station (Arbin Instruments) was used and data were collected with MITS-Pro software (Arbin Instruments). Cathode was fed with pure O₂ (Air Liquide) flow rate of 200 ml·min⁻¹ and atmospheric pressure. Anode was fed with 2 M ethanol in 2 M KOH aqueous solution, with a flow rate of 1 ml·min⁻¹, without back pressure, using a peristaltic pump (Dinko Instruments) external to the station. Fuel cell temperature was 90 °C and the area of the MEAs was 4 cm².

3. Results and discussion

The membranes were characterised using different techniques and their performance was evaluated.

3.1 ^{13}C and ^1H -NMR

The NMR study was used to identify the presence of the polymers and the possible interaction between them. Fig. 2a shows the structure of PBI and PVA with numbered C atoms in order to make easier to assign the signals of the solid ^{13}C -NMR spectra of Fig. 2b. Assignment of peaks was made according to bibliography[27–30].

Fig. 2: (a) Structure of PBI and PVA molecules with numbered carbons, (b) Partial ^{13}C -NMR spectrum of PVA, PBI and PVA:PBI membranes with numbers of ascribed carbons.

For comparison between the spectra of PVA, PBI and PVA:PBI blend, normalization of the intensity of the peaks was used. In the range where PBI signals appear (170-100 ppm), the intensity of the peaks was normalized to the peak at 128.5 ppm (carbons 5, 6 and 7). Those carbons belong to the solitary aromatic ring, which probably suffered negligible influence from the mixture with PVA.

In the PVA region (90-30 ppm), normalization was done to the intensity of peak at 45 ppm (carbon 15). This peak is ascribed to the CH_2 of PVA, which shouldn't have significant differences in the mixture with PBI. The peaks 12, 13 and 14 were ascribed to the CHOH carbons whose alcohol group has two, one or none hydrogen bonds formed with neighbours respectively. They are also called isotactic, heterotactic (or atactic) and syndiotactic signals[30]. The differences in the spectra are not very noticeable but it can give some information about the possible presence of interaction between PVA and PBI. The increase of intensity in the 12 and 13 peaks and decrease of the 14 peak in the 4:1 spectrum respect to the single PVA spectrum might mean that hydrogen bonds are being formed with PBI. Also, it is interesting to note that carbon 1 appears with a sharper and taller peak in the 4:1 membrane

and carbons 4 and 8, 9, 10 move slightly (2.9 ppm) downfield. All of them, except to 8, belong to the imidazole structure near the nitrogens and so might present this small changes due to the presence of hydrogen bonds with the PVA. The peaks that appear in the PBI spectrum at 227 and 30ppm, showed in Fig. S1, are the rotational side bands[31].

Liquid ^1H -NMR, Fig. 3a, shows the structure of PBI and PVA with the numbered protons assigned to the spectra of Fig. 3b,c and Fig. S2a. The assignment of the peaks was done according to bibliography[32,33]. The chemical shift of the signals related to the corresponding hydrogens and the integration values are given in Table S1. The number of integrated hydrogens correlates perfectly with the hydrogens present in the PVA and PBI monomers.

The comparison of the PBI, PVA and 4:1 mix spectra shows some important changes. It is relevant to note that the interaction between the polymers occurs being both dissolved and it is expected to be more intense when the casting of the membranes is finished and there is further intimate contact between them. The peak at 13.25 ppm (peak 1), in Fig. 3b, ascribed to the N-H proton suffers an important decrease in intensity, expansion of the width and small shift of 0.06 ppm downfield. We consider this is a clear signal of the interaction of this protons with PVA via hydrogen bonds[33].

Another change that occur in the PBI region, showed with more detail in Fig. 3c, is the slight shift of 0.01 ppm downfield in the peak at 9.16 ppm (peak 2) which is ascribed to the solely proton of the aromatic ring and it might be produced from the effect of forming hydrogen bonds in the two near imidazole rings.

Also in Fig. 3c, relevant differences can be observed in the peaks between 8.1 and 7.6ppm (peaks 4-10). These peaks are ascribed to the aromatic ring of the benzimidazole and thus is logical to suppose that the aromatic electron cloud will be sensible to the hydrogen bonds established by the NH group. Fig. S2b shows the range in which PVA and solvent signals appear. Peaks not marked come from impurities. Peaks at 3.3 and 2.5ppm were ascribed to

protons of water present in the solution and the DMSO used as solvent respectively, similarly than other works elsewhere[33].

