



## Polymer Electrolyte Fuel Cells Based on Phosphoric Acid-Impregnated Poly(2,5-benzimidazole) Membranes

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Preparation and characterization of membranes of poly(2,5-benzimidazole) (ABPBI) (as thin as 20  $\mu\text{m}$ ) for polymer electrolyte membrane fuel cells are reported. These membranes were prepared by solution casting and then impregnated in phosphoric acid baths. Their characterization included thermogravimetric analyses, conductivity measurements, Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. These membranes have high thermal stability and good proton conductivity at temperatures up to 200°C ( $6.2 \times 10^{-2} \text{ S cm}^{-1}$  at 150°C and 30% relative humidity), similar to the well-known commercial polybenzimidazole (PBI). ABPBI membrane-electrode assemblies (MEAs) using commercially available E-TEK Pt/C electrodes were tested in  $\text{H}_2/\text{O}_2$  cells, obtaining power densities similar to those of PBI MEAs studied here as reference at temperatures of up to 180°C, humidifying the reactants at room temperature.

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Perfluorosulfonated polymers in general, and among them DuPont's Nafion in particular, are some of the polymers most widely used as proton conducting membranes in polymer electrolyte membrane fuel cells (PEMFCs). But membranes based on those materials present two main limitations: their high cost and their maximum operation temperature, limited to 100°C.<sup>1</sup> Above this temperature, the membrane dehydrates and the conductivity falls. The solid electrolyte membrane contributes a very important part to the cost of PEMFCs; therefore, cheaper alternative materials are of great importance. In addition, at the operation temperature of Nafion, traces of carbon monoxide, present as an impurity in  $\text{H}_2$  fuels, poisons the Pt catalysts, whereas at temperatures higher than 150°C, CO is not retained by Pt. Thus, to reduce or eliminate this poisoning, membranes with high proton conductivity at temperatures as high as 150–200°C are one of the main goals in current PEMFC research.<sup>1</sup>

In the emerging family of polybenzimidazoles, it is phosphoric acid that impregnates the polymers and is responsible for their proton transport, so water is not needed to keep a high conductivity, and the thermal stability is much higher. Among polybenzimidazoles, the most widely used acid-doped polymer is poly[2,2-(*m*-phenylene)-5,5-benzimidazole], generically referred to as polybenzimidazole (PBI). See Fig. 1. In the last few years, several research groups have been working on these new membranes.<sup>1–13</sup> Phosphoric acid-doped PBI is not as expensive as Nafion, is impermeable to gases and methanol, does not require humidification in PEMFC applications, and has an effective working temperature reaching almost 200°C, allowing the use of fuels with  $\text{H}_2$  containing 3% CO in volume with a very small power loss.<sup>9</sup> Acid-doped PBI has been studied mainly in  $\text{H}_2$  cells, but also when using methanol, ethanol, propanol, or even propane as fuel.<sup>8,9,14–23</sup>

PBI is the only commercially available polybenzimidazole (by Celanese) and is the only one under development for PEMFCs. Recently, Litt *et al.*<sup>3</sup> reported that another benzimidazole polymer, poly(2,5-benzimidazole) (ABPBI, see Fig. 1) has the same or even better conductivity and thermal stability than reported for PBI. We are interested in the preparation of benzimidazole-type membrane alternatives to PBI. We report here our results on the preparation of ABPBI membranes by casting from methanesulfonic acid (MSA), their doping with phosphoric acid, their characterization, and their application as membranes in polymeric  $\text{H}_2/\text{O}_2$  fuel cells. We also report a comparative study of those membranes with the better-known phosphoric acid-doped PBI membranes.

### Experimental

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) powder was purchased from Aldrich. The inherent viscosity (0.3 g in 100 mL of concentrated sulfuric acid at 30°C) is  $0.6 \text{ dl}\cdot\text{g}^{-1}$ . This viscosity is typical of PBIs of intermediate molecular weight (about 27,200).<sup>24</sup> The ABPBI monomer 3,4-diaminobenzoic acid (DABA) 97% and MSA 99% were obtained from Across Organics and used without further purification. Polyphosphoric acid (PPA) 85%  $\text{P}_2\text{O}_5$ , and phosphoric acid 85% were purchased from Panreac.

Chemical analyses of elemental C, N, H, and S, using a Carlo Erba Instruments EA1108 elemental analyzer, were systematically performed for the materials in their different forms, from the as-prepared polymer powders to the final doped membranes. A Cannon-Fenske 300 viscosimeter was used to measure the viscosities of the polymer solutions in  $\text{H}_2\text{SO}_4$  96%.

Both PBI and ABPBI membranes were studied by Fourier transform infrared spectroscopy (FTIRS). FTIRS spectra of the membranes were recorded on a Shimadzu FTIR-8300 spectrophotometer.

Thermogravimetric analyses (TGAs) were performed in a Mettler-Toledo TG50, under  $\text{N}_2$  or air at  $10^\circ\text{C min}^{-1}$ . X-ray diffraction (XRD) patterns were collected with a rotating anode Rigaku Rotaflex Ru-200B diffractometer ( $\lambda$  1.5418 Å, Cu K $\alpha$ )  $2\theta$  between 5 and  $60^\circ$  ( $0.02^\circ$  step,  $4^\circ \text{ min}^{-1}$ ). Scanning electron microscopy (SEM) was performed with a Jeol JSM 5310 electron microscope equipped with an Oxford Link Isis III energy-dispersive spectroscopy analyzer.

