

Effect of the addition of benzimidazole ionic liquid in ABPBI/H₃PO₄ proton exchange membranes

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ABSTRACT.

This paper reports the preparation and characterization of 3-butyl-1-ethyl-benzimidazole dihydrogenphosphate (BEBz-HP) ionic liquid (IL) and its effect on the addition of phosphoric acid (H₃PO₃) and poly(2, 5-benzimidazole) or ABPBI. The new IL was prepared from the consecutive reaction of benzimidazole with ethyl and butyl bromides yielding BEBz-HP which is compatible to H₃PO₃. ABPBI was added to provide thermo-mechanical support. We present the structural characterization by infrared spectroscopy (FTIR), thermal stability by thermogravimetric analysis (TGA), electrochemical stability by cyclic voltammetry (CV) and conductivity by impedance analysis.

INTRODUCTION.

The rapid increase of energy consumption and the need to preserve our environment had increased the research and development towards cleaner energy sources. The fuel cells¹ are electrochemical devices capable of electricity generation from a fuel (H₂, methanol, etc.) and an oxidant (O₂ or air directly). The most promising fuel cell technology in the field of portable power is the proton exchange membrane (PEM) fuel cell.² PEM materials must present high proton conductivity, good impermeability to gases and/or fuels, good water transport, high chemical and thermomechanical stability, good electrical insulation, etc.³ At low operation

temperatures ($<100^{\circ}\text{C}$) Pt/C electrodes are highly sensitive at small amounts of CO from the reactive gases, what generates a fast lost from their catalytic activity. Therefore, there is considerable interest to use PEM fuel cells at high temperature ($>150^{\circ}\text{C}$) to avoid the need of Pt/C catalyst eliminating CO poisoning thus reducing the need of ultrapure hydrogen resulting in cost decrease. This sort of temperature presents moisture management issues to the classical Nafion PEM. Therefore, there is a need to seek out new PEM systems whose proton conduction mechanism does not rely on water.

Currently, polybenzimidazole (PBI) membranes are receiving a great deal of attention due to their high temperature stability up to 200°C . To promote proton conduction, those membranes are usually doped with large amounts of H_3PO_4 . Particularly, ABPBI⁴ offers higher imidazolium group concentration per unit volume resulting in an increased capability to dissolve phosphoric acid and then increased proton conductivity. However, the use of these strong acids leads to corrosion problems affecting the lifetime of PEMFC. A plausible solution is to partially replace H_3PO_4 by suitable solvent as ionic liquids (LI's)⁵, which are molten salts formed by highly asymmetric ions and presents high chemical stability. Hence, the purpose of the present work is to study the effect of the addition of a novel benzimidazole ionic liquid in a polymer matrix ABPBI/ H_3PO_4 for possible application as proton exchange membranes in PEMFC.

EXPERIMENTAL.

Synthesis and characterization of 3-butyl-1-ethyl-benzimidazole dihydrogen phosphate (BEBz-HP) ionic liquid (IL).

The reagents used were: ethyl acetate (CTR), Phosphoric Acid 85% (CTR), Benzimidazole 98% (Aldrich), 99% 1-bromobutane (Sigma-Aldrich), bromoethane 99% (Sigma-Aldrich) and tetramethyl ammonium bromide 98% (Sigma-Aldrich). The synthesis was carried out in two stages: first the benzimidazole cation was prepared then the anion was added by

metathesis⁷. For the benzimidazole cation synthesis 11.81g of benzimidazole (98%) was placed in a 100 mL flask and 0.7g of ammonium tetramethylammonium bromide (98%) in 100 ml KOH 40% w/v were mixed in. Then, 15 ml of ethylbromide were added dropwise under vigorous stirring. After completing the addition, the reaction mixture was heated to 45° C for 24 hours until two phase formation. The product of interest, 1-ethyl benzimidazole (EBz), was washed with ethyl acetate and subsequently removed by low pressure distillation. Next, the EBz was transferred into a three-necked flask equipped with a condenser and 50 ml of toluene were added under vigorous stirring. After that, an equimolar amount of 1-bromobutane (freshly distilled) was added dropwise. The reaction mixture was stirred and heated up to 70° C for 24 hours. The product of interest (butyl 1-ethyl benzimidazolium bromide, [BEBz][Br]) was washed with toluene and dried inside a vacuum oven at 80° C for 8 hours. Finally, the [BEBz][HP] was prepared by a dropwise addition of one equivalent of phosphoric acid to a cooled solution of anhydrous [BEBz][Br] in dichloromethane. The mixture was refluxed for 48 h and the remaining solvent was removed using a vacuum oven at 70° C for 8 hours. Finally, the IL obtained is stored in a desiccator and characterized.

