

# Sulfonated poly(2,5-benzimidazole) (SABPBI) impregnated with phosphoric acid as proton conducting membranes for polymer electrolyte fuel cells

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## Abstract

Previously cast ABPBI membranes were sulfonated by doping with sulfuric acid followed by heat treatment at 450 °C for 5 min in air. Sulfonation degrees between 35 and 49% of the benzimidazole rings were achieved. The resulting SABPBI membranes were impregnated with phosphoric acid (H<sub>3</sub>PO<sub>4</sub> 85%/H<sub>2</sub>O, 70:30 bath). For concentrated phosphoric acid baths (above 65%), the capacity of these membranes for phosphoric acid uptake (and consequently also their conductivity) increased with the degree of sulfonation. Sulfonated and acid doped SABPBI membranes were characterized in terms of degree of sulfonation, thermal stability (TGA), X-ray diffraction, FTIR spectroscopy and proton conductivity in the dry state, and compared with phosphoric acid impregnated ABPBI studied earlier. The maximum conductivity measured in dry conditions was  $3.5 \times 10^{-2} \text{ S cm}^{-2}$  at 185 °C for SABPBI-4.6H<sub>3</sub>PO<sub>4</sub> (with a degree of sulfonation of 41%) which compares favorably with non-sulfonated ABPBI and makes feasible their application in PEM Fuel Cells working at temperatures of 150–200 °C. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Proton-conducting membranes; Polybenzimidazole; ABPBI; Sulfonated polybenzimidazole; Polymer electrolyte; PEMFC

## 1. Introduction

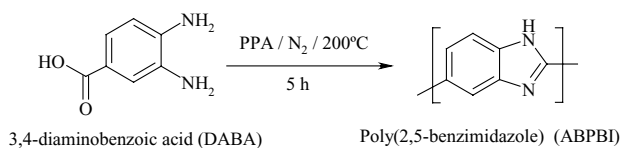
Current polymer electrolyte membrane fuel cells (PEMFC) technology is based on perfluorosulfonated materials, most frequently Nafion®. These membranes have two main limitations. First of all there is their high cost that make difficult future PEMFC commercialization. But in addition, Nafion® and other sulfonated membranes work as electrolytes within a relatively narrow temperature range, in all cases below 100 °C and require proper humidification to keep proton conduction high enough for PEMFC applications. Yet, below 150 °C CO impurities commonly present in H<sub>2</sub> from reforming result in the poisoning of the Pt/C catalyst, so electrolyte membranes with a higher thermal stability and lower costs are required for PEMFC development.

In recent years, polybenzimidazole (PBI) membranes impregnated with phosphoric acid have attracted the attention of many research groups. PBI, the only commercially available polybenzimidazole, is a basic polymer that when soaked in phosphoric acid solutions absorbs up to 75% of acid in the membrane, yielding the so called phosphoric acid “doped” polybenzimidazole [1–13]. Phosphoric acid doped PBI is less expensive than Nafion®, is impermeable to the gases and methanol, does not require humidification in PEMFC application, and its working temperature reaches almost 200 °C, allowing the use of H<sub>2</sub> containing 3% CO in volume with a very small power loss [9]. Acid doped PBI has been studied in PEMFC using many fuel types [8,9,14–23].

Aside from commercial PBI only poly(2,5-benzimidazole) (ABPBI), which is the simplest polybenzimidazole type polymer (Scheme 1) has been doped with phosphoric acid in the form of membranes [3,24].

Another way to increase the proton conductivity of PBI is the sulfonation of pre-cast membranes by sulfuric acid doping and heat treatment [25,26] but the conductivity of

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Scheme 1. Synthesis of ABPBI.

those membranes was not high enough for practical PEMFC applications.

We have studied the combined effect of sulfonation and acid impregnation in polybenzimidazole materials. Our first efforts were centered on polybenzimidazole derivatives that eventually did not lead to membrane formation but were useful to show that when doping with the same amount of acid two polybenzimidazoles, both with the same chemical structure but one sulfonated, the sulfonated one featured a dc conductivity of about two orders of magnitude higher [27].

