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# Incorporation of benzimidazolium ionic liquid in proton exchange membranes ABPBI-H<sub>3</sub>PO<sub>4</sub>

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# 1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) offers good prospects in the field of automotive and portable power [1]. High proton conductivity, adequate gas impermeability, good electrical insulation, high chemical and thermomechanical stability are desirable features [2] for polymeric membranes. Nafion® is the most used PEM material and is based on perfluorinated polymer [3] but inevitably lose proton conductivity when exposed to harsh operating conditions [4] (near 100 °C).

It is well known that the high-temperature PEMFCs provide several potential benefits such as improved electrode kinetics, high tolerance to fuel impurities and simplified thermal and water management systems. Polybenzimidazole (PBI) is a basic polymer with excellent thermal and chemical stability and has been realized that this system is a promising candidate for high-temperature PEM applications [5]. When it is dipped in aqueous phosphoric acid to form an acid—base complex, the PBI/H<sub>3</sub>PO<sub>4</sub> complex shows high proton conductivity at high temperatures even in the anhydrous state. Particularly, poly(2,5-benzimidazole) (ABPBI) offers [6] high imidazolium density per monomer unit resulting in higher capacity to incorporate inorganic additives as H<sub>3</sub>PO<sub>4</sub> enhancing ionic conductivity and thermal stability.

In order to overcome acid leaching, several approaches including sulfonation of main polymer backbone [7] and addition of heteropolyacids

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# ABSTRACT

This paper presents the development of proton exchange membranes (PEM) from the incorporation of poly (2,5-benzimidazole) (ABPBI) in phosphoric acid ( $H_3PO_4$ ) and ionic liquid (IL) 1-butyl-3-ethylbenzimidazolium dihydrogen phosphate (BEBzIm-H<sub>2</sub>PO<sub>4</sub>). We show structural, physicochemical and electrochemical characterization of synthesized IL and prepared membranes. The addition of IL in composite membranes of ABPBI-H<sub>3</sub>PO<sub>4</sub> increases thermal stability. Also, the conductivity of membranes increases with temperature and the amount of absorbed mixture. Conductivity at a range of  $10^{-4}$  S/cm was achieved at 150 °C by 50% IL and 50% phosphoric acid impregnation. This conducting composite membrane shows promise for operation in temperature proton exchange membrane fuel cells at working temperatures up to 100 °C.

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[8], polymer blends [9,10], zirconium oxide [11] and pyrophosphate [12], BPO<sub>4</sub> nanoparticles [13] and cerium sulfophenyl phosphate [14] to ABPBI membranes have been accomplished with moderated improvement of proton conductivity. Also, copolymer membranes based on poly(2,5-benzimidazole) had been attained [15,16] where membrane processability has been improved.

lonic liquids (ILs) incorporation into nafion membranes was proposed by Proulx [17] seeking plasticizer and thermal stability effect. ILs are molten salts at room temperature and have a variety of useful properties like low vapor pressure, high thermal and electrochemical stability, non-flammability, good solvent miscibility and high conductivity [18]. These qualities make them useful in a diversity of applications such as catalysis, electrochemistry, photochemistry, organic synthesis, solar cells, batteries and fuel cells.

There is a wide variety of PEM materials being doped by ILs [19,20]. In particular, J.Y. Sanchez [21] modified Nafion 117 by incorporating different degrees of ILs in the membrane. Sekhon [22] prepared membranes of polyvinylidene fluoride-co-hexafluoro propylene blended with 2,3-dimethyl-1-octylimidazolium hexafluorophosphate where conductivity depended upon IL concentration. Greenbaum [23] proposed the incorporation of 1-methyl-3-propyl-methyl-imidazolium dihydrogen phosphate in a PBI/H<sub>3</sub>PO<sub>4</sub> system and obtained homogeneous, flexible and thermally stable membranes presenting ionic conductivity up to  $2 \times 10^{-3}$  S/cm at 150 °C. Furthermore, porous PBI was recently doped [24] with IL 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl) imide where the pores were filled with IL by direct immersion of PBI. After impregnation the proton conductivity reached a value of  $1.86 \times 10^{-3}$  S/cm at 190 °C.