Synthesis and characterization of poly(2,5-benzimidazole) or ABPBI.

For the synthesis of ABPBI, 3.040g of 3,4-Diaminobenzoic acid 97% (Sigma-Aldrich) and 50g of polyphosphoric acid (Sigma-Aldrich) were mixed. Then the mixture was heated at 200° C for five hours under dry N₂⁸. Afterwards, the polymer was poured into water, the solid obtained was washed with deionized water and 10% NaOH overnight to remove any excess of unreacted acid. ABPBI finally dried under vacuum at 100 ° C for 12 hours.

[BEBz][HP]-H₃PO₄-ABPBI membrane preparation.

Films were prepared by dissolving 400mg of ABPBI in 6 ml methanesulfonic acid, the solution was poured onto a glass plate and heated to 150 °C until complete evaporation of the acid (about 8 hours to 20µm membranes thick).⁹ The prepared membranes were immersed for 24 hours inside doping baths with different [BEBz][HP]-H₃PO₄ proportions (Table I). Then, the samples were dried on absorbent paper for 12 hours.

Table I. [BEBz][HP]- H₃PO₄ ratio in doping baths.

Sample	% [BEBz][HP]	%H ₃ PO ₄
1	0	100
2	25	75
3	50	50
4	75	25
5	100	0

RESULTS AND DISCUSSION.

Synthesis and characterization of [BEBz][HP].

For the IL purification, the liquid-liquid extraction technique was used employing CH₂Cl₂. After, UV-Vis spectroscopy was used to discard remains of reagents in the product of interest as these impurities have an absorption band at 350 nm it clear that is not present in the pure ionic liquid (Figure 1).

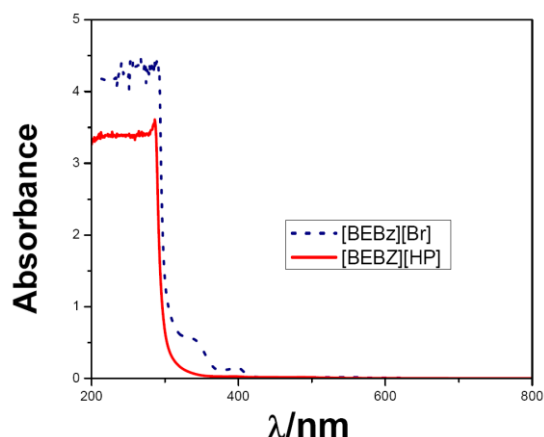


Figure 1. UV-Vis spectrum of [BEBz][Br] (dotted blue line) and [BEBz][HP] (red solid line).

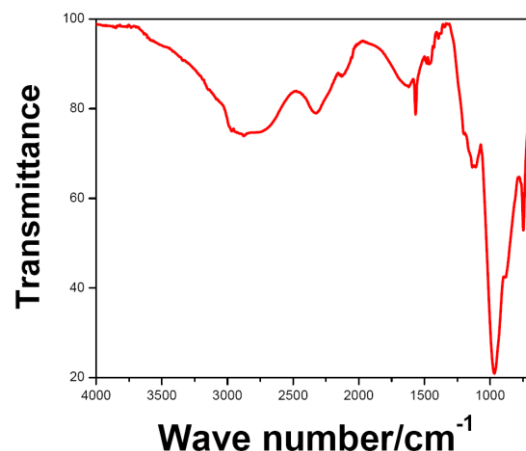


Figure 2. FTIR spectra of product [BEBz][HP]

On Figure 2 we present the FTIR spectra of the [BEBz][HP]. The band at 2950 cm^{-1} can alternatively be ascribed to a second overtone of P=O deformation vibration at 990 cm^{-1} . Further in 1740 and 1620 cm^{-1} we observe thermal vibrations of H^+ ions in an intermolecular phonon vibration associated with $\text{H}^+-\text{PO}_4^{-3}$ contacts¹⁰. The P=O stretching vibration leads to a distinct band at 1260 cm^{-1} . At room temperature, PO_4^{-3} is a symmetric complex anion. The P=O deformation vibrations are found between 840 and 1120 cm^{-1} . We observe the absence of N-H stretching (3460 cm^{-1}) as well as the nonexistence of the C=N stretching band (at 1689 cm^{-1}). On the other hand, we can see the bands corresponding to the vibrations of the polybenzimidazole ring¹¹ to 2971 , 2879 cm^{-1} and 749 cm^{-1} vibration out of plane.