In the PVA region, between 5 and 1 ppm, no great differences can be seen. The peaks at 4.67, 4.47 and 4.22 ppm come from the isotactic, heterotactic and syndiotactic alcohol groups respectively (similar to the signals observed in the ^{13}C spectra). None of them show a shifting of the peak in the 4:1 spectrum but it makes sense since the ratio of reacted PVA (via hydrogen bonds) to unreacted would be so low that the changes are probably neglected by the unreacted signals.

Fig. 3: (a) Structure of PBI and PVA molecules with numbered hydrogens, (b, c) Selected parts of ^1H -NMR spectrum of PVA, PBI and PVA:PBI membranes with numbers of ascribed hydrogens.

In the PVA region, between 5 and 1 ppm, no great differences can be seen. The peaks at 4.67, 4.47 and 4.22 ppm come from the isotactic, heterotactic and syndiotactic alcohol groups respectively (similar to the signals observed in the ^{13}C spectra). None of them show a shifting of the peak in the 4:1 spectrum but it makes sense since the ratio of reacted PVA (via hydrogen bonds) to unreacted would be so low that the changes are probably neglected by the unreacted signals.

When the spectrum of the dissolved membrane was compared with the spectrum of the mixed PVA and PBI solutions no relevant differences were observed in the described signals.

NMR, and more concretely liquid ^1H -NMR spectroscopy, has demonstrated to be an accurate technique to identify the interaction between PBI and PVA, showing clearly the formation of a bridge hydrogen bond between these two polymers. This demonstrates that the membrane is not just a physical mix of both polymers but there is chemical interaction between them.

3.2 TGA/DSC

In order to know if the synthesized membranes are appropriate to be used as a polymer electrolyte in exchange membrane fuel cells the thermal stability was evaluated. The behaviour of three different blend membranes with 2:1, 4:1 and 6:1 weight ratio of PVA:PBI was measured, in addition to that of PVA and PBI pristine membranes for comparison purposes. The thermal stability of these samples is showed in Fig. 4a. PBI membranes have been broadly studied previously[34–38], revealing that about 10–15 wt. % is lost before reaching 150 °C, due to absorbed water; above 150 °C, no relevant weight loss is observed up to 500 °C, indicating the excellent thermal stability of this polymer. In the range from 500 to 900 °C, another loss of mass occurs (10-15 wt. %), although still most of the original weight remains[39].

Fig. 4: a) TGA measurements and b) DSC of the blend membranes and pristine PVA and PBI membranes.

Regarding to the pure PVA membrane, three main loss regions are visible in TGA measurements. First, this material loses around 5 wt.% at 96 °C, probably due to the evaporation of absorbed water. The second step, between 200 and 375 °C with sharp decrease around 266 °C, comes from the degradation of the PVA polymer membrane, and an approximate loss of 80 wt.% is observed. This degradation starts with the process known as chain “stripping”, which consist on the elimination of water accompanied by the formation of polyene structures. After that, a second loss happens around 350 °C, in which these polyene structures are further converted to low-molecular weight aliphatic products, as described by other authors[40–42]. The third change occurs in the range of 400-500 °C, losing 12 wt. %, owing to the cleavage of C-C backbone of PVA polymer membrane (or so-called carbonation). Finally, the sample gradually degrades until reaching 880 °C, remaining 2.5 wt. % of residual ash.

As Fig. 4a shows, all studied PVA:PBI samples are stable at least up to 250 °C. This value is far superior to the normal PEMFCs operation temperature, around 90 °C, at which these membranes should work. It is also interesting to notice different behaviour between the membranes. In the region from 500 to 850 °C, the degradation of membranes is closely related to the PVA:PBI ratio. Thus, the higher the content of PVA in the membrane the lower remaining residual ash (in weight %) at 850 °C. This result seems logical since PBI still retains most of its original weight in this region, while PVA is almost completely degraded. Partial degradation of PBI in the same range of temperatures is also observed for the membranes with the highest content of PBI (2:1 and 4:1)[39].

The results of the differential scanning calorimetry (DSC) of the membranes are presented in Fig. 4b. The broad endothermic band observed for all samples around 100 °C comes from the evaporation of water. Pristine PVA and blend membranes present a clear melting transition (T_m) around 228 °C, similar to values reported elsewhere[42,43]. The intensity of the peak at

these temperatures is lower for blend membranes, this effect can be attributed to the reduction in crystallinity of PVA due to the mixture with PBI [42]. In summary, although the presence of PBI in blend membranes distorts slightly the PVA crystallinity, all blend membranes are suitable for being used in fuel cells at 90 °C.

