

# POLYBENZIMIDAZOLES BASED ON HIGH TEMPERATURE POLYMER ELECTROLYTE FUEL CELLS

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# ABSTRACT

This work presents an interesting approach in order to enhance the performance of Polymer Electrolyte Membrane Fuel Cells (PEMFC) by means of an increase in the operational temperature. For this, two polymeric materials, Poly(2,5-bibenzimidazole) (ABPBI) and Poly[2,2'-(m-phenylen)-5,5' bibenzimidazol] (PBI), impregnated with phosphoric acid have been utilized. These have shown excellent properties, such as thermal stability above 500°C, reasonably high conductivity when impregnated with H<sub>3</sub>PO<sub>4</sub> and a low permeability to alcohols compared to Nafion<sup>®</sup>. Preliminary fuel cells measurements on hydrogen based Polymer Electrolyte Membrane Fuel Cell (PEMFC) displayed an interestingly reasonable good fuel cell performance, a quite reduced loss when the hydrogen stream was polluted with carbon monoxide, and finally, when the system was tested with an ethanol/water (E/W) fuel, it displayed quite promising results that allows placing this system as an attractive option in order to increase the cell performance and deal with the typical limitations of low temperature Nafion<sup>®</sup>-based PEMFC.

# KEY WORDS

Key words: PBI ; ABPBI . High temperature ; PEMFC ; Ethanol crossover

# **1. INTRODUCTION**

Proton exchange membrane fuel cells (PEMFC) that operate at high temperatures (120-200  $^{\circ}$ C) are considered the next fuel cell generation, due to its advantages on the fuel cell that operates at lower temperatures (usually lower than 85  $^{\circ}$ C). The advantages include high kinetics, thermal control, simple water management, and high tolerance to pollutants [1,2]. In the last years, there is a strong research activity focused on the development of membranes that can be used in fuel cells at high temperature operation [3]. The most widely used membrane in PEMFC is the perfluorosulfonic-based Nafion<sup>®</sup> membrane, which presents some limitations, such as high cost, and low maximum operation temperature [4]. The polibenzimidazol family (PBI, ABPBI) have shown good results when membranes synthesized from these polymers are employed on tests

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in fuel cells that operates at high temperatures [5]. ABPBI is the simplest member of this family and is reported to have proton conductivity as good as the well-known commercial phosphoric acid doped PBI. Phosphoric acid is generally used for impregnation because it has got a high boiling point, high thermal stability, and high protonic conductivity. Compared to PBI, the ABPBI synthesis is simpler since it is synthesized from an unique monomer (3,4-diaminobenzoic acid), which is cheaper than the two monomers used to synthesize PBI. However, its solubility is very limited compared to PBI [6], which, in fact, might be the reason for the lower attention in literature, compared to its homonymous PBI. This material, on the contrary, has been extensively studied, developing both the own membranes, and the structure and formulation of the electrodes, with several interesting approaches that are addressed in a recent review carried out by Li et al. [5]. The structure of both polymers is shown in Figure 1.



Figure 1. Structure of: (a) ABPBI, and (b) PBI

When PBIs are impregnated with  $H_3PO_4$ , a conductivity of almost 0.1 S cm<sup>-1</sup> can be reached at 200°C, and its thermal stability is above 500°C in air [7-10]. Also, measurements of methanol and ethanol permeability on PBI displayed values 10-fold lower than Nafion<sup>®</sup> ones [11-13]. In addition, ethanol is a larger molecule compared to methanol, giving rise to a lower permeation [14], so that the beneficial effects of a low alcohol crossover can be reinforced. All these properties place this material as an interesting candidate for being used as electrolyte for high temperature PEMFC, both operating on hydrogen, and on simple organic molecules, such as methanol, ethanol or formic acid [5,15,16].

In this line, this work pretends to demonstrate how the polybenzimidazoles can be considered as an attractive alternative for being used at high temperatures, showing firstly some key physico-chemical properties, such as the thermal stability, the proton conductivity, and the alcohol permeation rate through the membrane. Afterwards, fuel cell measurements on hydrogen were carried out, completing the work by the use of PBIs in an ethanol-based PEMFC at high temperature.