The thermal stability of [BEBz][HP] was tested in an air atmosphere from 25 to $500\text{ }^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$, this compound showed relatively high thermal stability up to $300\text{ }^\circ\text{C}$. The density was $1,616\text{ g}/\text{cm}^3$ determined at 30°C . In addition, we studied the dependence of

viscosity with temperature from 30 to 100 ° C, showing a behavior of quasi-Arrhenius in the range of work where the calculated activation energy was 44.16 J/mol (see figure 3). On figure 4 we present the conductivity vs. temperature of the [BEBz][HP] IL conductivity. It also shows a cuasi-Arrhenius type behavior within the temperature range studied. The activation energy calculated was 33.06 J/mol. The electrochemical stability of LI was analyzed by cyclic voltammetry (Figure 5) at room temperature using as working electrode, counter electrode and pseudoreference electrode platinum wires (scanning rate was 5 mV/s). The cyclic voltammogram of the ionic liquid shows that the potential window of 0.7 V which indicates that the synthesized compound is stable under the conditions of operation of the cell since according to data reported in literature¹² in a fuel cell can generate potential differences between 0.6 and 0.7 V.

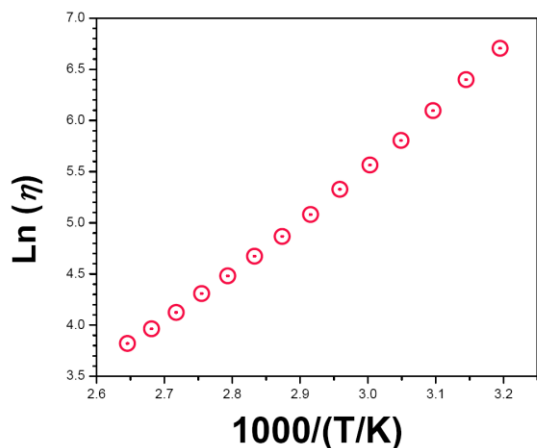


Figure 3. Dependence of viscosity with temperature in a temperature range of 30 to 100 ° C.

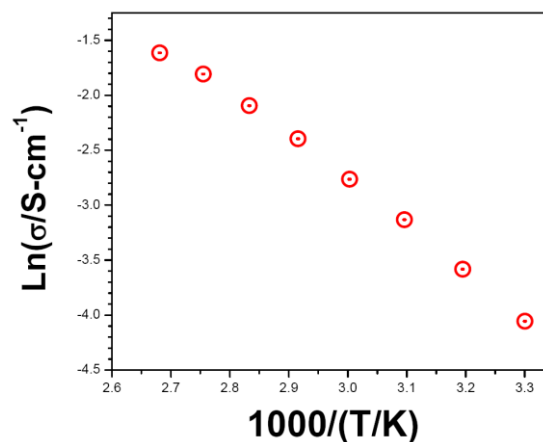


Figure 4. Dependence of ionic conductivity with temperature in a temperature range of 30 to 100 ° C, which is due to an Arrhenius type behavior.