3.3 FT-IR and Raman.

FTIR and Raman measurements of the membranes were carried out in order to identify the functional groups present in their structures and to obtain information about the possible interaction between PVA and PBI. The recorded spectra of PVA, PBI and PVA:PBI (2:1, 4:1 and 6:1) membranes have been included in Fig. 5.

The FTIR spectrum of PVA membrane shows a very strong broad peak centred at 3270 cm^{-1} for the intermolecular hydrogen bonding and the hydroxyl (O-H) stretching vibration. The C-H asymmetrical and symmetrical stretching vibration occurs at 2940 cm^{-1} and 2910 cm^{-1} respectively, and the transmission peak at 1093 cm^{-1} corresponds to the stretching vibration of C-O of the remaining non hydrolysed vinyl acetate group of the PVA [44]. Another two peaks appear at 1425 cm^{-1} and 1328 cm^{-1} due to -C-H and -O-H bending, in agreement with Panero et al.[45]. The FTIR spectra of the PVA:PBI membranes show the same characteristic transmission peaks of the PVA (see Fig. 5a). On the other hand, the most significant bands observed for the pristine PBI membrane appear in the region $2000\text{-}1000\text{ cm}^{-1}$. These signals are composed of the relatively narrow peaks which can be assigned to the cycle vibrations as well as in plane deformation modes (δ_{NH} and δ_{CN}). Bands derived from aromatic (C=C) and (C=N) stretching

modes (ca. 1630 cm^{-1}), in-plane deformation of benzimidazole (1536 cm^{-1} and 1443 cm^{-1}) and breathing mode of the imidazole rings (1289 cm^{-1}) were observed (see Fig. 5a) [35,38]. It is worth noting that PBI characteristic peaks are not clearly visible for the blend membranes in IR.

Fig. 5. a) FT-IR/ATR and b) Raman spectra of undoped PBI, PVA and PVA:PBI membranes (2:1, 4:1, 6:1).

Regarding the Raman spectra (Fig. 5b), the most relevant information for the blend membranes is obtained from PBI typical signals: 958 (weak), 998 (weak), 1293 (strong), 1447 (medium), 1537 (very strong) and 1592 cm^{-1} (very strong). All membranes containing PBI

showed peaks mounted on a high broad band due to fluorescence. Even when the base-line correction was performed, the signal of PBI-based membranes was approximately 20 times stronger than those observed for pristine PVA. For this reason, PVA signals are masked and the Raman spectra of PVA:PBI membranes are so similar to the PBI one. The peaks at 1545 cm^{-1} and 1299 cm^{-1} come from N-H stretching and breathing modes of imidazole rings, respectively [11]. The region between 900 and 1000 cm^{-1} shows different signals assigned to aromatic rings vibrations. IR and Raman spectra have been useful to identify the presence of PVA and PBI in membranes, although a NMR study have been necessary to have further insights in the interaction between the polymers (in section 3.1).

On the other hand, the ionic conductivity of as-synthesised membranes is very low, as it will be discussed in section 3.8, and therefore doping is required to reach adequate conductivity of the ions through the membrane. For this purpose, aqueous solutions of KOH are commonly used in alkaline PEMFCs [35,46]. The effect of doping on membrane structure was analysed using FT-IR and Raman spectroscopy, and the most relevant information is shown in Fig. 6. All blend membranes display similar IR and Raman spectra, and only slight changes in relative intensities are observed by changing the ratio of polymers. Characteristic peaks observed in the IR spectra at 1144 and 1093 cm^{-1} , from C-O stretching, and at 1019 and 952 cm^{-1} , from the in-plane aromatic C-H bending, reveal the presence of both polymers. Moreover, a signal around 1400 cm^{-1} assigned to the O-H bending mode of the hydroxide (1411 cm^{-1} in Raman and 1397 cm^{-1} in IR) can be observed in all samples, which is a clear indication of the presence of “free KOH” within the membrane structure [35]. Additionally, a strong band at 1625 cm^{-1} (IR) is attributed to the –O-H stretching of the absorbed water [11]. Regarding N-containing groups, a band at 1370 cm^{-1} (IR) might be attributed to free amino moieties coming from the hydrolysis of PBI in a strongly alkaline environment [35]. Moreover, the reaction of NH groups with KOH produces a shift of the C=N stretching vibration to lower energies, giving a broader band around 1600 cm^{-1} in the Raman spectrum. It is worth noting that the signal assigned to N-

H stretching of imidazole rings (1545 cm^{-1} in Raman) disappears completely for PBI doped membranes and suffers an important reduction for the PVA:PBI 4:1 ones. This can corroborate the substitution of the acid H^+ of the imidazole rings by K^+ coming from KOH.

