BENZIMIDAZOLE EFFECT ON THE PERFORMANCE OF POLYELECTROLYTE MEMBRANES BASED ON SULFONATED HYDROCARBON RESIN

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Abstract: It is well known that polybenzimidazole electrolyte membranes do not have water dependence as nafion® membrane and it could be used at intermediate and higher temperatures (T>100ºC). Otherwise benzimidazole groups can act promoting próton conduction in sulphonated membrane improving the polyelectrolyte efficiency. This paper discusses an alternatively use of heterocycles (benzimidazole and a derivative benzimidazole) as protogenic groups for sulfonated hydrocarbon resins (SR) and poly(vinyl alcohol) semi-interpenetrated polymer network (SR/PVA) operating at low temperatures. The PVA, a water soluble polymer, was reticulated with glutaraldehyde and the membranes modified with benzimidazole compounds were prepared by casting technique from water solution. The SR/PVA membranes were characterized by water uptake measurements, FTIR spectroscopy, thermogravimetric analysis (TGA) and the conductivity were assessed by impedance spectroscopy. The presence of benzimidazole leads to moderate water uptake and this increased with increasing the heterocycles content and the sulfonic acid functionalized membrane showed reasonable properties. The polyelectrolyte membranes with 40 and 50% (wt%) of benzimidazole showed the highest conductivity values and the 1,4- Bis(N benzimidazolyl) butane reduced the membrane conductivity.

Keywords: polymer electrolyte membrane, hydrocarbon resin, benzimidazole, impedance spectroscopy

1. INTRODUCTION

Polyelectrolyte membranes have attracted attention due to their promising applications in fuel cell (Saga et al., 2008). Nafion® membranes are limited in their operation temperature range to around 80°C and have poor barrier properties, allowing methanol crossover from the anode to the cathode in a DMFC (Rozière et al., 2003) The perfluorosulfonic acid (PFSA) membranes only exhibit sufficient proton conductivity at high degrees of hydration and these electrolytes are two phases system when fully hydrated, been the water the dispersed phase. The protons mobility through the membranes is facilitated by solvation or hydration of the sulfonic groups followed by transport via structure diffusion and the water molecules are vital for mobility of protonic charge carriers. Therefore, at high temperatures PSFA membranes are unstable and proton conductivity decrease due to water deficit restricting the fuel cell operating temperature to the water boiling point. In addition, the PFSA high cost is another limiting factor (Saga et al.,2008, Paddison et al., 2006). For this reason, cheaper and high temperature tolerant polymer electrolyte membranes have been investigated. Recently the sulfonation of hydrocarbon polyelectrolyte membranes have been reported as alternative polyelectrolyte membrane due their low cost and disposable (Yifeng et al., 2006). The membrane performance restrictions are determined by membrane itself and passive transport through these occurs as consequence of a driving force, as a difference in chemical potential by a gradient across the membrane or by electrical field (Ulbricht, 2006). Promising alternative membranes from composite or blend of acidic and basic polymers, such as sulfonated polysulfones and polybenzimidazole, have been made (Jorissen et al., 2002) and these membranes have showed excellent thermal, mechanical and dimensional stability. According Günday et al. (2007), membranes comprising aromatic heterocyclic protogenic solvents such imidazole or benzimidazole have been reported to exhibit high conduction in the anhydrous state. The proton mobility in these proton solvents at temperatures relative to their respective melting points shows similar behavior to the water mobility in PFSA membranes (Münch et al., 2001). The interesting in hydrogen bonding and proton conductivity in heterocycles is due speculations about the participation of hydrogen bonds in energy and charge transfer in biological systems, concerning the participation of NH-N bonds between the imidazole groups of histidine in proton transport in transmembrane proteins (Kreuer et al., 2004). In this work benzimidazole and benzimidazole derivative (1,4-Bis(N benzimidazolyl)butane were added to sulfonated hydrocarbon resin (SR) and poly(vinyl alcohol) (PVA) blends to evaluate the protogenic heterocyclic effect on the membrane properties. The SR/PVA blends were obtained as semi-interpenetrating polymer network (semi-IPN) by crosslinking PVA with glutaraldehyde. The membranes were evaluated by water uptake measurements, FT- IR spectroscopy, termogravimetry (TGA) and impedance spectroscopy.