Four-probe ac conductivity measurements, as a function of temperature and relative humidity (RH), were made in the laboratory of Dr. R. F. Savinell, at Case Western Reserve University (Ohio). Samples were cut as strips of  $3 \times 0.6 \text{ cm}$ . Current was applied between the ends of the sample, and the voltage drop was measured by two platinum wires placed in the middle and separated by 1 cm. The conductivity cell was placed inside a stainless steel container and a vacuum was made. The RH was controlled by injecting a precisely measured amount of water.

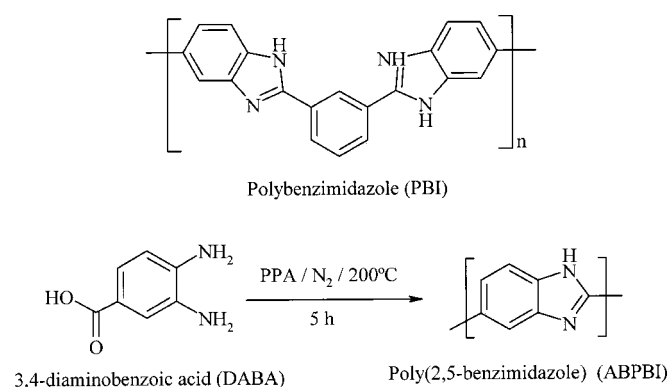
The fuel cell used for the final characterization of the title membranes was a commercial unit model FC05-01SP-REF by Electrochem Inc. We used homemade fiber glass-reinforced-silicone gaskets to adapt it for the use of  $1 \text{ cm}^2$  membrane electrode assemblies (MEAs).

### Results and Discussion

**Polymer synthesis.**—ABPBI was obtained by condensation of DABA monomers in PPA, as reported earlier.<sup>25</sup> In the optimal polymerization conditions, 3.040 g (20 mmol) of DABA was dissolved in 50 g of PPA (85%  $\text{P}_2\text{O}_5$ ), under  $\text{N}_2$  atmosphere at 150°C for

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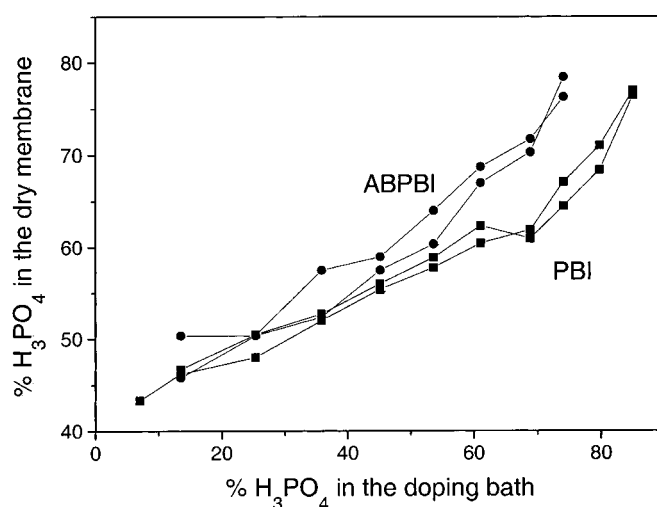
**Figure 1.** Commercially available PBI and the synthesis of ABPBI.

one-half h using a magnetic stirrer. Then, the temperature was raised to 200°C for one-half h more. Suddenly, stirring became impossible, but the temperature was maintained for 4 more h. The hot mixture was then poured into a large volume of water. This mixture coagulated and was washed until the water was neutral. Elemental analysis showed 15-30% phosphoric acid remaining in the polymer. To eliminate this acid, the polymer was washed in 10% NaOH with stirring overnight and washed with water again to neutrality. Finally, the ABPBI obtained was dried at 100°C, yielding 2.32 g. Elemental analyses did not show any residue different from C, H, or N that could be assigned to traces of phosphoric acid.

The typical inherent viscosity of a 0.5 g dl<sup>-1</sup> solution was 2.3-2.4 dl g<sup>-1</sup> measured in 96% H<sub>2</sub>SO<sub>4</sub> at 30°C. A higher molecular weight ABPBI can be polymerized if the monomer is recrystallized previously (see Ref. 3a) or by adding P<sub>2</sub>O<sub>5</sub> to the PPA/DABA solution, but 2.4 dl g<sup>-1</sup> is high enough for membrane casting. Good membranes are obtained, even when doped with high phosphoric acid amounts, when prepared as indicated in the next section. The Mark-Howink equation described in the literature (see Ref. 3b) for capillary viscosimetry of ABPBI in concentrated sulfuric acid is  $[\eta] = 8.7 \cdot 10^{-3} \cdot DP^{1.10}$ , where  $DP$  is the degree of polymerization ( $DP = Mw/116$  for ABPBI). This equation allows us to calculate a Mw of 23,800 for 2.4 dl g<sup>-1</sup> ABPBI.

**Membrane casting.**—Membranes of ABPBI were prepared by evaporation of an MSA solution,<sup>26,27</sup> dissolving 400 mg in 6 mL of MSA. Films of this solution were cast on a glass and evaporated on a heating plate inside a ventilated hood, at about 200°C. The membranes were heated until no evolution of MSA was observed (for at least 2 h), and were peeled off by immersion in water. The resulting membranes were analyzed by elemental analysis, and a large amount of MSA was detected (about 5-6% S). This remaining MSA could be extracted by washing the membrane in boiling water, but as is shown later, this step was finally not necessary.