Fig. 6. FT-IR/ATR and Raman spectra of PVA (pristine), PBI (pristine and doped), and PVA:PBI 4:1 (undoped and doped).

3.4 Mechanical properties

In general, before the alkaline doping process in KOH 6M, PVA:PBI membranes display good mechanical flexibility, light transparent yellow-brown colour, and homogeneous appearance (Fig. 1a). In addition, they possess enough consistency to be easily cut into different size and used as solid electrolyte in low temperature fuel cells. Mechanical properties of 2:1 and 4:1 PVA:PBI membranes were investigated, since these blends performed the best results in single cell measurements. The stress vs. elongation graph shows the behaviour of doped and undoped membranes compared to PBI (Fig. 7). Detailed results with averages and standard deviations are in table S2. These results reveal that the resistance of undoped PBI is higher than those of PVA:PBI membranes (2:1, 4:1), whereas blend membranes show similar stress values. On the other hand, the mechanical resistance for doped membranes decreases in all cases. Pristine PBI is reduced to a similar stress value than the undoped blend membranes.

Meanwhile, the mechanical strength of doped blend membranes becomes similar for both samples, although the loss is much lower than for PBI.

Fig. 7. Stress vs. elongation measurements of pristine PBI and blend PVA:PBI membranes.

Regarding to ductility, the presence of PVA in blend membranes means a clear improvement, and the elongation values observed for these samples, both undoped and doped, are several times larger than for pristine PBI. It was also observed that the ductility was further improved by the doping of the blend membranes while remaining unaffected in the pure PBI doped membrane.

One possible explanation of these results may arise from the process of degradation of the membranes in the strong alkali media. Probably, some bonds are broken in PBI, as was suggested by Linares et al. [35], giving rise to lower modulus and resistance of pristine PBI membranes without significant difference in elongation. In blend membranes, added to the degradation of PBI, small gaps may be formed between PBI chains in the surface and PVA, which would allow larger elongation of the membrane. The results obtained from the mechanical properties of PBI are in good agreement to other results found in literature [11,34] and the values obtained for the PVA:PBI membranes are sufficient to be used as AEMs.

3.5 SEM/EDX

Scanning electron micrographs of the membrane surfaces and cross sections were obtained to investigate the homogeneity of as-synthesised membranes and possible changes after the doping process. The homogeneity of undoped membrane's surface can be observed in Fig. S3. In addition, the mean composition determined by EDX was similar throughout the membrane. After the doping process, differences were observed in the surface of the membrane, especially in those with lower PVA content, Fig. S3. Some circular islands are formed, which are composed mainly by PBI. This composition was deduced from the differences on the N/O ratio: 1.16 in the circular white islands vs. 0.16 in the undoped membrane and the dark zones of the doped membrane. Probably these islands are created due to the removal of superficial PVA during the doping process. However, no tunnel-like forms are observed in the cross-section, therefore it may be just a surface effect, Fig. S3c,d.

3.6 KOH and water uptake

Anion exchange membranes based on PBI are able to absorb water and KOH, undergoing dimensional changes during both alkaline doping and fuel cell measurements. The amount of water and KOH absorbed during the doping is represented in Fig. 8a as weight percentage of the undoped membranes. These values correspond to the optimal doping time for each membrane.

Fig. 8. a) KOH and water absorbed in the membrane due to the doping process. As percentage of the undoped membrane's weight.
b) Dimensional changes due to the doping process.

Regarding PBI membranes, they are able to absorb above 85 wt. % of water and around 40 wt. % of KOH. The presence of PVA in blend membranes results in a decrease KOH uptake (32% is the minimum value, for 2:1 membrane) and in water uptake. However, increasing the amount of PVA in the blend, the membrane can absorb more KOH and water (for example PVA:PBI 8:1 reach values of KOH and water uptake similar to pristine PBI).