Furthermore, and in relation to membrane-forming materials, we have recently communicated the enhanced proton conductivity of ABPBI membranes induced by polyanion integration in the polymer (either inorganic polyoxometalates or sulfonate groups) [28]. In this work we present a full account of the latter derivative, including the synthesis of ABPBI, membrane casting, a detailed description of the sulfonation of these ABPBI membranes, and finally their phosphoric acid impregnation, as well as their chemical and electrochemical characterization, in comparison to non-sulfonated ABPBI.

## 2. Experimental

The monomer 3,4-diaminobenzoic acid (DABA) 97% and methanesulfonic acid (MSA) 99% were obtained from Across Organics and used without further purification. Polyphosphoric acid (PPA) 85% P<sub>2</sub>O<sub>5</sub>, phosphoric acid 85%, and sulfuric acid 96% were purchased from Panreac.

Thermogravimetric Analyses (TGA) were recorded with a Mettler-Toledo CR50 thermobalance in air at 10 °C min<sup>-1</sup>. 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 Canon-Fenske 300 viscosimeter was used for the measurement of viscosities of polymer solutions in H<sub>2</sub>SO<sub>4</sub> 96%.

FTIR spectra of the membranes were recorded on a Shimadzu FTIR-8300 spectrophotometer.

X-ray diffraction patterns were collected with a rotating anode Rigaku Rotaflex Ru-200B diffractometer ( $\lambda = 1.5418 \text{ \AA}$ , K $\alpha$  Cu)  $2\theta$  between 5 and 60° (0.02° step, 4° min<sup>-1</sup>).

Four probe ac conductivity measurements as a function of temperature were made in air at a fixed frequency of 500 Hz–2 kHz measuring almost pure resistive behavior.

Samples were cut as strips of 3 cm × 0.6 cm. Current was applied between the ends of the sample, and the voltage drop was measured by two Ag wires placed in the middle and separated 1 cm. In order to eliminate the effect of absorbed humidity of the sample, the cell was heated at 185 °C and the measurements were recorded while cooling. A more complete description of ac conductivity method for proton conducting membranes can be found in the literature [29].

## 3. Polymer synthesis

Poly(2,5-benzimidazole) (ABPBI) was prepared by condensation of 3,4-diaminobenzoic acid (DABA) monomers in polyphosphoric acid (PPA) as reported earlier [27]. Typical inherent viscosity of a 0.5 dl g<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. Higher molecular weight ABPBI can be polymerized if the monomer is recrystallized previously [3] or 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 obtaining good membranes, even when doped with high phosphoric acid amounts, prepared as follows.

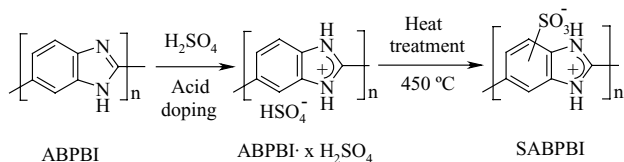
## 4. Membrane casting

Membranes of ABPBI were prepared by evaporation of a methanesulfonic acid (MSA) solution [30–32] dissolving 400 mg of finely ground polymer in 6 ml of MSA. Films were cast on a glass plate, and evaporated in a heating plate inside a ventilated hood, at about 200 °C. The membranes were heated until no evolution of MSA was observed, during at least 2 h, and were peeled off by immersion into water. The resulting membranes were characterized by elemental analysis, and a big amount of MSA was detected (about 5–6% S).

## 5. Sulfonation of ABPBI membranes

The sulfonation of preformed PBI membranes, by doping in sulfuric acid and heat treating the sulfuric acid membranes, has been described earlier [25,26,33]. Based on those reports we have optimized the same procedure for the sulfonation of ABPBI membranes.