# 2. OBJECTIVES

This work aims at demonstrating that polybenzimidazoles impregnated with phosphoric acid can be an interesting approach for High Temperature PEMFC, further helping to increase the efficiency and performance of the system. In order to achieve this overall objective, this work has been divided into a series of partial ones listed below:

- Characterisation of some important properties of ABPBI and PBI for its use in a fuel cell: thermal stability, membrane conductivity and ethanol crossover.
- Implementation of these materials on a high temperature PEMFC operating on different fuels (hydrogen, methanol and ethanol).

#### 3. METHODOLOGY

ABPBI was synthesized according to the following process: 6.046 g of monomer 3,4diaminobenzoic acid (DABA, 97 %) in 100 g of polyphosphoric acid (PPA, 99 % in 85 %  $P_2O_5$ ), both purchased from Aldrich and used without previous purification, as reported by Asensio [17]. The condensation occurred in a glass reactor equipped with a mechanical stirrer and reflux condenser, under a flow of N<sub>2</sub> at 150 °C for 0.5 h using a mechanical stirrer due to the high



viscosity of the medium during the reaction. Then, the temperature was raised to 180  $\degree$  for 0.5 h more and maintained for 4 more hours under constant mechanical stirring. The polymer was removed from the glass reactor by adding a large volume of purified water (Milli-Q) and washed until the pH of the filtrates remained unchanged. To eliminate the acid remaining inside the polymer structure, it was washed in 10 % NaOH solution with stirring for 12 h and washed with water again until neutrality. Finally, the polymer was dried at 100  $\degree$  until no weight change was observed and later dried in a vacuum oven at 40  $\degree$ . After drying, the polymer was milled and dried again at 100  $\degree$ . ABPBI membranes were prepared by dissolution of the polymer in methanesulfonic acid (MSA). The polymer and MSA were mixed and maintained under magnetic stirring at room temperature for 17 h. The films obtained were cast on a glass surface and evaporated on a heating plate at 200  $\degree$  for 2 h. The membranes were peeled off by adding distilled water.

In the case of PBI, 3.24 g (15.1 mmol) of 3,3',4,4'-tetraaminobiphenyl (Sigma-Aldrich, 99 %) and 2.51 g (15.1 mmol) of isophthalic acid (Sigma-Aldrich, 99 %) were mixed in 180 g of polyphosphoric acid (Riedel de Haen, > 83,5 % P<sub>2</sub>O<sub>5</sub>). The reaction system consisted of a 250 mL three-neck flask with a forth threaded neck, equipped with a calcium chloride (Panreac) drying tube and nitrogen inlet. Stirring was supplied magnetically by a heating/stirring mantle. The mixture was heated up to 200 °C for 9 hours, observing a progressive increase of its viscosity as reaction proceeded. Once the time elapsed, the dark purple reaction mixture was poured down into deionised (DI) water in order to isolate the polymer, and neutralised with potassium hydroxide (Panreac, 85 % pellets). Afterwards, the polymer powder was rinsed several times with DI water until reaching neutrality and left to dry up overnight at 150 °C inside an oven. Finally, the polymer was ground in order to obtain a fine gold-brownish powder. This was dissolved in N.N'-dimethylacetamide (Across) and lithium chloride (Panreac). The dissolving system consisted of a stainless steel reactor in which all those compounds were mixed until obtaining a 5 % wt. PBI solution with 1.5 % of LiCl. Nitrogen was bubbled previous to the closure of the reactor in order to expel all the oxygen. After closing it, it was heated up to 250°C (above DMAc normal boiling point, 166 °C) for 5 hours. The homogeneous solution obtained was subsequently used to cast the membranes. In order to cast films, 5 % wt. PBI solution in DMAc was spread onto a glass plate. The plate was next introduced inside an oven where a temperature ramp from 60 °C to 190 °C was programmed in order to evaporate slowly the solvents for 12 hours. Once this time elapsed, the plate was immersed in DI water in order to detach the membrane from the plate. The membrane was boiled in DI water during the following two days in order to remove traces of the solvent and the stabiliser, and stored in DI water until future uses. The removal of the solvent was later confirmed by FTIR analyses.