PVA and PBI show high affinity to water, PVA membranes gain 36% weight in water (water absorbed relative to the dry membrane), which corresponds to 0.9 water molecules per PVA r.u. (repeating unit) as reported by Lim et al.[47] and PBI membranes gain up to 23% in water, which corresponds to 4 water molecules per PBI r.u.[35] Since PVA gains more water in % of

weight than PBI, it should be expected that the addition of PVA to pure PBI would increase the water and KOH absorbed. But as described above, the effect measured in the 2:1 membrane is the opposite. It may be explained by the interaction between PVA and PBI, in which probably many chains are mixed and hydrogen bonds appear between the polymers as explained before. This may give rise to a more condense structure in which water has more difficulty to penetrate (as can be observed since the increase of thickness in the blend membranes is significantly lower than in pure PBI) and less available groups for the interaction with water. Opposite to this effect is the fact that PVA gains more water than PBI, so increasing the proportion of PVA increases the water and KOH uptake.

When the membranes are kept in alkaline medium, an increase in the water uptake was observed due to the existence of water molecules solvating the K^+ and OH^- ions that enter the membrane (above 10 molecules of water per r.u. for PBI) [35].

The dimensional changes undergone by membranes during the doping process are depicted in Fig. 8b. Length and width of membranes suffer slight variations as compared to thickness. A contraction of length and width above 10% is observed for PBI, while the presence of PVA favours the expansion of the membranes up to 6% for PVA:PBI 8:1. Nevertheless, for the pristine PBI, a thickness increase of 140% is observed after doping membranes, whereas the expansion of PVA containing membranes is close to 50%.

Expansion of thickness in aqueous alkaline media will be an important factor to take into account when membranes are used to prepare membrane-electrodes assemblies (MEA) for alkaline fuel cells. Thus, in order to avoid the effects of water and KOH uptake during cell operation, it is necessary to dope the membranes before sandwich them between the carbon sheets impregnated with the catalysts.

3.7 XPS measurements

Further information on the chemistry of the membranes and on their behaviour during the doping process can be obtained using XPS. Fig. 9a shows the evolution of the O 1s spectra measured on the PVA:PBI 4:1 sample for different doping times up to 6 days. The spectrum labelled as PVA:PBI 4:1 corresponds to the sample with no doping. This spectrum can be deconvoluted using solely a synthetic peak with Gaussian-Lorentzian shape at 532.5 eV, which could be attributed to oxygen in the --C--OH bonds of the PVA. With increasing doping time, this peak becomes broader and a new feature clearly appears in the low binding energy (BE) side. Such changes can be attributed to the successful doping on the membrane.

Spectra of the doped samples can be properly deconvoluted using two peaks, the first one at the BE indicated above, and the second one at 531.2 eV, which could be attributed to oxygen in the HO^-K^+ bonds appearing during the doping process. This results is in good agreement with H. Hou et al. [23], who proposed a mechanism involving hydrogen bonding between OH^- and --N= in the imidazole ring of PBI, while K^+ is introduced in the polymer connected with OH^- to balance the charge during alkaline doping. It should be pointed out that the O 1s spectrum of alkali doped graphene oxide membranes display a peak at around 531 eV that has been also attributed[48] to oxygen in OH^- therefore supporting the assignation proposed above. The N 1s spectrum of PVA:PBI4:1 membrane is shown in Fig. S4. As can be observed, it can be deconvoluted using two peaks at 400.4 eV and 398.6 eV, which could be attributed to the nitrogen of amine (--NH--) and imine (=N--) in the imidazole rings, respectively, in good agreement with previously published results [11,49]. In addition to that, Fig. 9 shows b) the C 1s and c) the K 2p spectra measured on the PVA:PBI 4:1 sample doped 1 day. The C 1s spectrum can be deconvoluted using three synthetic peaks with Gaussian-Lorentzian shape at 285, 286.4 and 287.8 eV. The interpretation of the C 1s spectrum is somewhat controversial. However, there is a general consensus to attribute the peak at 285 eV (used as binding energy

reference) to C–C and to C–H bonds [50,51]. In the case of CN compounds, polarization occurs due to the difference of electronegativity between carbon and nitrogen atoms leading to a transfer of negative charge from carbon to nitrogen atoms, which increases the binding energy of the C 1s level and decreases the binding energy of the N 1s level. Since this charge transfer is dependent of the nature of the bonding between carbon and nitrogen[51] (either C–N or C=N), the other two peaks could be attributed to C–N and C=N bonds, respectively. The K 2p spectrum of Fig. 9c is characterized by a doublet with the peak $2p_{3/2}$ at 292.9 eV and a spin-orbit splitting of ~ 3 eV. The binding energy of metallic K $2p_{3/2}$ has been reported at 294.6 eV whereas oxidized and nitrated potassium appears shifted ~ 1.7 eV to lower binding energies [52,53]. Therefore, the peak observed in Fig. 9c could be attributed to potassium in both $=N-HO^-K^+$ and $-N-K$ bonds, which appear during the doping process.