When doping a PBI membrane in a sulfuric acid/water bath, this membrane absorbs acid, which appears in the FTIR spectrum at 1200–1000 cm<sup>-1</sup> [4]. The same happens for ABPBI membranes (Scheme 2). In order to study its doping process, a 20  $\mu\text{m}$  ABPBI membrane was soaked in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O (10:90 by volume) for 24 h and dried at 100 °C. Since ABPBI is  $(\text{C}_7\text{H}_4\text{N}_2)_n$ , the doping level was calculated as the molar ratio S/C<sub>7</sub> and S/N<sub>2</sub> from elemental analyses, finding a composition of ABPBI-0.6H<sub>2</sub>SO<sub>4</sub>. These membranes could have been washed in boiling water before acid doping in order to eliminate the remaining MSA (detected



Scheme 2. Sulfonation of ABPBI membranes.

from its FTIR spectra). However, this was not necessary since, as it is also the case for phosphoric acid doped ABPBI membranes, the MSA is displaced and completely eliminated during the process of acid doping.

First attempts to sulfonate 20  $\mu\text{m}$  sulfuric acid doped membranes for 30 or 10 min in air, or for 15 min in Ar, produced a dark and fragile membrane, but the FTIR spectra showed bands at 1200 and 1050  $\text{cm}^{-1}$  similar to those found in other sulfonated benzimidazole polymers [27,34–37] as well as bands characteristic of MSA. Since the atmosphere did not seem to help in reducing the fragilization of the membrane, we did carry out all the following heat treatments in air.

We noticed shorter times led to membranes which were less fragile. Thus, we decided to optimize the minimal time needed to sulfonate ABPBI membranes in air at 450  $^{\circ}\text{C}$ , previously cast and doped in  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  (10:90 by volume) for 24 h. Three 20  $\mu\text{m}$  membranes were doped as described above, dried at 100  $^{\circ}\text{C}$ , and heat treated at 450  $^{\circ}\text{C}$  for 3, 5 and 10 min. In all cases, new FTIR bands, not present in the spectra before the heat treatment could be observed at 1230, 1178 and 1048  $\text{cm}^{-1}$ . For heat treatments over 5 min, the intensities of these bands did not decrease when washed in boiling water for 24 h, whereas the bands assigned to sulfuric acid at smaller wave number disappeared after the heat treatment. We have therefore assigned these new bands to the sulfonated ABPBI associated to the sulfonation of the benzene ring.

After washing, the sulfonation degree was calculated from the molar ratios  $\text{S}/\text{C}_7$  and  $\text{S}/\text{N}_2$  as determined from elemental analyses. The composition of our sulfuric acid doped membrane was ABPBI·0.6 $\text{H}_2\text{SO}_4$ , so in the sulfonation reaction, the limiting reagent is the acid, not the benzimidazole, therefore, the yield of this sulfonation reaction has to be calculated as 0.6 times the degree of sulfonation (Table 1). It should be noted that in the spectra of the membrane treated for just 3 min bands characteristic of sulfuric acid are still clearly visible. Therefore, we conclude that the optimum heating

Table 1

Degree of sulfonation of the ABPBI·0.6 $\text{H}_2\text{SO}_4$  membrane as a function of the heat treatment time

Sample (min)	Degree of sulfonation		Yield of sulfonation (%)
	$\text{S}/\text{C}_7$ (%)	$\text{S}/\text{N}_2$ (%)	
3	39	41	67
5	43	43	72
10	49	49	82