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Surprisingly, there is no literature available on IL incorporation in ABPBI matrix for FC applications. ABPBI material has great potential as PEM material due to facile preparation and high proton conductivity. Stability issues are yet to be improved in order to accomplish this prospective. Therefore, this work proposes the development of ABPBI proton exchange membranes impregnated with mixtures of H<sub>3</sub>PO<sub>4</sub> and 1-butyl-3-ethylbenzimidazolium dihydrogen phosphate (BEBzIm] [H<sub>2</sub>PO<sub>4</sub>]) in order to obtain a material with good thermal and conductivity properties to be applied as electrolyte in high temperature PEMFCs.

# 2. Experimental

The chemicals were ethyl acetate 98% (Control Técnico y Representaciones, CTR), phosphoric acid 85% (CTR), and the rest from Aldrich: benzimidazole 98%, bromobutane 99%, bromoethane 99%, tetramethyl ammonium bromide 98%, 3,4-diaminobenzoic acid 97% and polyphosphoric acid 85%. All were used as received. For 1-ethylbenzimidazole (EBzIm) preparation, we dissolved in a flask 12.06 g (100 mmol) of benzimidazole and 0.70 g (4.5 mmol) of tetramethyl ammonium bromide as catalyst in 100 ml of 40% KOH aqueous solution. Then, 11.00 g (100 mmol) of bromoethane was added dropwise. After, the mixture was heated at 45 °C for 12 h. The resulting product was washed with ethyl acetate, and then removed by distillation. For 1-butyl-3-ethylbenzimidazolium bromide ([BEBzIm][Br]) preparation, we placed 2.3 g (50 mmol) of EBzIm in a three-necked flask with reflux condenser followed by addition of 50 ml toluene. Then 6.92 g (50 mmol) of 1-bromobutane was added dropwise and solution was stirred at 70 °C for 24 h. Finally, for [BEBzIm][H<sub>2</sub>PO<sub>4</sub>] preparation, 11.32 g (40 mmol) of [BEBzIm] [Br] was dissolved in 100 mL of anhydrous dicloromethane and 2.5 mL (40 mmol) of phosphoric acid was added dropwise. The mixture was stirred for 48 h, after the remaining solvent was removed in a vacuum oven at 70 °C overnight. An amber liquid was obtained. The 1-butyl-3-ethylbenzimidazolium dihydrogen phosphate, FTIR (ATR, v/cm-1): 3147, 2964, 2880, 2753, 2300, 2127, 1621, 1565, 1485, 1462, 1124, 960, 890, 741. 1H NMR (500 MHz, DMSO-d6): 0.90 (t,3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.13 (m,2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.52 (t, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.87 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.81 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.48 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 7.66 (m, 2H, Ph), 8.03 (m, 2H, Ph), 9.77 (s, 1H, NCHN) y 10.04 (s, 1H, OH).

The ABPBI was obtained by heating a solution of 3.14 g (20 mmol) of 3,4-diaminobenzoic acid in 50 g of polyphosphoric acid at 200 °C for 5 h under N<sub>2</sub> atmosphere. The product was isolated by water precipitation, filtered and washed repeatedly with water. After, the dark powder was washed with 10% NaOH for 12 h to remove polyphosphoric acid residuals. For ABPBI membrane preparation, 400 mg of ABPBI powder was dissolved in 6 ml of methanesulfonic acid, the solution was poured into a petri dish and evaporated over a hot plate at 150 °C for about 8 h to obtain a dark film (200-micrometer thick in average). For  $H_3PO_4$  and IL impregnation,  $2 \times 2$  cm samples were cut and immersed in different phosphoric acid-ionic liquid baths. Table 1 shows bath composition in which ABPBI membranes were impregnated for 24 h. Then, sample squares were dried in a vacuum oven at 80 °C overnight. The polymer was dried under vacuum at 100 °C overnight. FTIR (ATR, v/cm-1): 3349, 3121, 2987, 2325, 1622, 1550, 1426, 1271, 1131, 1064, 976, 858, 801, 723. Elemental analysis: C7H4N2•2H2O: C, 55.26; H, 18.42; N, 5.26.