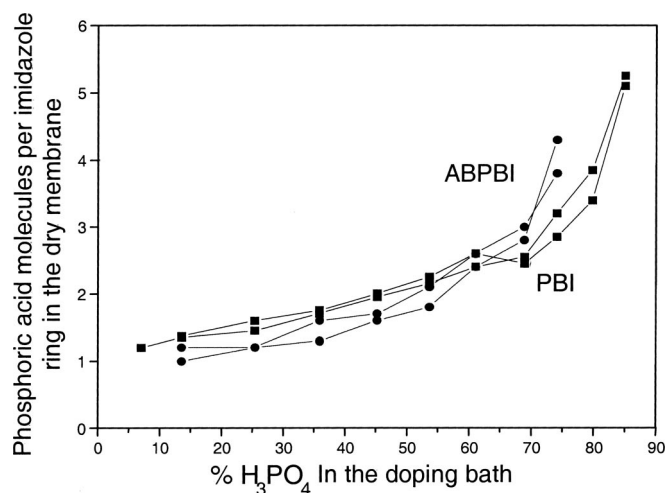
**Acid impregnation of the membranes.**—Samples of about 2 × 3 cm were cut and immersed in different phosphoric acid solutions for 3 days and dried at 100°C to eliminate the water absorbed from the doping bath. The amount of PO<sub>4</sub><sup>3-</sup> was determined by elemental analysis of C, H, N, and S. The residue of the elemental analysis that is different from C, H, and N is attributed to PO<sub>4</sub><sup>3-</sup>. This allows us to calculate the number of acid molecules  $x$  per polymer repeating unit (ABPBI ·  $x$ H<sub>3</sub>PO<sub>4</sub> and PBI ·  $x$ H<sub>3</sub>PO<sub>4</sub>). No S was found after the doping with phosphoric acid (<0.1%) into baths of any concentration, even after only 5 min in a bath of about 50% H<sub>3</sub>PO<sub>4</sub>; therefore, the final washing step of the undoped membranes was not necessary. We also studied the time necessary to achieve the maximum doping level at a given concentration of the doping bath. After a few minutes, a membrane reached almost 100% of the maximum acid that can be absorbed. A big increase in the conductivity of PBI occurs after about 11 h of doping.<sup>5,6</sup> For this



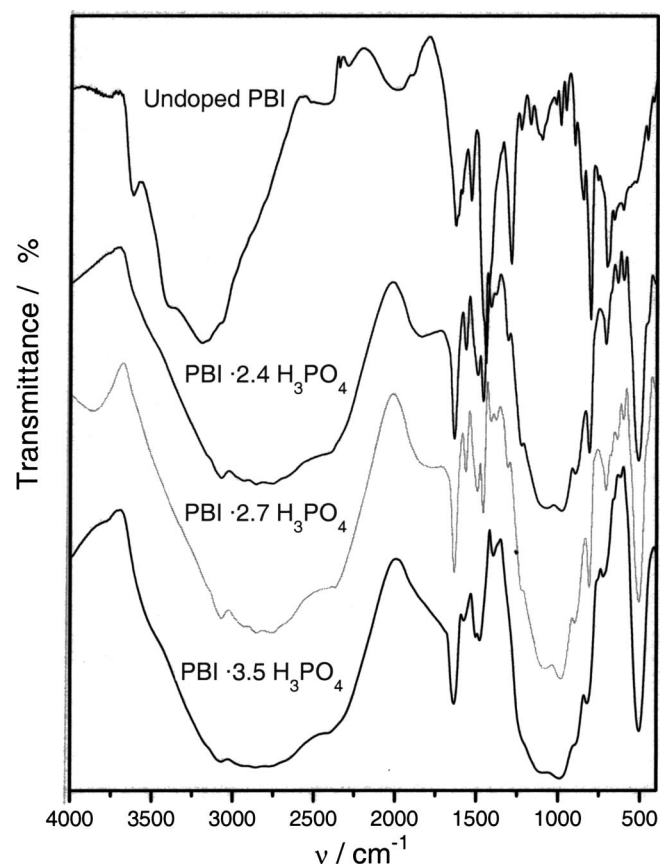
**Figure 2.** Phosphoric acid percentage absorbed as a function of the doping bath concentration. ● ABPBI membranes and ■ PBI membranes.

reason, we let the membranes stay for a much longer time in the doping bath. Membranes of PBI were cast by the well-known dimethyl acetamide (DMAc) method,<sup>1,4-6,28</sup> washed in boiling water, and doped in phosphoric acid in the same way used before for ABPBI. The membranes used to study phosphoric acid uptake and FTIRS were about 20 μm thick. Thicker membranes (70-120 μm) were prepared following the same procedure for MEA preparation and fuel cell tests.

**Phosphoric acid uptake.**—The amount of acid absorbed by both types of polybenzimidazoles studied can be compared as a function of the acid percentage in the doping bath. For low concentrations of H<sub>3</sub>PO<sub>4</sub> baths, PBI and ABPBI absorb almost the same amount of acid, but above concentrations of H<sub>3</sub>PO<sub>4</sub> 50-60%, ABPBI absorbs much more acid than PBI in acid percentage. For a better comparison, we have plotted the absorbed acid by weight percent vs. the bath concentration (Fig. 2). A comparison in terms of phosphoric acid molecules per benzimidazole ring is also of interest, see Fig. 3 (do not forget that PBI has two imidazoles while ABPBI has only one per repeating unit of the polymer). To obtain an impregnated polymer membrane containing 75% H<sub>3</sub>PO<sub>4</sub>, we need a bath of concentrated commercial phosphoric acid (85%) for PBI, whereas ABPBI membranes absorb the same amount of acid by immersion in



**Figure 3.** Phosphoric acid molecules per imidazole ring as a function of the doping bath concentration. ● ABPBI membranes and ■ PBI membranes.



