



## Spray-Casting ABPBI Membranes for High Temperature PEM Fuel Cells

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The preparation and characterization of membranes of poly[2,5-benzimidazole] (ABPBI) by spray casting at room temperature from an ethanol solution is described. The prepared membranes doped with 11 M H<sub>3</sub>PO<sub>4</sub> sorbed 1.5 molecules of acid per imidazole ring exhibiting a proton conductivity of 0.05 S · cm<sup>-1</sup> at 153°C. The 80 μm thick, homogeneous, membranes obtained were used for the preparation of a membrane electrode assembly (MEA). Fuel cell test conducted with the prepared MEA at temperatures between 100 and 180°C shows an increase in the performance with temperature, with a maximum power density of 200 mW · cm<sup>-2</sup> at 180°C. The described ABPBI membrane preparation method from an ethanol solution at low temperature opens a simple route for overcoming the processability problems of the aforementioned polymer.

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High temperature proton exchange membrane fuel cells (HT-PEMFC) operating above 100°C (typically at 150–200°C) render several advantages as compared to conventional PEMFC. Namely, enhanced rates of electrochemical kinetics (mainly the ORR), higher tolerance to impurities in the reformed hydrogen, easier water management, and co-generation of heat and power.<sup>1,2</sup>

It is well known that Nafion, the most extensive membrane used in PEMFCs, dehydrates above 90°C, with an inevitable loss of proton conductivity,<sup>3</sup> even in the presence of fillers that extend a few degrees the upper temperature of operation.<sup>4</sup> Chandan et al.<sup>2</sup> have pointed out that, with the exception of durability issues, only acid doped polybenzimidazole (PBI) membranes meet the US DOE targets for high temperature membranes operating under no humidification on both anode and cathode sides, and also exhibit good mechanical and chemical properties.<sup>5</sup>

Poly[2,2'-m-(phenylene)-5,5'-bibenzimidazole] is the most extensively used PBI. Nevertheless, poly(2,5-benzimidazole) (ABPBI) has also deserved great attention due to its simple synthesis procedure from a polycondensation mechanism using a low cost commercial monomer.<sup>6</sup> ABPBI is soluble in very few solvents,<sup>7</sup> mainly strong acids such as phosphoric (PA), polyphosphoric, sulfuric, formic, trifluoroacetic, and methanesulfonic (MSA) acid, as well as in ethanol/NaOH, limiting ABPBI membrane preparation to casting at high temperature from MSA solution,<sup>8–11</sup> and casting at low temperature from alkalized ethanol,<sup>12–15</sup> or formic acid.<sup>11</sup>

High temperature casting is usually performed by pouring ABPBI solutions (5% w/w) in MSA on a glass plate kept at 200°C in a ventilated hood, and solvent evaporation requires several hours. Low temperature casting from formic acid was conducted at room temperature and it demands several hours.<sup>11</sup> Casting of ABPBI from ethanol/NaOH also can be performed at low temperature.<sup>12–14</sup> However, the proposed methods require special conditions such as pour the solution on a Teflon plate cooled at 0°C with liquid N<sub>2</sub> and nitrogen stream in order to kept evaporation rate as low as possible (overnight) to obtain a homogeneous membrane,<sup>15</sup> cast on a level glass plate in a glove box under a stream of nitrogen,<sup>12,14</sup> or the drying in vacuo at 40°C for 24 h, of the casted solution on glass plates.<sup>13</sup> Casting at intermediate temperature from N-methylpyrrolidinone/LiCl, or trifluoroacetic acid (TFA)-PA mixture have been also reported for ABPBI.<sup>7,16</sup> Thus, to the best of our knowledge, alternative procedures to long casting for homogeneous ABPBI membrane fabrication are not available.

It is also important to emphasize that the number of components and steps involved in the MEA fabrication process has a great impact on the massive production of fuel cells,<sup>17,18</sup> and the fuel cell performance,<sup>17–20</sup> by influencing the microstructure of the triple phase boundary (TPB) region.<sup>21</sup> In order to generate the TPB, the catalyst is dispersed in a solution of the same ionomeric polymer that composes the membrane, which acts as a binder between the catalyst and the substrate, and allows the ionic charge transport.

Briefly, MEA preparation steps are: the catalyst ink preparation; the application of the catalyst layer on the membrane, or on the gas diffusion layers, and the hot pressing of the components. In the case of ABPBI-based MEAs, the lack of a polymer solution easy to handle forced the use of a binder different that ABPBI in the ink formulation. Thus, Nafion,<sup>22</sup> PBI,<sup>23,24</sup> PTFE,<sup>25–27</sup> and PVDF<sup>28</sup> were employed in the catalyst formulation, even when the last two are not proton conductors. Wang et al.<sup>10</sup> have prepared an ABPBI-MEA using ABPBI in the catalyst ink, but the preparation process required the use of methanesulfonic acid at 100°C, implying a highly impractical method.

In the present work, an ABPBI membrane prepared through a simple procedure is presented. The membranes were formed by spraying an ABPBI solution at room temperature (ca. 20°C). Moreover, a more environmental friendly solvent as ethanol/ KOH was employed in the dissolution of ABPBI. The feature properties of the obtained membranes, such as doped level, water uptake, and ionic conductivity were determined. Furthermore, the ABPBI solution in ethanol/KOH was employed in the formulation of a catalyst ink for the MEA preparation procedure, based on a direct paint method. Finally, the MEA performance was evaluated in a fuel cell at temperatures up to 180°C. The simplicity of these membrane and MEA preparation methods could allow a facile massive fabrication of ABPBI fuel cells.