Fig. 10a shows the evolution of K 2p / N 1s peak area ratio as a function of the doping time in days (black lines). Peak areas have been normalized to the corresponding sensitivity factors S_K (4.04) and S_N (1.77) provided by the manufacturer.

As can be observed, this ratio increases with increasing the doping time, however according to the reaction mechanism proposed by H. Hou et al./ L. Zeng et al. for the alkaline doping process, this ratio should remain constant and equal to one. Therefore, this behaviour points to the incorporation of more K species within the PVA:PBI 4:1 membrane framework during the alkali doping process, different from the above mentioned reaction mechanism.

Fig. 9. a) Evolution of the O 1s spectra measured on the PVA:PBI 4:1 sample for different doping times up to 6 days. The spectrum labelled as 4:1 corresponds to the sample with no doping; b) C 1s and c) K 2p spectra measured on the membrane doped 1 day. The synthetic peaks used for deconvolution as explained in the text are also shown.

Fig. 10. a) Evolution of the peak area ratio $K\ 2p/N\ 1s$ and peak area ratio of the $O\ 1s$ related to HO^-K^+ bonds to the $O\ 1s$ related to $-C-OH$ bonds in the PVA molecule as a function of the doping time in days for the PVA:PBI 4:1 membrane. The peak areas have been normalized to the corresponding sensitivity factors S_K and S_N , respectively. The dotted line is given to guide the eye. b) Evolution, during the doping of the PVA:PBI 4:1 membrane, of the $K\ 2p$ intensity as a function of the intensity of the oxygen peak at 531.2 eV in the $O\ 1s$ spectrum (black squares). The intensities (peak areas) have been normalized to the sensitivity factors, S_K and S_O , respectively. The red line represents the experimental data fit to a straight line (slope= 0.78), whereas the black line represents the expected linear dependence $I_K/S_K = I_O/S_O$.

Fig. S5 shows the ratio of amine ($-NH-$) to imine ($=N-$) in the imidazole rings as a function of the doping time. It can be observed that the ratio remains constant and equal to one, as expected from the structure of the PBI molecule involved in the PVA:PBI 4:1 membrane. This result indicates that the reaction produced during the membrane formation does not alter neither the number, nor the type, of N species of the imidazole rings present in the PBI molecule.

The ratio of oxygen present in the HO–K⁺ bonds (appeared during the doping process) to the oxygen in the –C–OH bonds of the PVA molecule, is depicted in Fig. 10a as a function of the doping time (red lines). As can be observed, this ratio tends to saturate for doping times above 3 days. According to the reaction mechanism proposed by H. Hou et al.[23] for the alkaline doping process, a ratio of 0.25 (1:4) should be expected. However, at saturation, the ratio is well above this value, indicating again the incorporation of more K species than expected from the above mentioned reaction mechanism.

The evolution of the K 2p intensity is shown as a function of the intensity of the oxygen peak at 531.2 eV in the O 1s spectrum Fig. 10b (black squares). Intensities (peak areas) have been normalized to the corresponding sensitivity factors S_K (4.04) and S_O (2.85) provided by the manufacturer. Red line in Fig. 10b represents the fit of the experimental data to a straight line (slope= 0.78) whereas the black line represents the expected linear dependence $I_K/S_K = I_O/S_O$. Experimental results of this figure indicate that the oxygen peak at 531 eV in the O 1s spectrum should be composed not only of oxygen in HO–K⁺ but also of oxygen (HO– species) coming from water which would incorporate within the membrane framework during the alkaline doping process. This incorporation could explain the deviation of experimental data from the above mentioned expected linear dependence $I_K/S_K = I_O/S_O$.