2. EXPERIMENTAL

2.1 Materials and sample preparation

Poly(vinyl alcohol) (PVA) provided by VETEC, glutaraldehyde 25% (MERCK), ethanol (Quimex), benzimidazole (Aldrich), 1,4 dibromobutane (Aldrich) were used as received. Low molecular weight (5,000 dalton) hydrocarbonic resins were kindly donated by Quattor S.A.. 1,4-Bis(N-benzimidazolyl) butane was synthesized according Shi and Thummel (1995). The hydrocarbon resin was sulfonated with acetyl sulfate according to procedure currently used in previous work (Celso et al., 2003, Becker, 2007) and the sulfonation degree (mol sulfonic acid/100 mol of resin repeated unit) was 48%. Solutions of PVA (10% w/v) and sulfonated hydrocarbon resin were prepared using distilled water, and benzimidazole and 1,4-Bis(N benzimidazolyl) butane solutions were prepared using ethanol and acetonitrile, respectively. The PVA/SR/BZ membranes were prepared according to Table 1, using PVA/SR weight ratio of 1:2, by mixing PVA (1 g) and sulfonated resin (2 g) solutions during 15 min, in an ultra-sound under mechanical stirrer at 25ºC, followed by the glutaraldehyde (80 μL) addition into the polymers mixture that was kept under agitation for 30 min. From the solutions films were cast in polypropylene plates, and the water was carefully evaporated and further dried under vacuum at 45ºC for several days. Transparent and homogeneous films with thicknesses between 2 and 3 mm were obtained for all the semi-IPNs. The films were flexible at room temperature and very hygroscopic.

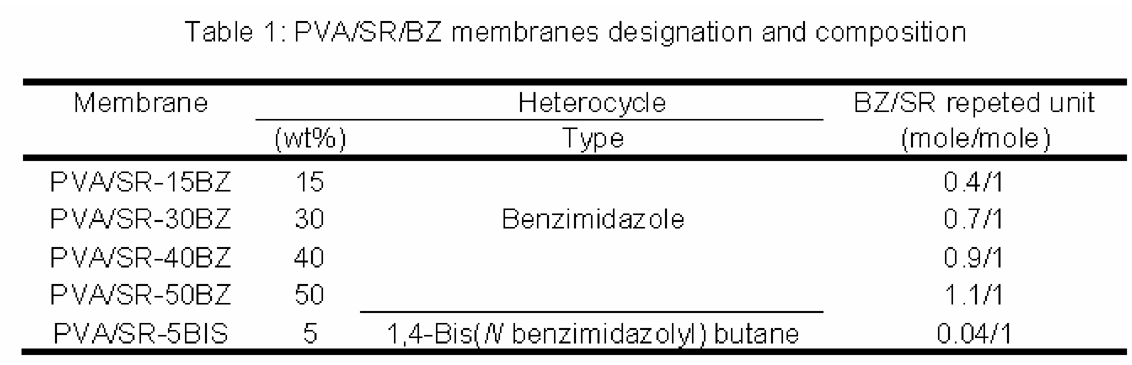


Table 1: PVA/SR/BZ membranes designation and composition

Membrane	Heterocycle (wt%)	Type	BZ/SR repeted unit (mole/mole)
PVA/SR-15BZ	15	Benzimidazole	0.4/1
PVA/SR-30BZ	30		0.7/1
PVA/SR-40BZ	40		0.9/1
PVA/SR-50BZ	50		1.1/1
PVA/SR-5BIS	5	1,4-Bis(*N* benzimidazolyl) butane	0.04/1

2.2 Materials Characterizations

The FT-IR spectra of the samples were recorded using a Perkin Elmer spectrophotometer, Spectrum 1000. The membranes thermal stability was evaluated in a TA Instrument 2050 analyzer from 25 to 1000°C at a heating rate of 20°C/min under nitrogen flow. Measurement of membranes water uptake was determined by the difference in weight between the hydrated membranes (Wwet), soaked in water during 24h, and the dried membranes (Wdry), after being kept at 45°C until they reached a constant weight, calculated by the Eq. (1).