### Experimental

**Materials.**—H<sub>3</sub>PO<sub>4</sub> (Merck), H<sub>2</sub>SO<sub>4</sub> (Fluka), 3,4-diaminobenzoic acid, 97% (Aldrich), polyphosphoric acid 85% (Aldrich), KOH (Mallinckrodt), ethanol absolute (Aldrich) all analytical grade were used as received. Water was deionized and passed through a Millipore filter. The commercial ABPBI membrane was Fumapem A (Fumatech).

**ABPBI synthesis.**—Poly(2,5-benzimidazole) was obtained using the method described elsewhere.<sup>6</sup> Briefly, ABPBI was prepared by condensation of 3,4-diaminobenzoic acid (DABA) monomer in polyphosphoric acid (PPA) at 200°C during five hours. On a three

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neck round-bottom flask, DABA and PPA without any previous purification were added. The reaction mixture was stirred mechanically and maintained under nitrogen stream during all polymerization time. The product obtained was poured in deionized water and the PPA was neutralized by using NaOH. Following, the polymer was washed with hot water during 24 hours using a Soxhlet apparatus. Finally, the washed polymer was dried at 180°C for 24 hours and then finely ground.

Polymer molecular weight was determined by the intrinsic viscosity measurement. Typically ABPBI was completely dissolved in H<sub>2</sub>SO<sub>4</sub> 98%, and four solutions with different concentrations were prepared and kept stirred at least for 72 hours before their use. A Cannon–Fenske viscosimeter thermostated at 30°C was employed for viscosity measurements. The reduced ( $\eta_{red}$ ) and inherent ( $\eta_{inh}$ ) viscosities were calculated for each solution and the intrinsic viscosity ( $\eta_{int}$ ) was determined from the equation:

$$\eta_{int} = \lim_{c \rightarrow 0} \eta_{red} = \lim_{c \rightarrow 0} \eta_{inh} \quad [1]$$

The polymer molecular weight can be calculated by using the Mark-Houwink equation,<sup>6</sup> which for ABPBI adopts the form:

$$\eta_{int} = 8.7 \cdot 10^{-3} DP^{1.1} \quad [2]$$

where DP is the polymerization degree. Molecular weight was calculated as the product of DP times the mass of the repeating unit (116 g · mol<sup>-1</sup>).

**Membrane preparation process.**—The ABPBI prepared as described above was dissolved in absolute ethanol/KOH. The solution contains typically ca. 2 wt% of ABPBI, and between 2 and 4 wt% of KOH is added to provide the ABPBI dissolution. The dissolution step took around 5 days. The mix was kept in reflux until complete dissolution of the ABPBI. Once cooled the solution was filtered with a stainless steel sieve (mesh 500) and stored until further use. A spray casting method was used to prepare the membrane.<sup>29</sup> Briefly, the solution was sprayed homogeneously with dry air as a carrier over a glass plate at room temperature (20–25°C). The solution was finely and continuously sprayed over the substrate, with homogeneous linear and transverse movements, by using a dual action gravity feed airbrush with a nozzle 0.5 mm in diameter. Carrier gas pressures between 0.5 and 3 bar were evaluated, and the best results were obtained with a pressure of 1 bar. At this pressure the solution lost was minimized to ca. 30%, while the membrane obtained was smooth. The airbrush-substrate distance was approximately 10–15 cm. The amount of solution used was calculated on the basis of the area to be sprayed and the desired membrane thickness. Once the sprayed ABPBI membrane (sABPBI) was formed, the coated glass was immersed in a water bath at room temperature for peeling off the film. The resulting membranes were subjected to a thermal treatment at 180°C during 10 hours and finally washed with ultrapure water in a Soxhlet apparatus. The spray-casting method allows the preparation of membranes with homogeneous thickness in the range of 40–120 μm. Membranes 80 μm in thickness, and area of 20 cm<sup>2</sup> were employed to prepare the MEAs and perform the fuel cell tests. The thicknesses of the membranes were measured with a Mahr XL1-57B-15 dead load gauge.

**Membrane characterization.**—The sABPBI membranes were previously doped with different concentrations of aqueous H<sub>3</sub>PO<sub>4</sub> (PA) for 7 days in capped polypropylene flasks at ca. 20°C.

The acid doping level measurements were performed by the titration method. Before the titration, the residual acid on the membrane surface was removed by fast immersion in deionized water, and superficially dried with filter paper. The membrane was placed in a Metrohm cell, containing 20 mL of water, and titrated by adding, drop by drop with a syringe pump, 0.15 M NaOH solution. During the whole titration, the solution was stirred with a magnetic bar while N<sub>2</sub> was bubbled. The pH was measured with combined glass electrode connected to HP a HP multimeter (Agilent 34970) through a high-input-impedance operational amplifier. In order to obtain the dry

mass of the membranes, they were washed in a Soxhlet apparatus for 24 hours and then dried until constant weight.

The mass of H<sub>3</sub>PO<sub>4</sub> sorbed ( $m_a$ ) was calculated using the following equation:

$$m_a = C_b V M_a \quad [3]$$

where  $C_b$  is the molarity of the NaOH solution,  $V$  is the volume consumed until the equivalent point is reached, and  $M_a$  is the H<sub>3</sub>PO<sub>4</sub> molar mass.

The H<sub>3</sub>PO<sub>4</sub> mass sorbed by the membrane ( $m_{a0}$ ), per gram of dry membrane, was calculated according to the equation:

$$m_{a0} = \frac{m_a}{m_0} \quad [4]$$

where  $m_0$  is the mass of dry membrane.

Water uptake was determined by weight difference. The doped membranes were dried superficially with a tissue paper. The equilibrium mass for each membrane was named as the wet membrane mass ( $m_h$ ). Then, they were immersed in a 5 wt% NaOH bath and washed in a Soxhlet apparatus until a constant pH value. Finally, in order to obtain the mass of dry membranes ( $m_a$ ) the samples were dried in a vacuum oven at 120°C until constant weight (usually 20 hours). The water mass sorbed ( $m_w$ ) was calculated by using the following equation:

$$m_w = m_h - m_a - m_0 \quad [5]$$

where  $m_h$  and  $m_0$  are the wet and dry membrane masses, respectively.