Membranes were impregnated by immersing them in phosphoric acid of different concentrations for at least 3 days, in order to assure the complete saturation with the acid. Subsequently, different characterization techniques were applied in order to analyze some interesting properties of the membranes.

The thermal stability of the samples was evaluated by a thermogravimetry. In the case of ABPBI, this analysis was carried out in a in a Shimadzu TGA–50, under N<sub>2</sub> atmosphere, gas flow 20 mL min<sup>-1</sup>, at 20 °C min<sup>-1</sup>. In the case of PBI, a Perkin-Elmer Thermogravimetric Analyzer TGA7 equipped with a Gas Selector and a Thermal Analysis Controller TAC7/DX was utilized. The sample was heated up from 25 °C to 700 °C at 5 °C/min in an air atmosphere.

Measurements of the membrane conductivity were carried out in the actual fuel cell by impedance spectroscopy. This was carried out with the aid of potentiostat/galvanostat Autolab PGSTAT 30 (Ecochemie, The Netherlands), equipped with a Frequency Response Analyser (FRA) module. The cell voltage was fixed at 0.6 V, and the frequency was varied from 10 KHz to 0.1 Hz, with a wave amplitude of 5 mV rms. The intercept of the impedance spectrum with the X-axis at high frequency is considered to be the ohmic resistance (R) of the system [18], whose main contribution is the membrane conductivity ( $\sigma$ ) [19]. This can be calculated according to equation 1, where L is the thickness of the membrane, and S is the active area of the MEA.



$$\sigma = \frac{1}{R} \cdot \frac{L}{S}$$
(1)

Limiting ethanol permeation currents through the membrane in the real fuel cell were measured voltammetrically [20]. This method consists of inverting the cell polarity with respect to that used in the fuel cell normal mode, so that a limiting current density is measured due to the transport-controlled methanol oxidation at the former cathode (now the anode) of the fuel cell fed with inert N<sub>2</sub>. In the former anode (now the cathode) hydrogen evolution takes place, serving as a counter and reference electrode. The actual crossover current is somewhat larger than the measured limiting current density. This is due to the counter ethanol flux associated with the electro-osmotic drag of fluid by the protonic current corresponding to the limiting current [20]. Ren et al. developed an expression to obtain the crossover current ( $J_{crossover}$ , mA cm<sup>-2</sup>) depending on the limiting current density ( $J_{lim}$ , mA cm<sup>-2</sup>), the electro-osmotic drag coefficient ( $\epsilon$ ) and the ethanol concentration ( $x_0$  corresponding to the ethanol molar fraction).

$$\frac{J_{crossover}}{J_{lim}} = \frac{12 \cdot \varepsilon \cdot x_{0}}{\ln(1 + 12 \cdot \varepsilon \cdot x_{0})}$$
(2)

However,  $H_3PO_4$ -doped PBI membranes have an electro-osmotic drag coefficient that is almost negligible [21], so that the limiting current density can be considered as equal to the crossover one.

The preparation of the electrode for the ABPBI-cell was as follows. A very viscous ink consisting of 30 % platinum on carbon black (ETEK-Inc, USA), ABPBI, and a mixture of N,N'-dimethylacetamide and LiCl as solvent was prepared, and subsequently magnetically stirred. This ink was deposited on a carbon cloth previously treated by brushing, until reaching a platinum loading of 0.5 mg cm<sup>-2</sup>, and a PBI loading corresponding to 20 % with respect to the total catalyst loading. After that, the electrode was immersed in Milli-Q water for 24 hours, impregnated with a solution of 5 % H<sub>3</sub>PO<sub>4</sub>. Finally, the electrode was dried in on oven at 110 °C.

In the case of the PBI-based electrodes, Toray graphite paper (TGPH-120, 10 % wet-proofed, Etek Inc., USA) was used as gas diffusion and supporting layer. On top of it, it was sprayed (using as carrier gas N<sub>2</sub>) a catalytic ink composed by 20 % Pt on carbon black Vulcan XC-72 (Etek Inc., USA), PBI as ionomer and DMAc as solvent, until obtaining a double loading of 0.5 mg/cm<sup>2</sup> for Pt and ABPBI. Afterwards, these were impregnated with 10 % H<sub>3</sub>PO<sub>4</sub> in a ratio of 6:1 with respect to the amount of polymer and left to soak overnight. In order to prepare the assembly, a piece of membrane was taken out from the H<sub>3</sub>PO<sub>4</sub> doping bath (75 % acid), and placed between the electrodes (active area of 4.65 cm<sup>2</sup>). Hot pressing was carried out with the aid of a press, applying a load of 1 tonne and 130 °C for 15 minutes.