FTIR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer with universal attenuated total reflectance accessory. Nuclear magnetic resonance spectra was obtained using a Bruker Avance II 300 with QNP-z sensor using DMSO-d<sup>6</sup> as solvent. For elemental analysis we used a Eurovector 3011 elemental analyzer with a Mettler Toledo MX5 microbalance connected to a gas chromatographer. The thermal stability was determined using a TA Instruments SDT 2960 thermogravimetric analyzer between with heating rate of 10 °C/min. Viscosity was measured using a Viscolab 3000 viscometer

#### Table 1

Doping bath composition of [BEBzIm][H <sub>2</sub> PO <sub>4</sub> ]:H <sub>3</sub> PO <sub>4</sub> mixtures used in the im	pregna-
tion of ABPBI.	

Sample	Bath composition IL:H <sub>3</sub> PO <sub>4</sub>	Membrane weight before doping/g	Membrane weight after doping/g	% absorption
M1	0:100	0.2430	0.2824	16.21
M2	25:75	0.2750	0.6172	124.43
M3	50:50	0.3493	0.6540	87.23
M4	75:25	0.2174	0.3066	41.03
M5	100:0	0.1195	0.1218	1.92

(Cambridge Viscosity, Medford, MA) at 10 °C intervals with 30 min equilibration at each temperature. Accordingly, 1 mL samples were transferred inside a stainless steel cylinder sample holder and then hermetically closed in the upper end. Electrical conductivities were determined from complex impedance technique using a frequency response analyzer (PCI4-750, Gamry Instruments) where an AC voltage signal of 10 mV was applied at a frequency range of 1 Hz-100 kHz. Gold was deposited on polymer membranes (10 mm diameter, thickness ~0.2 mm) on both sides using a cathode sputter coater (Pelco SC-7). The samples were sandwiched between two nickel electrodes in a closed stainless steel-bodied cell and measurements were carried out under a slow dry nitrogen flow (30 mL/min). IL electrochemical stability was measured employing a potentiostat/galvanostat Biologic Science Instrument model VMP3. A conventional three-electrode electrochemical cell was used. Glassy carbon electrode was used as working electrode, Pt wire as counter electrode and a silver wire was used as pseudo-reference (Ag-QR) electrode. The experiments were performed at different scan rates from 50 to 500 mV/s.

# 3. Results and discussion

Results from temperature stability testing of [BEBzIm][H<sub>2</sub>PO<sub>4</sub>] using DTA/TGA show expected thermal behavior (see Fig. 1). On Table 2, we tabulated thermal decomposition temperatures at 90% weight on TGA experiment along similar compounds from literature. We notice that thermal stability strongly depends on the nature of the anion. Thus, weight losses of our IL will be associated to dihydrogen anion decomposition where DTA peaks are linked to the following discussion. Weight loss up to510 K is associated to adsorbed moisture. Within 510–610 K we relate weight losses to the first dehydration of the anion according to Prinsloo [25] where pyrophosphoric unit (H<sub>2</sub>PO<sub>7</sub>)<sup>-2</sup> is formed. A second dehydration occurs immediately at 630–700 K range where metaphosphoric unit (PO<sub>3</sub>)<sup>-</sup> is produced. Subsequent weight losses are associated to thermal decomposition of aliphatic chains attached to benzimidazolium ring at 760–860 K range and



Fig. 1. Thermal behavior of [BEBzIm][H<sub>2</sub>PO<sub>4</sub>] in air atmosphere at 10 °C/min.

Table 2

Thermal properties of several 1-R<sub>1</sub>-3-R<sub>2</sub>-benzimidazoliums with different anions (X).

R <sub>1</sub>	R <sub>2</sub>	Х	T/K at 90% weight	Reference
Butyl	Ethyl	H <sub>2</sub> PO <sub>4</sub>	510.0	This work
Pentafluoro-benzyl	2,4,6-trimethylbenzyl	Br	458.1	[34]
Butyl	Ethyl	Br	529.1	[35]
Butyl	Ethyl	BF <sub>4</sub>	603.1	[35]
Butyl	Ethyl	PF <sub>6</sub>	640.1	[35]

after we interpreted it as heterocycle decomposition [26]. DTA/TGA data is accurate for the chosen IL only, in which the molecules are highly mobile; the incorporation into a polymer membrane changed the thermal stabilities of the mixtures. This situation will be discussed later on.