The water content per gram of dry membrane ( $m_{w0}$ ) was obtained by resorting to the following equation:

$$m_{w0} = \frac{m_w}{m_0} \quad [6]$$

The in-plane membrane conductivity was measured between 80 and 153°C by the four point method. The measurements were carried out by placing the doped membrane in a homemade Teflon cell with a design similar to the BT 112 commercial cell.<sup>30</sup> The cell has four platinum wire electrodes 0.5 mm in diameter, 5 mm length, and separated 5 mm among them. Humidification was carried out by introducing nitrogen at ca. 30% RH into the cell (corresponding to the water activity in 11 M PA at 25°C),<sup>31</sup> which was obtained by sparging the gas through a MgCl<sub>2</sub> saturated solution at atmospheric pressure and room temperature. Impedance spectroscopy was performed with a potentiostat/galvanostat (AUTOLAB PGSTAT302N, Eco Chemie) equipped with a frequency response analyzer (FRA). A potential of 0 V was fixed, varying the frequency between 100 kHz and 1 Hz with amplitude of 100 mV. The ohmic resistance ( $R$ ) was obtained by fitting the experimental results with an equivalent circuit at the first intercept ( $Z''$ ) of the impedance spectrum. The membrane conductivity was calculated using the following equation:

$$\sigma = \frac{l}{R e b} \quad [7]$$

where  $l$  is the distance between electrodes,  $R$  ohmic resistance,  $e$  and  $b$  are the thickness and the width of the membrane, respectively. The thickness value used was an average obtained along the membrane using a digital microscope and processed with ImagenJ software.

The structure of the washed and dried membrane, without metallization, was observed by a scanning electron microscope (SEM) - FEI Company (Quanta FEG 250), in high vacuum mode with Large Field Detector (LFD). In order to obtain a cross-section image the membrane was broken after immersion in liquid N<sub>2</sub>.

The X-ray diffraction patterns of undoped and doped in 11 M PA sprayed membranes were performed with a PHILIPS PW 1730/10 X-ray diffractometer, using CuK<sub>α</sub> radiation. The data were recorded at 2θ between 5° and 50°, 0.01 step size and 1.0 s per step.

**MEA fabrication and fuel cell testing.**—Pt/C 20 wt% (E-Tek Division) was used as anode and cathode catalysts. The catalyst ink was prepared by using ethanolic ABPBI as binder, that is, a polymer

with the same structure as the employed membrane. The calculated amount of ethanol was added quickly to the vial containing the catalyst in order to avoid the formation of sparks, a normal occurrence when low MW alcohol like methanol are mixed with nanoparticulated Pt. The formulation of the ink was adjusted for yielding 15% wt of ABPBI in the final electrode.<sup>32,33</sup> The catalyst suspension was prepared by mixing the catalyst with ethanol and the ABPBI solution in a 2:82:16% wt, respectively. Toray C paper TGP-H 60 (10% PTFE coated, Fuel Cell Technologies) was used as gas diffusion layer (GDL). Anode and cathode suspension were applied with an airbrush on one side of the square pieces of GDL of 5 cm<sup>2</sup> area. No temperature control was employed while depositing the ink over the electrode. The electrode loading was ca. 0.6 mg · cm<sup>-2</sup>. The sABPBI membranes, 80 μm in thickness, were placed in between the electrodes and then hot pressed at 140°C and 40 bars for 25 min. The formed MEAs were doped by immersion in 11 M H<sub>3</sub>PO<sub>4</sub> solution during 7 days at ca. 20°C.

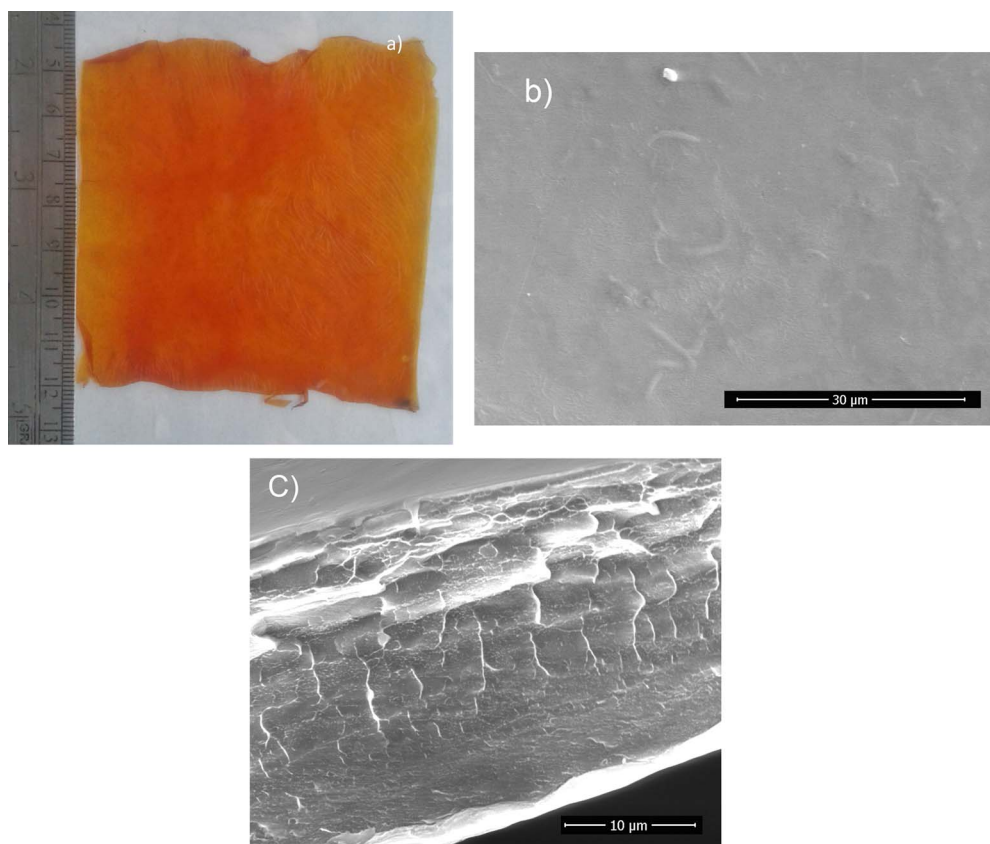
Fuel cell tests were performed in a mono-cell by using a commercial test station and fuel cell hardware (Fuel Cell Technologies, Inc.). Galvanodynamic polarization tests were performed at different temperatures from the open circuit voltage (OCV) to a voltage close to short circuit (0.05 V) with increments of 0.05 A every 90 s. H<sub>2</sub> and O<sub>2</sub> were humidified at 100% RH (at 90°C) before feed them into the cell. The humidifying bottles and the cell temperatures were controlled individually. The cell was tested with humidified H<sub>2</sub> and O<sub>2</sub> at a flow of 200 and 250 sscm, respectively. Activation of the MEA was performed at 80°C by conducting a series of fast polarizations, current increments every 5–10 s, followed by maintaining the maximum current reached (around 4 A) for 2–3 hours. The initial internal resistance of the MEA was assessed after conditioning of the cell by electrochemical impedance spectroscopy (EIS) in a frequency range of 100 kHz to 1 kHz at 0.0 V, and sinusoidal perturbation of 10 mV in amplitude. This resistance gives an indication of the fuel cell performance. Also, the resistance value has a dependency with