$$Wateruptake = \frac{W_{wet} - W_{dry}}{W_{dry}} x100 \qquad (1)$$

The Electrochemical Impedance Spectroscopy (EIS) measurements were performed at 25°C, under dry conditions, using an Autolab PGSTAT 30/FRA 2. Appropriated sized films were cut and sandwiched between two electrodes with area of 1.5 cm2. The films thickness was between 2 and 3 mm determined by a Byko-test 7500 (BYK GARDNER). The frequency range was 106 to 10-1 and the amplitude of the sinusoidal voltage was 10 mV. Conductivities of the membranes were determined through the equation:

$$\delta = \frac{1}{R}\frac{l}{A} \qquad (2)$$

Where: δ = conductivity; R = material resistance; l = membranes thickness and A = membrane area.

3. RESULTS AND DISCUSSION

The PVA was used in a network form to limit its water solubility and to improve the mechanical properties of the PVA/RS films since the sulfonated hydrocarbon resin does not have a high molecular weight. The 1,4-Bis(N-benzimidazolyl) butane, a benzimidazole derivative without active protogenic groups, since the active H gives place to the butane, was used comparatively to the protogenic benzimidazole groups, aiming the membranes uses in intermediated temperatures under anhydrous conditions. The PVA/SR films with benzimidazole were very homogeneous whereas the films with 1,4-Bis(N benzimidazolyl) butane showed phase separation what limited its use in the mixture around 5% (wt%). Phase separation in these films shows a low interaction between the benzimidazole derivtive and the resin sulfonic groups.

FT-IR spectrum of SR-50BZIm is showed in Figure 1 with the main peaks assigned. The IR spectrum as already confirmed by Günday et al. (2007) and Rodrigues et al. (2007) shows absorption bands at 3400 cm-1 due the stretching of O-H and N-H groups, and at 1084 and 1452 cm-1 related to C-O bonds of PVA. The absorption peak
at 1620 cm-1 can be attributed to C=N bond of benzimidazole and peaks in the interval 1150 – 1120 cm-1 are characteristic absorptions of sulfonic groups.