Generally, ILs have higher viscosity than regular solvents (For example, water viscosity at room temperature is 0.9 cP). Indeed, their viscosities typically range from 30 cP-100 cP at room temperature; however, values as high as 500-800 cP are typically reported. The chemical nature of anions and cations has a huge effect on viscosity. With respect to anion moiety, higher basicity, size, and relative capacity to form hydrogen bonds result in more viscous ILs. Polymer electrolytes containing ionic liquid 2,3-dimethyl-1-alkyl-imidazolium dihydrogen phosphate ( $[MMRIm][H_2PO_4] R = Octyl, and Butyl)$  where previously reported [27] showed possibility of use as high temperature membranes for fuel cell applications. Fig. 2 shows [BEBzIm][H<sub>2</sub>PO<sub>4</sub>] viscosity behavior along [MMOIm][H<sub>2</sub>PO<sub>4</sub>] and [MMBIm][H<sub>2</sub>PO<sub>4</sub>] ILs for comparison. The different behavior observed for viscosity results is probably due to the difference in bulk viscosity - which is measured experimentally and local viscosity - which is related to mobility of the ionic species. The imidazolium-based IL with octyl group ([MMOIm][H<sub>2</sub>PO<sub>4</sub>]) has higher viscosity whereas the imidazolium-based IL with butyl group ([MMBIm][H<sub>2</sub>PO<sub>4</sub>]) has lower value. Our benzimidazolium-based IL [BEBzIm][H<sub>2</sub>PO<sub>4</sub>] has an intermediate viscosity value. The length of alkyl group affects the viscosity of the resulting IL. The exact contribution of alkyl group on the modification of viscosity cannot be estimated, as some other parameters such as ion size, degree of dissociation also affect the properties of IL. Moreover, the viscosities of ionic liquids appear to be ruled by Van der Waals (VdW) interactions, where long octyl chain group provides higher Van der Waals interactions increasing IL viscosity. On the other hand, benzimidazolium cation has larger size than imidazolium and consequently increases the internal resistance to flow as well as the viscosity of [BEBzIm][H<sub>2</sub>PO<sub>4</sub>] in comparison to  $([MMBIm][H_2PO_4]).$ 



**Fig. 2.** Viscosity behavior of several dihydrogen phosphate ionic liquids.  $(\odot)$  [BEBzIm]<sup>+</sup> from this work, ( $\blacktriangle$ ) MMOIm<sup>+</sup> and ( $\blacksquare$ ) MMBIm<sup>+</sup> both from reference no. 27. Insert displays Arrhenius plot. In all cases, dotted line represents VTF fitted line.

On the insert of Fig. 2, we display an Arrhenius type plot of the viscosity data. Fitting lines were calculated using the Vogel–Tammann– Fulcher (VTF) equation [18]:

$$\eta = \eta_0 e^{\left(\frac{B}{T-T_0}\right)} \tag{1}$$

where  $\eta$  represents the viscosity of the ionic liquid at temperature *T*,  $\eta_0$  is a pre-exponential constant, *B* is a factor related to the activation energy and  $T_0$  is the ideal glass transition temperature (see Table 3 for calculated values). From this data, the strength parameter, *D*, was calculated as  $D = B/T_o$  and could be used as a measure of fragility [28]. In the strength–fragility scheme, originally proposed by Angell [29], a *D* value lower than 10 represents fragile behavior, and higher values (around 100) are typical for strong liquids, similar to SiO<sub>2</sub>. The calculated *D* value decreases in the order MMOIm<sup>+</sup> > BEBzIm<sup>+</sup> > MMBIm<sup>+</sup> suggesting a relationship among fragility and viscosity with VdW interactions.