the membrane thickness. A value ca. 20 mΩ is acceptable for MEAs employing Nafion 212. Doping of ABPBI in 11 M PA was performed after the MEA preparation. The results shown below correspond to ABPBI MEA with a resistance around 100 to 200 mΩ. ABPBI MEA with resistance above 500 mΩ exhibited a very poor performance and the results were discarded. Also, MEAs doped before pressing tested, and their resistance was consistently in the range 1–2 Ω with a poor or null performance.

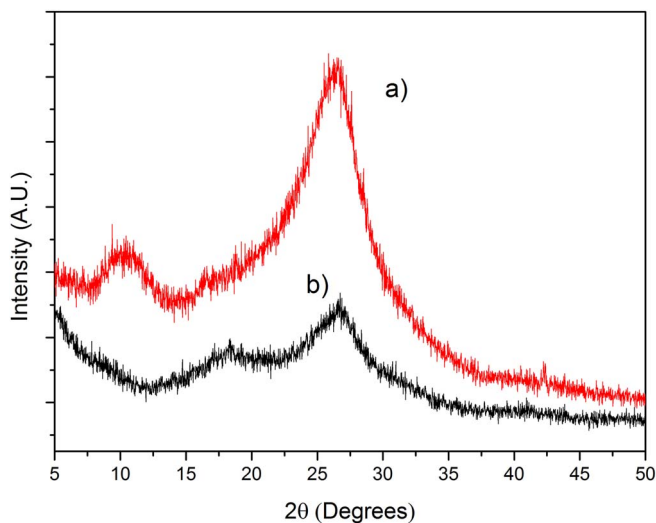
## Results and Discussion

**Polymer molecular weight.**—The ABPBI synthesized was dissolved in H<sub>2</sub>SO<sub>4</sub> and the viscosity was measured at 30°C. A typical value of inherent viscosity obtained was of 2.2 dL · g<sup>-1</sup>. Through Mark-Houwink equation<sup>2</sup> the polymerization degree and molecular weight were calculated. The MW for ABPBI synthesized without any previous purification of the reactive was 17,900 g · mol<sup>-1</sup>. This result is slightly lower than those found in the literature<sup>6,11,13</sup> with values ca. 23,000 g · mol<sup>-1</sup>. Nevertheless, robust membranes with handling properties that allowed the manipulation without compromising size or shape were obtained.

**Membrane structure and morphology.**—Heat treatment and washing steps were included in the preparation procedure in order to obtain a dense membrane and prevent changes in size during high temperature operation. Moreover, the washing steps eliminate residual KOH and water soluble impurities from the membrane. After these treatments, the membrane shrinks around 40%. Figure 1a shows images of a typical sABPBI membrane, with area ca. 30 cm<sup>2</sup>, obtained after the complete procedure of spraying and washing. Also, SEM top view image of the membrane (Fig. 1b) and a cross view of the membrane obtained by freeze-fracture method (Fig. 1c) can be observed.



**Figure 1.** a) Image of sABPBI membrane obtained after heat-treatment. SEM images b) from top view, and c) cross section of the membrane.



**Figure 2.** XRD pattern of undoped sABPBI membrane (a), and sABPBI membrane doped in 11 M  $\text{H}_3\text{PO}_4$  bath (b).

The dense membrane exhibits a uniform morphology and the absence of defects or holes can be appreciated.

The spray casting method prompted a fast solvent evaporation and proved to be a successful way to obtain a membrane with good handling properties. Moreover, the fact that the temperature does not need to be controlled implied a fast and simple procedure. In contrast, when ABPBI was cast by the Dr. Blade method from the same ethanol solution, without controlled conditions of temperature and humidity, the membranes obtained showed no uniform shape and broke easily when handled.