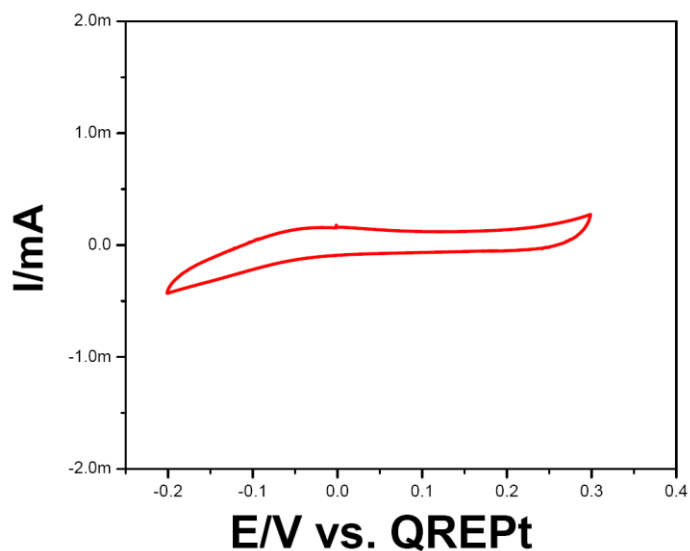


Figure 5. Cyclic voltammetry using as a working electrode. QREPt = quasi-reference electrode of platinum

Synthesis and characterization of ABPBI.

The ABPBI FTIR spectra is displayed on Figure 6 and it is similar as previously reported¹³. We observe bands due to absorbed water (3590 cm^{-1}), unassociated N-H tension (3340 cm^{-1}) and associated to hydrogen bridge (3200 cm^{-1}). The aromatic C-H stretching at about 3075 cm^{-1} is hidden behind the N-H stretching. Bands at 1623 , 1550 , and 1428 cm^{-1} can be assigned to the C=N and C=C stretching. The 1283 cm^{-1} signal is associated to the breathing mode of imidazol ring and 812 cm^{-1} and 725 cm^{-1} to out-of-the plane benzene ring bends.

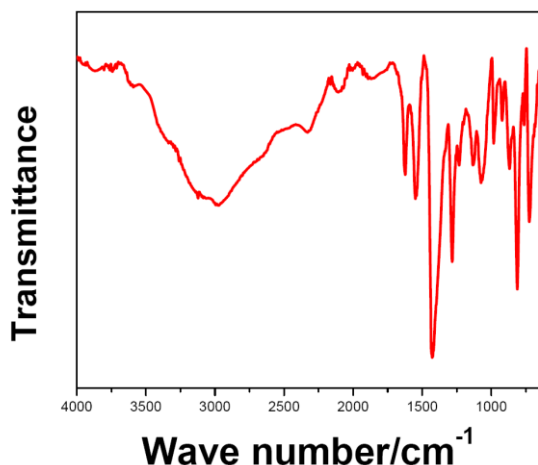


Figure 6. FTIR spectrum of ABPBI.

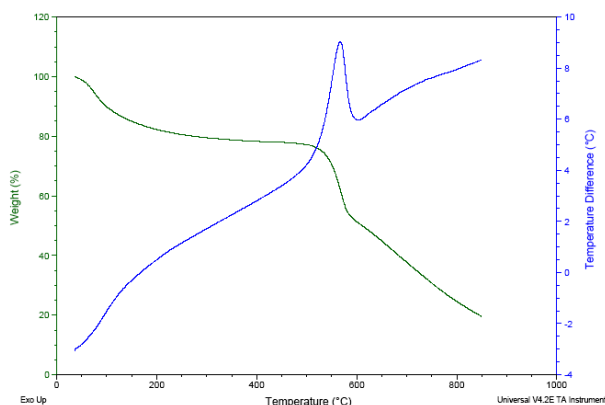


Figure 7. Thermogram of ABPBI.

The thermal stability of the polymer was determined by TGA from 25°C to 800°C in air at 10°C/min. (Figure 7). Finding a first exothermic event around 100-200°C due to absorbed water, then a exothermic event started at 500°C and is attributed to dehydration of residual polyphosphoric acid remains on in the polymer. Conductivity tests on ABPBI were measured at 25, 100 and 150 ° C by impedance applying a sinusoidal voltage signal of 10 mV in a range of 0.5Hz to 100kHz. The results (Table II) reveal that it has typical insulating conductivity values. In order to increase the conductivity to acceptable levels for PEM applications we proceed to incorporate the synthesized ionic liquid and H₃PO₄.