Ionic conductivity is one of the most important properties of ILs considered as electrolytes. Generally, ILs have better ionic conductivities compared with organic solvents/electrolyte systems. However, at room temperature, their conductivities are usually lower than those of concentrated aqueous electrolytes, based on the fact that ionic liquids are composed exclusively of ions. There is a difference on thermal dependence of conductivity when compared to similar ILs as 2,3-dimethyl-1-alkyl-imidazolium dihydrogen phosphate ([MMRIm]  $[H_2PO_4] R = Octyl and Butyl and)$  [27]. At room temperature, conductivity values of BEBzIm<sup>+</sup> are lower compared to MMRIm<sup>+</sup>. However, as temperature rises there is marked increase and this behavior should be associated to the benzilimidazolium ion contribution. Since BEBzIm<sup>+</sup> cation is rather bulky compared to MMBIm<sup>+</sup> cation and the former has higher viscosity we could think at this point that this increase on ionic conductivity is due to higher decoupling of the  $H_2PO_4^-$  anion with benzimidazolium ion compared to the imidazolium ion. In a recent study, Goward [30] demonstrated that benzimidazolium ring is somehow sluggish compared to imidazolium rings in analogous salts. This situation favors the mobility of added phosphonate groups thus increasing proton dynamics and conductivity as well. Another plausible explanation to this conductivity increase relies on the fact that liquids benzimidazoliums are prone to water adsorption. According to Alselmi [31] (BzImH)<sup>+</sup> in molten state, after short exposure to (humid) ambient air, absorbed water molecules may remove protons from (BImH)<sup>+</sup> groups, thereby enabling a chain mechanism of proton-hopping through non-protonated BIm sites, enhancing conduction properties remarkably.

On the other hand, the curved behavior of the Arrhenius type plot (see insert, Fig. 3) suggests the highly viscous nature of those ILs and this variation can be explained by VTF behavior. The VTF equation for conductivity is

$$\sigma = \sigma_0 e^{\left(-\frac{B}{1-T_0}\right)} \tag{2}$$

where  $\sigma$  represents the viscosity of the ionic liquid at temperature *T*,  $\sigma_0$  is a pre-exponential constant, *B* is a factor related to the activation energy and  $T_0$  is the ideal glass transition temperature (see Table 3 for calculated values).

Electrolytes for electrochemical devices should have large stability against oxidation-reduction processes. The electrochemical window (EW) is a term commonly used to indicate both the potential range and the potential difference in which the ionic liquid is stable. Fig. 4

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VTF parameters for the viscosity and conductivity of the prepared IL [BEBzIm][H<sub>2</sub>PO<sub>4</sub>].

	Ao	В	T <sub>o</sub> /K	D
Viscosity	0.09	1273.4	173	7.6
Conductivity	3.50	563.4	260	-



**Fig. 3.** Conductivity behavior of several dihydrogen phosphate ionic liquids.  $(\odot)$  [BEBzIm]<sup>+</sup> from this work, ( $\blacktriangle$ ) MMOIm<sup>+</sup> and ( $\blacksquare$ ) MMBIm<sup>+</sup> both from reference no. 27. Insert displays Arrhenius plot. In all cases dotted, line represents VTF fitted line.

displays the EW for [BEBzIm][H<sub>2</sub>PO<sub>4</sub>]. The resulting EW was 1.2 V vs. Ag-QR electrode and is limited by the reduction reaction of the cation (BEBzIm)<sup>+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> oxidation. This value is comparable to 1.3 V reported [32] for benzimidazole-bis(trifluoromethanesulfonyl)imide 1:1 melt and is suitable for PEM applications [33].

Comparing the amount of absorbed IL:H<sub>3</sub>PO<sub>4</sub> mixture in the ABPBI polymer (see Table 1) we observe a marked increase of doping mixture absorption at 25% of IL compared to sole H<sub>3</sub>PO<sub>4</sub> impregnation. Then, a gradual diminution of doping mixture incorporation is observed as IL amount is increased. This is attributed to the increase of the bath viscosity so that there is greater difficulty for mixture integration into the ABPBI polymer. It should be mentioned that the difference in weight in sample M1 is mainly attributed to the dissolution of the membrane in the H<sub>3</sub>PO<sub>4</sub> thus no acid uptake by the ABPBI. To account for IL-H<sub>3</sub>PO<sub>4</sub>-ABPBI interactions, Fig. 5 displays several FTIR spectra obtained for ABPBI membranes impregnated with H<sub>3</sub>PO<sub>4</sub> and IL according to Table 1. First, in the undoped ABPBI membrane, the remaining MSA absorbs at 1200 and 1100 (sulfonated group); the bands assigned to O–H stretching at 3300 cm<sup>-1</sup>, the free N–H stretching band is situated at 3121 and that for hydrogen bonded N–H stretching