The morphology of the membrane can be modified according to the casting procedure or solvent used during the membrane formation.<sup>34</sup> Asensio et al.<sup>8</sup> have shown that ABPBI membranes prepared by direct casting from MSA and PA are more crystalline than those prepared by casting from MSA followed by phosphoric doping. Moreover, the degree of crystallinity can be increased by heat-treatment or stretching the membrane.<sup>13,35</sup> Changes in the structure of the formed membrane have been studied through WAXD analysis. In Figure 2, diffraction patterns of undoped and doped (in 11 M  $\text{H}_3\text{PO}_4$ ) sABPBI membranes are shown.

Undoped membrane shows a sharp peak at  $26^\circ$  which corresponds to benzimidazole chains forming a stacked structure of ABPBI with a  $d$ -spacing of 0.33 nm. The sharpness of the peak at  $26^\circ$  should indicate the highly crystalline nature of the membrane.<sup>36</sup> Other broader peak at about  $10^\circ$  is attributed to the crystalline phase of ABPBI,<sup>6,37,38</sup> which it would be promoted by the heat-treatment suffered by the membrane during the formation procedure. During the doping step crystalline order can be lost due to the fact that PA, and also water molecules, act as plasticizers, staying in the intermolecular free volume space. In doped sprayed membranes, the increasing fraction of amorphous phase can be visualized by the lack of the peak at about  $10^\circ$  and the diminished intensity and broadening of the peak at  $26^\circ$ . Moreover, the new broad peak at  $18^\circ$  can be assigned to an increased  $d$ -spacing (0.47 nm) of the stacked ABPBI structure, as the result of the presence of PA and water, in good agreement with reported experimental<sup>39</sup> and simulated<sup>40</sup> results.

#### Phosphoric acid content, water uptake and ionic conductivity.—

Figure 3a shows the acid content in the PA doped membrane at different acid concentrations. At this range of doping bath, a linear trend of the acid content with the PA concentration is observed. The membrane doped in 11 M  $\text{H}_3\text{PO}_4$  takes 1.3 g of acid per gram of sABPBI, which correspond to 1.5  $\text{H}_3\text{PO}_4$  molecules per imidazole ring. Moreover, at higher doping concentrations (ca. 13 M), the membranes showed mechanical instability and easily break in parts with handling.

ABPBI membranes prepared by casting from MSA solution have shown the same trend with the doping concentrations, although, generally a higher acid content (around 3 per imidazole ring) have been reported<sup>16,7,15</sup> for an 11 M PA doping bath. Also, a content of 3.5  $\text{H}_3\text{PO}_4$  molecules per imidazole ring for cast membrane from formic acid has been reported.<sup>11</sup> More recently, Diaz et al.<sup>15</sup> reported studies of a membrane formed by a casting method from alkalized ethanol, at low temperature ( $0^\circ\text{C}$ ) and  $\text{N}_2$  atmosphere, showing comparable results to those obtained with membranes casted from MSA, reporting an acid content of 2.5  $\text{H}_3\text{PO}_4$  molecules per imidazole ring from 11 M PA doping bath. These results indicate that the membranes obtained by spray method reach a lower doping level than those ones formed by low and high temperature casting.

A dramatic rise of the water uptake with the increment of the acid concentration of the doping bath can be observed in Fig. 3b. Thus, the PA content, expressed as acid sorbed by total mass of membrane as in Fig. 3c, decreases with acid concentration of the bath.

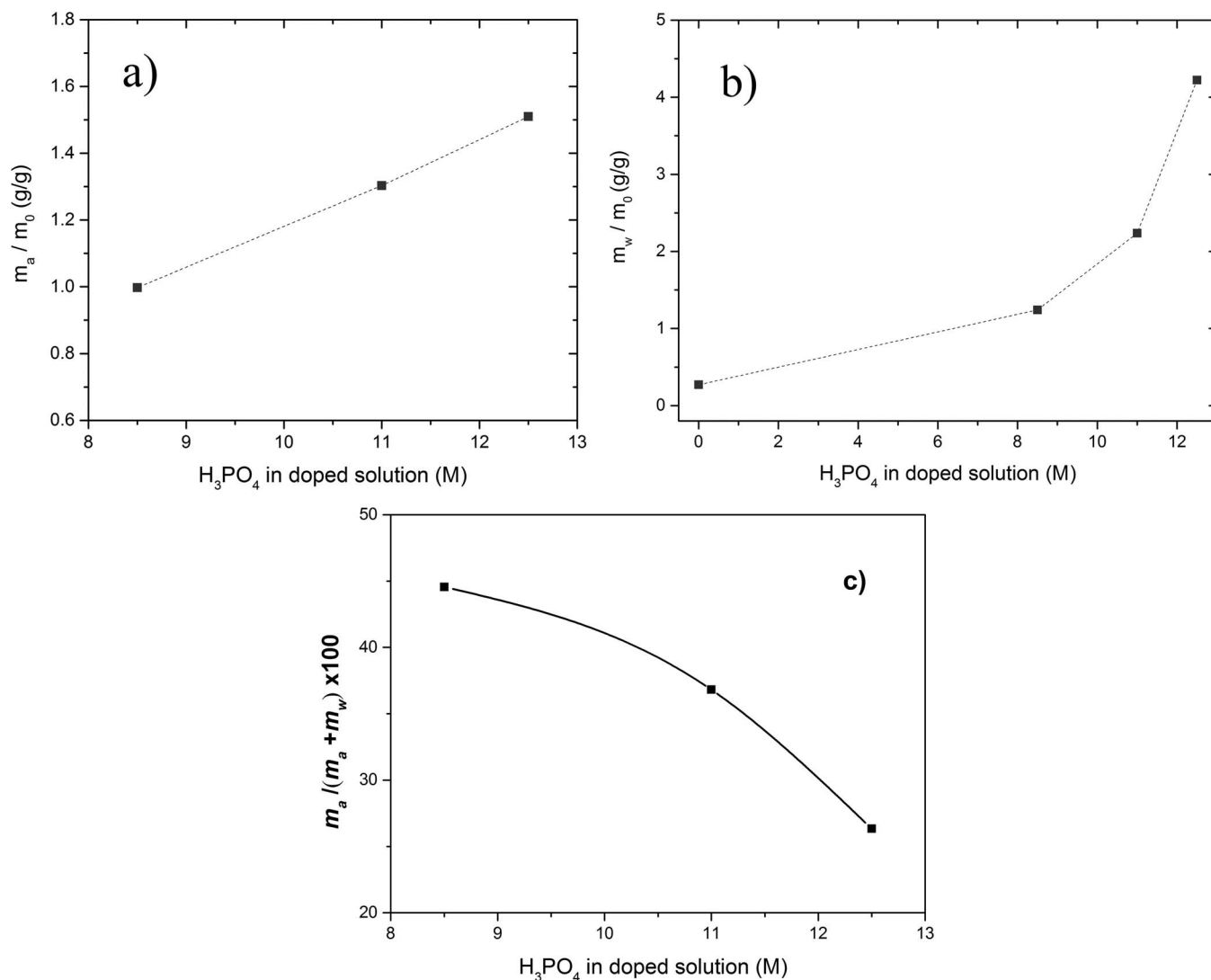
It can be noted that undoped dry membrane showed a water uptake ca. 25% wt, a value comparable to 15–19% wt reported for PBI membranes,<sup>41</sup> corresponding to ca. 1.5 water molecules per imidazole ring due to intermolecular hydrogen bonding with the imidazol-N atoms and other water molecules.