3.8 Conductivity measurements

The ionic conductivity of the blend membranes with progressive doping days was measured and the results were included in Table 1. It was observed that the higher the PVA content of the membrane, the higher the conductivity maximum was reached and the shorter the doping time required to get it. The presence of higher amount of PVA enhances the conductivity, probably due to the abundance of –OH groups in the polymer that helps to absorb water and KOH by hydrogen bonds formation. This effect may produce shorter doping time and make

easier the conductivity of ions through the membrane. After reaching the maximum conductivity at certain days of doping, the degradation of the membranes could be due to being maintained in a strong alkaline medium. This was reflected in a decrease in the conductivity of the samples.

Membrane	σ / $\text{mS}\cdot\text{cm}^{-1}$ at 90 °C	E_a / $\text{kJ}\cdot\text{mol}^{-1}$	Optimal doping time / days	E_a (4 days of doping) / $\text{kJ}\cdot\text{mol}^{-1}$
PVA:PBI 8:1	103	9.08	1	8.75
PVA:PBI 6:1	93	9.89	2	9.73
PVA:PBI 4:1	70	6.48	3	12.66
PVA:PBI 2:1	38	4.59	3	13.18
PBI	28	6.54	5	6.47

Table 1. Best conductivity (σ) and activation energy (E_a) for each membrane at their optimal doping time and for each membrane at 4 days of doping.

The best conductivity values for the different PVA:PBI blend membranes are showed in Table 1. The best performance is observed for PVA:PBI 8:1, which reaches a conductivity of $103 \text{ mS}\cdot\text{cm}^{-1}$ at 90 °C. This value decreases with the decreasing content of PVA in membranes, as observed for 4:1 blend membrane ($70 \text{ mS}\cdot\text{cm}^{-1}$ at 90 °C). Thus, pristine PBI shows the lowest value of the series ($28 \text{ mS}\cdot\text{cm}^{-1}$ at 90 °C, that is 3.6 and 2.5 times less than 8:1 and 4:1 membranes, respectively), which is in the range of conductivities observed by other authors [11,54].

These results clearly reveal that the increment in PVA enhances the ionic conductivity of the membrane.

In order to study the dependence of the OH^- conductivity of the membranes with the temperature and the possible mechanisms behind, the activation energy (E_a) was calculated from the conductivity vs. temperature data. The ionic conductivity of all membranes significantly increases with increasing temperature (25 °C – 90 °C) due to the improved mobility of OH^- species within polymeric membranes. The linear fitting of the results presented in Fig. 11 allow us to calculate the activation energy following the Arrhenius law. The obtained values are in the range of those previously mentioned from literature, which are consistent with some possible mechanisms for the hydroxyl transportation: Grotthuss mechanism, surface site hopping, diffusion and convection via permeation, and osmotic drag could take place [35,55]. OH^- could diffuse via the hydrogen-bonded network of water molecules, through the formation/breaking of covalent bonds combined with diffusion/migration transport process (vehicular mechanism).

Fig. 11. Activation energy at their corresponding optimum days of doping for all PVA:PBI membranes and pristine PBI membrane.

The activation energies are compared at 4 days of doping in KOH 6M for each membrane in Table 1. The results show that activation energy decreases with the increasing content in PVA, and thus the membranes have lower dependence with the temperature the higher the content of PVA is. The activation energy reported in literature for pristine PBI membrane is 22-23

kJ/mol in KOH 4 mol L⁻¹ one week [35]. To conclude, all doped blend membranes present conductivity values higher than 10 mS cm⁻¹, which is considered the limit value for an acceptable polymer electrolyte membrane [38].

3.9 Single cell

After confirming the suitability of blend membranes, single cell measurements with different membranes as electrolytes are carried out to check the final applicability of these materials. Fig. 12 shows the polarization and power density curves of MEAs with different membranes in single direct ethanol fuel cell. The MEA was prepared using commercial Pt-based catalysts as cathode and anode materials, and KOH-doped PVA:PBI and commercial PBI membranes as electrolytes. Performance measurements were carried out at 90 °C feeding the fuel cell with 2 M EtOH in 2 M KOH aqueous solution. The backpressure of the oxygen flow was 0.5 atm (7 psi). Doped PVA:PBI membranes present more structural problems than doped standard PBI membranes and they show more O₂ crossover. This problem is more noticeable when the PVA:PBI weight ratio increases, and it becomes impossible to have any measure for PVA:PBI 8:1. Open circuit potentials of different MEAs display the same trend as expected: PBI (744 mV), PVA:PBI 2:1 (647 mV), PVA:PBI 4:1 (651 mV) and PVA:PBI 6:1 (530 mV). As previously was reported (section 3.4), PBI membranes have better mechanical properties than blend membranes PVA:PBI and, according to that, it is not an unexpected result. When the PVA content is increased in blend membranes, the mechanical stability of the membrane is worst. In addition, some crossover of the oxygen from cathode to anode is observed, decreasing the open circuit potential. For example, PVA:PBI 6:1 OCP is 29% worse than standard PBI membrane.