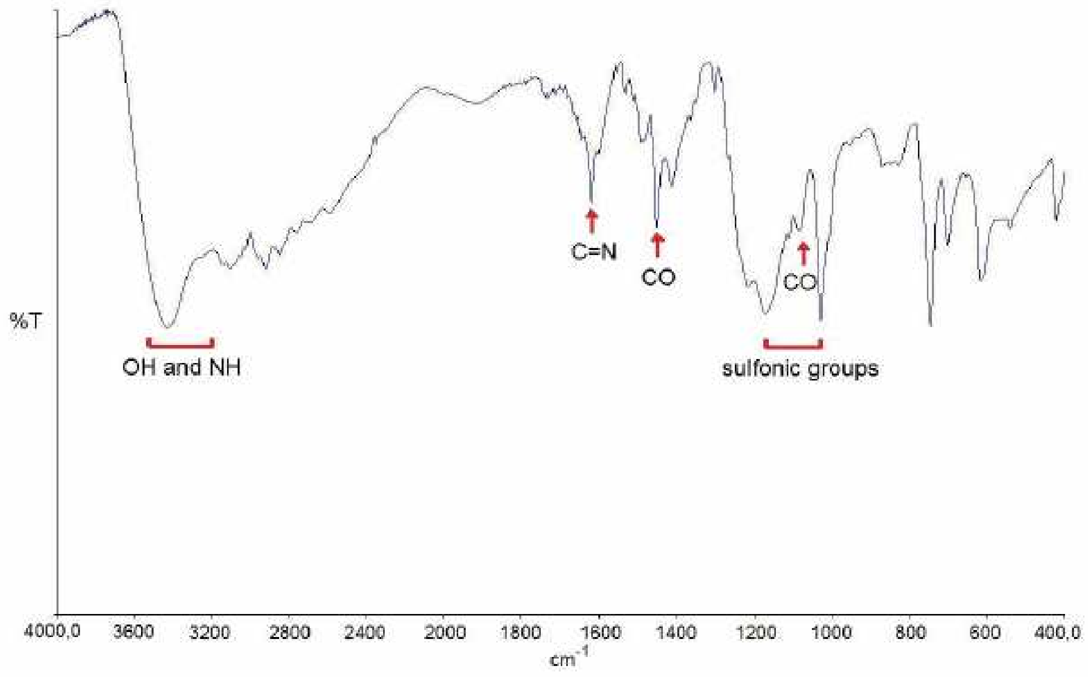


Figure 1: FT-IR spectra of the PVA/SR-50BZIm film

The TGA thermogram of PVA/SR-15BZ is shown in Figure 2, and the PVA/SR/BZ vfilms were dried for 2 days at 45ºC prior to TG measurements. The PVA/SR/BZ samples presented the same thermal behavior and were thermally stable up to approximately 180°C. A small exponential decay above this temperature may be due to the loss of sulfonic groups (Smitha et al., 2003) and to melting of benzimidazole (Yifeng et al., 2006) followed by decomposition through three weights loss events, as consequence of polymer degradation.

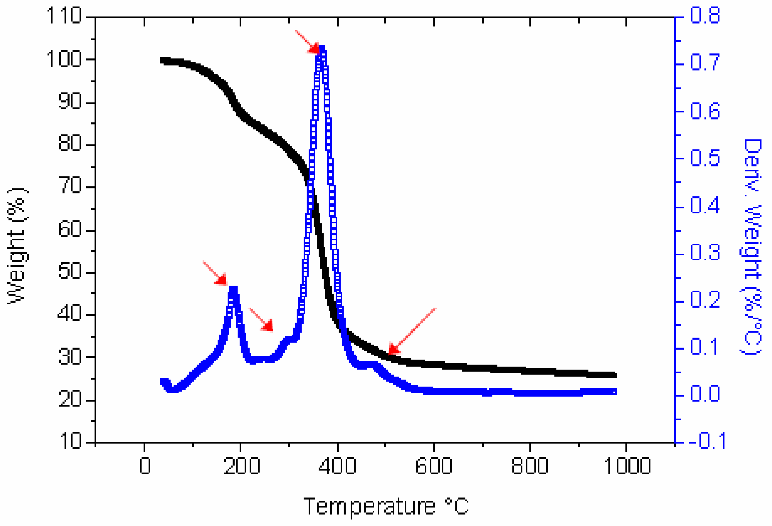
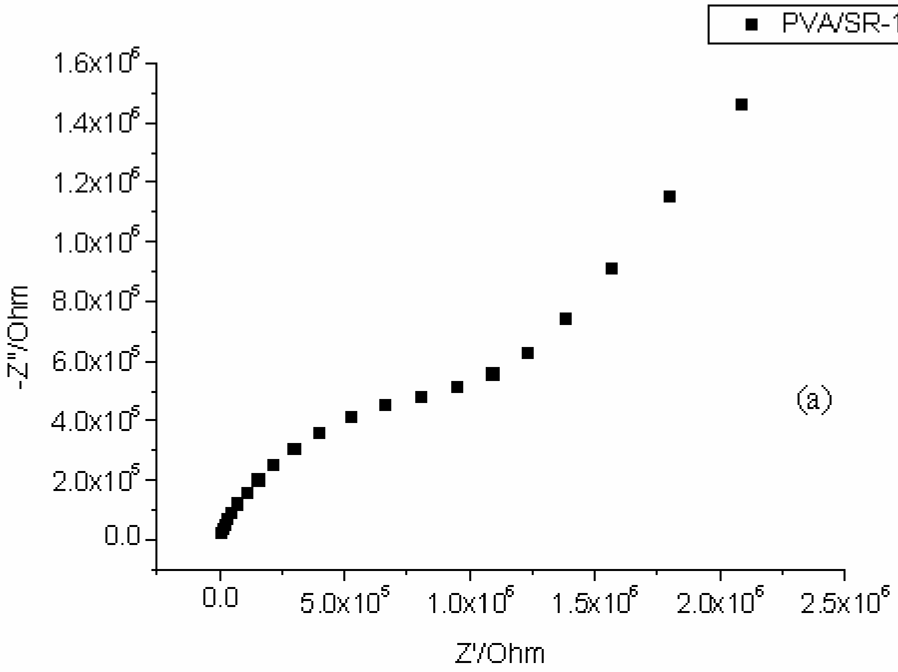