As the concentration of the PA in the doping bath is increased, the water sorption increases due to the hygroscopic behavior of the acid.<sup>42</sup> At 11 M  $\text{H}_3\text{PO}_4$ , the water content,  $m_{\text{wo}}$ , was  $2.2 \text{ g} \cdot \text{g}^{-1}$ , equivalent to 14  $\text{H}_2\text{O}$  molecules per imidazole ring. This result is remarkably higher than those reported in the literature, almost 5 times more water content than in the doped membrane cast from ethanol,<sup>15</sup> and 12 times more water than membranes cast from MSA.<sup>11</sup> A plausible explanation for the higher water uptake could be that in the sprayed membrane is promoted a looser packaging of the polymeric chains (free volume space) than the traditional casting during the doping procedure, as has been shown by WAXD analysis (Figure 2).

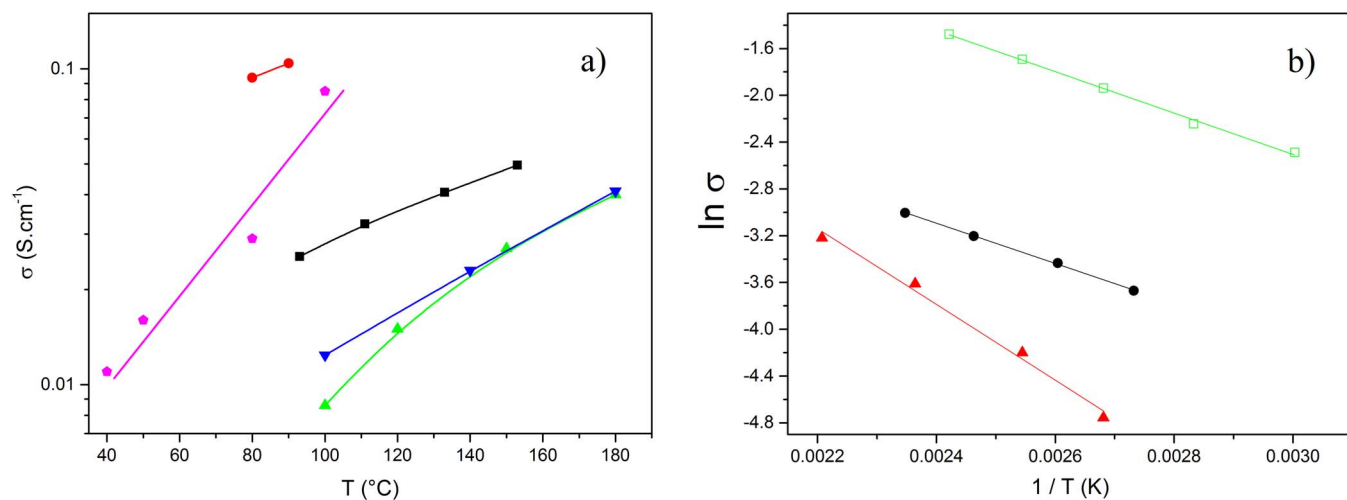
Although the doping level reached by the spray membranes was slightly lower, their proton conductivity was good enough for fuel cell application, probably as the result of their high water uptake, as it will be discussed below.

**Membrane proton conductivity.**—In Figure 4a the proton conductivity of Nafion and sABPBI are shown. sABPBI conductivity was measured between  $80^\circ\text{C}$  and  $153^\circ\text{C}$ . The RH was fixed at 30% (at the cell inlet) but, since this one is an open system, RH decreases at higher working temperatures reaching values between 3% ( $80^\circ\text{C}$ ) and 0.5% ( $153^\circ\text{C}$ ). We have adopted this open system conductivity setup because it matches the high temperature PEM fuel cell operation conditions. Probably, this procedure would lead to lower measured membrane proton conductivity as compare to the real conductivity in the PEM fuel cell, because of the water production and transport in the cell. However, the measured open-system conductivity would be closer to the real one than that obtained with a typical isopiestic conductivity cell.