For the tests with ethanol, the same procedure was followed, except that the composition of the anode and cathode varied. For the anode, the composition was 40 % Pt and 20 % Ru on Vulcan XC-72R (ETEK-Inc, USA). For the cathode, the components were the same except that the catalyst was 60 % Pt on Vulcan XC-72R carbon (ETEK-Inc, USA). The applied Pt loadings were 2 mg cm<sup>-2</sup> and 1 mg cm<sup>-2</sup> for the anode and the cathode, respectively. In the case of the PBI, the respective loadings were 1 and 0.33 mg cm<sup>-2</sup>.

#### 4. RESULTS

Figure 2 shows the corresponding Thermogravimetric Analyses (TGA) corresponding to the PBI [Fig. 2(a)], and ABPBI [Fig. 2(b)].As it can be seen, in both cases, for the pristine membranes, there is an initial weight drop until 150 °C, whose maximum is achieved at approximately 60-65 °C. In the case of the impregnated membranes, there is a second drop in the range of low temperatures, whose maximum is at approx. 250 °C, and finally, at temperatures above 500 °C, and for all the samples, the thermal decomposition of the polybenzimidazoles starts.



Nonetheless, it is noteworthy how this latest process becomes slower for the impregnated samples.

Figure 3 shows the values of the conductivity of a PBI sample at different temperatures and doping levels. As it can be seen in Figure 3, the higher is the doping level of the PBI, the higher is the proton conductivity. On the other hand, the temperature increases the conductivity up to value of 150  $^{\circ}$ C. Above this, the conductivity remains almost constant, or even slightly decreases.



Figure 2. TGA spectra of: (a) PBI, and (b) ABPBI membranes. Solid lines correspond to pristine membranes; dashed lines correspond to membranes impregnated with phosphoric acid.



**Figure 3.** Proton conductivity of a PBI membrane at different temperatures and doping levels ( 4.7; **1**.7; **1**.7; **1**.4.5).

Figure 4 shows the values of the limiting current densities values for the ethanol permeability at different temperatures and ethanol/water (E/W) weight ratios. As it can be seen, this values increases both with the temperature and with the E/W weight ratio. All the values obtained are in the ranges of 2-5 mA cm<sup>-2</sup>, lower that those obtained for Nafion<sup>®</sup> 117 membranes operated on ethanol, which are in the range of 50-100 mA cm<sup>-2</sup>, depending on the operating conditions, for much lower ethanol concentrations in the fuel mixture [21].

Figure 5 shows the cell performance for PBI and ABPBI membranes at different temperatures when the cell was operated on hydrogen. As it can be seen, the performance increases with the temperature, even though it is significant that this increase lowers the higher the temperature is, especially in the case of the ABPBI measurements.



Figure 6 displays the cell performance when the hydrogen stream contains impurities of carbon monoxide, observing a certain decrease in the cell voltage typical of the inclusion of a poison in the fuel.

Figure 7 shows the cell performance for a PBI-based PEMFC operating on ethanol at different temperatures and ethanol concentration. As expected, the temperature increases the cell performance, whereas in the case of the ethanol concentration, there is an optimum value corresponding to an ethanol/water weight ratio of 0.5.





Figure 4. Ethanol permeation currents for PBI at different temperatures and E/W weight ratios



Figure 5. Fuel Cell Performance of PBI's based PEMFC at different temperatures for (a) PBI membranes, and (b) ABPBI membranes





Figure 6. Polarization curves showing the influence of the inclusion of a poison in the fuel stream

### 5. DISCUSSION

Figure 2 shows the results of the thermal analyses carried out on different PBI's sample. As it was previously demonstrated [10], polybenzimidazoles show exceptional high-temperature stability up to temperatures higher than 500 °C in all the cases. The presence of aromatic rings increases the intermolecular forces, and hence, properties such as thermal stability are improved notably compared to other thermoplastic polymers. Furthermore, it can be seen that the doped membranes are thermally more stable than the non-doped ones. In US Patent 4,927,909 [22], this feature was also observed, although explanations were not given. It could be possible that the formation of strong hydrogen bonds between imidazole rings and acid molecules may increase the membrane stability. In any case, this result is of extremely high importance since it reveals the high thermal resistance of this material, confirming the chance of being utilized as electrolyte at high temperature.