**Figure 4.** FTIRS spectra of PBI ·  $x\text{H}_3\text{PO}_4$  membranes. Spectrum of the undoped PBI is included here for comparison.

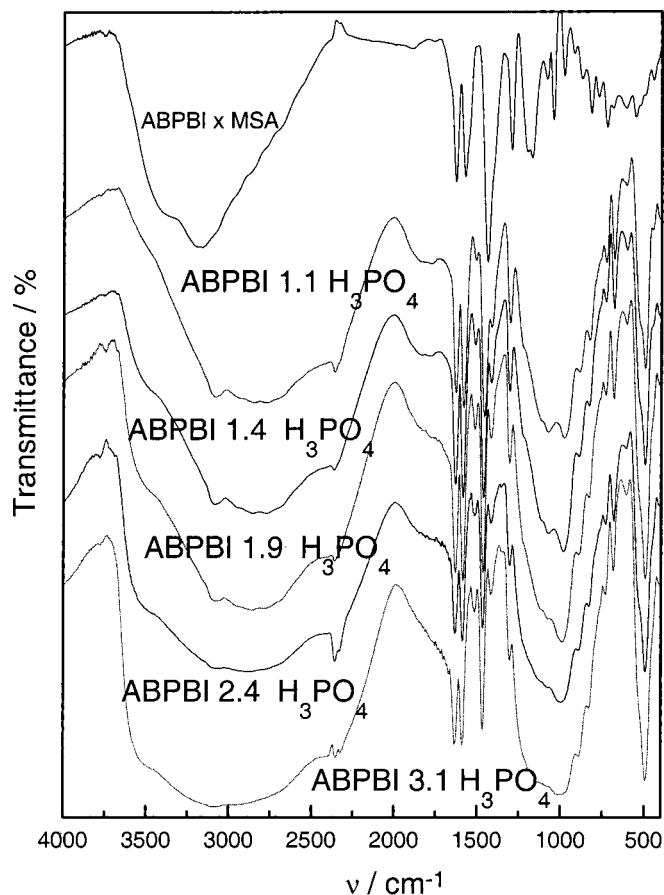
a solution of only about 70-75%  $\text{H}_3\text{PO}_4$ . When an ABPBI membrane ( $\eta_{\text{inh}} = 2.4 \text{ dl} \cdot \text{g}^{-1}$ ) was immersed in concentrated 85% phosphoric acid, it was completely dissolved.

Water absorption of both polymers in the doping bath can be calculated by the weight loss taking place when the doped membranes are dried, when we know the polymer/acid ratio. These measurements allow us to calculate that the acid/water absorbed is almost the same in the doping baths, about 80-85% acid and 20-15% water.

When impregnating PBI, it is known that for very low doping levels the mechanical properties improve, but when the acid amount increases, these mechanical properties get worse. The same behavior has been observed for ABPBI, but both polymers allowed their impregnation with a phosphoric acid concentration near 75%.

**FTIRS.**—FTIRS of PBI (Fig. 4) has been studied before.<sup>29</sup> In the region between 4000 and 2500  $\text{cm}^{-1}$ , we detect the bands assigned to O—H stretching at 3616  $\text{cm}^{-1}$  (absorbed water), free N—H stretching at 3390  $\text{cm}^{-1}$ , hydrogen bonded N—H stretching at 3191  $\text{cm}^{-1}$ , and C—H stretching at 3075  $\text{cm}^{-1}$ . Typical polybenzimidazole C=C and C=N stretching bands appear at 1629  $\text{cm}^{-1}$ , and the “breathing” mode of the imidazole ring appears at 1285  $\text{cm}^{-1}$  for both polymers. The absence of the DMAc band at 2940  $\text{cm}^{-1}$  (due to the C—H stretching of  $\text{CH}_3$  in DMAc) indicates the complete evaporation of the solvent during the casting of the undoped membrane.

When PBI is doped with phosphoric acid, a very broad band appears between 2500-3000  $\text{cm}^{-1}$  due to  $\text{N}^+\text{—H}$  stretching. The O—H stretching leads to a broad band at 2500-2250  $\text{cm}^{-1}$ . As reported earlier by Glipa,<sup>5</sup> the spectrum of phosphoric acid-doped PBI presents one region around 1250-750  $\text{cm}^{-1}$  and one at 500  $\text{cm}^{-1}$

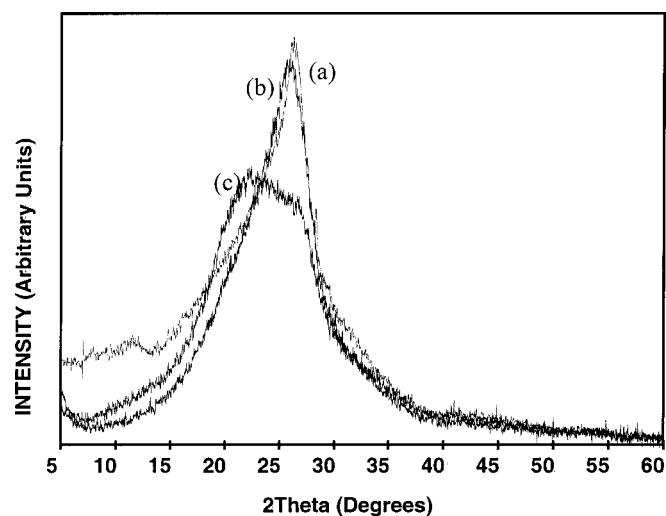


**Figure 5.** FTIRS spectra of ABPBI ·  $x\text{H}_3\text{PO}_4$  membranes. Spectrum of the undoped ABPBI is included for comparison.

that concentrates the main absorption bands of phosphoric acid and phosphates.