Nafion conductivity was measured, at 80 and  $90^\circ\text{C}$  at 100% RH, and the results are in agreement with those reported by the supplier.<sup>43</sup> Additionally, conductivity values of MSA-cast ABPBI membrane<sup>6</sup> at 5% RH, trifluoroacetic acid cast PBI membrane<sup>44</sup> at 5% RH, and ethanol/NaOH cast ABPBI membrane<sup>15</sup> at ca. 30% RH were included for comparison. It can be seen that the conductivity increases with temperature obeying Arrhenius law, as observed in Figure 4b. The activation energy for proton conduction of sABPBI membrane was  $E_a = 14.3 \text{ kJ} \cdot \text{mol}^{-1}$ . Instead, Asensio et al.<sup>6</sup> reported  $E_a = 26.7 \text{ kJ} \cdot \text{mol}^{-1}$  while Wannek et al.<sup>26</sup> obtained  $E_a = 14.7 \text{ kJ} \cdot \text{mol}^{-1}$  for the commercial crosslinked ABPBI membrane (Fumatech) at 20% RH. The proton conductivity of all ABPBI membranes has the same behavior as the temperature increases. sABPBI membrane reached a proton conductivity of  $0.05 \text{ S} \cdot \text{cm}^{-1}$  at  $153^\circ\text{C}$  at ca. 0.5% RH, which is higher than the values reported for MSA cast ABPBI ( $0.03 \text{ S} \cdot \text{cm}^{-1}$ ), and TFA cast PBI ( $0.023 \text{ S} \cdot \text{cm}^{-1}$  at  $140^\circ\text{C}$  and 5% RH).<sup>6,44</sup> Although these comparisons should be taken with caution because of the different humidity conditions, it is clear that the conductivity of



**Figure 3.** a) Acid content in sABPBI membranes vs.  $\text{H}_3\text{PO}_4$  concentration of the doping bath (-■-); b) Water sorption versus  $\text{H}_3\text{PO}_4$  concentration of the doping bath concentrations for sABPBI membranes; c) Acid concentration in the membrane vs.  $\text{H}_3\text{PO}_4$  concentration of the doping bath.



**Figure 4.** a) Specific conductivity of Nafion 117 (-●-) at 100% RH and sABPBI doped with  $\text{H}_3\text{PO}_4$  11 M (-■-) as a function of temperature. For comparison, conductivity of cast acid-doped ABPBI<sup>7</sup> (-▲-), cast acid-doped PBI<sup>36</sup> (-▼-) at 5% RH, cast acid-doped ABPBI from ethanol/NaOH<sup>15</sup> (-●-) at 33% RH were included. b) Temperature dependence of conductivity of sABPBI membrane at 5–0.3% RH. For comparison, values of cast acid-doped at 5% RH (-▲-)<sup>7</sup> and commercial (-□-)<sup>28</sup> ABPBI membranes at 20% RH were included.

sABPBI at a very low RH looks promising as compared with other PBI and ABPBI membranes at a higher RH (5%). This is probably a consequence of the much higher water content of the sABPBI membrane, which could be retained even in very low humidity conditions.

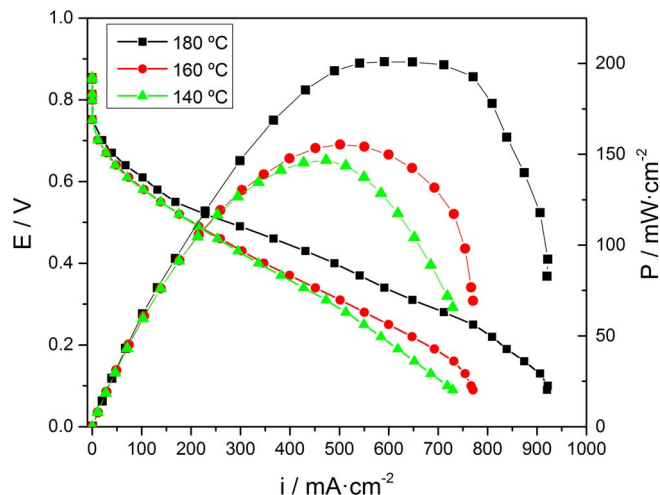
In the case of ABPBI membranes cast from ethanol/NaOH,<sup>15</sup> the proton conductivity at 100°C and 33% RH are comparable to that observed for Nafion membranes at 80°C and 100% RH, as shown in Figure 4a. The conductivity of these membranes is even higher than that of Nafion in the temperature interval 80–120°C at 55% RH, but it should be noted that these ABPBI membranes had neither a homogeneous thickness nor a long size for use in fuel cells.

In a PBI doped membrane, Grotthuss and vehicle mechanisms are responsible of proton conduction, while their contribution is affected by the conditions of the doping level, the temperature, and water content.<sup>6</sup> The Grotthuss mechanism implies charge transfer without proton displacement, being responsible for conductivity at temperatures below 100°C.<sup>7,44</sup> The vehicular mechanism, which consists of the  $\text{H}_3\text{O}^+$  migration (water acts as vehicle) through the membrane, becomes more significant at higher temperatures. Several works have been devoted to study the proton conduction in polybenzimidazole acid doped membranes and high water content has demonstrated to improve the proton conduction by both mechanisms.<sup>41,44–47</sup> For PA-doped ABPBI membrane casted from ethanol solution, Diaz et al.<sup>15</sup> showed the strong dependence of the conductivity with the water content, indicating that water molecules act as enabler of the proton transport. In that previous work we concluded that the conductivity of the PA-doped ABPBI membranes as a function of the PA concentration inside the membrane resembles that of the phosphoric acid aqueous solution, that is, the conductivity reaches a maximum for acid concentration around 50 wt%. In our case, the acid concentration inside the sprayed membrane was 37 wt% (for 11 M doping bath), that is close to the best conditions to obtain high proton conductivity.

