



Recent Developments on Proton Conducting Poly(2,5-benzimidazole) (ABPBI) Membranes for High Temperature Polymer Electrolyte Membrane Fuel Cells^x

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Abstract

Commercial polybenzimidazole (PBI) membranes impregnated with phosphoric acid have become a serious candidate as electrolytes for high temperature PEMFC. Much research effort has been devoted to the study of this proton conducting membrane.[1, 2] On the other hand, PBI is not the simplest nor the cheapest of this family and many other polybenzimidazoles would also be of great interest in this respect. Among them, poly(2,5-benzimidazole) (ABPBI) is one of the best choices [3]. ABPBI is easy to polymerize from a single monomer, even without previous purification, it

absorbs more acid than PBI in the same bath concentration, and it has the same thermal stability and high proton conductivity at temperatures up to 200 °C. Here we review all the recent developments on the preparation of proton conducting ABPBI membranes, mainly by phosphoric acid impregnation, but also by sulfonation or doping with heteropolyacids to form hybrid organic-inorganic membranes.

Keywords: ABPBI, High Temperature PEM, Hybrids, Membrane, PBI, PEMFC

1 Introduction

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have been most frequently based on the use of sulfonated membranes, and among them the most widely studied and used has been Nafion[®]. All these membranes require that they be highly hydrated to keep their proton conductivity. Thus, the working temperature of the resulting PEMFCs is limited to ca. 100 °C. On the other hand, the hydrogen used in those fuel cells has to be extremely pure, because CO traces in the fuel lead to the poisoning of the Pt catalyst typically used in the electrodes. Yet, if the working temperature of the cell was increased up to about 150 °C, the susceptibility of the catalyst to CO would be substantially reduced, and at 200 °C up to 3% CO can be tolerated.[4]

Many membranes have been proposed for the design of increased-temperature fuel cells, working above 100 °C,[5] but the only membrane that can work at temperatures as high

as 200 °C is phosphoric acid doped (impregnated) polybenzimidazole (PBI). This membrane, first developed by Savinell et al., [6, 7] has a high conductivity at low humidity [6] and a high thermal stability [8], among other interesting properties that make it a prime choice for high-temperature PEMFCs.[1] Many other research groups [2, 9–12] have focused their interest on PBI membranes, and Celanese, the only producer of PBI, is already investing in the commercialization of PBI MEAs.[13, 14]

On the other hand, PBI is the only polybenzimidazole polymer that is commercially available, but is not the only one that could be used as a high temperature membrane once doped with phosphoric acid or other dopants. Many other polybenzimidazoles can be easily synthesized [15–17], though a high enough molecular weight and good processability are necessary to cast membranes. Among the many possible benzimidazole polymers, poly(2,5-benzimidazole) has the simplest structure (see Figure 1), and is polymerized from a single commercial

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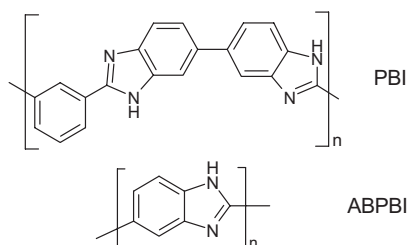


Fig. 1 Structures of Poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (polybenzimidazole, PBI) and Poly(2,5-benzimidazole) (ABPBI).

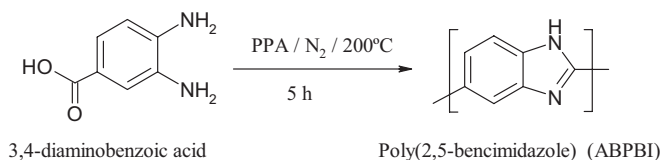


Fig. 2 Synthesis of ABPBI.

monomer (see Figure 2) without previous monomer purification,[3, 18] though if a higher molecular weight is needed, the monomer can be purified easily [19].

We review here recent work on the different aspects of ABPBI development including up to date work on ABPBI synthesis, preparation of ABPBI membranes, phosphoric acid doping, and fabrication and characterization of MEAs based on this polymer. Furthermore, work on derivatives based on several other strategies for the preparation of high-temperature proton-conducting ABPBI membranes, such as sulfonation or combination with inorganic species such as heteropolycids will also be presented and discussed.

2 ABPBI Structure and Synthesis

Poly(2,5-benzimidazole) (ABPBI) is the simplest benzimidazole polymer (see Figure 1). Compared to PBI, ABPBI does not contain the phenylene ring in the polymer backbone. This different structure gives ABPBI a higher affinity towards phosphoric acid than PBI, as discussed below.