Figure 2: TGA termogram of PVA/SR-15BZ film recorded under nitrogen flow at rate of 20°C/min.

The Impedance spectroscopy measurements were carried out using dried membranes and the results compared with that obtained for a Nafion membrane analyzed at the same conditions. Proton conductivity under anhydrous conditions would reflect the hopping of protons between sulfonic groups of sulfonated hydrocarbon resin and imidazole groups (Fu et al., 2008) of the benzimidazole compound added to the membrane at different concentrations. Figure 3 shows the Nyquist plots of the PVA/SR-15BZ and PVA/SR-40BZ membranes from low to high frequency range. At high frequency a capacitive loop is detected and at lower frequencies the diffusion of charge transfer in the polymer film dominates the impedance results.



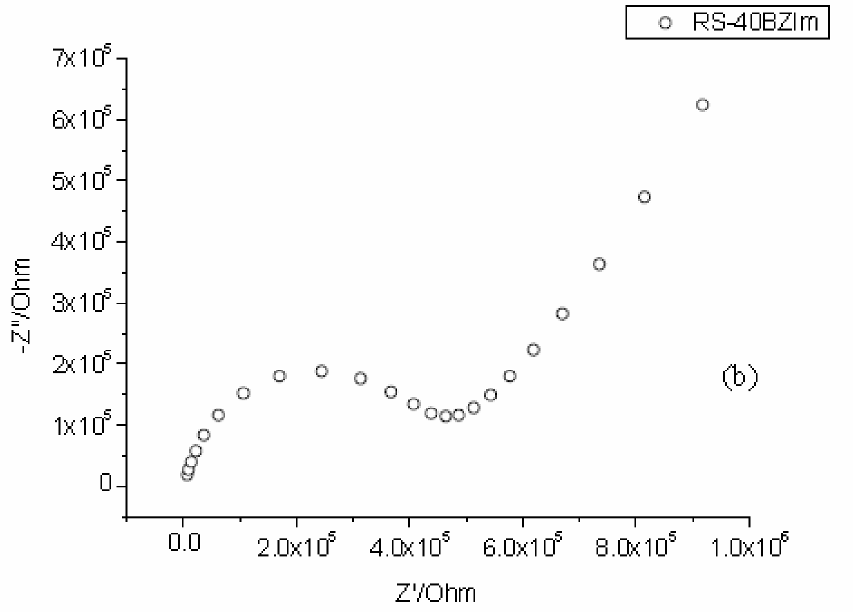


Figure 3: Nyquist plots of the SR/PVA-15BZ (a) and SR/PVA-40BZ (b) membranes.

As can be seen in Nyquist diagram, the membrane with higher amount of benzimidazole or 40% (wt%) (Fig 3b) has a diameter capacitive loop smaller than the membrane with 15% of protogenic groups compound, thus lower is the membrane resistance showing that the benzimidazole improved the proton conductivity through the membrane. The electric equivalent circuit (EC) shown in Figure 4, which can be satisfactorily used for fitting the EIS diagrams of membranes PVA/SR/BZ is R1(CPE[RbW]). The capacitance was replaced by a CPE impedance, which takes account the phenomena related to surface roughness and inhomogeneous of the electrode surface. The Warburg impedance (W) takes into account the diffusion process and Rb represents the bulk resistance. The CPE is the impedance related to a constant phase element and R1 represents the polymer-electrode interfacial resistance. The combination of Rb, CPE and W corresponds to the bulk properties and the effects of dielectric relaxations (Rodrigues et al., 2007, Becker, 2007). The simulated values corresponding to the membranes PVA/SR/BZ and the correspondent water uptake values are shown in Table 2. The conductivity of the membranes was determined from equation 2 and and parameters calculated from the impedance data (Fig. 3) using the proposed equivalent circuit (Fig.4).