The spectrum of impregnated ABPBI (Fig. 5) is similar, and the bands have been assigned on the basis of pure<sup>29</sup> and phosphoric acid-doped PBI.<sup>5</sup> Both PBI and ABPBI polymers are very hygroscopic. In the undoped or washed ABPBI membranes, the remaining MSA absorbs at 1202, 1174, and 1046  $\text{cm}^{-1}$  (sulfonate group). The FTIRS spectrum of pure ABPBI (washed in boiling water until no S due to MSA was found in the elemental analysis) shows the absorbed water at about 3615  $\text{cm}^{-1}$  even after drying at 100°C. The free N—H stretching band is situated at 3415  $\text{cm}^{-1}$  and that for hydrogen bonded N—H stretching at 3184  $\text{cm}^{-1}$ . In ABPBI the aromatic C—H stretching at about 3075  $\text{cm}^{-1}$  is hidden behind the N—H stretchings. Both spectra sets are almost identical. There are only small differences in the bands due to the polymer backbone. Bands at 1628, 1550, and 1437  $\text{cm}^{-1}$  can be assigned to the C=N and C=C stretchings for undoped ABPBI and at about 1628, 1581, and 1460 for the doped ABPBI samples. As observed for PBI ·  $x\text{H}_3\text{PO}_4$ , phosphoric acid bands appear at around 1250-750  $\text{cm}^{-1}$  and at 500  $\text{cm}^{-1}$ .

**XRD.**—The crystal lattice of ABPBI fibers has been reported<sup>30</sup> to present an orthorhombic unit cell with  $a = 7.16$ ,  $b = 3.49$ , and  $c$  (fiber axis) = 11.7 Å. This cell was proposed based on the similarity of ABPBI to poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO) that was reported earlier.<sup>31</sup> We have recorded the XRD spectra of doped ABPBI membranes (Fig. 6), and an undoped ABPBI membrane washed with boiling water and dried at 100°C to eliminate the residual MSA (no S was found by elemental analysis after washing). Both the doped and undoped polymer membranes are amorphous, and only a broad diffraction peak at

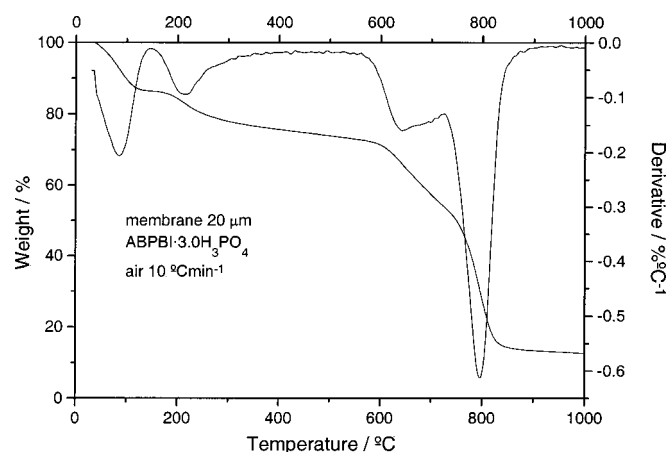


**Figure 6.** XRD spectra of (a) undoped ABPBI membrane washed with boiling water and dried at 100°C, (b) ABPBI · 1.5H<sub>3</sub>PO<sub>4</sub> membrane, and (c) ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub>.

about 26° is found. This peak is attributed to a  $d$  spacing of 3.4 Å between chains in a coplanar alignment.<sup>26</sup> When an undoped membrane was washed in boiling water and heated at 300°C, we observed another peak at about 10°. This is consistent with the recently reported effect of heating on the structures of ABPBT and ABPBO fibers, showing that the heat-treatment strongly increased their crystallinity.<sup>32</sup>

**Thermal stability.**—The TGAs, were recorded with a Mettler-Toledo CR50 thermobalance. The TGA of ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub> (Fig. 7) was performed in air from 30 to 1000°C at 10°C min<sup>-1</sup>. The initial weight loss from the beginning to 150°C is due to absorbed water. It is known that phosphoric acid-doped PBI is very hygroscopic. During the sample preparation and handling for the TGA, the “dry” membrane absorbed 14% of water from air.

There is a second loss starting at 150°C and centered at 205–210°C due to phosphoric acid. In dry atmospheres, the dehydration of phosphoric acid leads to the formation of pyrophosphoric acid, and the conductivity drops (see the section on conductivity). For this reason, when we measured the conductivity of ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub> at 200°C and 5% RH, we found a conductivity lower than the conductivity obtained at 180°C (also at 5% RH), though still high



**Figure 7.** TGA plot of ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub> membrane in air at 10°C min<sup>-1</sup>.

enough for fuel cell applications. In this 5% RH, dehydration takes place at a higher temperature than in the dry air used for the TGA experiments.

After this loss, the next dehydration step of the acid is observed above 600°C as observed by Samms for phosphoric acid-doped PBI,<sup>33</sup> and finally the polymer decomposes around 800°C.

We also performed the TGA of different acid-doped PBI membranes, observing the same weight losses, at the same temperatures, observed for the phosphoric acid-doped ABPBI.