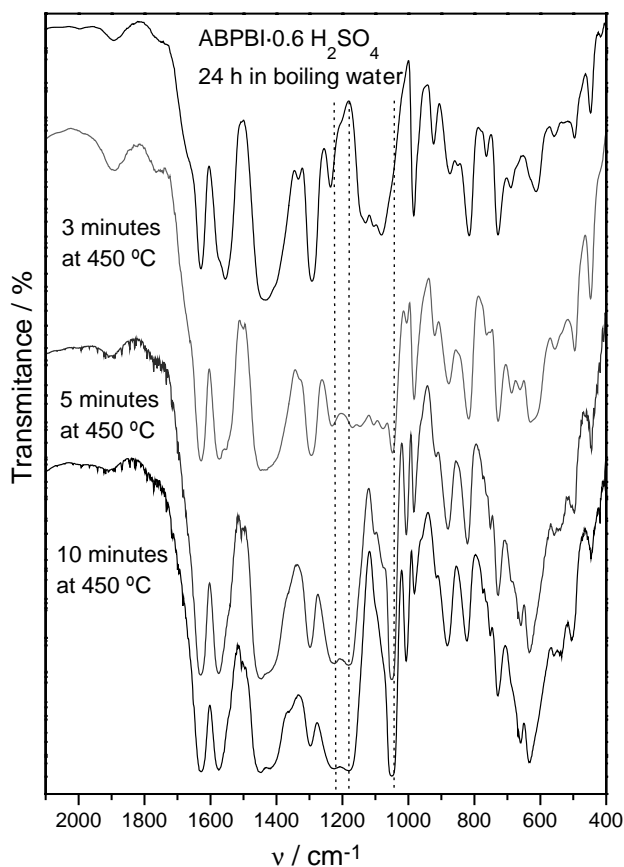


Fig. 1. FTIR of ABPBI·0.6 $\text{H}_2\text{SO}_4$  heat treated at 450  $^{\circ}\text{C}$  in air for 3–10 min, and washed in boiling water for 24 h. Bands at 1200  $\text{cm}^{-1}$   $\times$  1050  $\text{cm}^{-1}$  are assigned to sulfonates.

time, long enough to complete the sulfonation with the minimal fragilization, is 5 min at 450  $^{\circ}\text{C}$ . Fig. 1 and Table 2 summarize the evolution of the FTIR spectra of sulfuric acid doped ABPBI membranes heat treated for 5 min, where the markedly different positions of sulfuric acid and sulfonate bands is conveniently used to follow the sulfonation process.

## 6. Phosphoric acid impregnation of the membranes

The 20  $\mu\text{m}$  membrane heat at 450  $^{\circ}\text{C}$  for 3 min described above was washed in boiling water and doped in phosphoric acid, finding that the degree of sulfonation was lower after doping. That means that during the doping process the remaining sulfuric acid is eliminated much better than by washing in boiling water, so it is not necessary to wash the membranes before doping. For the membranes heat treated for 5 min or more we obtained the same calculated degree of sulfonation before and after doping, so almost all the sulfuric acid has reacted and the rest has been eliminated in the boiling water washing.

In order to study the doping of the sulfonated membrane with phosphoric acid and the conductivity of the resulting electrolytic sulfonated membranes, thicker membranes were

Table 2

Evolution of the FTIR bands in an ABPBI membrane doped in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O (10:90 by volume) for 1 and heat treated in air at 450 °C for 5 min

$\nu$ (cm <sup>-1</sup> )				Assignment
ABPBI·H <sub>2</sub> SO <sub>4</sub>	ABPBI·H <sub>2</sub> SO <sub>4</sub> washed 24 h	ABPBI·H <sub>2</sub> SO <sub>4</sub> 5 min at 450 °C	ABPBI·H <sub>2</sub> SO <sub>4</sub> 5 min at 450 °C washed 24 h	
		1233	1226	-SO <sub>3</sub> H
		1177	1183	-SO <sub>3</sub> H
	1141			H <sub>2</sub> SO <sub>4</sub>
1168	1130			H <sub>2</sub> SO <sub>4</sub>
1117	1104			H <sub>2</sub> SO <sub>4</sub>
1082	1080			H <sub>2</sub> SO <sub>4</sub>
1045		1048	1050	-SO <sub>3</sub> H

prepared following the same procedure. These membranes had the thickness used in PEMFC (about 80–150 μm). Samples of about 2 cm × 3 cm were cut and immersed in different phosphoric acid solutions for 3 days. The amount of PO<sub>4</sub><sup>3-</sup> as well as the degree of sulfonation was determined by elemental analyses of C, H, N and S after doping. As the polymer is partially sulfonated, an average C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>xSO<sub>3</sub> formula can be calculated from the C, N, and S elemental analysis. Hydrogen is excluded from this calculation because belongs both to the polymer and the phosphoric acid. Then, knowing this average formula, H<sub>3</sub>PO<sub>4</sub> can be calculated from the elemental analysis (C, H, N, and S) and the residue.