at 2977. The aromatic C–H stretching at about 2600 is hidden behind the N–H stretchings. The spectra for the impregnated membranes are quite similar. There are only small differences in the intensity of bands due to the polymer impregnation grade. A very broad band appears between 2500 and 3000 cm<sup>-1</sup> due to the protonation of the imine to the polymer by the interaction of this with the other system components. N–H stretching; the O–H stretching leads to a broad band at 2500–2250 cm<sup>-1</sup>. Bands at 1550 and 1620 can be assigned to the C=N and C=C stretchings for the doped ABPBI samples. The phosphoric acid and dihydrogen phosphate anion (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) bands appear at around 1200–650 cm<sup>-1</sup>.

The thermal stability of impregnated membranes was determined by thermogravimetric analysis in air atmosphere from room temperature to 400 °C with a heating rate of 10 °C/min. In Fig. 6, the thermogram of ABPBI before impregnation (undoped) shows weight loss on the 25–150 °C range and is due to absorbed water, after which the weight is almost constant. Membrane M5 displays weight loss pattern similar to undoped ABPBI and IL itself suggesting a little amount of impregnation. The rest of the doped membranes showed better thermal stability. The first weight loss is due to the elimination of moisture absorbed by the membrane and is equivalent to 5% by weight. This suggests a strong interaction between the IL and ABPBI causing an increase in the thermal stability of material itself.

Conductivity was measured in the range of 25–150 °C. Only we tested membranes M3 to M5 because they could be properly handled. M1 and M2 membranes were soft to measure under the present experimental conditions. Fig. 7 displays membrane conductivity as a function of temperature. In the impregnated membranes, the conductivity increases as a function of the temperature and the amount of mixture (H<sub>3</sub>PO<sub>4</sub>/BEBIm-HP) absorbed by the membrane. The values obtained are on the  $10^{-4}$  S/cm range for the tested materials. We also observe that above 100 °C there is a conductivity increase. We believe that conductivity behavior below 100 °C is performed through a hopping mechanism and as temperature increases, the diffusion of charges occurs more easily due to vehicular mechanism. Membranes containing IL with conductivity higher than  $10^{-3}$  S/cm above 100 °C can find potential use in various electrochemical devices. However, for their use in PEM fuel cells, the conductivity has to be improved by more than one order of magnitude and secondly protons should be the mobile species. Although cations and anions are the main mobile species in ILs yet the presence of



Fig. 4. Cyclic voltammetry of [BEBzIm][H<sub>2</sub>PO<sub>4</sub>].



Fig. 5. FTIR characterization of doped membranes.

acidic dihydrogenphosphate anion  $(H_2PO_4)^-$  and phosphoric acid  $(H_3PO_4)$  suggests that protons also contribute to the conductivity of these membranes. It is important for their future use as proton conducting membranes. However, more experimental studies are required to establish the nature of mobile species in these membranes containing ionic liquids.

# 4. Conclusions

lonic liquid with acidic  $(H_2PO_4)^-$  counteranion and having composition: 1-butyl-3-ethylbenzimidazolium dihydrogen phosphate ([BEBzIm] [H\_2PO\_4]) has been prepared and characterized and its conductivity and viscosity behavior has been studied. ABPBI/H\_3PO\_4/[BEBzIm][H\_2PO\_4] membranes were prepared. The incorporation of the IL into polymer



Fig. 7. Ionic conductivity of doped membranes.

matrix increases the thermal stability of the membrane. The conductivity of the membranes impregnated is directly proportional to temperature and the amount absorbed by ABPBI polymer. The membranes have an acceptable ionic conductivity up to  $9.02 \times 10^{-4}$  S/cm at 150 °C. The graphs of conductivity obtained suggest that the proton conduction is performed by two mechanisms, the first occurs below 100 °C through the hydrogen bond network by a hopping mechanism above this temperature the predominant mechanism is a transport vehicle.

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Fig. 6. TGA characterization of doped membranes.

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