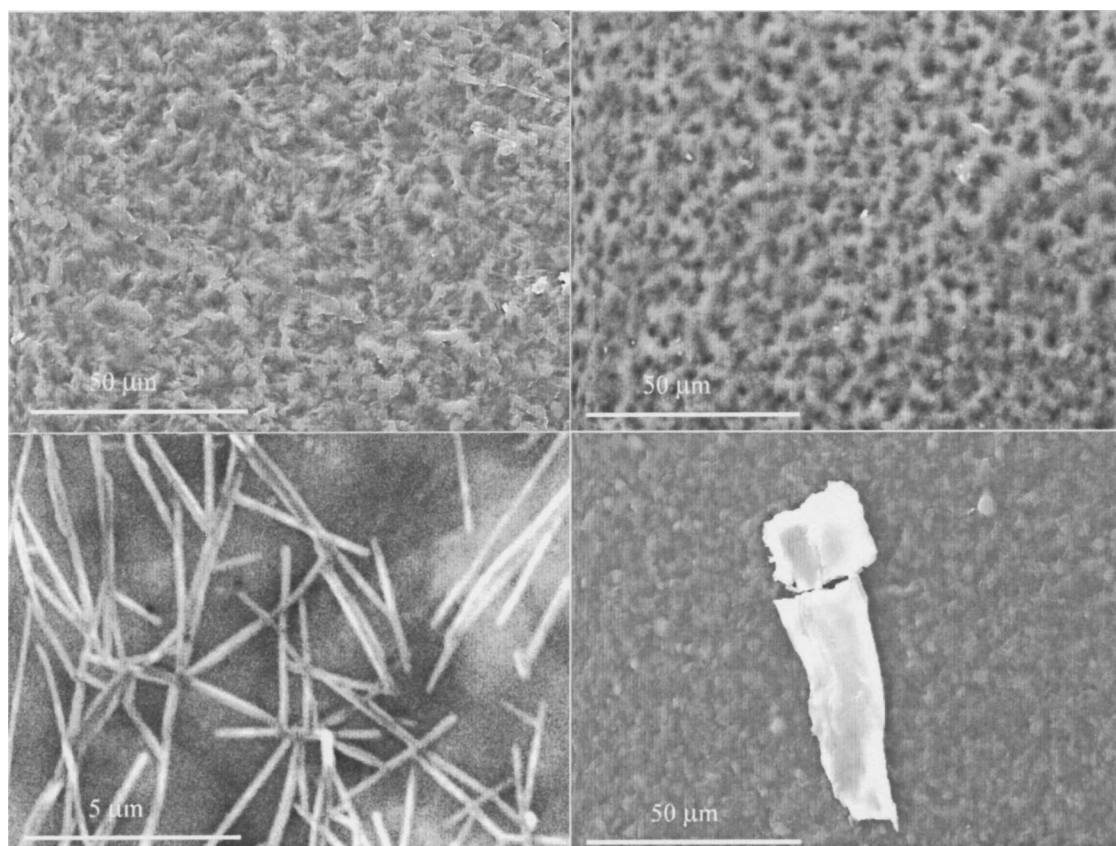
**SEM.**—The surface microstructure of ABPBI membranes was studied by SEM (Fig. 8). As the membranes were prepared by drying on a glass surface, we studied both faces of the membrane. The upper one was exposed to air during casting and drying, whereas the bottom face was in contact with glass. The SEM pictures show different microstructures for both faces (Fig. 8). Both are smooth surfaces, but they are quite different. The bottom face presents microscopic “holes” that could be due to boiling of the MSA on the glass surface. However, no pinholes were found in any membrane. But, for membranes with higher doping levels, we found segregation of needle-like phases during the drying process at 100°C in air, visible to the naked eye (Fig. 8). For the ABPBI · 2.1H<sub>3</sub>PO<sub>4</sub> and higher doping levels, after drying at 100°C, very thin needles (about 5 μm long and less than 1 μm thin) can be observed (Fig. 8 bottom, left). Despite the crystalline appearance of this phase, no extra peaks are observed in the XRD pattern in addition to the peak at 26° and a broad shoulder at lower angles for ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub>.

**Conductivity.**—AC conductivity was measured as indicated in the experimental section following a procedure previously described in detail (see Ref. 25b and 34). The conductivity of an ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub> sample (72% H<sub>3</sub>PO<sub>4</sub> by weight) was measured in the range of 50–200°C and 5–30% RH (Fig. 9 and 10). Conductivities as high as 6.2 × 10<sup>-2</sup> S cm<sup>-1</sup> at 150°C and 30% RH were measured. The conductivity, as expected, increases with temperature and RH; only between 180 and 200°C, the conductivity decreases at 5% RH. As mentioned in relation to TGAs, this decrease is due to the dehydration of phosphoric acid in the membrane at this low RH. The conductivity of a sample of PBI doped with a similar amount of acid (PBI · 7.7H<sub>3</sub>PO<sub>4</sub>, 71% by weight) was measured for comparison at 5% RH, yielding almost the same conductivity that was measured for ABPBI doped with 72% of acid (3.4 × 10<sup>-2</sup> S cm<sup>-1</sup> for PBI 71% H<sub>3</sub>PO<sub>4</sub> 5% RH and 3.9 × 10<sup>-2</sup> S cm<sup>-1</sup> for ABPBI 72% H<sub>3</sub>PO<sub>4</sub> at 180°C and 5% RH).