The high water content in the membrane decreases the viscosity of the PA solution within the membrane and prevents the pyrophosphoric acid formation which does not contribute to proton conduction.<sup>6,42,46,48</sup> Moreover, high water content enhances the  $\text{H}_2\text{PO}_4^-$  ions formation (essential for both mechanisms) and promotes the faster Grotthuss mechanism through  $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$  paths.<sup>15,44,49</sup> This influence of the high water content ( $m_{wo} = 2.2$ ) in the conduction mechanism could explain the good conductivity value of sABPBI membrane at moderated doping levels ( $m_{ao} = 1.3$ ).

**Fuel cell performance.**—The sABPBI membranes were evaluated as proton exchange membrane in  $\text{H}_2$  fed PEM fuel cells. As stated in the previous section, doped membranes were adequate for manipulation, allowing all the steps required for the preparation of the membrane-electrode assembly (MEA). The doping of the membrane before or after the hot pressing step to form the MEA is a controversial issue. Doping the membrane before the MEA preparation implied, not only immersion of the membrane in PA, but also the need of immersing the gas diffusion electrodes (GDE) as the ABPBI contained inside de GDE has to be doped as well.<sup>28</sup> On contrary, doping after the MEA preparation implies the immersion of the whole MEA, which in principle is a much simple process. Doping with  $\text{H}_3\text{PO}_4$  was carried out by immersing the membrane or the MEA in 11 M  $\text{H}_3\text{PO}_4$  for a period of 7 days, as indicated in Membrane characterization section, in order to evaluate the differences between both processes. In most studies reporting fuel cell results, the membrane is doped before MEA preparation.<sup>6,23,28,50</sup> In the present study poor results were obtained using that process. In most cases, the membrane broke during the MEA pressing step and in the few cases where a MEA was obtained, the performance was low or null. On the other hand, no problems came out during MEA preparation with the undoped membrane and further soaking in  $\text{H}_3\text{PO}_4$  acid.

Figure 5 shows the polarization and power plots obtained for a sABPBI MEA at temperatures between 140 and 180°C. The cell presented an OCV of 0.87 V at all the studied temperatures. The performance showed an improvement with temperature reaching a



**Figure 5.** Polarization and power plot of sABPBI-based PEM fuel cell fed with humidified  $\text{H}_2/\text{O}_2$  at 200 and 250 sscm, respectively, at three temperatures and ambient pressure.

maximum power density of  $200 \text{ mW} \cdot \text{cm}^{-2}$  at 180°C. The maximum current density attained was  $930 \text{ mA} \cdot \text{cm}^{-2}$  at the same temperature.

The performance was comparable to that observed in other works employing ABPBI membranes. The OCV reported by Linares et al.<sup>23,50</sup> and Asensio et al.<sup>6</sup> was ca. 0.8 V, Wang et al.<sup>10</sup> and Wanek et al.<sup>26</sup> reported 0.95 V, while Liang et al.<sup>28</sup> reached 1.0 V. Wang et al.<sup>10</sup> obtained a very high peak power density (ca.  $450 \text{ mW} \cdot \text{cm}^{-2}$  at  $900 \text{ mA} \cdot \text{cm}^{-2}$ ), while Linares et al.<sup>50</sup> achieved the highest maximum current density of ca.  $1600 \text{ mA} \cdot \text{cm}^{-2}$ . In comparison with MEAs using Nafion membrane, ABPBI-based MEAs tends to present a higher  $\text{H}_2$  crossover, particularly at low current densities and, probably, this is the reason for the low OCV, as was indicated by Linares et al.<sup>23</sup> The high OCV (1.0 V) reported by Liang et al.<sup>28</sup> was obtained by employing a commercial ABPBI membrane from FuMA-Tech, which appears to have some degree of crosslinking. Besides the mentioned crossover, another issue affecting fuel cells with ABPBI or PBI as a membrane is the presence of phosphoric acid as dopant, as it strongly adsorbs on platinum affecting the catalytic activity.<sup>23</sup> Wang et al.<sup>10</sup> observed a decrease in performance by increasing the PA doping level. However, that behavior was not observed by Wanek et al.,<sup>26</sup> but the controversy could be explained by differences in the amount of catalyst employed. The aim of the present work was to assess the performance of a membrane and MEAs prepared by a simple and direct method. Improving of the doping process should be possible and a detailed evaluation of the effect of the phosphoric acid doping level on the fuel cell performance is in progress.

## Conclusions

In the present work, the innovative preparation of an ABPBI membrane spray-casted from an ethanol/KOH solution is reported. Doped level, proton conductivity, and fuel cell performance of the membrane were characterized.

An ABPBI polymer with relatively low molecular weight was used to obtain a homogenous membrane by spray casting. The method proposed is an easy and versatile way to obtain ABPBI membranes at low temperature, where the size and thickness were parameters of simple control.

The prepared membrane reached a lower acid doped level than those obtained from casting of formic acid, methanesulfonic acid, even from the alkaline ethanol solution. However, the conductivity showed acceptable values which could be attributed to the high water content that would favor the proton transport inside the membrane.

The ABPBI solution in ethanol allowed the preparation of the MEA by the direct paint method incorporating ABPBI as a binder. The

process avoided corrosive acid and the need of temperature control. Furthermore, the sABPBI MEA was doped in a single step after pressing all the components together. All these facts represented a simplification of the whole fabrication process.

The fuel cell prepared with a sABPBI membrane presented a satisfactory performance at the tested temperature reaching a power density of  $200 \text{ mW} \cdot \text{cm}^{-2}$  at  $180^\circ\text{C}$ .

In summary, ABPBI membranes were obtained through a simple procedure. In this case, ethanol is a friendly solvent with a low temperature of evaporation. The results are comparable to those obtained with ABPBI membranes prepared by casting from methanesulfonic acid. Potentially, this method could open the possibilities to form blend membrane or fiber reinforced membranes without phase separation due to fast evaporation solvent procedure. Moreover, this method possesses high versatility and could mark a milestone in modified membrane preparation, which will be the discussion subject of further studies.

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