Fig. 2 shows that for almost all the concentrations of the doping bath, the non-sulfonated membranes absorb more acid than the sulfonated ones. Since sulfonated ABPBI is an anionic polymer, that behavior is easy to understand. However, when immersed in baths of a concentration higher than about 65% H<sub>3</sub>PO<sub>4</sub>, it is the sulfonated membrane that uptakes more acid. For this change in behavior we have not found any reasonable explanation.

In Fig. 3 is plotted the acid uptake as a function of the sulfonation degree of membranes doped in H<sub>3</sub>PO<sub>4</sub> 85%/H<sub>2</sub>O (70:30 by volume). Interestingly, in this highly concentrated bath, membranes with a higher degree of sulfonation show a higher capacities for phosphoric acid uptake expressed as the number of phosphoric acid molecules per benzimidazole unit or even as % weight of the acid in the membrane. This higher amount of acid will have a significant effect in the conductivity of these membranes as it will be discussed below.

## 7. X-ray diffraction

The X-ray diffraction pattern of a 41% sulfonated ABPBI membrane shows a single peak at  $2\theta$  26.4° (Fig. 4a) which could be associated to the d spacing resulting from stacked chains of benzimidazole rings on the same plane of the membrane as it has been found for ABPBI membranes cast from MSA solutions [30]. It can be noted that after doping with

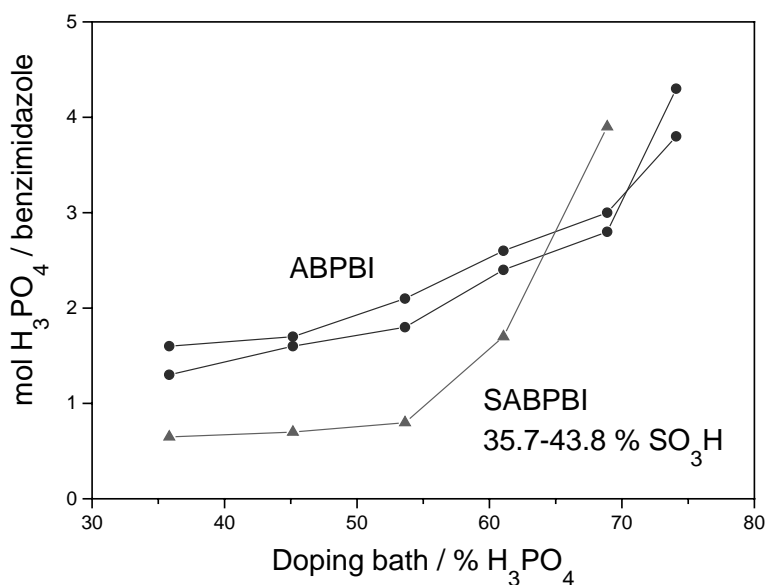


Fig. 2. Phosphoric acid absorption for SABPBI (degree of sulfonation 35.7–43.8%) (▲) and ABPBI (●) as a function of the doping bath concentration.

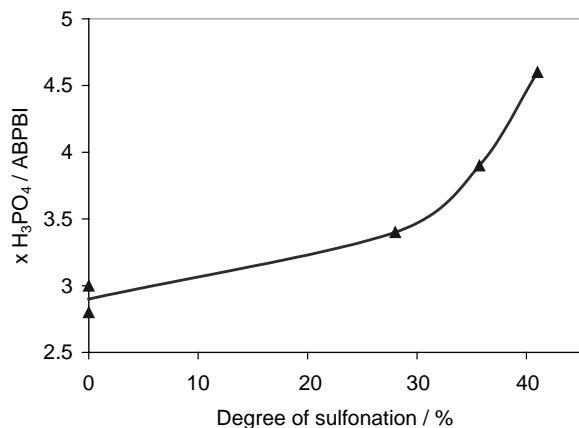


Fig. 3. Phosphoric acid absorption of sulfonated SABPBI membranes in H<sub>3</sub>PO<sub>4</sub> 85%/H<sub>2</sub>O (70:30 by volume) as a function of the degree of sulfonation.