Table II. ABPBI conductivity obtained by Impedance

Temperature (K)	Conductivity + (S/cm)
298	3.9457×10^{-13}
373	1.6573×10^{-12}
423	1.3846×10^{-11}

The preparation of the membranes consisted in evaporating solutions of ABPBI in methanesulfonic acid, then sliced into 2 x 2 cm pieces and immersed inside H_3PO_4 and ionic liquid baths at different proportions (see Table I). After 24 hours, the immersed membranes were allowed to stand for 24 hours on absorbent paper to remove excess liquid. Afterwards, we proceeded to analysis by FTIR spectroscopy (Figure 8). The ABPBI doped membranes have some changes that give information about the interaction between H_3PO_4 and the imidazole ring. The bands of free and associated NH hydrogen bonds have a tendency to disappear ($3500\text{-}3000\text{ cm}^{-1}$), while a wide band appears around $3000\text{-}2500\text{ cm}^{-1}$ which is due to the formation of $\text{N}^+\text{-H}$ by the interaction of H_3PO_4 and the polymer. At the same time the bands due to H_3PO_4 appear around $1100\text{-}900\text{ cm}^{-1}$. In the case of ABPBI only impregnated with IL (sample1), it retains all the characteristic peaks of pure [BEBz][HP] and unmodified polymer which indicates the ability of the ionic liquid to penetrate through the polymer membrane

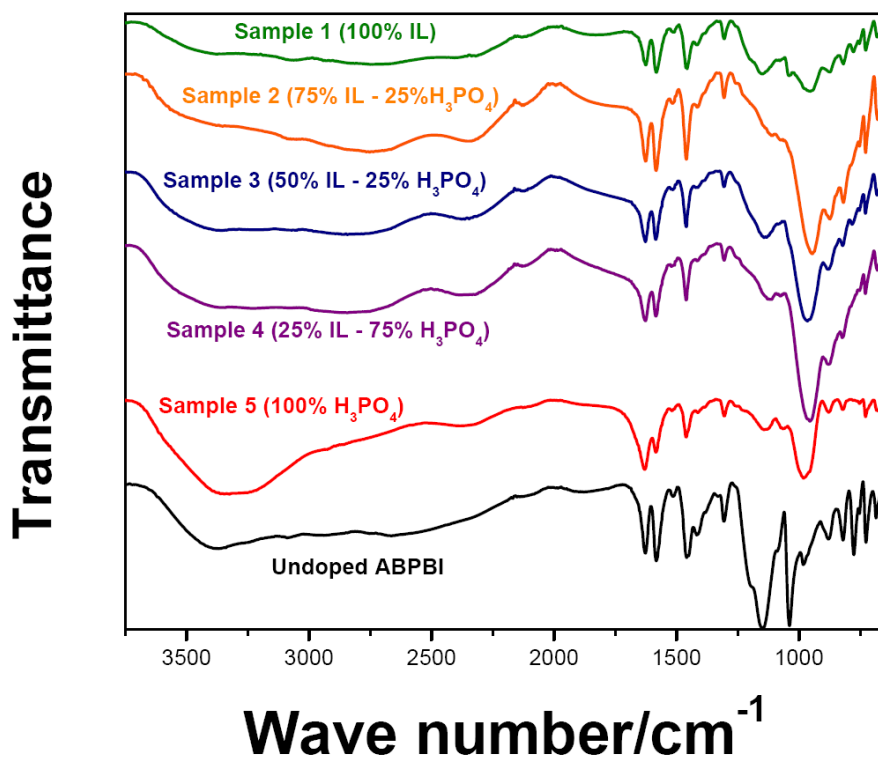


Figure 8. FTIR spectra for membranes prepared and undoped ABPBI.

Conclusions.

This work reports the synthesis of benzimidazole type ionic liquid 3-butyl-1-ethyl-benzimidazole dihydrogenphosphate ([BEBz][HP]). FTIR spectroscopy confirmed the structure of the compound by the identification of functional groups present in the molecule. Also, we determined the viscosity and ionic conductivity dependence with temperature. This compound showed a good thermal stability up to 300 °C according to TGA results. ABPBI was synthesized by reaction condensation of 3,4-Diaminobenzoic acid in polyphosphoric acid. The as-prepared polymer showed excellent thermal stability below 500°C and its conductivity was $3.9\text{--}138 \times 10^{-13}$ S/cm between 25-150°C. ABPBI/H₃PO₄/[BEBz][HP] flexible membranes were prepared by

controlled soaking. FTIR confirmed the absorption of both the IL and H_3PO_4 by ABPBI. The increment of H_3PO_4 content results in more fragile membranes.

Acknowledgements.

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