The activation energy between 100 and 150°C calculated from the Arrhenius plot, ln(σ) vs. 1000/T (K) (not shown) decreases when the RH increases. At low RH values, the dehydration of the membrane leads to more dehydrated acids (pyrophosphoric). Greenwood<sup>35,36</sup> measured the conductivity of H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> 0.5 H<sub>2</sub>O, finding that conductivity increased with the addition of water to the acid. From his data, we have calculated the average activation energy at 25–70°C, which is lower for the hydrated acid (23.05 kJ mol<sup>-1</sup> for pure H<sub>3</sub>PO<sub>4</sub> and 20.82 kJ mol<sup>-1</sup> for H<sub>3</sub>PO<sub>4</sub> 0.5 H<sub>2</sub>O).

**Preliminary tests of ABPBI and PBI membranes in PEMFCs.**—For electrochemical testing of the membranes in fuel cells, we prepared 1 cm<sup>2</sup> MEAs of both PBI and ABPBI doped with phosphoric acid. Pt/C materials for the fabrication of electrodes were commercially available E-TEK Pt/C (20% Pt) 0.35 mg Pt cm<sup>-2</sup> supported on carbon cloth. Electrodes were cut (1 × 1 cm), soaked for 5 min in 5 M H<sub>3</sub>PO<sub>4</sub>/ethanol (1:7 v/v), and dried at 100°C. MEAs were made by hot-pressing at 150°C and 5 ton cm<sup>-2</sup> for 5 min. All the fuel cell measurements were made using flowing H<sub>2</sub>/O<sub>2</sub> at atmospheric pressure, H<sub>2</sub> 62 mL min<sup>-1</sup> and O<sub>2</sub> 82 mL min<sup>-1</sup>.

The gases were introduced in the cell either dried or humidified at room temperature. Figure 11 shows the increase of the current density when the working temperature of an ABPBI fuel cell (ABPBI2.8H<sub>3</sub>PO<sub>4</sub> MEA, thickness 120 μm) is increased from 100



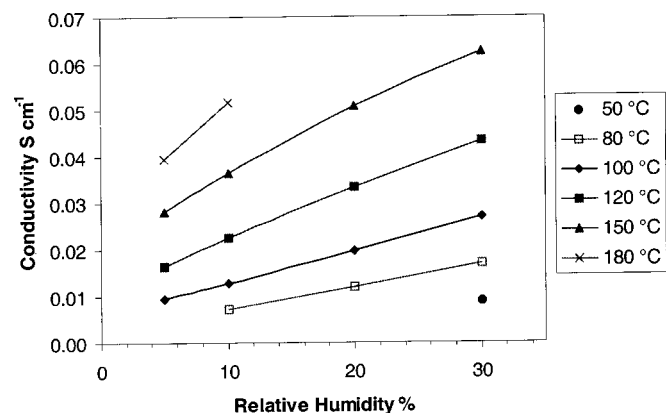
**Figure 8.** SEM images of ABPBI membranes. (Top, left) Upper face of ABPBI · xMSA, (top, right) ABPBI · xMSA down face, (bottom, left) ABPBI · 2.1H<sub>3</sub>PO<sub>4</sub>, and (bottom, right) ABPBI · 2.1H<sub>3</sub>PO<sub>4</sub>.

to 150°C without humidification of the gases. To check the effect of humidification, a single run was performed with the cell working at 150°C with humidification of H<sub>2</sub> and O<sub>2</sub> at room temperature. In these conditions, a 50% increase of the power density was obtained.

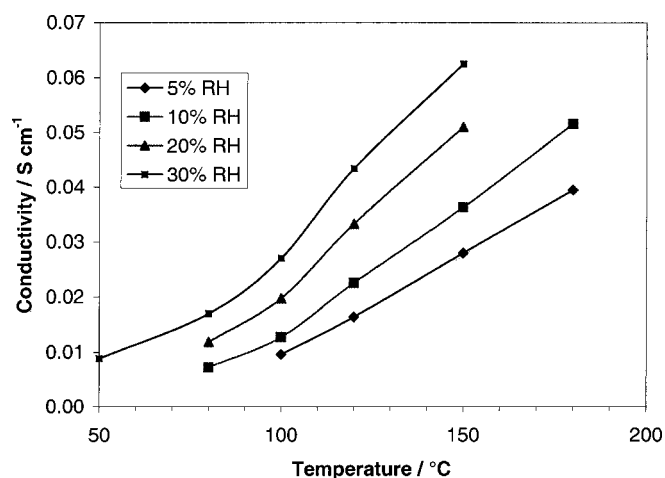
Maximum power densities of 185 mW cm<sup>-2</sup> (for PBI MEAs) and 175 mW cm<sup>-2</sup> (for ABPBI MEAs) were obtained (see Fig. 12). These values are already reached at 130°C (see Fig. 12). At this temperature, our results are close to those described earlier by other groups for PBI.<sup>9</sup> However, at temperatures higher than 130°C and contrary to earlier PBI reports,<sup>9</sup> the power density does not increase further. We have found similar power densities at 130°C and at

temperatures as high as 180°C measuring only a small decrease in the maximum power density (Fig. 13).