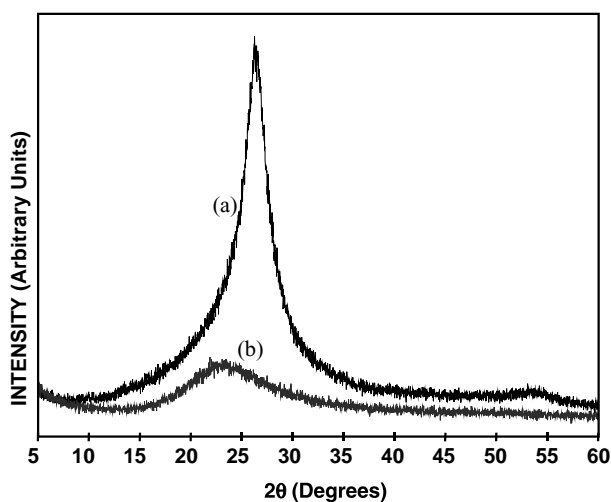


Fig. 4. X-ray diffraction of (a) SABPBI (41% SO<sub>3</sub>H) and (b) SABPBI (41% SO<sub>3</sub>H)-4.6H<sub>3</sub>PO<sub>4</sub>.

4.6H<sub>3</sub>PO<sub>4</sub> molecules per benzimidazole unit (Fig. 4b), the crystallinity of the membrane decreases as it is shown by the lower intensity and larger width of the peak, whereas the spacing increases as shown by the shift of the peak to lower angles when compared with that of Fig. 4a.

## 8. Thermal stability

Thermogravimetric analyses of SABPBI (41% SO<sub>3</sub>H) and phosphoric acid doped SABPBI (41% SO<sub>3</sub>H and 4.6H<sub>3</sub>PO<sub>4</sub>) were performed in air from 30 to 700 °C at 10 °C min<sup>-1</sup> and are shown in Fig. 5.

Sulfonated SABPBI is stable up to 400 °C. Above this temperature, a weight loss centered at 490 °C and assigned to the decomposition of sulfonate groups is detected (Fig. 5). Finally, the polymer decomposition starts at 540 °C (centered at ca. 630 °C). Upon doping, the membrane is more hygroscopic, absorbing about 15% of water by weight during

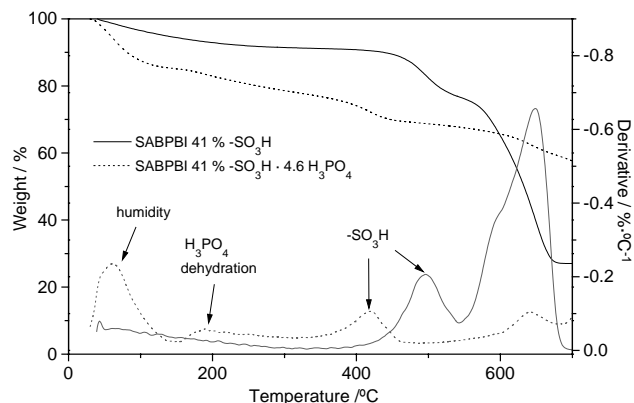


Fig. 5. TGA of SABPBI (41% SO<sub>3</sub>H) and SABPBI (41% SO<sub>3</sub>H)-4.6H<sub>3</sub>PO<sub>4</sub> in air at 10 °C min<sup>-1</sup>.

handling. Phosphoric acid dehydrates as expected in these acid doped polymers [27,38] between 150 and 300 °C (process centered at about 200 °C). It should be noted that the sulfonate groups is less stable in the presence of the phosphoric acid. On the other hand, the ABPBI backbone is stabilized by the acid, and its decomposition is detected centered at 750 °C.