ABPBI was first synthesized in 1961 by Vogel from 3,4-diaminebenzoate by melt polymerization.[20] The first synthesis in polyphosphoric acid (PPA) was later reported by Imai in 1965.[21] As with most polybenzimidazoles, ABPBI can be very easily produced at laboratory scale by diamine-acid condensation in polyphosphoric acid (PPA) (see Figure 2) [21–27].

Table 1 Inherent viscosity of ABPBI as a function of the monomer purity. C = 0.5 g dl⁻¹ in H₂SO₄ 96% at 30 °C.

Monomer	g PPA / 20 mmol DABA	$\eta_{inh} / \text{dl}\cdot\text{g}^{-1}$
DABA 95% Fluka	50	1.4
DABA 95% Fluka	50	1.8
DABA 97% Acros	50	2.3
DABA 97% Acros	50	2.4
DABA 97% Acros	100	2.3
DABA 97% Acros	25	2.7

Table 1 shows the inherent viscosity as a function of the monomer purity when ABPBI is prepared in PPA without adding P₂O₅. [18] When monomers of high enough purity are used, the condensation reaction yields polymers with a high molecular weight. Since ABPBI is synthesized from a single monomer, purity is not as critical as in the case of polymers prepared from two different monomers. If the monomer is purified [19], the molecular weight of the resulting ABPBI is increased (see Table 1), but polymers having molecular weight high enough to cast robust membranes can be synthesized even from commercial 3,4-diaminobenzoic acid as received (97%). [28]

Another suitable way to prepare ABPBI or other polybenzimidazoles at laboratory scale is by self-condensation of 3,4-diaminobenzoic acid in methanesulfonic acid / P₂O₅. That is also a very well-known synthesis of benzazole polymers. [29, 30] Recently ABPBI has been synthesized in this medium, and membranes have been cast directly from the reaction mixture. [31] Since polymerization takes place directly in the casting solvent, and provided the polymer concentration is adequate, this procedure allows one to save one step.

ABPBI has been synthesized by different groups, achieving different viscosities as summarized on Table 2. The higher viscosities are reported by Wainright et al. [1], but suitable membranes have been cast with polymers with viscosities as low as 1.81. [31] From our own experience, an ABPBI polymer with inherent viscosity around 2.3–2.4 dl g⁻¹ is enough to prepare good membranes from methanesulfonic acid as detailed below. [3, 18, 28] When we carried out these syntheses, only Acros supplied 97% pure monomer. Now also Aldrich supplies 98% or even 99% in the form of dihydrochloride salt.

Since PPA acts as reaction medium and dehydrating reagent, another parameter that allows the preparation of higher molecular weight polymers is the addition of P₂O₅ to the PPA, in order to enhance the dehydrating properties of PPA. The addition of P₂O₅ is limited by the associated increase of viscosity of the reaction mixture. If too much P₂O₅ is added the PPA mixture cannot be easily stirred specially as the reaction proceeds and the degree of polymerization increases. The higher molecular weight was achieved by

Table 2 Polymerization conditions and viscosity achieved by different laboratories (only those who have reported the preparation of membranes using the so obtained ABPBI polymer).

Polymerization conditions	Viscosity / dl g ⁻¹ and molecular weight / g mol ⁻¹ achieved	Reference
2 hours at 200 °C recrystallized DABA DABA/P ₂ O ₅ /PPA : 1/7/3.22	$[\eta] = 7.33$ $M_w = 53,000$	[1]
5 hours at 200 °C under N ₂ as received 97% DABA DABA/PPA : 2.4/50	$\eta_{inherent} = 2.4$ $[\eta] = 3.04$ $M_w = 23,800$	[18]
1.5–12 hours at 160 °C DABA / PPA : 1/35	$\eta_{inherent} = 0.86$	[10]
2 hours at 200 °C recrystallized DABA DABA / P ₂ O ₅ / MSA : 2/3/20 40 minutes at 150 °C under N ₂	$\eta_{inherent} = 1.81$	[31]

Wainright et al. [1], obtaining up to $53,000 \text{ g mol}^{-1}$. Such a high molecular weight must be due to high purity of the monomer (which was recrystallized before polymerization), as well as to the addition of P_2O_5 .