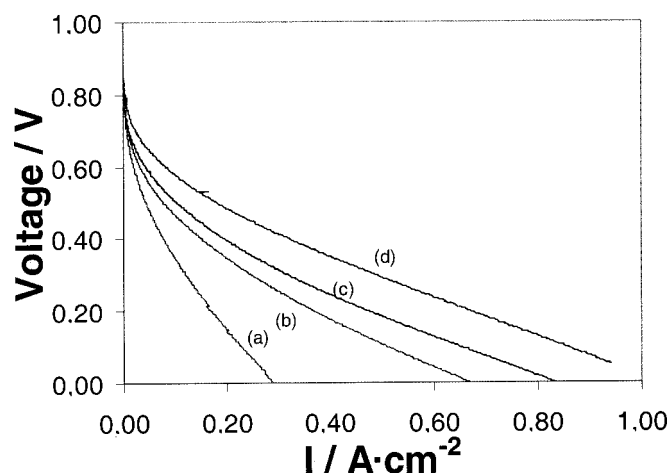
In principle, the performance of our membrane materials should keep improving up to temperatures of *ca.* 180-200°C. We believe that if this is not the case in our present preliminary results, it is due to a combination of factors, including the possible dehydration of the membranes at temperatures higher than 130-150°C and the need



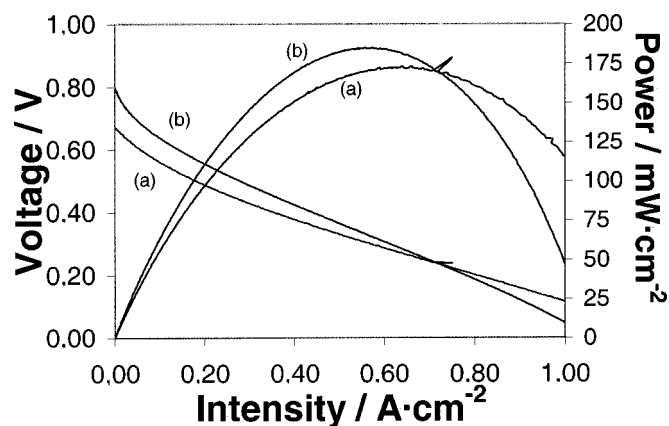
**Figure 9.** Conductivity of ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub> as a function of RH (5-30%) for different temperatures (50-180°C).



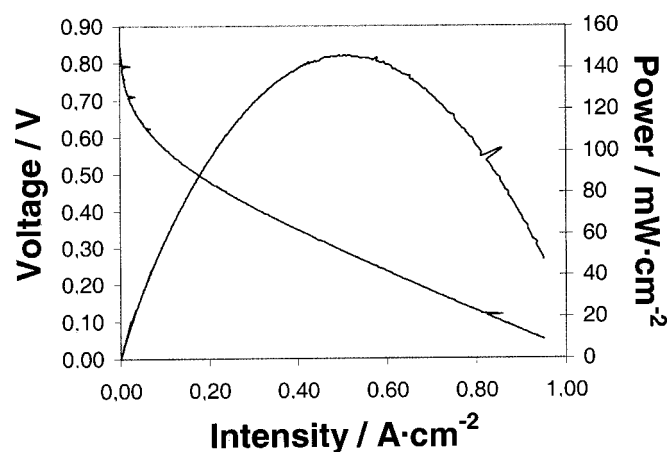
**Figure 10.** Conductivity of ABPBI · 3.0H<sub>3</sub>PO<sub>4</sub> as a function of temperature (50-180°C) for different RH values (5-30%). Average activation energy at 100-150°C is 27.9 kJ mol<sup>-1</sup> at 5% RH, 27.2 at 10% RH, 24.6 at 20% RH, and 21.7 at 30% RH.



**Figure 11.** ABPBI · 2.8H<sub>3</sub>PO<sub>4</sub> 120 μm dry H<sub>2</sub>/O<sub>2</sub> at (a) 100, (b) 120, and (c) 150°C, and (d) humidified H<sub>2</sub>/O<sub>2</sub> (at room temperature) with a cell working temperature of 150°C.



**Figure 12.** Power densities for (a) ABPBI · 2.8H<sub>3</sub>PO<sub>4</sub> 70 μm and (b) PBI · 6.4H<sub>3</sub>PO<sub>4</sub> 70 μm. Cell at 130°C, and H<sub>2</sub>/O<sub>2</sub> humidified at room temperature.



**Figure 13.** Power density for ABPBI · 2.8H<sub>3</sub>PO<sub>4</sub> 120 μm cell at 180°C and H<sub>2</sub>/O<sub>2</sub> humidified at room temperature.

to further optimize cell parameters or customized ABPBI electrodes. We are presently working on the modification of fuel cell operation parameters to provide a self-hydration regime for the membrane with the water produced in the cathode as reported by Qingfeng *et al.*<sup>9</sup>

### Conclusions

It is known that acid-doped PBI is a promising membrane for use in PEMFCs. We have found that ABPBI is a polybenzimidazole-type polymer as good for use in PEMFC as commercially available PBI. It has a high proton conductivity upon H<sub>3</sub>PO<sub>4</sub> doping (up to  $6.2 \times 10^{-2}$  S cm<sup>-1</sup> at 150°C and 30% RH). Conductivity increases with temperature and RH as for PBI, reaching similar values. We have also recorded FTIRS spectra of both polymers that show the same interaction with the acid. Phosphoric acid protonates the N of the imidazole rings, forming a polybenzimidazole-phosphate salt. TGAs of both benzimidazole-type polymers show that both have the same thermal stability, up to 150-200°C, before the phosphoric acid dehydrates. Finally, we have found similar performances in final PEMFCs.

ABPBI is even preferable to commercial PBI concerning its maximum acid uptake capability as well as its foreseeable cost, because the corresponding monomers (a single chemical in the case of ABPBI) are commercially available, inexpensive, and environmentally friendly (as opposed to diaminobenzidine, which is used for the synthesis of PBI). Finally, fuel cell tests have shown similar performances of MEAs prepared from both PBI- and ABPBI-doped membranes.

To sum up, ABPBI is a promising polymer for use in PEMFCs at temperatures as high as 200°C, as has been reported earlier for phosphoric acid-doped PBI.

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