## 9. Conductivity

Fig. 6 shows plots of the conductivity of three ABPBI and SABPBI membranes with different degrees of sulfonation, all them doped in H<sub>3</sub>PO<sub>4</sub> 85%/H<sub>2</sub>O (70:30 by volume). These data show that the conductivity of the membrane with higher sulfonation is larger than that of the membrane with lower sulfonation which in turn is larger than for the non-sulfonated ABPBI membrane. As discussed above (Fig. 3), the higher the sulfonation degree of our SABPBI membranes the larger it is their capacity to uptake phosphoric acid. This trend, which is kept for the samples in Fig. 6,

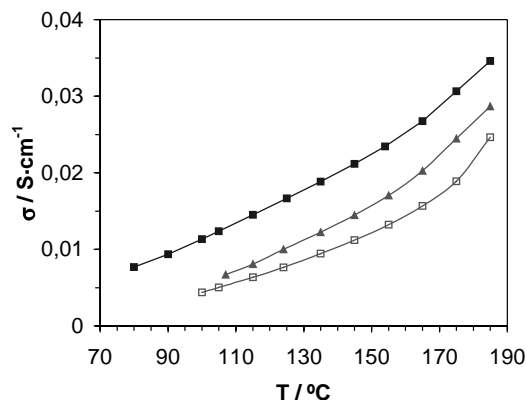


Fig. 6. Conductivity of SABPBI (41% SO<sub>3</sub>H and 4.6H<sub>3</sub>PO<sub>4</sub>) (■), SABPBI (28% SO<sub>3</sub>H and 3.4H<sub>3</sub>PO<sub>4</sub>) (▲), ABPBI-2.7H<sub>3</sub>PO<sub>4</sub> (□), these three membranes have been doped in H<sub>3</sub>PO<sub>4</sub> 85%/H<sub>2</sub>O (70:30 by volume) for 3 days.

can explain the behavior described. On the other hand, earlier work on different benzimidazole polymers showed that a sulfonated benzimidazole derivative presented a conductivity up to two orders of magnitude higher than its non-sulfonated analogue doped with the same amount of acid [27]. For this reason we cannot rule out an intrinsic contribution of the sulfonate groups themselves to the increased conductivity reported here.

The average activation energies ( $E_a$ ) for the conduction processes can be calculated from the slope of the Arrhenius plots,  $\ln(\sigma)$  versus  $1000/T$  (K). Not surprisingly,  $E_a$  decreases when the degree of sulfonation and the phosphoric acid content increase (ABPBI-2.7H<sub>3</sub>PO<sub>4</sub>,  $E_a = 27.37$  kJ mol<sup>-1</sup>; SABPBI 28% SO<sub>3</sub>H-3.4H<sub>3</sub>PO<sub>4</sub>,  $E_a = 26.54$  kJ mol<sup>-1</sup>; SABPBI 41% SO<sub>3</sub>H-4.6H<sub>3</sub>PO<sub>4</sub>,  $E_a = 18.7$  kJ mol<sup>-1</sup>).

## 10. Conclusions

We have successfully sulfonated previously cast ABPBI membranes by doping them with sulfuric acid and heat treating the doped membranes at 450 °C for 3–10 min in air, with an optimal time of 5 min. The degree of sulfonation achieved is between 35 and 49% of the benzimidazole rings. When impregnating these SABPBI membranes in a phosphoric acid bath (H<sub>3</sub>PO<sub>4</sub> 85%/H<sub>2</sub>O, 70:30) according to well-established procedures for polybenzimidazole membranes, we found that the acid absorption increases with the degree of sulfonation, and in consequence its conductivity increases too. The maximum conductivity measured in dry conditions was  $3.5 \times 10^{-2}$  S cm<sup>-2</sup> at 185 °C for SABPBI-4.6H<sub>3</sub>PO<sub>4</sub> with a degree of sulfonation of 41%. These membranes have the same thermal stability as phosphoric acid doped ABPBI and PBI, all of which make them interesting for practical application as membrane in PEMFC at temperatures as high as 150–200 °C.

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