The molecular weights of ABPBI polymers and their viscosities in concentrated sulfuric acid are correlated by the Mark-Houwink equation, [1, 32] where DP is the degree of polymerization and $[\eta]$ is the intrinsic viscosity. This allows one to calculate a molecular weight of about $23,800 \text{ g mol}^{-1}$ for a 2.4 dl g^{-1} ABPBI.

$$[\eta] = 8.7^{-3} \cdot DP^{1.10} \quad DP = Mw / 116$$

3 Phosphoric Acid Impregnated ABPBI Membranes

ABPBI is soluble in very few solvents, mainly strong acids such as phosphoric, polyphosphoric acid (PPA), sulfuric, formic acid, trifluoroacetic (TFA), methanesulfonic (MSA), as well as in ethanol/NaOH, or N-methylpyrrolidone/LiCl. [1, 18]

ABPBI is very easy to dissolve in MSA, and the first films or membranes described in the literature were cast from this acid solvent. [33–35] A typical membrane casting procedure dissolves 400 mg of ABPBI in 6 ml of MSA, stirring overnight at room temperature, after which a homogeneous mixture is obtained. The resulting viscous solution can be spread onto a glass plate, and MSA can be evaporated by heating the plate at $150\text{--}200 \text{ }^\circ\text{C}$. [3, 18] This procedure can lead to membranes as thin as 20 microns when ABPBI with a minimal inherent viscosity of $2.3\text{--}2.4 \text{ dl g}^{-1}$ is used. These membranes are too thin to prepare MEAs, but allow one to follow the acid casting, to see some remaining MSA in the membrane that is eliminated during the bath doping, [3] and even allow a sulfonation procedure detailed below. [36] Wereta [33] reported

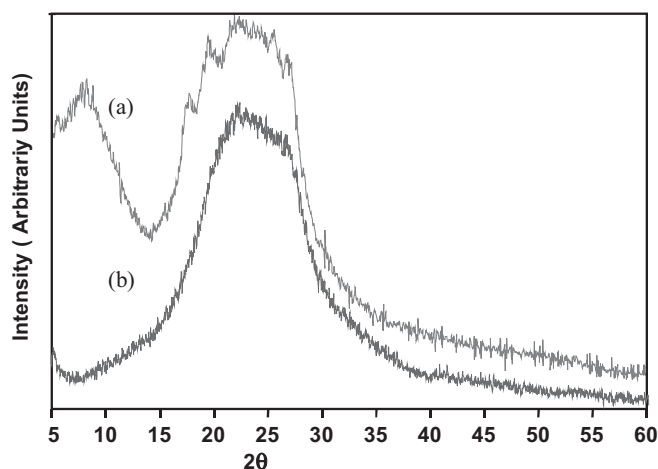


Fig. 3 X ray diffraction pattern of (a) $\text{ABPBI} \cdot 3.0 \text{ H}_3\text{PO}_4$ simultaneously cast and doped and (b) $\text{ABPBI} \cdot 3.0 \text{ H}_3\text{PO}_4$ prepared by MSA casting and subsequent phosphoric acid bath doping.

that MSA cast ABPBI films had a semicrystalline structure where benzimidazole rings were stacked parallel to the film surface as shown by the main X ray diffraction peak at $2\theta = 25^\circ$ (see Figure 3b).

When these MSA-cast membranes are doped by soaking them in a concentrated phosphoric acid bath, the phosphoric acid is absorbed and equilibrium is achieved in a few minutes, absorbing more acid than commercial PBI membranes. [3] Figure 4 shows the acid uptake by MSA-cast ABPBI membranes as a function of the phosphoric acid bath concentration. Since ABPBI and PBI do not have the same molecular structure (ABPBI does not contain a benzene ring in the backbone), the absorbed acid has to be compared in terms of acid% by weight. If ABPBI and PBI are compared (in terms of the number of acid molecules per benzimidazole unit), ABPBI conductivity is higher because in weight% the ABPBI membrane retains more acid.

The phosphoric acid bath step could be avoided by a direct acid casting procedure from an MSA/ABPBI/ H_3PO_4 solution, yielding directly the ABPBI membrane doped exactly with the desired amount of phosphoric acid. [37] But this procedure is limited because MSA is eliminated completely only for phosphoric acid compositions above $\text{ABPBI} \cdot 3.0 \text{ H}_3\text{PO}_4$. On the other hand, the membranes thus prepared have a higher crystallinity but a lower conductivity than those prepared by MSA casting and H_3PO_4 bath doping. This fact is not fully understood yet and is in opposition to the trend observed by Savinell, who found for PBI that the higher the crystallinity, the higher the conductivity because phosphoric acid is forced to the amorphous phase. [1, 19] These PBI results are in good agreement with the recent results by Ma et al, who have found that free phosphoric acid is the most conductive species in phosphoric acid doped membranes. [7]. In the case of direct acid doped ABPBI, one of the possible explanations is the dehydration of phosphoric acid during