Fig. 12. Polarization and power density curves of PVA:PBI and pristine PBI membranes.

The maximum power density was achieved by PVA:PBI 4:1 (76 mW cm^{-2}) at potential $E_p = 310 \text{ mV}$, whereas PVA:PBI 2:1 and PVA:PBI 6:1 reach 45 mW cm^{-2} at 279 mV and 11 mW cm^{-2} at 220 mV , respectively. The result obtained in the same operating conditions by PBI, a typical commercial electrolyte for these devices, achieves a maximum power density of 53 mW cm^{-2} at 260 mV .

The best results obtained for the PVA:PBI 4:1 blend membrane as solid electrolyte is 43% better in power density than standard PBI membrane under same conditions. Although other synthesised membranes as 6:1 and 8:1 PVA:PBI presented better ionic conductivity, the single-cell test performances do not show the same trend. PVA:PBI 6:1 membrane presents important issues and it is clearly deteriorated after short times under test conditions presenting after stabilization polarization curve the worst performance. In the case of PVA:PBI 8:1 membranes, which present the best conductivity values, the study of single-cell performance was not possible owing to the O_2 crossover. It was not possible the use of these membranes in real operation conditions in single cell.

These presented results are very promising and demonstrate that incorporating PVA to standard PBI polymer is a good way to improve not only the conductivity but also the final

performance in operation conditions in alkaline fuel cell. The PVA polymer increases the conductivity of the final material, whereas the PBI polymer improves the stability and durability of final blend membrane. Nevertheless, both of them possess some drawbacks and it is important to achieve the adequate PVA:PBI ratio in order to avoid them. In this study we demonstrate that a PVA:PBI ratio of 4:1 is the best one in order to have good performance in direct ethanol fuel cell. It demonstrates that PVA:PBI membranes are better anion conductors than membranes based on only PBI.

4. Conclusions

PVA:PBI blend membranes were successfully prepared using the casting method and characterized, demonstrating the presence of both polymers in the final membrane and the interaction between them by hydrogen bonds. The thermal and mechanical stability were also studied and determined to be adequate. The doping process was carefully investigated giving evidence of the successful incorporation of KOH in the structure of the membrane by FTIR, EDX and XPS. XPS was also used to have further relevant information about the relation of the atoms in the doped membranes. Due to the doping, good ionic conductivity values were obtained for the blend membranes, with increasing conductivity as the PVA content in the membranes increased. The high conductivity obtained, with the rest of characterizations were promising of the applicability for alkaline direct ethanol fuel cells, as the single test results corroborate. The PVA:PBI 4:1 membrane had the optimal behaviour in the fuel cell, giving a power density of 76 mW cm^{-2} , approximately 50% higher than the doped PBI in the same conditions. PVA:PBI 6:1 and 8:1 membranes presented better ionic conductivity than 4:1 but the single cell tests do not show same trend. Deterioration after short times appears as big problem. The degradation problem should still be solved and our actual research works in that way, by chemical cross-linking of the membrane. After all we consider that these membranes

have promising qualities to be used in alkaline polymeric electrolyte fuel cells for high efficiency conversion of energy.

5. Acknowledgements

This work has been partially supported by the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) under projects ENE2016-77055-C3-1-R and CTQ2015-68844-REDT, and by the Madrid Regional Research Council (CAM) under project S2013/MAE-2882 (RESTOENE-2).

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Highlights

PVA:PBI (KOH doped) anion exchange membranes are prepared.

Hydrogen bridge between PVA and PBI is identified by ^1H -NMR spectroscopy.

Ionic conductivity of $70\text{ mS}\cdot\text{cm}^{-1}$ at $90\text{ }^\circ\text{C}$ is attained with PVA:PBI 4:1 weight ratio.

The maximum power density in the single cell is 76 mW cm^{-2} .

Single cell performance of PVA:PBI 4:1 is 43% better than that of pure PBI.