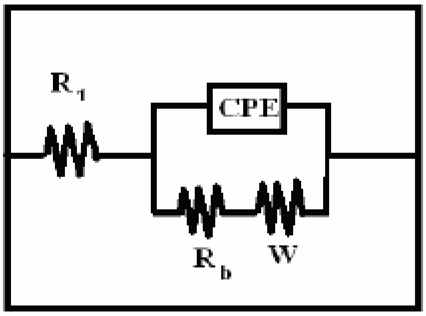
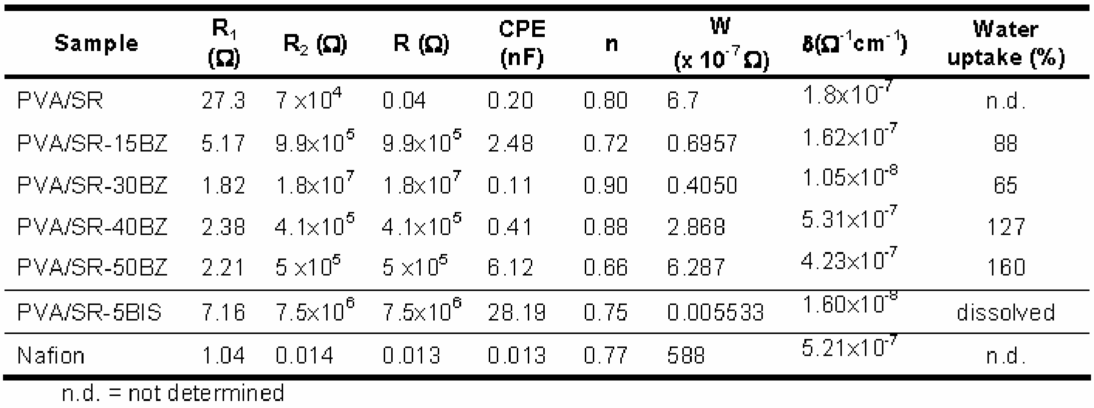


Figure 4: Equivalent circuit (EC) for the EIS diagram

Table 2: Resistance and conductivity of the PVA/SR/BZ membranes and parameters calculated from the impedance data (Fig. 3) and proposed equivalent circuit (Fig.4)



Sample	**R_1 (Ω)**	**R_2 (Ω)**	**R (Ω)**	**CPE (nF)**	**n**	**W (x 10^{-7} Ω)**	**δ($\Omega^{-1}cm^{-1}$)**	**Water uptake (%)**
PVA/SR	27.3	7×10^{4}	0.04	0.20	0.80	6.7	1.8×10^{-7}	n.d.
PVA/SR-15BZ	5.17	9.9×10^{5}	9.9×10^{5}	2.48	0.72	0.6957	1.62×10^{-7}	88
PVA/SR-30BZ	1.82	1.8×10^{7}	1.8×10^{7}	0.11	0.90	0.4050	1.05×10^{-8}	65
PVA/SR-40BZ	2.38	4.1×10^{5}	4.1×10^{5}	0.41	0.88	2.868	5.31×10^{-7}	127
PVA/SR-50BZ	2.21	5×10^{5}	5×10^{5}	6.12	0.66	6.287	4.23×10^{-7}	160
PVA/SR-5BIS	7.16	7.5×10^{6}	7.5×10^{6}	28.19	0.75	0.005533	1.60×10^{-8}	dissolved
Nafion	1.04	0.014	0.013	0.013	0.77	588	5.21×10^{-7}	n.d.