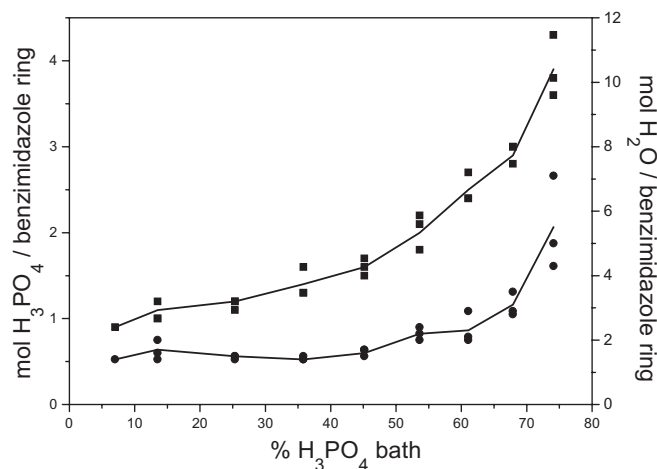


Fig. 4 Phosphoric acid (squares) and water (circles) uptake by MSA cast ABPBI membranes as a function of the phosphoric acid bath concentration. Reproducibility of the measurements is higher for the lower acid concentration. Near 75% H_3PO_4 the humidity absorbed introduced a higher uncertainty. [18]

the casting, but the membranes are allowed to rehydrate after the casting and are dried again at a lower temperature, and the analysis of the membranes did not show any proof of the acid dehydration.

Phosphoric acid impregnated ABPBI membranes were first cast by Litt et al. [19] from an ethanol/NaOH solution, finding that ABPBI absorbed more phosphoric acid (as weight%) than previously known PBI. But later, Litt and Savinell cast their ABPBI membranes from TFA/ABPBI/H₃PO₄ solutions.[1] These membranes have the same conductivity as those prepared from MSA solutions and further bath doping as described above, and have the same acid composition ABPBI·3.0 H₃PO₄, both measured by the same procedure.[38] As TFA is more volatile than MSA, membrane casting can be done at room temperature, but whether there is any remaining TFA on the membrane should be studied.

Akita et al. have also cast PBI and ABPBI membranes from TFA solutions, doping this ABPBI with phosphoric acid derivatives such as diphenyl phosphoric acid (less hydrophilic than phosphoric acid), in order to reduce phosphoric acid leaching during MEA hot-pressing and by the water formed inside the working fuel cell.[10]

In order to compare benzimidazole and benzoxazole polymers, poly(2,5-benzoxazole) (ABPBO) was synthesized by the same PPA procedure, and membranes were prepared casting MSA/ABPBO solutions from an ABPBI polymer with 2.4–3.2 dl g⁻¹ viscosity. These membranes had very poor mechanical properties due to insufficiently high molecular weight, but allowed one to ascertain that phosphoric acid absorption of ABPBO was much lower than that of ABPBI as can be seen on Table 3.[39] Thus, the second nitrogen present in the molecular structure of polybenzimidazoles seems to be very important for the phosphoric acid uptake. Indeed, the higher basicity of ABPBI and PBI polymers must be at the origin of their much higher acid uptake.

Table 3 Comparison of the phosphoric acid uptake of ABPBI and ABPBO membranes as a function of the bath concentration.[39]

% H ₃ PO ₄ bath	ABPBI		ABPBO	
	% H ₃ PO ₄ membrane	mol H ₃ PO ₄ membrane	% H ₃ PO ₄ membrane	mol H ₃ PO ₄ membrane
53.6	60.3–64.9	1.8–2.2	28.9	0.30
67.9	70.3–71.3	2.8–3.0	44.7	0.73
85	soluble		31.6	0.55

4 Properties of Phosphoric Acid Doped ABPBI Membranes

As for PBI membranes, those based on ABPBI have a very high conductivity at temperatures up to 200 °C under dry or very low humidity conditions.[3] This conductivity increases with humidity and temperature. Figure 5 plots the change in conductivity of ABPBI·3.0 H₃PO₄ cast from MSA solutions and doped in a phosphoric acid bath. The plot includes data from 0–20% relative humidity and from 0–180 °C. The conductivity of ABPBI·3.0 H₃PO₄ formed by direct acid casting