**Figure 7.** Fuel Cell Performance of PBI's based DEFC at: (a) different temperatures, (b) different ethanol concentrations (ethanol/water weight ratio: E/W)

Having a look more in detail at the TGA curves, it can be seen that the doped membranes presents two consecutive drops at low temperatures (below 350 °C), whereas the pristine PBI only has one. In the former cases, the first drop corresponds to the loss of free water contained in the membrane, whereas the second one is associated to the dehydration of phosphoric acid, forming oligomers of the original acid (pyrophosphoric and methaphosphoric acid).

Figure 3 shows the conductivity of a PBI membrane. As it can be seen, when doped with phosphoric acid, the membranes present acceptable values of conductivity in order to be used



as electrolyte for a high temperature PEMFC [23]. Furthermore, it can be observed how the membrane conductivity increases with the temperature, due to the increase in the mobility of the charge carriers within the membrane. Nevertheless, at the highest temperature, the conductivity does not increase any more. The reason for this fashion is the self-dehydration of phosphoric acid that occurs when the temperature exceeds 150 °C, generating the less conductive species pyrophosphoric acid [24]. It has to be taken into account that measurements were performed under fairly "dry" conditions (membranes equilibrated with the room environment), which favours that dehydration process. In addition, this can also explain why the values obtained in this work are lower than other reported in literature [25]. Water is an active element in the conduction of PBI, so that its absence may be responsible for the lower proton conductivity values obtained here. On the other hand, it can be seen that the higher the doping level, the higher the conductivity, indicating that the main source for protons conduction in PBI membranes is the acid.

Ethanol permeation rate, assessed from the limiting permeation current density, displays an increase as the temperature and/or E/W increases. Logically, the temperature favours the diffusion process through the membrane, so that a constant increase for any E/W is expected, and experimentally observed. In the case of the E/W, for any temperature, the crossover current also increases. However, the trend in this case is different. From E/W of 0.25 to 0.5, the current crossover sharply increases. However, this notably reduces from E/W of 0.5 to 1. This is not easily interpreted. Pu and Liu [26] found that in the case of methanol the permeability decreases with the concentration at high values. They adduced the possibility of the formation of hydrogen bonds between the methanol molecule and the own PBI. This might be also happening for ethanol. Nevertheless, further studies must be carried out to achieve a deeper understanding of this particular behaviour.

In Fig. 4, the values of the crossover currents were in the range 2-7 mA cm<sup>-2</sup> for E/W ratio between 0.25 and 1. In the case of methanol, following the same methodology, Lobato et al.[12] found values in the range of 5-25 mA cm<sup>-2</sup>. As expected, the ethanol permeability is also lower in PBI. With Nafion<sup>®</sup>, typical ethanol permeability values are in the range of 50-100 mA cm<sup>-2</sup> (depending on the operating conditions) for much lower ethanol concentrations in the fuel mixture [27]. This explains why this type of cells can be operated with concentrated ethanol solutions, which of interest from a practical point of view [28]. Therefore, in terms of fuel crossover, PBI can be considered as a suitable candidate for DEFC.

Cell performance based on hydrogen (Figure 5) displays the typical behaviour of PBI-based system, with an improvement the higher the temperature is. This is due to the enhancement on the kinetic of the electrochemical process that takes place in the cell, both the hydrogen oxidation and the oxygen reduction, along with the increase of the electrolyte conductivity, as it was previously showed. Concomitantly with the values of the conductivity, the increase of the cell performance diminishes the higher is the temperature, more likely due to the previously mentioned dehydration process of the phosphoric acid, which offsets the intrinsic improvements on the kinetic of the electrodes. Nevertheless, the obtained values are quite promising and seem to postulate the polybenzimidazoles as interesting and attractive candidate for polymer electrolyte operating at high temperatures.