n.d. = not determined

Previous studies (Forte et al, 2008) on the PVA/SR membranes with same composition but without benzimidazole showed lower conductivity values (first line Tab.2). The membranes PVA/SR/BZ with 40 and 50% benzimidazole showed the highest values of proton conductivity due to the enhancement of proton conduction by the imidazole groups. The Nafion conductivity was analyzed through same method and according results the membranes with 40 and 50% of benzimidazole present competitive values under anhydrous conditions. These two membranes presented similar results to that obtained for the Nafion membrane. Comparing the PVA/SR/BZ membranes is possible to seen that the conductivity (δ) values change with the benzimidazole concentration suggesting that the proton conductivity is maximized at an optimum content as already reported (Fu et al., 2008). In the optimum concentration, the interactions between sulfonic and imidazole groups are such as that favors a easier way to the protons migration over these groups from the cathode to the anode as exemplified in Figure 5. Thus the imidazole groups seem to take an important par in the proton conductivity favors or not a preferable way, and the kind of interaction can reduce or disfavor the protons transport (Li et al., 2007) as observed in the membrane with 1,4-Bis(N-benzimidazolyl) butane, in which the imidazole H was changed by the butane and the N groups can interact with the proton inhibiting its movement.

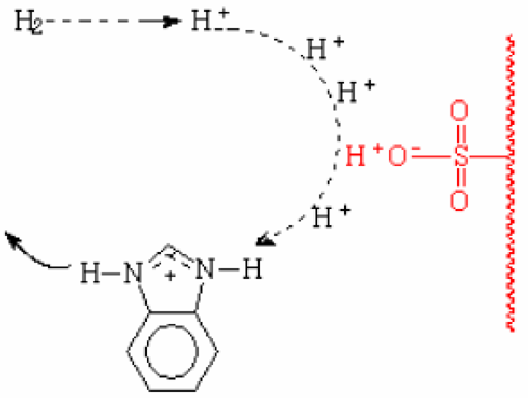


Figure 5: Schematic representation of proton conductivity through the sulfonic and imidazole groups of the benzimidazole (BZ)

As can be seen in Table 2, the PVA/SR-30BZ has showed different behavior from the others membranes what can be related to the roughness surface caused by na inhomogeneous system. Swelling due to water absorption is a factor regarding the mechanical integrity of the membranes and excessively high water content leads to dimensional changes and premature mechanical feature. Unsurprised the membrane PVA/SR-5BIS dissolved in the water during the uptake test, what suggests a low crosslink content of the PVA molecules caused by the 1,4-Bis(N-benzimidazolyl) butane that could have interfered in the reaction, which must be better investigated. As can be seen the water uptake increased with the benzimidazole increasing in the membrane. Hande et al. (2008) verified that water uptake of membranes with different crosslinker degree, as the crosslinker concentration increased, the water uptake decreased. On the other hand, the higher water uptake of the PVA/SR/BZ membranes as higher the benzimidazole content can be a consequence of imidazole groups and water interaction through hydrogens bonds. Water uptake plays an important role in polymer electrolyte membrane used at low temperatures (T<100ºC) since proton transport involves coordination of water molecules to facilitate the proton movement through the membrane. Thus these membranes can exhibit better values of conductivity in humidity conditions.

4. CONCLUSIONS

The reticulated PVA improved the membrane consistency and the benzimidazole groups improving its conductivity. The membranes SR/PVA/BZ were homogeneous and thus there was a good interaction between the benzimidazole groups and the sulfonic groups. The 1,4- Bis(N-benzimidazolyl) butane showed low solubility in the semi-IPN medium and na inhomogeneous system was obtained. The membrane water uptake was found to increase with increasing the benzimidazole content and this as well reduced the film fragility. The membranes with 40 and 50% (wt/wt) of benzimidazole (SR-40BZIm and SR-50BZIm) showed high levels of conductivity and must be better investigated. Otherwise, the Bis(Nbenzimidazolyl) ompound was not soluble in the polymer mixture and decreased the membrane conductivity since it is a Inhibitor of the proton transport. Copyrights The authors are the sole responsible for the paper. Acknowledgements The authors are grateful to CNPq and CAPES (Brazil) for the financial support and to Quattor S/A for supplying the polymeric resins.

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