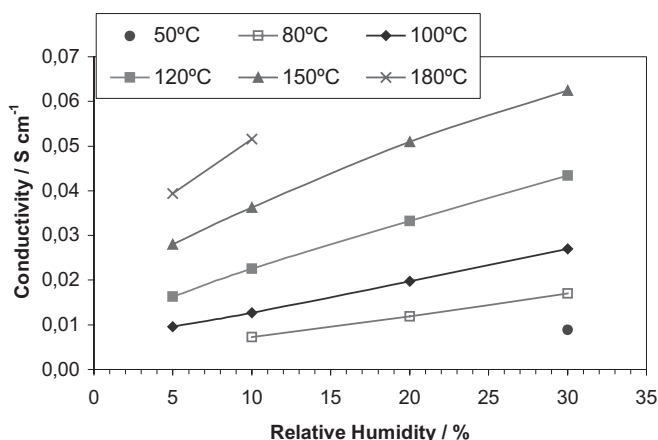


Fig. 5 Conductivity of ABPBI · 3.0 H₃PO₄ as a function of relative humidity.[3] Similar results were found by Savinell et al for a membrane of the same composition, prepared by TFA direct acid casting.[38]

from ABPBI/TFA/H₃PO₄ has a very similar conductivity and activation energy.[38] Since the conductivity is provided by the acid it increases also when the acid percentage increases (see Figure 6). Typical conductivity values are about 1.5·10⁻² S cm⁻¹ at temperatures as high as 180 °C in dry conditions for MSA/H₃PO₄ direct cast ABPBI·3.0 H₃PO₄ membranes. MSA-cast membranes under the same dry conditions prepared by the soaking method showed a conductivity of 2.5·10⁻² S cm⁻¹ for ABPBI·2.7 H₃PO₄ at 180 °C, higher than the conductivity obtained for the membranes direct cast from ABPBI/MSA/H₃PO₄ solutions. Kim et al. have reported higher conductivities (2.6·10⁻² S cm⁻¹ for ABPBI·1.6 H₃PO₄, 4.1·10⁻² S cm⁻¹ for ABPBI·2.4 H₃PO₄, and 6.0·10⁻² S cm⁻¹ for ABPBI·2.4 H₃PO₄ at 110 °C).[31]

These trends suggest the same conduction mechanism taking place in phosphoric acid doped PBI membranes, based on proton jumping between a complex network of imidazole rings, water molecules and phosphoric acid molecules as suggested by Ma.[7] This is also supported by the FT Infrared spectrum of undoped ABPBI which shows free N-H, hydro-

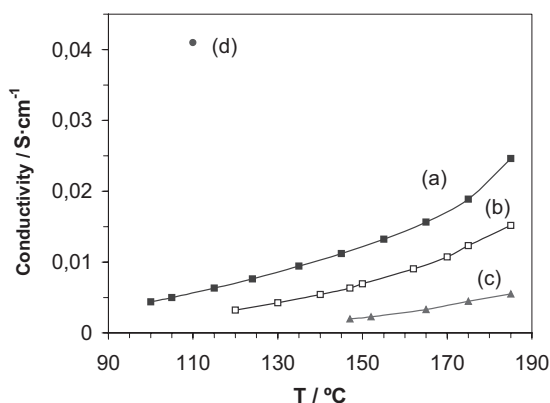


Fig. 6 Conductivity of ABPBI · 2.7 H₃PO₄ (69%) (a), ABPBI·2.5 H₃PO₄ (68%) (b), and ABPBI · 1.9 H₃PO₄ (62%) (c) anhydrous, as a function of temperature.[3, 18] This plot shows the effect of the acid percentage present in the membrane. The conductivity of ABPBI · 2.4 H₃PO₄ reported by Kim et al.[31] (d) has been included for comparison.

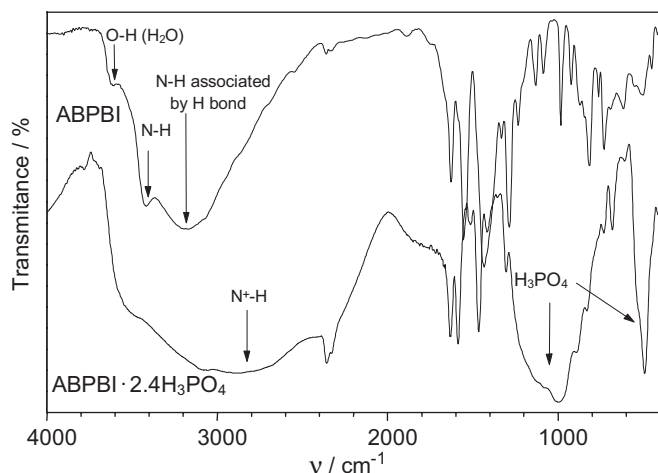


Fig. 7 FT Infrared spectra of ABPBI and ABPBI · 2.4 H₃PO₄ membranes.