Indeed, the increase in the temperature is probably the best option in order to mitigate the effects of the presence of poisons (e.g. carbon monoxide). As a matter of fact, in Figure 6, it can be seen how the loss in the performance of the cell is quite small (in terms of power density is ~10 %), something completely unthinkable for the same situation on PEMFC operating at lower temperatures (e.g. 85 °C), using Nafion<sup>®</sup> membranes, which typically experiment loss of performance near 80 % [29].

The good predisposition of the PBI's to be used as polymeric electrolyte for high temperature DEFC (high conductivity and low alcohol permeability) are fully confirmed by the results showed in Figure 7. As expected, an increase in the temperature causes an enhancement in the cell performance. Indeed, for a current density of 50 mA cm<sup>-2</sup> the corresponding cell voltages were



255 mV at 125 °C, 371 mV at 150 °C, 442 mV at 175 °C and 496 mV at 200 °C. The increase in the electrolyte conductivity with the temperature, along with the enhancement in the kinetic of the electrodic processes, especially for the ethanol oxidation [30], account for this fashion. Contrarily to what it is observed for H<sub>2</sub> PBI-based PEMFC, the increase of the performance with the temperature is monotonic. In the DEFC, as the fuel is a mixture of ethanol and water, the electrolyte might not undergo such a strong dehydration process. In consequence, its conductivity continuously increases with the temperature. This trend is similar to that reported when the PBI membrane conductivity is measured under humid conditions [8,31]. Also, the enhanced conductivity of the electrolyte is beneficial for the electrode kinetic as it takes part in the electrochemical reaction by carrying the protons. Moreover, the solubility of the fuel might be also improved if the PBI is hydrated, as Liu et al. [32] demonstrated for O<sub>2</sub>.

Figure 7(b) shows the influence of the ethanol concentration on the cell performance. Having a look at the polarization curves, in the range of current densities below 200 mA cm<sup>-2</sup>, the best performance is achieved for the E/W of 0.25, reducing as the E/W increases, i.e., as there is more ethanol present in the fuel. Two reasons may explain this behaviour: (i) ethanol oxidation takes place more rapidly in the presence of water [15], and (ii) the electrolyte conductivity enhances the higher is the water content. However, when the current exceeds 200 mA cm<sup>-2</sup> the trends reverse. This could be explained as follows. For methanol, a low permeability was reported for PBI [11,12], and even this could be even lower for ethanol due to the larger size of the molecule. Although this is beneficial from a membrane point of view, it might not be so desirable from the point of view of the electrodic architecture, since ethanol has to diffuse through the thin electrolyte layer that surrounds the catalytic sites. In consequence, the combination of the low PBI ethanol permeability and a low E/W may give rise to the appearance of mass transfer limitations, causing the decrease of the cell performance at high current densities are reached with the E/W of 1.

Although these performances are far from other values reported in literature for the wellestablished perfluorosulphonated systems, they allow postulating polybenzimidazoles as interesting candidates for high temperature PEMFC. Thus, its high thermal stability, the enhancement in the membrane conductivity with the temperature, the promising performance both with hydrogen, and with ethanol are quite promising results for this two alternative materials of the same polybenzimidazole family. Further work must be carried out in order to further improve the most important characteristic of these candidate polymeric materials, its fuel cell performance.

# 6. CONCLUSIONS

This work presents two types of polybenzimidazoles, ABPBI and PBI, as quite interesting candidate materials to be used as polymeric electrolyte for high temperatures PEMFC. As the most significant features, these materials possess a high thermal stability, a low ethanol crossover (especially compared to the classical Nafion<sup>®</sup> membranes), and a high conductivity at high temperatures. The fuel cell performance displayed quite promising and interesting results, with a reasonable performance operating the cell on hydrogen, a negligible performance loss when the fuel stream was contaminated with carbon monoxide, and satisfactory results operating on ethanol. All these results allow confirming that polybenzimidazoles can be considered as interesting alternative in order to increase the operational temperature of Polymer Electrolyte Membrane Fuel Cells above 100°C.

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