gen-bonded N-H and water O-H stretchings, while the spectra of the protonated membranes show mainly protonated N⁺-H stretchings (see Figure 7).[3, 18] Thus, protons can jump from a protonated imidazole to a non-protonated one, to a phosphoric acid molecule or along a chain of phosphoric acid molecules.[7]

Another key feature of ABPBI membranes is their high thermal stability. Below 100 °C only absorbed moisture is lost, and under low humidity atmospheres ABPBI membranes can work in fuel cells at temperatures up to 180–200 °C.[3]

Concerning the mechanical properties of these membranes, Kim et al.[31] reported tensile strengths of 88–121 MPa with elongations of 31–65% for ABPBI membranes with a relatively low associated inherent viscosity of 1.48–1.81 dl g⁻¹, which was nevertheless enough to cast membranes and prepare cells [40]. Wainright et al have reported that the moduli of comparably doped PBI and ABPBI films are about the same, but the higher molecular weight achievable by ABPBI yields higher elongation and toughness.[1] When a PBI membrane is doped, first, the modulus increases after doping, but when the acid percentage increases, the modulus decreased with the acid contents.[1]

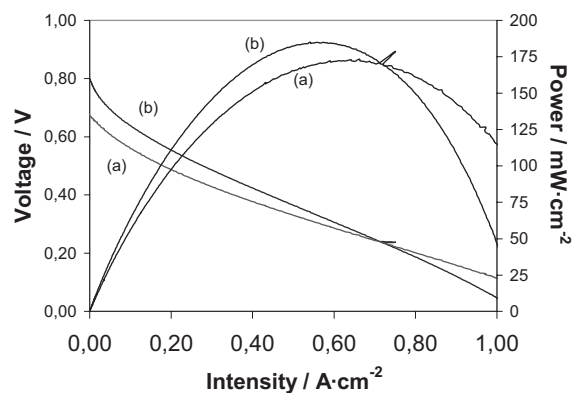


Fig. 8 Polarization curves for cells of (a) ABPBI · 2.8 H₃PO₄ 70 μm, and (b) PBI-6.4 H₃PO₄ 100 μm. Cells at 130 °C, and H₂ / O₂, both cells were humidified at room temperature.

ABPBI membranes have been preliminarily tested in H₂/O₂ PEMFC for comparison with PBI membranes.[3, 18] Cells of both polymers working under the same conditions achieved similar performances, with power values of 165–185 mW cm⁻² at 130–150 °C. Even though ABPBI MEAs were able to work at temperatures up to 180 °C [3], these performances are far from the best published results for PBI membranes [4, 13] because MEAs were prepared using standard 0.35 mg_{Pt} cm⁻² E-TEK electrodes, not designed for these high temperatures. Figure 8 shows polarization curves for cells with ABPBI and PBI doped with a similar amount of phosphoric acid.[3, 18] In this figure, the low open circuit voltage shows that there is some porosity on the membrane, indicating that the casting conditions (concentrations, temperatures,...) should be further optimized. Similar results were reported very recently by Kim et al. [40], achieving 280 mA cm⁻² at 0.5 V (140 mW cm⁻²) at 160 °C with a catalyst loading of 0.35 mg_{Pt} cm⁻² and PBI in the electrodes, and ABPBI·3.7 H₃PO₄ as membrane and oxygen/hydrogen without external humidification as fuels. These low power results were not discussed by the authors. In the same reference [40], Kim et al tested ABPBI membranes in hydrogen/air cells with pure H₂ or H₂/100 ppm CO without significant power losses when CO impurities were present in the fuel. When they used ABPBI as a binder for the electrodes instead of Nafion[®], the power and the open circuit voltage increased, which confirms the importance of preparing optimized electrodes specially adapted for ABPBI membranes.

5 Sulfonation of Previously Cast ABPBI Membranes and Phosphoric Acid Doping

It has been previously shown that a sulfonated polybenzimidazole, suitably impregnated with phosphoric acid, presents a conductivity which is up to two orders of magnitude higher than that of its non-sulfonated analog equally impregnated.[15, 41] This made us explore the possibility of synthesizing sulfonated ABPBI derivatives. It is well known that sulfonated polybenzimidazoles can be prepared through two main types of procedures, namely, direct polymerization of the corresponding sulfonated monomers,[25], or by sulfonation of the preformed benzimidazole, by grafting a side chain on the benzimidazole N.[41]

A simple way to obtain sulfonated polybenzimidazole membranes is to sulfonate a previously cast H₂SO₄-doped membrane by a treatment at high temperatures.[42–44] This approach can be very useful for the preparation of sulfonated ABPBI membranes [36, 45] (see Figure 9). When these sulfonated membranes are soaked in phosphoric acid baths of concentrations above ca. 65%, the sulfonated membranes absorb more acid than the non-sulfonated ones in the same bath; and as is shown in Figure 10, the higher the sulfonation degree, the higher the resulting acid absorption. As it might be expected this increased absorption leads to a higher conductivity (see Figure 11). Yet, since it is known that the introduc-

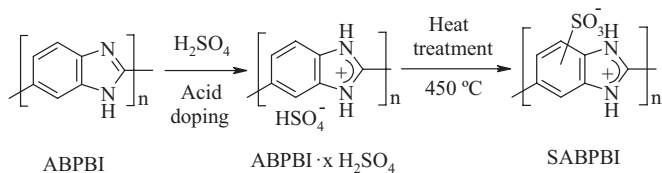


Fig. 9 Sulfonation of ABPBI membranes.

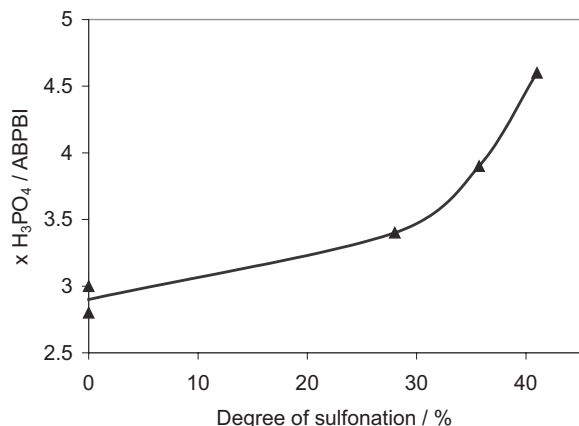


Fig. 10 Phosphoric acid absorption of sulfonated ABPBI membranes in H₃PO₄ 85% / H₂O (70 : 30 by volume).

tion of sulfonate groups helps increase the proton conductivity of acid doped polybenzimidazoles, we do not rule out a contribution from the sulfonate groups themselves to the increased conductivity of these sulfonated ABPBI derivatives. It should be remarked that on Figure 11, all the ABPBI membranes were doped in the same phosphoric acid bath. In order to compare these membranes to PBI, a PBI membrane was doped, but since PBI absorbs a lower acid percentage than ABPBI [18], the PBI membrane was doped in a more

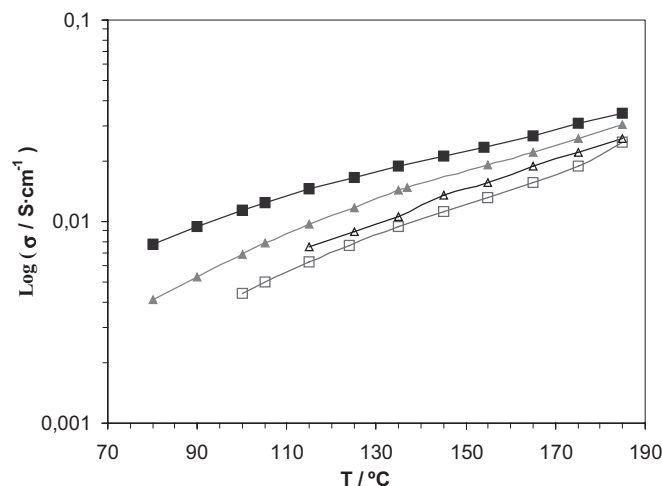


Fig. 11 Conductivity of membranes based on SABPBI (-SO₃H 41%) · 4.6 H₃PO₄ (■), ABPBI · 45% H₃PMO₁₂O₄₀ · x H₃PO₄ (▲), ABPBI · 2.7 H₃PO₄ (□), and PBI · 6.7 H₃PO₄ (△). For a meaningful comparison the three ABPBI membranes were doped in the same acid bath (H₃PO₄ 85% / H₂O 70:30 v/v).

concentrated phosphoric acid bath in order for it to reach an acid uptake comparable to that of the ABPBI membranes.

Concerning thermal stability of these derivatives it might be expected that the sulfonic acid groups would suffer decomposition at temperatures much lower than the 600 °C withstood by polybenzimidazoles. Yet, since the sulfonate groups decompose at temperatures much higher than those corresponding to the first phosphoric acid dehydration processes, we can conclude that from the point of view of their use as PEM electrolytes, the thermal stability of sulfonated ABPBI membranes doped with phosphoric acid is as high as the corresponding acid-doped non-sulfonated ABPBI membranes.[36, 45]

6 ABPBI/Heteropolyacids Hybrid Membranes and Impregnation with Phosphoric Acid

Heteropolyacids are among the best solid proton-conducting inorganic compounds,[46] and the incorporation of these inorganic conductors into sulfonated and perfluorosulfonated conventional membranes constitutes a significant research trend.[47–52] This approach has also been followed in the preparation of PBI membranes, but the conductivity achieved was not high enough.[53–56].

ABPBI membranes have also been prepared incorporating phosphomolybdic acid (PMo12) [45] as well as other heteropolyacid clusters [57]. As it is also the case for dry ABPBI or PBI membranes, a dry 45% PMo₁₂ / ABPBI hybrid membrane also has a very low proton conductivity.[18] Yet, once doped with phosphoric acid by immersion in a concentrated phosphoric acid bath, its conductivity increases well beyond the conductivity of an ABPBI membrane doped in the same bath as is shown in Figure 11.[18, 45, 57] The integration of heteropolyacids therefore works in a similar manner to the incorporation of sulfonate groups to the polybenzimidazole network. By means of FT Infrared spectroscopy it has been shown that the heteropolyacid is not lost in the phosphoric acid bath during the doping step. The high conductivity and the very flexible mechanical appearance of these hybrid membranes after doping are typical of high acid doping levels in ABPBI/phosphoric acid membranes.

7 Other Possible Dopants and Co-Dopants for ABPBI and Related Hybrid Membranes

PMo₁₂ is just one of the many known inorganic solid proton conductors.[58, 59] We have found that phosphotungstic acid (PW₁₂) can also be incorporated into the ABPBI matrix [39], and many other heteropolyacids can be tested.

There is also another very important family of solid proton conductors, which present a sharp increase in conductivities associated with phase transitions. One of the best known members of this family is CsHSO₄. [60–62] We have prepared hybrid ABPBI/CsHSO₄ membranes with up to 50% CsHSO₄

leading to materials which maintain the crystal structure of the CsHSO_4 in the hybrid and which are presently still under study.[39]

8 Conclusions

Poly(2,5-benzimidazole) (ABPBI) is the simplest member of the polybenzimidazole family and the easiest to synthesize. It can be obtained easily by condensation of a single commercial monomer (3,4-diaminobenzoic acid) without any further purification, yielding materials with viscosities and molecular weights suitable for the preparation of membranes bearing good mechanical properties, by means of several different casting technologies summarized here (included the single-step direct acid casting procedure).

This ABPBI polymer can be easily impregnated with phosphoric acid, resulting in PEM membranes with excellent conductivities. Indeed, values of $1.5 \cdot 10^{-2} \text{ S cm}^{-1}$ at temperatures as high as 180°C in dry conditions were obtained for MSA/ H_3PO_4 direct acid cast membranes (ABPBI-3.0 H_3PO_4). MSA-cast membranes under the same dry conditions prepared by the soaking method showed a conductivity of $2.5 \cdot 10^{-2} \text{ S cm}^{-1}$ for ABPBI-2.7 H_3PO_4 at 180°C .

ABPBI can also be very easily sulfonated by sulfuric acid doping followed by a further heat treatment. The introduction of the sulfonate groups increases the capacity for acid uptake of these membranes, in comparison with the non-sulfonated ones under the same conditions, leading to a consequent increase of the conductivity.

Furthermore, ABPBI also provides additional ground for novel materials development by means of integration of a variety of inorganic proton-conducting species, both molecular clusters and extended phases. Thus, heteropolyacids such as PMo_{12} or PW_{12} can be integrated into ABPBI to form hybrid organic-inorganic membranes with increased conductivities after impregnation with phosphoric acid.

Most of the work reviewed here has been devoted to the preparation of ABPBI membranes. Yet there are still many possible ways to increase the proton conductivity of ABPBI using many other proton conducting co-dopants, and much work remains to be done on the preparation of MEAs optimized *ad hoc*, using specially designed formulations, and leading to electrodes, and fuel cell studies. Summarizing, recent studies have shown ABPBI to be comparable to PBI in many respects (including conductivity) and superior in others (including synthesis). This makes ABPBI and their polymeric and hybrid materials deserving of further efforts to develop PEMFC as promising as phosphoric acid doped PBI which is already a commercial product.[13, 14]

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